

CO₂-in-water emulsion injection for dual-purpose enhanced methane hydrate recovery and hydrate-based CO₂ storage: A numerical assessment of performance and operational limits

2026

BAHMAEE Aabes

Abstract

Rising atmospheric concentrations of carbon dioxide (CO₂) and methane (CH₄) are the primary anthropogenic drivers of contemporary climate change. Methane hydrates—vast stores of CH₄ found in Arctic permafrost and continental-margin sediments—represent both a potential energy resource and a long-term climate risk should warming-triggered dissociation release methane to the ocean–atmosphere system. Class 2 methane-hydrate (MH) deposits, characterized by hydrate-bearing layers underlain by a mobile aquifer, are particularly attractive for production because aquifer flow supplies heat that accelerates hydrate dissociation. However, the same aquifer flow commonly induces uneconomic water production and rapid pressure recharge, limiting recoverable methane. Consequently, researchers have suggested forming an in-situ seal, via chemical agents or CO₂ hydrate, to isolate the MH-bearing layer (MHBL) from the underlying aquifer. While the injection of liquid CO₂ into the CO₂ hydrate stability zones (HSZs) of the aquifer can create such a seal, it typically causes rapid clogging and a total loss of injectivity. Accordingly, this thesis demonstrates that such clogging can be successfully exploited to form a CO₂ hydraulic barrier if injectivity is managed using optimized CO₂-in-water (C/W) emulsion injection schemes. This thesis develops, validates, and applies a coupled Thermo-Hydro-Chemical (T-H-C) numerical framework, implemented within the MATLAB Reservoir Simulation Toolbox (MRST), to evaluate and optimize a dual-purpose strategy. This strategy involves injecting a C/W emulsion into the aquifer beneath MH-bearing layers to create stable CO₂ hydrate seals, thereby enhancing methane production while ensuring secure CO₂ sequestration.

The research is organized into model development (Chapter 2) and validation (Chapter 3), operational optimization for injectivity and hydrate-based CO₂ storage (Chapters 4 and 5), and field-scale performance of the CO₂ hydrate seal on enhanced methane recovery and aquifer influx control (Chapter 6). A robust, multiphase T–H–C model was developed to represent C/W emulsion flow, CO₂ mass transfer, hydrate nucleation and growth kinetics, and coupled heat and fluid transport. Model credibility was established through systematic validation against 1D core-scale experiments. Calibration showed the model accurately reproduced the dissolution-dominated pre-induction thermal responses with a dissolution rate constant for liquid CO₂ droplets in water (β) of 0.04 s⁻¹ and a pressure adjustment parameter for heat of dissolution of CO₂ in water (C) of 0.15, while averaged post-induction thermal patterns were

captured using a CO₂ hydrate particle formation rate constant (γ) of 0.012 s⁻¹·MPa⁻¹ and an average volume fraction of CO₂ hydrate film in the CO₂ hydrate particle (α) of 0.55. The model reproduced sustained injectivity for low CO₂ volume fraction tests (CE10) and correctly identified limitations in higher-fraction experiments (CE20, CE30), and successfully reproduced water-alternating-emulsion (WAE) pressure and temperature trends, thereby completing the model validation objective.

Using the validated framework, operational sensitivity studies identified two dominant controls on injectivity: CO₂ hydrate particle diameter (D_p) and α . Smaller D_p reduces particle attachment and plugging, making dispersed liquid CO₂ droplet size control at injection a key design parameter. Low α (e.g., 0.15) in high-CO₂ emulsions produced near-immediate pore blockage, underscoring α as the integrative parameter linking initial droplet size, hydrate growth kinetics, and film evolution. Salinity was found to be a stabilizing factor: absence of salt accelerates CO₂ hydrate formation due to higher thermodynamic driving force and reduces operational viability. To mitigate injectivity loss, the WAE strategy was demonstrated to be highly effective: even the most challenging parameter set ($\alpha = 0.15$) allowed full 1 pore-volume (PV) injection under WAE by dissolving or sweeping attached hydrate particles and temporarily restoring permeability.

The study quantified HBCS capacity by applying operationally realistic injection schemes. Cumulative injected CO₂ mass scaled linearly with emulsion CO₂ fraction and reached up to 0.128 Mt CO₂ per single-well scenario for tested conditions. WAE not only preserved injectivity but increased the total CO₂ converted to hydrate by enabling full PV delivery. Long-term (100-yr) post-shut-in simulations show durable storage: roughly 60% of sequestered CO₂ is immobilized as hydrate and ~40% by solubility trapping, with less than 0.02 wt% escaping the modeled domain after 100 years. Downward density-driven migration of CO₂-enriched brine was captured by the model and validated qualitatively against 3D reactor experiments that exhibited self-trapping and flow-channeling—mechanisms that improve sweep efficiency and locally produce hydrate saturations > 40%.

Field-scale T–H–C simulations demonstrated the technical viability of the C/W emulsion strategy for establishing a robust hydraulic barrier. The study evaluated the trade-off between thermal stimulation and radial seal expansion across varying soaking durations. While an extended 5-year soak (S5y) was initially hypothesized to maximize conversion and exothermic thermal stimulation, results indicate that the resulting thermal stimulus is transient and

dissipates rapidly during production. In contrast, a shorter 6-month soaking period (S6m) proved superior by allowing unreacted liquid CO₂ to migrate and radially expand the composite CO₂-CH₄ seal during the production phase. This radial expansion was identified as more critical for sustained reservoir isolation than the initial thermal effect and in-situ hydrate formation.

Under the optimal scenario (50% CO₂ emulsion, 75% initial MH saturation, and a 6-month soak), field-scale results include a 58.93% increase in cumulative methane recovery and a 60.70% reduction in cumulative produced water, with 33.59% of the injected CO₂ retained primarily as CO₂ hydrate. Seal longevity remains strongly dependent on the injected CO₂ mass and the native MH saturation. Advection-driven dissolution caused by warm aquifer brine was identified as the principal failure mechanism, eroding the seal from the perimeter inward. To manage this, operational pathways such as cyclic huff-and-puff strategies—short injection/production cycles that leverage early-time gains while mitigating late-time collapse—and the re-emulsification of produced water for seal reinforcement were proposed to maximize long-term CO₂ retention and maintain reservoir isolation.

This thesis demonstrates that C/W emulsion injection into CO₂ hydrate stability zones beneath Class 2 MH deposits is a technically viable and operationally robust approach that simultaneously enhances methane recovery and achieves long-term CO₂ storage. The coupled T-H-C framework provides a validated tool for designing injection parameters (droplet size, α , salinity) and schedules (WAE, huff-and-puff) to balance injectivity and seal formation and to maximize the multi-cycle performance of the CO₂ hydrate barrier for enhanced methane production and aquifer influx control. Collectively, the results establish a promising route for the responsible development of Class 2 MH resources while contributing to long-term CO₂ mitigation strategies.

Acknowledgments

I would like to express my sincere and deepest gratitude to my supervisor, Professor Sumihiko Murata. He provided me with the opportunity and resources to conduct this research, and his invaluable advice, wisdom, insight, and sincerity have profoundly influenced my development as a researcher. His guidance led directly to the successful publication of three co-authored publications. I am especially thankful for his mentorship in establishing rigorous research methods and effectively communicating our findings. It has been a great joy and privilege to work and study under his supervision.

I wish to express my profound appreciation to Professor Yoshihiro Masuda, Professor Emeritus at the University of Tokyo. The core research ideas presented in this dissertation were initially conceived in his laboratory during my master's studies. I am deeply grateful for his significant contributions to the development of the governing equations and for his guidance in mastering the fundamental concepts of this field. Our collaboration resulted in the publication of my first journal paper, which established the essential foundation for my subsequent research and the work presented in this dissertation.

I extend my sincere appreciation to Assistant Professor Kazuya Kobayashi. His consistently constructive comments and technical insights during our laboratory meetings were instrumental in refining the methodology, significantly improving the overall quality of this work, and co-authoring one of my publications.

I offer profound gratitude to the Ministry of Education, Culture, Sports, Science and Technology (MEXT) for bestowing upon me the prestigious MEXT scholarship. This invaluable financial support made it possible for me to pursue my higher education in Japan and realize both my academic and personal goals.

Finally, I owe immeasurable thanks to my beloved parents, my sister, and my friends. Their unwavering love, encouragement, and continuous support were the foundation that enabled me to successfully complete this dissertation.

Table of Contents

Chapter 1	1
Introduction.....	1
1.1 The dominance of CO ₂ and CH ₄ in global warming.....	1
1.2 CH ₄ hydrates: Resource and challenge	2
1.3 Dual-purpose CO ₂ injection.....	5
1.4 Thesis objectives and outline	9
Chapter 2	13
Numerical modeling framework.....	13
2.1 Challenges in modeling emulsion-hydrate flow	15
2.2 Core numerical model assumptions	15
2.3 Emulsion stability justification	16
2.4 Governing equations	17
2.4.1 Darcy equations	17
2.4.2 Treatment of governing conservation equations	18
2.5 Constitutive and phenomenological models	18
2.5.1 Constitutive models for kinetics and thermal processes	18
2.5.2 Constitutive models for rock properties and flow.....	29
2.6 Physical properties	37
2.6.1 Density model	37
2.6.2 Viscosity model.....	43
2.6.3 Molar internal energy	47
2.6.4 Molar enthalpy	51
2.6.5 Effective thermal conductivity of porous media.....	54
Chapter 3	58
Numerical model validation.....	58
3.1 Overview of the experimental system and data	58
3.2 Mathematical formulation of the 1D validation model.....	60
3.3 Numerical implementation and solution strategy	62
3.3.1 Discretization and flow operators	63
3.3.2 System solver	63
3.4 Physical simulation setup for validation	64

3.4.1	Thermal boundary conditions	65
3.4.2	Injection conditions and CO ₂ partitioning	65
3.4.3	Model calibration and tuning	66
3.5	Initial model validation: Heat transfer coefficient calibration	66
3.6	Simulation results and validation for CO ₂ injection schemes.....	67
3.6.1	Continuous injection of C/W emulsion.....	67
3.6.2	Water-alternating C/W emulsion injection.....	72
3.6.3	Comparative analysis of different injection schemes	76
3.7	Sensitivity analysis of CO ₂ in water dissolution parameters	78
3.8	Conclusion	81
Chapter 4.....		82
C/W emulsion injectivity optimization		82
4.1	Introduction.....	82
4.2	Mathematical formulation.....	83
4.3	Simulation framework	84
4.3.1	Numerical simulation setup	85
4.3.2	Initial reservoir and injected fluid conditions	86
4.3.3	Numerical discretization and injection safety constraints	87
4.4	Simulation results and discussion	88
4.4.1	Grid convergence analysis	88
4.4.2	CO ₂ hydrate particle diameter sensitivity analysis	90
4.4.3	Sensitivity analysis of CO ₂ hydrate particle formation rate constant	92
4.4.4	Influence of α on C/W emulsion flow behavior	94
4.4.5	Water alternating C/W emulsion injection.....	98
4.4.6	Comparison of C/W emulsion behavior in seawater and pure water.....	100
4.5	Conclusion	102
Chapter 5.....		104
Hydrate-based CO ₂ storage and CO ₂ fate assessment		104
5.1	Introduction.....	104
5.2	Hydrate-based CO ₂ storage capacity in emulsion injection scenarios.....	104
5.3	Long-term CO ₂ fate in a seawater aquifer	108
5.4	Qualitative validation against 3D reactor experiments	112
5.5	Conclusion	115

Chapter 6.....	116
Enhanced methane recovery and aquifer influx control	116
6.1 Introduction.....	116
6.2 Mathematical formulation.....	116
6.2.1 Wellbore formulation and operational constraints	118
6.3 Simulation framework	119
6.3.1 Reservoir model and geological basis.....	119
6.3.2 Numerical discretization	122
6.4 Simulation results and discussion	123
6.4.1 Grid convergence analysis	124
6.4.2 Justification of single-component gas phase approximation	125
6.4.3 Case 1.....	125
6.4.4 Case 2.....	137
6.4.5 CO ₂ fate investigation	140
6.4.6 Influence of soaking time on sealing efficiency	142
6.5 Strategic implications for cyclic huff-and-puff operations	145
6.6 Conclusion	146
Chapter 7.....	147
Conclusion	147
References.....	151

List of Figures

Figure 1.1 Schematic illustration of the three primary gas hydrate reservoir types (Based on reservoir classification concepts from Moridis and Sloan [15], and Xia et al. [17]).	3
Figure 1.2 Schematic of CO ₂ hydrate utilization as a sealing agent to restrict pressure gradient propagation within the MHLB.	5
Figure 1.3 Comparing different approaches for CO ₂ injection. (a) Pore blockage mechanism during liquid CO ₂ injection in porous media; (b) Hydrate particles swept downstream during C/W emulsion injection (Reproduced from Bahmaee & Murata, [55], licensed under CC BY 4.0.).	6
Figure 1.4 Thesis structure. Roman numbers indicate published and submitted papers on these topics mentioned in each chapter (I: Bahmaee et al. [63]; II: Bahmaee and Murata [55]; III: Bahmaee et al. [68]).	12
Figure 2.1 Integrated research framework.	14
Figure 2.2 CO ₂ hydrate particle formation mechanism. The dark blue ring represents the CO ₂ hydrate film encasing the red liquid CO ₂ droplet core.	19
Figure 2.3 Conceptualization of CO ₂ dissolution in the aqueous phase (Based on Dahlgren and Lennernäs [91]).	23
Figure 2.4 Liquid CO ₂ droplets as nucleation sites for CO ₂ exsolution (Reproduced from Bahmaee & Murata, [55], licensed under CC BY 4.0.).	26
Figure 2.5 Conceptual schematic illustrating the sequential CO ₂ hydrate particle accumulation process in a porous medium. The sequence demonstrates how initial particle adsorption on the pore walls narrows the pore throats, leading to subsequent straining and entrapment of incoming particles, which results in permeability reduction.	31
Figure 3.1 Diagram of the core-flooding experimental setup utilized by Masuda lab for C/W emulsion injection (Reproduced from Bahmaee et al., [63], licensed under CC BY-NC-ND).	59
Figure 3.2 Measurement points for pressure and temperature within the core-flooding experimental setup (Reproduced from Bahmaee et al., [63], licensed under CC BY-NC-ND).	59
Figure 3.3 Computational flow work.	63
Figure 3.4 Schematic detailing the numerical boundary conditions applied to the core model, including flow boundaries (inlet and outlet) and prescribed thermal conditions.	64
Figure 3.5 Time evolution of the core temperature during water injection.	67
Figure 3.6 Time evolution of temperature for CE10: Comparison of experimental data (Exp) and numerical simulation results (Sim) at various core plug locations.	68
Figure 3.7 Time evolution of inlet and outlet pressures for CE10: Comparison of experimental data (Exp) and numerical simulation results (Sim).	69
Figure 3.8 Time evolution of temperature for CE20: Comparison of experimental data (Exp) and numerical simulation results (Sim) at various core plug locations.	70
Figure 3.9 Time evolution of inlet and outlet pressures for CE20: Comparison of experimental data (Exp) and numerical simulation results (Sim).	70

Figure 3.10 Time evolution of temperature for CE30: Comparison of experimental data (Exp) and numerical simulation results (Sim) at various core plug locations.	71
Figure 3.11 Time evolution of inlet and outlet pressures for CE30: Comparison of experimental data (Exp) and numerical simulation results (Sim).....	72
Figure 3.12 Time evolution of temperature for WAE20: Comparison of experimental data (Exp) and numerical simulation results (Sim) at various core plug locations.	73
Figure 3.13 Time evolution of inlet and outlet pressures for WAE20: Comparison of experimental data (Exp) and numerical simulation results (Sim).....	74
Figure 3.14 Time evolution of temperature for WAE30: Comparison of experimental data (Exp) and numerical simulation results (Sim) at various core plug locations.	75
Figure 3.15 Time evolution of inlet and outlet pressures for WAE30: Comparison of experimental data (Exp) and numerical simulation results (Sim).....	76
Figure 3.16 Temporal changes in the mean hydrate particle saturation across different injection scenarios.....	77
Figure 3.17 Time evolution of temperature for WAE30 up to the induction time ($\beta = 0.002 \text{ s}^{-1}$ and $C = 1$).	78
Figure 3.18 Time evolution of temperature for WAE30 up to the induction time ($\beta = 0.12 \text{ s}^{-1}$ and $C = 0.1$)......	79
Figure 3.19 Time evolution of temperature for CE10 up to the induction time ($\beta = 0.12 \text{ s}^{-1}$ and $C = 0.1$).....	80
Figure 4.1 Boundary conditions of reservoir domain (bottom boundary identical to top boundary).	85
Figure 4.2 Distribution of the reservoir's initial pressure, along with the well's perforated zone.	87
Figure 4.3 Sensitivity of injection pressure to grid resolution (NC and $8 NC$) as a function of injected pore volume (PV) for the CE10 scenario ($\alpha = 0.45$).	89
Figure 4.4 Total CO_2 hydrate saturation distribution for the CE10 scenario ($\alpha = 0.45$) comparing resolutions: (a) $8NC$. (b) NC	90
Figure 4.5 Sensitivity of injection pressure to hydrate particle diameter (DP) as a function of PV for the CE10 injection scenario ($\alpha = 0.45$).	91
Figure 4.6 Total hydrate particle saturation distribution for the CE10 injection scenario ($\alpha = 0.45$) at varying particle diameters: (a) $DP = 5 \text{ }\mu\text{m}$. (b) $DP = 10 \text{ }\mu\text{m}$. (c) $DP = 15 \text{ }\mu\text{m}$. (d) $DP = 20 \text{ }\mu\text{m}$	92
Figure 4.7 Injection pressure sensitivity to γ for the CE20 injection scenario ($\alpha = 0.45$).....	93
Figure 4.8 Concept of CO_2 hydrate particle formation.	94
Figure 4.9 Injection pressure sensitivity to average hydrate film volume fraction (α) for. (a) CE10. (b) CE15. (c) CE20.	96
Figure 4.10 Liquid CO_2 saturation distribution (CE10). (a) $\alpha = 0.45$. (b) $\alpha = 0.35$	97
Figure 4.11 Total CO_2 hydrate and liquid CO_2 saturation distribution (CE20). (a) Top row: $\alpha = 0.45$. (b) Bottom row: $\alpha = 0.15$	98
Figure 4.12 Injection pressure evolution as a function of injected PV for: (a) WAE15. (b) WAE20.	99

Figure 4.13 Injection pressures versus injected PV for pure water and seawater cases: (a) CE10 and (b) CE15.	100
Figure 4.14 Aquifer temperature distribution (CE15). (a) Pure water aquifer. (b) Seawater aquifer.	101
Figure 4.15 Dissolved CO ₂ and liquid CO ₂ saturation distribution in the aquifer (CE10 with $\alpha = 0.45$). (a) Top row: Pure water aquifer. (b) Bottom row: Seawater aquifer.	101
Figure 5.1 CO ₂ mass partitioning evolution within the simulated domain as a function of injected PV ($\alpha = 0.45$). (a) CE10. (b) CE20.	106
Figure 5.2 CO ₂ mass partitioning evolution within the simulated domain as a function of injected PV (WAE20).	108
Figure 5.3 Dissolved CO ₂ volume fraction distribution in the aquifer for CE15 ($\alpha = 0.25$) at various time points.	109
Figure 5.4 Spatial distribution of temperature in the aquifer for CE15 ($\alpha = 0.25$) at various time points.	110
Figure 5.5 Spatial distribution of liquid CO ₂ droplets in the aquifer for CE15 ($\alpha = 0.25$) at various time points.	110
Figure 5.6 Spatial distribution of CO ₂ hydrate particles in the aquifer for CE15 ($\alpha = 0.25$) at various time points.	111
Figure 5.7 Spatial distribution of temperature in the aquifer for CE15 ($\alpha = 0.45$) at various time points.	113
Figure 5.8 Spatial distribution of CO ₂ hydrate in the aquifer for CE15 ($\alpha = 0.45$) at various time points.	114
Figure 6.1 Three-dimensional Cartesian grid representation of the reservoir model. The domain is layered vertically: OB (0–5 m); MHBL (5–30 m); aquifer (30–40 m); and UB (40–45 m). The production interval is set within the MHBL (10–25 m) and the injection interval is in the aquifer (32.5–37.5 m).	122
Figure 6.2 Grid convergence analysis of (a) gas production rate (Q_g) and (b) water production rate (Q_w).	124
Figure 6.3 Comparison of CO ₂ solubility in seawater: theoretical versus simulated values.	125
Figure 6.4 Time evolution over the 3-year production period of (a) gas production rate (Q_g) and (b) water production rate (Q_w) for Base_75, Base75_CE30, and Base75_CE50.	126
Figure 6.5 Time evolution of Gas-water ratio for different scenarios in Case 1.	127
Figure 6.6 Thermal homogenization during soaking (Base75_CE30). Comparison of reservoir temperature distribution at (a) the end of the 60-day injection phase ($t = 60$ d) and (b) the end of the 5-year soaking phase ($t = 1885$ d).	127
Figure 6.7 Spatiotemporal evolution of stationary hydrate saturation (Sh) for the Base_75 scenario.	130
Figure 6.8 Spatiotemporal evolution of reservoir pressure for the Base_75 scenario.	130
Figure 6.9 Spatiotemporal evolution of reservoir temperature for the Base_75 scenario. ...	131
Figure 6.10 Spatiotemporal evolution of stationary hydrate saturation (Sh) for the Base75_CE30 scenario.	132
Figure 6.11 Spatiotemporal evolution of reservoir temperature for the Base75_CE30 scenario.	132

Figure 6.12 Spatiotemporal evolution of reservoir pressure for the Base75_CE30 scenario.	133
Figure 6.13 Spatiotemporal evolution of gas saturation for Base75_CE30. The results highlight secondary dissociation near the end of the production period, driven by high-temperature water influx from the UB.	134
Figure 6.14 Spatiotemporal evolution of stationary hydrate saturation (Sh) for the Base75_CE50 scenario.	134
Figure 6.15 Spatiotemporal evolution of liquid CO ₂ droplets for: (a) Base75_CE50 and (b) Base75_CE30.	135
Figure 6.16 Spatiotemporal evolution of reservoir temperature for the Base75_CE50 scenario.	135
Figure 6.17 Spatiotemporal evolution of reservoir pressure for the Base75_CE30 scenario.	136
Figure 6.18 Spatiotemporal evolution of volume fraction of dissolved CO ₂ for the Base75_CE50 scenario.	137
Figure 6.19 Time evolution over the 3-year production period of (a) gas production rate (Q_g) and (b) water production rate (Q_w) for Base_50, and Base50_CE50.	138
Figure 6.20 Spatiotemporal evolution of stationary hydrate saturation (Sh) for the Base_50 scenario.	139
Figure 6.21 Spatiotemporal evolution of stationary hydrate saturation (Sh) for the Base50_50 scenario.	139
Figure 6.22 CO ₂ mass partitioning over time for: (a) Base75_CE30, (b) Base75_CE50, and (c) Base50_CE50.	141
Figure 6.23 Conversion of CO ₂ phases during soaking (Base75_CE30). Comparison of liquid CO ₂ saturation (left) decay and resultant total hydrate saturation (right) growth from the end of injection ($t = 60$ d) to the end of soaking ($t = 1885$ d).	141
Figure 6.24 Impact of soaking duration on production performance across different initial MH saturations: (a, b) gas production rate (Q_g) and (c, d) water production rate (Q_w) for Base75_CE50 and Base50_CE50 scenarios, respectively.	143
Figure 6.25 Spatiotemporal evolution of stationary hydrate saturation (Sh) for the Base75_CE50_S6m scenario.	143
Figure 6.26 Spatiotemporal evolution of stationary hydrate saturation (Sh) for the Base50_CE50_S6m scenario.	144

List of Tables

Table 1.1 Characteristics of hydrate cavities.	2
Table 2.1 Coefficients for the liquid CO ₂ fugacity correlation.	21
Table 2.2 Coefficients for CO ₂ hydrate equilibrium temperature in seawater.	22
Table 2.3 Coefficients for the CH ₄ fugacity correlation.	28
Table 2.4 Comparison of calculation value and literature data for molar density of water.	38
Table 2.5 Coefficients used for the molar density correlation of liquid CO ₂	39
Table 2.6 Parameters for the partial molar volume of dissolved CO ₂ in water.	39
Table 2.7 Coefficients used for the water viscosity correlation.	43
Table 2.8 Coefficients used for the liquid CO ₂ viscosity correlation.	44
Table 2.9 Coefficients used for the calculation of NaCl brine viscosity.	45
Table 2.10 Coefficients used for the correlation of the molar internal energy of water.	48
Table 2.11 Coefficients used for the correlation of the molar internal energy of CO ₂	49
Table 2.12 Coefficients used for the correlation of the molar enthalpy of water.	52
Table 2.13 Coefficients used for the correlation of the molar enthalpy of CO ₂	53
Table 2.14 Coefficients used for the correlation of the molar enthalpy of CH ₄	54
Table 2.15 Coefficients for the water thermal conductivity correlation.	55
Table 2.16 Coefficients for the CO ₂ thermal conductivity correlation.	55
Table 2.17 Coefficients for the CO ₂ hydrate thermal conductivity correlation.	56
Table 2.18 Coefficients for the CH ₄ thermal conductivity correlation.	56
Table 3.1 Summary of experimental conditions for model validation (Adapted from Bahmaee et al. [63]).	60
Table 3.2 CO ₂ partitioning in injected C/W emulsions (Adapted from Bahmaee et al. [63]).	65
Table 3.3 Thermal performance of different scenarios of injection (Adapted from Bahmaee et al. [63]).	76
Table 4.1 Initial reservoir and injected fluid conditions.	86
Table 4.2 Results of grid convergence analysis for the CE10 injection scenario ($\alpha = 0.45$).	89
Table 4.3 Key parameters for WAE injection scenarios.	98
Table 5.1 Partitioning of injected CO ₂ and hydrate characteristics after 1 PV injection for different CE Cases.	105
Table 5.2 Phase composition of CO ₂ leaving the computational domain for various CE scenarios.	106
Table 5.3 Performance comparison of WAE and CE injection scenarios for $\alpha = 0.15$	107
Table 5.4 CO ₂ partitioning for the CE15 ($\alpha = 0.25$) case at well shut-in (Day 102) and Year 100.	112
Table 6.1 Reservoir and emulsion modeling parameters (key physical properties and operational settings).	121
Table 6.2 Cumulative output parameters for grid convergence analysis during the 3-year production period.	124
Table 6.3 Summary of final performance and efficiency indicators for C/W emulsion injection scenarios for Case 1.	129

Table 6.4 Summary of final performance indicators for Case 2 C/W emulsion injection. ...	140
Table 6.5 CO ₂ mass partitioning at the end of simulation.....	142
Table 6.6 Performance and efficiency indicator changes for S6m scenarios relative to S5y baselines.	144

Nomenclature

Abbreviations

CH	CO ₂ hydrate
HSZ	Hydrate stability zone
MH	Methane hydrate
MHBL	Methane hydrate bearing layer
OB	Overburden
UB	Underburden
PV	Pore volume

Mathematical symbols

A_{CH_4}	Active reaction surface area of MH (m ²)
A_{CO_2}	Surface area of liquid CO ₂ droplets (m ²)
A_{HT}	Heat-transfer area per unit of the porous medium (m ⁻¹)
A_{p0}^{body}	Initial surface area of pore body (m ²)
A_{p0}^{throat}	Initial surface area of pore throats (m ²)
A_{PA}^{body}	Surface area of accumulated hydrate particles (m ²)
A_{PA}^{throat}	Surface area of accumulated hydrate particles in pore throats (m ²)
C	Pressure adjustment parameter for heat of dissolution of CO ₂ in water
C_{gr}	Specific heat capacity of grains (J/(kg·K))
C_{wCO_2}	Concentration of dissolved CO ₂ in water (mol/m ³)
$C_{wCO_2}^S$	Saturation solubility of CO ₂ in water (mol/m ³)
$C_{HCO_2}^S$	Saturation solubility of CO ₂ at the aqueous solution-hydrate interface (mol/m ³)
D	Diffusion coefficient of CO ₂ droplets in water (m ² /s)
D_{gr}	Average grain diameter of the porous medium (m)
D_{HP}	Molecular diffusion coefficient (m ² /s)
D_P	Hydrate particle diameter (m)
D_t	Pore throat diameter (m)
$\frac{dn}{dt}$	Dissolution rate of liquid CO ₂ droplets (mol/s)
E_L	Longitudinal convective dispersion coefficient (m ² /s)
F_A	Area adjustment factor
f_{CH_4}	Fugacity of CH ₄ (MPa)
$f_{CH_4}^{eq}$	Methane fugacity at equilibrium under the given temperature (MPa)
f_{CO_2}	Fugacity of CO ₂ (MPa)
$f_{CO_2}^{eq}$	Fugacity of CO ₂ in three-phase equilibrium of liquid water-CO ₂ hydrate-liquid CO ₂ (MPa)
g	Gravity (m/s ²)
h	Molar enthalpy (J/mol)
H	Heat transfer coefficient (W/(m ² ·K))
k	Kozeny constant
k_{ads}	Adsorption rate constant of flowing hydrate particles on pore surface (s ⁻¹)
k_{att}	Attachment rate constant for flowing CO ₂ hydrate particles on pore surface (s ⁻¹)

k_{det}	Detachment rate constant for CO ₂ hydrate particles on pore surface (s ⁻¹)
k_{trap}	Trapping rate constant for CO ₂ hydrate particles (s ⁻¹)
k_{rl}	Relative permeability of liquid phase
k_{rg}	Relative permeability of gas phase
K_D	Permeability (m ²)
K_D^{body}	Permeability of pore body (m ²)
K_D^{throat}	Permeability of pore throats (m ²)
K_{D0}	Initial permeability (m ²)
K_L	Longitudinal dispersion coefficient [m ² /s]
K_{MH_0}	Intrinsic kinetic constant for MH dissociation (mol/(m ² ·MPa·s))
M_{CO_2}	Molecular weight of CO ₂
M_{H_2O}	Molecular weight of water
K_{MH}	Kinetic rate constant for MH formation (mol/(m ² ·s·MPa))
N_{MH}	Hydration number of water
n_l	Empirical exponent of liquid relative permeability
n_g	Empirical exponent of gas relative permeability
P_0	Gas entry pressure (Pa)
P_{Ca}	Capillary pressure (Pa)
P_{fp}	Fracture pressure (Pa)
P_{ob}	Overburden pressure (Pa)
P_l	Pressure of liquid phase (Pa)
P_g	Pressure of gas phase (Pa)
$\dot{q}_{Patt}$	Attachment rate of flowing hydrate particles (mol/(m ³ ·s))
$\dot{q}_{dsol}$	Dissolution/exsolution rate of liquid CO ₂ in/from water (mol/(m ³ ·s))
$\dot{q}_{Ptrap}$	Trapping rate of flowing hydrate particles (mol/(m ³ ·s))
$\dot{q}_{CH}^{form}$	Rate of CO ₂ hydrate generation (mol/(m ³ ·s))
$\dot{q}_{CO_2}^{CH}$	Rate of conversion of liquid CO ₂ droplets to CO ₂ hydrate particles (mol/(m ³ ·s))
$\dot{q}_{CH_4}^{MH form}$	Rate of methane gas consumed during MH formation (mol/(m ³ ·s))
$\dot{q}_{CH_4}^{MH diss}$	Rate of methane gas released during MH dissociation (mol/(m ³ ·s))
$\dot{q}_{H_2O}^{CH form}$	Consumption rate of water during CO ₂ hydrate particle generation (mol/(m ³ ·s))
$\dot{q}_{H_2O}^{CH diss}$	Water generation due to dissociation of CO ₂ hydrate film (mol/(m ³ ·s))
$\dot{q}_{H_2O}^{CH dsol}$	Rate of water generation due to hydrate particle dissolution (mol/(m ³ ·s))
$\dot{q}_{H_2O}^{MH diss}$	Water generation due to dissociation of MH (mol/(m ³ ·s))
$\dot{q}_{H_2O}^{MH form}$	Rate of water generation due to MH formation (mol/(m ³ ·s))
$\dot{q}_{Patt}^{dsol}$	Dissolution rate of attached CO ₂ hydrate particles (mol/(m ³ ·s))
$\dot{q}_{PF}^{dsol}$	Dissolution rate of flowing CO ₂ hydrate particles (mol/(m ³ ·s))
$\dot{q}_{Pimm}^{dsol}$	Dissolution rate of trapped CO ₂ hydrate particles (mol/(m ³ ·s))
$\dot{q}_{PT}^{dsol}$	Dissolution rate of total CO ₂ hydrate particles (mol/(m ³ ·s))
$\dot{q}_{wCO_2}^{dsol}$	Rate of CO ₂ dissolution in water from dissolution of CO ₂ hydrate particles (mol/(m ³ ·s))
$\dot{q}_{CH}^{dsol}$	Dissolution rate of CO ₂ hydrate film (mol/(m ³ ·s))
$\dot{q}_{Ptrap}^{diss}$	Trapped CO ₂ hydrate particle consumption rate due to dissociation of hydrate film (mol/(m ³ ·s))
$\dot{q}_{Patt}^{diss}$	Attached CO ₂ hydrate particle consumption rate due to dissociation of hydrate film (mol/(m ³ ·s))
$\dot{q}_{PF}^{diss}$	Flowing CO ₂ hydrate particle consumption rate due to dissociation of hydrate film (mol/(m ³ ·s))
$\dot{q}_{CH}^{diss}$	Dissociation rates of CO ₂ hydrate film around CO ₂ hydrate particles (mol/(m ³ ·s))
$\dot{q}_{LCO_2}^{diss}$	Liquid CO ₂ generation rate due to dissociation of CO ₂ hydrate film of CO ₂ hydrate particles (mol/(m ³ ·s))

$\dot{q}_{MH}^{form}$	Rate of MH formation (mol/(m ³ ·s))
$\dot{q}_{MH}^{diss}$	Rate of MH dissociation (mol/(m ³ ·s))
$\dot{q}_p$	Rate of CO ₂ hydrate particle generation (mol/(m ³ ·s))
Q	Generated heat during hydrate formation (J/mol)
Q_g	Gas flow rate (SC m ³ /day)
Q_w	Water flow rate (SC m ³ /day)
r_h	Hydraulic radius (m)
r_{h0}	Initial hydraulic radius (m)
r_h^{body}	Pore body hydraulic radius (m)
r_{h0}^{body}	Initial pore body hydraulic radius (m)
r_h^{throat}	Pore throat hydraulic radius (m)
r_{h0}^{throat}	Initial pore throat hydraulic radius (m)
S_{CO_2}	Saturation of total CO ₂
S_{CH}	CO ₂ hydrate saturation
S_e	Saturation of emulsion
S_g	Saturation of methane gas
$S_{gr,e}$	Effective residual gas saturation
S_h	Total hydrate saturation in porous media
S_{H_2O}	Water saturation
S_l	Liquid phase saturation
$S_{lr,e}$	Effective residual saturation of liquid phase
S_{LCO_2}	Liquid CO ₂ saturation
S_{MH}	Saturation of MH
S_{NaCl}	NaCl saturation
S_{PA}	Saturation of accumulated hydrate particles
S_{pads}	Saturation of adsorbed hydrate particles on pore surface
S_{patt}	Saturation of attached CO ₂ hydrate particles on pore surface
S_{PF}	Saturation of flowing CO ₂ hydrate particles
S_{Ptrap}	Immobilized CO ₂ hydrate saturation
S_{PT}	Total saturation of CO ₂ hydrate particles
t	Time (s)
t_h	Diffusion layer thickness (m)
t_p	Production time (s)
T	Temperature (K)
T_∞	Surrounding temperature (K)
$\vec{u}_e$	Darcy velocity of the emulsion (m/s)
$\vec{u}_l$	Darcy velocity of the liquid phase (m/s)
$\vec{u}_g$	Darcy velocity of the gas phase (m/s)
U	Molar internal energy (J/mol)
V_b	Bulk volume (m ³)
V_g	Grain volume (m ³)
V_{p0}	Initial volume of pore (m ³)
V_{PA}^{body}	Volume of accumulated hydrate particles in the pore body (m ³)
V_{PA}^{throat}	Volume of accumulated hydrate particles in the pore throats (m ³)
V_{wCO_2}	Partial molar volume of dissolved CO ₂ in water (m ³ /mol)
W	Work done by hydrate formation/generation (J/mol)

Greek letters

α	Volume fraction of CO ₂ hydrate film in the CO ₂ hydrate particle
β	Dissolution rate constant for liquid CO ₂ droplets in water (s ⁻¹)
ε	Simulation tolerance
ε_a	Absolute tolerance level of simulation
ε_r	Relative tolerance level of simulation
γ	CO ₂ hydrate particle formation rate constant (s ⁻¹ ·MPa ⁻¹)
ζ	Threshold value for $\frac{D_t}{D_p}$ determining k_{trap}
ΔE_{MH}	MH dissociation activation energy (J/mol)
ΔH_{CH}	Heat of CO ₂ hydrate formation/dissociation (J/mol)
ΔH_{MH}	Heat of MH formation/dissociation (J/mol)
ΔH_S	Dissolution heat of CO ₂ in water (J/mol)
λ	Overall thermal conductivity (W/(m·K))
ρ_{brine}	Molar density of brine (mol/m ³)
ρ_{CH}	Molar density of CO ₂ hydrate film around liquid CO ₂ droplets [mol/m ³]
ρ_g	Molar density of methane gas (mol/m ³)
ρ_{H_2O}	Molar density of water (mol/m ³)
ρ_{LCO_2}	Molar density of liquid CO ₂ (mol/m ³)
ρ_{MH}	Molar density of MH (mol/m ³)
ρ_{NaCl}	Molar density of sodium chloride (mol/m ³)
ρ_P	Molar density of CO ₂ hydrate particles (mol/m ³)
ρ_{wCO_2}	Molar density of dissolved CO ₂ in water
$\hat{\rho}_g$	Methane gas density (kg/m ³)
$\hat{\rho}_{gr}$	Mass density of rock (kg/m ³)
$\hat{\rho}_{H_2O}$	Mass density of water (kg/m ³)
$\hat{\rho}_e$	Mass density of the C/W emulsion (kg/m ³)
$\hat{\rho}_l$	Mass density of the liquid phase (kg/m ³)
ϕ	Porosity
ϕ_0	Initial porosity
χ_{H_2O}	Volume fraction of water in emulsion
χ_{LCO_2}	Volume fraction of liquid CO ₂ droplets in the emulsion
χ_{NaCl}	Volume fraction of NaCl in the emulsion
μ_b	Viscosity of brine (Pa·s)
μ_{CO_2}	Viscosity of CO ₂ (Pa·s)
μ_{H_2O}	Viscosity of water (Pa·s)
μ_e	Effective viscosity of emulsion (Pa·s)
μ_g	Methane gas viscosity (Pa·s)
μ_l	Effective viscosity of liquid phase (Pa·s)
ϑ	Poisson's ratio
θ	Degree of inhomogeneity
σ_w	Water pressure gradient (Pa/m)
σ_b	Rock overburden pressure gradient (Pa/m)

Chapter 1

Introduction

1.1 The dominance of CO₂ and CH₄ in global warming

The buildup of greenhouse gases in Earth's atmosphere is causing global warming, which presents a major danger to our planet. Since the start of the industrial age, the increase in atmospheric carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) has been the dominant cause of climate change attributed to human activity [1].

Bhaskar et al. quantified that the combined effect of CO₂ and CH₄ accounts for approximately 43% of the observed variability in recent global temperatures, with CO₂ providing a larger share at ~24% and CH₄ contributing ~19% [2]. Fossil fuel combustion, cement production, and land-use change are driving the escalating atmospheric CO₂ concentration [3], [4], [5]. Sources of atmospheric CH₄ originate at the Earth's surface, where anthropogenic (human-caused) emissions account for the majority (60%), while natural emissions contribute the remaining 40% [6]. Methane concentrations have escalated by about 150% since the preindustrial age, significantly outpacing the increase in CO₂ concentrations, which have risen by less than 50% [7]. To successfully meet the temperature goals outlined in the Paris Agreement, addressing greenhouse gases other than CO₂ is a required component of global warming limitation efforts [1].

Of the substantial CH₄ reservoirs that naturally exchange with the ocean and atmosphere, gas hydrates are of particular relevance to global climate [7]. Specifically, ocean warming related to climate change has been proposed to cause their dissociation and methane leakage on the seafloor [8], a process considered important in the global carbon cycle and the Earth's climate in a long-term (e.g., 10³ years) perspective [8]. Given the profound impact of both escalating anthropogenic CO₂ emissions and the potentially massive, long-term threat posed by CH₄ release from natural stores like gas hydrates, it is imperative to develop coupled mitigation and resource development strategies. Therefore, the following sections will delve into the mechanisms of methane hydrate (MH) production and the opportunity for simultaneously and securely storing CO₂ within these geological formations.

1.2 CH₄ hydrates: Resource and challenge

Gas hydrates are non-stoichiometric clathrate compounds composed of hydrogen-bonded water molecules that form a crystalline, cage-like structure trapping guest gas molecules (chiefly methane) [9]. This structure persists only under high-pressure and low-temperature conditions, maintaining the gas in a solid, ice-like phase. Natural gas hydrates are predominantly Structure I or Structure II; Structure H is rare in nature [10]. Details on the geometry and characteristics of these clathrate hydrate structures are presented in **Table 1.1** [11].

Table 1.1 Characteristics of hydrate cavities.

Properties of the cages	I		II		H		
Cavity	Small	Large	Small	Large	Small	Medium	Large
Description	5 ¹²	5 ¹² 6 ²	5 ¹²	5 ¹² 6 ⁴	5 ¹²	4 ³ 5 ⁶ 6 ³	5 ¹² 6 ⁸
Cavity count in unit cell	2	6	16	8	3	2	1
Water molecules count within each cavity	20	24	20	28	20	20	36
Total number of water molecules per unit cell	46		136		34		
Examples of guest molecules	CH ₄ , CO ₂		Propane, Iso-butane		Methane + Neohexene, Methane + Cyclohep		

The differences in cage sizes and shapes determine which guest molecules (e.g., CH₄ or CO₂) can be stably hosted, and therefore strongly influence phase behavior in hydrate systems.

Global studies place the estimated size of methane hydrate reserves between 0.2×10^{15} to 120×10^{15} m³ at standard temperature and pressure (STP) conditions [9], a range that greatly exceeds the 0.15×10^{15} m³ of methane at STP of conventional gas reserves [10]. Therefore, the successful development of methane hydrates represents a strategic opportunity to diversify the global energy supply and enhance long-term energy security [12].

MH-bearing layers (MHBLs) are found in abundance within Arctic permafrost regions and in the shallow sediments beneath deep-ocean continental margins [10], [12], [13], [14]. Due to these varying geological settings, effective development and production of these immense

reserves require detailed knowledge of the local geological structure. Gas hydrate reservoirs are thus categorized into three distinct classes based on their subsurface architecture, as depicted in **Figure 1.1** [15], [16], [17].

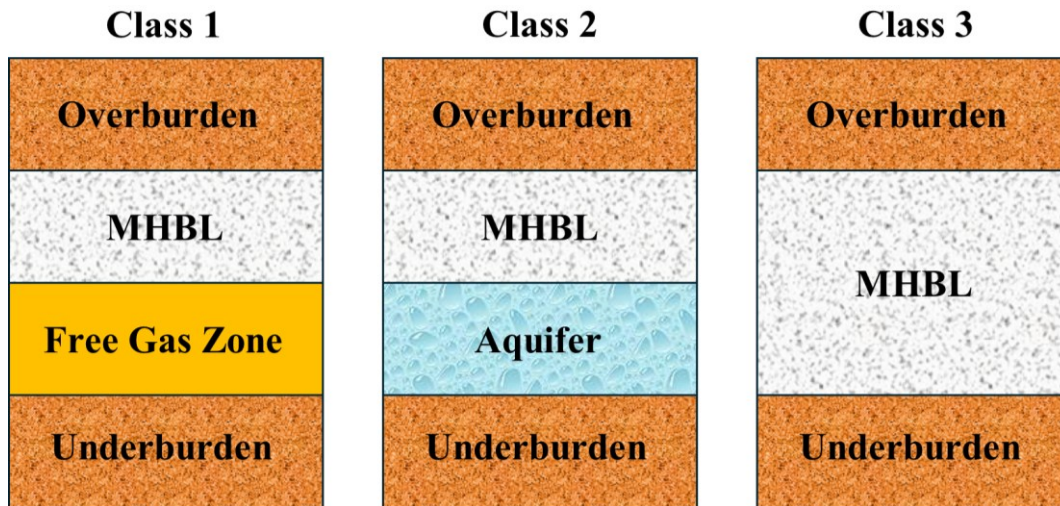


Figure 1.1 Schematic illustration of the three primary gas hydrate reservoir types (Based on reservoir classification concepts from Moridis and Sloan [15], and Xia et al. [17]).

Class 1 accumulations represent the most favorable reservoir type for gas production, characterized by a permeable MHBL resting directly atop a permeable free gas zone. Key global examples of this Class 1 architecture include the Messoyakha field [18] in West Siberia, Russia, and the major regional accumulations on the North Slope, Alaska, such as the Eileen and Tarn Gas Hydrate Trends and the extensively studied Mount Elbert site [19], and the Krishna-Godavari Basin in India [20].

Class 2 deposits consist of MHBLs overlying a mobile water zone, or aquifer. This configuration, exemplified by the Mallik gas hydrate reservoir in the Mackenzie Delta, Canada [21], [22], and the Ullung Basin accumulations in South Korea's East Sea [23], [24], is considered moderately favorable for hydrate production. The underlying water flow acts as a natural heat source promoting hydrate dissociation. However, this benefit is counterbalanced by the significant operational risk of uneconomic water production at the wellhead.

Class 3 reservoirs are the least favorable for production, defined by an MHBL that lacks an underlying permeable free gas or mobile water zone, forcing MH dissociation to rely on slow, inefficient heat conduction from the surrounding rock. Examples of these reservoir types include certain portions of the Gulf of Mexico (offshore USA) [24], [25] and complex areas within the Shenhu Area of the South China Sea [17], [25], [26], [27].

Many reservoirs exhibit mixed behavior: the Nankai Trough in Japan, for example, is a Class 2/3 hybrid where upper layers function as Class 3 (silt/sand) and lower layers function as Class 2 (sand-dominated) [24], [28]. Similarly, the Shenhu Area in the South China Sea contains sites that are dominantly Class 3, yet specific, characterized sites have been confirmed as a Class 1 accumulation due to the presence of an underlying free gas layer [29], [30].

To produce gas from MH reservoirs, a disruption in the thermodynamic equilibrium of hydrates is necessary, which is typically achieved through methods such as depressurization, thermal stimulation [31], [32], chemical inhibitor injection [33], [34], combined methods, carbon dioxide injection [35], [36], [37], or direct mining [38].

The depressurization method is currently regarded as the most viable and promising technique due to its potential for a high energy profit ratio. [39]. The Messoyakha gas field (a Class 1 accumulation) is the sole project to achieve commercial exploitation of gas hydrates worldwide [40]. This success was achieved by perforating the underlying Free Gas Zone, which induced decomposition of the hydrate layer due to pressure drop. This co-production strategy was highly effective, yielding $6.9 \times 10^9 \text{ m}^3$ (out of $13.3 \times 10^9 \text{ m}^3$ total gas) of gas from hydrate dissociation alone [41], and, critically, proved beneficial for maintaining reservoir stability [42].

Two trial tests were conducted using depressurization in the Nankai Trough offshore Japan in 2013 and 2017. While these tests partially verified technical feasibility, they were primarily hindered by sand production, which prematurely shut down the 2013 well and one of the 2017 wells [43]. The numerical simulation indicates that the core challenge of depressurization in the Nankai Trough is the high water production from permeable, water-rich layers, highlighting the necessity of zone isolation to separate the MHBL from the underlying aquifer for economic gas production [44]. To overcome these limitations, researchers have proposed strategies to seal MHBL. Numerical simulations suggest that such seals can mitigate water invasion, enhance pressure gradient propagation within the MHBL, and improve gas recovery [45], [46].

Beyond these fluid and sediment issues, low matrix permeability represents another critical obstacle to depressurization. The low gas production rate observed during the first offshore test in the Shenhu Area is attributed to the reservoir's low permeability (2–5 mD), indicating that the single depressurization method is insufficient for commercial exploitation [47]. Therefore, hydraulic fracturing is considered a promising solution to create highly conductive paths through the hydrate formation and enhance productivity [47].

While depressurization remains the primary method, other techniques face significant efficiency and operational limitations. The inhibitor injection method, which shifts the hydrate equilibrium curve by injecting chemicals, is hampered by high cost, low efficiency, and the difficulty of ensuring wide and rapid diffusion of the inhibitors throughout the formation [47]. Similarly, the gas replacement method—in which CH_4 is replaced by injecting CO_2 or other hydrate-forming gases—is subject to high operational costs and a low CH_4 replacement rate [47]. Field trials further revealed that this method introduces additional challenges, as the secondary CO_2 hydrate formation near the wellbore reduces permeability and hinders gas exchange, severely limiting its commercial viability [48], [49]. The rapid formation of stable CO_2 hydrate, which hinders the replacement method, can be paradoxically utilized to create a seal, isolating the MHL from the underlying aquifer to mitigate the critical problem of water invasion.

1.3 Dual-purpose CO_2 injection

The influx of warmer water from the permeable underburden (UB) significantly weakens the depressurization process and poses a major obstacle to long-term production by requiring additional energy for water lifting [50]. The paradox identified in the previous section, where the clogging tendency of CO_2 hydrate formation can be utilized for hydraulic isolation of the MH layer from the underlying aquifer, motivates the focus on CO_2 hydrate as a sealing agent to be coupled with depressurization for enhanced recovery from MH reservoirs (**Figure 1.2**).

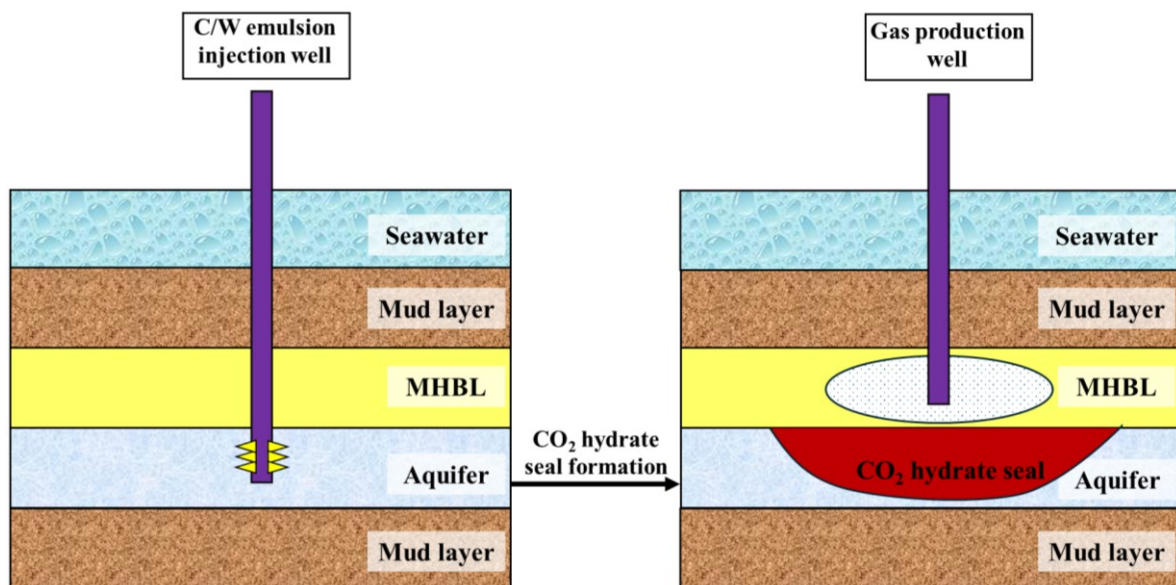


Figure 1.2 Schematic of CO_2 hydrate utilization as a sealing agent to restrict pressure gradient propagation within the MHL.

Research has shown that CO₂ hydrate provides both pore sealing and mechanical reinforcement [51]. Studies on the mechanical properties of hydrates have found that CO₂ hydrate samples exhibit greater strength than natural gas hydrates [52]. This enhanced strength contributes to reservoir stability, with research suggesting that a thicker CO₂ hydrate cap can increase a submarine slope's resistance to landslides during gas exploration [51].

Furthermore, forming a seal below the MHL also serves as a significant method for hydrate-based CO₂ storage (HBCS). HBCS offers enhanced storage capacity, as converting free CO₂ into solid hydrate structures can store up to 160 volumes of CO₂ gas per unit volume of CO₂ hydrate under standard conditions [53]. This process also offers faster reaction kinetics compared to other CO₂ trapping methods, such as mineral trapping [54].

Experimental work by Gauteplass et al. [54] showed that direct injection of liquid CO₂ into brine-saturated cores often led to pore blockage, hindering injectivity. Numerical simulations further indicated that maintaining injectivity within the CO₂ hydrate stability zone (HSZ) often requires active pressure management—such as water production—to keep the reservoir pressure below CO₂ hydrate formation pressure [5].

CO₂-in-water (C/W) emulsions are now considered a strong candidate for enhanced hydrate-based sequestration because the emulsion flow effectively sweeps the formed CO₂ hydrate particles downstream (**Figure 1.3**). This method addresses the traditional storage difficulties, which include achieving high sweep efficiency and sufficient injectivity, as well as overcoming the tendency for CO₂ to dominate as a free phase over hydrate formation [55].

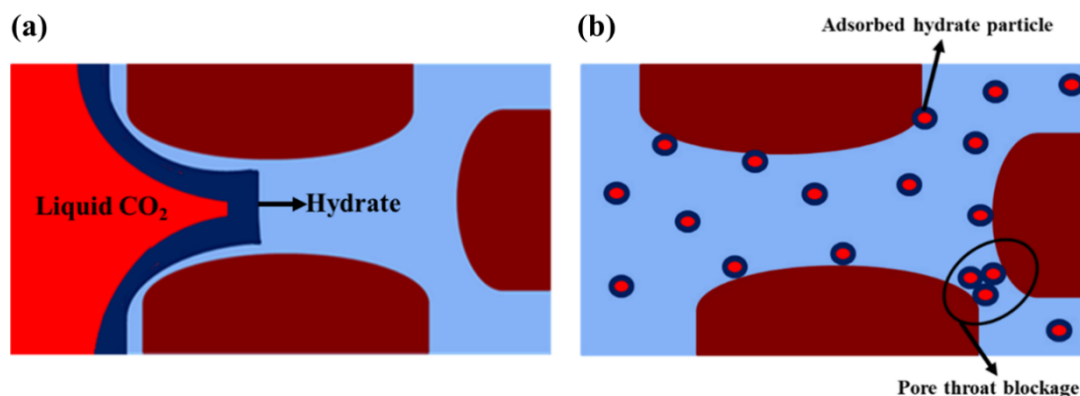


Figure 1.3 Comparing different approaches for CO₂ injection. (a) Pore blockage mechanism during liquid CO₂ injection in porous media; (b) Hydrate particles swept downstream during C/W emulsion injection (Reproduced from Bahmaee & Murata, [55], licensed under CC BY 4.0.).

Pore-scale studies further confirmed low sweep efficiency and hydrate nucleation occurring at the CO₂–water interfaces, causing immobilization of liquid CO₂ [56]. Experimental comparisons have demonstrated the substantial superiority of C/W emulsions over liquid CO₂ injection. Studies by Chen et al. [57] found that the C/W emulsion improved pore water displacement, delayed breakthrough, and increased hydrate phase sequestration density by a factor of 2.42. These benefits were attributed to the emulsion's large interfacial area and its tunable CO₂-to-water ratio. Further research consistently supports these findings, reporting that C/W emulsion injection leads to a 45% to 62% enhancement in displacement effectiveness and nearly triples the CO₂ hydrate conversion rate compared to using pure liquid CO₂ [58].

Despite the benefits of C/W emulsion injection, sustaining the process remains challenging due to the high risk of CO₂ hydrate plugging. Factors such as low temperatures and slow injection rates exacerbate this risk, significantly impeding CO₂ sequestration efforts [58]. To mitigate this known challenge, experiments by Ikegawa et al. [59] demonstrated that continuous injection is possible only when the C/W emulsion is injected at the CO₂ hydrate equilibrium temperature (~10 °C) to avoid rapid formation.

To address the water influx problem, Sridhara et al. [60] introduced a single-well, three-stage "huff-and-puff" method for Class 2 deposits. Their approach utilized the injection of liquid CO₂ at an elevated temperature (13 °C) into the aquifer underlying MHBL, followed by a soaking and depressurization phase. This specific thermal approach was designed to preclude immediate hydrate formation near the wellbore. Simulations of this process showed it successfully achieved a substantial increase in methane recovery and concurrent reduction in water production.

Alternatively, Sun et al. [61] conducted controlled experiments to assess cap formation by injecting either liquid CO₂ or C/W emulsions at around 15 °C into the overburden (OB). They observed that the emulsion-based approach was universally more effective, producing more methane while substantially limiting CO₂ production compared to liquid CO₂. They tested emulsions with 30%, 50%, and 70% CO₂ volume fractions, finding that the 50% fraction was optimal for maximizing recovery and minimizing water production. The study demonstrated two key failure points: the 30% emulsion proved insufficient to form a continuous, impermeable seal, thereby allowing undesirable water invasion. Conversely, the 70% emulsion contained residual liquid CO₂ droplets that migrated and formed secondary hydrates within the MHBL, resulting in lower methane recovery than the 50% case.

Despite these advancements, two key uncertainties persist: managing low temperature injectivity and defining long-term seal viability. Preheating CO₂ for injection, as used in earlier studies [60], [61], is costly, especially in permafrost settings. Furthermore, experiments show that decreasing the CO₂ emulsion injection temperatures promote emulsion stability and the formation of a continuous, low-permeability CO₂-hydrate seal; whereas higher injection temperatures cause the emulsion to delaminate and produce inhomogeneous hydrate structures with reduced mechanical stability [62], indicating injection at or near in-situ temperatures is thermodynamically and economically desirable. Experimental studies by Masuda laboratory [63] under CO₂ hydrate stability conditions (~7 MPa, ~7 °C) showed sustained injection of C/W emulsion only under CO₂ volume fractions as low as 10%, while higher CO₂ fractions (20% and 30%) immediately blocked porous media. Crucially, they demonstrated that water-alternating-emulsion (WAE) cycles significantly delayed the onset of porous media clogging and temporarily improved injectivity of higher CO₂ volume fractions; however, sustained injection was not achieved. The delay in clogging is attributed to the water slugs dissolving or sweeping away hydrate particles accumulated near the wellbore (**Figure 1.3b**). Nonetheless, this key finding was established using small laboratory cores (~10 cm), which cannot fully represent the complex, heterogeneous conditions and pressure/temperature gradients of a field-scale reservoir, necessitating a comprehensive numerical framework for operational design.

However, even with optimized low-temperature injectivity, the long-term efficacy of a CO₂ hydrate seal remains uncertain due to conflicting laboratory results on dissolution under realistic flow conditions [64], [65]. While static CO₂ hydrate dissolution rates are approximately 194 cm/year, advection-driven dissolution can reach rates as high as 365 cm/year, which would severely shorten cap lifetime [65], particularly when thermodynamically accelerated by warm UB water influx [66], [67]. Cui et al. [62] determined that the durability of CO₂ hydrate seals formed by C/W emulsions is sensitive to the confining pressure, noting that elevated pressure leads to erosion of the seal and a shorter effective pressure-bearing lifespan. The combination of these factors highlights that the general fate of CO₂ and the long-term integrity of the seal require a comprehensive, field-scale, coupled Thermo-Hydro-Chemical (T-H-C) assessment to evaluate practical longevity.

1.4 Thesis objectives and outline

The preceding sections have established a critical paradox in the utilization of Class 2 MH deposits: while CO₂ hydrate formation is essential for creating the hydraulic isolation seal needed to mitigate water influx and enhance CH₄ recovery, its rapid formation simultaneously poses the major operational barrier of near wellbore injectivity loss. The literature review highlights that previous research has primarily addressed these issues in isolation, often relying on energy-intensive thermal strategies or failing to prove long-term field-scale operational injectivity and CO₂ hydrate seal viability.

This research addresses this gap by developing and validating a coupled T-H-C numerical framework, which is subsequently used to design and prove a novel, dual-purpose C/W emulsion injection strategy for both enhanced methane hydrate recovery and secure HBCS. The ultimate aim is to analyze the operational factors and criteria for low-temperature C/W emulsion injection strategy that overcomes the critical barrier of near-wellbore injectivity loss and simultaneously establishes a viable methodology for HBCS and provides effective long-term hydraulic isolation of MHL from underlying aquifer, thereby mitigating excessive water production and maximizing CH₄ recovery in Class 2 MH deposits.

This overarching goal is broken down into three distinct, yet interconnected, objectives:

1. Framework development and validation: To develop and validate a coupled T-H-C numerical framework capable of accurately simulating the non-isothermal, multi-phase flow and CO₂ hydrate formation kinetics of C/W emulsion injection within porous media. This step will lay the fundamental model groundwork for all subsequent optimizations.
2. Injectivity optimization, HBCS quantification, and long-term CO₂ security assessment: To utilize the validated framework to investigate operational strategies, define criteria for sustained CO₂ injection, and simultaneously quantify the resulting HBCS capacity, assess the long-term fate of the sequestered CO₂, and confirm the model's robustness via 3D reactor experiment validation (as presented in Chapters 4 and 5).
3. Operational viability of CO₂ hydrate seal for enhanced methane recovery: To numerically evaluate the CO₂ hydrate seal integrity and performance, quantifying the resulting enhanced CH₄ recovery, aquifer influx control and partitioning and sequestration of injected CO₂.

The structure of this thesis is logically organized to reflect the progression from fundamental model development to field-scale operational optimization:

Chapter 1 provides the background on climate change, the dual importance of CH₄ hydrates (as both a vast potential energy resource and a significant climate change hazard), the challenges of conventional production, and the motivation for CO₂ dual-purpose injection.

Chapter 2 details the comprehensive T-H-C numerical framework developed for simulating C/W emulsion injection and CO₂ hydrate formation within porous media. It presents the full suite of governing equations for non-isothermal, multi-phase flow, including the specific constitutive relationships used to model the unique properties of the emulsion and the dynamic kinetics of CO₂ hydrate formation. This chapter establishes the fundamental theoretical and mathematical basis for all subsequent numerical studies.

Chapter 3 presents the application of the T-H-C framework to a 1D numerical domain and validates the resulting flow behavior and hydrate formation against experimental data. This validation step provides crucial insights into the various phenomena occurring in porous media, confirming the model's accuracy in capturing the complex interactions between C/W emulsion flow and hydrate kinetics. The results are used to identify the initial injection challenges and lay the groundwork for developing optimized injection schemes.

Chapter 4 focusing on Objective 2, utilizes the validated framework to systematically investigate operational strategies for low-temperature C/W emulsion and WAE injection scheme. It investigates the influence of operational factors—such as hydrate film volume fraction around liquid CO₂ droplet (α), salinity effects, and the use of WAE injection—on injectivity, thereby defining the critical operational criteria for sustained CO₂ delivery.

Chapter 5, a key part of Objective 2, assesses the overall performance and security of the storage strategy resulting from the operational criteria defined in Chapter 4. It quantifies and partitions the CO₂ storage capacity, evaluating both HBCS and dissolution-based CO₂ storage (DBCS). This is followed by an analysis of the long-term 100-year simulation tracking the sequestration fate of CO₂, thereby establishing the long-term stability criteria. Finally, the chapter includes the 3D reactor experiment validation, which confirms the model's robustness and scalability for complex flow regimes.

Chapter 6 focusing on Objective 3, applies an optimized C/W emulsion strategy into the aquifer of an arctic Class 2 hydrate deposits, simulating a single injection-soaking-production cycle to demonstrate the twofold advantage of enhanced CH₄ recovery and mitigation of excessive water production, alongside CO₂ storage quantification. The chapter subsequently uses the observed seal failure dynamics to establish the long-term stability criteria and operational limits for the technology.

Chapter 7 integrates the results of this work, summarizing the model calibration and validation, injectivity optimization, hydrate-based CO₂ storage performance, and the gains in methane recovery and aquifer inflow control achieved through in-situ CO₂ hydrate seal formation in Class 2 MH deposits, and discusses their implications for field-scale MH development.

The structure of this thesis is logically organized to reflect the progression from fundamental model development to full-scale reservoir applications (**Figure 1.4**).

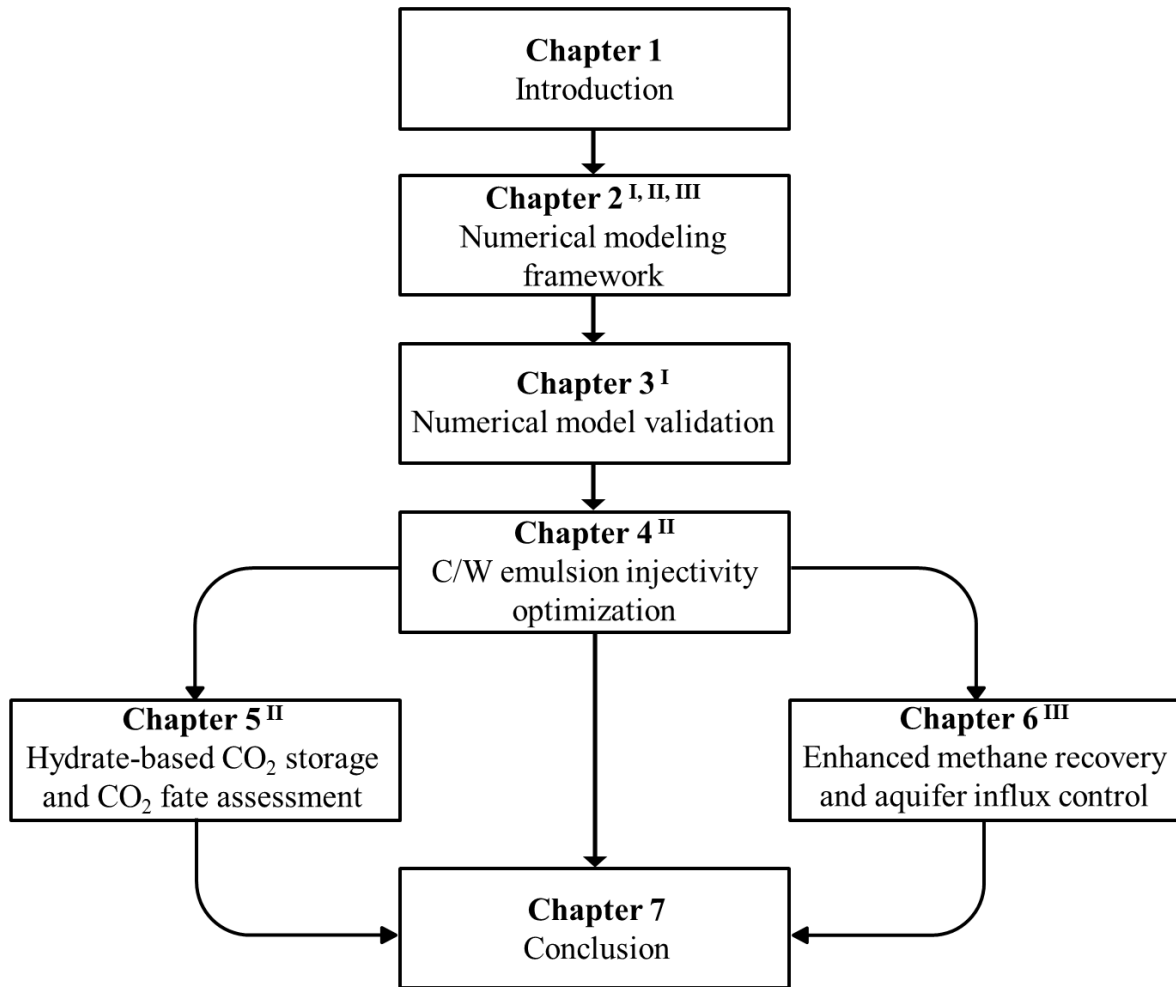


Figure 1.4 Thesis structure. Roman numbers indicate published and submitted papers on these topics mentioned in each chapter (I: Bahmaee et al. [63]; II: Bahmaee and Murata [55]; III: Bahmaee et al. [68]).

Chapter 2

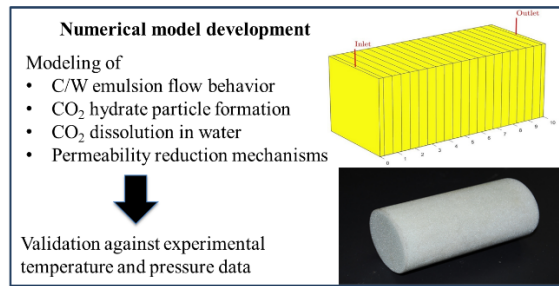
Numerical modeling framework

The numerical framework implemented in this study is a substantial evolution and extension of the core T-H-C model originally developed in Professor Masuda's laboratory [69]. To meet the requirements of simulating C/W emulsion injection and its complex near-wellbore behavior, the following key improvements and extensions have been implemented for this study:

1. Modeling the dissolution of CO₂ hydrate particles in water.
2. Correcting the heat of dissolution of CO₂ in water for high pressure conditions.
3. Modifying the mechanism and modeling of CO₂ hydrate particle formation.
4. Improving the constitutive model for C/W emulsion viscosity.
5. Refining the density model for dissolved CO₂ and developing a new brine-CO₂ density correlation.
6. Rigorous validation with a finer grid resolution (21 grid cells in this study compared to 10 in the previous work).
7. Extending the validity and application of the numerical model for 3D field scale reservoir simulations.

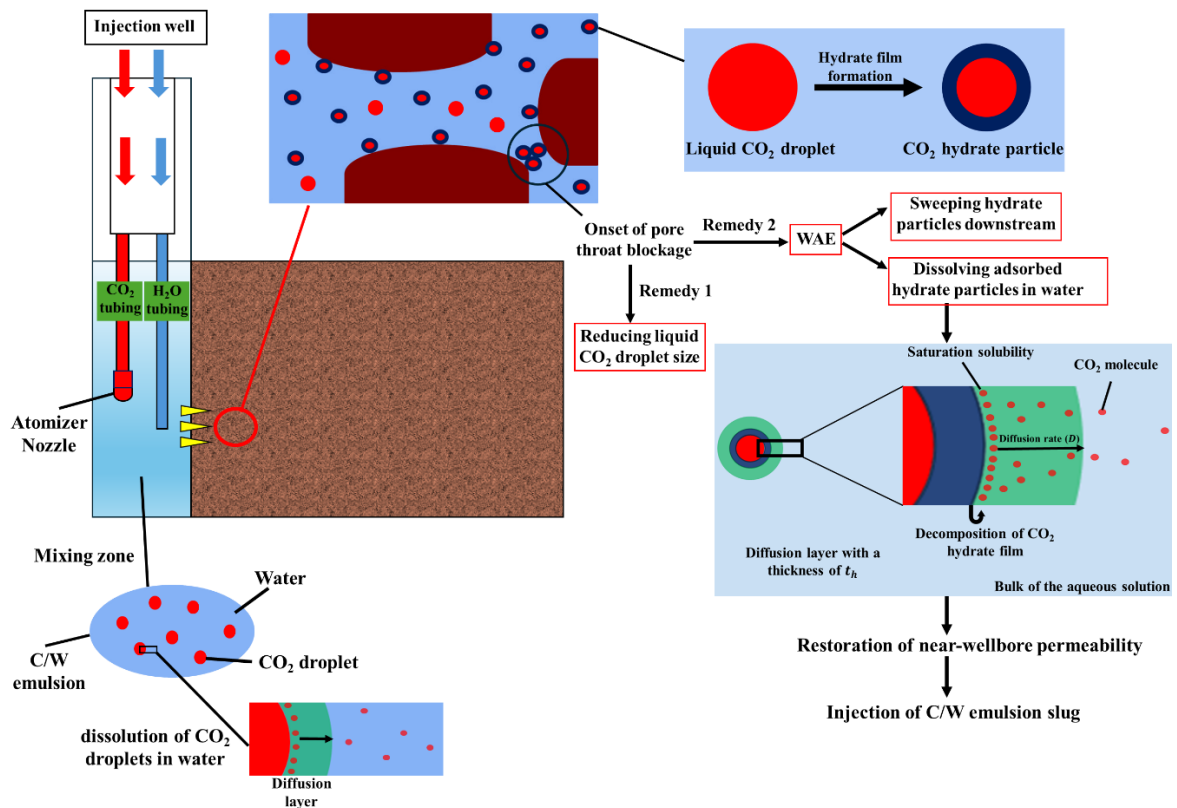
The integration of these numerical developments and their progression from core-scale validation to field-scale application is visually summarized in the integrated research framework shown in **Figure 2.1**.

Chapters 2 and 3



Chapters 4 and 5

Injection optimization and CO₂ storage



Chapter 6

Enhanced methane recovery and aquifer influx control

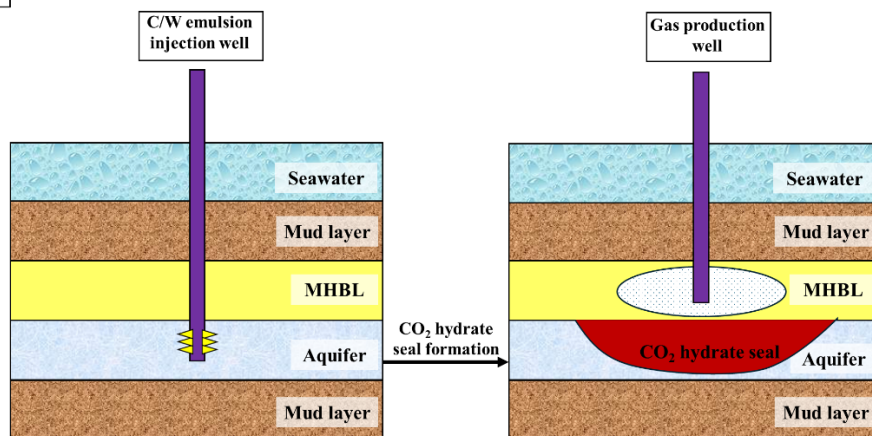


Figure 2.1 Integrated research framework.

2.1 Challenges in modeling emulsion-hydrate flow

Modeling the flow behavior of a C/W emulsion undergoing hydrate formation within a porous medium presents significant complexities. A high-fidelity model must account for the distinct effects of CO₂ hydrate particle accumulation on both pore throats and pore bodies, as done in this study, which enhances the model's accuracy but contributes substantially to the overall computational cost. Further complexity arises from accounting for dynamic variations in parameters as the hydrate particle formation rate (γ), the volume fraction of hydrate film around liquid CO₂ droplets (α), and the hydration number (stoichiometry). Additionally, accurately modeling the diffusion processes and the inherent stochastic nature of hydrate generation is difficult. To address these collective challenges and strike a necessary balance between predictive accuracy and computational feasibility for large-scale simulations, the numerical framework relies on a set of strategic assumptions.

2.2 Core numerical model assumptions

The numerical model is built upon the following foundational assumptions to simplify the multi-component, multi-phase T-H-C interactions for simulating C/W emulsion injection within the methane hydrate reservoir:

1. Hydrate formation is assumed to occur exclusively within the porous medium and not before the C/W emulsion enters the porous medium.
2. The C/W emulsion fluid is treated as stable throughout the simulation, with no separation or phase breakdown occurring between the liquid CO₂ and water components.
3. Liquid CO₂ droplets undergo a conversion process into hydrate particles, with a defined hydrate film thickness forming around the CO₂ droplets at a specified rate after a defined induction time [s].
4. Due to the small size and well-dispersed nature of the liquid CO₂ droplets and hydrate particles, the C/W emulsion and the dispersed hydrate particles are modeled as a single, continuous fluid phase.

5. Hydrate particles influence the flow behavior by becoming trapped or adsorbed onto the pore surfaces and at the pore throats, which is the primary mechanism for reducing the permeability of the porous medium.
6. Based on established practices in the literature [70], [71], [72]—and to enable a robust comparison with the baseline depressurization method—methane dissolution in the water phase is assumed to be negligible.
7. In-situ $\text{CO}_2\text{-CH}_4$ hydrate replacement reactions are excluded to reduce simulation complexity. This assumption is justified because the effective exchange layer is confined to a thin shell (5 μm) after which the reaction rate becomes negligible (smaller than 0.5 $\mu\text{m/day}$) due to mass transfer limitations [73].
8. No multi-component phase equilibrium (i.e., CO_2 and CH_4 mixing in the gas phase) was incorporated. This simplification treats methane as a pure component in the gas phase. The validity of this phase approximation is demonstrated in Section 6.2.

These assumptions serve as the foundation for the numerical model, allowing for the representation of the key flow and hydrate formation phenomena in the C/W emulsion within the porous medium.

2.3 Emulsion stability justification

The operational longevity of the C/W emulsion in the reservoir is a critical consideration. Although C/W emulsions are thermodynamically unstable systems, their behavior within porous media differs significantly from that in open fluid environments. In an open system, droplet coarsening, typically driven by Ostwald ripening, is the expected outcome [74]. However, studies have observed an anti-coarsening effect within porous media, where smaller droplets grow at the expense of larger ones [75]. Furthermore, the high shear forces inherent in field-scale injections promote emulsion stability by breaking down larger droplets into a more uniform, smaller size distribution [76], [77]. Enhanced stability is also provided by the high density of CO_2 droplets under the high-pressure and low-temperature conditions of the HSZ [78], which minimizes buoyancy-driven separation. Given this evidence of stabilization and homogenization within the porous medium, the model is justified in treating the C/W emulsion as a single effective fluid phase.

2.4 Governing equations

2.4.1 Darcy equations

Darcy velocities for gas (composed solely of methane) and liquid phase are defined as below:

$$\vec{u}_l = -\frac{k_{rl}}{\mu_l} K_D (\nabla P_l - \hat{\rho}_l g \nabla z) \quad (2.1)$$

$$\vec{u}_g = -\frac{k_{rg}}{\mu_g} K_D (\nabla P_g - \hat{\rho}_g g \nabla z) \quad (2.2)$$

The variables in the model include the Darcy velocities, $\vec{u}_l$ (m/s) and $\vec{u}_g$ (m/s), for the liquid and gas phases, respectively. K_D (m²) is the permeability of the porous medium, while k_{rl} and k_{rg} are the relative permeabilities of the liquid and methane gas phases. The effective viscosity of the liquid is μ_l (Pa·s), and the viscosity of methane gas is μ_g (Pa·s). The mass densities are $\hat{\rho}_l$ and $\hat{\rho}_g$ (kg/m³) for the liquid phase and methane gas. P_l and P_g (Pa) are the respective liquid and gas pressures. Finally, g (m/s²) represents the gravitational acceleration, and z (m) is the vertical distance.

The capillary pressure (P_{ca}), which is the pressure difference between the gas phase and the liquid phase, is described by a modified Brooks-Corey model [79].

$$P_{ca} = P_g - P_l = P_0 \left(\frac{S_{l,e} - S_{lr,e}}{1 - S_{lr,e} - S_{gr,e}} \right)^{-nc} \quad (2.3)$$

where P_0 is the gas entry pressure, 10⁴ Pa [43]. $S_{l,e}$ and $S_{g,e}$ are the liquid and gas phase saturations based on the effective pore volume [79]. $S_{lr,e}$ and $S_{gr,e}$ are the residual saturations of the liquid and gas phases, taken as 0.25 and 0.01, respectively [43], also defined relative to the effective pore volume [79]. The parameter nc represents the pore-size distribution index, set to 0.65 [80].

The relative permeabilities, k_{rl} and k_{rg} , are calculated using the modified Corey formula [79]. These relationships express the permeability of each phase as a power function of its respective saturation defined relative to the effective pore volume:

$$k_{rl} = \left(\frac{S_{l,e} - S_{lr,e}}{1 - S_{lr,e}} \right)^{n_l}, \quad k_{rg} = \left(\frac{S_{g,e}}{1 - S_{lr,e}} \right)^{n_g} \quad (2.4)$$

$$S_{l,e} = \frac{s_l}{s_l + s_g}, S_{g,e} = \frac{s_g}{s_l + s_g} \quad (2.5)$$

where the empirical exponents (n_l and n_g) are both assumed to be 3 [60].

2.4.2 Treatment of governing conservation equations

The T-H-C framework is completed by the mass conservation equations for the individual components (CH₄ gas, CH₄ hydrate, water, CO₂ dissolved, CO₂ liquid droplets, and CO₂ hydrate particles) and the overall energy conservation equation. Due to the evolving nature of the model's constitutive relationships—particularly improvement of constitutive equations across the published studies forming this thesis—the full, operational set of mass and energy conservation equations used for each chapter's specific simulation is detailed in the corresponding appendix.

These conservation equations are constructed via a series of constitutive relationships that describe the unique physical phenomena central to this study. These critical equations are detailed in the following sections.

2.5 Constitutive and phenomenological models

This section details the specific, empirical equations and physical relationships necessary to model complex, system-specific behaviors such as chemical kinetics, phase transformation rates, and flow resistance and serve as the key constitutive elements of the governing conservation equations.

2.5.1 Constitutive models for kinetics and thermal processes

The governing equations integrate several key mechanisms, including liquid CO₂ droplets dissolution and exsolution, CO₂ hydrate particle generation and dissolution, and CO₂ hydrate film dissociation. The models for the primary C/W emulsion injection processes were developed and rigorously validated against experimental data from the Masuda laboratory [63], while the CO₂ hydrate film dissociation and all MH dissociation/generation equations were adopted directly from established literature.

2.5.1.1 CO₂ hydrate particle generation model

CO₂ hydrate particle initiation (induction time) is treated as arbitrary input data because it is a random process sensitive to the experimental environment. The measured induction time corresponds to the period needed for hydrates to become macroscopically observable—a duration covering both the initial, small-scale nucleation and the subsequent growth phase [10].

The mechanism for hydrate growth involves the assumption that once a defined critical volume fraction of the CO₂ hydrate film (α) has encased the liquid CO₂ droplets, mass transport through that layer—specifically the diffusion of liquid CO₂ and water—is considered insignificant, thereby halting further hydrate expansion. **Figure 2.2** visually represents this particle formation concept.

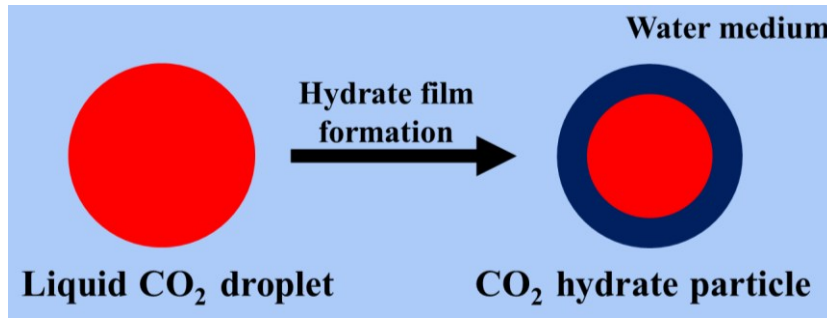


Figure 2.2 CO₂ hydrate particle formation mechanism. The dark blue ring represents the CO₂ hydrate film encasing the red liquid CO₂ droplet core.

The model assumes molar equivalence between the consumed liquid CO₂ droplets and the generated CO₂ hydrate particles to describe the hydrate formation process. This facilitated the use of a correlated rate expression (Equation 2.6), where the rate of consumption of liquid CO₂ droplets ($\dot{q}_{CO_2}^{CH}$ in mol/(m³·s)) or generation rate of CO₂ hydrate particles ($\dot{q}_P$ in mol/(m³·s)) is proportional to initial porosity (ϕ_0), liquid CO₂ saturation ($S_e \chi_{LCO_2}$), and liquid CO₂ molar density (ρ_{LCO_2}):

$$\dot{q}_P = \dot{q}_{CO_2}^{CH} \propto c_1 \phi_0 S_e \chi_{LCO_2} \rho_{LCO_2} \quad (2.6)$$

where c_1 (s⁻¹) is a constant, S_e is the C/W emulsion saturation, and χ_{LCO_2} is the volume fraction of liquid CO₂ droplets in C/W emulsion.

The rate of conversion of liquid CO₂ droplets to CO₂ hydrate particles is adversely affected by temperature increases stemming from heat generation, which lowers the thermodynamic

potential. Based on the equation derived by Malegaonkar et al. [81] this influence is captured by the correlation:

$$\dot{q}_P = \dot{q}_{CO_2}^{CH} \propto (f_{CO_2}^{eq} - f_{CO_2}) \quad (2.7)$$

The variables $f_{CO_2}^{eq}$ (MPa) and f_{CO_2} (MPa) represent the three-phase equilibrium fugacity (liquid water-CO₂ hydrate-liquid CO₂) and the instantaneous fugacity of liquid CO₂, respectively. Combining the right-hand sides of Equation (2.6) and Equation (2.7) yields the following correlation:

$$\dot{q}_P = \dot{q}_{CO_2}^{CH} \propto c_1 \phi_0 S_e \chi_{LCO_2} \rho_{LCO_2} \quad (2.8)$$

To achieve the necessary equivalence between the terms, the integrated correlation was scaled by multiplying the right-hand side of Equation (2.8) by a constant, c_2 (MPa⁻¹):

$$\dot{q}_P = \dot{q}_{CO_2}^{CH} = c_1 c_2 \phi_0 S_e \chi_{LCO_2} \rho_{LCO_2} (f_{CO_2}^{eq} - f_{CO_2}) \quad (2.9)$$

By setting $\gamma = c_1 c_2$ the final form of the CO₂ hydrate particle generation equation becomes:

$$\dot{q}_P = \dot{q}_{CO_2}^{CH} = \gamma \phi_0 S_e \chi_{LCO_2} \rho_{LCO_2} (f_{CO_2}^{eq} - f_{CO_2}) \quad (2.10)$$

where γ (s⁻¹·MPa⁻¹) is the CO₂ hydrate particle generation rate constant. This parameter, together with α , was determined by comparison with experimental results presented in Chapter 3 [63].

The rates of CO₂ hydrate layer formation and the associated water consumption are defined as follows:

$$\dot{q}_{CH}^{form} = \dot{q}_{H_2O}^{CH_{form}} / N_{CH} = \dot{q}_P \frac{\rho_{CH}}{\rho_P} \alpha \quad (2.11)$$

where N_{CH} represents the hydration number of water.

The fugacity of liquid CO₂ (f_{CO_2}) was modeled using a specific correlation developed by the former research group's work in Masuda Laboratory [69].

$$f_{CO_2} = \left(A_1 \left(\frac{P}{P_0} \right)^2 + A_2 \left(\frac{P}{P_0} \right) + A_3 \right) T^2 + \left(A_4 \left(\frac{P}{P_0} \right)^2 + A_5 \left(\frac{P}{P_0} \right) + A_6 \right) T + \left(A_7 \left(\frac{P}{P_0} \right)^2 + A_8 \left(\frac{P}{P_0} \right) + A_9 \right) \quad (2.12)$$

where $P_0 = 1$ MPa.

The coefficients (A_1 through A_9) for the liquid CO₂ fugacity correlation (Equation 2.12) are presented in **Table 2.1**.

Table 2.1 Coefficients for the liquid CO₂ fugacity correlation.

A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9
6.00E-07	-1.10E-07	0.000161	-0.00033	0.00201	-0.03804	0.045923	-0.41377	0.9192

For calculating the equilibrium fugacity ($f_{CO_2}^{eq}$), a correlation was used to determine the equilibrium temperature (T^{eq}) at each pressure. For the equilibrium temperature of CO₂ hydrate in pure water, Equation (2.13) was developed in Masuda laboratory [69] based on the data reported by Ng and Robinson [82]:

$$T^{eq} = A_1 P + A_2 \quad (2.13)$$

where $A_1 = 1.06E-07$ Pa⁻¹, and $A_2 = 282.3289$ K.

However, field scale simulations were conducted considering seawater with salinity of 3.5 wt%. The change in local salinity caused by hydrate phase transitions is a critical modeling consideration. Salt rejection during CO₂ hydrate formation salinity increases, which then acts as an inhibitor by decreasing water activity [83], [84]. Conversely, the release of pure water during hydrate dissociation (relevant to WAE strategies) causes a pronounced salinity reduction. To model these dynamic salinity changes accurately, especially for pressures above 4.331 MPa, this study adopted a specific correlation for T^{eq} based on comparative hydrate formation data from pure water [85] and seawater [86].

$$T_{eq} = A_1 + A_2 \left(\frac{P}{P_0} \right) + A_3 \left(\frac{P}{P_0} \right)^2 + A_4 \ln \left(\frac{P}{P_0} \right) - A_5 w_s \quad (2.14)$$

where $P_0 = 1$ MPa, and w_s is the weight fraction of salt in the seawater. For modeling purposes, the brine is represented as a single-salt NaCl solution.

The coefficients (A_1 to A_5) for Equation (2.14) are presented in **Table 2.2**.

Table 2.2 Coefficients for CO₂ hydrate equilibrium temperature in seawater.

A_1	A_2	A_3	A_4	A_5
281.97895752	0.03666088	0.00029353	0.64361042	42.5672141

2.5.1.2 Dissolution of liquid CO₂ droplets in water

The rate of liquid CO₂ droplet dissolution into water ($\frac{dn}{dt}$) is determined using the Noyes-Whitney equation [87]. This formulation incorporates the CO₂ diffusion coefficient (D), the thickness of the diffusion layer (t_h), and the concentration difference between the CO₂ saturation solubility ($C_{wCO_2}^S$ in mol/m³) and the current dissolved concentration (C_{wCO_2} in mol/m³).

$$\frac{dn}{dt} = DA_{CO_2} \frac{(C_{wCO_2}^S - C_{wCO_2})}{t_h} = D \left(\frac{6}{D_e} \right) V_b \phi_0 S_e \chi_{LCO_2} \frac{(C_{wCO_2}^S - C_{wCO_2})}{t_h} \quad (2.15)$$

The total surface area of the liquid CO₂ droplets (A_{CO_2} in m²) is calculated by multiplying the specific surface area of a single droplet by the overall volume of liquid CO₂ present within the porous medium.

$$A_{CO_2} = \frac{4\pi \left(\frac{D_e}{2} \right)^2}{\frac{4}{3}\pi \left(\frac{D_e}{2} \right)^3} V_b \phi_0 S_e \chi_{LCO_2} = \left(\frac{6}{D_e} \right) V_b \phi_0 S_e \chi_{LCO_2} \quad (2.16)$$

where D_e (m) denotes the diameter of the CO₂ droplets, and V_b (m³) is the bulk volume.

Equation (2.17) then calculates the dissolution rate per bulk volume ($\dot{q}_{dsol}$ in mol/m³·s), which introduces a dissolution rate constant ($\beta = \frac{D \left(\frac{6}{D_e} \right)}{t_h}$) with a unit of (s⁻¹).

$$\dot{q}_{dsol} = \beta \phi_0 S_e \chi_{LCO_2} (C_{wCO_2}^S - C_{wCO_2}) \quad (2.17)$$

where $C_{wCO_2}^S$ is calculated as a function of pressure and temperature, using the correlation developed by Duan and Sun [88]. Crucially, the dissolution rate constant β was rigorously determined and validated against experimental data obtained from the Masuda laboratory [63] in Chapter 3.

When liquid CO₂ is introduced into water, an extremely thin hydrate film typically forms around the droplets [89], [90]. The dissolution rate constant, β , accounts for the diffusional resistance across this film. Importantly, this study simplifies the continuity equations by treating these film-coated droplets as liquid CO₂ droplets, rather than classifying them as distinct hydrate particles. **Figure 2.3** conceptually illustrates CO₂ dissolution in water.

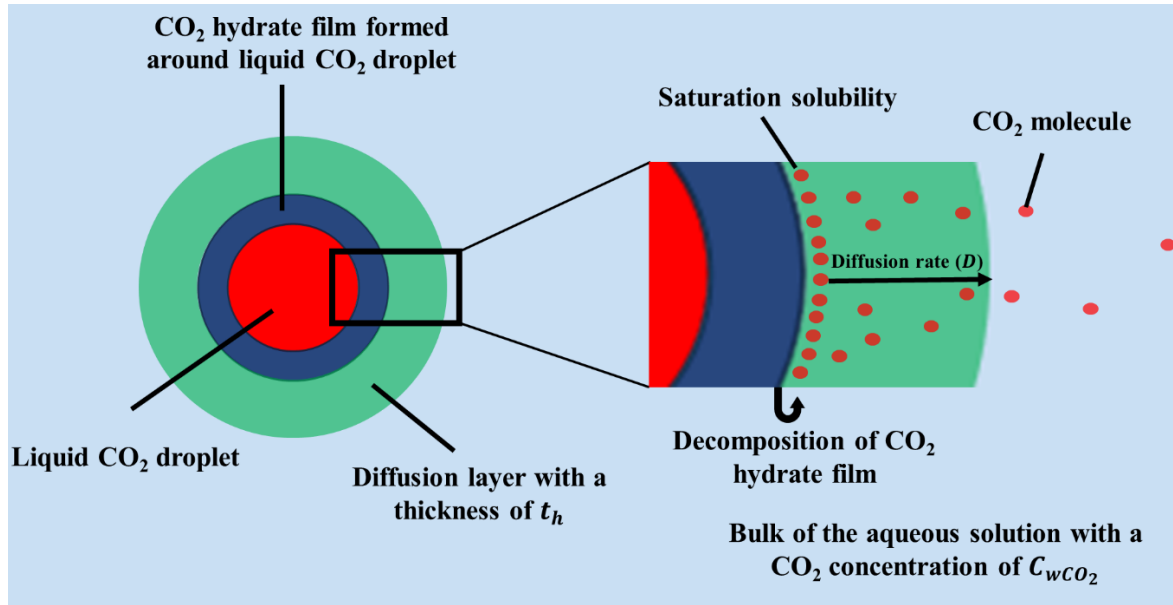


Figure 2.3 Conceptualization of CO₂ dissolution in the aqueous phase (Based on Dahlgren and Lennernäs [91]).

The heat of dissolution (ΔH_S in J/mol) for CO₂ in water is calculated using Equation (2.18), which is based on a low-pressure correlation by Carroll et al. [92].

$$\Delta H_S = C \left(106.5 - \frac{62634}{T} + \frac{7475000}{T^2} \right) \times 10^3 \quad (2.18)$$

Since the original Carroll equation (derived from Henry's law) does not account for the pressure-dependent decrease in dissolution heat observed by Koschel et al. [93], a pressure adjustment coefficient (C) was introduced into Equation (2.18). This adjustment was validated against experimental data (presented in Chapter 3) obtained from C/W emulsion injection into water-saturated core experiments conducted in the Masuda laboratory [63].

2.5.1.3 Dissolution of CO₂ hydrate particles driven by solubility

The dissolution process is fundamentally driven by the fact that the aqueous solution is undersaturated with dissolved CO₂, creating a concentration gradient between the saturation solubility and the bulk aqueous concentration. The author utilized the concept of the Noyes-

Whitney equation to determine this dissolution rate from the CO₂ hydrate particles in water. By employing a similar approach as shown in **Figure 2.3**, Equation (2.19) was derived.

$$\dot{q}_{PT}^{dsol} = \dot{q}_{wCO_2}^{dsol} = \beta \phi_0 S_{PT} (C_{HCO_2}^S - C_{wCO_2}) \quad (2.19)$$

where $\dot{q}_{PT}^{dsol}$ (mol/(m³·s)) and $\dot{q}_{wCO_2}^{dsol}$ (mol/(m³·s)) are the total dissolution rates of CO₂ hydrate particles in water. S_{PT} is the total CO₂ hydrate particles saturation (encompassing all states: flowing in the emulsion body or attached to the sand surface). $C_{HCO_2}^S$ (mol/m³) is the saturation solubility of CO₂ at the aqueous solution-hydrate interface which is determined as a function of temperature based on the work of Y. Zhang et al. [67].

The initial numerical model validation, based on 1D experimental data from the Masuda Laboratory (Chapter 3) [63], utilized the liquid CO₂ solubility saturation term, $C_{wCO_2}^S$. This approach sets the dissolution driving force as the difference between the bulk aqueous phase's saturation solubility and its current dissolved concentration.

However, when CO₂ hydrate is present, the true equilibrium solubility at the interface, $C_{HCO_2}^S$, is not equal to $C_{wCO_2}^S$. These two solubility terms exhibit opposing temperature and pressure dependencies:

1. The liquid CO₂ solubility ($C_{wCO_2}^S$) increases as temperature decreases and pressure increases [88].
2. The CO₂ hydrate equilibrium solubility ($C_{HCO_2}^S$) decreases as temperature decreases and pressure increases, reflecting the enhanced thermodynamic stability of the hydrate at lower temperatures and higher pressures [66], [67].

Therefore, for the dissolution of CO₂ hydrate particles in the bulk aqueous phase, the correct driving force was subsequently redefined (in Chapters 4 to 6) as the difference between the CO₂ solubility at the hydrate-water interface ($C_{HCO_2}^S$) and the current solubility in the bulk aqueous phase.

2.5.1.4 Exsolution of CO₂ from aqueous water-CO₂ solutions

The prevailing understanding is that a reduction in pore pressure causes CO₂ solubility in water to decrease, thereby inducing gradual CO₂ exsolution as the injected fluid moves away from the high-pressure injection zone [94], [95].

However, this study identifies the hydrate particle formation process itself as the primary driver of CO₂ exsolution. This mechanism works by consuming pure water during the reaction at the liquid CO₂-water interface, which leads to dissolved CO₂ supersaturation in the surrounding aqueous phase. This supersaturation effect is further intensified by the resulting increase in seawater salinity, which simultaneously reduces the CO₂ solubility saturation.

Based on the foundational work of Gao et al. [96] and Zhao and Ioannidis [97], the exsolution mechanism observed in this model is attributed to four sequential physical phenomena:

1. Activation of nucleation sites.
2. Transport of CO₂ molecules from the bulk aqueous solution to the diffusion layer.
3. Diffusion of CO₂ molecules through the diffusion layer to the nucleation site.
4. Subsequent growth of liquid CO₂ droplets.

In this specific model, the thermodynamic conditions often approach equilibrium due to the heat generated during hydrate formation, which results in a low driving force for further hydrate growth from supersaturated dissolved CO₂. Consequently, each liquid CO₂ droplet is treated as a single nucleation site (**Figure 2.4**).

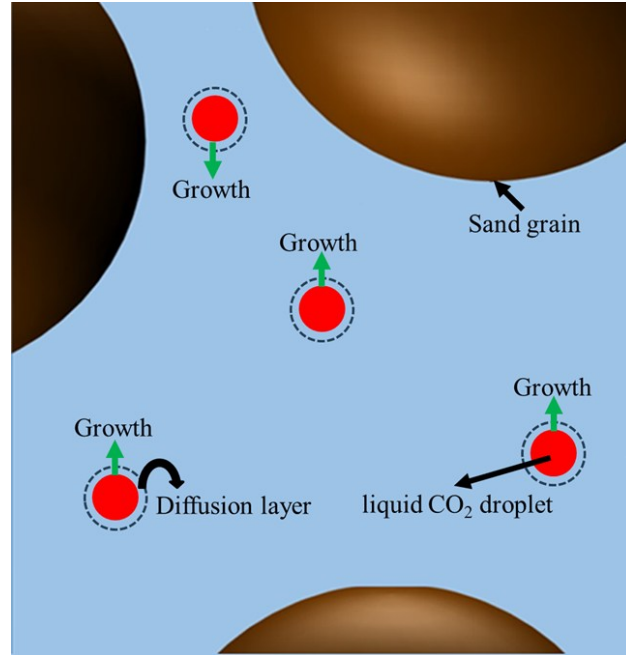


Figure 2.4 Liquid CO₂ droplets as nucleation sites for CO₂ exsolution (Reproduced from Bahmaee & Murata, [55], licensed under CC BY 4.0.).

Therefore, since the exsolution process occurs in the opposite direction of CO₂ dissolution into water, the diffusion-limited equation originally used for liquid CO₂ dissolution (Equation 2.17) was adopted to quantify the exsolution rate.

2.5.1.5 CO₂ hydrate dissociation model

During simulations of C/W emulsion injection, poor heat transfer from the reservoir (Chapters 4 to 6) often maintains relatively constant temperatures extending far from the wellbore, whereas pressure decreases with distance from the wellbore. This combination can result in localized conditions near the wellbore that fall just outside the hydrate stability zone.

This study adopts a kinetic control dissociation model [98] to quantify the rate of CO₂ hydrate film dissociation ($\dot{q}_{CH}^{diss}$ in mol/(m³·s)) around CO₂ hydrate particles:

$$\dot{q}_{CH}^{diss} = \dot{q}_{H_2O}^{CHdiss} / N_{CH} = K_{CH} A_{sp} (f_{CO_2} - f_{CO_2}^{eq}) \quad (2.20)$$

where $\dot{q}_{H_2O}^{CHdiss}$ is the water release rate and N_{CH} is the hydration number.

The effective area for dissociation is accounted for by the specific surface area of hydrate particles per unit porous medium, A_{sp} (m⁻¹). Assuming spherical particles, A_{sp} is calculated

based on the CO₂ hydrate particle diameter (D_p) and the total CO₂ hydrate particle saturation (S_{PT}), as shown in Equation (2.21):

$$A_{sp} = \frac{4\pi\left(\frac{D_p}{2}\right)^2}{\frac{4}{3}\pi\left(\frac{D_p}{2}\right)^3} \phi_0 S_{PT} = \left(\frac{6}{D_p}\right) \phi_0 S_{PT} \quad (2.21)$$

The CO₂ hydrate dissociation rate constant, K_{CH} (mol/(m²·s·MPa)), accounts for the temperature dependence of the reaction using the Arrhenius equation [99]:

$$K_{CH} = K_{CH0} e^{\left(-\frac{\Delta E_{CH}}{RT}\right)} \quad (2.22)$$

where K_{CH0} is the intrinsic dissociation rate constant (1.83×10^{14} mol/(m²·s·MPa)), ΔE_{CH} is the activation energy (102900 J/mol), R is the universal gas constant, and T is the temperature.

2.5.1.6 CH₄ hydrate dissociation and formation kinetics

The kinetic rate models for both MH dissociation and formation are based on a linear driving-force relationship, following the established formulations proposed by Birkedal et al. [100] and Sun et al. [79].

The MH dissociation rate ($\dot{q}_{MH}^{diss}$ in mol/s), which equals the methane gas generation rate ($\dot{q}_{CH_4}^{MHdiss}$ in mol/s), is governed by Equation (2.23):

$$\dot{q}_{MH}^{diss} = \dot{q}_{CH_4}^{MHdiss} = K_{MH0} e^{-\Delta E_{MH}/RT} A_{CH_4} F_A (f_{CH_4}^{eq} - f_{CH_4}) \quad (2.23)$$

The rate is controlled by the difference between the equilibrium methane fugacity ($f_{CH_4}^{eq}$) and the instantaneous methane gas fugacity (f_{CH_4}). The key parameters used are:

- K_{MH0} (3.6×10^{10} mol/(m²·MPa·s)): The intrinsic kinetic constant for MH dissociation.
- ΔE_{MH} (81,000 J/(mol·K)): MH dissociation activation energy.
- R (8.314 J/mol): The Universal Gas Constant.
- A_{CH_4} (m²): The active reaction surface area of MH, which is calculated as $A_{CH_4} = V_b \phi_0 S_{MH} A_{0CH_4}$, where A_{0CH_4} is the surface area to volume ratio (3.75×10^5 m²/m³) and V_b is the bulk volume.

- F_A (0.065): An area adjustment factor that corrects for irregularities in grain shape and hydrate morphology [100].

The MH formation rate ($\dot{q}_{MH}^{form}$ in mol/s), which is equivalent to the methane gas consumption rate ($\dot{q}_{CH_4}^{MHform}$ in mol/s), is given by Equation (2.24):

$$\dot{q}_{MH}^{form} = \dot{q}_{CH_4}^{MHform} = K_{MH} A_{CH_4} F_A (f_{CH_4} - f_{CH_4}^{eq}) \quad (2.24)$$

The parameters for MH formation are introduced below:

- K_{MH} (0.5875×10^{-5} mol/(m²·MPa·s)): The kinetic rate constant for MH formation.
- A_{CH_4} : The active reaction surface area, which is calculated differently for formation based on porosity (ϕ), permeability (K_D) and gas (S_g), water (S_{H_2O}), and MH (S_{MH}) saturations: $A_{CH_4} = \sqrt{\frac{\phi^3}{2K_D}} (S_g S_{H_2O} S_{MH})^{2/3} V_b$.

Spycher and Reed [101] calculated the CH₄ gas fugacity (f_{CH_4}) using Equation (2.25), and they demonstrated that the result agreed very well with the experimental data:

$$f_{CH_4} = \left(\frac{P}{P_0}\right) \times \exp \left[\left(\frac{A_1}{T^2} + \frac{A_2}{T} + A_3 \right) \times \left(\frac{P}{10^5} \right) + \left(\frac{A_4}{T^2} + \frac{A_5}{T} + A_6 \right) \times \frac{\left(\frac{P}{10^5} \right)^2}{2} \right] \quad (2.25)$$

where $P_0 = 1$ MPa.

Table 2.3 presents the coefficients (A_1 through A_6) used in the CH₄ fugacity correlation (Equation 2.25).

Table 2.3 Coefficients for the CH₄ fugacity correlation.

A_1	A_2	A_3	A_4	A_5	A_6
-537.779	1.54946	-92.7827E-05	120.861E-02	-370.814E-05	333.804 E-08

Methane gas equilibrium fugacity ($f_{CH_4}^{eq}$) is determined by the equilibrium pressure (P_e), calculated as shown in the following relationship [102]:

$$P_e = 1.15 \exp \left(49.3185 - \frac{9459}{T} \right) \quad (2.26)$$

2.5.2 Constitutive models for rock properties and flow

This section defines the key constitutive relations governing the transport phenomena and hydraulic property alteration within the porous medium. Specifically, it details the kinetic models for CO₂ hydrate particle accumulation and the corresponding permeability reduction models used to quantify the flow resistance induced by MH saturation and CO₂ hydrate saturation.

2.5.2.1 Hydrate particle accumulation modelling

Hydrate particles accumulate within the porous medium through two primary mechanisms: adsorption to the pore surfaces and trapping at the pore throats. The total accumulation term for hydrate particles (S_{PA}) is therefore defined as the sum of these two components: the adsorption saturation term (S_{Pads}) and the trapping saturation term (S_{Ptrap}).

The accumulation of CO₂ hydrate particles on the pore surfaces (adsorption) and within the pore throats (trapping) is modeled using a general kinetic rate formula (Equation 2.27) adapted from Rodriguez and Bryant [103]:

$$k_i \text{ (s}^{-1}\text{)} = A_i \left(\frac{D_p}{D_{gr}} \right)^{B_i} \quad i = \text{ads, trap} \quad (2.27)$$

For the initial 1D numerical model validation (Chapter 3), the following parameters were used for simplicity:

- D_{gr} is grain diameter.
- The exponent was set to $B_i = 1$.
- The adsorption constant was set to $A_{ads} = 0.0095 \text{ s}^{-1}$.
- The trapping constant $A_{trap} = 0.03 \text{ s}^{-1}$ was chosen as it successfully predicted the pressure behavior observed in the experimental work [63].
- A detachment rate of $k_{det} = 0.00095 \text{ s}^{-1}$ was applied to both adsorbed and trapped particles, falling within the ranges reported by previous studies [104], [105].

The possibility of particle trapping is highly dependent on the particle concentration and the ratio of pore throat diameter (D_t) to CO₂ hydrate particles diameter (D_p). Generally, when the

$\frac{D_t}{D_p}$ ratio exceeds six, particle trapping is typically avoided [106]. However, the critical threshold ratio (ζ) that governs trapping is not constant and its value increases as the particle concentration increases [107].

To account for this dependency, a quadratic function was devised [63] from the experimental data of Gruesbeck and Collins [106] (Equation 2.29) that calculates the threshold value (ζ). This threshold concentration is based on the ratio of particle saturation to total fluid saturation ($\frac{S_{PF}}{S_{PF}+S_e}$) in the porous medium. The calculated ζ value then acts as a critical condition that determines the value of the trapping constant (k_{trap}) using the piecewise function in Equation (2.28). Trapping is activated based on comparing the threshold ζ against the actual ratio of pore throat diameter to particle diameter ($\frac{D_t}{D_p}$).

$$k_{trap} = \begin{cases} A_{trap} \left(\frac{D_p}{D_g} \right)^{B_{trap}} & \text{if } \frac{D_t}{D_p} < \zeta \text{ or during soaking period} \\ 0 & \text{if } \frac{D_t}{D_p} \geq \zeta \text{ and not during the soaking period} \end{cases} \quad (2.28)$$

$$\zeta = \begin{cases} 6 & \frac{S_{PF}}{S_{PF}+S_e} \geq 0.3167 \\ -36.502 \left(\frac{S_{PF}}{S_{PF}+S_e} \right)^2 + 25.706 \left(\frac{S_{PF}}{S_{PF}+S_e} \right) + 1.52 & \frac{S_{PF}}{S_{PF}+S_e} < 0.3167 \end{cases} \quad (2.29)$$

Figure 2.5 illustrates the progression of CO₂ hydrate accumulation, moving from initial adsorption to final pore throat trapping.

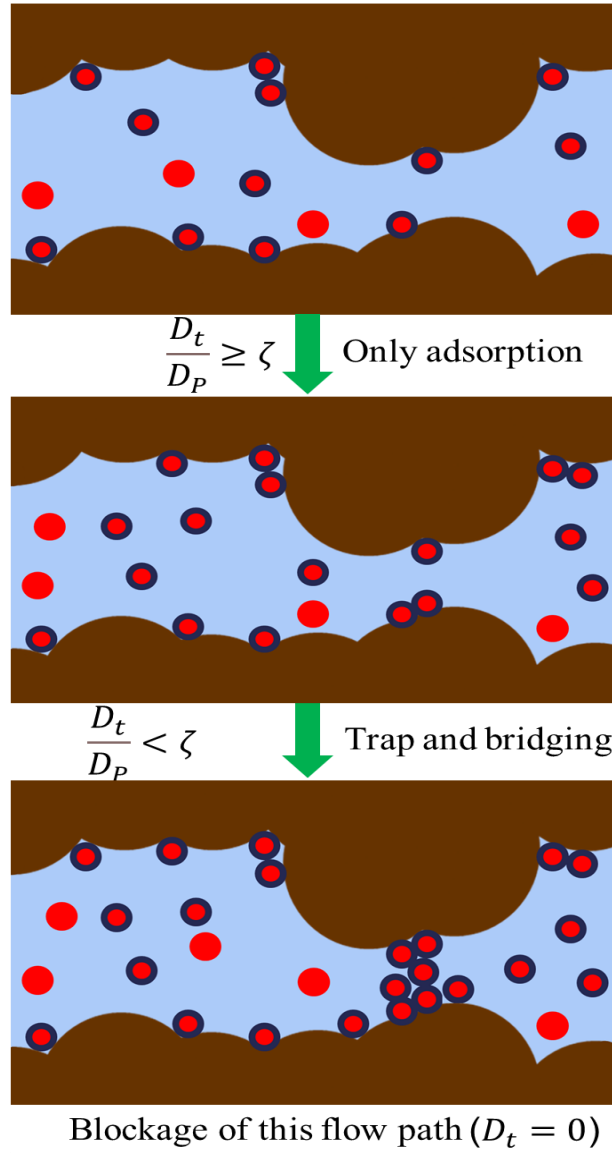


Figure 2.5 Conceptual schematic illustrating the sequential CO₂ hydrate particle accumulation process in a porous medium. The sequence demonstrates how initial particle adsorption on the pore walls narrows the pore throats, leading to subsequent straining and entrapment of incoming particles, which results in permeability reduction.

In Chapters 4 to 5, the model was simplified due to the computational cost of the field-scale study. The author did not differentiate between adsorption and trapping and used a simplified permeability model (Section 2.4.4.2). To ensure the robustness of this simplification, the following parameters were used:

- The exponent was set to $B_i = 1.5$ [108].
- A single attachment constant (A_{att}) of 0.03 s^{-1} was used to represent both adsorption and trapping.

- Due to simplifications, the detachment rate (k_{det}) was conservatively reduced tenfold to 0.00009 s^{-1} , a value within reported ranges [104], [105], to ensure a more rigorous assessment of near-wellbore blockage.

Chapter 6 adopted the same general methodology as the 1D validation (Chapter 3), but incorporated further simplifications consistent with the field-scale context:

- The exponent was set to $B_i = 1.5$ [108].
- Both the adsorption constant (A_{ads}) and the trapping constant (A_{trap}) were set equal to 0.03 s^{-1} .
- $k_{det} = 0.00009 \text{ s}^{-1}$ consistent with the value utilized in the field-scale study presented in Chapter 4.
- The total saturation of trapped particles (via straining, bridging, or agglomeration) was modeled as permanently immobilized across all operational periods (injection, soaking, and production), resulting in a zero particle detachment rate for trapped particles.

This assumption of irreversible consolidation is warranted by two coupled physical factors:

1. Adhesive consolidation by the Quasi-Liquid Layer (QLL) [109]: Premelting of the hydrate surface creates a QLL that promotes capillary bridging and adhesion between particles and the pore wall. This adhesive strength increases with contact time, and under the low-shear conditions of the soaking period, these forces overcome detaching stresses, rendering the particles immobile [109], [110].
2. Geometric constraint and permanent bridging [106]: In zones of high hydrate saturation and fine sediments, the reduction in pore-throat diameters fosters the mechanical interlocking of hydrate particle aggregates, a well-established mechanism for particle bridging [106].

These combined effects guarantee the permanent structural integrity of the consolidated aggregates against fluid shear, aligning with the expected behavior of native methane hydrate and supported by experimental studies showing successful CO_2 caps formed via C/W emulsion injection [61], [62].

2.5.2.2 Permeability model

Permeability, a fundamental rock property, quantifies the ability of a porous medium to transmit fluids [69]. For 1D validation of the numerical model, the present study developed a permeability equation based on the distinct effect of hydrate particles adsorbed on the pore bodies or trapped in the pore throats. The model used to calculate the reduction in absolute permeability (K_D (m²)) is based on the Kozeny-Carman (K-C) equation [111], which relates permeability to porosity and specific surface area.

$$K_{D0} = \frac{\phi_0^3}{k(1-\phi_0)^2 A_{grs}^2} \quad (2.30)$$

$$A_{grs} = \frac{A_{gr}}{V_{gr}} = \frac{4\pi\left(\frac{D_{gr}}{2}\right)^2}{\frac{4}{3}\pi\left(\frac{D_{gr}}{2}\right)^3} = \frac{6}{D_{gr}} \quad (2.31)$$

$$r_{h0} = \frac{V_{p0}}{A_{p0}} = \frac{\phi_0}{(1-\phi_0)A_{gr}} = \frac{\phi_0 D_{gr}}{6(1-\phi_0)} \quad (2.32)$$

$$K_{D0} = \frac{\phi_0 r_{h0}^2}{k} \quad (2.33)$$

The variables used in these equations include K_{D0} (intrinsic permeability in m²), A_{gr} (grain surface area in m²), V_{gr} (grain volume in m³), A_{grs} (grain specific surface area in m⁻¹), and r_{h0} (initial hydraulic radius in m).

Based on the structure of Equation (2.33) and maintaining the critical assumption that the Kozeny constant k remains invariant despite the accumulation of hydrate particles, the generalized formula for instantaneous permeability is expressed as follows:

$$K_D = \frac{\phi r_h^2}{k} \quad (2.34)$$

$$\phi = \phi_0(1 - S_{PA}) \quad (2.35)$$

It is important to note that the Kozeny constant is not a universal constant, but rather a geometric parameter that depends on pore shape, tortuosity, and flow-path assumptions. In the classical Kozeny–Carman model for random granular packings, when the hydraulic radius is defined according to Equation (2.32), the Kozeny constant (k) typically is assumed to be 5.

In contrast, the pore-scale representation adopted in this study models pore throats and pore bodies as idealized straight circular tubes. Under this assumption, permeability can be directly related to the Hagen–Poiseuille equation for laminar flow in a circular straight tube with a radius of r_h (m); therefore, the value of k is set to 2.

The permeability reduction model treats pore throats and pore bodies independently, as hydrate particle adsorption and trapping exert fundamentally different hydraulic effects in these two domains. The total accumulated CO₂ hydrate particle saturation (S_{PA}) is partitioned as:

$$S_{PA}^{throat} = S_{P_{trap}} + \varepsilon_{t0} S_{P_{ads}} \quad (2.36)$$

$$S_{PA}^{body} = (1 - \varepsilon_{t0}) S_{P_{ads}} \quad (2.37)$$

where ε_{t0} is the initial ratio of the pore throat volume to the total pore volume, set to 0.159 based on the methodology used by German [112].

The permeability of the pore throats (K_D^{throat}) and pore bodies (K_D^{body}) are calculated using a form analogous to a Kozeny–Carman model (similar to Equation 2.34), which relates permeability to the square of the hydraulic radius:

$$K_D^{throat} = \frac{\phi r_h^{throat^2}}{2} \quad (2.38)$$

$$K_D^{body} = \frac{\phi r_h^{body^2}}{2} \quad (2.39)$$

The key step is calculating the instantaneous change in the hydraulic radius as hydrate particles accumulate. Equations (2.40) and (2.41) express the changing hydraulic radius for the pore throats and pore bodies, respectively:

- Pore throat hydraulic radius:

$$\frac{D_t}{4} = r_h^{throat} = \frac{V_{p0}\varepsilon_{t0} - V_{PA}^{throat}}{A_{p0}^{throat} + A_{PA}^{throat}} = \frac{V_{p0}\varepsilon_{t0} \left(1 - \frac{S_{PA}^{throat}}{\varepsilon_{t0}}\right)}{A_{p0}^{throat} + V_{p0}\varepsilon_{t0} S_{PA} \frac{6}{D_P}} = \frac{1 - \frac{S_{PA}^{throat}}{\varepsilon_{t0}}}{\frac{1}{r_{h0}^{throat}} + S_{PA} \frac{6}{D_P}} \quad (2.40)$$

- Pore body hydraulic radius:

$$r_h^{body} = \frac{V_{p0}(1-\varepsilon_{t0}) - V_{PA}^{body}}{A_{p0}^{body} + A_{PA}^{body}} = \frac{V_{p0}(1-\varepsilon_{t0})(1 - \frac{S_{PA}^{body}}{1-\varepsilon_{t0}})}{A_{p0}^{body} + V_{p0}(1-\varepsilon_{t0})S_{PA} \frac{6}{D_p}} = \frac{1 - \frac{S_{PA}^{body}}{1-\varepsilon_{t0}}}{\frac{1}{r_{h0}^{body}} + S_{PA} \frac{6}{D_p}} \quad (2.41)$$

These equations incorporate the initial pore volume (V_{p0}), the volume of accumulated particles (V_{PA}), and the total surface area of the pore space (A_{p0}) and the accumulated particles (A_{PA}).

The initial hydraulic radius for the throats (r_{h0}^{throat}) and bodies (r_{h0}^{body}) are scaled to the grain diameter (D_{gr}) based on the findings of Glover and D  ry [113]:

$$\frac{D_{t0}}{4} = r_{h0}^{throat} = 0.0425D_{gr} \quad (2.42)$$

$$r_{h0}^{body} = 0.07D_{gr} \quad (2.43)$$

Finally, the total permeability (K_D) of the porous medium is calculated by treating the pore bodies and pore throats as elements connected in harmonic average (series), weighted by the initial volume ratio (ε_{t0}):

$$K_D = \frac{1}{\frac{\varepsilon_{t0}}{K_D^{throat}} + \frac{1-\varepsilon_{t0}}{K_D^{body}}} \quad (2.44)$$

To reduce computational costs for field-scale studies in Chapters 4 to 6, this work employed a simplified permeability reduction model. For modeling the absolute reduction in permeability, the widely recognized Tokyo model, which is frequently applied in reservoir simulations and numerical modeling studies [80], [114], [115], was adopted:

$$K_D = K_{D0}(1 - S_h)^N \quad (2.45)$$

$$S_h = S_{pads} + S_{ptrap} + S_{MH} \quad (2.46)$$

where K_{D0} is the intrinsic permeability and S_h is the stationary hydrate saturation, encompassing all CO₂ and methane hydrates. The permeability-saturation exponent, N , is set to 3 in this work.

The value of the exponent N dictates the severity of permeability reduction. While the theoretical geometric value is $N = 2$ [116], experimental and numerical studies report a wide variation, ranging from 1.25 to 25 [117], [118]. Higher N values are generally observed when hydrate preferentially accumulates in flow-restricting pore throats [116]. Reported values often show a dependence on the extent of saturation, such as $N = 2.6$ for $S_h \leq 40\%$ and $N = 9.7$ for higher saturations [119], or $N = 3$ (up to 35%) and $N = 5$ (up to 50%) [120]. This variability confirms that the permeability reduction is more severe at higher hydrate accumulation levels. Furthermore, Pan et al. [121] confirmed that no single fixed exponent or theoretical model adequately captures all experimental observations, but found that a curve using $N = 3$ provided a reasonable average that lay near the center of the total data spread.

The kinetic-theory-based pore-network modeling (KT-PNM) study by Zhang et al. [122] further supports these constraints. The KT-PNM explicitly simulates the two-stage hydrate evolution in realistic pore networks (reconstructed from X-CT images of sandy samples) and found that the exponent for sandy hydrate-bearing sediments lies within a narrow range of 3 to 4.

Based on this evidence, this study adopted $N = 3$ for several reasons. First, this selection aligns with the modeling framework used to determine the CO₂ hydrate particle attachment rate during the 1D numerical validation (Chapter 3). Furthermore, this choice is supported by the initial conditions of the clean aquifer model (Chapters 4 and 5), where injection into a system with zero initial hydrate saturation aligns with literature suggesting permeability exponents equal to or lower than 3 are appropriate for modeling the low-to-moderate hydrate saturation range ($S_h \leq 40\%$). Second, choosing $N = 3$ is strongly supported by external data, as Pan et al. [121] demonstrated that this value represents a reasonable average that lies near the center of the wide experimental data spread. Moreover, it represents the lower, conservative bound of the robust KT-PNM range (3 to 4) established for sandy sediments [122]. Finally, this choice is appropriate because the model already explicitly accounts for severe flow-restriction mechanisms, specifically modeling the bridging, plugging, and agglomeration of hydrate particles in pore throats. Selecting a higher exponent would introduce redundancy and potentially lead to unrealistically strong permeability reductions, thereby overestimating the sealing efficiency of the CO₂ hydrate and the resulting methane recovery enhancement.

2.6 Physical properties

This section details the governing constitutive relationships and phase behavior models used to calculate the physical properties of the system components (water, CO₂, CH₄, CO₂ hydrate, MH) within the simulation domain.

2.6.1 Density model

In this simulation, while the continuity equations were calculated using molar density of the fluid (ρ_F in mol/m³), the Darcy equation's gravity term requires the use of mass density of the fluid ($\hat{\rho}_F$ in kg/m³). To convert between these two quantities, the molar density must be multiplied by the fluid's molar mass (M_F in kg/mol), as shown in Equation (2.47):

$$\hat{\rho}_F = \rho_F \times M_F \quad (2.47)$$

2.6.1.1 Molar density of water

The molar density of water (ρ_{H_2O}) is calculated as a function of temperature and pressure using Equation (2.48), which is based on data from Wagner and Kretzschmar [123].

$$\rho_{H_2O} \times M_{H_2O} = \left(A_1 \left(\frac{P}{P_0} \right)^2 + A_2 \left(\frac{P}{P_0} \right) + A_3 \right) T^2 + \left(A_4 \left(\frac{P}{P_0} \right)^2 + A_5 \left(\frac{P}{P_0} \right) + A_6 \right) T + \left(A_7 \left(\frac{P}{P_0} \right)^2 + A_8 \left(\frac{P}{P_0} \right) + A_9 \right) \quad (2.48)$$

where $P_0 = 1$ MPa and molar mass of water (M_{H_2O}) is 18.02×10^{-3} kg/mol.

Table 2.4 shows the values of coefficients used in Equation (2.48). It should be noted that the literature data provided in this table originally represented specific volume (m³/kg) in the source material by Wagner and Kretzschmar [123]. The values were converted to mass density ($\hat{\rho}_{H_2O}$) for direct comparison with the developed equation. Furthermore, for improved readability, the coefficients utilized in Equation (2.48) are presented with four digits following the decimal point.

Table 2.4 Comparison of calculation value and literature data for molar density of water.

P [MPa]	T [K]	Literature data [kg/m ³]	Calculation value [kg/m ³]	Relative error (%)		Coefficient
5.0	277.15	1002.39	1002.40	0.00	A_1	$-1.8878\text{E}-05$
5.0	279.15	1002.33	1002.32	0.00	A_2	$3.2927\text{E}-04$
5.0	281.15	1002.20	1002.19	0.00	A_3	$-6.9864\text{E}-03$
5.0	283.15	1002.03	1002.02	0.00	A_4	$1.0670\text{E}-02$
5.0	285.15	1001.80	1001.80	0.00	A_5	$-1.8861\text{E}-01$
10.0	277.15	1004.81	1004.83	0.00	A_6	$3.8692\text{E}+00$
10.0	279.15	1004.72	1004.72	0.00	A_7	$-1.5080\text{E}+00$
10.0	281.15	1004.58	1004.57	0.00	A_8	$2.7479\text{E}+01$
10.0	283.15	1004.39	1004.37	0.00	A_9	$4.6421\text{E}+02$
10.0	285.15	1004.13	1004.12	0.00		
15.0	277.15	1007.23	1007.23	0.00		
15.0	279.15	1007.11	1007.10	0.00		
15.0	281.15	1006.93	1006.93	0.00		
15.0	283.15	1006.71	1006.71	0.00		
15.0	285.15	1006.44	1006.44	0.00		

2.6.1.2 Molar density of CO₂

The molar density of liquid CO₂ (ρ_{LCO_2}) is calculated as a function of temperature and pressure using the empirical correlation originally developed by Span and Wagner [124]. This correlation was previously implemented, fitted, and validated as part of the former research group's work in Professor Masuda's laboratory [69], [125]. The correlation is valid for a temperature range of 275–285 K and a pressure range of 5–15 MPa. The general form used in this work is:

$$\rho_{LCO_2} \times M_{CO_2} = \left(A_1 \left(\frac{P}{P_0} \right)^2 + A_2 \left(\frac{P}{P_0} \right) + A_3 \right) T^2 + \left(A_4 \left(\frac{P}{P_0} \right)^2 + A_5 \left(\frac{P}{P_0} \right) + A_6 \right) T + \left(A_7 \left(\frac{P}{P_0} \right)^2 + A_8 \left(\frac{P}{P_0} \right) + A_9 \right) \quad (2.49)$$

where molar mass of CO₂ is $M_{CO_2} = 44.01 \times 10^{-3}$ kg/mol.

The coefficients (A_1 through A_9) required for the calculation of the liquid CO₂ molar density using Equation (2.49) are listed in **Table 2.5**

Table 2.5 Coefficients used for the molar density correlation of liquid CO₂.

A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9
-0.00150	0.04174	-0.3108	0.8148	-22.565	162.9572	-110.822	3058.703	-20424.91

2.6.1.3 Molar density of dissolved CO₂ in water

For the 1D numerical validation study presented in Chapter 3, a simplification was employed where the molar density of dissolved CO₂ was assumed to be equivalent to that of liquid CO₂. However, this assumption was corrected for the subsequent 3D field scale simulations in Chapters 4 to 6 using the empirical equation developed by McBride-Wright et al. [126], which accurately captures the influence of the aqueous phase on CO₂ density. This empirical equation calculates the partial molar volume of dissolved CO₂ in water (V_{wCO_2} in m³/mol) as a function of temperature (T) and pressure (P):

$$V_{wCO_2} = 10^{-6} \cdot \left(\sum_{i=0}^2 \sum_{j=0}^1 a_{ij}(T)^i \left(\frac{P}{P_0}\right)^j \right) \quad (2.50)$$

The molar density of dissolved CO₂ (ρ_{wCO_2}) is then computed as the inverse of the partial molar volume:

$$\rho_{wCO_2} = \frac{1}{V_{wCO_2}} \quad (2.51)$$

The parameters for Equation (2.50) are given in **Table 2.6**.

Table 2.6 Parameters for the partial molar volume of dissolved CO₂ in water.

$a_{0,0}$	$a_{1,0}$	$a_{2,0}$	$a_{0,1}$	$a_{1,1}$	$a_{2,1}$
51.19	-0.15575	3.2955E-04	-6.0708E-02	5.5026E-04	-1.2114E-06

2.6.1.4 Molar density of brine with dissolved CO₂

A critical result of CO₂ dissolving into the formation water is an increase in brine density. This triggers natural convection by creating a state of negative buoyancy, thereby accelerating the uptake of CO₂ and thus speeding up solubility trapping [126], [127]. To capture this density increase for the field scale study in Chapters 4 to 6, a new empirical correlation for the mass density of the brine with dissolved CO₂ ($\hat{\rho}_{b-CO_2}$ in kg/m³) was developed in this work by fitting

the tabulated experimental data reported by Calabrese et al. [128]. The correlation is applicable for temperatures between 274.73 K and 296.22 K and is given by:

$$\hat{\rho}_{b-CO_2} = 1062.589 - 0.2129T + 0.4016\left(\frac{P}{P_0}\right) + 57.7301m + 475.4109x_{wCO_2} - 0.0746Tm \quad (2.52)$$

here x_{wCO_2} is the mole fraction of dissolved CO₂ in seawater, and m (mol/kg) is the molality of the saline solution. For modeling purposes, the brine is represented as a single-salt NaCl solution.

The molar density of the brine with dissolved CO₂ (ρ_{b-CO_2}) is calculated by dividing the mass density ($\hat{\rho}_{b-CO_2}$) by the average molar mass of the brine solution (M_{brine}), which is derived from the following relationship:

$$\rho_{b-CO_2} = \frac{\hat{\rho}_{b-CO_2}(1 + M_{H_2O}M_{NaCl})}{(M_{H_2O}(1 + mM_{NaCl}))} \quad (2.53)$$

in this equation M_{NaCl} is the molar mass of NaCl which is 58.44×10^{-3} kg/mol.

The developed correlation (Equation 2.52) successfully models the experimental data from Calabrese et al. [27], achieving an Average Absolute Relative Error (AARE) of only 0.0626% and yielding an R-squared (R^2) value of 0.999455.

2.6.1.5 Molar density of CO₂ hydrate

CO₂ hydrate typically forms Structure I (sI) and its ideal unit cell contains 46 water molecules ($n_{H_2O} = 46$) and the general formula of sI hydrates is $6(5^{12}6^{12}) \cdot 2(5^{12}) \cdot 46H_2O$ [10], [129]. This study assumed the hydration number is greater than its theoretical value of 5.75, indicating that CO₂ molecules do not occupy all the cavities. This study adopts is $N_{CH} = 6.2$, a value supported by X-ray diffraction results from Udachin et al. [130]. The mass density ($\hat{\rho}_H$) and molar density (ρ_{CH}) of the hydrate are calculated using the following unit cell relationships:

$$\hat{\rho}_{CH} = \frac{(n_{H_2O}M_{H_2O} + \left(\frac{n_{H_2O}}{N_{CH}}\right)M_{CO_2})}{N_A l^3} \quad (2.54)$$

$$\rho_{CH} = \frac{\hat{\rho}_{CH}}{M_{CH}} \quad (2.55)$$

where, N_A is the Avogadro constant which is equal to $6.022 \times 10^{23} \text{ mol}^{-1}$, l is the cell constant which is $1.2 \times 10^{-9} \text{ m}$, M_{CH} is the molar mass of CO_2 hydrate ($\text{CO}_2 \cdot 6.2 \text{ H}_2\text{O}$).

2.6.1.6 Mass density of C/W emulsion

For the 1D numerical validation study presented in Chapter 3, the mass density of the emulsion was calculated using the arithmetic mean of the mass densities of the constituent water and CO_2 , weighted by their respective volume fractions:

$$\hat{\rho}_e = \chi_{H_2O} \rho_{H_2O} M_{H_2O} + (1 - \chi_{H_2O}) \rho_{CO_2} M_{CO_2} \quad (2.56)$$

where χ_{H_2O} is the volume fraction of water in the C/W emulsion.

In contrast, for the field-scale simulations in Chapters 4, 5, and 6, where the influence of dissolved CO_2 on brine density is accounted for (as detailed in Section 2.6.1.4), Equation (2.57) was employed. This formulation calculates the emulsion density by weighting the mass density of the liquid CO_2 droplets with the mass density of the brine-dissolved CO_2 mixture ($\hat{\rho}_{b-\text{CO}_2}$):

$$\hat{\rho}_e = \chi_{LCO_2} \rho_{CO_2} M_{CO_2} + (1 - \chi_{LCO_2}) \hat{\rho}_{b-\text{CO}_2} \quad (2.57)$$

where χ_{LCO_2} is the volume fraction of the liquid CO_2 droplets in the C/W emulsion.

The mass density of the liquid phase ($\hat{\rho}_l$) in the Darcy equation (2.1) is equivalent to the effective emulsion mass density ($\hat{\rho}_e$) in the context of two-phase flow simulations (Chapter 6).

2.6.1.7 Molar density of CO_2 hydrate particle

The molar density of the CO_2 hydrate particles (ρ_P) is calculated by finding the arithmetic mean of the volume ratios of the two main components within the particles: the CO_2 hydrate film and the liquid CO_2 droplet which is encaged by the CO_2 hydrate film (as defined in Equation 2.58).

$$\rho_P = \alpha \rho_{CH} + (1 - \alpha) \rho_{CO_2} \quad (2.58)$$

2.6.1.8 Molar density of CH₄ gas

According to Chierici [131], the molar density of methane gas (ρ_g) can be derived through a sequential set of calculations, beginning with the determination of the compressibility factor (z). The compressibility factor is calculated using the following empirical correlation:

$$z = A + \frac{1-A}{\exp B} + C P_r^D \quad (2.59)$$

the parameters A , B , C , and D are functions of the reduced temperature (T_r) and reduced pressure (P_r), and are defined by Equations (2.60) through (2.64):

$$T_r = \frac{T}{T_c}, P_r = \frac{P}{P_c} \quad (2.60)$$

$$A = 1.39 (T_r - 0.92)^{0.5} - 0.36 T_r - 0.101 \quad (2.61)$$

$$B = (0.62 - 0.23 T_r) P_r + \left(\frac{0.066}{T_r - 0.86} - 0.037 \right) P_r^2 + \frac{0.32}{\text{antilog}\{9 (T_r - 1)\}} P_r^6 \quad (2.62)$$

$$C = (0.132 - 0.32 \log T_r) \quad (2.63)$$

$$D = \text{antilog}(0.3106 - 0.49 T_r + 0.1824 T_r^2) \quad (2.64)$$

After calculating the value of the compressibility factor (z), the molar density of methane gas (ρ_g) is then determined using the following thermodynamic relationship:

$$\rho_g = \frac{P}{zRT} \quad (2.65)$$

2.6.1.9 Molar density of CH₄ hydrate

The molar density of methane hydrate (ρ_{MH}) can be determined using a unit cell approach, based on the hydrate's mass density ($\hat{\rho}_{MH}$) and the composition of the hydrate lattice. The mass density of the methane hydrate is calculated using the following unit cell relationship:

$$\hat{\rho}_{MH} = \frac{n_{H_2O} M_{H_2O} + \left(\frac{n_{CH_4}}{N_{MH}} \right) M_{CH_4}}{N_A l^3} \quad (2.66)$$

where N_{MH} is the hydration number ($= 6.2$), M_{CH_4} is the molar mass of methane, N_A is the Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$), l is the cell constant which is $1.2 \times 10^{-9} \text{ m}$, and n_{H_2O} is the number of water molecules in the unit cell ($= 46$).

The molar density (ρ_{MH}) is then calculated by dividing the mass density by the molar mass of the methane hydrate (M_{MH}):

$$\rho_{MH} = \frac{\hat{\rho}_{MH}}{M_{MH}} \quad (2.67)$$

2.6.2 Viscosity model

The viscosity of the fluids (μ_F in Pa·s) present in the reservoir is a key transport property that governs fluid mobility through the porous medium. Accurate modeling of these viscosities is critical for the reliable simulation of flow rates in the multiphase system. This section presents the empirical correlations used to calculate the viscosity for each fluid component and fluid phase as a function of local pressure and temperature.

2.6.2.1 Water viscosity

Since the 1D numerical model in Chapter 3 was validated against core flood experiments where a C/W emulsion was injected into a pure water-saturated core conducted in Professor Masuda's laboratory, the viscosity of the pure water phase (μ_{H_2O}) was modeled using a specific correlation developed by the former research group's work in Masuda Laboratory [69], [125] based on the published data of Kestin et al. [132] and is valid for a temperature range of 273.15–293.15 K.

$$\mu_{H_2O} \times 10^6 = A_1 T^2 + A_2 T + A_3 \quad (2.68)$$

The coefficients (A_1 , A_2 , and A_3) required for calculating the viscosity of pure water using Equation (2.68) are provided in **Table 2.7**.

Table 2.7 Coefficients used for the water viscosity correlation.

A_1	A_2	A_3
0.901118	−549.4863	84647.4177

2.6.2.2 CO₂ viscosity

The correlation used to model the viscosity of CO₂ (μ_{LCO_2}) as a function of temperature and pressure is originally based on the data reported by Fenghour et al. [133]. This correlation was previously implemented and validated as part of the former research group's work in Professor Masuda's laboratory [69], [125]. The model is valid for a temperature range of 260–300 K and a pressure range of 5–12.5 MPa, which covers the experimental conditions of this study.

The viscosity of CO₂ is expressed as:

$$\mu_{LCO_2} \times 10^6 = \left(A_1 \left(\frac{P}{P_0} \right)^2 + A_2 \left(\frac{P}{P_0} \right) + A_3 \right) T^2 + \left(A_4 \left(\frac{P}{P_0} \right)^2 + A_5 \left(\frac{P}{P_0} \right) + A_6 \right) T + \left(A_7 \left(\frac{P}{P_0} \right)^2 + A_8 \left(\frac{P}{P_0} \right) + A_9 \right) \quad (2.69)$$

The coefficients (A_1 through A_9) required for the calculation of the liquid CO₂ viscosity using Equation (2.69) are listed in **Table 2.8**.

Table 2.8 Coefficients used for the liquid CO₂ viscosity correlation.

A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9
−0.000231	0.006138	−0.03063	0.12311	−3.265	14.3612	−16.3951	436.2560	−1544.22

2.6.2.3 Brine viscosity

Since the 3D field scale simulations focused on injection in seawater (modeled as NaCl brine) instead of pure water, the brine viscosity (μ_b) equation was adopted from the study developed by Calabrese et al. [128], based on the foundational work of Kestin and Shankland [134]. This model calculates the brine viscosity as a function of pressure (P), temperature (T), and molality (m):

$$\mu_b(P, T, m) = \mu_{b0}(T, m)[1 + k(T, m)P] \quad (2.70)$$

where the pressure-dependence term, $k(T, m)$, is defined by the coefficients for pure water (k_w) and an excess term (k^E) related to salinity:

$$k(T, m) = k_w(T) + k^E(T, m) \quad (2.71)$$

the pure water viscosity pressure coefficient (k_w) is expressed by a third-order polynomial in temperature (T in K) [134]:

$$k_w(T) = -0.7879 + 0.02927(T - 273.15) - 1.584 \times 10^{-4}(T - 273.15)^2 + 3.775 \times 10^{-7}(T - 273.15)^3 \quad (2.72)$$

the excess pressure coefficient (k^E) related to the NaCl salt type and molality (m) is given by:

$$k^E(T, m) = -0.3974m + \frac{0.6125m}{\left(\frac{T}{142} - 1\right)} \quad (2.73)$$

the viscosity of the brine at atmospheric pressure, μ_{b0} , is calculated using the Othmer model correlation [128]:

$$\ln\left(\frac{\mu_{b0}(T, m)}{\mu_{H_2O}(T)}\right) = A + B \cdot \ln\left(\frac{\mu_{H_2O}(T)}{\mu_{H_2O}(293.15 \text{ K})}\right) \quad (2.74)$$

the parameters A and B in Equation (2.74) are expressed as functions of molality (m):

$$A = \sum_{i=1}^3 A_i m^i \quad (2.75)$$

$$B = \sum_{i=1}^3 B_i m^i \quad (2.76)$$

The parameters utilized in Equations (2.75) and (2.76) for the calculation of NaCl brine viscosity are listed in **Table 2.9**.

Table 2.9 Coefficients used for the calculation of NaCl brine viscosity.

A_1	A_2	A_3	B_1	B_2	B_3
8.6075E-02	2.3522E-03	3.5710E-04	-3.5198E-02	5.4401E-03	-4.2694E-05

2.6.2.4 C/W emulsion viscosity

For the C/W emulsion viscosity (μ_e) used in the 1D numerical validation study presented in Chapter 3, a geometric mean model was employed [55], [69], [125]:

$$\mu_e = \mu_{H_2O}^{\chi_{H_2O}} \mu_{LCO_2}^{(1-\chi_{H_2O})} \quad (2.77)$$

where χ_{H_2O} is the volume fraction of the water in the C/W emulsion.

However, The present model is deficient because it underestimates the true viscosity and incorrectly predicts an inverse relationship between CO₂ saturation and viscosity. Observations confirm that emulsion viscosity is greater than the continuous phase and increases with CO₂ saturation. Recognizing this critical shortcoming, this study sought to establish a more accurate model for the emulsion's continuous phase.

For aqueous solutions containing dissolved CO₂, the viscosity increases with the concentration of dissolved CO₂ [126], [135]. To address the noted discrepancy in Equation (2.77), the influence of dissolved CO₂ saturation is accounted for by correcting the base brine viscosity (μ_b). The viscosity of the brine solution containing dissolved CO₂ (μ_{b-CO_2}) is therefore modeled using a linear correction factor, which was developed in the study by Calabrese et al. [128] as follows:

$$\ln(\mu_{b-CO_2}(P, T, m, x_{wCO_2})) = \ln(\mu_b(P, T, m)) + 65.56 \exp\left[-2.468\left(\frac{T}{142} - 1\right)\right] x_{wCO_2} \quad (2.78)$$

Furthermore, the overall emulsion viscosity (μ_e) is significantly affected by the presence of dispersed liquid CO₂ droplets and solid CO₂ hydrate particles. Research has shown that the interfacial tension directly influences droplet size [136], and subsequently, smaller droplet sizes lead to a notable increase in emulsion viscosity [137]. This is due to the greater total surface area of the interfaces, which increases internal friction within the fluid. Additionally, the formation of hydrate particles causes a substantial increase in viscosity [138]

To comprehensively account for the coupled effects of CO₂ droplets and flowing CO₂ hydrate particles on the continuous phase, this study utilized a hybrid model combining the principles of Taylor [139] and Einstein [140]. The effective emulsion viscosity (μ_e) is calculated by applying a correction factor to the corrected continuous phase viscosity (μ_{b-CO_2}):

$$\mu_e = \mu_{b-CO_2} \left(1 + \frac{S_e \chi_{LCO_2}}{S_{PF} + S_e} \left[\frac{2\mu_{b-CO_2} + 5\mu_{LCO_2}}{2\mu_{b-CO_2} + 2\mu_{LCO_2}} \right] + \frac{2.5S_{PF}}{S_{PF} + S_e} \right) \quad (2.79)$$

For the two-phase flow simulations in Chapter 6, the effective emulsion viscosity used in the Darcy equation (2.1) is denoted as:

$$\mu_l = \mu_e \quad (2.80)$$

2.6.2.5 CH₄ gas viscosity

The correlation used in this study to determine methane gas viscosity (μ_g) was adopted from Chierici [131] and is presented as follows:

$$\mu_g = A \exp \left[X \left(\frac{\rho_g M_{CH_4}}{1000} \right)^Y \right] \times 10^{-7} \quad (2.81)$$

the parameters A , X , and Y in the above equation are defined by the following auxiliary correlations:

$$A = \frac{(12.61 + 0.027 M_{CH_4}) T^{1.5}}{116.11 + 10.56 M_{CH_4} + T} \quad (2.82)$$

$$X = 3.5 + \frac{547.8}{T} + 0.01 M_{CH_4} \quad (2.83)$$

$$Y = 2.4 - 0.2X \quad (2.84)$$

2.6.3 Molar internal energy

The specific internal energy (internal energy per unit mass) of the fluid denoted as $\hat{U}_F$ (J/kg), and the molar internal energy (internal energy per mole) of the fluid, denoted as U_F (J/mol) follow the same hat notation convention used for density. The relationship between these two quantities is given by Equation (2.85):

$$\hat{U}_F = \frac{U_F}{M_F} \quad (2.85)$$

2.6.3.1 Molar internal energy of water

The molar internal energy of water (U_{H_2O}) is modeled as a function of temperature and pressure using a correlation that was previously implemented and validated by the former research group's work in Professor Masuda's laboratory [69], [125]. This correlation is valid for a temperature range of 273.15–313.15 K and a pressure range of 5–15 MPa, which covers the experimental conditions of this study. The internal energy is expressed as follows:

$$U_{H_2O} \times \frac{10^{-3}}{M_{H_2O}} = \left(A_1 \left(\frac{P}{P_0} \right)^2 + A_2 \left(\frac{P}{P_0} \right) + A_3 \right) T^2 + \left(A_4 \left(\frac{P}{P_0} \right)^2 + A_5 \left(\frac{P}{P_0} \right) + A_6 \right) T + \left(A_7 \left(\frac{P}{P_0} \right)^2 + A_8 \left(\frac{P}{P_0} \right) + A_9 \right) \quad (2.86)$$

The coefficients (A_1 through A_9) required for the calculation of the molar internal energy of water using Equation (2.86) are listed in **Table 2.10**.

Table 2.10 Coefficients used for the correlation of the molar internal energy of water.

A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9
-2.50E-07	2.63E-05	-0.00045	0.000162	-0.01897	4.45334	-0.02588	3.24386	-1182.91

The numerical model uses 5 MPa and 274 K as the standard reference state for calculating all internal energy values. Consequently, the coefficient A_9 in Equation (2.86) is corrected to this reference state using Equation (2.87):

$$A_{9_{calc}} = A_9 - \hat{U}_{H_2O \text{ at } 5 \text{ MPa}, 274 \text{ K}} = -1186.51 \quad (2.87)$$

The molar internal energy of brine was approximated by that of pure water to simplify the simulation.

2.6.3.2 Molar internal energy of CO₂

The molar internal energy of CO₂ (U_{CO_2}) is modeled as a function of temperature and pressure using a correlation originally derived from the data published by Span and Wagner [124]. This specific correlation was previously implemented and validated by the former research group's work in Professor Masuda's laboratory [69], [125]. The correlation is valid for a temperature range of 275–285 K and a pressure range of 5–15 MPa, which matches the conditions utilized in the current model. U_{CO_2} is expressed by the following equation:

$$U_{CO_2} \times \frac{10^{-3}}{M_{CO_2}} = \left(A_1 \left(\frac{P}{P_0} \right)^2 + A_2 \left(\frac{P}{P_0} \right) + A_3 \right) T^2 + \left(A_4 \left(\frac{P}{P_0} \right)^2 + A_5 \left(\frac{P}{P_0} \right) + A_6 \right) T + \left(A_7 \left(\frac{P}{P_0} \right)^2 + A_8 \left(\frac{P}{P_0} \right) + A_9 \right) \quad (2.88)$$

The coefficients (A_1 through A_9) required for the calculation of the molar internal energy of water using Equation (2.88) are listed in **Table 2.11**.

Table 2.11 Coefficients used for the correlation of the molar internal energy of CO₂.

A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9
0.000288	-0.00795	0.058436	-0.15637	4.2887	-29.3821	21.25649	-580.641	3362.389

Similar to the previous adjustment, the coefficient A_9 is corrected by Equation (2.89) to align with the 5 MPa and 274 K reference state:

$$A_{9_{calc}} = A_9 - \hat{U}_{CO_2 \text{ at } 5 \text{ MPa}, 274 \text{ K}} = 3673.9 \quad (2.89)$$

2.6.3.3 Molar internal energy of CO₂ hydrate

The molar internal energy of CO₂ hydrate (U_{CH}) is calculated by accounting for the internal energy of the constituent molecules (water and CO₂) and then subtracting the internal energy change associated with the hydrate formation process. This relationship, which includes a correction factor for the reference state, is expressed as:

$$U_{CH} = N_{CH}U_{H_2O} + U_{CO_2} - (Q - W) + (Q - W)_{ref} \quad (2.90)$$

The terms Q (heat exchange) and W (work done) relate to the phase change. Following Holder et al. [141], the enthalpy change (ΔH_{CH}) due to the phase change during one mole of hydrate formation is modeled as:

$$\Delta H_{CH} = -4.18(A + BT) \quad (2.91)$$

where $A = 19200 \text{ J/mol}$ and $B = -15 \text{ J/(mol}\cdot\text{K)}$.

The heat transferred (Q) and the enthalpy change (ΔH_{CH}) are related by the following approximation:

$$Q = -\Delta H_{CH} \quad (2.92)$$

The amount of work (W) done during the formation of one mole of hydrate is calculated as $P\Delta V$, where ΔV is the change in volume of the components:

$$W = P\Delta V = P \times \left(\frac{1}{\rho_{CO_2}} + \frac{N_{CH}}{\rho_{H_2O}} - \frac{1}{\rho_{CH}} \right) \quad (2.93)$$

Finally, the reference state correction term $(Q - W)_{ref}$ is derived from these equations by evaluating Q and W at the standard conditions (5 MPa and 274 K):

$$(Q - W)_{ref} = Q_{at\ 5\ MPa, 274\ K} - W_{at\ 5\ MPa, 274\ K} = 6.30 \times 10^4 \quad (2.94)$$

2.6.3.4 Molar internal energy of CO₂ hydrate particles

The molar internal energy of the CO₂ hydrate particles (U_p) is calculated as the arithmetic mean of the molar internal energies of its constituent phases, weighted by their respective volume fractions. This relationship is given by Equation (2.95):

$$U_p = \alpha U_{CH} + (1 - \alpha) U_{CO_2} \quad (2.95)$$

2.6.3.5 Molar internal energy of CH₄ gas

The molar internal energy (U_{CH_4}) of methane gas is related to its molar enthalpy (h_{CH_4}) through the fundamental thermodynamic definition:

$$U_{CH_4} = h_{CH_4} - \left[\left(\frac{P}{\rho_g} \right) - \left(\frac{P}{\rho_g} \right)_{ref} \right] \quad (2.96)$$

Since the molar enthalpy of methane gas (h_{CH_4}) is the primary input calculated in the simulation, it is necessary to first determine this value. The specific correlation and detailed calculation procedure for h_{CH_4} are described in Section 2.6.4.4.

2.6.3.6 Molar internal energy of CH₄ hydrate

The molar internal energy of methane hydrate (U_{MH}) is modeled to be dependent on the pressure and temperature of its constituent components, a necessary approach given that the specific heat capacity of MH is a function of both parameters [142]. The molar internal energy of MH is obtained by subtracting the internal energy change associated with hydrate formation ($\Delta U = Q - W$) from the total molar internal energy of the constituent water and methane molecules:

$$U_{MH} = N_{MH} U_{H_2O} + U_{CH_4} - (Q - W) + (Q - W)_{ref} \quad (2.97)$$

the heat exchange term (Q) and the work term (W) relate to the energy change during hydrate formation. The enthalpy change (ΔH_{MH}) due to the phase change in one mole of MH is expressed by the linear temperature-dependent model:

$$\Delta H_{MH} = -4.18(A_{MH} + B_{MH}T) \quad (2.98)$$

the model parameters, referenced from Holder et al. [141], are $A_{MH} = 13500$ J/mol and $B_{MH} = -4$ J/(mol·K).

The heat source/sink term (Q) in the energy balance is related to the enthalpy change by:

$$Q = -\Delta H_{MH} \quad (2.99)$$

The work done (W) by the system per mole of hydrate generation is determined by the pressure-volume work ($P\Delta V$):

$$W = P\Delta V = P \times \left(\frac{1}{\rho_{CH_4}} + \frac{N_{MH}}{\rho_{H_2O}} - \frac{1}{\rho_{MH}} \right) \quad (2.100)$$

The reference state correction term, $(Q - W)_{ref}$, is derived by evaluating the energy change terms at the numerical standard state of 5 MPa and 274 K:

$$(Q - W)_{ref} = Q_{at\ 5\ MPa, 274\ K} - W_{at\ 5\ MPa, 274\ K} \quad (2.101)$$

2.6.4 Molar enthalpy

The specific enthalpy (enthalpy per unit mass) of the fluid, denoted as $\hat{h}_A$ (J/kg), and the molar enthalpy (enthalpy per mole) of the fluid, denoted as h_A (J/mol), follow the same hat notation convention established for density and internal energy. The relationship between these two quantities is given by Equation (2.102):

$$\hat{h}_A = \frac{h_A}{M_F} \quad (2.102)$$

2.6.4.1 Molar enthalpy of water

The correlation used to determine the molar enthalpy of water (h_{H_2O}) as a function of temperature and pressure was developed and validated by the author's previous work during

the research conducted in Professor Masuda's laboratory [69]. This correlation is valid for a temperature range of 273.15–313.15 K and a pressure range of 5–20 MPa, which covers the water phase conditions simulated in this study. The molar enthalpy is calculated according to the following expression:

$$h_{H_2O} \times \frac{10^{-3}}{M_{H_2O}} = \left(A_1 \left(\frac{P}{P_0} \right)^2 + A_2 \left(\frac{P}{P_0} \right) + A_3 \right) T^2 + \left(A_4 \left(\frac{P}{P_0} \right)^2 + A_5 \left(\frac{P}{P_0} \right) + A_6 \right) T + \left(A_7 \left(\frac{P}{P_0} \right)^2 + A_8 \left(\frac{P}{P_0} \right) + A_9 \right) \quad (2.103)$$

The coefficients (A_1 through A_9) required for the calculation of the molar enthalpy of water using Equation (2.103) are listed in **Table 2.12**.

Table 2.12 Coefficients used for the correlation of the molar enthalpy of water.

A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9
-1.57E-07	2.72E-05	-0.00045	0.000164	-0.01732	4.478789	-0.02567	3.406698	-1188.75

To ensure consistency with the established 5 MPa and 274 K reference state for enthalpy, the coefficient A_9 from Equation (2.103) must be adjusted. This correction is performed by subtracting the specific enthalpy of water at the reference point, yielding the corrected coefficient $A_{9_{calc}}$:

$$A_{9_{calc}} = A_9 - \hat{h}_{H_2O \text{ at } 5 \text{ MPa}, 274 \text{ K}} = -1197.12 \quad (2.104)$$

2.6.4.2 Molar enthalpy of CO₂

The molar enthalpy of CO₂ (h_{CO_2}) is modeled by the author's previous work [69] as a function of temperature and pressure using a correlation originally derived from the data reported by Span and Wagner [124]. The model is valid for a temperature range of 275–285 K and a pressure range of 5–15 MPa. The molar enthalpy is calculated as follows:

$$h_{CO_2} \times \frac{10^{-3}}{M_{CO_2}} = \left(A_1 \left(\frac{P}{P_0} \right)^2 + A_2 \left(\frac{P}{P_0} \right) + A_3 \right) T^2 + \left(A_4 \left(\frac{P}{P_0} \right)^2 + A_5 \left(\frac{P}{P_0} \right) + A_6 \right) T + \left(A_7 \left(\frac{P}{P_0} \right)^2 + A_8 \left(\frac{P}{P_0} \right) + A_9 \right) \quad (2.105)$$

The coefficients (A_1 through A_9) necessary for the calculation of the molar enthalpy of CO_2 using Equation (2.105) are listed in **Table 2.13**.

Table 2.13 Coefficients used for the correlation of the molar enthalpy of CO_2 .

A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9
0.000289	-0.007879	0.058666	-0.15666	4.2545	-29.4941	21.29593	-575.421	3682.148

The coefficient A_9 is adjusted to meet the 5 MPa and 274 K reference state by subtracting the specific enthalpy ($\hat{h}_{\text{CO}_2}$) of the component at these conditions, as shown:

$$A_{9\text{calc}} = A_9 - \hat{h}_{\text{CO}_2 \text{ at } 5 \text{ MPa}, 274 \text{ K}} = 3682.15 \quad (2.106)$$

2.6.4.3 Molar enthalpy of flowing CO_2 hydrate particles

The molar enthalpy of the flowing CO_2 hydrate particles (h_p) is derived from the fundamental thermodynamic definition relating enthalpy to internal energy ($h = U + PV$). The molar enthalpy is calculated from the molar internal energy (U_p) plus the pressure-volume work term ($\frac{P}{\rho_p}$), with a correction for the reference state:

$$h_p = U_p + \left(\frac{P}{\rho_p}\right) - \left(\frac{P}{\rho_p}\right)_{\text{ref}} \quad (2.107)$$

2.6.4.4 Molar enthalpy of CH_4 gas

The correlation used to calculate the molar enthalpy of methane gas (h_{CH_4}) as a function of temperature and pressure was developed in this study based on the enthalpy data reported by Friend et al. [143]. This correlation is valid within the operational range of 1 MPa to 40 MPa and 270 K to 300 K. The final form of the correlation is expressed as follows:

$$h_{\text{CH}_4} = A_1 T^3 + \left(A_2 \left(\frac{P}{P_0}\right) + A_3\right) T^2 + \left(A_4 \left(\frac{P}{P_0}\right)^2 + A_5 \left(\frac{P}{P_0}\right) + A_6\right) T + \left(A_7 \left(\frac{P}{P_0}\right)^3 + A_8 \left(\frac{P}{P_0}\right)^2 + A_9 \left(\frac{P}{P_0}\right) + A_{10}\right) \quad (2.108)$$

The coefficients (A_1 through A_{10}) required for calculating the molar enthalpy of CH_4 gas via Equation (2.108) are listed in **Table 2.14**.

Table 2.14 Coefficients used for the correlation of the molar enthalpy of CH₄.

Coefficient values	
A_1	0.16769
A_2	0.0672606
A_3	-141.942
A_4	-0.162387
A_5	-30.6658
A_6	40040.8
A_7	-0.00906371
A_8	48.8787
A_9	3083.65
A_{10}	-3.75484E+06

The coefficient A_{10} is adjusted to meet the 5 MPa and 274 K reference state by subtracting the specific enthalpy (h_{CH_4}) of the component at these conditions, as shown:

$$A_{10_{\text{calc}}} = A_{10} - h_{CH_4 \text{ at } 5 \text{ MPa}, 274 \text{ K}} = -3.763025956\text{e}+06 \quad (2.109)$$

The accuracy of this correlation was validated by comparison against the Friend et al. [143] data, yielding an R^2 value of 0.9897 and an average absolute relative error (AARE) of 2.033%. These metrics confirm the correlation's suitability for the pressure and temperature conditions encountered in the MH reservoir simulations.

2.6.5 Effective thermal conductivity of porous media

The overall thermal conductivity (λ) of the porous media, expressed in W/(m·K), is determined using a geometric mean model. This model accounts for the thermal conductivity of each component distributed within the system, weighted by its respective saturation (S) within the porous space. The overall relationship is given by Equation (2.110):

$$\lambda = \lambda_{H_2O}^{\phi_0 S_{H_2O}} \lambda_{CO_2}^{\phi_0 S_{CO_2}} \lambda_{CH}^{\phi_0 S_{CH}} \lambda_{CH_4}^{\phi_0 S_{CH_4}} \lambda_{MH}^{\phi_0 S_{MH}} \lambda_{gr}^{(1-\phi_0)} \quad (2.110)$$

where λ_{H_2O} , λ_{CO_2} , λ_{CH} , λ_{CH_4} , λ_{MH} , and λ_{gr} are the thermal conductivities of water, CO₂, CO₂ hydrate, CH₄ gas, methane hydrate, and rock grains, respectively.

2.6.5.1 Thermal conductivity of water

A correlation originally derived from the data of Ramires et al. [144] is employed to calculate the thermal conductivity of water. This specific correlation, which depends on temperature, was previously implemented and validated by the former research group in Professor Masuda's laboratory [69], [125]. The correlation is valid for a temperature range of 275–290 K and is expressed as follows:

$$\lambda_{H_2O} = A_1 T + A_2 \quad (2.111)$$

Table 2.15 lists the required coefficients (A_1 and A_2) used in Equation (2.111) for modeling the thermal conductivity of water.

Table 2.15 Coefficients for the water thermal conductivity correlation.

A_1	A_2
0.002073	−0.00917

2.6.5.2 Thermal conductivity of CO₂

A specific correlation, whose underlying data originated from the work of Vesovic et al. [145], is used to calculate the temperature and pressure-dependent thermal conductivity of CO₂. This model was previously implemented and validated by research conducted in Professor Masuda's laboratory [69], [125].

$$\lambda_{CO_2} \times 10^3 = \left(A_1 \left(\frac{P}{P_0} \right)^2 + A_2 \left(\frac{P}{P_0} \right) + A_3 \right) T^2 + \left(A_4 \left(\frac{P}{P_0} \right)^2 + A_5 \left(\frac{P}{P_0} \right) + A_6 \right) T + \left(A_7 \left(\frac{P}{P_0} \right)^2 + A_8 \left(\frac{P}{P_0} \right) + A_9 \right) \quad (2.112)$$

The coefficients (A_1 through A_9) for the CO₂ thermal conductivity correlation (Equation 2.112) are presented in **Table 2.16**.

Table 2.16 Coefficients for the CO₂ thermal conductivity correlation.

A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9
−3.10E−05	0.001289	−0.01152	0.01504	−0.63911	4.694902	−1.8307	80.48626	−318.299

2.6.5.3 Thermal conductivity of CO₂ hydrate

The thermal conductivity of CO₂ hydrate is modeled as a function of temperature using a correlation developed by the author's previous work [69], which utilized data originally reported by Wan et al. [146]. The correlation is valid for a temperature range of 260–300 K and a pressure range of 5–12.5 MPa. The general form used is:

$$\lambda_{CH} = A_1 T^2 + A_2 T + A_3 \quad (2.113)$$

Table 2.17 lists the required coefficients (A_1 to A_3) used in Equation (2.113) for modeling the thermal conductivity of the CO₂ hydrate.

Table 2.17 Coefficients for the CO₂ hydrate thermal conductivity correlation.

A_1	A_2	A_3
0.01263822	−6.98833371	966.759827

2.6.5.4 Thermal conductivity of CH₄ gas

To model the thermal conductivity of methane gas across the operational range 1 MPa to 50 MPa and 270 K to 300 K, a new correlation was developed in this study. This correlation utilizes enthalpy data reported by Friend et al. [143] and is presented below:

$$\lambda_{CH_4} = A_1 T^2 + A_2 \left(\frac{P}{P_0}\right)^2 + A_3 \left(\frac{P}{P_0}\right) T + A_4 T + A_5 \left(\frac{P}{P_0}\right) + A_6 \quad (2.114)$$

The coefficients (A_1 through A_6) for the CH₄ gas thermal conductivity correlation (Equation 2.114) are presented in **Table 2.18**.

Table 2.18 Coefficients for the CH₄ thermal conductivity correlation.

A_1	A_2	A_3	A_4	A_5	A_6
0.0000015	−0.000007997	−0.000009679	−0.000740	0.004627	0.1182

The correlation was validated using the Friend et al. [143] data showing high accuracy with an R^2 of 0.9961 and AARE of 2.997%. This performance ensures the correlation is suitable for calculating CH₄ gas thermal conductivity under the relevant pressure and temperature ranges.

2.6.5.5 Thermal conductivity of CH₄ hydrate

The thermal conductivity of methane hydrate (λ_{MH}) has been characterized by Waite et al. [142] through empirical relationships showing weak dependence on temperature:

$$\lambda_{MH} = -(2.78 \pm 0.05) \times 10^{-4}(T - 273.15) + (0.62 \pm 0.02) \quad (2.115)$$

and pressure:

$$\lambda_{MH} = (2.54 \pm 0.06) \times 10^{-4} \left(\frac{P}{P_0} \right) + (0.61 \pm 0.02) \quad (2.116)$$

where $P_0 = 1$ MPa. Given the weak nature of these dependencies, a constant thermal conductivity value of $\lambda_{MH} = 0.6$ W/(m·K) was used throughout this study.

Chapter 3

Numerical model validation

Chapter 2 detailed the theoretical and mathematical foundation of the T-H-C numerical framework developed for simulating CO₂ dual-purpose injection. The transition from theoretical formulation to reliable 3D application necessitates rigorous validation against empirical evidence. This chapter, therefore, presents the crucial steps taken to establish the T-H-C model's accuracy and predictive capability.

3.1 Overview of the experimental system and data

The reliability of the developed numerical framework was rigorously established by validating its performance against six distinct sets of experimental data sourced from the Masuda laboratory [63], [69]. These experiments were specifically designed to investigate the process of injecting a C/W emulsion into a porous medium composed of sintered glass beads, initially saturated with water. The physical tests were carried out on a cylindrical core sample, which measured 10 cm in length and 5 cm in diameter, housed within a specialized apparatus. As illustrated in **Figure 3.1**, the setup permitted precise control over experimental conditions. Key components included a back pressure regulator for maintaining constant outlet pressure, a separator to effectively isolate gas from the liquid production stream, and dedicated pumps for supplying both water and liquid CO₂. These fluids were routed to a mixer before entering the core. Temperature stability was ensured by a temperature-controlled water bath, and a computer system continuously logged all temperature and pressure measurements .

Crucially, the CO₂ emulsion was synthesized by introducing liquid CO₂ into the mixer through a mesh filter tube. This filter had a controlled pore size optimized to create highly uniform CO₂ droplets with a diameter of approximately 10 μm . This controlled droplet size was key to ensuring the emulsion's stability and uniformity. The resulting C/W emulsion, which consists of CO₂ droplets dispersed throughout the aqueous phase, maintained stability primarily through the electrostatic repulsion forces acting between the similarly charged droplets. This uniformity ensured effective and stable transport of CO₂ through the water-saturated porous core. Throughout the experimental runs, the ambient temperature of the system was maintained at approximately 7.0 °C via water circulation [63].

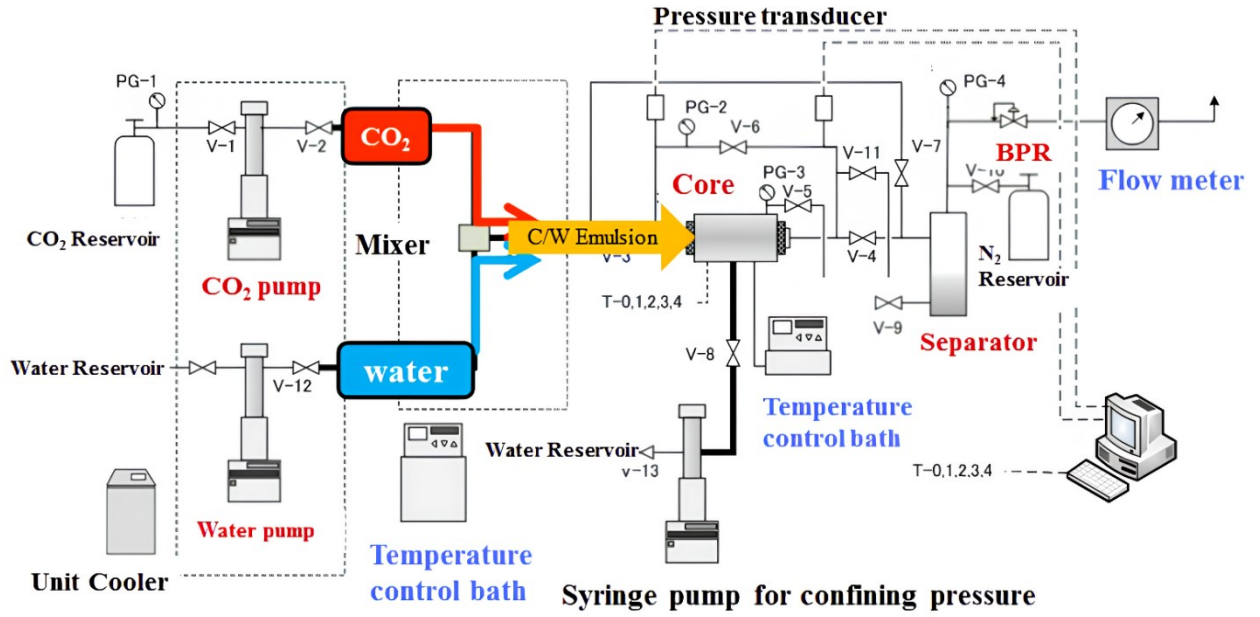


Figure 3.1 Diagram of the core-flooding experimental setup utilized by Masuda lab for C/W emulsion injection (Reproduced from Bahmaee et al., [63], licensed under CC BY-NC-ND).

Real-time monitoring of the experiment involved tracking key parameters. High-accuracy pressure transducers were positioned at both the inlet and outlet of the core sample. Temperature data was collected at five distinct points: at the inlet, outlet, and three intermediate locations along the core surface (specifically 2.5 cm, 5 cm, and 7.5 cm from the inlet). The placement of these sensors, along with the end caps, is schematically presented in **Figure 3.2**. All measured data were continuously recorded by a dedicated computer system at regular intervals for subsequent analysis.

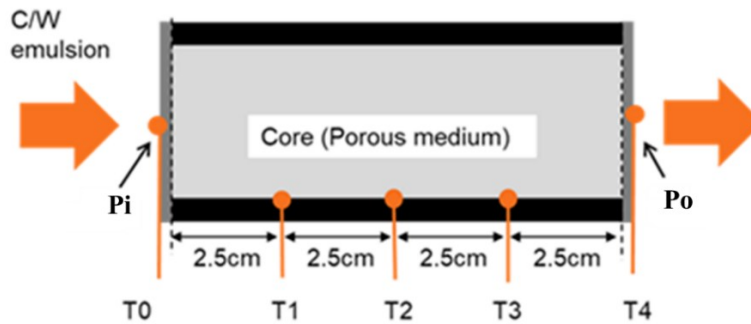


Figure 3.2 Measurement points for pressure and temperature within the core-flooding experimental setup (Reproduced from Bahmaee et al., [63], licensed under CC BY-NC-ND).

The experimental program investigated several injection strategies. Specifically, the study included one baseline water injection experiment, which was used primarily for calculating the system's overall heat transfer coefficient. This was followed by three scenarios involving continuous emulsion (CE) injection and two scenarios using water-alternating-emulsion (WAE) injection. The core purpose of the CE and WAE runs was to systematically investigate

the influence of varying the liquid CO₂ volume fraction within the injected emulsion. The WAE tests utilized uniform water and emulsion slugs of 0.25 pore volume (PV). The flow rate of all injection scenarios was 2 mL/min.

Based on the soda lime glass beads physical properties data reported by Bahmaee [69], the sintered glass bead core had a porosity of 37%, a thermal conductivity of 1.1 W/(m·K), a grain mass density of 2600 kg/m³, and a grain specific heat capacity of 837 J/(kg·K). Permeability was estimated using Equation (2.44). The calculated permeability varied based on the bead size: 7.12 Darcy (7.027 μm²) for the core with a bead diameter of 0.1 mm and 1.78 Darcy (1.757 μm²) for the core with a bead diameter of 0.05 mm. For the core with a bead diameter of 0.1 mm, the Reynolds number at the core inlet is approximately 0.002, and for the 0.05 mm bead diameter, it is approximately 0.001. These values, being much less than 1, confirm that the flow is strictly laminar, justifying the use of Darcy equations for the numerical validation. The specific conditions for all experiments used for validation are summarized in **Table 3.1**.

Table 3.1 Summary of experimental conditions for model validation (Adapted from Bahmaee et al. [63]).

Experiment	Grain diameter (mm)	Permeability (μm ²)	CO ₂ volume fraction in the emulsion (%)	Initial Pressure (MPa)
Water injection	0.1	7.027	-	7.27
CE10	0.1	7.027	10	7.23
CE20	0.1	7.027	20	7.08
CE30	0.1	7.027	30	7.14
WAE20	0.05	1.757	20	7.25
WAE30	0.05	1.757	30	7.19

Most experiments showed a rapid inlet pressure rise indicating hydrate-induced core plugging, which necessitated immediate termination of the emulsion flow. The injection phase was sustained for 4 to 5 hours only in the absence of clogging.

3.2 Mathematical formulation of the 1D validation model

The core-scale flow domain used in the Masuda lab experiments is considered inherently one-dimensional (1D). The cylindrical geometry, combined with the fact that fluid is injected only at one end and produced at the opposite end, establishes a single, primary flow axis along the core's length. Furthermore, all physical measurements (pressure, P_i , P_o , and temperature, T_0 to T_4) were taken either at the end faces or along the axial length, confirming that the

experiment measures changes only in the direction of flow. Hence, this section presents the necessary governing equations and simplifications for the 1D numerical validation.

Due to the assumption of 1D single-phase flow, the gravity term in the Darcy equation is omitted, and the liquid phase is treated as the emulsion flowing through the core:

$$\vec{u}_e = -\frac{K_D}{\mu_e} \nabla P \quad (3.1)$$

The material balance equations for the individual transported components—which include water, liquid CO₂, total CO₂ (dissolved CO₂ plus liquid CO₂), and the three states of CO₂ hydrate particles (flowing, adsorbed, and trapped)—and the overall energy conservation equation are presented as follows:

Water :

$$-\nabla \cdot (\vec{u}_e S_e \chi_{H_2O} \rho_{H_2O}) - \dot{q}_{H_2O}^{CH_{form}} + \dot{q}_{H_2O}^{CH_{dsol}} = \phi_0 \frac{\partial}{\partial t} (S_e \chi_{H_2O} \rho_{H_2O}) \quad (3.2)$$

Liquid CO₂:

$$-\nabla \cdot (\vec{u}_e S_e \chi_{LCO_2} \rho_{LCO_2}) - \dot{q}_{CO_2}^{CH} - \dot{q}_{dsol} = \phi_0 \frac{\partial}{\partial t} (S_e \chi_{LCO_2} \rho_{LCO_2}) \quad (3.3)$$

Total CO₂:

$$-\nabla \cdot (\vec{u}_e S_e (1 - \chi_{H_2O}) \rho_{LCO_2}) - \dot{q}_{CO_2}^{CH} + \dot{q}_{wCO_2}^{dsol} = \phi_0 \frac{\partial}{\partial t} (S_e (1 - \chi_{H_2O}) \rho_{LCO_2}) \quad (3.4)$$

Flowing CO₂ hydrate particles:

$$\begin{aligned} & -\nabla \cdot (\vec{u}_e S_{PF} \rho_P) + \nabla \cdot (K_L \nabla S_{PF} \rho_P) + \dot{q}_P - \dot{q}_{PF}^{dsol} - \phi_0 (k_{trap} S_{PF} - k_{det} S_{Ptrap}) \rho_P - \\ & \phi_0 (k_{ads} S_{PF} - k_{det} S_{Pads}) \rho_P = \phi_0 \frac{\partial}{\partial t} (S_{PF} \rho_P) \end{aligned} \quad (3.5)$$

where $\dot{q}_{PF}^{dsol}$ is the dissolution rate of flowing hydrate particles and K_L (m²/s) is the longitudinal dispersion coefficient.

The overall longitudinal dispersion coefficient (K_L) in porous materials is traditionally the sum of molecular diffusion (D_{HP}) and convective dispersion (E_L), as per Perkins and Johnston [147] (Equation 3.6). However, in this numerical work, molecular diffusion was neglected due

to its small magnitude. By further assuming a uniform particle diameter for the porous medium, the convective dispersion term was simplified, resulting in the degree of inhomogeneity (θ) being set to 1.

$$K_L = D_{HP} + E_L \approx E_L \quad (3.6)$$

$$E_L = 0.5\theta D_{gr} \frac{\vec{u}_e}{\phi} \quad (3.7)$$

Adsorbed CO₂ hydrate particles:

$$\phi_0(k_{ads}S_{PF} - k_{det}S_{Pads})\rho_P - \dot{q}_{Pads}^{dsol} = \phi_0 \frac{\partial}{\partial t} (S_{Pads}\rho_P) \quad (3.8)$$

Trapped CO₂ hydrate particles:

$$\phi_0(k_{trap}S_{PF} - k_{det}S_{Ptrap})\rho_P - \dot{q}_{Ptrap}^{dsol} = \phi_0 \frac{\partial}{\partial t} (S_{Ptrap}\rho_P) \quad (3.9)$$

Energy conservation equation:

$$\begin{aligned} \nabla \cdot (\lambda \nabla T) - \nabla \cdot \vec{u}_e (\rho_{LCO_2} S_{CO_2} h_{CO_2} + \rho_{H_2O} S_{H_2O} h_{H_2O} + S_{PF} \rho_P h_P) + \nabla \cdot (K_L \nabla (S_{PF} \rho_P h_P)) + \\ HA_{HT}(T_\infty - T) - \Delta H_{CH}(\dot{q}_{CH}^{form} - \dot{q}_{CH}^{dsol}) - \Delta H_S(\dot{q}_{dsol} + \dot{q}_{wCO_2}^{dsol}) = \frac{\partial}{\partial t} \left((1 - \phi_0) \hat{\rho}_{gr} C_{gr} T + \right. \\ \left. \phi_0 (\rho_{CH} S_{CH} U_{CH} + \rho_{LCO_2} (S_{CO_2} + S_{PT}(1 - \alpha) U_{CO_2}) + \rho_{H_2O} S_{H_2O} U_{H_2O}) \right) \end{aligned} \quad (3.10)$$

where $\hat{\rho}_{gr}$ (kg/m³) and C_{gr} (J/(kg·K)) are the mass density and specific heat capacity of grains constituting the porous medium (sintered glass beads). The term H (W/(m²·K)) is the heat transfer coefficient that governs heat exchange with the surrounding boundary, and A_{HT} is the specific heat-transfer area per unit bulk volume of the porous medium.

3.3 Numerical implementation and solution strategy

The numerical framework was developed within the MATLAB environment and integrated with the MATLAB Reservoir Simulation Toolbox (MRST), an open-source platform benchmarked against commercial simulation tools [148]. The overall computational workflow is presented in **Figure 3.3**.

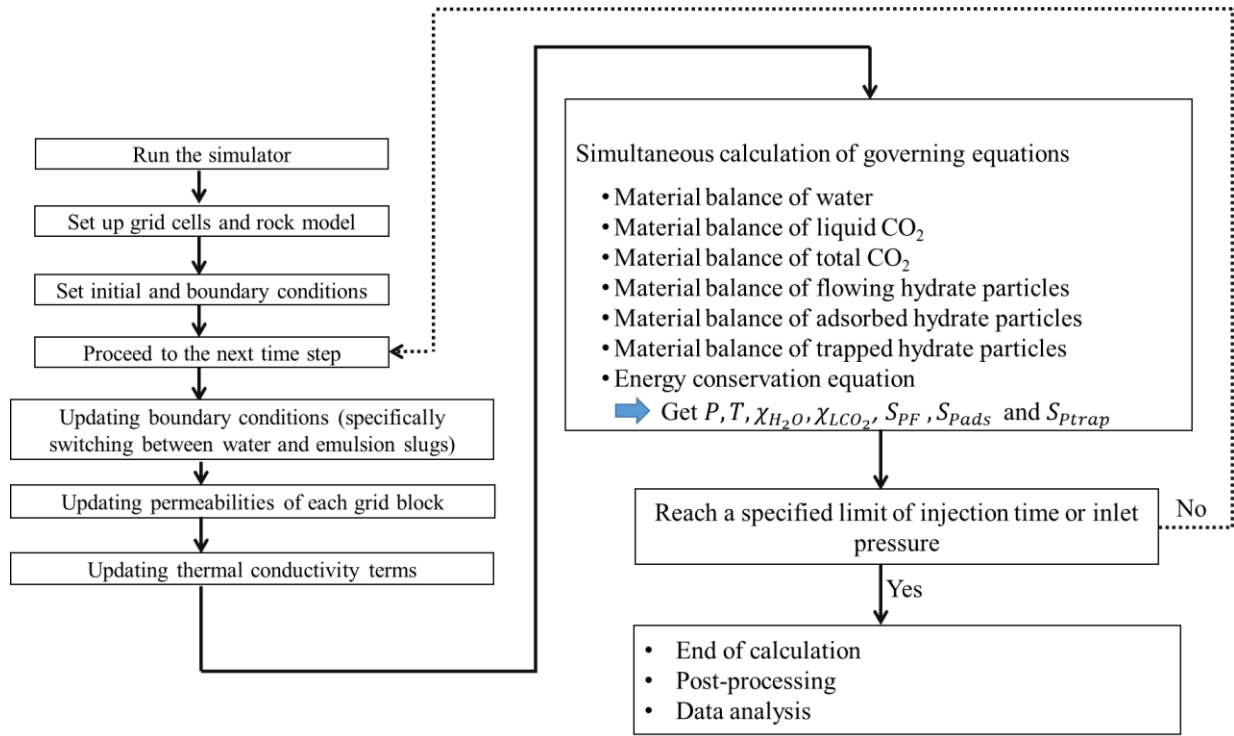


Figure 3.3 Computational flow work.

3.3.1 Discretization and flow operators

The system's governing continuity and energy balance equations were discretized utilizing the finite-volume method (FVM) across a Cartesian coordinate system for the porous domain. For these calculations, divergence and gradient operators were employed [148], [149]. Fluid flow between grid blocks was characterized using the concept of transmissibility, which was determined by calculations involving the grid-cross-sectional area, normal vector, and centroid vector [148], [149]. Furthermore, upwind operators were applied to compute the phase fluxes accurately at the interfaces between grid blocks.

3.3.2 System solver

A fully implicit solver based on the Newton-Raphson method was utilized to find solutions for the highly nonlinear set of governing equations at each time step. To improve efficiency in computing the Jacobian matrix, which is central to the Newton-Raphson scheme, Automatic Differentiation (AD) was leveraged. AD automated the process of generating the partial derivatives of the residuals with respect to the unknown variables, significantly reducing potential derivation errors and computational overhead [149]. The resulting large, sparse linear system was solved using the backslash (\) operator, a direct solver built into MATLAB. The

iterative solution process continued until the norm of the residuals converged to a tolerance level of 10^{-6} or lower.

3.4 Physical simulation setup for validation

To validate the model against the 1D experimental data, a regular Cartesian grid was constructed (**Figure 3.4**). Its dimensions were set to be identical to the experimental core, defining the bounded domain as $[0, 10]$ centimeters in the flow direction and $[0, 4.45] \times [0, 4.45]$ centimeters in the cross-section. Although the simulation utilized a cuboid geometry and the experimental core was cylindrical, this configuration ensured that the simulated core shared a comparable volume and cross-sectional area with the actual cylindrical core. The core was discretized into 21 grid blocks along the x-direction (the flow path), with the end cells (first and last) having half the length of the internal cells.

For validation, temperature values corresponding to the four measurement points were selected. These included the inlet temperature sensor, T0, and three internal points, T1, T2, and T3, represented by grid centers located 2.5, 5, and 7.5 centimeters from the inlet (**Figure 3.2**). Pressure measurements were validated at the inlet (Pi) and outlet (Po) boundaries.

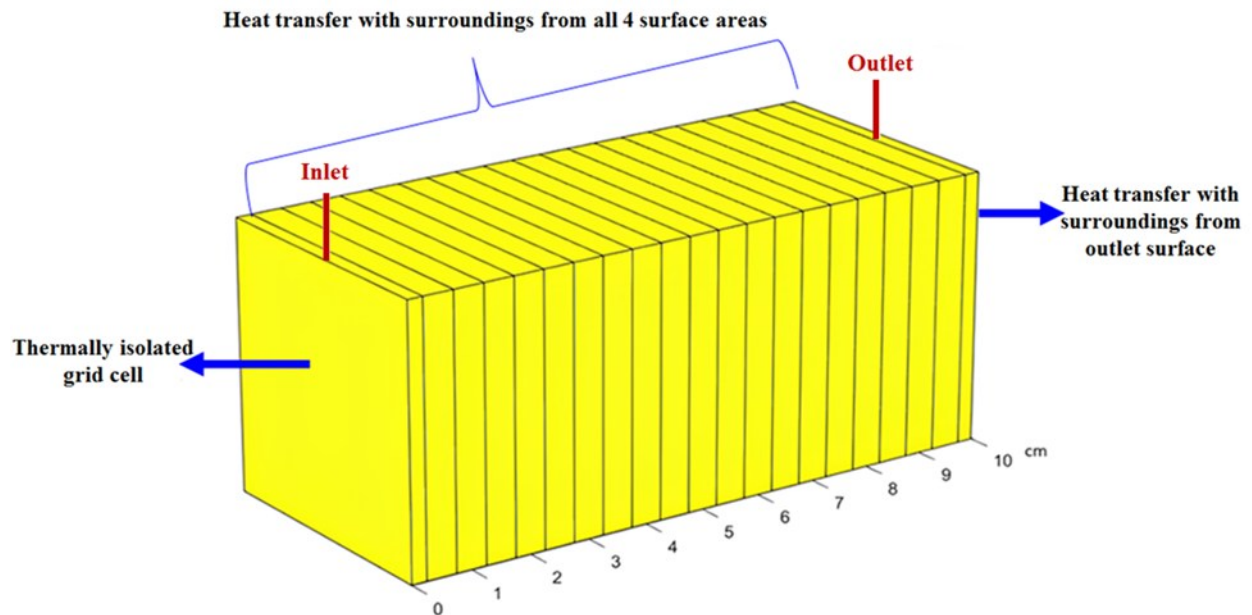


Figure 3.4 Schematic detailing the numerical boundary conditions applied to the core model, including flow boundaries (inlet and outlet) and prescribed thermal conditions.

3.4.1 Thermal boundary conditions

To accurately represent the thermal influence of the end caps, specific conditions were applied to the first and last grid cells. The inlet cell was modeled without internal heat transfer or conduction, which ensures its temperature output aligns with the experimental T0 value under stable, steady-state conditions (**Figure 3.2**). Crucially, this cell's heat capacity was assigned to be higher than that of the rest of the core to effectively replicate the observed initial, transient temperature rise at the T0 monitoring point during the start of the experiment. At the other end, the last grid cell transfers heat to the environment from its entire external surface area, including both the outlet face and the lateral surfaces, using an equivalent heat transfer coefficient as that of the lateral surface. Furthermore, the injection temperature for each experiment was dynamically defined by an equation that is a function of the time evolution of the experimental T0 reading and the measured temperature of the injected fluid line (which was consistently approximately 14 °C).

3.4.2 Injection conditions and CO₂ partitioning

The initial conditions and boundary conditions for the simulation are established using the data presented in Section 3.1. **Table 3.2** details the injection boundary conditions, specifically the partitioning of liquid CO₂ between the dissolved state in water and the liquid droplets dispersed within the emulsion. The injection temperature for the fluid mixture was set to that of injection line which is approximately 14 °C.

Table 3.2 CO₂ partitioning in injected C/W emulsions (Adapted from Bahmaee et al. [63]).

Experiment	Liquid CO ₂ volume fraction in the emulsion (%)	Dissolved CO ₂ volume fraction in the emulsion (%)	Solubility fraction
Water injection	-	-	-
CE10	0.042	0.058	0.8
CE20	0.1419	0.0581	0.9
CE30	0.2435	0.0565	1
WAE20	0.142	0.058	0.9
WAE30	0.2437	0.0563	1

For the WAE30 and CE30 experiments, the amount of CO₂ dissolved in the water phase of the injected emulsion was assumed to be at saturation solubility (a solubility fraction of 1). However, for the CE10 and CE20 experiments, the dissolved CO₂ was set as a fraction of the saturation solubility. This lower fractional solubility value was also applied to the WAE20

simulation. This choice was necessary because the experimental temperature profiles, particularly before the hydrate induction time, suggested that continuous CO₂ dissolution was still occurring in these runs. The reason for this lower initial solubility is hypothesized to be due to a slower dissolution rate with a lower available volume fraction of liquid CO₂ relative to water (based on Equation 2.17).

3.4.3 Model calibration and tuning

In this study, four key parameters— CO₂ hydrate particle generation rate constant (γ), volume fraction of CO₂ hydrate film formed around liquid CO₂ droplet (α), CO₂ dissolution rate constant (β), and pressure adjustment coefficient for CO₂ dissolution heat (C)—were adjusted to ensure the numerical model accurately matched the experimental temperature behavior, both before and after the hydrate induction time.

The parameters γ and α were calibrated using the temperature response after the induction time, when the thermal signal is primarily governed by the kinetics of hydrate formation and growth. Conversely, the parameters β and C were validated using the temperature data before the hydrate induction time, a period dominated by the heat effect of CO₂ dissolution. The calibrated values of β and C were initially validated against the WAE30 and CE30 experimental data before being used to predict the other experimental data sets with their assigned solubility fractions.

3.5 Initial model validation: Heat transfer coefficient calibration

The first step in the validation process was the determination of the heat transfer coefficient, H . This was achieved by simulating the injection of pure water into the core. Water, slightly warmer than the initial core temperature of 6.97 °C, was injected into the water-saturated medium. The measured temperatures at various core locations were used to validate the numerical model, which successfully predicted the temperature time evolution (**Figure 3.5**). This procedure yielded a calibrated heat transfer coefficient of 30 W/(m²·K).

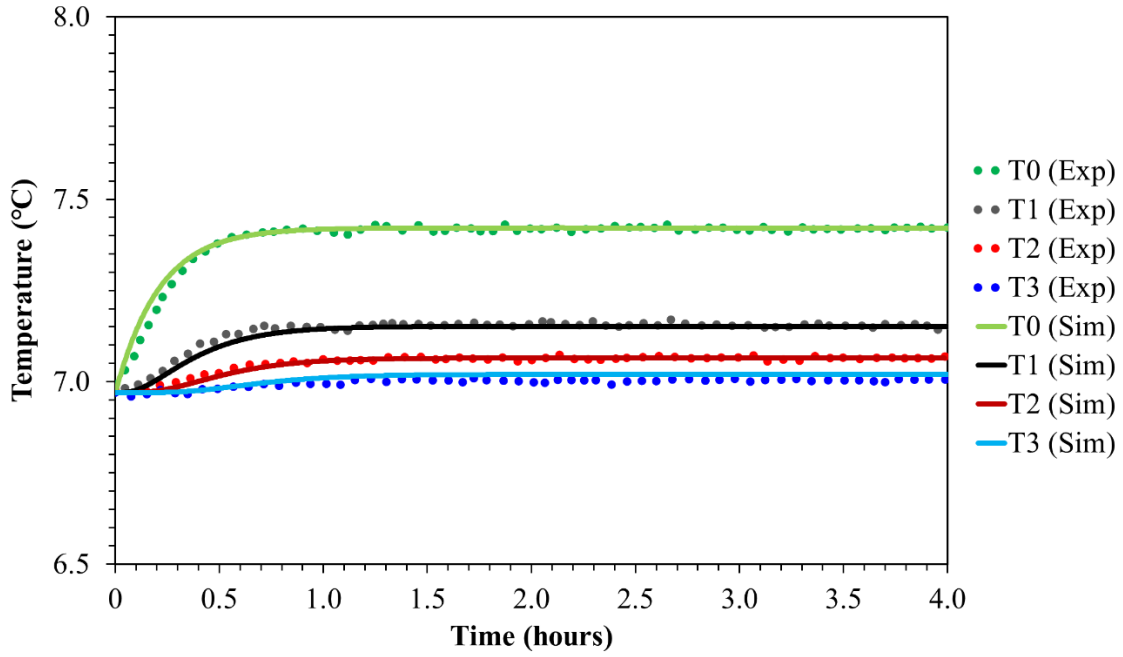


Figure 3.5 Time evolution of the core temperature during water injection.

This determined value for the heat transfer coefficient, along with the calibrated heat capacity assigned to the first grid cell (as detailed in Section 3.4.1), was subsequently applied consistently across all simulations involving the C/W emulsion injection.

3.6 Simulation results and validation for CO₂ injection schemes

This section presents the results from the continuous (CE) and water-alternating C/W emulsion (WAE) injection scenarios, focusing on validating the model's ability to capture temperature trends, pressure behavior, and porous media blockage.

In all injection scenarios, the average liquid CO₂ droplet diameter was assumed to be 10 μm , consistent with the reported size passing the mesh filter tube. However, it is recognized that the actual average diameter might be smaller than the mesh filter size, especially due to subsequent dissolution upon mixing or during the alternating injection of the C/W emulsion with water.

3.6.1 Continuous injection of C/W emulsion

Three experiments (CE10, CE20, and CE30) were conducted under continuous injection conditions. Following C/W emulsion formation, CO₂ dissolution occurred in the injection line. Across all continuous injection scenarios, the numerical model demonstrated strong predictive capability:

1. Pre-induction temperature: By setting the CO₂ dissolution rate constant $\beta = 0.04 \text{ s}^{-1}$ and the pressure adjustment coefficient $C = 0.15$, the model accurately predicted the temperature behavior throughout the core, particularly during the critical pre-induction period.
2. Post-induction temperature: By setting the hydrate particle generation rate constant $\gamma = 0.012 \text{ s}^{-1} \cdot \text{MPa}^{-1}$ and the hydrate film volume fraction $\alpha = 0.55$, the model moderately predicted the temperature evolution after the induction time.

3.6.1.1 CE10 experiment validation

In this scheme, 10% CO₂ was mixed with water and subsequently injected into the core plug. The resulting thermal evolution (**Figure 3.6**) showed a slight temperature increase during the first 1.5 hours of injection, followed by a sharp rise at the induction time. This initial 1.5-hour period is accurately attributed to the dissolution of liquid CO₂ droplets in water and was well predicted using the calibrated dissolution parameters $\beta = 0.04 \text{ s}^{-1}$ and $C = 0.15$.

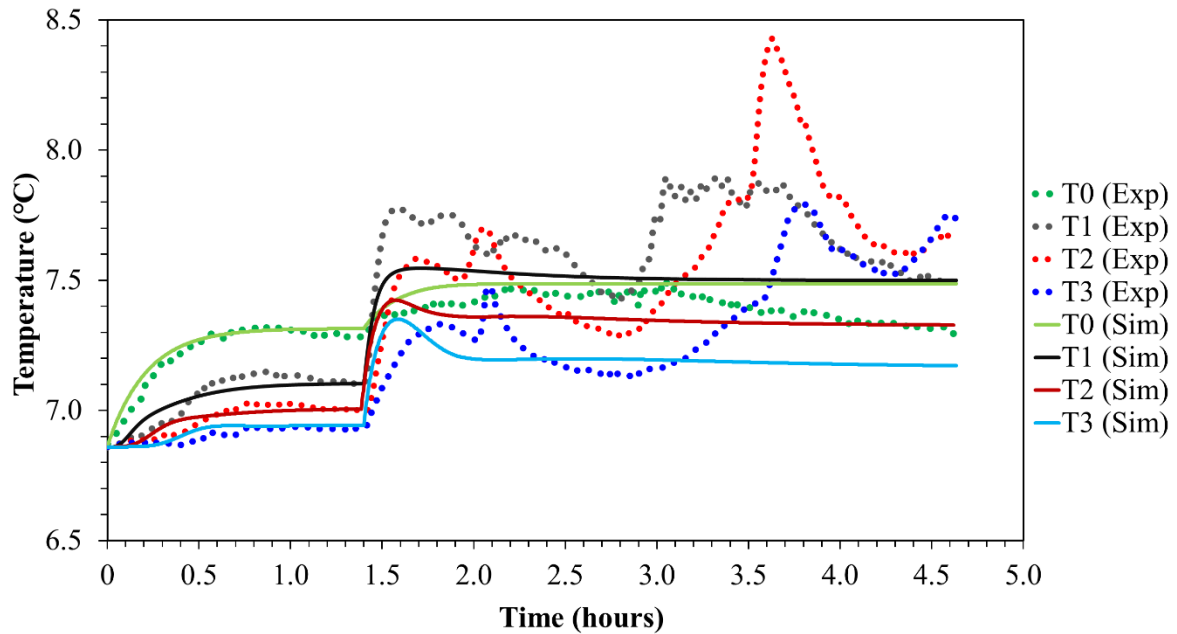


Figure 3.6 Time evolution of temperature for CE10: Comparison of experimental data (Exp) and numerical simulation results (Sim) at various core plug locations.

Following the induction time, the experimental temperature trend exhibited a fluctuating manner, confirming the known stochastic nature of hydrate kinetics [10]. These dynamic changes are compelling evidence of intricate, non-constant interactions within the system, suggesting that parameters such as the hydrate particle formation rate constant (γ), the volume

fraction of the hydrate film (α) within hydrate particles, or the hydration number may not remain constant throughout the process. However, the selected constant parameters ($\gamma = 0.012 \text{ s}^{-1}\cdot\text{MPa}^{-1}$ and $\alpha = 0.55$) allowed the model to successfully predict the general temperature behavior despite the experimental fluctuations.

Crucially, pressure remained stable throughout the injection (**Figure 3.7**). This stability in pressure confirms that no porous media blockage occurred, indicating that the formed CO_2 hydrate particles were likely carried downstream, thus preserving injectivity.

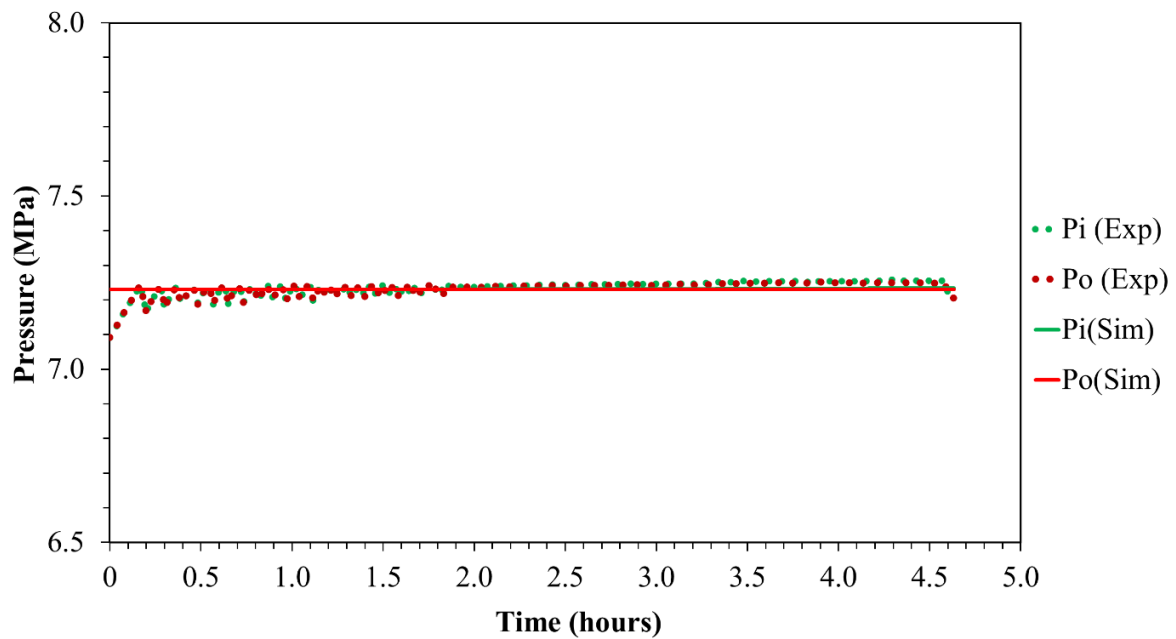


Figure 3.7 Time evolution of inlet and outlet pressures for CE10: Comparison of experimental data (Exp) and numerical simulation results (Sim).

3.6.1.2 CE20 experiment validation

In this scheme, although the injected CO_2 volume was double that of the CE10 experiment, the onset of hydrate formation—as indicated by the corresponding temperature increase—occurred after 4.5 hours (**Figure 3.8**). Crucially, the simulator accurately predicted the temperature trends observed in the experiment up until this induction time. This successful prediction, which is primarily driven by the dissolution of liquid CO_2 in water, affirms the reliability of the chosen dissolution parameters.

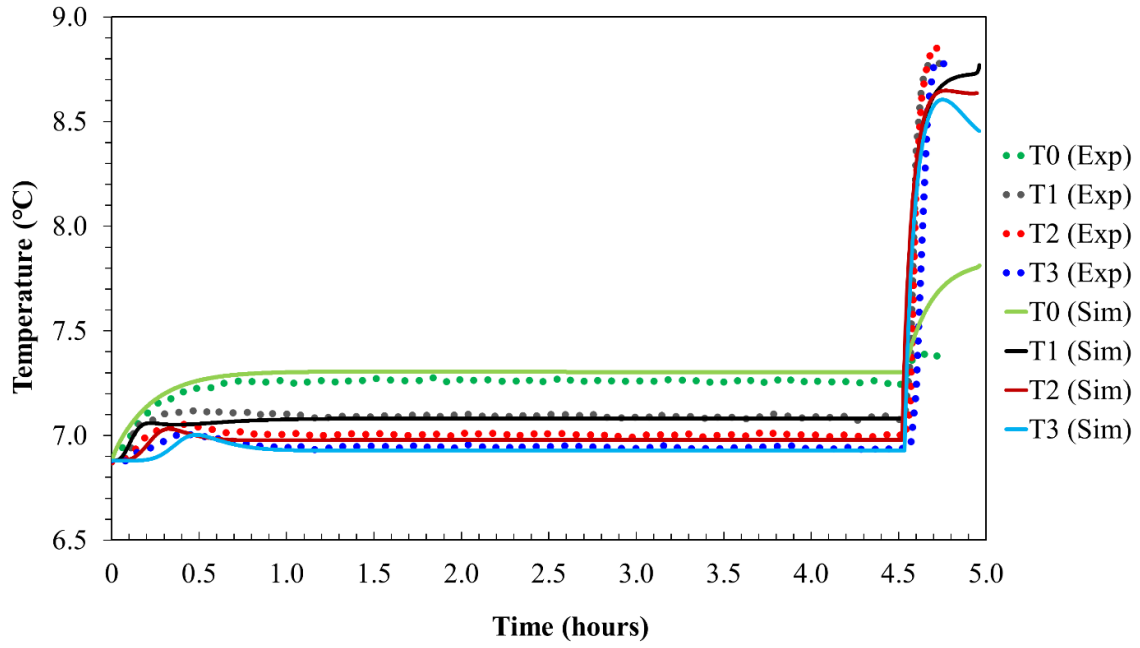


Figure 3.8 Time evolution of temperature for CE20: Comparison of experimental data (Exp) and numerical simulation results (Sim) at various core plug locations.

The model matched the experimental observation of porous media blockage and inlet pressure buildup immediately following the hydrate induction time (**Figure 3.9**). However, the modeled blockage time showed a slight delay; the simulation was terminated after 4.96 hours, occurring approximately 24 minutes later than the corresponding inlet pressure spike recorded in the experiment.

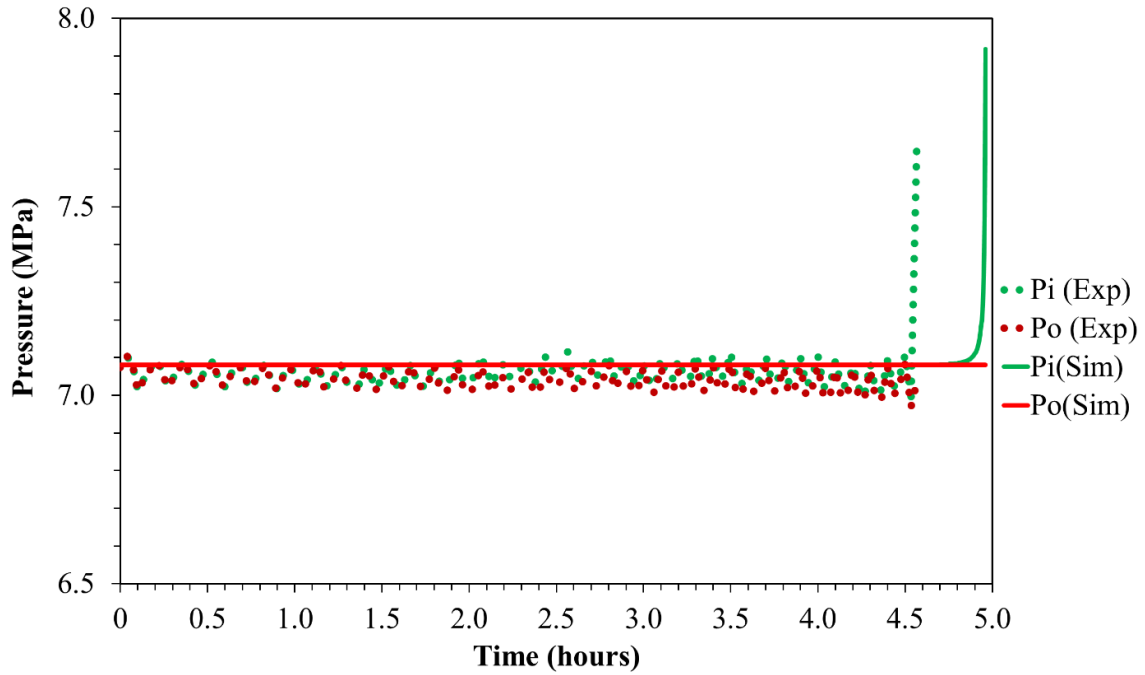


Figure 3.9 Time evolution of inlet and outlet pressures for CE20: Comparison of experimental data (Exp) and numerical simulation results (Sim).

3.6.1.3 CE30 experiment validation

Figure 3.10 further demonstrates the model's accuracy, showing that our simulator accurately reproduced the temperatures observed at different locations within the core plugs. This excellent agreement strongly confirms the reliability of the dissolution model.

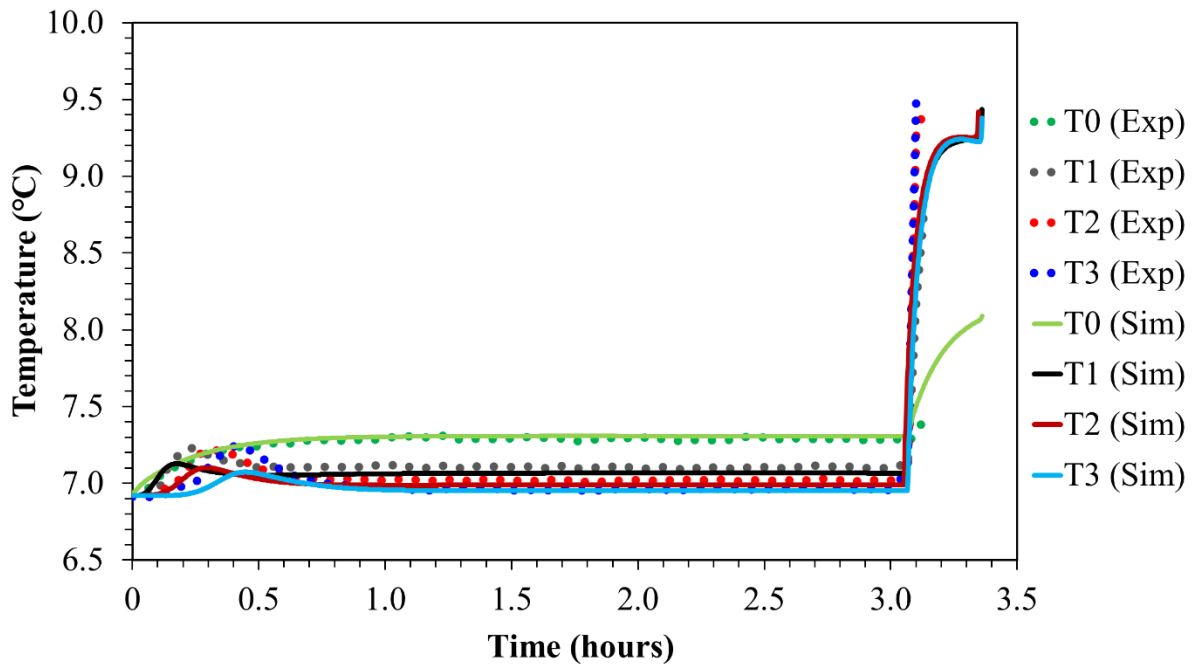


Figure 3.10 Time evolution of temperature for CE30: Comparison of experimental data (Exp) and numerical simulation results (Sim) at various core plug locations.

Upon induction time, the inlet pressure in the experiment exhibited a critical pressure transition (**Figure 3.11**). This transition involved a smooth, preceding pressure increase followed by a sharp surge immediately after induction. This sharp surge is attributed to the sudden formation and agglomeration of hydrate particles, causing rapid pore throat blockage and permeability reduction. Despite setting the detachment rate parameter to zero in the numerical model, the simulator still lagged this observation, as the porous media blockage predicted by the model occurred approximately 18 minutes later than the pressure spike recorded in the experiment.

A separate, preceding smooth and gradual inlet pressure rise commenced approximately 2.5 hours after injection. This gradual rise is consistent with the Jamin effect. The 2.5-hour delay reflects the time required for the CO₂ droplets to travel through the porous medium and begin causing a measurable, bulk flow restriction via the Jamin effect [150], [151]. The flow resistance is primarily governed by CO₂ droplet size relative to pore throat diameters [150], a

factor corroborated by the effect's observation only in the CE30 injection case (and not the CE10 or CE20). The lower concentration mixtures exhibit no clear and visible Jamin resistance due to initially lower number of liquid CO₂ droplets and enhanced CO₂ dissolution in the greater volume of water, mitigating the average CO₂ droplet radius.

The Jamin mechanism involves droplets becoming partially trapped or adsorbed at constrictions, which drastically reduces the flow radius and facilitates the sequential blockage of following droplets [150]. Mobilizing these droplets requires overcoming the differential capillary pressure generated across each segment, where the leading meniscus's smaller radius of curvature necessitates a proportionally higher viscous driving pressure. The observed smooth, sustained pressure rise, including the slight dips or noise confirming the discontinuous nature of droplet trapping and remobilization [152], reflects the cumulative increase in resistance prior to the onset of massive CO₂ hydrate particle formation. However, the developed numerical model does not consider Jamin effect.

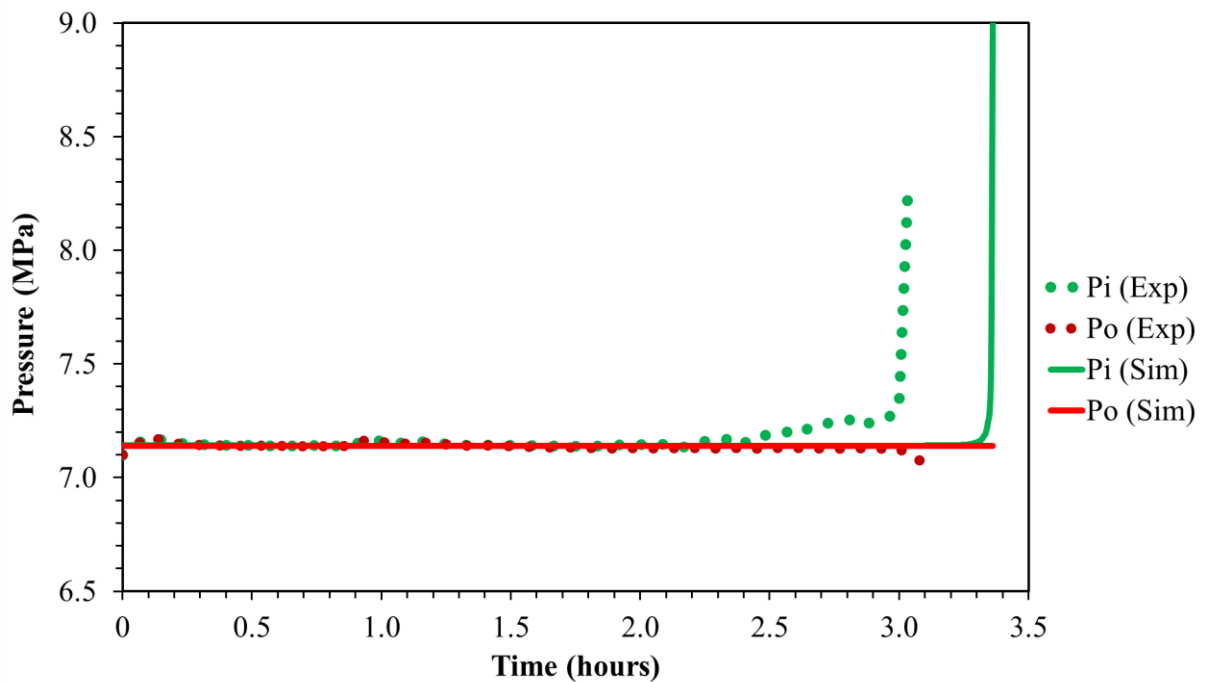


Figure 3.11 Time evolution of inlet and outlet pressures for CE30: Comparison of experimental data (Exp) and numerical simulation results (Sim).

3.6.2 Water-alternating C/W emulsion injection

The WAE scheme was employed to investigate the potential of water slugs to enhance injectivity. Water slugs were alternated with C/W emulsion slugs containing 20% (WAE20) and 30% (WAE30) CO₂ volume fractions. The same calibrated parameters ($\beta = 0.04 \text{ s}^{-1}$ and

$C = 0.15$, $\gamma = 0.012 \text{ s}^{-1}\cdot\text{MPa}^{-1}$ and $\alpha = 0.55$) were applied. The numerical model demonstrated a reasonable prediction of the core temperature behavior across both WAE scenarios.

3.6.2.1 WAE20 experiment validation

In this scheme, by alternately injecting slugs of water with C/W emulsion, the goal was to sweep the flowing hydrate particles downstream and dissolve the particles attached to the pore surface in the pure water slug. The induction time happened after 1 hour of alternating C/W emulsion and water injection (**Figure 3.12**), a shorter time than all continuous injection schemes observed, highlighting the stochastic nature of CO₂ hydrate formation.

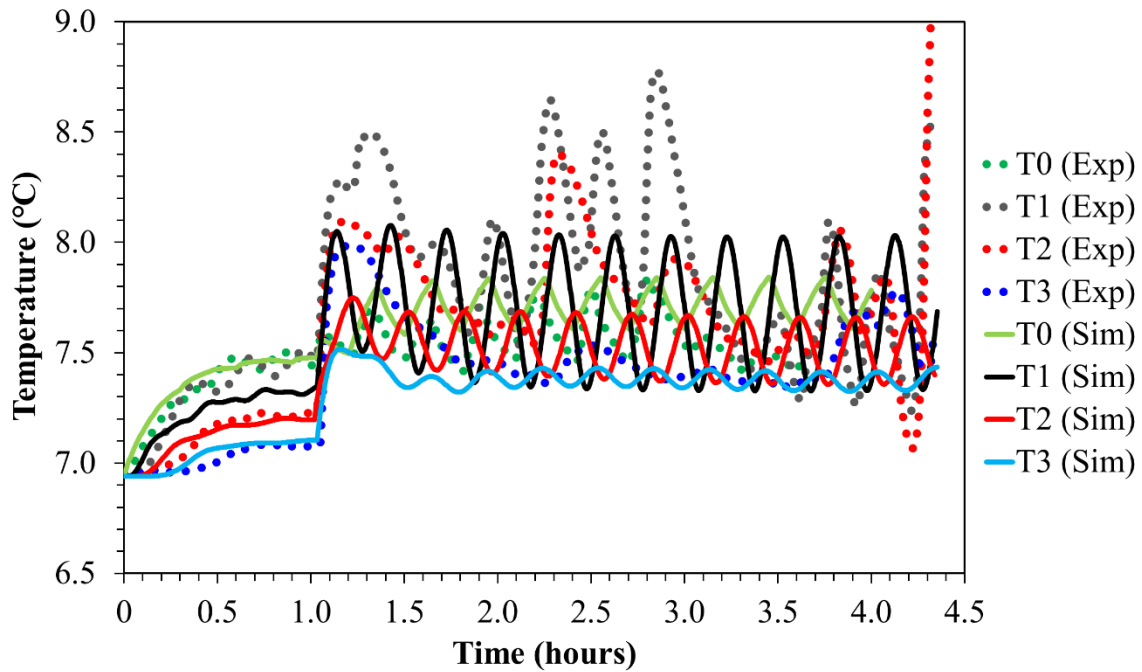


Figure 3.12 Time evolution of temperature for WAE20: Comparison of experimental data (Exp) and numerical simulation results (Sim) at various core plug locations.

The continuous temperature fluctuations are a direct result of the alternating injection. When the water slug is injected, a sharp temperature reduction occurs because the primary heat source, the liquid CO₂ droplets that drive exothermic CO₂ hydrate formation, is rapidly dissolved, and consequently, lost near the inlet. The subsequent flow of pure water then promotes the endothermic dissociation of attached CO₂ hydrate particles, which further exacerbates the temperature reduction. This dual cooling effect is most pronounced near the inlet, where the simulated temperature fluctuations are the largest. The complexity of modeling dynamic

changes in hydrate formation is evident from the T1(Exp) fluctuations, where the peaks and troughs show different values for each injected slug.

Nonetheless, the high value of $\gamma = 0.012 \text{ s}^{-1} \cdot \text{MPa}^{-1}$ successfully models the rapid conversion of available liquid CO₂ droplets to CO₂ hydrate particles near the wellbore. This high conversion efficiency causes the highest temperature increases upstream but depletes the system of liquid CO₂ fuel, leading to a subsequent loss of heat downstream. This thermal trend, characterized by high upstream temperatures and low downstream temperatures due to insufficient liquid CO₂ to sustain the reaction, is consistent with the CE10 numerical validation results.

Furthermore, the injection of alternating water slugs mitigated the clogging of pore throats by hydrate particles and significantly delayed blockage by around 3.5 hours (**Figure 3.13**). The simulator could well predict the timing of pressure increase observed in the experiment.

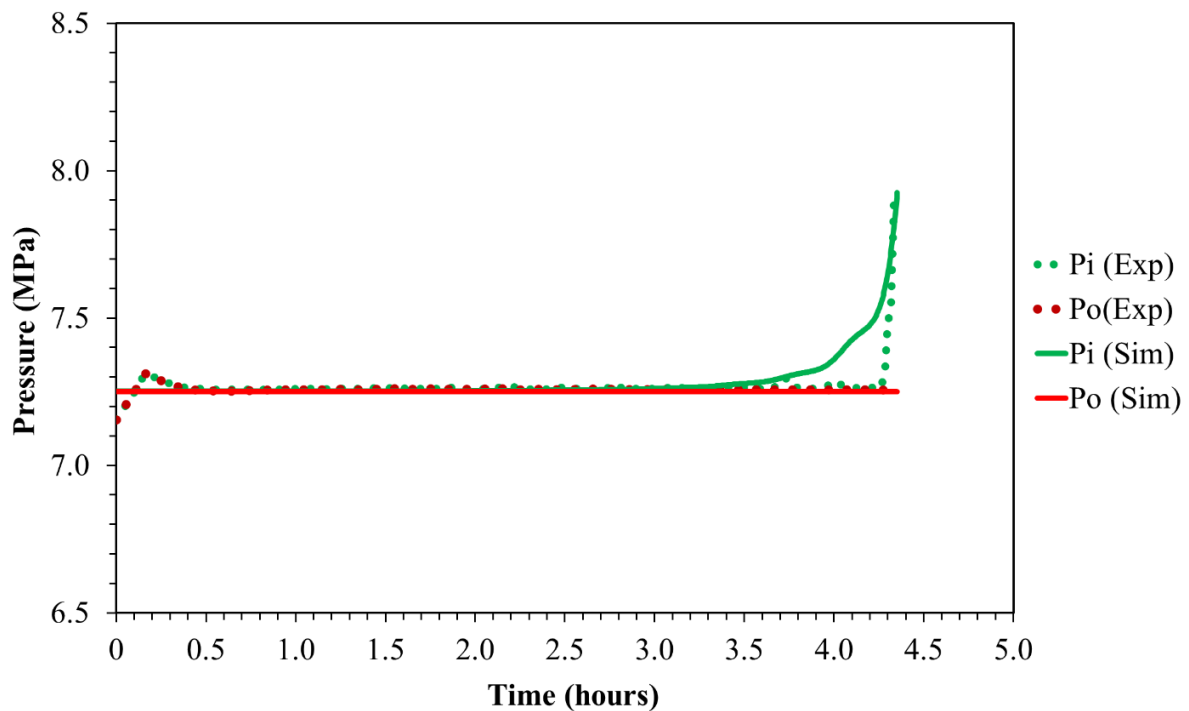


Figure 3.13 Time evolution of inlet and outlet pressures for WAE20: Comparison of experimental data (Exp) and numerical simulation results (Sim).

3.6.2.2 WAE30 experiment validation

In this scheme, similar to WAE20, a similar oscillatory temperature response due to the alternating injection of pure water was observed throughout the injection period (**Figure 3.14**).

The injected water slugs significantly improved the injectivity of the emulsion. However, blockage occurred approximately 1 hour after induction time (**Figure 3.14**), which necessitated stopping the injection.

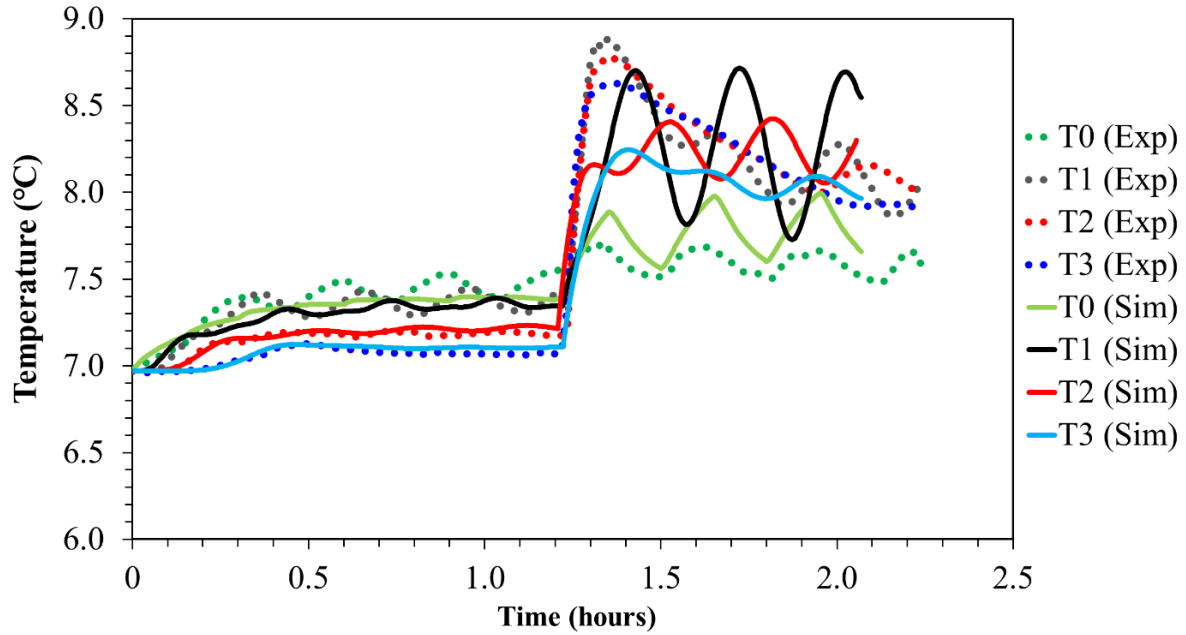


Figure 3.14 Time evolution of temperature for WAE30: Comparison of experimental data (Exp) and numerical simulation results (Sim) at various core plug locations.

The effectiveness of WAE injection is clearly evident from the experiment inlet pressure response (**Figure 3.15**). Specifically, the pressure oscillation observed during the 1-to-2-hour period—where pressure briefly increases and then decreases—is a key indicator. This behavior suggests that CO₂ hydrate particles that were adsorbed on the pore bodies and trapped in the pore throats were exposed to dissolution during the subsequent water slug injection, thereby mitigating the pore throat blockage near the injection inlet.

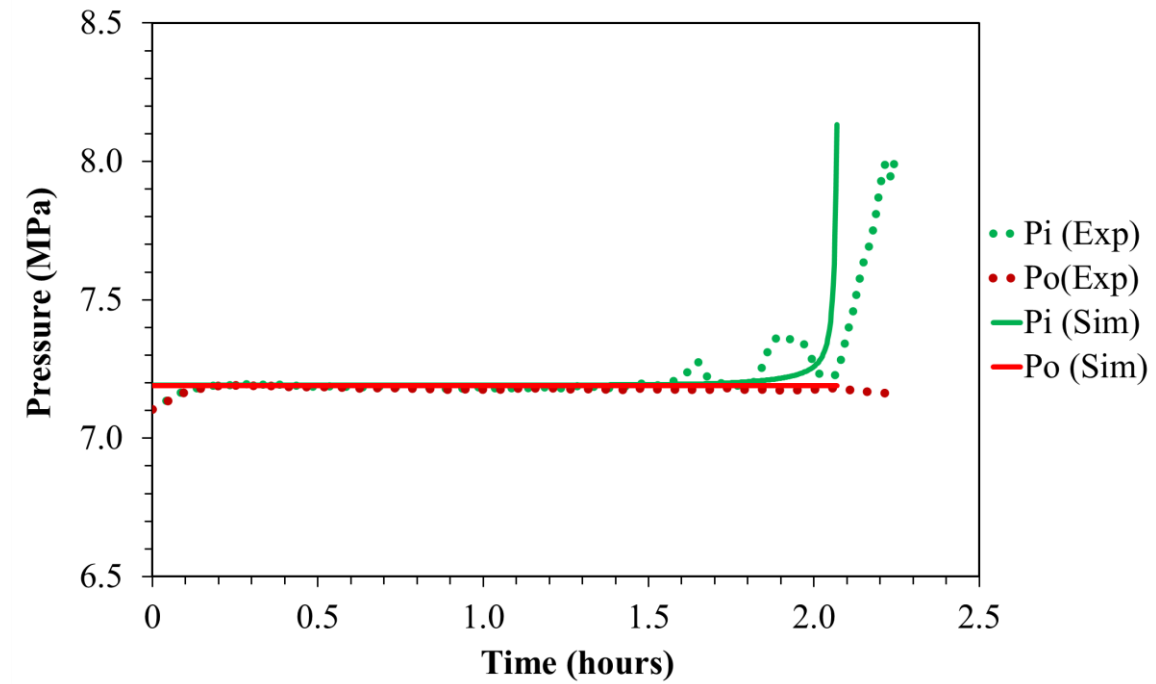


Figure 3.15 Time evolution of inlet and outlet pressures for WAE30: Comparison of experimental data (Exp) and numerical simulation results (Sim).

3.6.3 Comparative analysis of different injection schemes

This section provides a comprehensive, quantitative comparison of the thermal and chemical implications of the different injection methods. **Table 3.3** presents the calculated energy balances, including the net heat supplied to the surrounding environment per cubic meter of the porous medium.

Table 3.3 Thermal performance of different scenarios of injection (Adapted from Bahmaee et al. [63]).

Experiment	Hydrate formation heat [MJ/m ³]	CO ₂ dissolution heat [MJ/m ³]	Hydrate dissociation heat [MJ/m ³]	Supplied heat [MJ/m ³]
CE10	17.63	3.05	4.79	17.45
CE20	11.84	2.07	0.11	12.21
CE30	12.90	0.59	0	9.0
WAE20	27.93	7.89	15.25	21.65
WAE30	14.81	3.78	3.25	12.28

The data presented in **Table 3.3**, specifically concerning CO₂ dissolution heat and hydrate dissociation heat, underscores the multifaceted benefits of the WAE injection approach. This technique provides a path toward optimized dissolution-based carbon sequestration by promoting the efficient dissolution of CO₂ within the aqueous phase. Furthermore, the ability of the water slugs to dissolve formed hydrate particles is crucial for maintaining prolonged

injectivity. Due to this prolonged injection, the WAE method delivers superior thermal performance: the measurable increase in net heat supplied to the surrounding formation would potentially contribute to providing a better thermal stimulation source for MH reservoirs. Notably, the comparative results in **Table 3.3** likely represent a conservative estimate of the WAE method's advantages. For the CE20 and CE30 cases, the actual experimental durations were shorter than the simulation times used for the thermal performance calculations, meaning the simulated heat supply for these cases is likely overestimated. In contrast, for the WAE30 case, the experimental duration exceeded the simulation time due to a premature blockage predicted by the numerical model. Consequently, the true thermal benefits and injectivity improvements offered by the WAE strategy are likely even more significant than the simulated comparative results suggest.

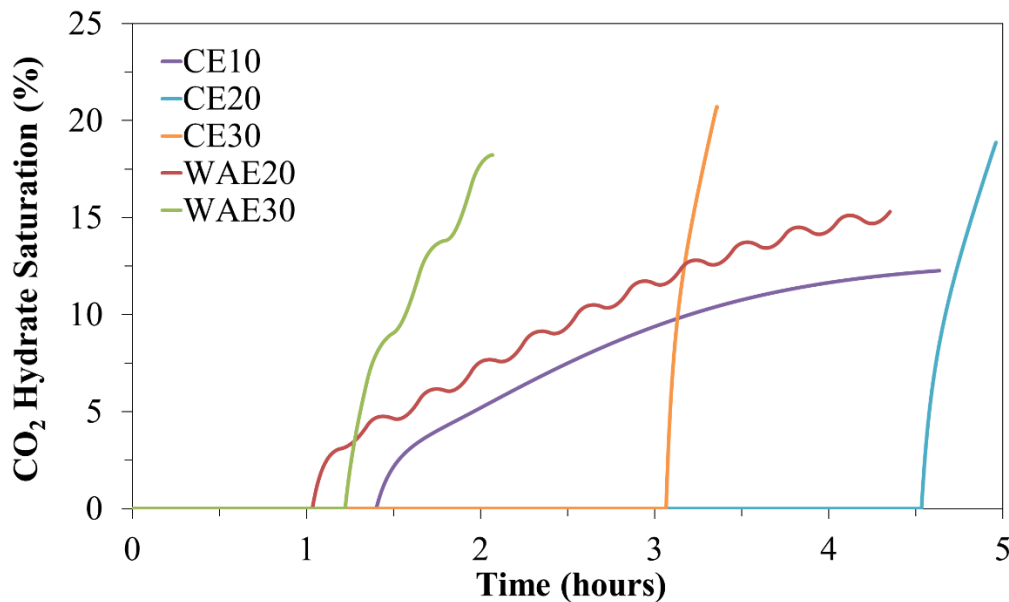


Figure 3.16 Temporal changes in the mean hydrate particle saturation across different injection scenarios.

The data presented in **Figure 3.16** offers key insights into the dynamics of hydrate formation across different injection scenarios. Specifically, continuous injection involving a low CO_2 volume fraction (CE10) indicates the system is stabilizing, characterized by the hydrate particle saturation approaching a steady state plateau. Conversely, the WAE injection, even at higher CO_2 fractions (20% and 30%), successfully delayed the onset of porous media blockage. This performance is particularly significant given that the WAE core utilized smaller grain diameters than the CE core, which naturally resulted in reduced permeability and elevated trapping and adsorption risks. These findings collectively demonstrate the high potential of the WAE technique for achieving prolonged injectivity in field-scale reservoir operations.

3.7 Sensitivity analysis of CO₂ in water dissolution parameters

To evaluate the robustness of validated parameters for the dissolution models (β , C), a series of sensitivity analyses was conducted. A primary objective was to address the potential for equifinality, where different combinations of dissolution parameters might yield similar temperature trends. This section demonstrates that these parameters are identifiable by matching the coupled spatial and temporal temperature evolution across the core.

In my previous research conducted at Professor Masuda's laboratory [69], the pressure adjustment parameter for the heat of dissolution of CO₂ in water was not applied (i.e., $C = 1$). This necessitated the use of a dissolution rate ($\beta = 0.002 \text{ s}^{-1}$) that was 20 times lower than the value validated in the current study to prevent excessive heat generation near the injection inlet. However, as illustrated in **Figure 3.17**, this lower β value could not accurately predict the temperature behavior prior to the induction time at the various monitoring points.

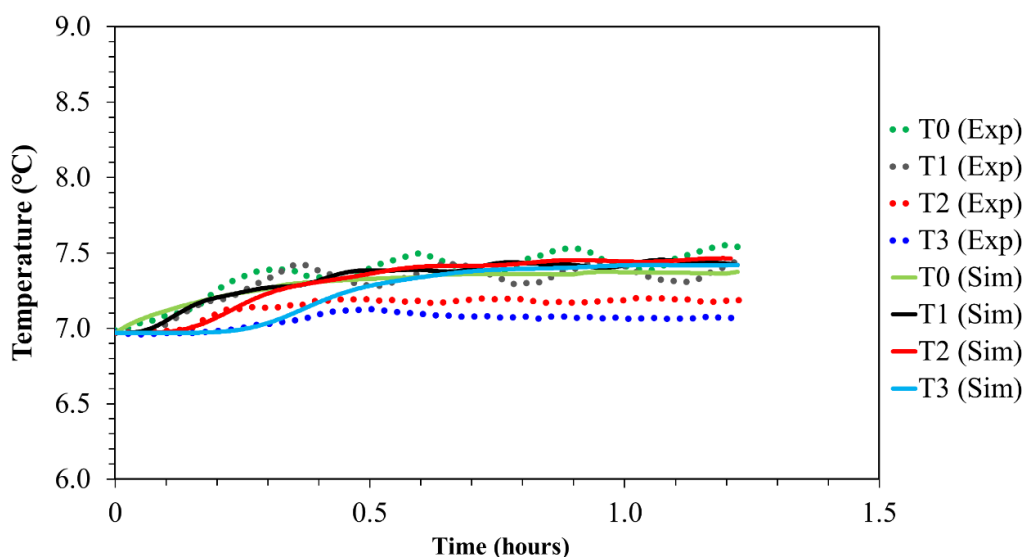


Figure 3.17 Time evolution of temperature for WAE30 up to the induction time ($\beta = 0.002 \text{ s}^{-1}$ and $C = 1$).

These temperature trends indicate that the lower beta value underestimates the CO₂ solubility rate near the inlet, resulting in an artificially uniform thermal distribution throughout the core plug. Following the findings of Koschel et al. [93], which indicate that the heat of dissolution for CO₂ decreases with increasing pressure, it was determined that the parameter C must be incorporated into the expression for the heat of dissolution (Equation 2.18) to reduce the calculated heat generation. This reduction allows for the employment of a higher β value, facilitating faster dissolution near the injection inlet. Consequently, the solubility driving force becomes significantly lower downstream, and heat generation due to solubility reduces

accordingly. This accurately reproduces the observed temperature gradient from the upstream to the downstream locations.

However, increasing β beyond the optimal range also creates discrepancies. For instance, if β is increased to 0.12 s^{-1} and C is decreased to 0.1, the water becomes saturated with CO_2 immediately at the injection inlet. In this case, the dissolution heat is concentrated at the very beginning of the core and dissipates before reaching the downstream positions, leading to an underestimation of the temperature response at T1(Exp), T2(Exp), and T3(Exp) (**Figure 3.18**). In this scenario, the T0(Sim) and T1(Sim) values do not overlap as they do in **Figure 3.14**. Furthermore, the peaks and troughs in the T1(Sim) and T2(Sim) curves are dampened, failing to capture the correct dynamics of CO_2 dissolution through time.

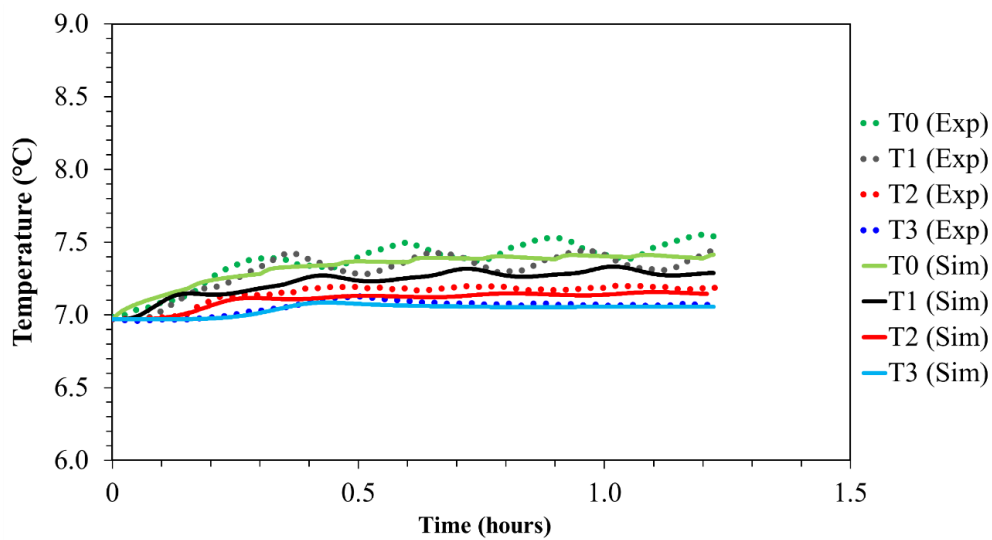


Figure 3.18 Time evolution of temperature for WAE30 up to the induction time ($\beta = 0.12 \text{ s}^{-1}$ and $C = 0.1$).

The values of $\beta = 0.12 \text{ s}^{-1}$, and $C = 0.1$ were also tested for case CE10 (**Figure 3.19**). In contrast to the primary results (**Figure 3.6**), the T0(Sim) in **Figure 3.19** lies above the experimental T0. Despite the reduction in the pressure adjustment parameter, the excessively high solubility rate causes a temperature overestimation at the inlet. Simultaneously, this combination causes the model to underpredict T2(Exp) and T3(Exp) downstream. This stands in contrast to the calibrated results shown previously in **Figure 3.6**, where T0(Sim), T2(Sim), and T3(Sim) closely follow their experimental counterparts.

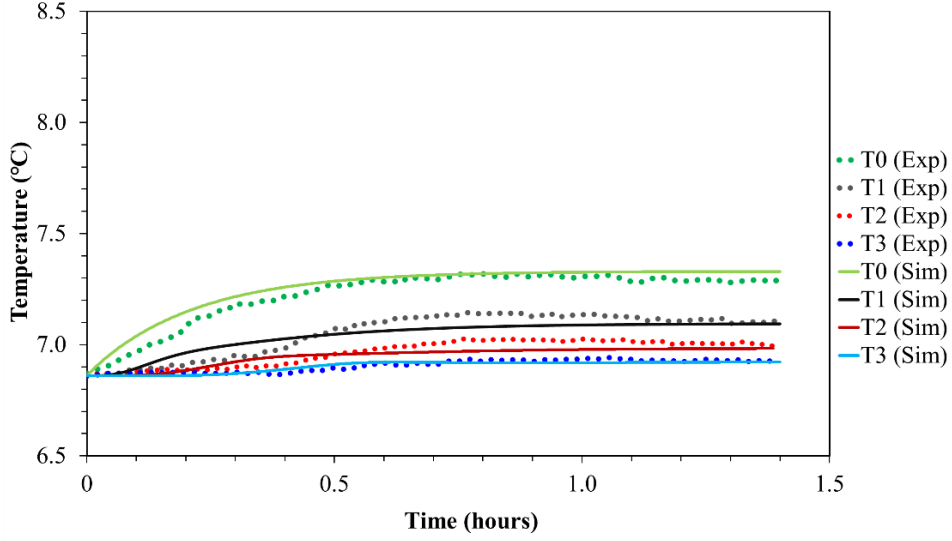


Figure 3.19 Time evolution of temperature for CE10 up to the induction time ($\beta = 0.12 \text{ s}^{-1}$ and $C = 0.1$).

These analyses confirm that β and C influence the thermal signature of the system in distinct ways, allowing for their effects to be decoupled. While the calibrated values are not claimed to be absolute constants, the sensitivity results demonstrate that the combination of $\beta = 0.04 \text{ s}^{-1}$, and $C = 0.15$ provides the most physically consistent representation of the experimental data across all monitoring points. By matching the temperature evolution at multiple locations simultaneously, the risk of equifinality is significantly reduced, as alternative parameter combinations failed to accurately reproduce the observed spatial temperature gradient between the upstream and downstream positions. This confirms that the selected parameter set provides a robust and reliable fit for capturing the dynamics of CO_2 dissolution in the porous medium.

It is important to note that the injection conditions in these experiments fell within the hydrate stability zone. Upon contact between CO_2 and water under these conditions, a thin hydrate film forms around the CO_2 droplets, which can significantly hinder the dissolution rate. Additionally, the continuous formation and dissociation of this interfacial film during the dissolution process [89] causes fluctuations in the net heat generation. Therefore, to isolate and effectively measure the CO_2 dissolution rate and the specific impact of pressure on the heat of dissolution, it is recommended that future experiments be conducted at temperatures slightly above the CO_2 hydrate equilibrium threshold.

Since CO_2 hydrate particle generation is a stochastic phenomenon, the validation in this chapter focuses on capturing general temperature and pressure trends. To further explore the influence of hydrate kinetic parameters, additional field-scale sensitivity analyses are presented in Chapter 4.

3.8 Conclusion

In summary, the rigorous validation process demonstrated that the developed T-H-C numerical model possesses strong predictive capability, particularly in modeling the dissolution-dominated phase of the experiments. The calibrated dissolution parameters ($\beta = 0.04 \text{ s}^{-1}$ and $C = 0.15$) affirmed the reliability of the dissolution model by accurately capturing the temperature behavior prior to the induction time across five distinct experiments. The sensitivity analysis further demonstrated that these values are independently identifiable. By simultaneously matching the spatial temperature gradients across multiple monitoring points prior to the induction time, the model successfully overcame the challenge of equifinality, ensuring a robust and physically consistent representation of the experimental data. While the presence of an interfacial hydrate film likely influenced the local dissolution kinetics, the calibrated parameters effectively capture the net thermal signature of the system.

Conversely, the model's success in predicting the post-induction phase was more moderate due to the highly stochastic nature of hydrate kinetics; the selected constant kinetic parameters ($\gamma = 0.012 \text{ s}^{-1} \cdot \text{MPa}^{-1}$ and $\alpha = 0.55$) allowed the model to successfully capture the overall temperature trends rather than the localized stochastic fluctuations. Furthermore, the noted time lag in predicting porous media blockage for the CE20 and CE30 experiments highlights the inherent limitations of using constant parameters in such complex systems.

Significantly, the validation also confirmed the model's ability to accurately capture sustained injectivity for the CE10 continuous injection scenario, thereby demonstrating the operational viability of the C/W emulsion concept under lower CO_2 concentration conditions.

The validation ultimately confirmed the thermal and operational superiority of the WAE strategy over continuous injection for high CO_2 volume fractions. By using water slugs to dissolve formed CO_2 hydrate particles, WAE maintained injectivity even within cores characterized by lower permeability and higher particle adsorption and trapping rates.

Ultimately, the successful validation of the T-H-C framework against 1D experimental data marks the completion of Objective 1. The demonstrated reliability of the model in capturing thermal effects, combined with the clear injectivity challenge posed by continuous emulsion flow, establishes a credible foundation for the operational optimization studies presented in Chapter 4 addressing the injectivity optimization component of Objective 2.

Chapter 4

C/W emulsion injectivity optimization

4.1 Introduction

The foundational T-H-C numerical model, validated against 1D experimental data and calibrated for key chemical reactions in Chapter 3, now transitions to addressing the central operational objective of this thesis. This chapter focuses on Objective 2: utilizing the model to systematically investigate strategies that actively mitigate near-wellbore plugging and ensure sustained injectivity under desirable low-temperature conditions, with the practical goal of achieving 1 pore volume (PV) of fluid injection.

To accomplish this, the validated framework is used to systematically analyze the influence of several critical operational parameters. The study first addresses foundational numerical and parameter choices: a grid convergence analysis is conducted to confirm the numerical accuracy and resolution-independence of the chosen computationally efficient grid, and a sensitivity analysis on the CO₂ hydrate particle diameter (D_p) is performed to define a representative base case that presents a challenging yet sustainable injectivity scenario, consistent with the kinetic parameters calibrated in Chapter 3.

Following these initial checks, the main operational investigations proceed: First, the dynamic temperature responses throughout the injection in the experimental data of Chapter 3 motivated the analysis of the effect of varying α on injectivity. Then, the scenarios with the most challenging injectivity conditions are chosen to evaluate the effectiveness of WAE injection scheme in mitigating near-wellbore blockage. Furthermore, the impact of salinity on injectivity is analyzed.

This work defines the operational criteria necessary for sustained low-temperature injections, which are subsequently utilized for the HBCS quantification and final field-scale performance analysis presented in Chapter 5 and Chapter 6.

4.2 Mathematical formulation

The foundational T-H-C numerical framework introduced in Chapter 2 is applied here to investigate injectivity. This framework, used for all analyses in Chapters 4 and 5, is summarized below with governing equations for an emulsion-only flow carrying entrained hydrate particles.

The Darcy equation for the emulsion phase velocity, which dictates the advective transport terms in the subsequent conservation equations, is expressed as:

$$\vec{u}_e = -\frac{K_D}{\mu_e} (\nabla P - \hat{\rho}_e g \nabla z) \quad (4.1)$$

where $\hat{\rho}_e$, μ_e are expressed based on Equations (2.57) and (2.79), respectively.

The general form of the governing equations is as follows:

Water :

$$-\nabla \cdot (\vec{u}_e S_e \chi_{H_2O} \rho_{H_2O}) - \dot{q}_{H_2O}^{CH_{form}} + \dot{q}_{H_2O}^{CH_{dsol}} + \dot{q}_{H_2O}^{CH_{diss}} = \phi_0 \frac{\partial}{\partial t} (S_e \chi_{H_2O} \rho_{H_2O}) \quad (4.2)$$

Liquid CO₂:

$$-\nabla \cdot (\vec{u}_e S_e \chi_{LCO_2} \rho_{LCO_2}) - \dot{q}_{CO_2}^{CH} - \dot{q}_{dsol} + \dot{q}_{LCO_2}^{diss} = \phi_0 \frac{\partial}{\partial t} (S_e \chi_{LCO_2} \rho_{LCO_2}) \quad (4.3)$$

where $\dot{q}_{LCO_2}^{diss}$ is the liquid CO₂ generation rate due to dissociation of CO₂ hydrate film of CO₂ hydrate particles (mol/(m³·s)).

Dissolved CO₂:

$$-\nabla \cdot (\vec{u}_e S_e (1 - \chi_{H_2O} - \chi_{LCO_2} - \chi_{NaCl}) \rho_{wCO_2}) + \dot{q}_{dsol} + \dot{q}_{wCO_2}^{dsol} = \phi_0 \frac{\partial}{\partial t} (S_e (1 - \chi_{H_2O} - \chi_{LCO_2} - \chi_{NaCl}) \rho_{wCO_2}) \quad (4.4)$$

Flowing CO₂ hydrate particles:

$$-\nabla \cdot (\vec{u}_e S_{PF} \rho_P) + \nabla \cdot (K_L \nabla S_{PF} \rho_P) + \dot{q}_P - \dot{q}_{PF}^{dsol} - \phi_0 (k_{att} S_{PF} - k_{det} S_{Patt}) \rho_P - \dot{q}_{PF}^{diss} = \phi_0 \frac{\partial}{\partial t} (S_{PF} \rho_P) \quad (4.5)$$

where $\dot{q}_{PF}^{diss}$ is flowing CO₂ hydrate particle consumption rate due to dissociation of hydrate film (mol/(m³·s)) and K_L is as expressed in Equation (3.6).

Attached CO₂ hydrate particles:

$$\phi_0(k_{att}S_{PF} - k_{det}S_{Patt})\rho_P - \dot{q}_{Patt}^{sol} - \dot{q}_{Patt}^{diss} = \phi_0 \frac{\partial}{\partial t} (S_{Patt}\rho_P) \quad (4.6)$$

where S_{Patt} represents both adsorbed and trapped particles, as defined in Section 2.5.2.1 to optimize computational efficiency.

NaCl:

$$-\nabla \cdot (\vec{u}_e S_e \chi_{NaCl} \rho_{NaCl}) = \phi_0 \frac{\partial}{\partial t} (S_e \chi_{NaCl} \rho_{NaCl}) \quad (4.7)$$

where χ_{NaCl} specifies the volume fraction of NaCl in the emulsion.

Energy conservation equation:

$$\begin{aligned} \nabla \cdot (\lambda \nabla T) - \nabla \cdot \vec{u}_e (\rho_{LCO_2} S_e \chi_{LCO_2} h_{CO_2} + S_e (1 - \chi_{H_2O} - \chi_{LCO_2} - \chi_{NaCl}) \rho_{wCO_2} h_{CO_2} + \\ \rho_{brine} (S_{H_2O} + S_{NaCl}) h_{brine} + S_{PF} \rho_P h_P) + \nabla \cdot (K_L \nabla (S_{PF} \rho_P h_P)) + H A_{HT} (T_\infty - T) - \\ \Delta H_{CH} (\dot{q}_{CH}^{form} - \dot{q}_{CH}^{diss} - \dot{q}_{CH}^{sol}) - \Delta H_S (\dot{q}_{dsol} + \dot{q}_{wCO_2}^{sol}) = \frac{\partial}{\partial t} ((1 - \phi_0) \hat{\rho}_{gr} C_{gr} T + \\ \phi_0 (\rho_{CH} S_{CH} U_{CH} + S_e (1 - \chi_{H_2O} - \chi_{LCO_2} - \chi_{NaCl}) \rho_{wCO_2} U_{CO_2} + \rho_{LCO_2} (S_e \chi_{LCO_2} + S_{PT} (1 - \\ \alpha) U_{CO_2}) + \rho_{brine} (S_{H_2O} + S_{NaCl}) U_{brine})) \end{aligned} \quad (4.8)$$

where λ_{brine} , h_{brine} , and U_{brine} are approximated by that of pure water for simplicity.

4.3 Simulation framework

The simulator was built and implemented in MRST using the same solvers, flow operators and FVM for discretization as it was implemented in Chapter 3. However, the convergence criteria for these specific injectivity analyses were implemented as follows:

$$\begin{aligned} MAX \{ \Delta P_i^2 - \varepsilon^2 P_i^2, \Delta \chi_{H_2O i}^2 - \varepsilon^2 \chi_{H_2O i}^2, \Delta S_{PF i}^2 - \varepsilon^2 S_{PF i}^2, \Delta T_i^2 - \varepsilon^2 T_i^2, \Delta \chi_{LCO_2 i}^2 \\ - \varepsilon^2 \chi_{LCO_2 i}^2, \Delta S_{Patt i}^2 - \varepsilon^2 S_{Patt i}^2, \Delta \chi_{NaCl i}^2 - \varepsilon^2 \chi_{NaCl i}^2 \} < 0 \end{aligned}$$

the index i refers to the grid cell location. The value $\varepsilon = 10^{-6}$ is the tolerance (or precision limit) used in the simulation.

4.3.1 Numerical simulation setup

This study sets up a simple 3D grid to study how pressure changes and blockages happen around the injection point within a fixed area of $300\text{m} \times 300\text{m} \times 25\text{m}$. The boundaries of this domain are shown in **Figure 4.1**.

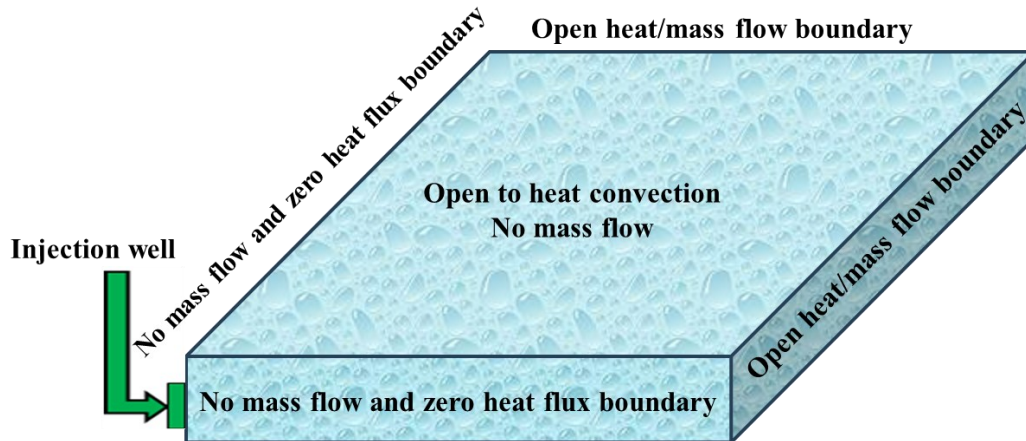


Figure 4.1 Boundary conditions of reservoir domain (bottom boundary identical to top boundary).

To prevent CO_2 hydrates from clogging the pipelines, field operations could potentially inject liquid CO_2 and water through separate pipelines. The fluids then mix underground at the injection zone according to a specific ratio. This procedure has the added benefit of easily allowing operators to stop the CO_2 flow and transition to the water-only injection, a crucial feature for WAE injection strategies.

In Chapter 3, it is observed that CO_2 hydrate formation starts some time after the pore water in the core plug is fully saturated with dissolved CO_2 . The large surface area of the CO_2 droplets leads us to assume immediate dissolution of the gas into the water upon mixing. This study used a 2.4-hour delay in the model to represent the time needed for the injected C/W emulsion into the reservoir to fully saturate the water surrounding the wellbore before any hydrates could begin to form. This induction time was chosen both to guarantee numerical stability and to match experimental evidence presented in Chapter 3 where hydrate formation took between 1 to 4.5 hours during core injection tests.

4.3.2 Initial reservoir and injected fluid conditions

The potential for Carbon Capture and Storage (CCS) in the zone where hydrates are stable was studied. The study was conducted under conditions simulating a deep seafloor at 900 m with an ambient temperature of 4 °C and a geothermal gradient of 30 °C/km. The entire simulated region was a small slice of the sub-seabed area, stretching only 25 meters vertically (100-125 mbsf), with the fluid being pumped into the layer between 105 and 120 mbsf. The initial reservoir and injected fluid parameters are detailed in **Table 4.1**.

Table 4.1 Initial reservoir and injected fluid conditions.

Properties and Parameters	Values and Unit	Properties and Parameters	Values and Unit
Initial porosity (ϕ_0)	30%	Salinity	3.5 wt%
D_{gr}	200 μm	CO ₂ volume fraction in emulsion	10%, 15%, 20%
K_{D0}	3.12 Darcy	Injection flow rate (Q_{inj})	900 m ³ /d
Thermal conductivity of rock	1 W/(m·K)	Initial temperature range	7.08–7.68 °C
Grain density [43]	2650 kg/m ³	Initial pressure range	10.02–10.22 MPa
Grain specific heat capacity [43]	792 J/(kg·K)	Wellbore radius (r_w)	0.1 m
Heat transfer coefficient	1 W/(m ² ·K)	Reynolds number at the wellbore sandface	~ 0.88

The porosity and permeability values chosen for the reservoir match those used by K. Zhang and Lau [5] in their field-scale model, although this study modeled the seafloor 100 m deeper. The injected fluid is a CO₂ and water emulsion. The water phase includes dissolved salt, unless the target reservoir is a pure water aquifer.

To account for the quarter-symmetry of the reservoir model, the Reynolds number (R_e) in **Table 4.1** was calculated at the wellbore sandface for a 90° sector as follows:

$$R_e = \frac{\hat{\rho}_e \times Q_{inj} \times D_{gr}}{\frac{2\pi r_w h}{4} \times \mu_e} \quad (4.9)$$

where h is the perforation length. For simplicity in the Reynolds number calculations, the density and viscosity of the emulsions were approximated using values of 1000 kg/m³ and 0.001 Pa·s, respectively. As $R_e \approx 0.88$ is well below the critical threshold of 1, the flow remains strictly laminar, justifying a Darcy-based approach.

4.3.3 Numerical discretization and injection safety constraints

The simulation was run on a $20 \times 20 \times 5$ grid (2,000 cells). To achieve better accuracy near the injection well, cells were refined (made smaller) in that area and gradually increased in size away from it (**Figure 4.2**). Of the five vertical layers, injection was focused only on the middle three, corresponding to the perforated section of the well.

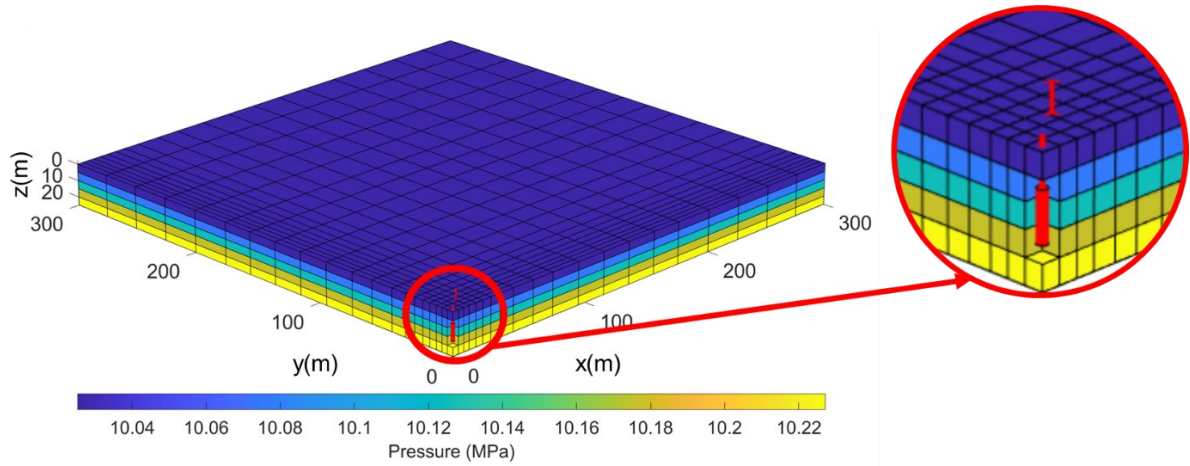


Figure 4.2 Distribution of the reservoir's initial pressure, along with the well's perforated zone.

This study distributed the injected fluid based on the permeability of each perforated grid cell to maintain a stable simulation and ensure that injection allocation was physically meaningful, correctly reflecting flow resistance.

Safety in CO₂ sequestration requires defining a maximum injection pressure to prevent exceeding the fracture pressure, which could cause the formation to crack and lead to leakage [153]. This critical pressure was calculated using Eaton's method [5], [154], as follows:

$$P_{fp} = \frac{1.5\theta}{1-\theta} (P_{ob} - P) + P \quad (4.10)$$

$$P_{ob} = \sigma_w h_w + \sigma_b h_b \quad (4.11)$$

$$P = \sigma_w (h_w + h_b) \quad (4.12)$$

The equations involve several variables that define the physical conditions. The calculated pressures are P_{fp} (fracture pressure) and P_{ob} (overburden pressure), both measured in Pascals. The other variables define the physical depths and pressure gradients: h_w is the water depth, and h_b is the buried depth below the seafloor, both measured in meters. The terms σ_w (10520

Pa/m) is the pressure increase per meter for the water column, and σ_b (26000 Pa/m) is the pressure increase per meter for the buried sediment. Finally, ν represents Poisson's ratio for the sandstone, and for simplification in these calculations, the factor $\frac{\nu}{1-\nu}$ was set to 0.5 [154].

The fracture pressure (P_{fp}) was calculated to be 12 MPa. This value was constantly compared to the reservoir pressure at the midpoint of the injection zone. Importantly, the real-world fracture pressure could potentially be greater because hydrate particles and pore trapping can act as a natural cementing agent [155]. This safety assessment serves as a pressure-limit criterion rather than a fully coupled hydro-mechanical assessment.

4.4 Simulation results and discussion

This section details the findings derived from the 3D numerical simulations. The analysis is presented systematically, adhering to the investigative plan set out in the chapter introduction.

The study first addresses the foundational numerical setup by conducting a grid convergence analysis and a CO₂ hydrate particle diameter (D_p) sensitivity study to ensure numerical accuracy and define a representative base case. These initial tests utilize the continuous injection scenario with 10% CO₂ volume fraction (CE10) and an average hydrate film volume fraction (α) of 0.45. (Note: Continuous injection is denoted CE, and water-alternating-emulsion is denoted WAE, followed by the CO₂ volume fraction, e.g., CE15, WAE20).

Following these initial checks, the main operational investigations proceed: The analysis assesses the effects of varying γ and α on emulsion flow behavior, evaluates the effectiveness of the WAE injection scheme in mitigating plugging for challenging scenarios, and examines the impact of salinity on injectivity.

4.4.1 Grid convergence analysis

To demonstrate that the 2,000-cell grid provides an acceptable level of accuracy for investigating the general challenges of C/W emulsion injection, this analysis used the CE10 scenario ($\alpha = 0.45$) to compare the 2,000-cell grid's results with those from a significantly finer grid of 16,000 cells. For clarity, the coarser 2,000-cell grid is designated as *NC* (number of cells) and the finer, eight-times-larger grid is designated as *8NC*. The errors resulting from the difference in grid resolution are summarized in **Table 4.2**.

Table 4.2 Results of grid convergence analysis for the CE10 injection scenario ($\alpha = 0.45$).

	<i>NC</i>	<i>8NC</i>	Error (%)
Final injection pressure (MPa)	11.514	11.74	1.9
Average hydrate saturation (%)	5.28	5.2	1.5

These calculated errors, which are less than 2% for both final injection pressure (1.9%) and average hydrate saturation (1.5%), are deemed small enough for this study. Beyond the quantitative error summarized in the table, qualitative validation of the grid's dynamic stability is essential. **Figure 4.3** displays the time evolution of injection pressure for both grid resolutions as a function of the injected pore volume. Comparing the *NC* and *8NC* curves confirms that the chosen coarse grid is numerically stable and accurately captures the transient flow behavior throughout the entire simulation duration.

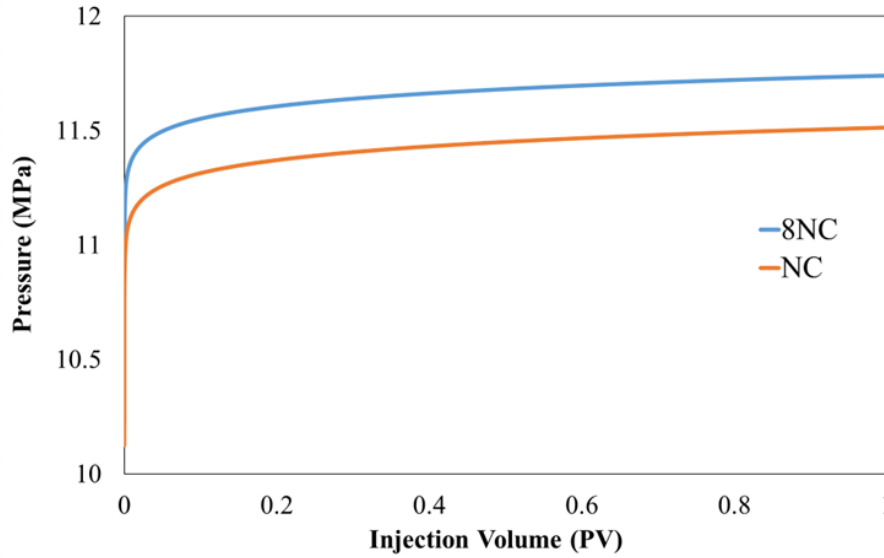


Figure 4.3 Sensitivity of injection pressure to grid resolution (*NC* and *8 NC*) as a function of injected pore volume (PV) for the CE10 scenario ($\alpha = 0.45$).

Finally, to confirm that the *NC* grid is physically representative and not just accurate on average, the resulting hydrate distribution is shown in **Figure 4.4**.

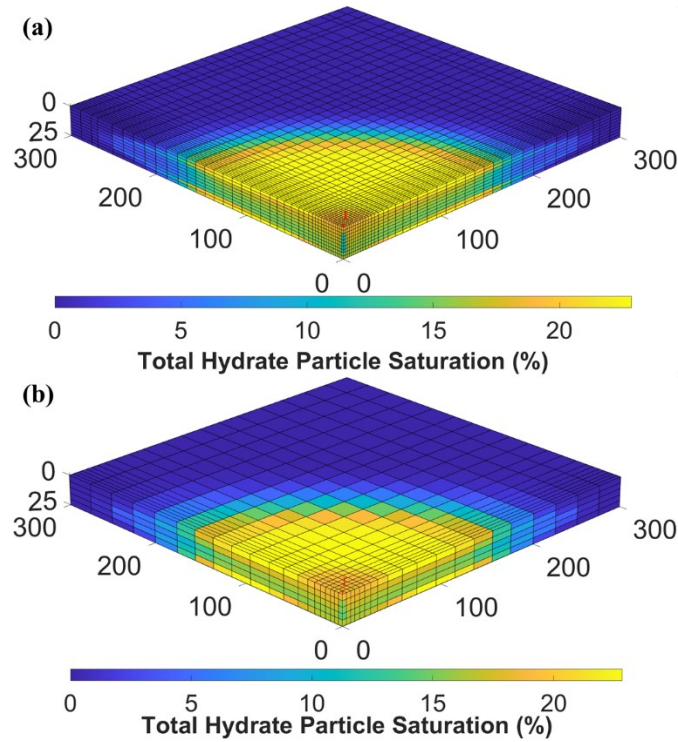


Figure 4.4 Total CO₂ hydrate saturation distribution for the CE10 scenario ($\alpha = 0.45$) comparing resolutions: (a) 8NC. (b) NC.

This comparison verifies that the *NC* grid correctly captures the spatial localization and extent of hydrate formation, ensuring that the minor error observed in the average saturation (**Table 4.2**) is not due to a physical misrepresentation. The minimal difference between the two resolutions allows us to confidently use the computationally efficient 2,000-cell grid (*NC*) resolution for capturing the essential physics while providing significant computational savings.

4.4.2 CO₂ hydrate particle diameter sensitivity analysis

The size of the injected CO₂ droplets plays a critical role in the physical clogging of reservoir pores. To assess the impact of this uncertainty on injectivity, a sensitivity analysis on the CO₂ hydrate particle diameter (D_p) was performed using the CE10 base case ($\alpha = 0.45$). This analysis specifically examined how variations in this parameter influence the maximum injection pressure and the resultant plugging radius around the wellbore. **Figure 4.5** illustrates the sensitivity of injection pressure evolution to the hydrate particle diameter (D_p) as a function of the injected pore volume.

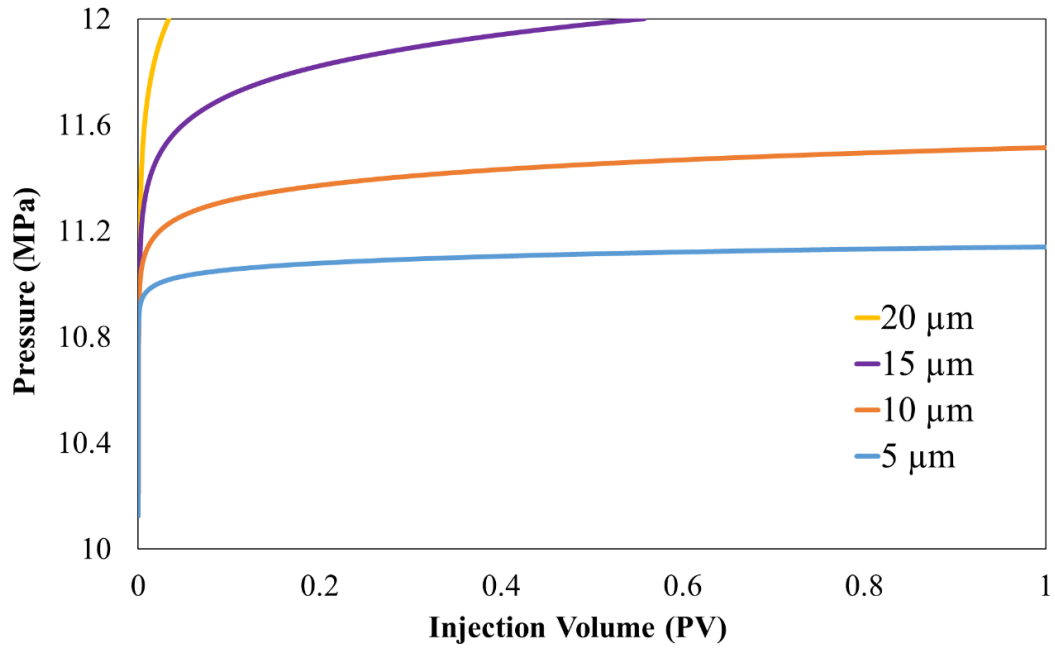


Figure 4.5 Sensitivity of injection pressure to hydrate particle diameter (D_p) as a function of PV for the CE10 injection scenario ($\alpha = 0.45$).

A clear dependency on particle size was demonstrated: Scenarios using particle diameters of 5 μm and 10 μm were able to successfully reach 1 Pore Volume (PV) of injection and achieve a stable, steady-state pressure condition. In contrast, the injection scenario using a 15 μm particle diameter was stopped prematurely after only 0.56 PV. Furthermore, the case with a 20 μm particle diameter showed an immediate pressure increase, which strongly implies significant plugging near the injection wellbore. The resulting plugging radius for these different hydrate particle diameters is shown in **Figure 4.6**.

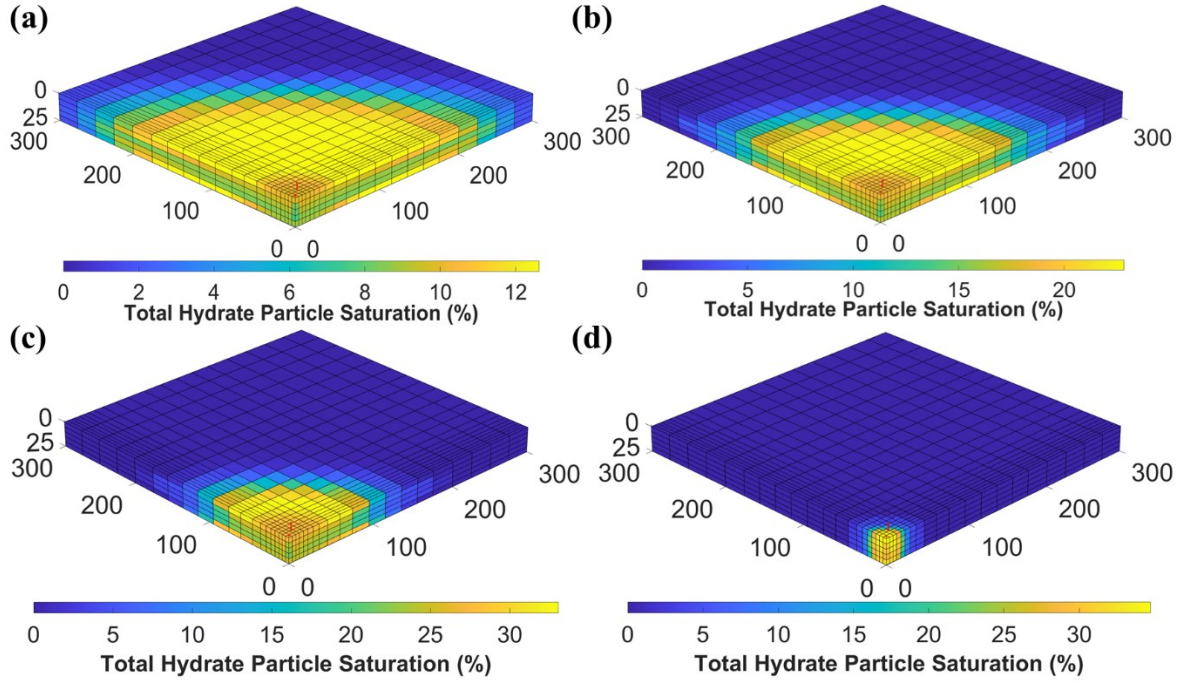


Figure 4.6 Total hydrate particle saturation distribution for the CE10 injection scenario ($\alpha = 0.45$) at varying particle diameters: (a) $D_p = 5 \mu\text{m}$. (b) $D_p = 10 \mu\text{m}$. (c) $D_p = 15 \mu\text{m}$. (d) $D_p = 20 \mu\text{m}$.

These analyses confirm forming an emulsion with smaller liquid CO_2 droplets is key to achieving continuous injection by reducing attachment rates (Equation 2.27) and straining of hydrate particles.

For the remainder of this study, all subsequent simulations were conducted using a particle diameter of $D_p = 10 \mu\text{m}$. This value was chosen because it aligns with the kinetic parameters calibrated in Chapter 3, where particle size directly influences the surface area available for hydrate growth and liquid CO_2 dissolution. Although the $D_p = 5 \mu\text{m}$ case is also physically valid—given that liquid CO_2 droplets dissolve in water after passing the mesh filter, potentially leading to a smaller average diameter for hydrate formation—the $10 \mu\text{m}$ diameter was selected as the representative base case because it presents a more challenging injectivity scenario (higher pressure increase) especially for C/W emulsion injection cases with higher CO_2 volume fractions.

4.4.3 Sensitivity analysis of CO_2 hydrate particle formation rate constant

To evaluate the sensitivity of the CO_2 hydrate particle formation rate constant (γ) on injection pressure, a series of simulations was conducted using the CE20 scenario as a baseline ($\alpha = 0.45$). The CE20 case was specifically selected for this analysis as it contains the highest

number of liquid CO₂ droplets dispersed in the aqueous phase, representing the most kinetically active scenario. Values of 0.012 (validated in Chapter 3), 0.024, and 0.006 s⁻¹·MPa⁻¹ were tested to evaluate the impact of reaction speed on pressure evolution. **Figure 4.7** illustrates the sensitivity of injection pressure evolution to different values of the hydrate formation rate constant (γ) as a function of the injected pore volume (PV), where 1 PV is equivalent to 750 days of simulated injection.

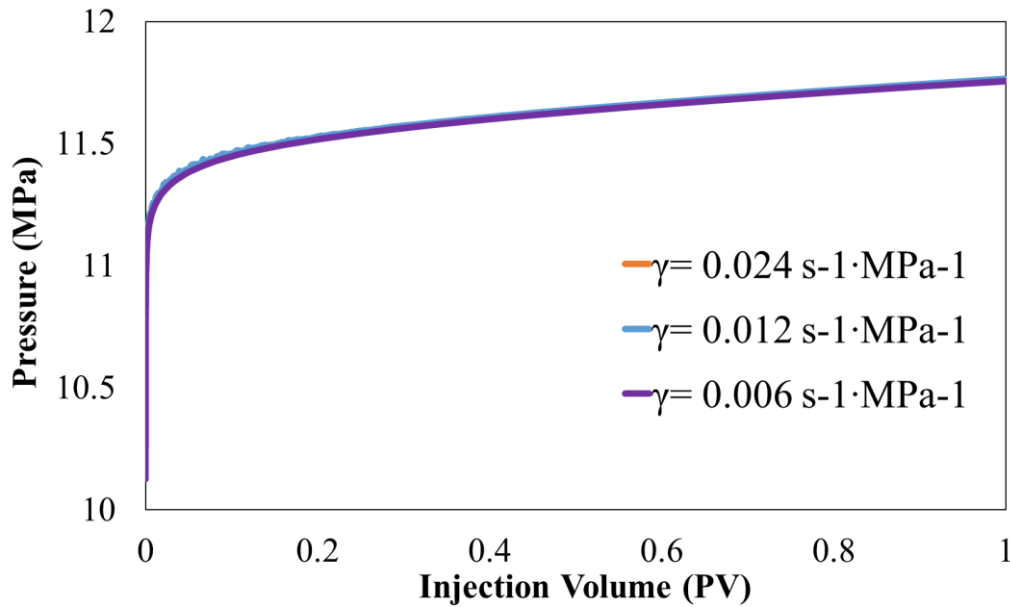


Figure 4.7 Injection pressure sensitivity to γ for the CE20 injection scenario ($\alpha = 0.45$).

The simulation results indicated that the model is insensitive to variations in γ within this range, as the resulting injection pressure curves for all three cases overlapped almost identically. This behavior suggests that under field-scale reservoir conditions, the process of CO₂ hydrate formation is primarily governed by thermodynamic equilibrium rather than by the speed of the kinetic reaction. Due to the massive reservoir column and the low heat transfer efficiency in the reservoir ($H = 1 \text{ W}/(\text{m}^2\cdot\text{K})$), the local temperature reaches the hydrate equilibrium point almost instantaneously. Upon achieving thermal equilibrium, the thermodynamic driving force dissipates, resulting in the cessation of the reaction, irrespective of the kinetic rate constant.

This confirms that in a massive reservoir column, hydrate formation is limited by the system's ability to dissipate heat rather than the inherent kinetics of the CO₂-water interface. Consequently, the hydrate film volume fraction (α) emerges as the primary governing parameter for injectivity risk. In this study, $\gamma = 0.012 \text{ s}^{-1}\cdot\text{MPa}^{-1}$ was consistently employed for the remainder of the study.

4.4.4 Influence of α on C/W emulsion flow behavior

The process of CO₂ hydrate particle formation is governed by the modeling parameter α , which is defined as the fraction of the hydrate film relative to the overall hydrate particle volume. This relationship is conceptually depicted in **Figure 4.8**. Since the conversion of liquid CO₂ droplets to solid hydrate is an exothermic reaction, it immediately elevates the local temperature to the hydrate equilibrium point, a state that then inhibits further hydrate formation thermodynamically.

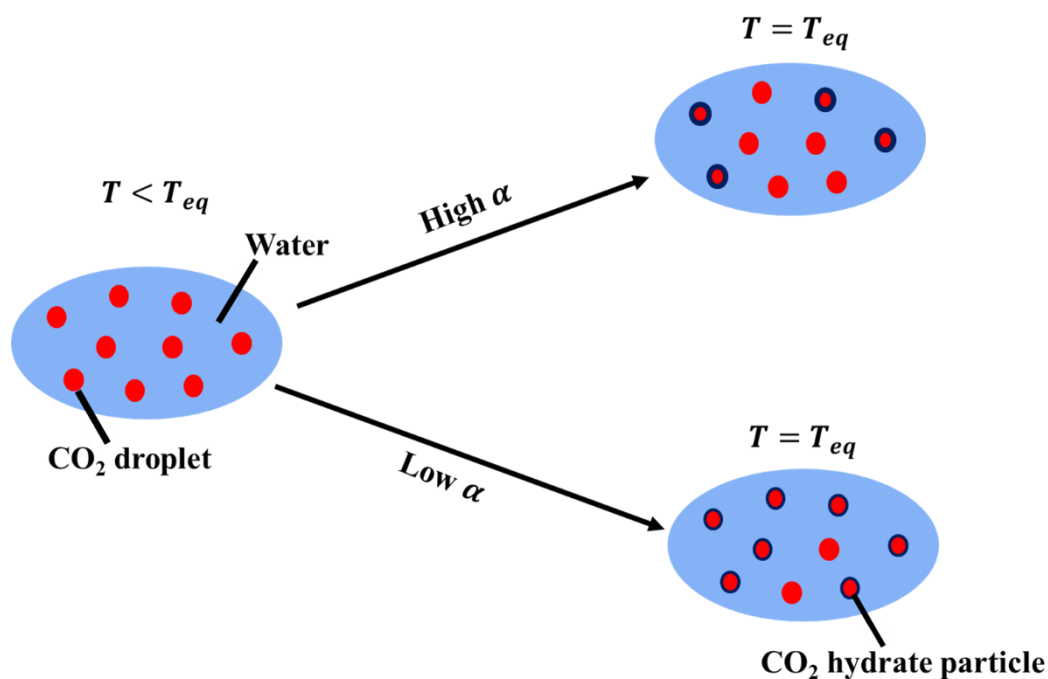


Figure 4.8 Concept of CO₂ hydrate particle formation.

The amount of heat generated—and thus the point at which formation stops—is directly controlled by α . A high α value means the hydrate film accounts for a large particle volume fraction, requiring only minimal liquid CO₂ conversion to reach the equilibrium temperature. Conversely, a low α necessitates a substantially greater conversion of liquid CO₂ to generate enough heat to achieve this thermal equilibrium (illustrated in **Figure 4.8**). As the local temperature approaches equilibrium, any remaining liquid CO₂ droplets will no longer contribute to hydrate growth in that volume.

Experimental studies report significant variations in the resulting hydrate film thickness, showing a strong dependence on droplet size and flow conditions. For instance, observations have demonstrated that film thicknesses can be as large as 20 μm under stagnant conditions,

yet decrease to 5 μm at higher flow speeds [156], clearly indicating that increased flow velocity leads to reduced film thickness. Due to this considerable uncertainty in the literature (with reported film thicknesses ranging from 0.13 μm to 20 μm [90], [156], [157]), a systematic injectivity sensitivity analysis for α was conducted. The analysis utilized a conservative α range of 0.15 to 0.45, which corresponds to film thicknesses from 0.27 μm to 0.90 μm for a 10 μm droplet diameter.

In Chapter 3 a fixed $\alpha = 0.55$, showed potential modeling inconsistencies when compared to experimental findings. In the CE10 case, the experimental temperatures were higher than simulated, suggesting that the model underestimated the effective average α . For the CE20 and CE30 cases, while both model and experiment reached the equilibrium temperature, the simulated pressure rise was delayed up to 24 minutes compared to the immediate experimental pressure rise. This indicates an overestimation of the effective average α in the model, resulting in insufficient conversion of liquid CO_2 droplets to CO_2 hydrate particles and consequently delayed clogging.

A lower α would have required more CO_2 conversion to generate the same heat (**Figure 4.8**), leading to faster clogging and eliminating the observed delay in pressure increase. This phenomenon, coupled with the observation that smaller liquid CO_2 droplet radii increase the likelihood of forming CO_2 hydrate particles with a high α [158], suggests the CE10 discrepancy may stem from greater CO_2 dissolution, leading to smaller droplet diameters and a plausibly higher effective α in that specific experimental case. To systematically investigate the resulting injectivity impacts, this analysis examined the temporal evolution of injection pressure for the defined α range, terminating simulations if the fracture pressure was reached.

4.4.4.1 Sensitivity analysis of α on injectivity under varying CO_2 volume fractions

An α value of 0.45 was selected as the operational baseline for the simulations in this section, despite earlier analysis of Chapter 3 suggesting that the true average α for the CE10 case should be greater than 0.55. This choice is necessitated by the substantial differences between the two study environments. The conditions in experimental setup of Masuda laboratory—injection into a small, pure-water-saturated core with a high heat transfer coefficient ($H = 30 \text{ W}/(\text{m}^2\cdot\text{K})$)—are unlike the present model. This study simulates injection into a massive 25-meter reservoir column utilizing a drastically lower heat transfer efficiency ($H = 1 \text{ W}/(\text{m}^2\cdot\text{K})$).

The combination of the increased reservoir size and the lower H factor results in less efficient heat dissipation compared to the experimental core, leading to the expectation of a reduced effective α . Furthermore, the use of seawater introduces salinity, which acts as an inhibitor to the growth of hydrates [10].

Figure 4.9 illustrates the sensitivity of injection pressure evolution to α across the three different CO₂ concentration cases: CE10, CE15, and CE20. In these simulations, the temporal changes are presented as a function of the injected pore volume.

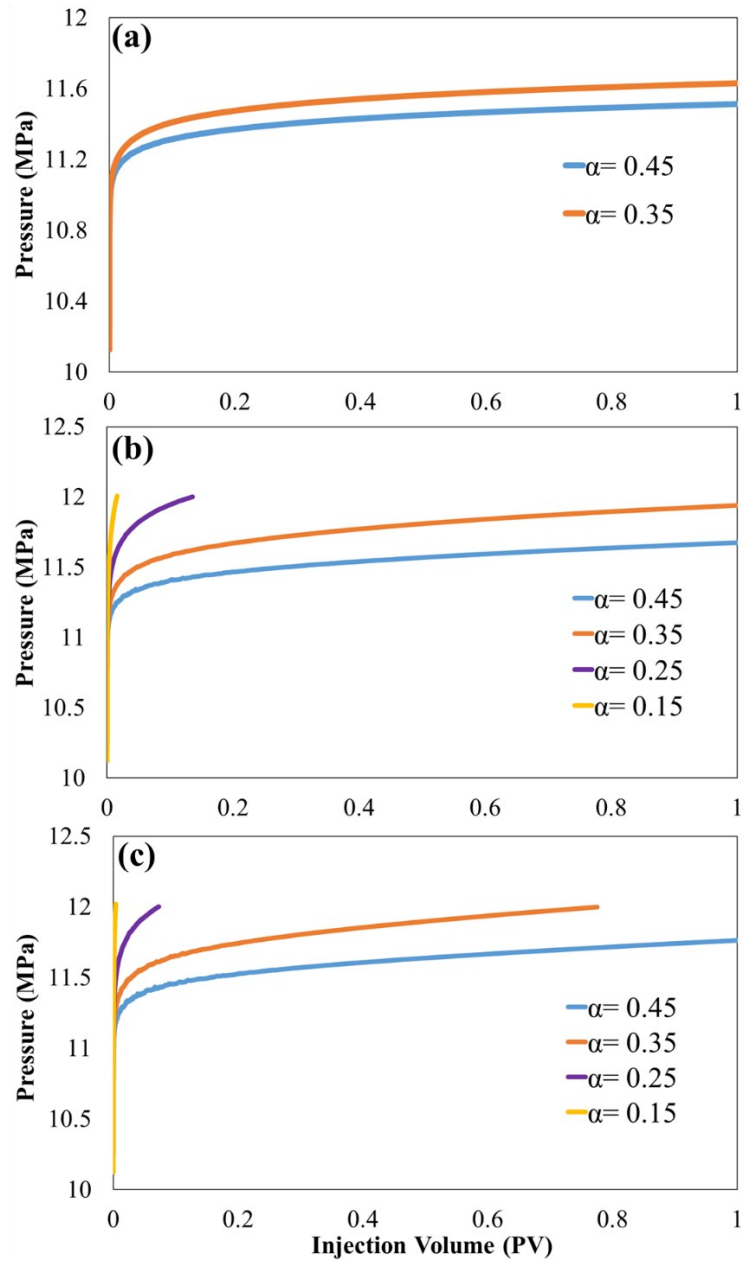


Figure 4.9 Injection pressure sensitivity to average hydrate film volume fraction (α) for. (a) CE10. (b) CE15. (c) CE20.

The C/W emulsion flow behavior demonstrated minimal sensitivity to α in the CE10 scenario; only negligible pressure differences were recorded between $\alpha = 0.35$ and $\alpha = 0.45$. This insensitivity resulted from the limited number of liquid CO₂ droplets available for hydrate particle generation (as shown in **Figure 4.10**), making injection pressure insensitive to α values impossible for this case.

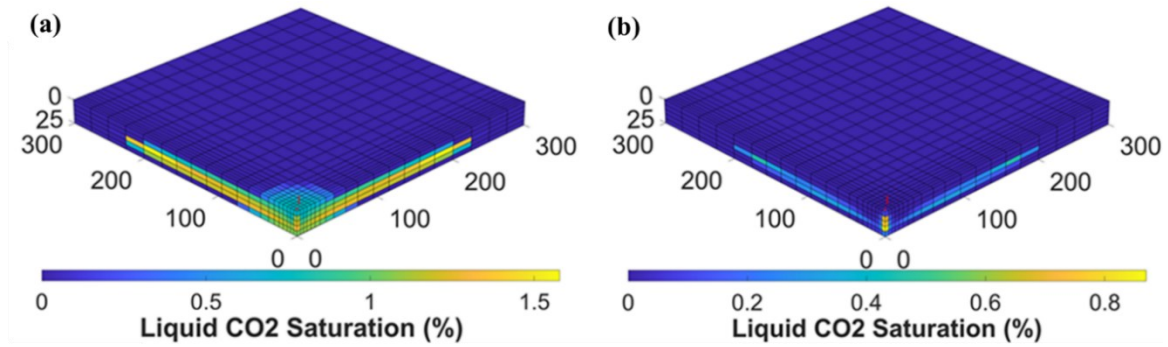


Figure 4.10 Liquid CO₂ saturation distribution (CE10). (a) $\alpha = 0.45$. (b) $\alpha = 0.35$.

Conversely, the impact of α is far more significant in the CE15 and CE20 cases. Injection maintains a stable trajectory and reaches the full 1 PV limit when α is set to 0.45 for all cases. The 0.35 setting also performs well, achieving the full 1 PV in the CE15 case but resulting in 0.78 PV injection in the CE20 case. However, further reduction in α (for example, to 0.15) immediately triggers a pronounced and rapid pressure spike early in the injection process. This behavior is attributed to the swift formation of thin hydrate films around a significantly greater number of liquid CO₂ droplets close to the wellbore, which induces severe pore blockage (illustrated in **Figure 4.11**).

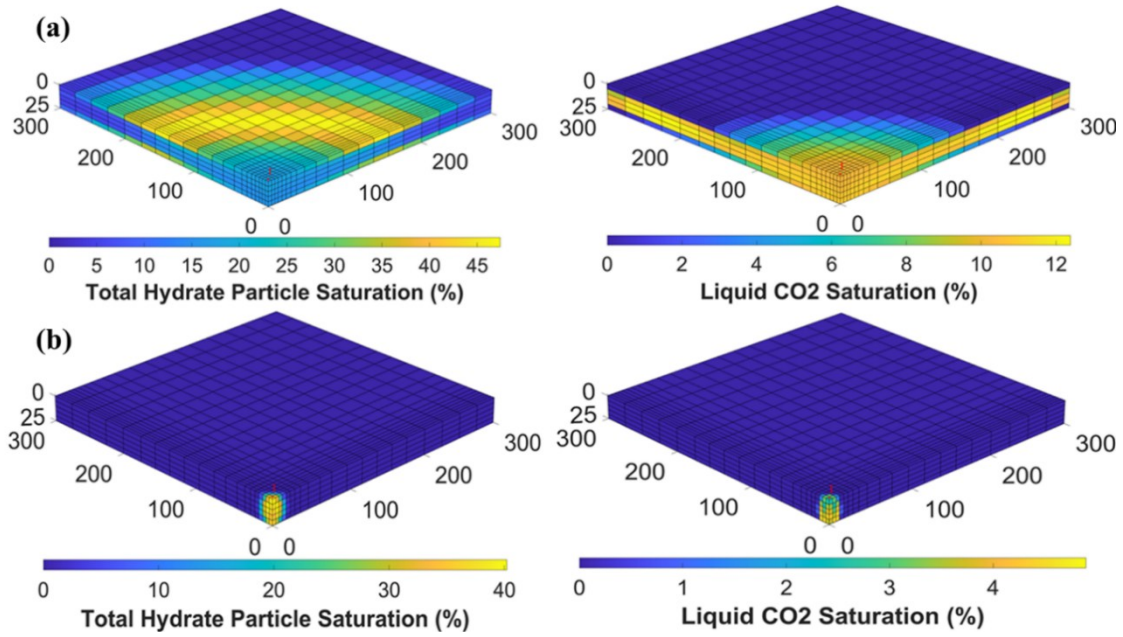


Figure 4.11 Total CO₂ hydrate and liquid CO₂ saturation distribution (CE20). (a) Top row: $\alpha = 0.45$. (b) Bottom row: $\alpha = 0.15$.

To effectively mitigate these critical injectivity issues and ensure prolonged, stable injection, particularly relevant for scenarios involving higher CO₂ volume fractions and lower α values, the WAE strategy was subsequently investigated as a prospective mitigation methodology.

4.4.5 Water alternating C/W emulsion injection

In Chapter 3, WAE laboratory scale experiments demonstrated significant improvement in injectivity of C/W emulsion with high CO₂ volume fractions. Building upon the severe injectivity challenges identified in the preceding section, WAE injection was simulated specifically for $\alpha = 0.15$, which represents the most demanding scenario in terms of hydrate-induced plugging. The decision to model this extreme condition (0.15) was made to demonstrate the robust applicability of the WAE technique under the most critical circumstances. For scenarios involving less severe conditions (higher α values), a longer injection cycle could be considered to manage near-wellbore blockage effectively. The key parameters defining the WAE injection scenarios are summarized in **Table 4.3**.

Table 4.3 Key parameters for WAE injection scenarios.

Scenario	Onset of water injection (MPa)	Injected water slug duration (hours)
WAE15	11.7	24
WAE20	11.7	24

The feasibility of incorporating the relatively brief 24-hour water injection period is supported by the operational flexibility afforded by having separate injection lines in a real-world setting (as detailed in Section 4.3.1).

Both the WAE15 and WAE20 simulations successfully managed near-wellbore blockage, ultimately facilitating the injection of the full 1 PV of total fluid (comprising both water and emulsion slugs). The time evolution of injection pressure for both scenarios is illustrated in **Figure 4.12**. A notable feature in both cases is the presence of significant pressure oscillations, which reflect the intricate and competing effects of hydrate dynamics during WAE cycles. On one hand, the permeability is restored, and pressure is reduced by the dissolution of attached CO₂ hydrate particles by the injected water. On the other hand, this dissolution simultaneously causes temporary pressure spikes due to the rapid release of pure water and trapped CO₂ from the collapsing hydrate structure. This complex interaction generally permitted WAE to manage injection pressures but resulted in occasional peak values that slightly exceeded 11.7 MPa.

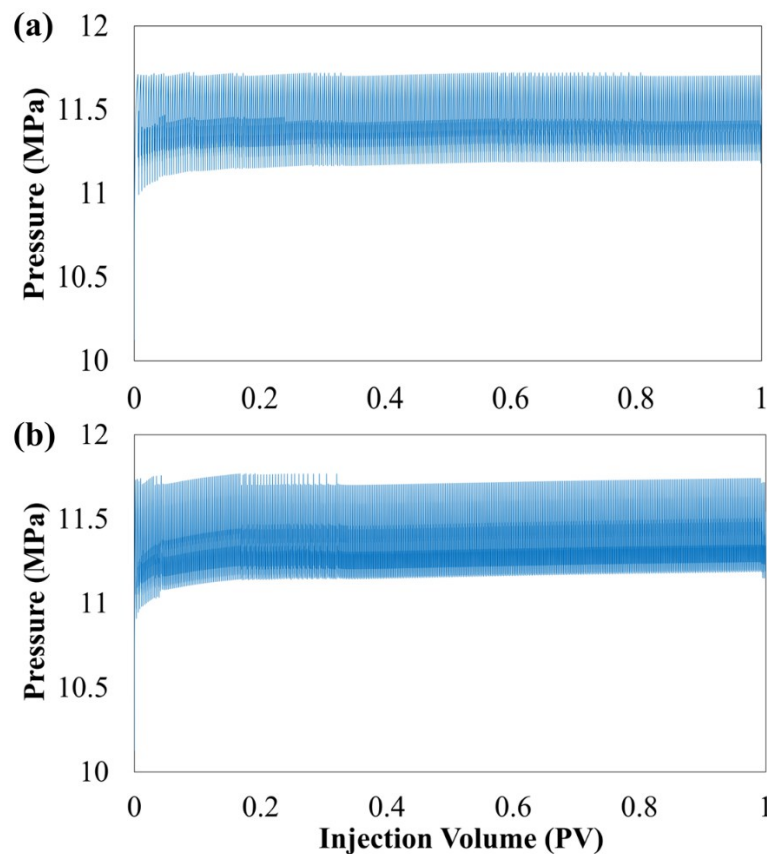


Figure 4.12 Injection pressure evolution as a function of injected PV for: (a) WAE15. (b) WAE20.

The dynamic response was more pronounced in the WAE20 case (**Figure 4.12b**) compared to WAE15 (**Figure 4.12a**), which is consistent with its higher initial CO₂ volume fraction. As

hydrates gradually accumulated downstream and continued to obstruct the porous media, the injectivity of the emulsion slugs diminished over time. This trend was quantitatively reflected in the decreasing duration of the subsequent emulsion slugs towards the conclusion of the simulations: the duration fell from approximately 103 hours to 29 hours for WAE15, and from roughly 34 hours to 14 hours for WAE20.

4.4.6 Comparison of C/W emulsion behavior in seawater and pure water

Unlike the analyses presented in the preceding sections, this investigation focuses on the introduction of a C/W emulsion into an aquifer containing pure water. This section sought to contrast the emulsion flow dynamics in seawater versus pure water environments specifically for the CE10 and CE15 cases (both using $\alpha = 0.45$). This direct comparison yielded contrasting outcomes for the two scenarios (**Figure 4.13**): The reduced salinity of the pure water environment led to a lower injection pressure for CE10, but critically, it caused the pressure in the CE15 case to escalate until it reached the reservoir's fracture limit.

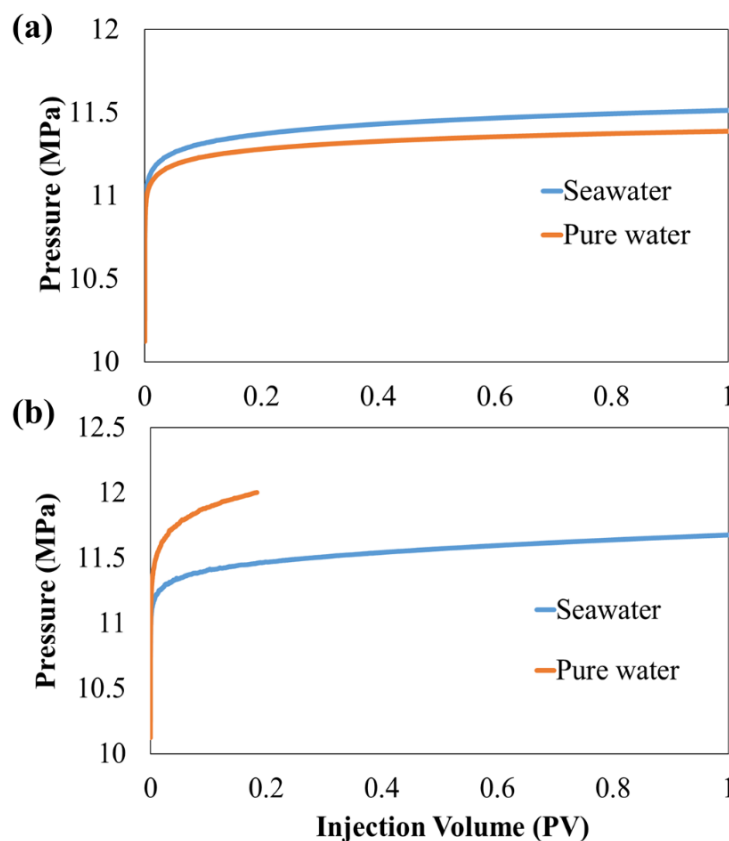


Figure 4.13 Injection pressures versus injected PV for pure water and seawater cases: (a) CE10 and (b) CE15.

The divergence in observed pressure behavior is rooted in the inhibitory effect salt has on hydrate crystallization. The absence of salt permits a greater degree of subcooling for hydrate

formation in pure water compared to seawater, which is evident from the temperature distribution for both cases at the end of injection in CE15 (**Figure 4.14**). As a direct consequence, the injection of emulsion into the pure water aquifer promotes more pervasive hydrate particle development near the injection point.

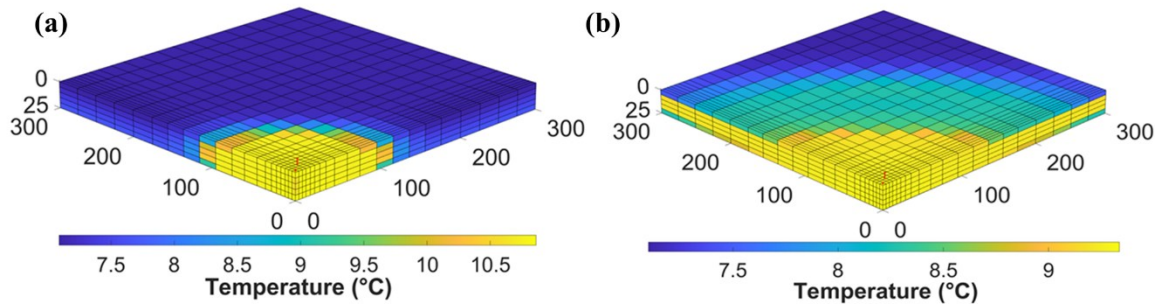


Figure 4.14 Aquifer temperature distribution (CE15). (a) Pure water aquifer. (b) Seawater aquifer.

This increased hydrate generation caused the pressure to climb steeply toward the fracture pressure in the CE15 scenario. Conversely, the lower injection pressure observed in the CE10 case can be explained by the significantly higher solubility of liquid CO₂ in pure water. This elevated solubility further diminishes the already small number of liquid CO₂ droplets present in the CE10 case. The resulting low liquid CO₂ saturation within the porous medium effectively suppresses overall hydrate particle generation (**Figure 4.15**).

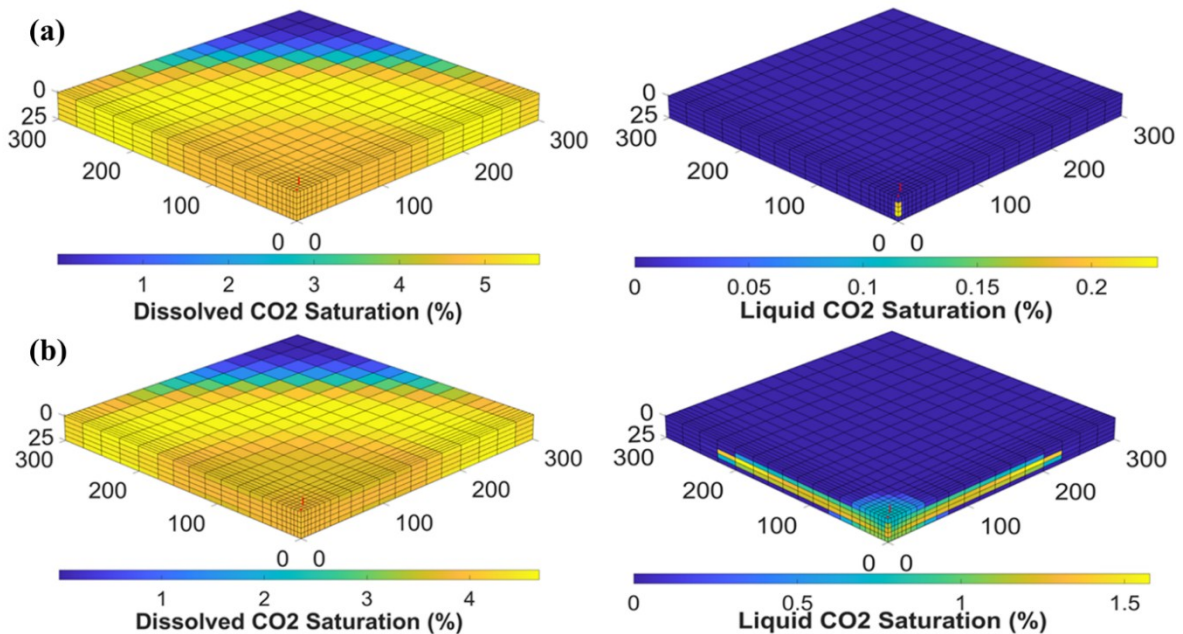


Figure 4.15 Dissolved CO₂ and liquid CO₂ saturation distribution in the aquifer (CE10 with $\alpha = 0.45$). (a) Top row: Pure water aquifer. (b) Bottom row: Seawater aquifer.

4.5 Conclusion

This chapter successfully utilized the validated T-H-C numerical framework to define the operational criteria for sustained low-temperature C/W emulsion injection. The robustness and scalability of the model were first confirmed. The robustness of the numerical setup for the injectivity study was confirmed through a grid convergence analysis, which demonstrated minimal error (with errors less than 2% for key parameters) between the computationally efficient and the fine grid.

The primary operational challenge for continuous emulsion (CE) injection schemes was identified as a critical trade-off between the CO₂ volume fraction in the emulsion and injectivity stability, necessitating the definition of strict operational criteria:

1. Critical parameter sensitivity: Loss of injectivity was highly dependent on the following factors:
 - Hydrate particle diameter (D_p): A critical sensitivity to D_p was observed, highlighting that a smaller particle diameter is essential for reducing particle attachment and mitigating plugging.
 - Thermodynamic vs. Kinetic control: The study revealed that the system is primarily governed by thermodynamic equilibrium rather than kinetic speed (γ), because the massive reservoir column and low heat transfer efficiency cause the system to reach the hydrate equilibrium point almost instantaneously, making injectivity insensitive to γ value validated in Chapter 3. This demonstrates that while the kinetic rate is a measurable factor in lab-scale core experiments, heat dissipation is the dominant controlling bottleneck at the field scale.
 - Influence of α and CO₂ concentration: The influence of α proved highly dependent on the CO₂ concentration; low α values (e.g., 0.15) for high-concentration cases (CE15, CE20) led to immediate, severe pore blockage. This emphasizes that achieving smaller liquid CO₂ droplet diameters is critical, as this simultaneously reduces attachment rates and promotes a higher effective α .
2. Salinity effect: The operational challenge was further intensified by the analysis of the inhibitory effect of salinity. The comparison showed that, in the absence of salt, high-concentration cases failed prematurely due to accelerated, pervasive hydrate formation

stemming from a greater thermodynamic driving force. This highlights the importance of the saline environment for controlling hydrate formation kinetics.

To overcome these critical injectivity challenges, the water-alternating-emulsion (WAE) strategy proved to be a highly robust mitigation technique. By successfully managing the most demanding scenario ($\alpha = 0.15$), WAE facilitated the injection of the full 1 PV of total fluid for both WAE15 and WAE20. The success is attributed to the brine slug's ability to restore permeability by dissolving attached hydrate particles.

This work establishes the WAE method and the associated optimized operational parameters (D_p , α , CO₂ concentration) as the viable criteria for sustained, high-capacity, low-temperature C/W emulsion injection, laying the essential groundwork for subsequent HBCS quantification (Chapter 5) and for the performance evaluation of the dual-purpose strategy regarding enhanced methane recovery and aquifer influx control (Chapter 6).

Chapter 5

Hydrate-based CO₂ storage and CO₂ fate assessment

5.1 Introduction

This chapter transitions from defining the operational criteria for sustained injection (Chapter 4) to assessing the performance and long-term security of the C/W emulsion injection strategy. The work presented here fulfills the quantitative requirements of Objective 2 by rigorously analyzing the storage efficacy and confirming the reliability of the numerical framework for large-scale application.

The chapter begins by quantifying the CO₂ storage capacity for all successful injection scenarios identified in Chapter 4, detailing the partitioning of CO₂ into hydrate-based CO₂ storage (HBCS), dissolution-based storage (DBCS), and liquid-based CO₂ storage (LBCS). This analysis establishes the key trade-offs between injectivity stability and total sequestration volume.

Following the capacity quantification, the chapter addresses the critical issue of long-term CO₂ storage security. A 100-year simulation is conducted using a prematurely terminated injection scenario to track the post-shut-in CO₂ fate. This analysis confirms the secure trapping mechanism of CO₂ via density-driven migration of CO₂-rich brine and the complete conversion of residual liquid CO₂ to stable hydrate particles, demonstrating the long-term viability of the storage approach.

Finally, the robustness and scalability of the T-H-C numerical model are confirmed through a qualitative validation against 3D reactor experiments conducted by Chen et al. [57]. This validation step ensures the framework accurately captures the complex flow phenomena, specifically the thermal and hydraulic coupling that results in the crucial "cap-and-channel" flow regime, thereby establishing the model's readiness for the field-scale performance assessment in Chapter 6.

5.2 Hydrate-based CO₂ storage capacity in emulsion injection scenarios

The results, detailed in **Table 5.1**, compare the cumulative CO₂ mass injected (measured in Mt) and the resultant CO₂ partitioning performance achieved by each continuous emulsion

(CE) scheme that successfully completed 1 PV of injection. This study categorizes CO₂ partitioning into three primary storage forms within the domain: dissolution-based CO₂ storage (DBCS), liquid-based CO₂ storage (LBCS) in the form of dispersed CO₂ droplets, and hydrate-based CO₂ storage (HBCS). The HBCS category specifically accounts for the total mass of CO₂ stabilized by hydrate formation, which includes both CO₂ bound within the hydrate lattice and the liquid CO₂ encapsulated by the hydrate film. Unlike bulk liquid CO₂ storage, where thick hydrate films often inhibit mass transfer, the exceptionally thin films formed around the small emulsion droplets minimize this resistance. This allows for far more effective diffusion of water and CO₂, facilitating the efficient conversion of the encapsulated CO₂ into solid hydrate over time [159].

Table 5.1 Partitioning of injected CO₂ and hydrate characteristics after 1 PV injection for different CE Cases.

	α	Injected CO ₂ (Mt)	Hydrate particle saturation (%)	DBCS (wt%)	LBCS (wt%)	HBCS (wt%)	CO ₂ exited domain (wt%)
CE10	0.35	0.064	5.11	49.79	0.29	38.69	11.23
	0.45		5.3	49.58	2.67	36.40	11.35
CE15	0.35	0.096	9.7	31.52	11.33	48.94	8.21
	0.45		9.3	31.95	16.37	42.65	9.03
CE20	0.45	0.128	11.73	23.04	27.63	40.10	9.23

The findings demonstrate that the cumulative mass of injected CO₂ exhibits a linear relationship with the initial CO₂ volume fraction of the emulsion. Correspondingly, the porous media's final hydrate particle saturation increases as the initial CO₂ fraction is raised.

Analysis of the storage categories shows distinct trends: The contribution from DBCS generally declines as the total injected CO₂ mass rises (dropping sharply from approximately 49 wt% in CE10 to 23 wt% in CE20). Conversely, the LBCS component increases significantly with higher injection volumes (rising from negligible in CE10 to approximately 23 wt% in CE20), signifying a strong shift toward LBCS storage. The HBCS fraction initially rises sharply from CE10 to CE15, followed by a minor reduction for CE20. Across all scenarios studied, HBCS consistently represents a substantial portion of the immobilized CO₂ mass, ranging from 36.40 wt% to 48.94 wt%.

Notably, the mass of CO₂ exiting the domain remains low (below 12 wt%). The advantage of injecting liquid CO₂ as small droplets dispersed in water is highlighted by the fact that the vast majority of the CO₂ leaving the domain is in the dissolved form (**Table 5.2**).

Table 5.2 Phase composition of CO₂ leaving the computational domain for various CE scenarios.

	α	DBCS (wt%)	LBCS (wt%)	HBCS (wt%)
CE10	0.35	100	0	0
	0.45	100	0	0
CE15	0.35	99.3	0	0.7
	0.45	96.67	1.39	1.94
CE20	0.45	81.63	14.18	4.19

The increased interfacial surface area provided by the small droplets promotes dissolution, leading to a mobile dissolved CO₂ front that precedes other components, which likely explains its dominance in the CO₂ mass exiting the domain. Furthermore, the rising LBCS observed with higher CO₂ concentrations is not necessarily a long-term liability, as the remaining liquid CO₂ droplets are expected to fully convert into CO₂ hydrates after injection is stopped and temperatures rebound, contributing to long-term storage (further investigated in Section 5.3).

Figure 5.1 illustrates the temporal evolution of CO₂ mass partitioning (DBCS, LBCS, HBCS) within the computational domain, with mass ratios normalized by the total CO₂ mass present at each time step ($\alpha = 0.45$).

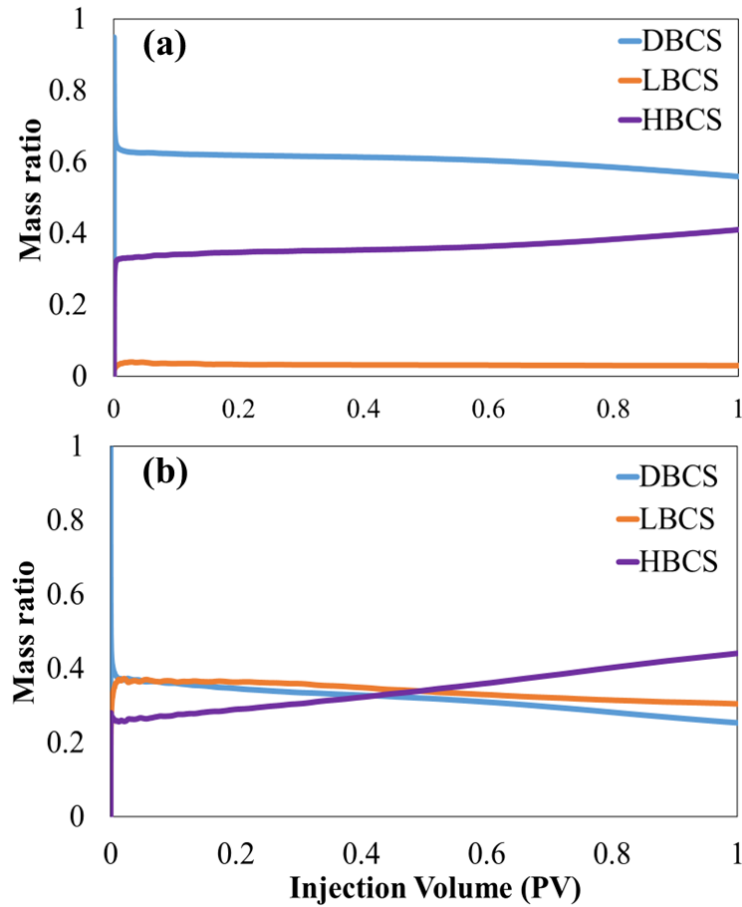


Figure 5.1 CO₂ mass partitioning evolution within the simulated domain as a function of injected PV ($\alpha = 0.45$). (a) CE10. (b) CE20.

The temporal trends reveal that HBCS accumulation is slow for CE10 but accelerates sharply for CE20. This suggests that while increasing the CO₂ volume fraction enhances the injected mass for high CO₂ volume fractions, the probability of blockage during prolonged injection periods dramatically increases. Consequently, CE10 offers superior control over the C/W emulsion process. Even with the CE10 scenario, however, mitigating potential blockage remains essential for sustained long-term injection, emphasizing the necessity of adopting a strategy like WAE.

The WAE scheme has been established as an effective solution for mitigating injectivity challenges during emulsion injection, even under extreme conditions like $\alpha = 0.15$. **Table 5.3** summarizes the key results for the WAE scenarios, providing a direct comparison against the immediate failure of their corresponding CE counterparts at $\alpha = 0.15$. This comparison clearly showcases the WAE method's efficacy in drastically improving emulsion injectivity and substantially increasing HBCS capacity.

Table 5.3 Performance comparison of WAE and CE injection scenarios for $\alpha = 0.15$.

	Injected water slug duration (hours)	PV of injected emulsion	Cumulative injected CO ₂ (Mt)	Hydrate particle saturation (%)
CE15	—	0.016	0.0015	0.16
WAE15	24	0.59	0.057	3.62
CE20	—	0.004	0.0005	0.05
WAE20	24	0.42	0.054	3.3

Figure 5.2 illustrates the temporal evolution of CO₂ mass partitioning during WAE20 injection. The alternation of emulsion with brine not only successfully manages hydrate accumulation near the wellbore but also actively promotes solubility trapping by enhancing the dissolution of existing CO₂ hydrate particles. However, as the CO₂ hydrate particles accumulate further downstream in the aquifer, the overall HBCS contribution within the simulated domain increases. This gradual downstream blockage explains the observed reduction in the duration of the subsequent emulsion slugs compared to the initial cycles.

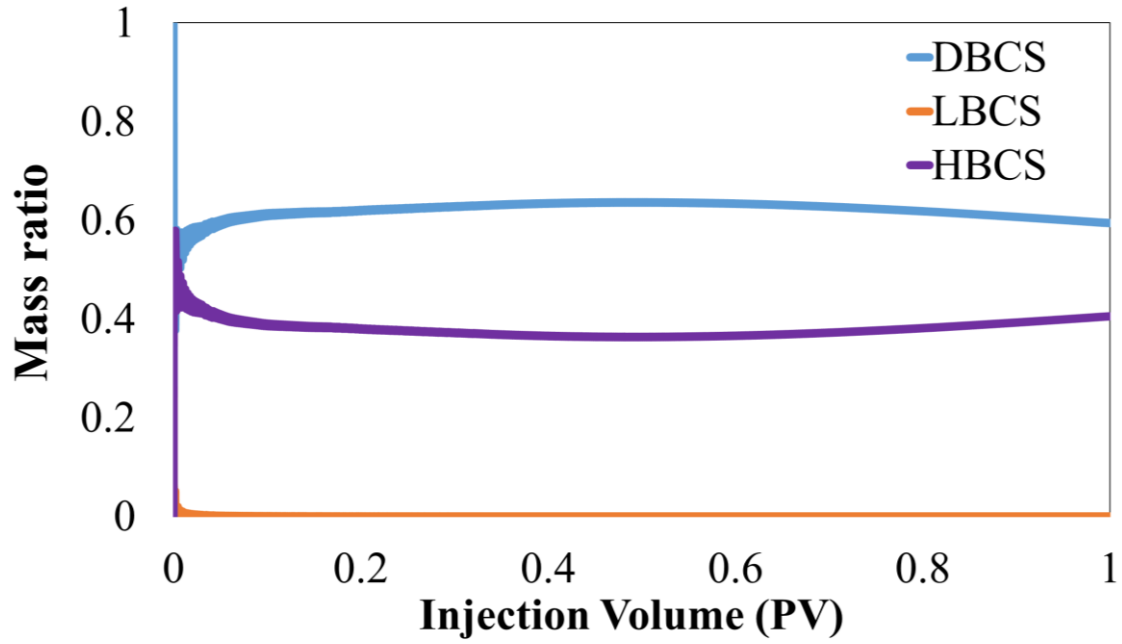


Figure 5.2 CO₂ mass partitioning evolution within the simulated domain as a function of injected PV (WAE20).

Given that higher CO₂ volume fractions generally yield greater cumulative injected mass and enhanced HBCS capacity, achieving the smallest possible liquid droplet diameter is recommended for optimization. A reduced liquid droplet diameter promotes the formation of particles largely composed of hydrate (i.e., a higher α) [158]. In this study, higher values correlated with a greater likelihood of achieving continuous emulsion injection. Furthermore, multiple studies suggest that smaller particle diameters are highly desirable; as described by Equations 2.28 and 2.29, they reduce the particle attachment rate while helping to maintain a high ratio of pore throat diameter to particle diameter (greater than 6), which prevents clogging and enables continuous injection [103], [106].

5.3 Long-term CO₂ fate in a seawater aquifer

Evaluating the long-term fate of injected CO₂ is fundamental to determining the effectiveness and safety of geological carbon storage. To monitor the CO₂ behavior after the well was shut in, the CE15 case with $\alpha = 0.25$ was selected for analysis. This scenario involved halting injection prematurely at 0.136 PV (after 102 days) because the pressure within the reservoir approached the fracture limit. This outcome simulates a more realistic operational constraint and provides sufficient unswept volume to track the spreading of dissolved CO₂, the thermal rebound, and potential leakage, unlike scenarios where the entire reservoir volume is largely filled. The total simulation duration was set to 100 years, encompassing both the active injection and the extended post-shut-in phases.

While mineral trapping is a recognized storage mechanism, it was excluded from this study as these geochemical reactions generally occur on timescales of centuries to millennia in typical sedimentary formations [160], [161]. Consequently, mineral trapping is considered to have a negligible impact on CO₂ storage security within the 100-year window modeled here. To investigate the long-term dynamics of solubility trapping, **Figure 5.3** presents spatial maps of the dissolved CO₂ volume fraction in the aquifer. Snapshots are provided at critical intervals—well shut-in (Day 102), 10 years, 50 years, and 100 years—illustrating the evolution and dispersion of the dissolved CO₂ front.

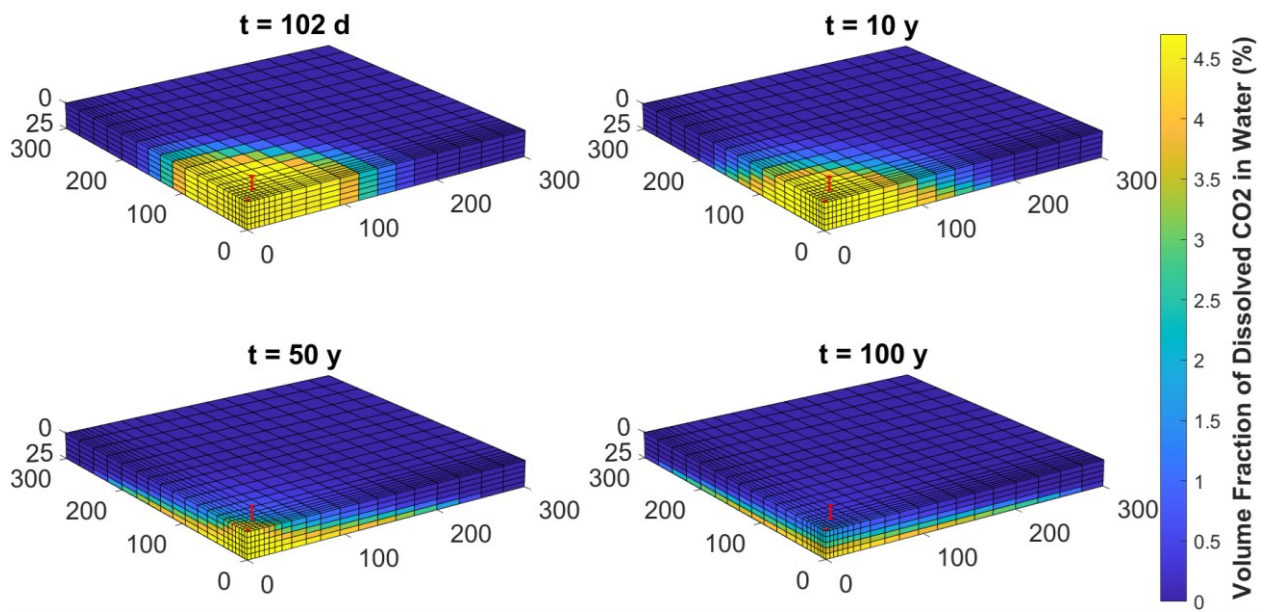


Figure 5.3 Dissolved CO₂ volume fraction distribution in the aquifer for CE15 ($\alpha = 0.25$) at various time points.

As depicted in **Figure 5.3**, the spatial distribution of dissolved CO₂ undergoes a marked change over the 100-year period following cessation of injection. While the dissolved CO₂ appeared relatively uniform at the point of shut-in, a distinct accumulation is evident at the reservoir base by the 100-year mark. This downward migration of the dissolved CO₂ is a direct result of the increased density of the brine following CO₂ dissolution. This negative buoyancy effect drives natural convection within the aquifer. The successful capture of this fundamental principle confirms the modified model's accuracy (Sections 2.6.1.3 and 2.6.1.4), demonstrating that the descent of CO₂-dense brine facilitates highly efficient mixing and significantly reduces the timescale required for permanent solubility trapping.

Beyond solubility trapping, understanding the thermal evolution is key to evaluating phase stability. **Figure 5.4** displays the temperature distribution from shut-in up to 10 years, the point at which the temperature largely reverts to its initial state.

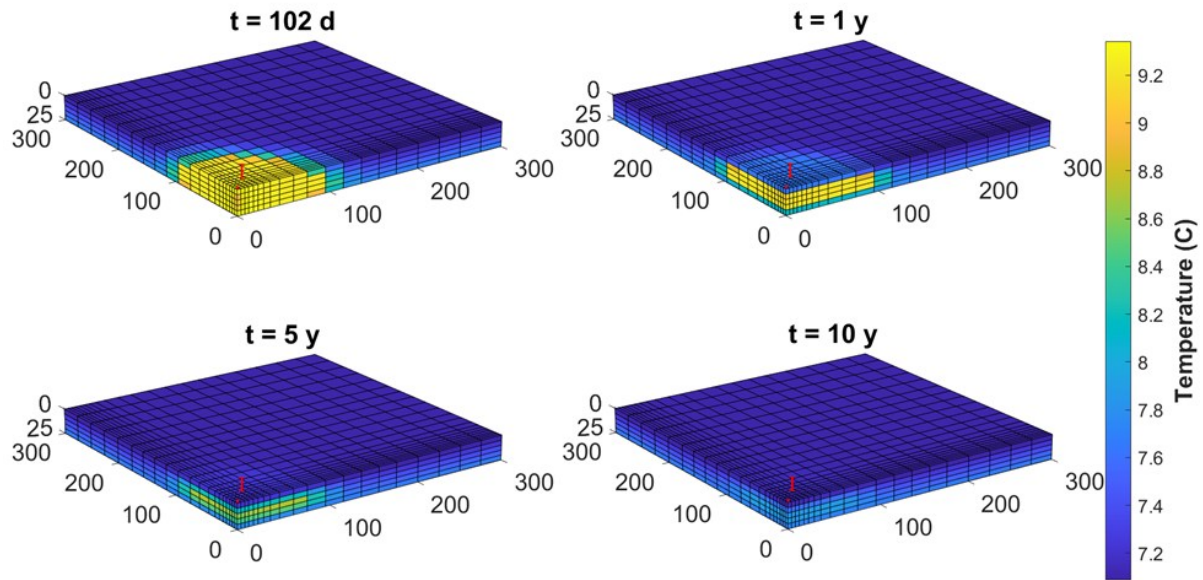


Figure 5.4 Spatial distribution of temperature in the aquifer for CE15 ($\alpha = 0.25$) at various time points.

To correlate this thermal recovery with CO_2 phase behavior, **Figure 5.5** details the spatial distribution of liquid CO_2 droplets.

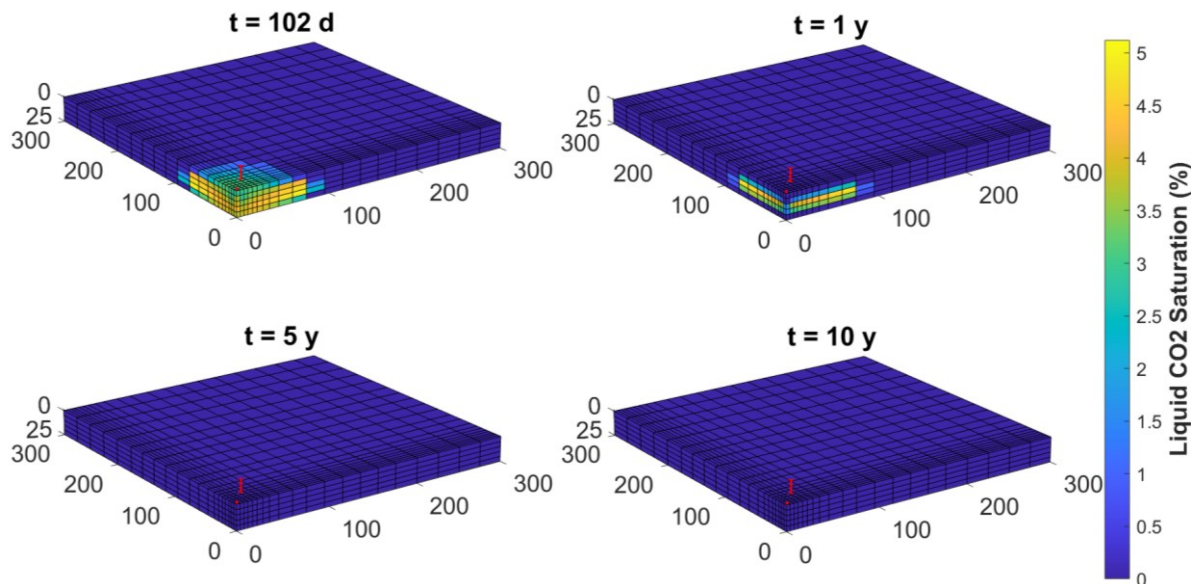


Figure 5.5 Spatial distribution of liquid CO_2 droplets in the aquifer for CE15 ($\alpha = 0.25$) at various time points.

It is evident that liquid CO_2 converts rapidly into hydrate particles in the top and bottom layers of the domain. In these outer zones, convective heat transfer enables quicker dissipation of the exothermic heat generated by hydrate formation, thereby accelerating the conversion of

liquid CO₂ to solid hydrate within the first year. Conversely, the more insulated central layers retain this exothermic heat for longer periods, resulting in localized temperature elevation visible in the Year 5 snapshot compared to the top and bottom regions. By Year 10, the entire domain nears thermal equilibrium, with temperatures having almost returned to their initial values, signifying the conclusion of major thermal transients and the virtual completion of further hydrate conversion.

Complementing the observed consumption of liquid CO₂ droplets and clarifying the long-term immobilization mechanisms, **Figure 5.6** illustrates the spatial distribution of hydrate particles. Snapshots covering the period from well shut-in (Day 102) up to 100 years provide insight into the persistence and evolution of hydrate formation throughout the post-injection period.

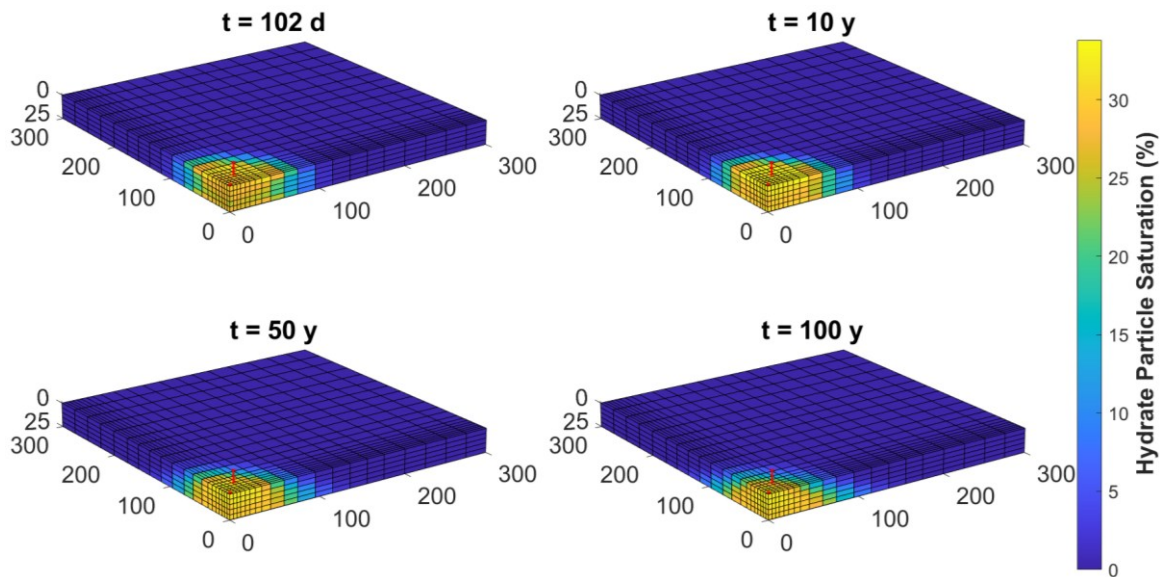


Figure 5.6 Spatial distribution of CO₂ hydrate particles in the aquifer for CE15 ($\alpha = 0.25$) at various time points.

Figure 5.6 shows how the hydrate particle spatial distribution evolves over the 100-year period. At shut-in, higher hydrate particle saturation is present in the upper and lower layers, consistent with the efficient convective heat transfer that promoted faster exothermic conversion discussed previously. By Year 10, following the near-total conversion of liquid CO₂ to hydrates (as confirmed by **Figure 5.5**), the hydrate saturation profile appears more uniform. However, by Year 100, the hydrate-saturated zone demonstrates a subtle downward movement. This indicates that the generated hydrate particles, which are entrained within the CO₂-laden fluid, can be carried by the general fluid flow. Crucially, while this descent is less dramatic than

the density-driven migration of dissolved CO₂, this long-term downward trend of hydrate accumulation in the deeper aquifer contributes robustly to secure immobilization, substantially reducing the risk of CO₂ migration upward.

The data presented in **Table 5.4** confirm the exceptional stability achieved during the post-injection phase. A clear phase transition occurs between well shut-in (Day 102) and Year 100: HBCS increased substantially, climbing from 51.58 wt% to 59.88 wt%, directly corresponding to the complete consumption of all liquid CO₂ droplets over the century. Concurrently, the DBCS maintained a near-constant contribution to storage, shifting only slightly from 40.38 wt% to 40.10 wt%).

Table 5.4 CO₂ partitioning for the CE15 ($\alpha = 0.25$) case at well shut-in (Day 102) and Year 100.

Time	DBCS (wt%)	LBCS (wt%)	HBCS (wt%)	CO ₂ exited domain (wt%)
Well shut-in	40.38	8.04	51.58	0
Year 100	40.10	0	59.88	0.02

This minor decline in DBCS is accounted for by the exsolution process detailed in the Chapter 2: Dissolved CO₂ is drawn from the aqueous phase onto the surfaces of liquid CO₂ droplets to fuel continued hydrate particle growth. This dynamic partitioning mechanism results in a highly secure trapping regime, with only a negligible fraction (0.02 wt%) of CO₂ exiting the domain after 100 years. The minimal risk of leakage confirms the long-term viability and effectiveness of this storage approach under an incomplete injection scenario.

5.4 Qualitative validation against 3D reactor experiments

To assess the reliability of the numerical model for 3D simulations, a qualitative comparison against the 3D reactor experiments performed by Chen et al. [57] was conducted. In the experimental work by Chen et al. [17], a C/W emulsion was introduced at an elevated temperature into a 3D vessel, whose walls were independently maintained at a controlled temperature. The distribution of internal temperatures was visually mapped across multiple planes, including triaxial cross-sections, a dedicated side view, and two depth slices from the top. Initial hydrate formation was consistently observed in the uppermost region for all fluid types, creating a solidified hydrate cap. The side-view visualization indicated this cap as a localized zone of elevated temperature, which effectively blocked upward fluid movement and redirected the injection stream into the vessel's central section. When tracing temperature evolution, the fronts for the two top-view depth slices showed similar upward trends, but the lower trace (50 mm) exhibited a delayed temperature rise, strongly suggesting the insulating

impact of the overlying hydrate cap. Spatially, top-view heat maps revealed that the warmest zones were immediately adjacent to the injection port, with temperatures decreasing gradually toward the producer well.

The reservoir model in this study simulated the injection of a C/W emulsion at the in-situ temperature. This study implemented no-flow conditions on the upper and lower reservoir boundaries but permit heat transfer with the overburden and underburden, which are treated as convective boundaries linked to adjacent rock layers. Consistent with the findings of Chen et al. [57], initial hydrate growth occurs in these thermally open strata, leading to a reduction in permeability that forces the flow into the intermediate layers. Because heat escapes more slowly from these middle layers, continued hydrate formation is subsequently delayed, thereby sustaining higher fluid flows in the center.

The simulated temperature distribution (**Figure 5.7**) successfully mirrors the characteristic "cap-and-channel" thermal signature: A top view perspective shows distinct hot spots near the injection well that become progressively cooler further downstream. Vertically, the warmer fluid demonstrates a preference for faster advancement through the middle layers. Time-series snapshots further demonstrate that the initial hot zone first expands before undergoing subsequent cooling and contraction. This reduction in the spatial extent of the elevated temperature region is attributed to increased hydrate particle saturation and reduced effective permeability and the resultant heat loss across the boundaries, thus providing supplementary evidence of the flow channeling phenomenon.

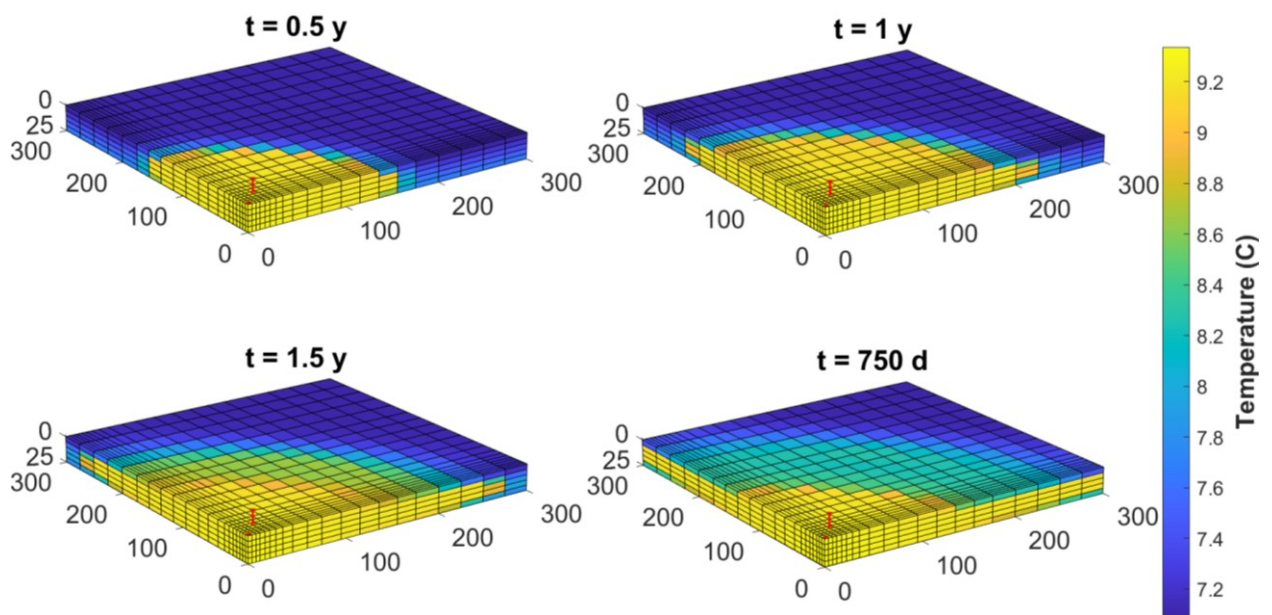


Figure 5.7 Spatial distribution of temperature in the aquifer for CE15 ($\alpha = 0.45$) at various time points.

Figure 5.8 presents hydrate saturation patterns of the numerical model of this study, confirming the development of a hydrate cap at the upper stratum and the resulting diversion of the emulsion into the central section—a configuration that precisely replicates the flow partitioning observed in the experimental work by Chen et al. [57].

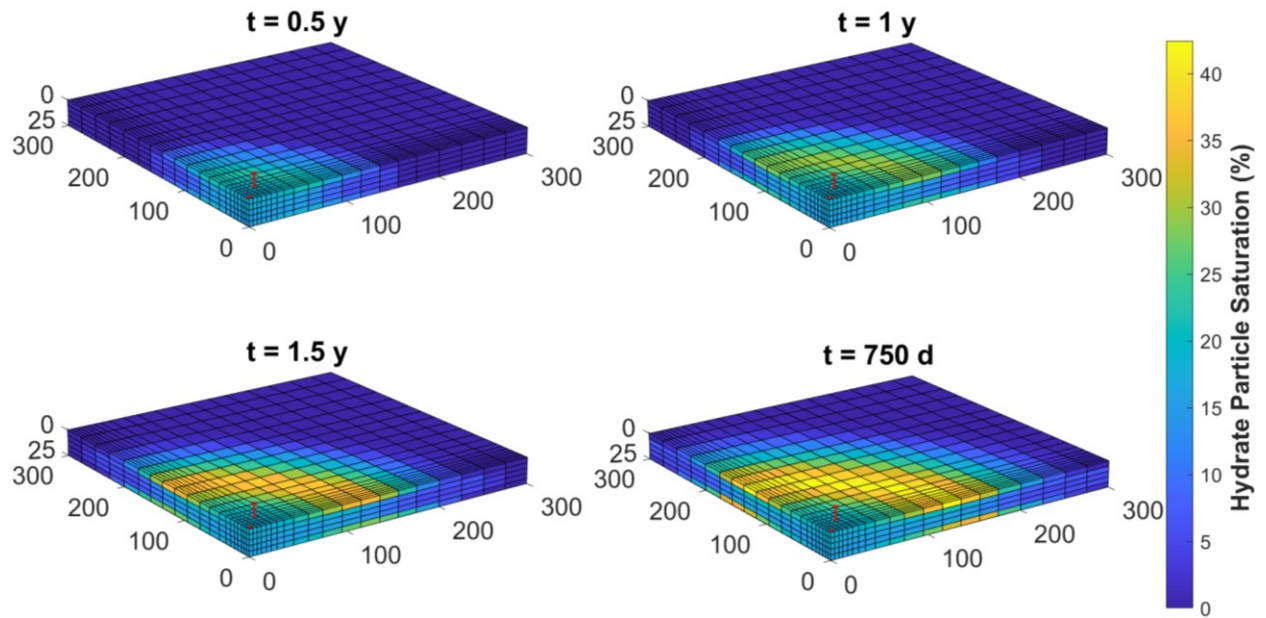


Figure 5.8 Spatial distribution of CO₂ hydrate in the aquifer for CE15 ($\alpha = 0.45$) at various time points.

The elevated hydrate particle saturation near the top and bottom boundaries supports a mechanism of self-trapping. When coupled with the C/W emulsion's proven sweep efficiency, this process significantly boosts the overall HBCS capacity within the targeted aquifer zone. This close qualitative correspondence confirms that the fundamental "cap-and-channel" flow behavior and associated thermal fingerprint remain consistent, regardless of whether the driving force is injected-fluid temperature and controlled boundary cooling (Chen et al. [57]) or hydrate exothermicity and conductive exchange with the reservoir strata (this study's model).

5.5 Conclusion

This chapter successfully transitioned from defining the operational injection criteria (Chapter 4) to rigorously assessing the resultant storage performance and establishing the full reliability of the T-H-C numerical framework. The findings presented herein provide the definitive quantitative evidence necessary to validate the C/W emulsion strategy as a viable mechanism for secure geological storage.

The analysis of hydrate-based CO₂ Storage (HBCS) capacity demonstrated the high sequestration potential of this methodology. Simulation results showed that cumulative injected CO₂ mass scales linearly with the initial CO₂ volume fraction, with schemes successfully injecting up to 0.128 Mt through a single well. Significantly, HBCS consistently constituted a substantial portion of the immobilized CO₂ mass, confirming the mechanism's efficacy. Furthermore, the WAE scheme, adopted to overcome critical injectivity challenges, not only facilitated full pore volume injection but also demonstrated a corresponding substantial increase in overall HBCS capacity, effectively linking the operational solution to enhanced storage performance.

The critical long-term viability of the storage approach was confirmed through a 100-year simulation encompassing the extended post-shut-in phase. This analysis provided two major contributions to the understanding of CO₂ fate in hydrate-bearing sediments: CO₂ was permanently immobilized via dominant hydrate trapping (nearly 60%) and effective solubility trapping (approximately 40%). The successful simulation of density-driven downward migration of CO₂-rich brine affirmed the model's accuracy in predicting long-term geological stability, while the resultant negligible fraction (0.02 wt%) of CO₂ exiting the domain after a century conclusively confirms the long-term security and effectiveness of this C/W emulsion storage approach.

Finally, the framework's robustness was validated by achieving a close qualitative match with 3D reactor experiments, confirming its ability to reproduce the self-trapping, flow-channeling mechanism that optimized C/W emulsion sweep efficiency and pore-space utilization, significantly boosting HBCS capacity and achieving local hydrate saturations exceeding 40%. This consistency establishes the predictive capability of the T-H-C framework for C/W emulsion flow, rendering it fully prepared for the comprehensive field-scale performance assessment presented in Chapter 6.

Chapter 6

Enhanced methane recovery and aquifer influx control

6.1 Introduction

The preceding chapters established the fundamental framework for simulating C/W emulsion injection (T-H-C model validation in Chapter 3), defined the necessary operational criteria for sustained injectivity (Chapter 4), and confirmed the model's robustness for complex flow regimes (3D validation in Chapter 5). This chapter, focusing on Objective 3, marks the transition from controlled-parameter study to the field-scale performance assessment of the dual-purpose C/W emulsion technology. (α), and the utilization of the WAE injection scheme.

While injectivity is paramount, the ultimate viability of this strategy hinges on its ability to enhance methane production over conventional methods, while simultaneously achieving acceptable long-term CO₂ storage security. This chapter addresses both by applying an optimized operational strategy—derived from observations in Chapter 4—to a representative benchmark domain of an arctic Class 2 methane hydrate deposit.

The core objective is to numerically evaluate the strategy's effectiveness over a single injection-soaking-production cycle. The analysis will rigorously quantify the twofold advantage of the CO₂ hydrate seal, measuring both enhanced CH₄ recovery and mitigation of aquifer influx, alongside a detailed CO₂ storage quantification. Fundamentally, this chapter will investigate the stability of the in-situ CO₂ hydrate seal over the production period, analyzing the dynamics of advection-driven dissolution. The results will establish the critical sensitivity of the technology's performance to geological and operational parameters, such as initial MH saturation and CO₂ volume fraction, thereby defining the necessary operational limits for the technology and laying the groundwork for optimizing future implementation strategies.

6.2 Mathematical formulation

In this chapter, the model is extended to simulate the full production phase, which requires the inclusion of MH dissociation and the resulting two-phase flow (liquid and gas). The governing equations presented below utilize the multiphase Darcy's Law framework established in Chapter 2 (Equations 2.1 and 2.2) for both the liquid and gas phases.

The advective transport of the emulsion components and the flowing CO₂ hydrate particles is dictated by the liquid-phase superficial velocity, $\vec{u}_l$. As the flowing hydrate particles are carried by the emulsion, their flux terms are expressed using the liquid velocity multiplied by the component's volume fraction relative to the entire flowing liquid material ($S_{PF} + S_e$). The general form of the governing equations is as follows:

Water :

$$-\nabla \cdot \left(\vec{u}_l \left(\frac{S_e}{S_{PF} + S_e} \right) \chi_{H_2O} \rho_{H_2O} \right) - \dot{q}_{H_2O}^{CH_{form}} + \dot{q}_{H_2O}^{CH_{dsol}} + \dot{q}_{H_2O}^{CH_{diss}} - \dot{q}_{H_2O}^{MH_{form}} + \dot{q}_{H_2O}^{MH_{diss}} = \phi_0 \frac{\partial}{\partial t} (S_e \chi_{H_2O} \rho_{H_2O}) \quad (6.1)$$

Liquid CO₂:

$$-\nabla \cdot \left(\vec{u}_l \left(\frac{S_e}{S_{PF} + S_e} \right) \chi_{LCO_2} \rho_{LCO_2} \right) - \dot{q}_{CO_2}^{CH} - \dot{q}_{dsol} + \dot{q}_{LCO_2}^{diss} = \phi_0 \frac{\partial}{\partial t} (S_e \chi_{LCO_2} \rho_{LCO_2}) \quad (6.2)$$

Dissolved CO₂:

$$-\nabla \cdot \left(\vec{u}_l \left(\frac{S_e}{S_{PF} + S_e} \right) (1 - \chi_{H_2O} - \chi_{LCO_2} - \chi_{NaCl}) \rho_{wCO_2} \right) + \dot{q}_{dsol} + \dot{q}_{wCO_2}^{dsol} = \phi_0 \frac{\partial}{\partial t} (S_e (1 - \chi_{H_2O} - \chi_{LCO_2} - \chi_{NaCl}) \rho_{wCO_2}) \quad (6.3)$$

Flowing CO₂ hydrate particles:

$$-\nabla \cdot \left(\vec{u}_l \left(\frac{S_{PF}}{S_{PF} + S_e} \right) \rho_P \right) + \dot{q}_P - \dot{q}_{PF}^{dsol} - \phi_0 k_{trap} S_{PF} \rho_P - \phi_0 (k_{ads} S_{PF} - k_{det} S_{Pads}) \rho_P - \dot{q}_{PF}^{diss} = \phi_0 \frac{\partial}{\partial t} (S_{PF} \rho_P) \quad (6.4)$$

Adsorbed CO₂ hydrate particles:

$$\phi_0 (k_{ads} S_{PF} - k_{det} S_{Pads}) \rho_P - \dot{q}_{Pads}^{dsol} - \dot{q}_{Pads}^{diss} = \phi_0 \frac{\partial}{\partial t} (S_{Pads} \rho_P) \quad (6.5)$$

Trapped CO₂ hydrate particles:

$$\phi_0 k_{trap} S_{PF} \rho_P - \dot{q}_{Ptrap}^{dsol} - \dot{q}_{Ptrap}^{diss} = \phi_0 \frac{\partial}{\partial t} (S_{Ptrap} \rho_P) \quad (6.6)$$

NaCl:

$$-\nabla \cdot \left(\vec{u}_l \left(\frac{S_e}{S_{PF} + S_e} \right) \chi_{NaCl} \rho_{NaCl} \right) = \phi_0 \frac{\partial}{\partial t} (S_e \chi_{NaCl} \rho_{NaCl}) \quad (6.7)$$

Methane hydrate (MH):

$$\dot{q}_{MH}^{form} - \dot{q}_{MH}^{diss} = \phi_0 \frac{\partial}{\partial t} (S_{MH} \rho_{MH}) \quad (6.8)$$

CH₄ gas:

$$-\nabla \cdot (\vec{u}_g S_g \rho_g) - \dot{q}_{CH_4}^{MHform} + \dot{q}_{CH_4}^{MHdiss} = \phi_0 \frac{\partial}{\partial t} (S_g \rho_g) \quad (6.9)$$

Energy conservation equation:

$$\begin{aligned} \nabla \cdot (\lambda \nabla T) - \nabla \cdot \vec{u}_l \left(\left(\frac{S_e}{S_{PF} + S_e} \right) (\chi_{LCO_2} \rho_{LCO_2} h_{CO_2} + (1 - \chi_{H_2O} - \chi_{LCO_2} - \chi_{NaCl}) \rho_{wCO_2} h_{CO_2} + \right. \\ \left. \rho_{brine} (\chi_{H_2O} + \chi_{NaCl}) h_{brine}) + \left(\frac{S_{PF}}{S_{PF} + S_e} \right) \rho_P h_P \right) - \nabla \cdot \vec{u}_g (S_g h_g) + H A_{HT} (T_\infty - T) - \\ \Delta H_{CH} (\dot{q}_{CH}^{form} - \dot{q}_{CH}^{diss} - \dot{q}_{CH}^{dsol}) - \Delta H_S (\dot{q}_{dsol} + \dot{q}_{wCO_2}^{dsol}) - \Delta H_{MH} (\dot{q}_{MH}^{form} - \dot{q}_{MH}^{diss}) = \frac{\partial}{\partial t} \left((1 - \right. \\ \left. \phi_0) \hat{\rho}_{gr} C_{gr} T + \phi_0 (\rho_g S_g U_g + \rho_{MH} S_{MH} U_{MH} + \rho_{CH} S_{CH} U_{CH} + S_e (1 - \chi_{H_2O} - \chi_{LCO_2} - \right. \\ \left. \chi_{NaCl}) \rho_{wCO_2} U_{CO_2} + \rho_{LCO_2} (S_e \chi_{LCO_2} + S_{PT} (1 - \alpha) U_{CO_2}) + \rho_{brine} (S_{H_2O} + S_{NaCl}) U_{brine}) \right) \end{aligned} \quad (6.10)$$

where λ_{brine} , h_{brine} and U_{brine} are approximated by that of pure water for simplicity.

6.2.1 Wellbore formulation and operational constraints

The reservoir model employs a vertical well with a physical radius (r_w) of 0.1 m. To integrate the well into the numerical framework, it is treated as a source/sink term rather than an explicit grid block. During the injection phase, a constant-rate boundary condition is applied, where the total flow rate is distributed among the perforated grid cells in the aquifer. During the production phase, the well is modeled using a radial flow approximation based on the Peaceman well index. This approach calculates gas and water production rates based on the pressure drawdown between the reservoir grid and the target bottom-hole pressure, accounting for phase mobility and grid-block geometry.

The equivalent radius (r_{eq}) for a rectangular grid block with an area of A_{grid} is calculated as:

$$r_{eq} = 0.2079 \sqrt{A_{grid}} \quad (6.11)$$

The production rate for the liquid phase (including water and emulsion components) is given by:

$$q_l = K_D k_{rl} (2\pi dz) \frac{(P_{grid} - P_{wf})}{\mu_l \log\left(\frac{r_{eq}}{r_w}\right)} \quad (6.12)$$

The gas production rate is calculated by:

$$q_g = K_D k_{rg} (2\pi dz) \frac{(P_{ca} + P_{grid} - P_{wf})}{\mu_g \log\left(\frac{r_{eq}}{r_w}\right)} \quad (6.13)$$

where P_{grid} is the grid block liquid pressure, P_{wf} is the bottom-hole flowing pressure, and dz is the grid cell thickness.

6.3 Simulation framework

For the numerical analysis in this chapter, the simulator employed the Newton-Raphson method to solve the governing nonlinear equations. To achieve this, the Jacobian matrices were constructed using the Automatic Differentiation (AD) capabilities of MRST [149]. The iterations proceeded at each time step until the following convergence criteria were met:

$$MAX \left\{ \begin{array}{l} \Delta P_i - (\varepsilon_r P_i + \varepsilon_a), \\ \Delta T_i - (\varepsilon_r T_i + \varepsilon_a), \\ \Delta \chi_{H_2O\ i} - (\varepsilon_r \chi_{H_2O\ i} + \varepsilon_a), \\ \Delta \chi_{LCO_2\ i} - (\varepsilon_r \chi_{LCO_2\ i} + \varepsilon_a), \\ \Delta \chi_{NaCl\ i} - (\varepsilon_r \chi_{NaCl\ i} + \varepsilon_a), \\ \Delta S_{MH\ i} - (\varepsilon_r S_{MH\ i} + \varepsilon_a), \\ \Delta S_{g\ i} - (\varepsilon_r S_{g\ i} + \varepsilon_a), \\ \Delta S_{Ptrap\ i} - (\varepsilon_r S_{Ptrap\ i} + \varepsilon_a), \\ \Delta S_{Pads\ i} - (\varepsilon_r S_{Pads\ i} + \varepsilon_a), \\ \Delta S_{PF\ i} - (\varepsilon_r S_{PF\ i} + \varepsilon_a) \end{array} \right\} < 0$$

the convergence criterion employs a mixed tolerance approach, combining a relative tolerance (ε_r) set at 10^{-6} with an absolute tolerance (ε_a) set at 10^{-7} .

6.3.1 Reservoir model and geological basis

The numerical model simulates a simplified, homogeneous system based on the geometry and average thermophysical properties of Zone A (the Upper MH Zone) within the Mallik Gas Hydrate Production Test Site, drawing representative data from the Mallik 2L-38 and Mallik 5L-38 well log interpretations [162], [163].

Despite confirming that the Overburden (OB) and Underburden (UB) shale zones possess some intrinsic permeability, Uddin et al. modeled them as impermeable due to the significantly higher intrinsic permeability of the connecting sand layer [162]. Assuming zero permeability for boundaries significantly distorts production forecasts. For example, Boswell et al. [164] showed that replacing an infinite aquifer with an impermeable boundary drastically enhanced productivity by nearly two orders of magnitude, highlighting the critical need for accurate hydraulic boundary definition to prevent flawed productivity predictions based on closed-system assumptions.

In modeling, the top and bottom boundaries (OB and UB) were represented using Robin boundary conditions for both mass and heat exchange, accounting for their typical permeability ranges (OB: several millidarcy; UB: several to hundreds of millidarcy [45]). This involved modeling mass flow with a finite-conductance connection to a fixed far-field pressure, and heat transfer as a convective boundary to a fixed external temperature. Initial data from the Mallik field shows variability in methane hydrate (MH) saturation: Well logs for 2L-38 suggest a 20% to 80% range, and 5L-38 shows significant lateral variation [162]. Conversely, some core and well-log studies indicate high saturation values, often exceeding 80% [163]. For instance, Rutqvist et al. used an average MH saturation value of 75% in their model [163], while Waite et al. reported 80% as typical hydrate saturations for Mallik 5L-38 [142].

To address this uncertainty, the current study examined two scenarios for average MH saturation: Case 1 (75%) and Case 2 (50%). Case 1 served as the base case; the most successful emulsion injection strategy employed there was subsequently tested on Case 2 to assess its ability to seal the MHL and enhance gas recovery. The initial physical properties and modeling parameters of the reservoir built in this study are listed in **Table 6.1**.

Table 6.1 Reservoir and emulsion modeling parameters (key physical properties and operational settings).

Properties and Parameters	Values and Unit	Properties and Parameters	Values and Unit
Reservoir domain	Thickness: 45 m (900-945 m) Areal extent: 120 m × 120 m	MH saturation	Case1: 75% Case2: 50%
MHBL depth	905-930 m	Pressure at the center of the top layer	9.0126 MPa
Perforation interval	Production: 910-925 m Injection: 932.5-937.5 m	Temperature at the center of the top layer	7.0375 °C
Sand layer interval	905-940 m	Geothermal gradient	30 °C/km
Initial porosity (ϕ_0) [163]	35%	Salinity	3.5 wt%
D_{gr}	150 μm	Emulsion injection flow rate	100 m ³ /d
Vertical/horizontal permeability	$\frac{k_v}{k_h} = 0.1$	Thermal conductivity of rock [165]	Sand: 6.6 W/(m·K) Mud: 1.5 W/(m·K)
Intrinsic horizontal permeability of mud layer	OB: 1 md UB: 50 md	CO ₂ hydrate particle parameters	$\alpha = 0.3$ $D_p = 5 \mu\text{m}$
Intrinsic horizontal permeability of sand layer	1200 md [163]	CO ₂ volume fraction in emulsion	30%, 50%
Grain density [43]	2650 kg/m ³	Wellbore radius	0.1 m
Grain specific heat capacity [43]	792 J/(kg·K)	Reynolds number at the wellbore sandface	~ 0.22
Heat transfer coefficient (top/bottom boundaries)	1 W/(m ² ·K)		

The average volume fraction (α) of the hydrate film on CO₂ hydrate particles is crucial. A smaller CO₂ droplet diameter increases α [158], which reduces the total number of CO₂ droplets that convert to hydrate particles [55]. This incomplete conversion is a self-limiting effect caused by the hydrate film's resistance to mass transfer and the local temperature increase around the droplet [55]. Given the wide range of reported film thicknesses (0.15 μm to 20 μm) as mentioned in Section 4.4.4, in this chapter α was set to 0.3 (corresponding to a 0.28 μm film thickness). Building on Chapter 4, which optimized droplet diameter (5 μm to 20 μm) and α to mitigate injection risks [55], the chosen values here represent a highly effective C/W emulsion, allowing the current analysis to focus entirely on the CO₂ seal integrity.

6.3.2 Numerical discretization

The simulation utilized a 4,312-cell grid ($14 \times 14 \times 22$) featuring local grid refinement near the wellbore (**Figure 6.1**), which is essential for capturing steep gradients during injection and production. Vertical cell sizing was based on established strategies [60], with minor adjustments for computational efficiency:

- Coarser cells (2.5 m) were used in the aquifer, mud layers (OB/UB) and the hydrate bearing layers where the production well is perforated.
- Finer resolution (1.25 m) was implemented at the critical MHBL boundaries (the OB and aquifer interfaces) where maximum phase changes occur.

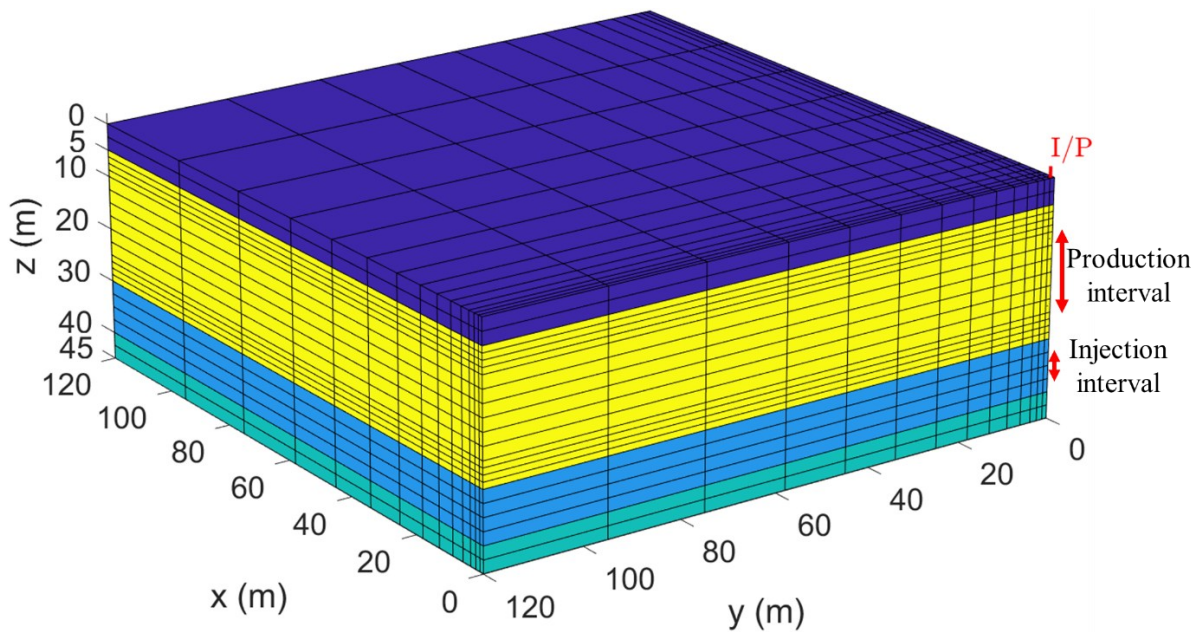


Figure 6.1 Three-dimensional Cartesian grid representation of the reservoir model. The domain is layered vertically: OB (0–5 m); MHBL (5–30 m); aquifer (30–40 m); and UB (40–45 m). The production interval is set within the MHBL (10–25 m) and the injection interval is in the aquifer (32.5–37.5 m).

Solution independence was confirmed by a grid-convergence study comparing the 4,312-cell grid with finer 5,488-cell and 7,056-cell meshes (Section 6.4.1).

6.4 Simulation results and discussion

This chapter presents the simulation results for Case 1 (initial MH saturation of 75%) and Case 2 (initial MH saturation of 50%), evaluating the effectiveness of aquifer-based C/W emulsion injection to form a stable CO₂ hydrate seal. Production under standard depressurization is referred to as Base_75 for Case 1 and Base_50 for Case 2. Case 1 is further compared against two emulsion-injection scenarios: a 30% liquid CO₂ volume fraction (Base75_CE30) and a 50% volume fraction (Base75_CE50). The most effective emulsion-injection scenario from Case 1 is then applied to Case 2 to examine its performance under lower MH saturation. The analysis focuses on key performance indicators, including enhanced gas production, reduction of water production, the Gas-Water ratio (GWR) (defined as the ratio of cumulative gas production to cumulative water production), and CO₂ storage partitioning.

The operational sequence includes a 60-day C/W emulsion injection phase, followed by a designated soaking period and a 3-year production stage. Two distinct soaking strategies were compared to determine how resting time influences seal integrity and thermal effects:

- **Extended 5-year soaking period (S5y):** This serves as the primary baseline for both cases. This duration aims to maximize the conversion of liquid CO₂ droplets into hydrates while allowing exothermic heat to migrate into the MHBL, potentially providing thermal stimulation during the subsequent production phase.
- **Shortened 6-month soaking period (S6m):** This was performed as a sensitivity analysis. In industrial settings, shorter soaking intervals are more desirable to minimize project durations and operational costs.

During these soaking periods, the lack of fluid flow enables hydrate particles to consolidate within the sand matrix before being subjected to production-induced pressure gradients. The production stage for all scenarios spans 3 years under a constant bottom-hole pressure (BHP) reflecting a 5 MPa drawdown. In this study, t represents the total simulation time starting from the onset of injection ($t = 0$), while t_p denotes the duration of the production phase.

6.4.1 Grid convergence analysis

Numerical convergence was verified using Base_75 by comparing the base grid (4,312 cells) with finer meshes of 5,488 and 7,056 cells. Final cumulative gas (G_{cum}) and water (W_{cum}) production outputs after three years are summarized in **Table 6.2**.

Table 6.2 Cumulative output parameters for grid convergence analysis during the 3-year production period.

Grid resolution	G_{cum} (SC m ³)	Absolute Relative Difference to 7056 Grid (%)	W_{cum} (SC m ³)	Absolute Relative Difference to 7056 Grid (%)
4312	1074576	0.06	644495	3.25
5488	1068792	0.6	650345	2.37
7056	1075252	0.0	666155	0.0

The absolute relative differences in cumulative gas (G_{cum}) and water (W_{cum}) production between the base and fine grids are small (gas: $\leq 0.6\%$; water: $\leq 3.25\%$), and the dynamic gas- (Q_g) and water-rate (Q_w) curves overlap closely (**Figure 6.2**). These results confirm that the chosen 4,312-cell mesh yields numerically stable and grid-independent predictions, particularly during the highly transient early production phase.

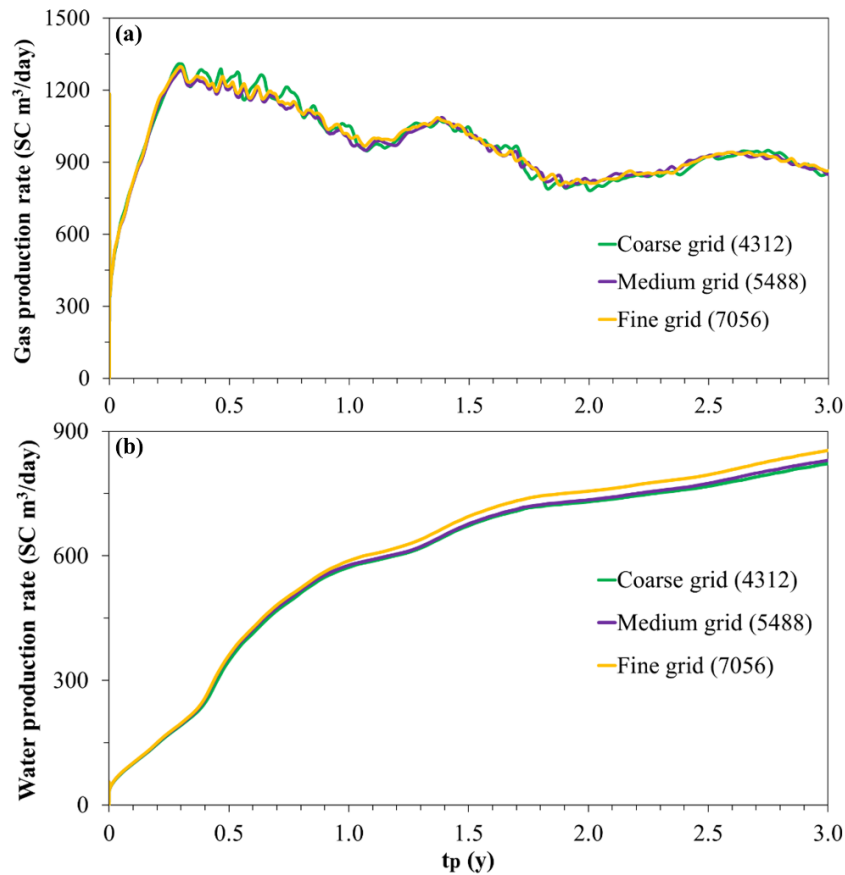


Figure 6.2 Grid convergence analysis of (a) gas production rate (Q_g) and (b) water production rate (Q_w).

6.4.2 Justification of single-component gas phase approximation

This section validates assumption number 8 of Section 2.2 (simplification of CO₂/CH₄ mixing in the gas phase). **Figure 6.3** compares simulated dissolved CO₂ concentrations in produced brine (extracted from the perforated cell at the base of the well) with theoretical solubility limits from Duan and Sun [88]. The Base75_CE50 run, which represents the scenario with the highest initial hydrate saturation (75%) and highest CO₂ concentration in the emulsion (50%), thus producing the largest dissolved-CO₂ concentrations near the well, remains undersaturated relative to the theoretical maximum for the majority of the production interval. This persistent undersaturation indicates that nearly all CO₂ mass resides in the aqueous phase as dissolved CO₂ rather than having a measurable partitioning into the existing CH₄ gas phase; thereby supporting the model assumption that the gas phase remains single-component CH₄ and neglecting the presence of CO₂ in the gas phase.

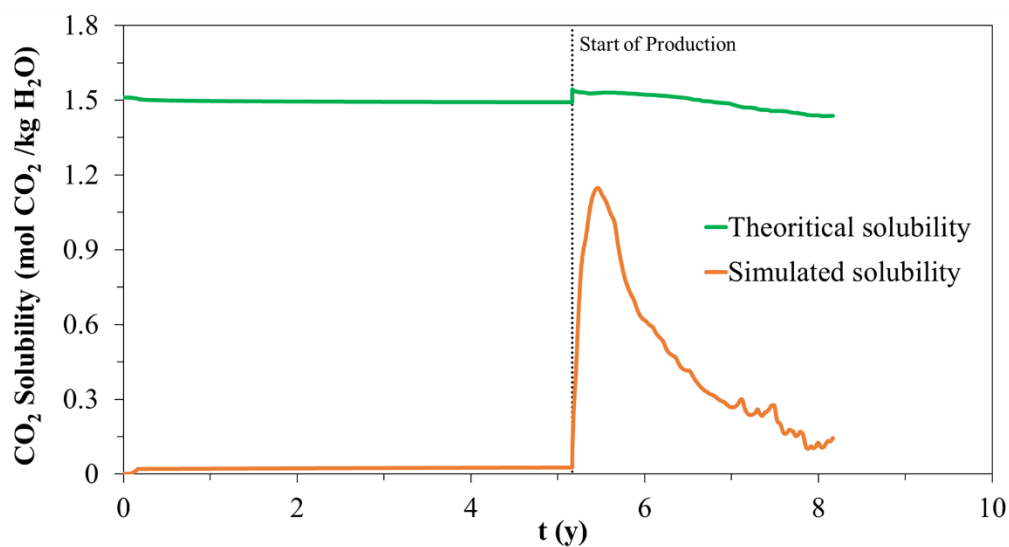


Figure 6.3 Comparison of CO₂ solubility in seawater: theoretical versus simulated values.

6.4.3 Case 1

This section examines the results for Case 1 (initial MH saturation of 75%). The base case (depressurization only, Base_75) is compared against two C/W emulsion injection scenarios: the 30% liquid CO₂ volume fraction (Base75_30) and the 50% volume fraction (Base75_50).

6.4.3.1 Performance comparison and transient rate analysis

The following analysis establishes the macro-scale effects of C/W emulsion injection by comparing the time evolution of production rates and the final cumulative performance across the three scenarios. **Figure 6.4** displays the gas (Q_g) and water (Q_w) production rates for the three Case 1 scenarios at standard conditions (SC, 0.1013 MPa and 15 °C). For the emulsion injection scenarios, Q_w represents the total aqueous production, consisting of brine and dissolved CO_2 .

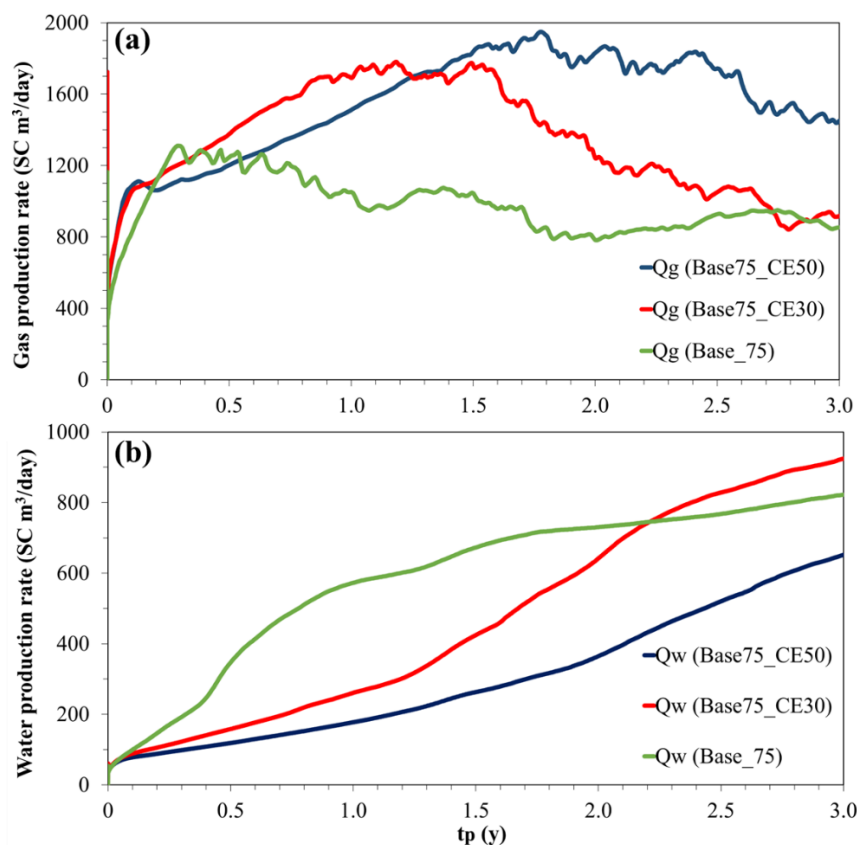


Figure 6.4 Time evolution over the 3-year production period of (a) gas production rate (Q_g) and (b) water production rate (Q_w) for Base_75, Base75_CE30, and Base75_CE50.

The time series for gas (Q_g) and water (Q_w) production rates (**Figure 6.4**) clearly show the significant positive impact of C/W emulsion injection on methane hydrate depressurization efficiency. The standard depressurization case, Base_75, achieves its gas production peak earliest, around 0.3 years, followed by a sustained decline. This behavior is expected when the pressure gradient decreases as the dissociation front rapidly moves away from the wellbore, and the observation aligns with previous studies [60], validating the numerical model's robustness.

In stark contrast, the two emulsion scenarios, Base75_CE30 and Base75_CE50, exhibit delayed but longer-sustained production peaks, signaling a fundamental change in reservoir flow control due to the hydrate seal. At the start of production ($t_p = 0$ y), the emulsion cases show superior initial performance (**Figure 6.4a**) and significantly higher initial GWR (**Figure 6.5**). The GWR reaches up to 31.1 SC m³ CH₄/SC m³ H₂O for the emulsion cases, compared to approximately 22.9 for the standard depressurization case.

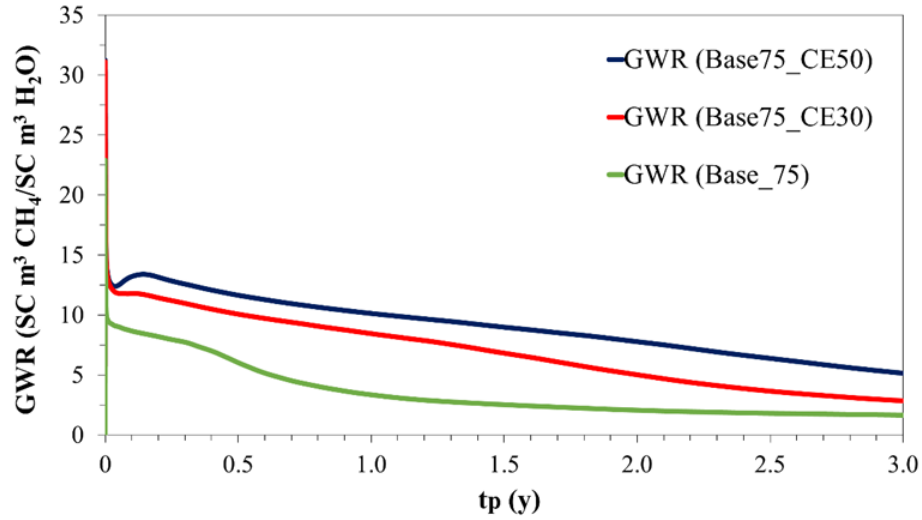


Figure 6.5 Time evolution of Gas-water ratio for different scenarios in Case 1.

This early advantage is attributed to a transient thermal stimulation created during the 5-year soaking period. The exothermic formation of CO₂ hydrate releases heat, which conducts into the adjacent, cooler MHL (Figure 6.6).

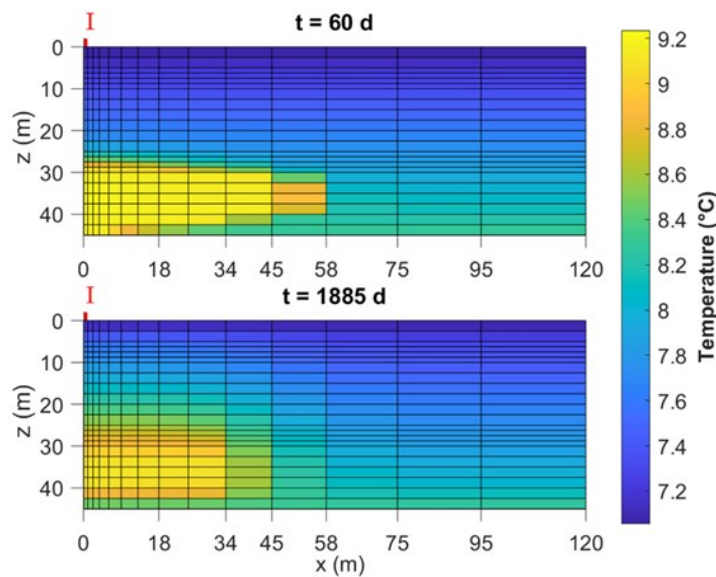


Figure 6.6 Thermal homogenization during soaking (Base75_CE30). Comparison of reservoir temperature distribution at (a) the end of the 60-day injection phase ($t = 60$ d) and (b) the end of the 5-year soaking phase ($t = 1885$ d).

This thermal increase locally raises the near-wellbore temperature, enhancing the thermodynamic drive for MH dissociation upon pressure reduction. This thermal effect is short-lived, corresponding with the sharp GWR peak that dissipates within the first 0.1 years, after which the hydraulic control of the CO₂ hydrate seal becomes the dominant factor in flow dynamics. The standard depressurization case, Base_75, exhibits a sharp GWR decline after approximately 0.3 years of production (**Figure 6.5**), which is directly caused by the loss of the natural hydrate barrier and the subsequent acceleration of water influx from the aquifer. Conversely, both emulsion cases show only a gradual GWR decline because the newly formed CO₂ hydrate seal effectively slows aquifer inflow and simultaneously concentrates the pressure drawdown within the MHBL. This sustained hydraulic control successfully prevents the rapid failure observed in the Base_75 case, confirming the long-term effectiveness of the sealing mechanism.

Water production (Q_w) data (**Figure 6.4b**) strongly supports this hydraulic interpretation. The Base_75 case exhibits the highest initial and continuously increasing Q_w , which reflects unrestricted water flow from the underlying aquifer. While this influx serves as a convective heat source that accelerates dissociation in the MHBL bordering the aquifer, it critically weakens the effective pressure gradient propagation, ultimately driving the sharp Q_g decline observed in **Figure 6.4a**. The Base75_CE50 scenario maintains the lowest water production throughout, signifying a robust CO₂ hydrate seal that effectively limits aquifer water influx into the wellbore.

This effective sealing mechanism allows Base75_CE50 to achieve the best long-term gas production (Q_g) performance, reaching a peak of nearly 2000 m³/day at 1.8 years. This long-term improvement occurs because the seal concentrates pressure drawdown exclusively inside the MHBL, thereby maintaining the production driving force across a wider reservoir radius. These observations are consistent with experimental findings reported by Sun et al. [61]. To quantify the overall outcomes, **Table 6.3** provides a quantitative summary of the final performance metrics for the three scenarios, detailing the cumulative gas (G_{cum}) and water (W_{cum}), GWR, methane recovery factor (Rf), and the percent improvements relative to the Base_75 scenario.

Table 6.3 Summary of final performance and efficiency indicators for C/W emulsion injection scenarios for Case 1.

	G_{cum} (SC m ³)	W_{cum} (SC m ³)	GWR (SC m ³ CH ₄ /SC m ³ H ₂ O)	Rf (%)	G_{cum} improvement (%)	W_{cum} reduction (%)
Base_75	1074576	644495	1.67	6.75	-	-
Base75_CE30	1469295	513358	2.86	9.23	36.74	20.35
Base75_CE50	1696098	328652	5.16	10.65	57.83	49.01

The final performance summary presented in **Table 6.3** clearly establishes the Base75_CE50 scenario as the most effective strategy. This case yielded substantial gains, demonstrating a 57.83% increase in cumulative gas production (G_{cum}) and achieving an approximate 49% reduction in cumulative water production (W_{cum}) compared to the unsealed Base_75 scenario. Importantly, the analysis shows that increasing the CO₂ volume fraction from 30% to 50% provided disproportionate benefits in hydraulic control. Although the G_{cum} improved by a factor of 1.5, the corresponding reduction in water production saw a much larger increase, improving by a factor of 2.5. While Base75_CE50 was optimal, the Base75_CE30 injection still provided a significant benefit, confirming the underlying efficacy of the CO₂ hydrate seal by delivering a 36.74% increase in G_{cum} and reducing water production by over 20%.

6.4.3.2 Spatiotemporal analysis of seal integrity and flow control mechanisms

This analysis focuses on how the CO₂ hydrate seal affects reservoir flow, contrasting the unsealed case (Base_75) with two sealed scenarios (Base75_CE30 and Base75_CE50) to explain the observed differences in gas and water production.

6.4.3.2.1 Mechanism of hydraulic recharge in the unsealed case (Base_75)

Analysis of the unsealed Base_75 scenario demonstrates the adverse impact of unrestricted aquifer inflow. **Figure 6.7**, **Figure 6.8**, and **Figure 6.9** present the spatiotemporal distributions of the stationary hydrate saturation (S_h), pressure and temperature for Base_75, with depressurization imposed at the wellbore ($x = 0$ m labeled ‘P’). To better capture dissociation onset, Base_75 panels are plotted from $t_p = 100$ days, whereas emulsion-case plots begin at $t_p = 0$ to show initial seal formation.

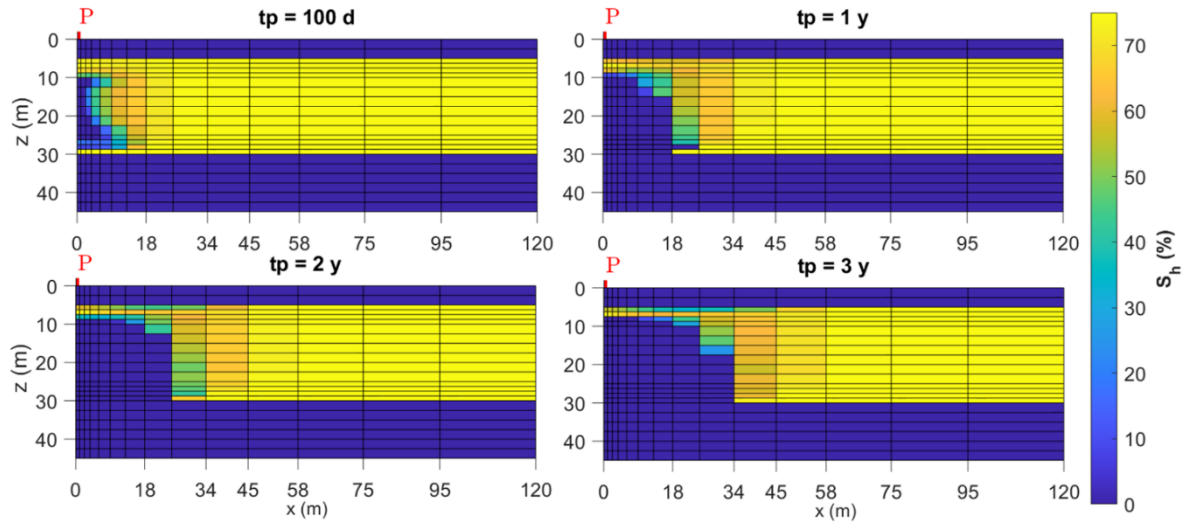


Figure 6.7 Spatiotemporal evolution of stationary hydrate saturation (S_h) for the Base_75 scenario.

The S_h profiles (**Figure 6.7**) confirm that the dissociation front is strongly confined; in this unsealed setting ($S_h = S_{MH}$) the front exhibits only limited radial advance and remains concentrated near the wellbore because the effective pressure gradient decays quickly (see pressure evolution in **Figure 6.8**).

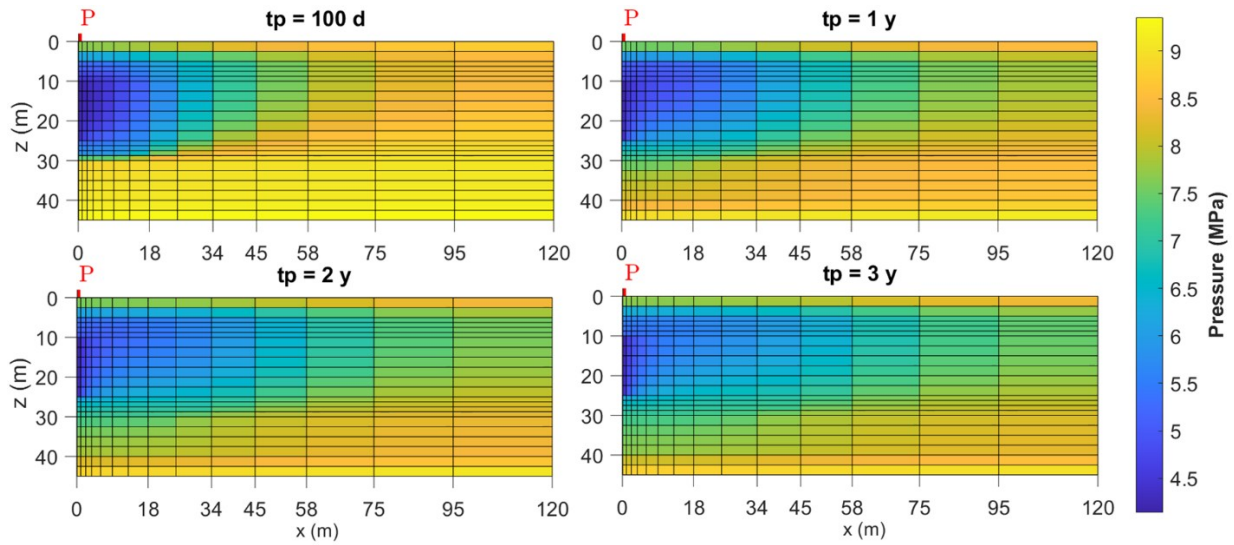


Figure 6.8 Spatiotemporal evolution of reservoir pressure for the Base_75 scenario.

Pressure profiles (**Figure 6.8**) directly support this interpretation: although the drawdown region grows rapidly during the first ~100 days, it is soon diluted by inflow of high-pressure aquifer fluid, indicating hydraulic recharge. Temperature fields (**Figure 6.9**) further corroborate the mechanism and reveal two notable thermal signatures.

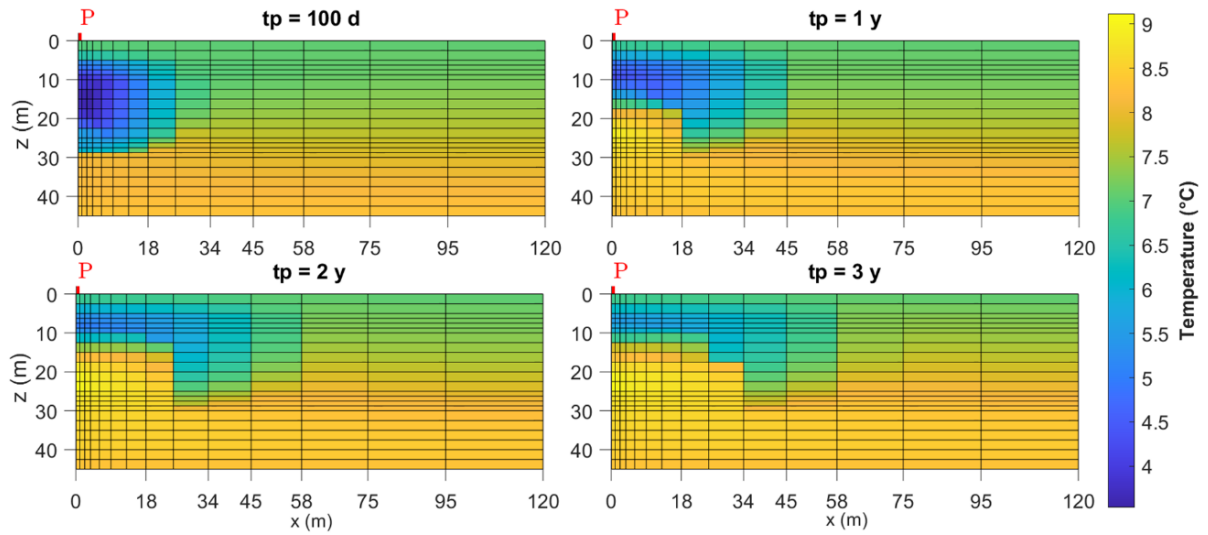


Figure 6.9 Spatiotemporal evolution of reservoir temperature for the Base_75 scenario.

First, warmer aquifer water induces bottom-up dissociation at the MHBL base, which promotes pressure-front propagation into the aquifer and produces the characteristic bottom-up dissociation pattern visible in **Figure 6.7** after one year. Second, a localized temperature increase appears immediately around the wellbore, attributed to Joule–Thomson heating associated with water entering the lower-pressure zone (consistent with water’s negative Joule–Thomson coefficient). These thermal patterns reduce the thermodynamic drive for MH dissociation in the MHBL, strengthen hydraulic recharge, and explain the high-water production and restricted radial progression of the dissociation front. The near-wellbore thermal distribution result is consistent with the findings of Sun et al. [166].

6.4.3.2.2 Mechanism evaluation of CO₂ hydrate seal stability (Base75_CE30)

Base75_CE30 aimed for hydraulic isolation but resulted in limited hydraulic performance due to the lower CO₂ fraction. **Figure 6.10** depicts this mixed behavior: the CO₂ hydrate seal formed at the base of the MHBL is spatially complex, forming locally while concurrently undergoing extensive dissolution at its outer margins.

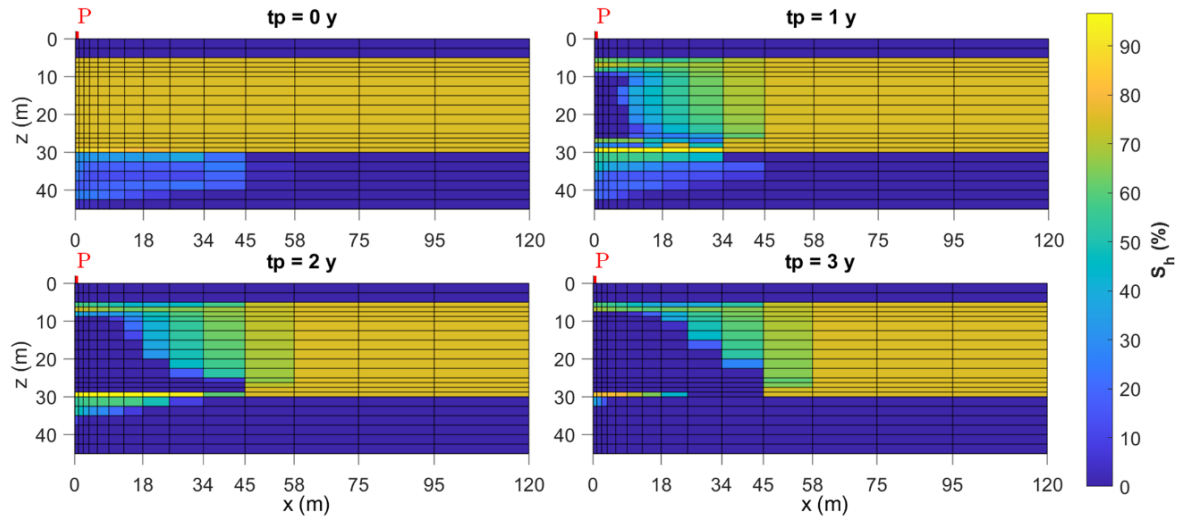


Figure 6.10 Spatiotemporal evolution of stationary hydrate saturation (S_h) for the Base75_CE30 scenario.

During the first production year ($t_p = 0$ y to $t_p = 1$ y) CO₂ hydrate saturation increases in the layer immediately below the MHBL (reaching ~50–60%) and exceeds ~90% at the very base of the MHBL. Upward migration of liquid CO₂ droplets from warmer intermediate layers encounters a cooler region sustained by endothermic MH dissociation (**Figure 6.11** at $t_p = 1$ y). The ensuing CO₂ hydrate formation is exothermic; heat released by droplet conversion into hydrate partially thermally stimulates adjacent MH dissociation while contributing to localized sealing of the MHBL.

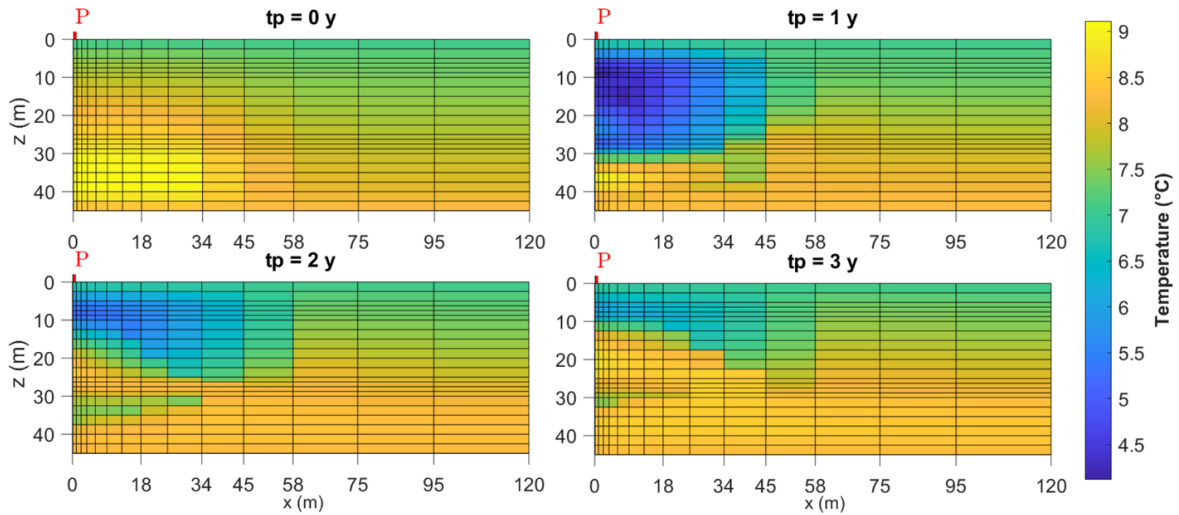


Figure 6.11 Spatiotemporal evolution of reservoir temperature for the Base75_CE30 scenario.

The principal failure mechanism, however, is lateral aquifer ingress of unsaturated seawater that dissolves hydrate at the seal perimeter (e.g., $x = 34$ m to 45 m at $t_p = 2$ y in **Figure 6.10**), causing the saturation front to retreat toward the aquifer interface (decreasing x and z). This dissolution is accompanied by localized cooling ($z = 30$ m to 40 m at $t_p = 2$ y; **Figure 6.11**),

consistent with endothermic CO₂ hydrate decomposition. Progressive, advection-driven dissolution degrades the CO₂ hydrate seal and eventually re-establishes hydraulic connectivity with the aquifer (pressure breach seen in **Figure 6.12**).

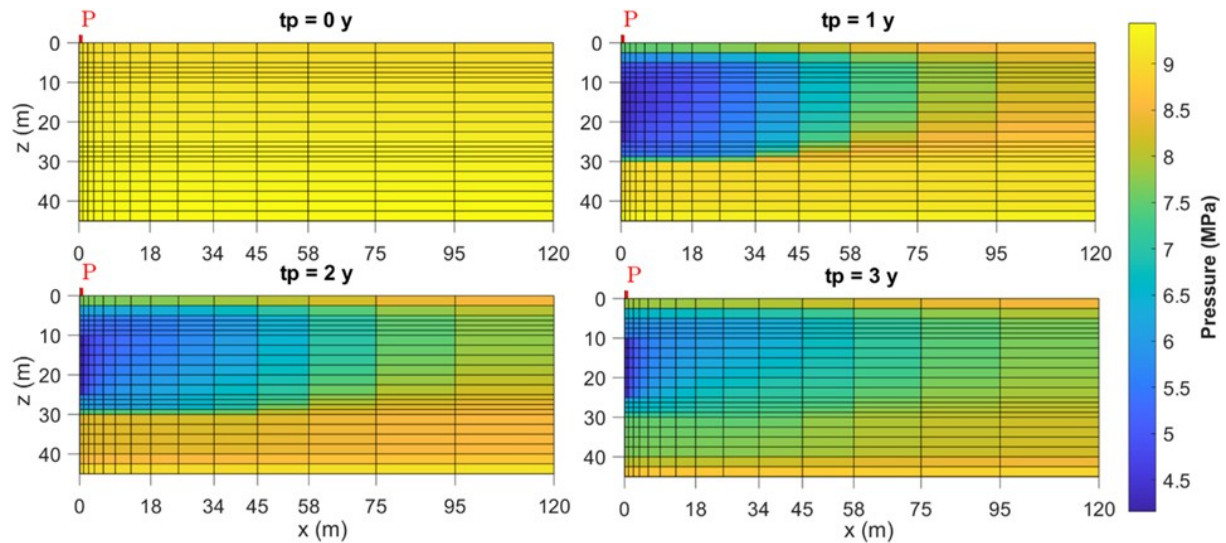


Figure 6.12 Spatiotemporal evolution of reservoir pressure for the Base75_CE30 scenario.

The hydraulic compromise is clearly reflected in the production dynamics shown in **Figure 6.4**. Following the weakening and dissolution of the CO₂ hydrate layers, Q_w for the Base75_CE30 case rises sharply during the second half of the simulation (**Figure 6.4b**). This high instantaneous water rate is a consistent physical response to the seal's earlier effectiveness. By maintaining isolation for the first two years, the Base75_CE30 case achieves a larger dissociation radius and deeper pressure drawdown than the Base75 case. Once the seal breaches, aquifer influx intensifies as it fills the expanded, low-pressure pore volume created by the enhanced methane recovery.

In contrast, Q_g drops significantly after a plateau between 0.9 and 1.5 years, falling below Base75 rates by 2.8 years (**Figure 6.4a**). This decline occurs because the breached seal prevents wellbore pressure drawdown from reaching distant regions of the methane hydrate bearing layer (MHBL), which limits further dissociation. A minor increase in Q_g between 2.8 and 3 years is linked to the influx of high-temperature water from the underburden (UB) into the dissociated MHBL (**Figure 6.11**). This thermal influx triggers late-stage dissociation and increases gas saturation (**Figure 6.13**).

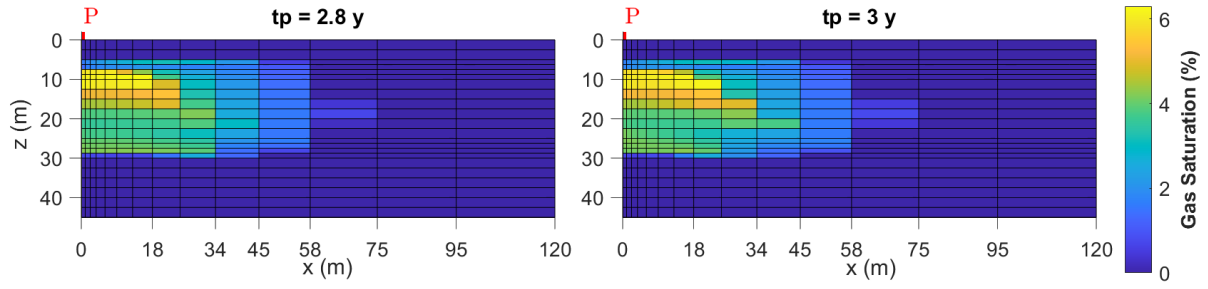


Figure 6.13 Spatiotemporal evolution of gas saturation for Base75_CE30. The results highlight secondary dissociation near the end of the production period, driven by high-temperature water influx from the UB.

Despite the seal instability, Base75_CE30 effectively expanded the dissociation front and reduced cumulative water production over the three-year period compared to the base case.

6.4.3.2.3 Mechanism evaluation of CO₂ hydrate seal stability (Base75_CE50)

Base75_CE50 yields the best long-term trade-off between recovery and water control (**Table 6.3**) because it forms a wider and more persistent CO₂ hydrate seal (**Figure 6.14**).

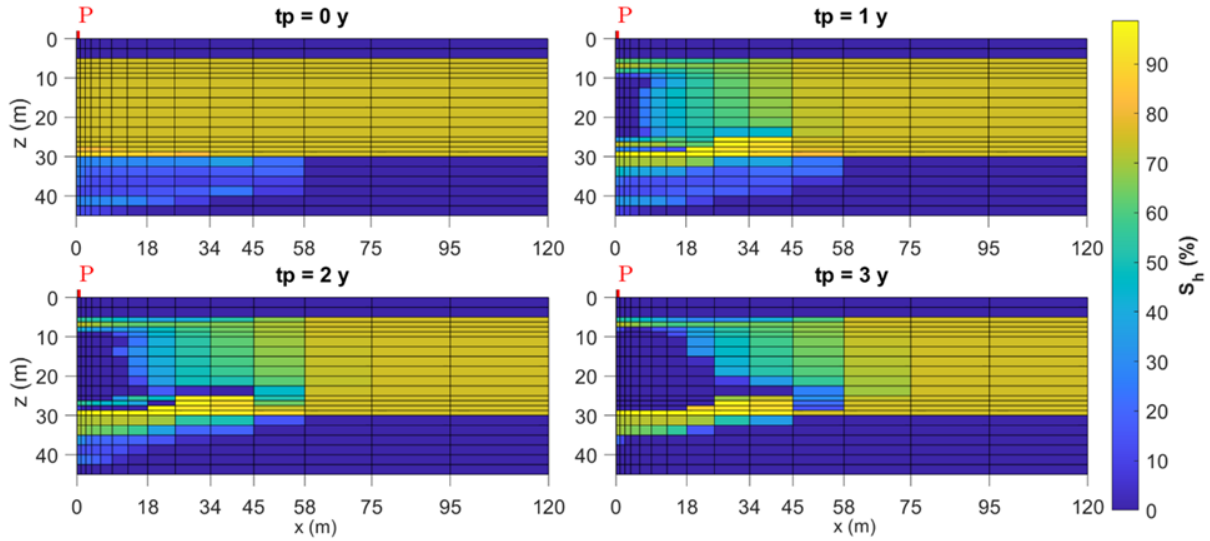


Figure 6.14 Spatiotemporal evolution of stationary hydrate saturation (S_h) for the Base75_CE50 scenario.

S_h profiles for Base75_CE50 (**Figure 6.14**) show a seal whose lateral and vertical extent greatly exceed those in Base75_CE30, a difference driven by the larger injected CO₂ mass (**Figure 6.15**).

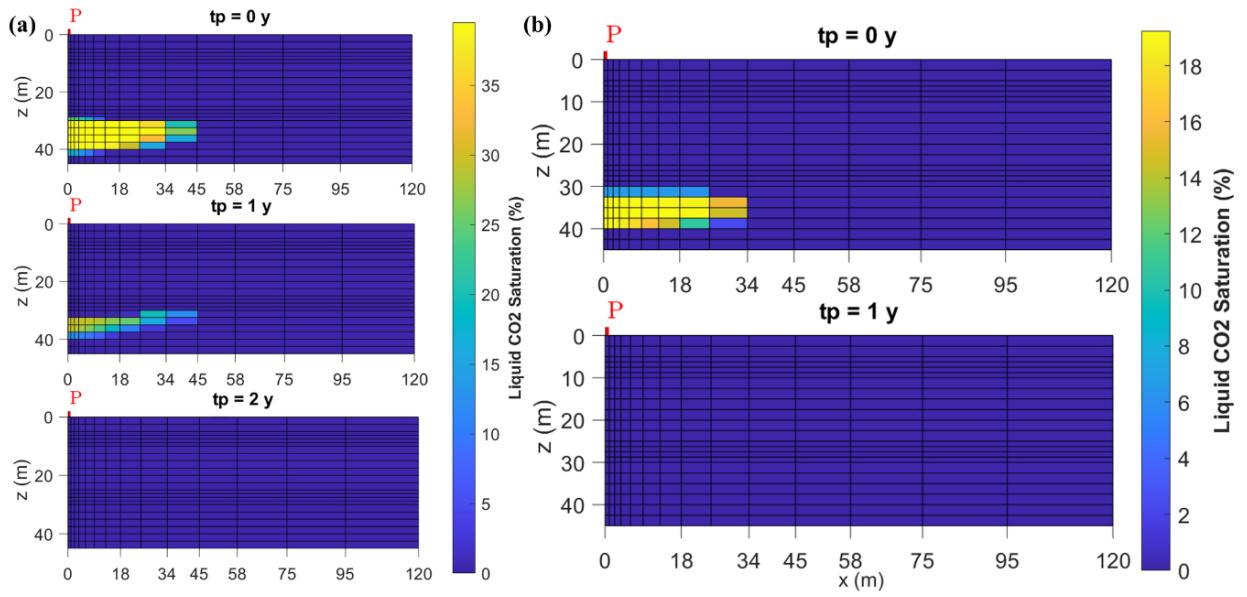


Figure 6.15 Spatiotemporal evolution of liquid CO₂ droplets for: (a) Base75_CE50 and (b) Base75_CE30.

The greater sealing length primarily explains why Base75_CE50 outperforms Base75_CE30, in agreement with prior studies that identify sealing length as a dominant control on cumulative gas production [45]. Although peripheral dissolution is observed, a substantial, high-saturation bulk seal endures through the three-year production period. Abundant liquid CO₂ droplets (**Figure 6.15**) support formation of a dense CO₂ hydrate layer beneath the MHL by $t_p = 1$ y, promoted locally by endothermic cooling from MH dissociation and conductive heat transfer (**Figure 6.16**). The outer lateral edges of the seal ($x = 45$ m to 58 m) begin to show significant dissolution only by $t_p = 3$ y, driven by persistent aquifer inflow.

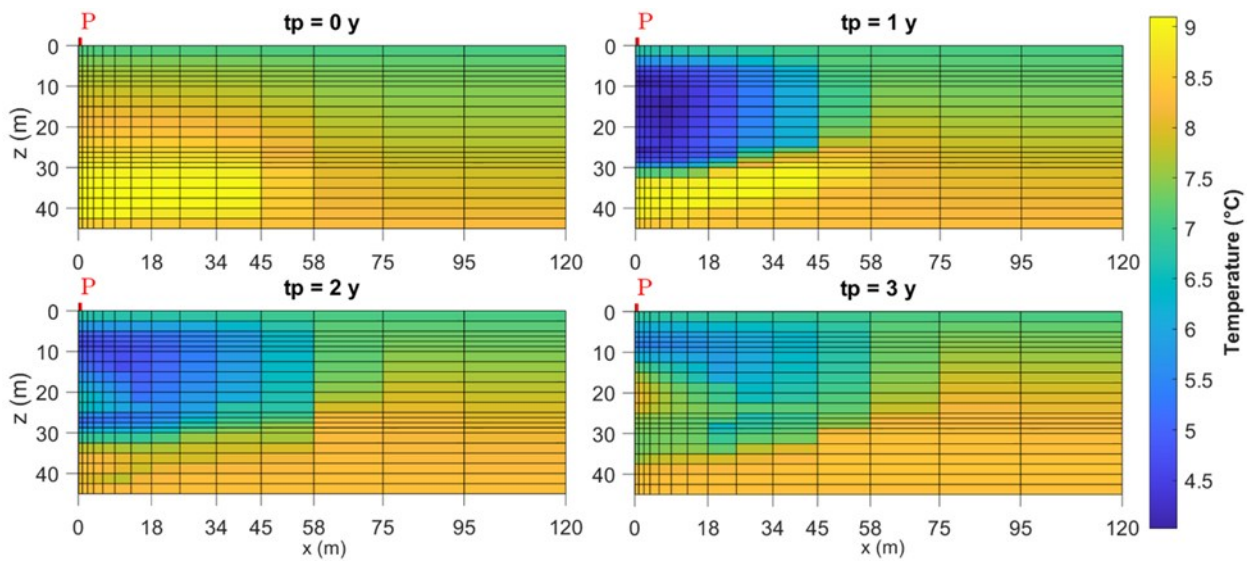


Figure 6.16 Spatiotemporal evolution of reservoir temperature for the Base75_CE50 scenario.

The outward propagating cold thermal front enhances the rate of liquid CO₂ droplets conversion into CO₂ hydrate particles, resulting in rapid agglomeration and subsequent pore-throat bridging up to $t_p = 1$ y (**Figure 6.14** and **Figure 6.16**). This process produces a sharp increase in S_h that extends vertically and laterally into the lower regions of MHBL (locally > 90%) and into adjacent aquifer layers (locally > 70%), leading to cementation that strongly isolates the MHBL's hydraulic connectivity to underlying aquifer. The resulting hydraulic isolation confines pressure drawdown to the MHBL (**Figure 6.17**) and thereby driving the MH dissociation front forward. This localized hydrate cementation and associated CH₄ trapping are consistent with experimental observations by Sun et al. [61], who reported formation of CO₂–CH₄ double hydrates from unreacted CO₂ droplets at high injected CO₂ fractions; such double hydrates mechanically stabilized sands and trapped CH₄, which explains the lower initial gas production for Base75_CE50 compared with Base75_CE30 during the first 1.3 years (**Figure 6.4a**).

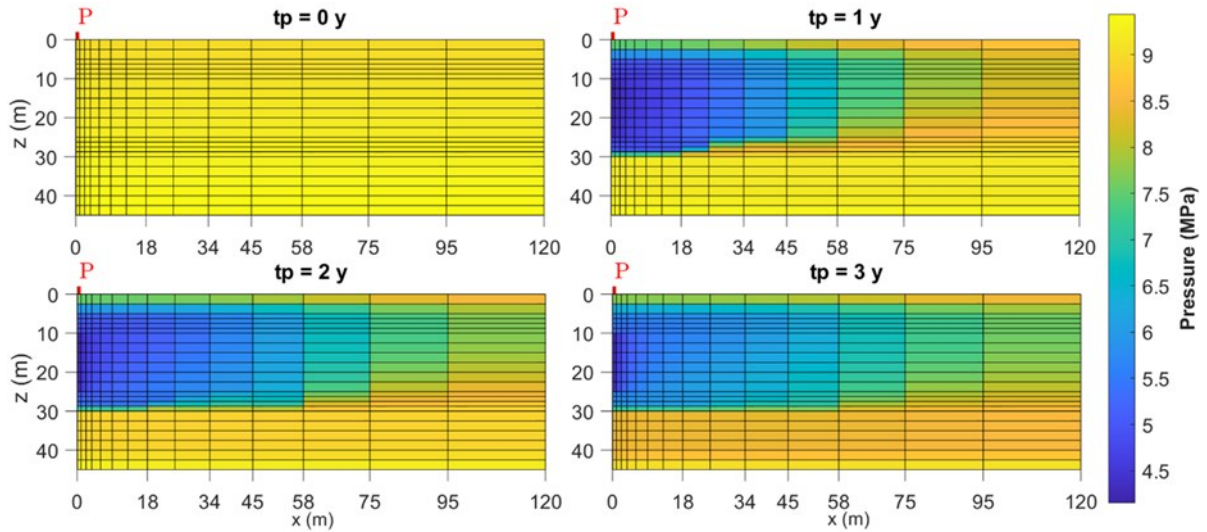


Figure 6.17 Spatiotemporal evolution of reservoir pressure for the Base75_CE30 scenario.

Pressure fields for Base75_CE50 (**Figure 6.17**) confirm the seal's success: a strong hydraulic gradient between MHBL and aquifer is maintained throughout production, with drawdown confined to the MHBL and the aquifer pressure field ($z > 30$ m) remaining largely unchanged between initial and final states. This persistent, highly localized pressure sink is essential for sustained dissociation and contrasts sharply with the Base75_CE30 case (**Figure 6.12**), where the drawdown zone is overcome and the aquifer pressure re-establishes by $t_p = 3$ y, producing pressure profiles similar to the unsealed Base_75 and limiting performance.

Figure 6.18 presents dissolved CO₂ volume fraction evolution in the aqueous phase for Base75_CE50. At $t_p = 0$ the dissolved CO₂ front extends substantially farther than both the solid CO₂ hydrate front (**Figure 6.14**) and the liquid CO₂ droplet front (**Figure 6.15a**).

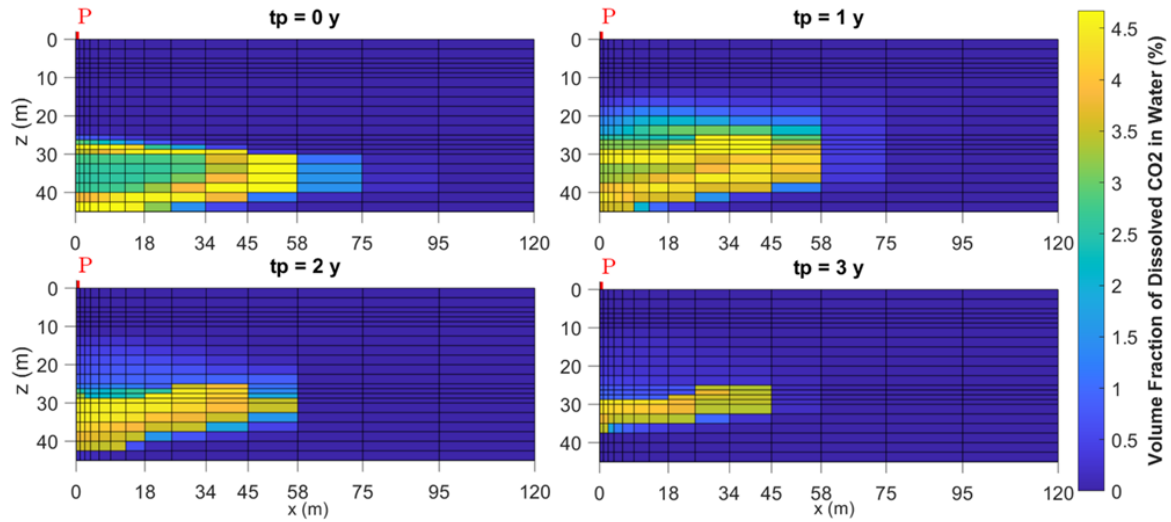


Figure 6.18 Spatiotemporal evolution of volume fraction of dissolved CO₂ for the Base75_CE50 scenario.

The more rapid and wider spread of dissolved CO₂ is attributable to the enhanced interfacial area for dissolution created by dispersing liquid CO₂ droplets within the aqueous phase. Because this study does not model replacement of CO₂ by CH₄, the reported methane recovery and the effectiveness of seal formation at the MHBL base may be conservative.

6.4.4 Case 2

Case 2 investigates production behavior when the MHBL has a lower initial methane hydrate saturation of 50%. The reference run (Base_50) represents depressurization without C/W emulsion injection, and its response is compared with the optimal emulsion configuration identified in Case 1—namely, injection of a C/W emulsion containing 50% liquid CO₂ by volume (Base50_CE50). Both scenarios are simulated over a three-year production window to assess how reducing the initial hydrate saturation influences seal performance and overall recovery.

Figure 6.19 presents the gas (Q_g) and water (Q_w) production rates at standard conditions for the two Case 2 scenarios. At the start of production, the emulsion case outperforms Base_50, showing higher Q_g and suppressed Q_w . However, this advantage persists only until approximately $t_p \sim 2.3$ years, after which the CO₂ hydrate seal fails.

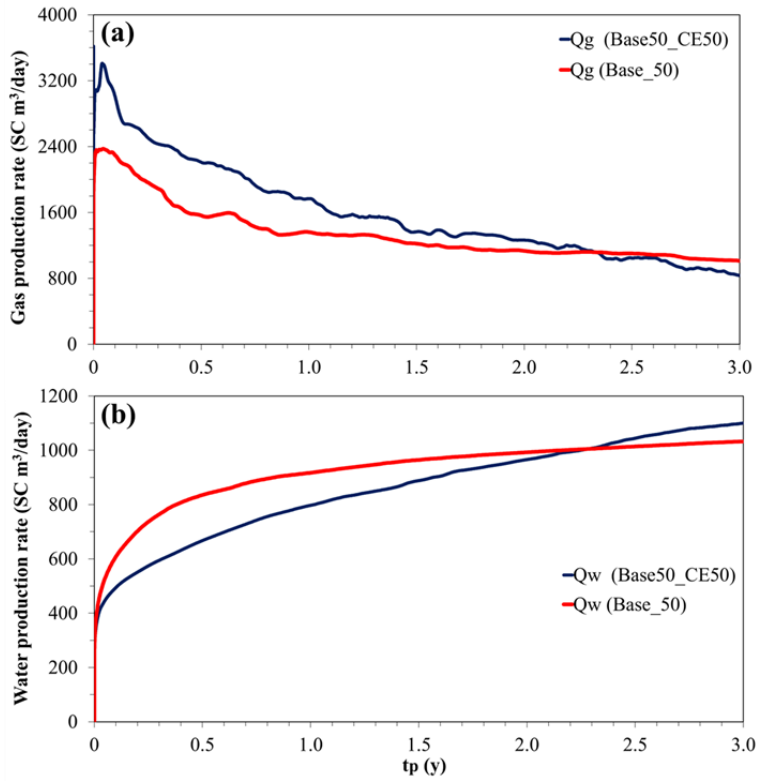


Figure 6.19 Time evolution over the 3-year production period of (a) gas production rate (Q_g) and (b) water production rate (Q_w) for Base_50, and Base50_CE50.

Once failure occurs, the production response reverses—a trend analogous to the Base75_CE30 behavior seen earlier. Following seal breach, Q_g drops below the Base_50 trajectory, while Q_w sharply increases. This deterioration in performance arises because the dissociation front in Base50_CE50 has expanded farther laterally than in Base_50 by the time the seal collapses. As a result, the compromised seal no longer sustains a localized pressure drawdown; the wellbore cannot effectively transmit depressurization into the more distant, still-MH-rich regions of the MHBL. At the same time, the increased open-contact area between the MHBL and aquifer enables vigorous aquifer inflow, causing the pronounced rise in Q_w and accelerating the decline in Q_g .

Figure 6.20 shows the evolution of hydrate saturation for the depressurization-only Base_50 case (where $S_h = S_{MH}$). Relative to the Base_75 scenario (**Figure 6.7**), the lower initial hydrate content in Base_50 allows the dissociation front to advance more deeply into the MHBL. This enhanced front progression explains the consistently higher Q_g values, since lower hydrate saturation corresponds to greater initial effective permeability and a more efficient transmission of pressure gradients into the reservoir.

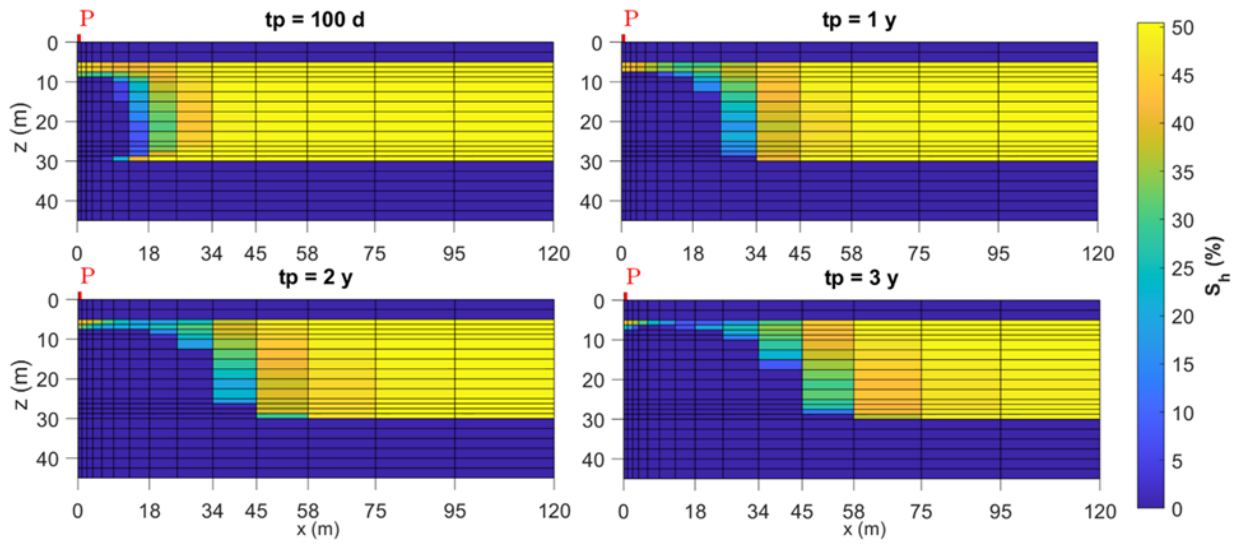


Figure 6.20 Spatiotemporal evolution of stationary hydrate saturation (S_h) for the Base_50 scenario.

The spatial distribution of S_h for the Base50_CE50 emulsion case is shown in **Figure 6.21**. In contrast to the behavior observed in Base75_CE50 (**Figure 6.14**), the reduced initial S_{MH} (50%) enhances native permeability within the MHL. This greater permeability permits both liquid CO₂ droplets and newly formed CO₂ hydrates to penetrate into multiple MHL layers adjacent to the injection well, instead of remaining concentrated at the base of the MHL and in the uppermost layer of the aquifer.

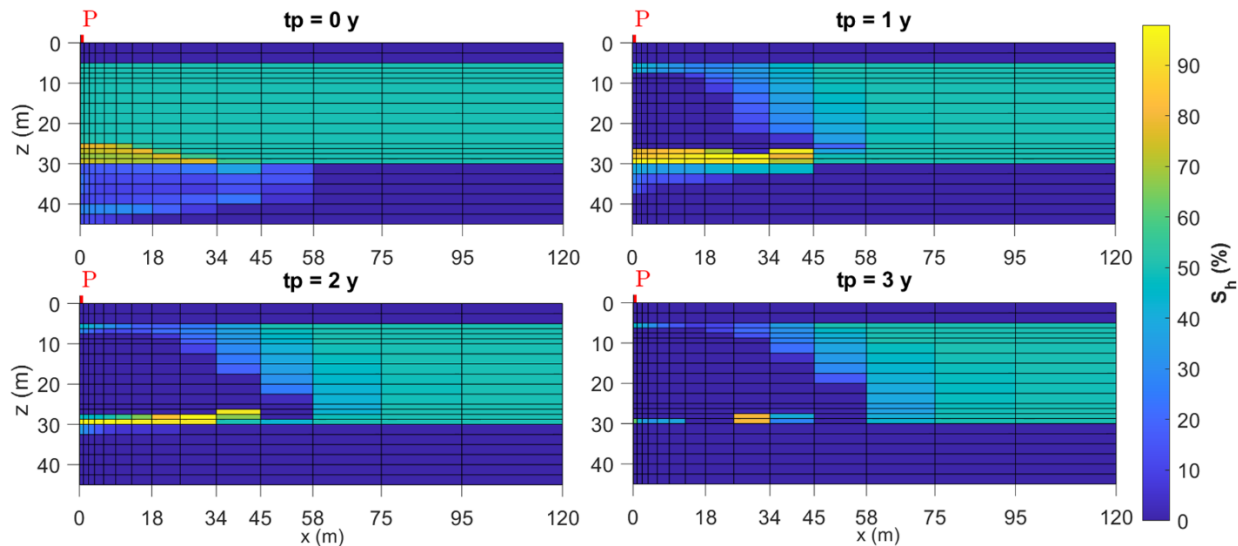


Figure 6.21 Spatiotemporal evolution of stationary hydrate saturation (S_h) for the Base50_50 scenario.

Because the resulting CO₂ hydrate seal beneath the MHL near the wellbore attains relatively low saturation, its structural integrity weakens quickly. While the dissociation front expands outward more rapidly than in Base75_CE50—reaching a larger lateral extent by $t_p = 2$ years—the seal simultaneously thins and breaks down both laterally and vertically. Once the

underlying seal largely disappears (apart from sparse, isolated hydrate cells), the dissociation front halts its lateral advance. From this point forward, only limited bottom-up dissociation occurs, driven by warmed aquifer inflow from below. This stagnation in front progression directly corresponds to the performance reversal in **Figure 6.19**.

Table 6.4 summarizes the performance metrics for Case 2 and highlights how quickly the benefits of C/W emulsion injection deteriorate once the seal fails between $t_p = 2$ and 3 years.

Table 6.4 Summary of final performance indicators for Case 2 C/W emulsion injection.

	G_{cum} (SC m ³)	W_{cum} (SC m ³)	GWR (SC m ³ CH ₄ /SC m ³ H ₂ O)	Rf (%)	G_{cum} improvement (%)	W_{cum} reduction (%)
Base_50	1468517	1010940	1.45	13.83	-	-
Base50_CE50	1744144	939851	1.86	16.43	$t_p = 2$ y: 26.89	$t_p = 2$ y: 12.55
					$t_p = 3$ y: 18.80	$t_p = 3$ y: 7.03

Table 6.4 quantifies the rapid loss of efficiency following the seal breach near $t_p = 2.3$ years. Although Base50_CE50 still yields a net benefit over the entire three-year period, the advantage erodes quickly: G_{cum} improvement drops from 26.89% at $t_p = 2$ years to only 18.80% at $t_p = 3$ years, and the water-reduction benefit falls from 12.55% to 7.03%. This sharp decline demonstrates that low initial MH saturation leads to a mechanically weaker CO₂ hydrate seal that cannot sustain hydraulic isolation over long timescales, even if early-time performance is favorable.

6.4.5 CO₂ fate investigation

Temporal partitioning of injected CO₂ mass is a key metric for assessing both storage potential and environmental performance. **Figure 6.22** displays the cumulative mass distribution among dissolution-based CO₂ storage (DBCS), hydrate-based CO₂ storage (HBCS), liquid-based CO₂ storage (LBCS) in the form of dispersed CO₂ droplets, CO₂ crossing boundaries (CCB), and produced CO₂ (PrC) for Base75_CE30 and Base75_CE50. Across all scenarios, CCB was minimal and assumed to re-enter the simulation domain during production.

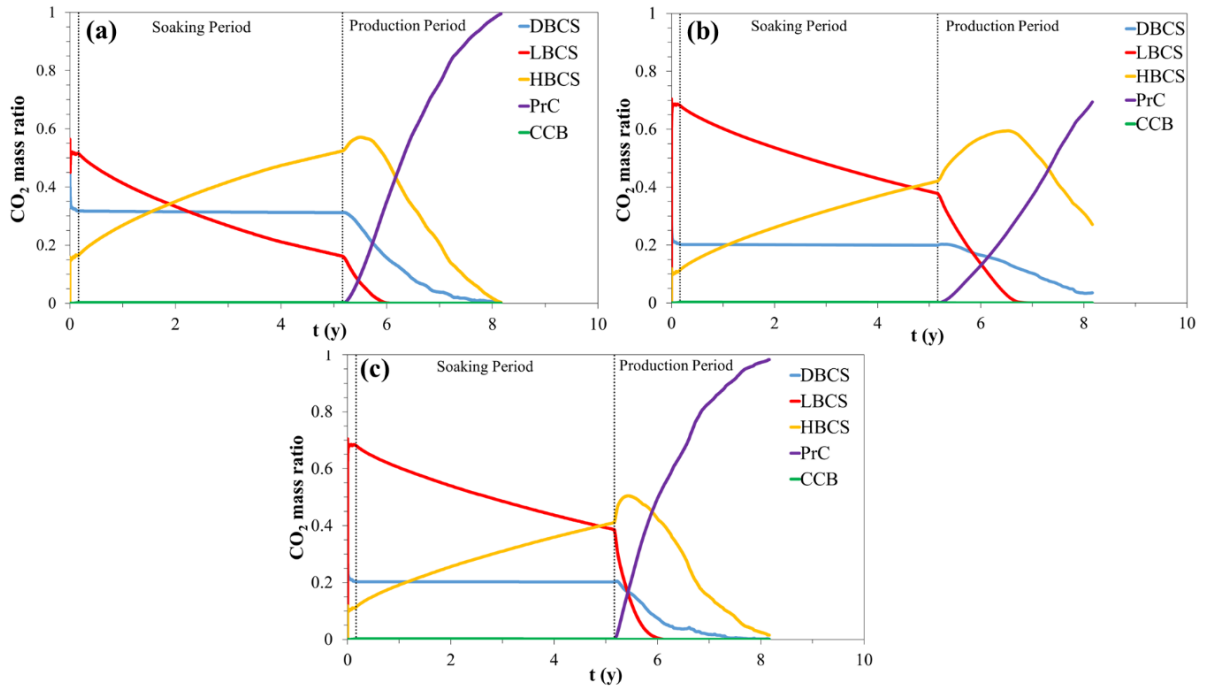


Figure 6.22 CO₂ mass partitioning over time for: (a) Base75_CE30, (b) Base75_CE50, and (c) Base50_CE50.

Mass-conversion dynamics follow a two-stage pattern. During soaking, injected liquid droplets convert into CO₂ hydrate particles that become embedded within the sand matrix (**Figure 6.23**); however, the conversion rate slows with time, indicating diminishing returns for extending the soak. This slowdown arises from decay of the initial thermal gradient as heat released by exothermic hydrate formation diffuses into surrounding media (**Figure 6.6**).

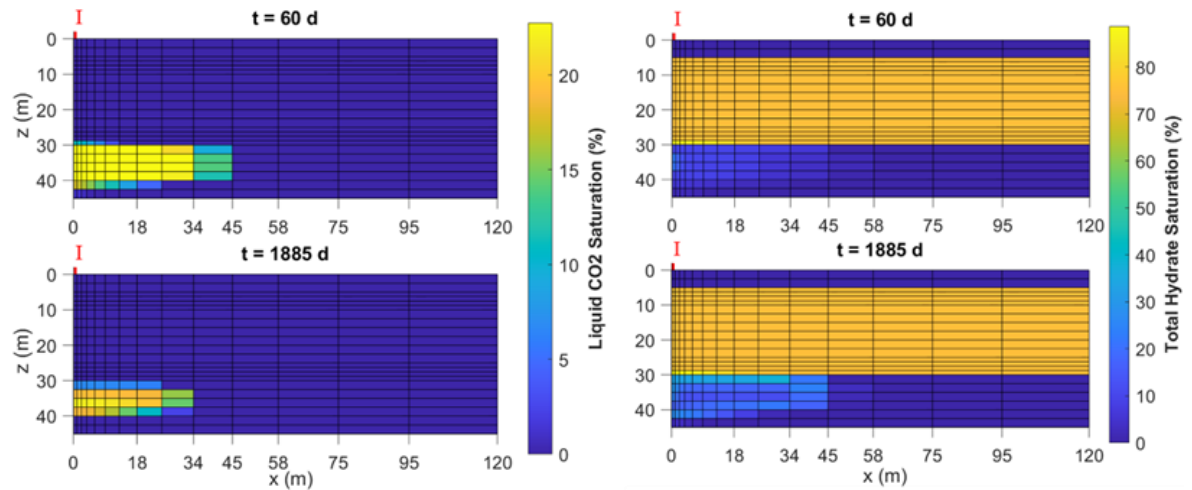


Figure 6.23 Conversion of CO₂ phases during soaking (Base75_CE30). Comparison of liquid CO₂ saturation (left) decay and resultant total hydrate saturation (right) growth from the end of injection ($t = 60$ d) to the end of soaking ($t = 1885$ d).

In contrast, HBCS rises sharply at production onset because CO₂ droplets encounter cooler zones produced by endothermic MH dissociation; this heat transfer to the colder environment

promotes fast hydrate formation. Subsequently, HBCS declines as seawater infiltration dissolves CO₂ hydrates. DBCS remains nearly steady through soaking but decreases during production. Produced brine never reaches CO₂ saturation under standard conditions in these simulations, which implies the produced gas is not contaminated by dissolved CO₂. **Table 6.5** summarizes the final mass partitioning for all scenarios.

Table 6.5 CO₂ mass partitioning at the end of simulation.

	Injected CO ₂ mass (t)	DBCS (%)	HBCS (%)	LBCS (%)	CCB (%)	PrC (%)
Base75_CE30	1684.565	0.17	0.3	0	0	99.53
Base75_CE50	2811.152	3.50	27.08	0	0	69.42
Base50_CE50	2811.152	0.11	1.56	0	0	98.33

the Base75_CE30 and Base50_CE50 scenarios result in the recovery of nearly all injected CO₂, with PrC of 99.53% and 98.33%, respectively. In contrast, the Base75_CE50 scenario retains 30.58% of the injected CO₂ mass within the reservoir through HBCS and DBCS sequestration. These results suggest that combining a higher-concentration emulsion with higher initial methane hydrate saturation can significantly enhance long-term CO₂ retention during the production phase.

6.4.6 Influence of soaking time on sealing efficiency

The 5-year soaking period (S5y) was initially intended to facilitate the conduction of exothermic heat from CO₂ hydrate synthesis into the MHL. However, transient data (**Figure 6.4a** and **Figure 6.5**) show that this thermal effect is short-lived. The observation that hydrate conversion slows during soaking but accelerates once production begins suggests that shorter resting intervals may offer better operational efficiency. To test this, a sensitivity analysis was performed using a 6-month soak (S6m) for the Base75_CE50 and Base50_CE50 cases. This section examines if hydrate formation triggered by production can successfully maintain seal integrity and optimize recovery.

Figure 6.24 demonstrates that while the shorter soak period effectively manages water production for both initial MH saturation levels, gas production for the Base75_CE50_S6m case initially lags behind the S5y baseline for two years before reaching a stable, high-production plateau in the final year.

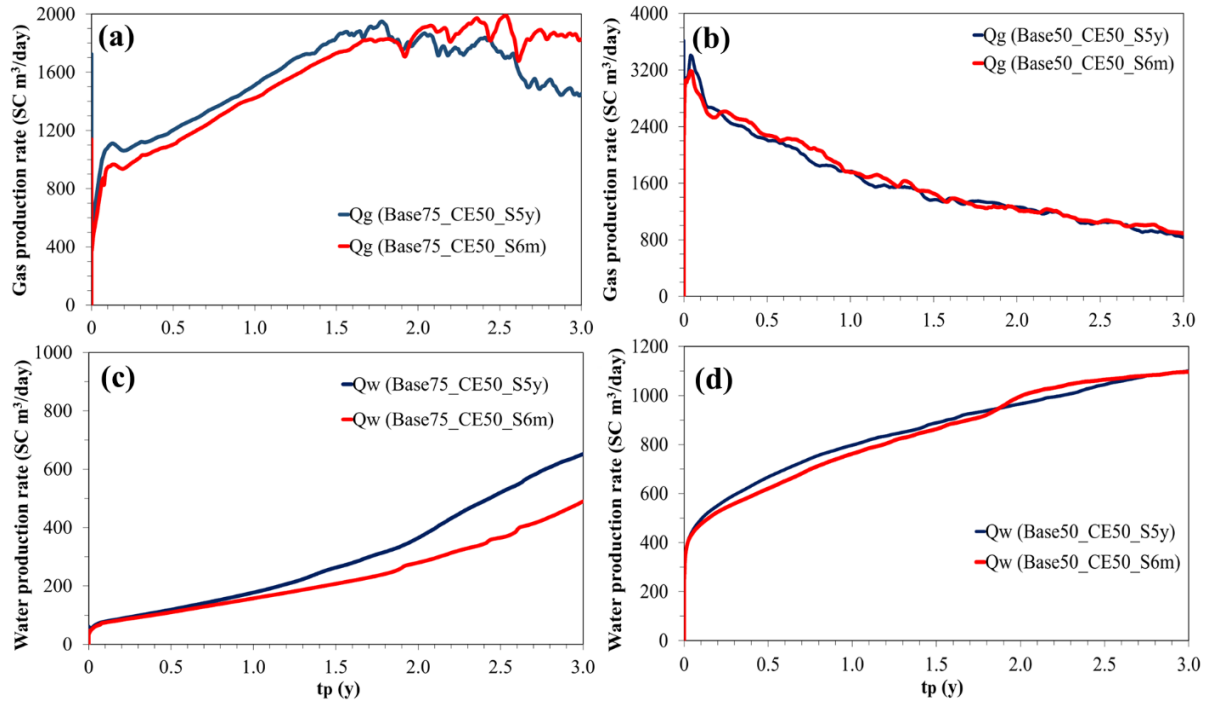


Figure 6.24 Impact of soaking duration on production performance across different initial MH saturations: (a, b) gas production rate (Q_g) and (c, d) water production rate (Q_w) for Base75_CE50 and Base50_CE50 scenarios, respectively.

The early suppression of gas flow seen in **Figure 6.24a** results from unreacted liquid CO_2 droplets entering the lower grid layers of the MHL, where it forms high-saturation ($> 90\%$) composite $\text{CO}_2\text{-CH}_4$ hydrates. This composite zone functions as a pressure barrier, shielding the MH in these layers from the production drawdown. Eventually, as unreacted CO_2 migrates to a radial distance of 58 m (**Figure 6.25**), this expanded seal supports the high production plateau reached during the last year of the simulation.

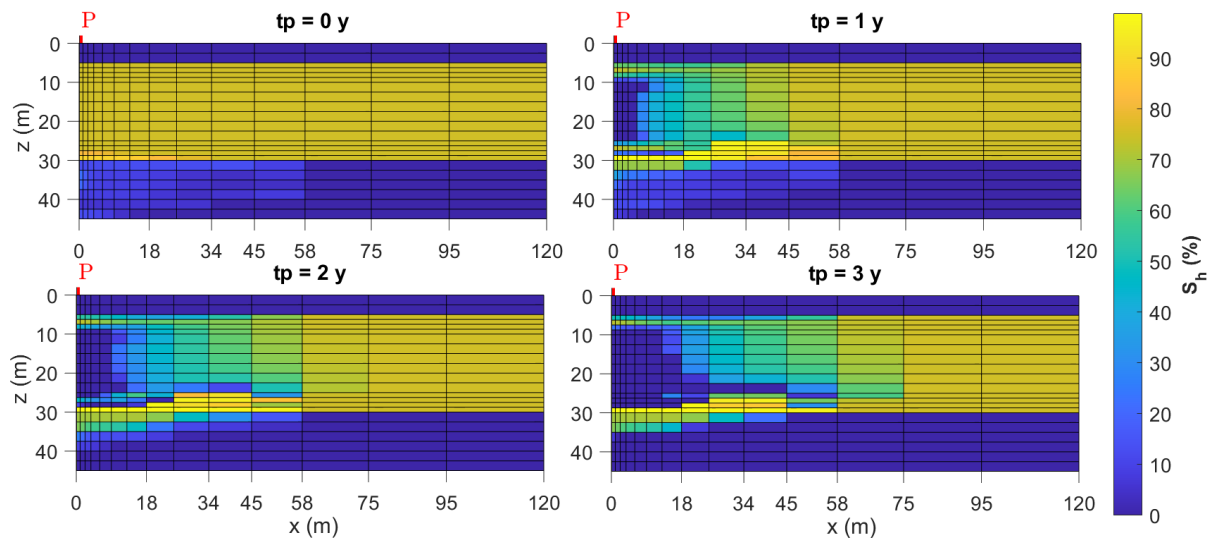


Figure 6.25 Spatiotemporal evolution of stationary hydrate saturation (S_h) for the Base75_CE50_S6m scenario.

In the Base50_CE50_S6m case, the 6-month soak results in a seal that extends further radially than the 5-year version. However, when this transient seal finally breaks down after 2 years of production (Figure 6.26), the pressure gradient between the aquifer and the low-pressure zone is more pronounced than in the S5y case. This causes a brief but more intense influx of aquifer water immediately after the seal fails.

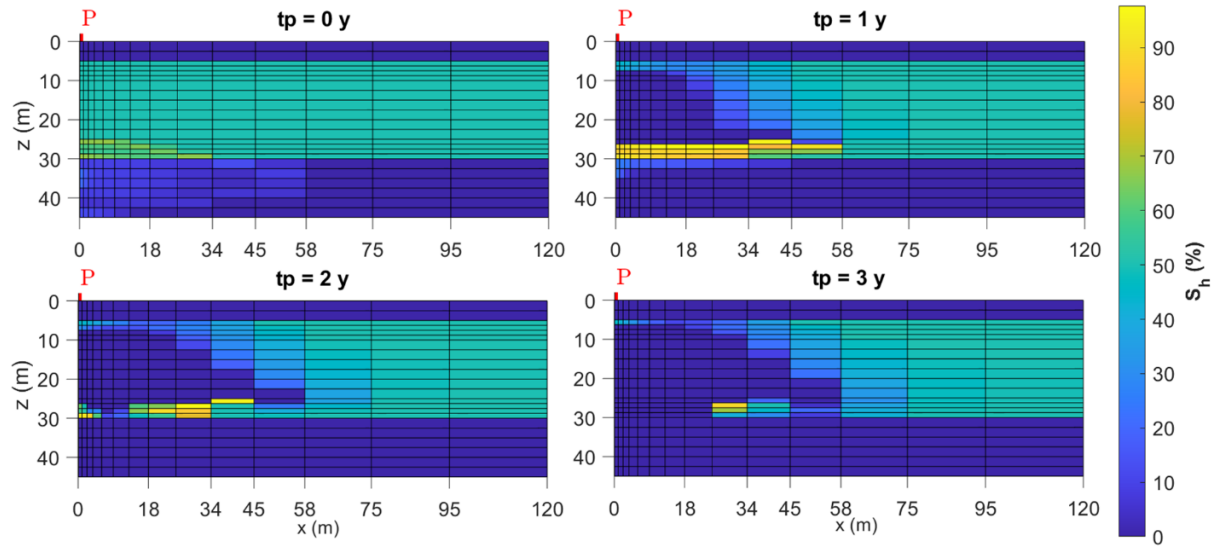


Figure 6.26 Spatiotemporal evolution of stationary hydrate saturation (S_h) for the Base50_CE50_S6m scenario.

The performance improvements of the S6m cases compared to the S5y baseline are summarized in Table 6.6. The results confirm that reduced soaking durations enhance key metrics, such as increasing gas recovery and decreasing water production. This improvement is driven by production-induced hydrate formation, which encourages liquid CO₂ droplets to move into the cooler MHBL and form dense (> 90%) composite hydrate barriers. Total CO₂ storage for Base75_CE50_S6m was 33.59%, with a 29.17% contribution from HBCS.

Table 6.6 Performance and efficiency indicator changes for S6m scenarios relative to S5y baselines.

	G_{cum} improvement (%)	W_{cum} reduction (%)	PrC changes (%)
Base75_CE50_S6m	0.69	22.93	−4.34
Base50_CE50_S6m	2.12	1.37	0.2

Relative to non-emulsion baselines, the observed production enhancements led to cumulative gas increases of 58.93% and 21.29%, and water reductions of 60.70% and 8.31% for the Base75_CE50_S6m and Base50_CE50_S6m cases, respectively. Comparing saturation profiles (Figure 6.25 and Figure 6.26 vs. Figure 6.14 and Figure 6.19) indicates that the radial extension of the seal—specifically the growth of high-saturation composite hydrates—is more

vital for performance than the thickness of the CO₂ hydrate seal in the aquifer, which degrades more rapidly in shorter soak scenarios.

6.5 Strategic implications for cyclic huff-and-puff operations

The dissolution of the CO₂ hydrate seal in the aquifer, especially during shorter soaking intervals, allows for the swift recovery of permeability near the injection well. This behavior indicates a specific operational opportunity for a closed-loop huff-and-puff approach. By mixing produced seawater with liquid CO₂ for extended re-injection phases, operators could target regions further from the wellbore as the MH dissociation front recedes. Specifically, if a high-saturation (exceeding 90%) composite seal is established during the first cycle, the near-wellbore MH zone eventually dissociates. This allows unreacted liquid CO₂ injected in the second "huff" to remain in thermal equilibrium rather than being immediately produced during the following "puff." Consequently, the CO₂ can bypass the initial impermeable layer and advance toward the retreating MH front to establish secondary composite seals. This method enables the selective reinforcement of local barriers and the radial expansion of the dissolved CO₂ front within the aquifer.

Such a strategy effectively manages seal failures at the lateral boundaries caused by aquifer encroachment while increasing the radial reach of the composite seal through successive cycles. Ultimately, this approach could maintain the isolation of the MHBL from the aquifer, ensuring high gas recovery and low water production while achieving CO₂ storage efficiency near 100%.

However, the long-term success of cyclic operations may be constrained by the receding MH front. As noted by Sridhara et al. [60], gas production peaks typically diminish because the pressure gradient weakens as the dissociation front moves away from the wellbore. This increased distance results in higher flow resistance, which can impair the efficiency of later cycles. Additionally, extended injection periods designed to reach these distant zones carry the risk of near-wellbore blockage. If the C/W emulsion forms CO₂ hydrates prematurely near the well, it could result in a permanent loss of injectivity, preventing the emulsion from reaching and strengthening the receding seal.

6.6 Conclusion

This research utilized numerical simulations to evaluate the injection of C/W emulsions into the aquifer beneath Class 2 methane hydrate reservoirs as a method for establishing a stable, in-situ CO₂ hydrate seal. Grid-convergence analysis and dissolved CO₂ comparisons with theoretical solubility confirm numerical stability and validate the modeling approximations used for CO₂ phase behavior. The coupled thermo-hydro-chemical model, developed using a simplified representation of the Mallik Upper Zone, provided results that qualitatively confirm the behaviors reported in previous experimental and numerical literature. These findings demonstrate that C/W emulsion injection creates a robust hydraulic barrier against aquifer encroachment, effectively focusing the pressure drawdown within the MHL.

The analysis of operational parameters revealed that during a 5-year soaking period, the conversion rate of liquid CO₂ droplets into hydrate particles decreases over time, and the associated thermal benefits dissipate quickly once production begins. This indicates that extremely long soaking durations may offer diminishing returns. In contrast, the start of production was found to accelerate the conversion process. A shorter 6-month soaking period proved more effective, as it allowed a larger volume of unreacted CO₂ to migrate and radially expand the composite CO₂-CH₄ seal, thereby enhancing overall reservoir performance.

The optimal scenario (50% CO₂ fraction, 75% initial MH saturation, and 6-month soak) achieved a 58.93% increase in gas recovery and a 60.70% reduction in water production, confirming seal durability over three years. However, stability proved highly sensitive to CO₂ fraction and MH saturation, with lower values leading to premature failure via advection-driven dissolution triggered by aquifer brine flow.

This configuration sequestered 33.59% of injected CO₂ through hydrate-based carbon storage without contaminating the produced methane. The observed failure dynamics suggest that a closed-loop, cyclic huff-and-puff strategy—incorporating produced-water re-emulsification—could achieve nearly 100% storage effectiveness. Such an approach maximizes the artificial barrier's reach and stability by facilitating the radial expansion of both the hydrate seal and the dissolved CO₂ front.

Chapter 7

Conclusion

This thesis addressed one of the fundamental obstacles in the commercial development of Class 2 methane hydrate (MH) deposits, namely excessive water production and strong pressure recharge from the underlying aquifer by numerically developing and validating a novel, dual-purpose strategy: the injection of CO₂-in-water (C/W) emulsion into the underlying aquifer of MH deposits to form a stable, in-situ CO₂ hydrate seal. Using a rigorously developed Thermo-Hydro-Chemical (T-H-C) numerical framework, which was supported by experimental validation and multi-scale simulations across Chapters 3 through 6, this work successfully met all research objectives. The results comprehensively demonstrate the technical viability, hydrate-based CO₂ storage performance, and field-scale impact of this strategy on enhanced methane recovery.

In Chapter 3, the rigorous validation process established the predictive reliability of the newly developed T-H-C model through systematic comparison with 1D core-scale experiments. The model accurately reproduced the dissolution-dominated stage of CO₂-water interaction, reflected by its ability to capture temperature evolution prior to hydrate induction using calibrated dissolution parameters ($\beta = 0.04 \text{ s}^{-1}$ and $C = 0.15$). Although hydrate formation kinetics exhibited inherent stochasticity, the model successfully reproduced the overall post-induction thermal trends using constant kinetic parameters ($\gamma = 0.012 \text{ s}^{-1} \cdot \text{MPa}^{-1}$ and $\alpha = 0.55$). Limitations were identified through the delayed prediction of flow impairment in CE20 and CE30 cases, illustrating the constraints of applying constant kinetic parameters to highly dynamic hydrate systems. A critical achievement of the validation stage was the model's successful reproduction of sustained injectivity in the CE10 experiment, demonstrating that the C/W emulsion concept remains operationally feasible at lower CO₂ volume fractions. Additionally, the model revealed clear operational advantages associated with the water-alternating-emulsion (WAE) method, which consistently outperformed continuous injection in terms of injectivity preservation. The ability of water slugs to dissolve CO₂ hydrate particles embedded in the core plug enabled WAE to maintain flow even in low-permeability cores and in samples exhibiting higher hydrate particle attachment and trapping tendencies. The successful alignment of numerical predictions with experimental data established the T-H-C framework as a reliable platform for developing and optimizing operational strategies, completing Objective 1.

In Chapter 4, the validated T-H-C numerical framework was utilized to define the operational criteria for sustained low-temperature C/W emulsion injection. The robustness of the numerical setup was confirmed through a grid convergence analysis, which demonstrated minimal error (less than 2 percent for key parameters). The modeling revealed that continuous emulsion (CE) injection faces a fundamental operational trade-off: higher CO₂ concentrations increase storage potential but simultaneously raise injectivity risk. Two physical parameters emerged as decisive in determining injectivity failure. First, the average hydrate film volume fraction (α) was found to be a key controlling factor; for high-concentration emulsions, low α values (e.g., 0.15) triggered immediate and severe pore blockage. Second, the CO₂ hydrate particle diameter (D_p) was identified as a critical design parameter, as smaller D_p values reduce attachment and plugging. This highlights the importance of controlling the initial liquid CO₂ droplet size during the injection stage; smaller droplets not only mitigate the attachment rates of hydrate particles within pore throats and bodies but, as suggested by Shindo et al. [158], also allow for higher α values.

The analysis also highlighted the crucial inhibitory role of salinity. Simulations without salt predicted rapid, pervasive hydrate formation due to stronger thermodynamic driving forces, causing premature blockage in high-CO₂ schemes. Thus, marine salinity is an important natural stabilizer for operational viability. To mitigate injectivity collapse, the WAE strategy proved extremely robust. Even the most challenging case ($\alpha = 0.15$) remained fully injectable for 1 PV when WAE was applied, confirming the unique capability of brine slugs to dissolve attached hydrate particles and temporarily restore permeability. Together, these results established the operational envelope for sustained, high-capacity C/W emulsion injection and completed the injectivity optimization component of Objective 2.

In Chapter 5 the other component of Objective 2 was investigated. After establishing operational feasibility, the framework was extended to quantify storage performance and assess long-term behavior. The analysis demonstrated strong linear scaling between the CO₂ volume fraction in the injected emulsion and the cumulative CO₂ mass successfully introduced into the formation—reaching up to 0.128 Mt CO₂ for the tested conditions. Across all scenarios, hydrate-based CO₂ storage (HBCS) consistently represented a major portion of immobilized CO₂, confirming it as a dominant and reliable trapping mechanism. The WAE strategy again showed a significant benefit beyond injectivity control: by enabling full pore-volume injection, it expanded the amount of CO₂ converted into hydrate, thereby substantially improving total

storage capacity. Long-term (100-year) post-injection simulations confirmed the security and persistence of this storage system. CO₂ retained in hydrate form (~60%) and dissolved in brine (~40%) dominated the storage structure, while less than 0.02 wt% exited the simulation domain after one century. Simulated density-driven downward migration of CO₂-enriched brine further validated the model's ability to represent long-term thermo-hydrodynamic behavior with high fidelity. A separate validation step was performed by qualitatively comparing the model with 3D reactor experiments. The framework successfully reproduced the self-trapping and flow-channeling behavior observed experimentally, which leads to improved sweep efficiency and hydrate saturations exceeding 40% locally. This agreement confirmed the physical soundness of the model and its applicability to 3D processes involving reactive flow and hydrate formation. These results collectively demonstrated the high sequestration potential, and long-term reliability of C/W-emulsion-based CO₂ storage, specifically in the solid hydrate forms.

In Chapter 6, the final objective was achieved by evaluating the field-scale application of the C/W emulsion strategy within a Class 2 MH deposit. The coupled T-H-C simulations demonstrated the twofold advantage of this technology: establishing a robust hydraulic barrier to mitigate excessive aquifer influx and providing a mechanism for significant CO₂ sequestration. For the optimal scenario (50% CO₂ emulsion, 75% initial MH saturation, and a 6-month soak), results showed a 58.93% increase in cumulative methane production and a 60.70% reduction in water production, with 33.59% of the injected CO₂ sequestered primarily via hydrate-based carbon storage (HBCS).

A critical finding of this performance assessment was the influence of the soaking period on seal expansion. While it was initially hypothesized that a 5-year soak would maximize thermal stimulation, the study revealed that the resulting exothermic heat is transient and dissipates rapidly during production. In contrast, a shorter 6-month soak proved more effective for long-term reservoir isolation. This duration allowed unreacted liquid CO₂ to migrate and radially expand the composite CO₂-CH₄ seal during the production phase, which proved more vital for sustained methane recovery than the in-situ CO₂ hydrate formation and thermal stimulation.

The analysis of seal integrity further highlighted that stability is highly sensitive to the injected CO₂ mass and native MH saturation. In cases with lower CO₂ fractions or lower initial hydrate saturations, the seal was susceptible to premature failure through advection-driven dissolution by encroaching aquifer brine. These observed failure dynamics define the operational limits of the technology and suggest that a cyclic huff-and-puff strategy, involving

the re-emulsification and reinjection of produced water, offers a promising pathway to maintain seal integrity and maximize CO₂ storage effectiveness over multiple cycles.

While this thesis establishes the feasibility of C/W emulsion injection for dual-purpose methane production enhancement and CO₂ storage, several areas warrant further investigation to refine the strategy for commercial application.

A primary recommendation for future experimental work is to isolate the fundamental dissolution parameters, β and C , from the complexities inherent to hydrate stability conditions. Because the experiments used in this study to validate our numerical model were conducted under conditions where hydrate was thermodynamically stable, the formation of an interfacial hydrate film likely hindered the dissolution rate and caused fluctuations in net heat generation. Future studies should therefore be conducted at temperatures slightly above the CO₂ hydrate equilibrium threshold to precisely measure the liquid CO₂ droplet dissolution rate and the impact of pressure on the dissolution heat without the interference of interfacial hydrate films.

Additionally, future work should incorporate fully coupled geomechanics to accurately model the complex interactions between hydrate cementation and formation stability. This includes evaluating poroelastic stress changes and how embedded CO₂ hydrate particles enhance formation strength and reduce sand production risk, as well as understanding the subsequent stress redistribution that influences the long-term integrity of the seal and potential fault reactivation. Additionally, operational optimization should focus on the development of specific huff-and-puff schedules designed to mitigate CO₂ hydrate seal dissolution and maintain enhanced methane recovery. Exploring the effectiveness of these cycles over multiple stages, particularly through the re-emulsification and reinjection of produced water, remains a vital step for maximizing total CO₂ storage and managing the produced water. Finally, the inclusion of reservoir heterogeneity, lateral connectivity, and field-scale complexity is essential for a more realistic assessment.

Overall, this thesis developed and validated a robust T-H-C numerical framework demonstrating that C/W emulsion injection into CO₂ hydrate stability zones of aquifers, whether for HBCS or as a CO₂ hydrate seal underlying MH-bearing layers, is a technically viable, operationally robust, and environmentally beneficial strategy. It simultaneously achieves substantial and long-lasting CO₂ sequestration through hydrate formation and dissolution trapping, enhances methane recovery, and mitigates excessive water production.

References

- [1] I. Melnikova *et al.*, “Carbon cycle and climate feedbacks under CO₂ and non-CO₂ overshoot pathways,” *Earth System Dynamics*, vol. 16, no. 1, pp. 257–273, Feb. 2025, doi: 10.5194/esd-16-257-2025.
- [2] A. Bhaskar, D. S. Ramesh, G. Vichare, T. Koganti, and S. Gurubaran, “Quantitative assessment of drivers of recent global temperature variability: an information theoretic approach,” *Clim. Dyn.*, vol. 49, no. 11–12, pp. 3877–3886, Dec. 2017, doi: 10.1007/s00382-017-3549-5.
- [3] P. Ciais *et al.*, “Five decades of northern land carbon uptake revealed by the interhemispheric CO₂ gradient,” *Nature*, vol. 568, no. 7751, pp. 221–225, Apr. 2019, doi: 10.1038/s41586-019-1078-6.
- [4] Y. Sun, S. Jiang, S. Li, X. Wang, and S. Peng, “Hydrate formation from clay bound water for CO₂ storage,” *Chemical Engineering Journal*, vol. 406, p. 126872, Feb. 2021, doi: 10.1016/j.cej.2020.126872.
- [5] K. Zhang and H. C. Lau, “Sequestering CO₂ as CO₂ hydrate in an offshore saline aquifer by reservoir pressure management,” *Energy*, vol. 239, p. 122231, Jan. 2022, doi: 10.1016/j.energy.2021.122231.
- [6] Y. Niwa *et al.*, “Multi-observational estimation of regional and sectoral emission contributions to the persistent high growth rate of atmospheric CH₄ for 2020–2022,” *Atmos. Chem. Phys.*, vol. 25, no. 13, pp. 6757–6785, Jul. 2025, doi: 10.5194/acp-25-6757-2025.
- [7] C. D. Ruppel and J. D. Kessler, “The interaction of climate change and methane hydrates,” *Reviews of Geophysics*, vol. 55, no. 1, pp. 126–168, Mar. 2017, doi: 10.1002/2016RG000534.
- [8] M. Ketzer *et al.*, “Gas hydrate dissociation linked to contemporary ocean warming in the southern hemisphere,” *Nat. Commun.*, vol. 11, no. 1, p. 3788, Jul. 2020, doi: 10.1038/s41467-020-17289-z.
- [9] A. V. Milkov, “Global estimates of hydrate-bound gas in marine sediments: how much is really out there?,” *Earth. Sci. Rev.*, vol. 66, no. 3–4, pp. 183–197, Aug. 2004, doi: 10.1016/j.earscirev.2003.11.002.
- [10] E. Dendy Sloan Jr. and Carolyn A. Koh, *Clathrate Hydrates of Natural Gases*, 3rd edition. CRC Press, 2007.
- [11] A. G. Aregbe, “Gas Hydrate—Properties, Formation and Benefits,” *Open Journal of Yangtze Oil and Gas*, vol. 02, no. 01, pp. 27–44, 2017, doi: 10.4236/ojogas.2017.21003.
- [12] J. Zhao, Y. Song, X.-L. Lim, and W.-H. Lam, “Opportunities and challenges of gas hydrate policies with consideration of environmental impacts,” *Renewable and*

- Sustainable Energy Reviews*, vol. 70, pp. 875–885, Apr. 2017, doi: 10.1016/j.rser.2016.11.269.
- [13] Z. R. Chong, S. H. B. Yang, P. Babu, P. Linga, and X.-S. Li, “Review of natural gas hydrates as an energy resource: Prospects and challenges,” *Appl. Energy*, vol. 162, pp. 1633–1652, Jan. 2016, doi: 10.1016/j.apenergy.2014.12.061.
 - [14] A. Tréhu *et al.*, “Gas Hydrates in Marine Sediments: Lessons from Scientific Ocean Drilling,” *Oceanography*, vol. 19, no. 4, pp. 124–142, Dec. 2006, doi: 10.5670/oceanog.2006.11.
 - [15] G. J. Moridis and E. D. Sloan, “Gas production potential of disperse low-saturation hydrate accumulations in oceanic sediments,” *Energy Convers. Manag.*, vol. 48, no. 6, pp. 1834–1849, Jun. 2007, doi: 10.1016/j.enconman.2007.01.023.
 - [16] C. Sahu, R. Kumar, and J. S. Sangwai, “Comprehensive Review on Exploration and Drilling Techniques for Natural Gas Hydrate Reservoirs,” *Energy & Fuels*, vol. 34, no. 10, pp. 11813–11839, Oct. 2020, doi: 10.1021/acs.energyfuels.0c02202.
 - [17] Z. Xia, X. Wang, and W. Ren, “Class-III Hydrate Reservoir Depressurization Production Enhancement by Volume Fracturing and Cyclic N₂ Stimulation Combination,” *ACS Omega*, vol. 8, no. 50, pp. 47678–47689, Dec. 2023, doi: 10.1021/acsomega.3c05923.
 - [18] J. Marcelle-De Silva and R. Dawe, “Towards Commercial Gas Production from Hydrate Deposits,” *Energies (Basel)*, vol. 4, no. 2, pp. 215–238, Jan. 2011, doi: 10.3390/en4020215.
 - [19] M. D. White, S. K. Wurstner, and B. P. McGrail, “Numerical studies of methane production from Class 1 gas hydrate accumulations enhanced with carbon dioxide injection,” *Mar. Pet. Geol.*, vol. 28, no. 2, pp. 546–560, Feb. 2011, doi: 10.1016/j.marpetgeo.2009.06.008.
 - [20] N. Satyavani, G. Alekhya, and K. Sain, “Free gas/gas hydrate inference in Krishna–Godavari basin using seismic and well log data,” *J. Nat. Gas Sci. Eng.*, vol. 25, pp. 317–324, Jul. 2015, doi: 10.1016/j.jngse.2015.05.010.
 - [21] G. J. Moridis, “Numerical Simulation Studies of Thermally-Induced Gas Production from Hydrate Accumulations with No Free Gas Zones at the Mallik Site, Mackenzie Delta, Canada,” in *SPE Asia Pacific Oil and Gas Conference and Exhibition*, SPE, Oct. 2002. doi: 10.2118/77861-MS.
 - [22] M. Kurihara *et al.*, “Analysis of Production Data for 2007/2008 Mallik Gas Hydrate Production Tests in Canada,” in *Proceedings of International Oil and Gas Conference and Exhibition in China*, Society of Petroleum Engineers, Jun. 2010. doi: 10.2523/132155-MS.
 - [23] G. J. Moridis, M. T. Reagan, S.-J. Kim, Y. Seol, and K. Zhang, “Evaluation of the Gas Production Potential of Marine Hydrate Deposits in the Ulleung Basin of the Korean

- East Sea,” *SPE Journal*, vol. 14, no. 04, pp. 759–781, Dec. 2009, doi: 10.2118/110859-PA.
- [24] J. Y. Lee, B. J. Ryu, T. S. Yun, J. Lee, and G.-C. Cho, “Review on the gas hydrate development and production as a new energy resource,” *KSCE Journal of Civil Engineering*, vol. 15, no. 4, pp. 689–696, Apr. 2011, doi: 10.1007/s12205-011-0009-3.
 - [25] J. Hou, E. Zhao, and Y. Ji, “Numerical simulation of gas production from Class III hydrate reservoirs using low-frequency electric heating-assisted depressurization with horizontal wells,” *Fuel*, vol. 357, p. 129906, Feb. 2024, doi: 10.1016/j.fuel.2023.129906.
 - [26] S. Yang, X. Lang, Y. Wang, Y. Wen, and S. Fan, “Numerical simulation of Class 3 hydrate reservoirs exploiting using horizontal well by depressurization and thermal co-stimulation,” *Energy Convers. Manag.*, vol. 77, pp. 298–305, Jan. 2014, doi: 10.1016/j.enconman.2013.09.046.
 - [27] P. Mao *et al.*, “Numerical study of gas production from fine-grained hydrate reservoirs using a multilateral horizontal well system,” *Appl. Energy*, vol. 301, p. 117450, Nov. 2021, doi: 10.1016/j.apenergy.2021.117450.
 - [28] T. Yu, G. Guan, A. Abudula, A. Yoshida, D. Wang, and Y. Song, “Application of horizontal wells to the oceanic methane hydrate production in the Nankai Trough, Japan,” *J. Nat. Gas Sci. Eng.*, vol. 62, pp. 113–131, Feb. 2019, doi: 10.1016/j.jngse.2018.11.027.
 - [29] W. Yuan *et al.*, “Assessing the prospect of long-term exploitation of Class 1 hydrate deposit with horizontal well in the South China Sea from energy, environmental, and economic perspectives,” *Appl. Energy*, vol. 400, p. 126552, Dec. 2025, doi: 10.1016/j.apenergy.2025.126552.
 - [30] X. Qin *et al.*, “Coexistence of natural gas hydrate, free gas and water in the gas hydrate system in the Shenhu Area, South China Sea,” *China Geology*, vol. 3, no. 2, pp. 210–220, 2020, doi: 10.31035/cg2020038.
 - [31] Y. Liu, J. Hou, Z. Chen, H. Su, E. Zhao, and G. Li, “A novel natural gas hydrate recovery approach by delivering geothermal energy through dumpflooding,” *Energy Convers. Manag.*, vol. 209, p. 112623, Apr. 2020, doi: 10.1016/j.enconman.2020.112623.
 - [32] Y. Song, L. Zhang, Q. Lv, M. Yang, Z. Ling, and J. Zhao, “Assessment of gas production from natural gas hydrate using depressurization, thermal stimulation and combined methods,” *RSC Adv.*, vol. 6, no. 53, pp. 47357–47367, 2016, doi: 10.1039/C6RA05526E.
 - [33] Q. Yuan *et al.*, “Gas Production from Methane-Hydrate-Bearing Sands by Ethylene Glycol Injection Using a Three-Dimensional Reactor,” *Energy & Fuels*, vol. 25, no. 7, pp. 3108–3115, Jul. 2011, doi: 10.1021/ef200510e.

- [34] T. Yagasaki, M. Matsumoto, and H. Tanaka, "Effects of thermodynamic inhibitors on the dissociation of methane hydrate: a molecular dynamics study," *Physical Chemistry Chemical Physics*, vol. 17, no. 48, pp. 32347–32357, 2015, doi: 10.1039/C5CP03008K.
- [35] M. Yasue, Y. Masuda, and Y. Liang, "Estimation of Methane Recovery Efficiency from Methane Hydrate by the N₂–CO₂ Gas Mixture Injection Method," *Energy & Fuels*, vol. 34, no. 5, pp. 5236–5250, May 2020, doi: 10.1021/acs.energyfuels.9b03898.
- [36] M. Yasue, Y. Masuda, and Y. Liang, "Enhancing the methane production from methane hydrate by cyclic N₂–CO₂ gas injection and soaking method: Significance of the slow diffusion-controlled process," *Appl. Energy*, vol. 379, p. 124912, Feb. 2025, doi: 10.1016/j.apenergy.2024.124912.
- [37] S. Yu, S. Uchida, E. M. Myshakin, Y. Seol, and C. Deusner, "Numerical Investigation of CH₄ Gas Production from CH₄ Hydrate-Bearing Sediments via CO₂ Injection," *Energy & Fuels*, vol. 38, no. 1, pp. 462–481, Jan. 2024, doi: 10.1021/acs.energyfuels.3c01304.
- [38] S. Fakher, Y. Elgahawy, and H. Abdelaal, "A Comprehensive Review on Gas Hydrate Reservoirs: Formation and Dissociation Thermodynamics and Rock and Fluid Properties," in *International Petroleum Technology Conference*, IPTC, Mar. 2019. doi: 10.2523/IPTC-19373-MS.
- [39] Y. Konno, Y. Masuda, Y. Hariguchi, M. Kurihara, and H. Ouchi, "Key Factors for Depressurization-Induced Gas Production from Oceanic Methane Hydrates," *Energy & Fuels*, vol. 24, no. 3, pp. 1736–1744, Mar. 2010, doi: 10.1021/ef901115h.
- [40] Y. F. Makogon and R. Y. Omelchenko, "Commercial gas production from Messoyakha deposit in hydrate conditions," *J. Nat. Gas Sci. Eng.*, vol. 11, pp. 1–6, Mar. 2013, doi: 10.1016/j.jngse.2012.08.002.
- [41] Y. F. Makogon, "Natural gas hydrates – A promising source of energy," *J. Nat. Gas Sci. Eng.*, vol. 2, no. 1, pp. 49–59, Mar. 2010, doi: 10.1016/j.jngse.2009.12.004.
- [42] B. Li *et al.*, "Production characteristics and sensitivity analysis on gas hydrate and shallow gas coexistence reservoirs: Focus on gas hydrate formation," *Appl. Energy*, vol. 386, p. 125572, May 2025, doi: 10.1016/j.apenergy.2025.125572.
- [43] T. Yu, G. Guan, and A. Abudula, "Production performance and numerical investigation of the 2017 offshore methane hydrate production test in the Nankai Trough of Japan," *Appl. Energy*, vol. 251, p. 113338, Oct. 2019, doi: 10.1016/j.apenergy.2019.113338.
- [44] Y. Konno *et al.*, "Key Findings of the World's First Offshore Methane Hydrate Production Test off the Coast of Japan: Toward Future Commercial Production," *Energy & Fuels*, vol. 31, no. 3, pp. 2607–2616, Mar. 2017, doi: 10.1021/acs.energyfuels.6b03143.

- [45] S. Li, D. Wu, X. Wang, and Y. Hao, “Enhanced gas production from marine hydrate reservoirs by hydraulic fracturing assisted with sealing burdens,” *Energy*, vol. 232, p. 120889, Oct. 2021, doi: 10.1016/j.energy.2021.120889.
- [46] S. Nie *et al.*, “Numerical study on the stimulation effect of boundary sealing and hot water injection in marine challenging gas hydrate extraction,” *Sci. Rep.*, vol. 14, no. 1, p. 15280, Jul. 2024, doi: 10.1038/s41598-024-66321-5.
- [47] J. Xu, H. Qin, H. Li, C. Lu, S. Li, and D. Wu, “Enhanced gas production efficiency of class 1,2,3 hydrate reservoirs using hydraulic fracturing technique,” *Energy*, vol. 263, p. 126003, Jan. 2023, doi: 10.1016/j.energy.2022.126003.
- [48] Y. Li *et al.*, “Enhancing CO₂ hydrate sequestration through underlying methane hydrate production: A novel strategy for carbon storage,” *Energy*, vol. 326, p. 136144, Jul. 2025, doi: 10.1016/j.energy.2025.136144.
- [49] R. Boswell, D. Schoderbek, T. S. Collett, S. Ohtsuki, M. White, and B. J. Anderson, “The Ignik Sikumi Field Experiment, Alaska North Slope: Design, Operations, and Implications for CO₂–CH₄ Exchange in Gas Hydrate Reservoirs,” *Energy & Fuels*, vol. 31, no. 1, pp. 140–153, Jan. 2017, doi: 10.1021/acs.energyfuels.6b01909.
- [50] Y. Gu *et al.*, “Enhancing gas recovery from natural gas hydrate reservoirs in the eastern Nankai Trough: Deep depressurization and underburden sealing,” *Energy*, vol. 262, p. 125510, Jan. 2023, doi: 10.1016/j.energy.2022.125510.
- [51] H. Ye *et al.*, “How shallow CO₂ hydrate cap affects depressurization production in deeper natural gas hydrate reservoirs: An example at Site W17, South China Sea,” *J. Clean. Prod.*, vol. 478, p. 143954, Nov. 2024, doi: 10.1016/j.jclepro.2024.143954.
- [52] W. Liu *et al.*, “Experimental measurements of mechanical properties of carbon dioxide hydrate-bearing sediments,” *Mar. Pet. Geol.*, vol. 46, pp. 201–209, Sep. 2013, doi: 10.1016/j.marpetgeo.2013.06.016.
- [53] M. Aminnaji *et al.*, “CO₂ Gas hydrate for carbon capture and storage applications – Part 1,” *Energy*, vol. 300, p. 131579, Aug. 2024, doi: 10.1016/j.energy.2024.131579.
- [54] J. Gauteplass, S. Almenningen, G. Ersland, and T. Barth, “Hydrate seal formation during laboratory CO₂ injection in a cold aquifer,” *International Journal of Greenhouse Gas Control*, vol. 78, pp. 21–26, Nov. 2018, doi: 10.1016/j.ijggc.2018.07.017.
- [55] A. Bahmaee and S. Murata, “A numerical study of hydrate-based CO₂ storage using CO₂-in-water emulsion: optimizing emulsion injectivity, and storage capacity,” *Fuel*, vol. 404, p. 136399, Jan. 2026, doi: 10.1016/j.fuel.2025.136399.
- [56] S. Almenningen, J. Gauteplass, P. Fotland, G. L. Aastveit, T. Barth, and G. Ersland, “Visualization of hydrate formation during CO₂ storage in water-saturated sandstone,” *International Journal of Greenhouse Gas Control*, vol. 79, pp. 272–278, Dec. 2018, doi: 10.1016/j.ijggc.2018.11.008.

- [57] H.-N. Chen *et al.*, “Enhanced CO₂ injection and hydrate conversion in unsealed submarine sediments for CO₂ hydrate sequestration by CO₂-H₂O emulsion injection,” *Chem. Eng. Sci.*, vol. 304, p. 121053, Feb. 2025, doi: 10.1016/j.ces.2024.121053.
- [58] M.-L. Wang *et al.*, “A new approach to high conversion CO₂ hydrate sequestration by CO₂/water emulsion injection into marine sediments,” *Chemical Engineering Journal*, vol. 503, p. 158375, Jan. 2025, doi: 10.1016/j.cej.2024.158375.
- [59] Y. Ikegawa, K. Miyakawa, K. Suzuki, Y. Masuda, H. Narita, and T. Ebinuma, “SS: Hydrates: Experimental results for long term CO₂ injection near methane hydrate formations,” in *All Days*, OTC, May 2010. doi: 10.4043/20575-MS.
- [60] P. Sridhara, B. J. Anderson, N. Garapati, Y. Seol, and E. M. Myshakin, “Novel Technological Approach To Enhance Methane Recovery from Class 2 Hydrate Deposits by Employing CO₂ Injection,” *Energy & Fuels*, vol. 32, no. 3, pp. 2949–2961, Mar. 2018, doi: 10.1021/acs.energyfuels.7b03441.
- [61] Z.-F. Sun *et al.*, “A novel method to enhance methane hydrate exploitation efficiency via forming impermeable overlying CO₂ hydrate cap,” *Appl. Energy*, vol. 240, pp. 842–850, Apr. 2019, doi: 10.1016/j.apenergy.2019.02.022.
- [62] J.-L. Cui *et al.*, “Study on the factors affecting the sealing performance and mechanical stability of CO₂ hydrate cap during gas production from methane hydrate,” *J. Nat. Gas Sci. Eng.*, vol. 93, p. 104050, Sep. 2021, doi: 10.1016/j.jngse.2021.104050.
- [63] A. Bahmaee, Y. Masuda, and S. Murata, “Numerical modelling of CO₂-in-water emulsion injection into a water-saturated core,” *Gas Science and Engineering*, vol. 131, p. 205485, Nov. 2024, doi: 10.1016/j.jgsce.2024.205485.
- [64] M. F. Qureshi, H. Khandelwal, A. Usadi, T. A. Barckholtz, A. B. Mhadeshwar, and P. Linga, “CO₂ hydrate stability in oceanic sediments under brine conditions,” *Energy*, vol. 256, p. 124625, Oct. 2022, doi: 10.1016/j.energy.2022.124625.
- [65] J.-R. Zhong *et al.*, “CO₂ Hydrate dissolution rates in unsaturated water quantified with laboratory experiments,” *Chemical Engineering Journal*, vol. 430, p. 133137, Feb. 2022, doi: 10.1016/j.cej.2021.133137.
- [66] I. Aya, K. Yamane, and H. Nariai, “Solubility of CO₂ and density of CO₂ hydrate at 30 MPa,” *Energy*, vol. 22, no. 2–3, pp. 263–271, Feb. 1997, doi: 10.1016/S0360-5442(96)00093-X.
- [67] Y. Zhang, G. D. Holder, and R. P. Warzinski, “Phase Equilibrium in Two-Phase, Water-Rich-Liquid, Hydrate Systems: Experiment and Theory,” *Ind. Eng. Chem. Res.*, vol. 47, no. 2, pp. 459–469, Jan. 2008, doi: 10.1021/ie070846c.
- [68] A. Bahmaee, K. Kobayashi, and S. Murata, “Numerical study of the effects of in-situ CO₂ hydrate seal formation by CO₂-in-water emulsion injection on methane production and aquifer inflow in Class 2 hydrate deposits,” *Fuel*, vol. 419, p. 138834, Sep. 2026, doi: 10.1016/j.fuel.2026.138834.

- [69] A. Bahmaee, “Thermal Effects of CO₂-in-Water Emulsion Injection into a Methane Hydrate Reservoir Aquifer,” Master’s Thesis, The University of Tokyo, 2023.
- [70] J. Grabowska *et al.*, “Solubility of Methane in Water: Some Useful Results for Hydrate Nucleation,” *J. Phys. Chem. B*, vol. 126, no. 42, pp. 8553–8570, Oct. 2022, doi: 10.1021/acs.jpcc.2c04867.
- [71] Z. Duan and S. Mao, “A thermodynamic model for calculating methane solubility, density and gas phase composition of methane-bearing aqueous fluids from 273 to 523K and from 1 to 2000bar,” *Geochim. Cosmochim. Acta*, vol. 70, no. 13, pp. 3369–3386, Jul. 2006, doi: 10.1016/j.gca.2006.03.018.
- [72] Z. Li, E. Spangenberg, J. M. Schicks, and T. Kempka, “Numerical Simulation of Hydrate Formation in the Large-Scale Reservoir Simulator (LARS),” *Energies (Basel)*, vol. 15, no. 6, p. 1974, Mar. 2022, doi: 10.3390/en15061974.
- [73] P. L. Stanwix, N. M. Rathnayake, F. P. P. de Obanos, M. L. Johns, Z. M. Aman, and E. F. May, “Characterising thermally controlled CH₄–CO₂ hydrate exchange in unconsolidated sediments,” *Energy Environ. Sci.*, vol. 11, no. 7, pp. 1828–1840, 2018, doi: 10.1039/C8EE00139A.
- [74] W. Ostwald, “Studien über die Bildung und Umwandlung fester Körper,” *Zeitschrift für Physikalische Chemie*, vol. 22U, no. 1, pp. 289–330, Feb. 1897, doi: 10.1515/zpch-1897-2233.
- [75] K. Xu, R. Bonnecaze, and M. Balhoff, “Egalitarianism among Bubbles in Porous Media: An Ostwald Ripening Derived Anticoarsening Phenomenon,” *Phys. Rev. Lett.*, vol. 119, no. 26, p. 264502, Dec. 2017, doi: 10.1103/PhysRevLett.119.264502.
- [76] B. Ding, M. Dong, Z. Chen, and A. Kantzas, “Enhanced oil recovery by emulsion injection in heterogeneous heavy oil reservoirs: Experiments, modeling and reservoir simulation,” *J. Pet. Sci. Eng.*, vol. 209, p. 109882, Feb. 2022, doi: 10.1016/j.petrol.2021.109882.
- [77] M. L’Estimé, M. Schindler, N. Shahidzadeh, and D. Bonn, “Droplet Size Distribution in Emulsions,” *Langmuir*, vol. 40, no. 1, pp. 275–281, Jan. 2024, doi: 10.1021/acs.langmuir.3c02463.
- [78] X. Kang *et al.*, “Stability influence factors and mechanism of produced emulsion from CO₂ flooding,” *J. Mol. Liq.*, vol. 333, p. 115974, Jul. 2021, doi: 10.1016/j.molliq.2021.115974.
- [79] X. Sun and K. K. Mohanty, “Kinetic simulation of methane hydrate formation and dissociation in porous media,” *Chem. Eng. Sci.*, vol. 61, no. 11, pp. 3476–3495, Jun. 2006, doi: 10.1016/j.ces.2005.12.017.
- [80] R. Song, S. Sun, J. Liu, and X. Feng, “Numerical modeling on hydrate formation and evaluating the influencing factors of its heterogeneity in core-scale sandy sediment,” *J. Nat. Gas Sci. Eng.*, vol. 90, p. 103945, Jun. 2021, doi: 10.1016/j.jngse.2021.103945.

- [81] M. B. Malegaonkar, P. D. Dholabhai, and P. R. Bishnoi, "Kinetics of carbon dioxide and methane hydrate formation," *Can. J. Chem. Eng.*, vol. 75, no. 6, pp. 1090–1099, Dec. 1997, doi: 10.1002/cjce.5450750612.
- [82] H.-J. Ng and D. B. Robinson, "Hydrate formation in systems containing methane, ethane, propane, carbon dioxide or hydrogen sulfide in the presence of methanol," *Fluid Phase Equilib.*, vol. 21, no. 1–2, pp. 145–155, Jan. 1985, doi: 10.1016/0378-3812(85)90065-2.
- [83] J. Guan *et al.*, "Effect of initial pore water content and salinity on the resistivity of methane hydrate-bearing fine sediments," *Gas Science and Engineering*, vol. 124, p. 205267, Apr. 2024, doi: 10.1016/j.jgsce.2024.205267.
- [84] J. Husebø, G. Ersland, A. Graue, and B. Kvamme, "Effects of salinity on hydrate stability and implications for storage of CO₂ in natural gas hydrate reservoirs," *Energy Procedia*, vol. 1, no. 1, pp. 3731–3738, Feb. 2009, doi: 10.1016/j.egypro.2009.02.172.
- [85] J. C. Cordeiro, M. A. Marcelino Neto, R. E. M. Morales, and A. K. Sum, "Phase Equilibrium of Carbon Dioxide Hydrates Inhibited with MEG and NaCl above the Upper Quadruple Point," *J. Chem. Eng. Data*, vol. 65, no. 1, pp. 280–286, Jan. 2020, doi: 10.1021/acs.jced.9b01001.
- [86] Z. Duan, "A model to predict phase equilibrium of CH₄ and CO₂ clathrate hydrate in aqueous electrolyte solutions," *American Mineralogist*, vol. 91, no. 8–9, pp. 1346–1354, Aug. 2006, doi: 10.2138/am.2006.2017.
- [87] A. A. Noyes and W. B. Whitney, "Ueber die Auflösungs geschwindigkeit von festen Stoffen in ihren eigenen Lösungen," *Zeitschrift für Physikalische Chemie*, vol. 23U, no. 1, pp. 689–692, Jun. 1897, doi: 10.1515/zpch-1897-2341.
- [88] Z. Duan and R. Sun, "An improved model calculating CO₂ solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar," *Chem. Geol.*, vol. 193, no. 3–4, pp. 257–271, Feb. 2003, doi: 10.1016/S0009-2541(02)00263-2.
- [89] J. Gabitto and C. Tsouris, "Dissolution mechanisms of CO₂ hydrate droplets in deep seawaters," *Energy Convers. Manag.*, vol. 47, no. 5, pp. 494–508, Mar. 2006, doi: 10.1016/j.enconman.2005.05.016.
- [90] K. Ogasawara, A. Yamasaki, and H. Teng, "Mass Transfer from CO₂ Drops Traveling in High-Pressure and Low-Temperature Water," *Energy & Fuels*, vol. 15, no. 1, pp. 147–150, Jan. 2001, doi: 10.1021/ef000151n.
- [91] D. Dahlgren and H. Lennernäs, "Oral Drug Delivery, Absorption and Bioavailability," in *Comprehensive Pharmacology*, Elsevier, 2022, pp. 406–437. doi: 10.1016/B978-0-12-820472-6.00022-0.
- [92] J. J. Carroll, J. D. Slupsky, and A. E. Mather, "The Solubility of Carbon Dioxide in Water at Low Pressure," *J. Phys. Chem. Ref. Data*, vol. 20, no. 6, pp. 1201–1209, Nov. 1991, doi: 10.1063/1.555900.

- [93] D. Koschel, J.-Y. Coxam, L. Rodier, and V. Majer, "Enthalpy and solubility data of CO₂ in water and NaCl(aq) at conditions of interest for geological sequestration," *Fluid Phase Equilib.*, vol. 247, no. 1–2, pp. 107–120, Sep. 2006, doi: 10.1016/j.fluid.2006.06.006.
- [94] L. Zuo and S. M. Benson, "CO₂ Exsolution – challenges and Opportunities in Subsurface Flow Management," *Energy Procedia*, vol. 63, pp. 5664–5670, 2014, doi: 10.1016/j.egypro.2014.11.599.
- [95] R. Enouy, M. Li, M. A. Ioannidis, and A. J. A. Unger, "Gas exsolution and flow during supersaturated water injection in porous media: II. Column experiments and continuum modeling," *Adv. Water Resour.*, vol. 34, no. 1, pp. 15–25, Jan. 2011, doi: 10.1016/j.advwatres.2010.09.013.
- [96] Y. Gao, D. Chen, M. Saccoccio, Z. Lu, and F. Ciucci, "From material design to mechanism study: Nanoscale Ni exsolution on a highly active A-site deficient anode material for solid oxide fuel cells," *Nano Energy*, vol. 27, pp. 499–508, Sep. 2016, doi: 10.1016/j.nanoen.2016.07.013.
- [97] W. Zhao and M. A. Ioannidis, "Gas exsolution and flow during supersaturated water injection in porous media: I. Pore network modeling," *Adv. Water Resour.*, vol. 34, no. 1, pp. 2–14, Jan. 2011, doi: 10.1016/j.advwatres.2010.09.010.
- [98] H. C. Kim, P. R. Bishnoi, R. A. Heidemann, and S. S. H. Rizvi, "Kinetics of methane hydrate decomposition," *Chem. Eng. Sci.*, vol. 42, no. 7, pp. 1645–1653, 1987, doi: 10.1016/0009-2509(87)80169-0.
- [99] X. Cao, K. Yang, W. Xia, G. Tang, and J. Bian, "Dissociation experiment and dissociation rate model of CO₂ hydrate," *Natural Gas Industry B*, vol. 8, no. 6, pp. 607–614, Dec. 2021, doi: 10.1016/j.ngib.2021.11.008.
- [100] K. A. Birkedal, C. M. Freeman, G. J. Moridis, and A. Graue, "Numerical Predictions of Experimentally Observed Methane Hydrate Dissociation and Reformation in Sandstone," *Energy & Fuels*, vol. 28, no. 9, pp. 5573–5586, Sep. 2014, doi: 10.1021/ef500255y.
- [101] N. F. Spycher and M. H. Reed, "Fugacity coefficients of H₂, CO₂, CH₄, H₂O and of H₂O- CO₂-CH₄ mixtures: A virial equation treatment for moderate pressures and temperatures applicable to calculations of hydrothermal boiling," *Geochim. Cosmochim. Acta*, vol. 52, no. 3, pp. 739–749, Mar. 1988, doi: 10.1016/0016-7037(88)90334-1.
- [102] J. Wang, F. Han, S. Li, K. Ge, and Z. Zheng, "Investigation of gas hydrate production with salinity via depressurization and thermal stimulation methods," *J. Pet. Sci. Eng.*, vol. 194, p. 107465, Nov. 2020, doi: 10.1016/j.petrol.2020.107465.
- [103] E. Rodriguez and S. L. Bryant, "Straining of Fine Particles in Gaps in Porous Media," in *All Days*, SPE, Nov. 2007. doi: 10.2118/110425-MS.

- [104] S. A. Bradford, J. Simunek, M. Bettahar, M. T. van Genuchten, and S. R. Yates, "Significance of straining in colloid deposition: Evidence and implications," *Water Resour. Res.*, vol. 42, no. 12, Dec. 2006, doi: 10.1029/2005WR004791.
- [105] S. Torkzaban, S. A. Bradford, M. Th. van Genuchten, and S. L. Walker, "Colloid transport in unsaturated porous media: The role of water content and ionic strength on particle straining," *J. Contam. Hydrol.*, vol. 96, no. 1–4, pp. 113–127, Feb. 2008, doi: 10.1016/j.jconhyd.2007.10.006.
- [106] C. Gruesbeck and R. E. Collins, "Particle Transport Through Perforations," *Society of Petroleum Engineers Journal*, vol. 22, no. 06, pp. 857–865, Dec. 1982, doi: 10.2118/7006-PA.
- [107] F. Civan, *Reservoir Formation Damage: Fundamentals, Modeling, Assessment, and Mitigation*, 3rd Edition. Gulf Professional Publishing, 2016.
- [108] W. A. Hall, "An Analysis of Sand Filtration," *Journal of the Sanitary Engineering Division*, vol. 83, no. 3, pp. 1–9, Jun. 1957, doi: 10.1061/JSEDAI.0000083.
- [109] N. N. Nguyen, R. Berger, and H.-J. Butt, "Premelting-Induced Agglomeration of Hydrates: Theoretical Analysis and Modeling," *ACS Appl. Mater. Interfaces*, vol. 12, no. 12, pp. 14599–14606, Mar. 2020, doi: 10.1021/acsami.0c00636.
- [110] X. Lv, B. Shi, S. Zhou, S. Wang, W. Huang, and X. Sun, "Study on the Decomposition Mechanism of Natural Gas Hydrate Particles and Its Microscopic Agglomeration Characteristics," *Applied Sciences*, vol. 8, no. 12, p. 2464, Dec. 2018, doi: 10.3390/app8122464.
- [111] J. B. Walsh and W. F. Brace, "The effect of pressure on porosity and the transport properties of rock," *J. Geophys. Res. Solid Earth*, vol. 89, no. B11, pp. 9425–9431, Oct. 1984, doi: 10.1029/JB089iB11p09425.
- [112] R. M. German, "Detailed linkages of powder characteristics to properties in press-sinter processing of powder metals," in *Advances in Powder Metallurgy and Particulate Materials*, 2006, vol. 2, p. 10.
- [113] P. W. Glover and N. Déry, "Streaming potential coupling coefficient of quartz glass bead packs: Dependence on grain diameter, pore size, and pore throat radius," *GEOPHYSICS*, vol. 75, no. 6, pp. F225–F241, Nov. 2010, doi: 10.1190/1.3509465.
- [114] K. Nazridoust and G. Ahmadi, "Computational modeling of methane hydrate dissociation in a sandstone core," *Chem. Eng. Sci.*, vol. 62, no. 22, pp. 6155–6177, Nov. 2007, doi: 10.1016/j.ces.2007.06.038.
- [115] J. Zhao, Z. Fan, H. Dong, Z. Yang, and Y. Song, "Influence of reservoir permeability on methane hydrate dissociation by depressurization," *Int. J. Heat Mass Transf.*, vol. 103, pp. 265–276, Dec. 2016, doi: 10.1016/j.ijheatmasstransfer.2016.05.111.

- [116] R. L. Kleinberg *et al.*, “Deep sea NMR: Methane hydrate growth habit in porous media and its relationship to hydraulic permeability, deposit accumulation, and submarine slope stability,” *J. Geophys. Res. Solid Earth*, vol. 108, no. B10, Oct. 2003, doi: 10.1029/2003JB002389.
- [117] Z. Zhang, L. Liu, W. Lu, C. Liu, F. Ning, and S. Dai, “Permeability of hydrate-bearing fine-grained sediments: Research status, challenges and perspectives,” *Earth. Sci. Rev.*, vol. 244, p. 104517, Sep. 2023, doi: 10.1016/j.earscirev.2023.104517.
- [118] S. Dai and Y. Seol, “Water permeability in hydrate-bearing sediments: A pore-scale study,” *Geophys. Res. Lett.*, vol. 41, no. 12, pp. 4176–4184, Jun. 2014, doi: 10.1002/2014GL060535.
- [119] H. Minagawa *et al.*, “Water Permeability of Porous Media Containing Methane Hydrate as Controlled by the Methane-hydrate Growth Process,” in *Natural Gas Hydrates—Energy Resource Potential and Associated Geologic Hazards*, American Association of Petroleum Geologists, 2009, pp. 734–739. doi: 10.1306/13201176M893367.
- [120] A. Kumar, B. Maini, P.R. Bishnoi, M. Clarke, O. Zatsepina, and S. Srinivasan, “Experimental determination of permeability in the presence of hydrates and its effect on the dissociation characteristics of gas hydrates in porous media,” *J. Pet. Sci. Eng.*, vol. 70, no. 1–2, pp. 114–122, Jan. 2010, doi: 10.1016/j.petrol.2009.10.005.
- [121] L. Pan, L. Lei, and Y. Seol, “Pore-scale influence of methane hydrate on permeability of porous media,” *J. Nat. Gas Sci. Eng.*, vol. 87, p. 103758, Mar. 2021, doi: 10.1016/j.jngse.2020.103758.
- [122] Y. Zhang *et al.*, “Investigating the effective permeability evolution as a function of hydrate saturation in the hydrate-bearing sands using a kinetic-theory-based pore network model,” *Comput. Geotech.*, vol. 150, p. 104930, Oct. 2022, doi: 10.1016/j.compgeo.2022.104930.
- [123] W. Wagner and H.-J. Kretzschmar, *International Steam Tables*. Berlin, Heidelberg: Springer Berlin Heidelberg, 2008. doi: 10.1007/978-3-540-74234-0.
- [124] R. Span and W. Wagner, “A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa,” *J. Phys. Chem. Ref. Data*, vol. 25, no. 6, pp. 1509–1596, Nov. 1996, doi: 10.1063/1.555991.
- [125] S. Shao, “Numerical Simulation on Optimum Scheme of CO₂-in-Water Emulsion Injection into Methane Hydrate Reservoirs,” Master’s Thesis, The University of Tokyo, 2020.
- [126] M. McBride-Wright, G. C. Maitland, and J. P. M. Trusler, “Viscosity and Density of Aqueous Solutions of Carbon Dioxide at Temperatures from (274 to 449) K and at Pressures up to 100 MPa,” *J. Chem. Eng. Data*, vol. 60, no. 1, pp. 171–180, Jan. 2015, doi: 10.1021/je5009125.

- [127] F. Tabasinejad *et al.*, “Water/CO₂ System at High Pressure and Temperature Conditions: Measurement and Modeling of Density in Equilibrium Liquid and Vapor Phases,” in *SPE EUROPEC/EAGE Annual Conference and Exhibition*, SPE, Jun. 2010. doi: 10.2118/131636-MS.
- [128] C. Calabrese, M. McBride-Wright, G. C. Maitland, and J. P. M. Trusler, “Extension of Vibrating-Wire Viscometry to Electrically Conducting Fluids and Measurements of Viscosity and Density of Brines with Dissolved CO₂ at Reservoir Conditions,” *J. Chem. Eng. Data*, vol. 64, no. 9, pp. 3831–3847, Sep. 2019, doi: 10.1021/acs.jced.9b00248.
- [129] Q. Sun and Y. T. Kang, “Review on CO₂ hydrate formation/dissociation and its cold energy application,” *Renewable and Sustainable Energy Reviews*, vol. 62, pp. 478–494, Sep. 2016, doi: 10.1016/j.rser.2016.04.062.
- [130] K. A. Udachin, C. I. Ratcliffe, and J. A. Ripmeester, “Structure, Composition, and Thermal Expansion of CO₂ Hydrate from Single Crystal X-ray Diffraction Measurements,” *J. Phys. Chem. B*, vol. 105, no. 19, pp. 4200–4204, May 2001, doi: 10.1021/jp004389o.
- [131] G. L. Chierici, *Principles of Petroleum Reservoir Engineering*. Berlin, Heidelberg: Springer Berlin Heidelberg, 1994. doi: 10.1007/978-3-662-02964-0.
- [132] J. Kestin, M. Sokolov, and W. A. Wakeham, “Viscosity of liquid water in the range –8 °C to 150 °C,” *J. Phys. Chem. Ref. Data*, vol. 7, no. 3, pp. 941–948, Jul. 1978, doi: 10.1063/1.555581.
- [133] A. Fenghour, W. A. Wakeham, and V. Vesovic, “The Viscosity of Carbon Dioxide,” *J. Phys. Chem. Ref. Data*, vol. 27, no. 1, pp. 31–44, Jan. 1998, doi: 10.1063/1.556013.
- [134] J. Kestin and I. R. Shankland, “Viscosity of aqueous NaCl solutions in the temperature range 25–200 °C and in the pressure range 0.1–30 MPa,” *Int J Thermophys*, vol. 5, no. 3, pp. 241–263, Sep. 1984, doi: 10.1007/BF00507835.
- [135] A. Kumagai and C. Yokoyama, “Viscosities of Aqueous NaCl Solutions Containing CO₂ at High Pressures,” *J. Chem. Eng. Data*, vol. 44, no. 2, pp. 227–229, Mar. 1999, doi: 10.1021/je980178p.
- [136] K. Rayatdoost Talooki, E. Omidbakhsh Amiri, and H. Salimi-Kenari, “Effects of high viscosity ratio and interfacial tension on droplet formation,” *Journal of the Brazilian Society of Mechanical Sciences and Engineering*, vol. 44, no. 5, p. 176, May 2022, doi: 10.1007/s40430-022-03478-y.
- [137] L. Yu, B. Ding, M. Dong, and Q. Jiang, “Plugging Ability of Oil-in-Water Emulsions in Porous Media: Experimental and Modeling Study,” *Ind. Eng. Chem. Res.*, vol. 57, no. 43, pp. 14795–14808, Oct. 2018, doi: 10.1021/acs.iecr.8b03805.
- [138] Y. Liu *et al.*, “Evolution of morphology and cohesive force of hydrate particles in the presence/absence of wax,” *RSC Adv.*, vol. 12, no. 23, pp. 14456–14466, 2022, doi: 10.1039/D2RA02266D.

- [139] G. I. Taylor, "The viscosity of a fluid containing small drops of another fluid," *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, vol. 138, no. 834, pp. 41–48, Oct. 1932, doi: 10.1098/rspa.1932.0169.
- [140] A. Einstein, "Berichtigung zu meiner Arbeit: „Eine neue Bestimmung der Moleküldimensionen“,” *Ann. Phys.*, vol. 339, no. 3, pp. 591–592, Jan. 1911, doi: 10.1002/andp.19113390313.
- [141] G. D. Holder, S. P. Zetts, and N. Pradhan, "Phase Behavior in Systems Containing Clathrate Hydrates: A Review," *Reviews in Chemical Engineering*, vol. 5, no. 1–4, pp. 1–70, Jan. 1988, doi: 10.1515/REVCE.1988.5.1-4.1.
- [142] W. F. Waite, L. A. Stern, S. H. Kirby, W. J. Winters, and D. H. Mason, "Simultaneous determination of thermal conductivity, thermal diffusivity and specific heat in sI methane hydrate," *Geophys. J. Int.*, vol. 169, no. 2, pp. 767–774, May 2007, doi: 10.1111/j.1365-246X.2007.03382.x.
- [143] D. G. Friend, J. F. Ely, and H. Ingham, "Thermophysical Properties of Methane," *J. Phys. Chem. Ref. Data*, vol. 18, no. 2, pp. 583–638, Apr. 1989, doi: 10.1063/1.555828.
- [144] M. L. V. Ramires, C. A. Nieto de Castro, Y. Nagasaka, A. Nagashima, M. J. Assael, and W. A. Wakeham, "Standard Reference Data for the Thermal Conductivity of Water," *J. Phys. Chem. Ref. Data*, vol. 24, no. 3, pp. 1377–1381, May 1995, doi: 10.1063/1.555963.
- [145] V. Vesovic, W. A. Wakeham, G. A. Olchowy, J. V. Sengers, J. T. R. Watson, and J. Millat, "The Transport Properties of Carbon Dioxide," *J. Phys. Chem. Ref. Data*, vol. 19, no. 3, pp. 763–808, May 1990, doi: 10.1063/1.555875.
- [146] L. Wan, D. Liang, D. Li, and J. Guan, "Characteristics of thermal conductivity and thermal diffusivity of carbon dioxide hydrate," *Huagong Xuebao/CIESC Journal*, vol. 67, no. 10, pp. 4169–4175, Oct. 2016, doi: 10.11949/j.issn.0438-1157.20160384.
- [147] T. K. Perkins and O. C. Johnston, "A Review of Diffusion and Dispersion in Porous Media," *Society of Petroleum Engineers Journal*, vol. 3, no. 01, pp. 70–84, Mar. 1963, doi: 10.2118/480-PA.
- [148] K. Bao, K.-A. Lie, O. Møyner, and M. Liu, "Fully implicit simulation of polymer flooding with MRST," *Comput. Geosci.*, vol. 21, no. 5–6, pp. 1219–1244, Dec. 2017, doi: 10.1007/s10596-017-9624-5.
- [149] K.-A. Lie, *An Introduction to Reservoir Simulation Using MATLAB/GNU Octave: User Guide for the MATLAB Reservoir Simulation Toolbox (MRST)*. Cambridge: Cambridge University Press, 2019. Accessed: Aug. 02, 2023. [Online]. Available: <http://www.cambridge.org/9781108492430>
- [150] M. M. Yousufi, I. bin Dzulkarnain, M. E. M. Elhaj, and S. Ahmed, "A Perspective on the Prospect of Pickering Emulsion in Reservoir Conformance Control with Insight

- into the Influential Parameters and Characterization Techniques,” *Processes*, vol. 11, no. 9, p. 2672, Sep. 2023, doi: 10.3390/pr11092672.
- [151] L. Yu, B. Ding, M. Dong, and Q. Jiang, “A new model of emulsion flow in porous media for conformance control,” *Fuel*, vol. 241, pp. 53–64, Apr. 2019, doi: 10.1016/j.fuel.2018.12.014.
- [152] B. Ding, M. Dong, and L. Yu, “A model of emulsion plugging ability in sandpacks: Yield pressure drop and consistency parameter,” *Chem. Eng. Sci.*, vol. 211, p. 115248, Jan. 2020, doi: 10.1016/j.ces.2019.115248.
- [153] Z. Chen, “Challenges and opportunities of CO₂ storage in depleted shallow gas reservoirs in Alberta Oilsands area, Western Canada Sedimentary Basin, Canada,” *Fuel*, vol. 381, p. 133384, Feb. 2025, doi: 10.1016/j.fuel.2024.133384.
- [154] J. Zhang and S.-X. Yin, “Fracture gradient prediction: an overview and an improved method,” *Pet. Sci.*, vol. 14, no. 4, pp. 720–730, Nov. 2017, doi: 10.1007/s12182-017-0182-1.
- [155] J. A. Priest and J. L. Hayley, “Strength of Laboratory Synthesized Hydrate-Bearing Sands and Their Relationship to Natural Hydrate-Bearing Sediments,” *J. Geophys. Res. Solid Earth*, vol. 124, no. 12, pp. 12556–12575, Dec. 2019, doi: 10.1029/2019JB018324.
- [156] Y. Abe, X. Ma, T. Yanai, and K. Yamane, “Development of formation and growth models of CO₂ hydrate film,” *AIChE Journal*, vol. 62, no. 11, pp. 4078–4089, Nov. 2016, doi: 10.1002/aic.15304.
- [157] T. Uchida, T. Ebinuma, J. Kawabata, and H. Narita, “Microscopic observations of formation processes of clathrate-hydrate films at an interface between water and carbon dioxide,” *J. Cryst. Growth*, vol. 204, no. 3, pp. 348–356, Jul. 1999, doi: 10.1016/S0022-0248(99)00178-5.
- [158] Y. Shindo, K. Sakaki, Y. Fujioka, and H. Komiyama, “Kinetics of the formation of CO₂ hydrate on the surface of liquid CO₂ droplet in water,” *Energy Convers. Manag.*, vol. 37, no. 4, pp. 485–489, Apr. 1996, doi: 10.1016/0196-8904(95)00198-0.
- [159] M.-L. Wang *et al.*, “Kinetics and morphology study of hydrate formation from CO₂-H₂O emulsion in glass beads,” *Chemical Engineering Journal*, vol. 513, p. 162936, Jun. 2025, doi: 10.1016/j.cej.2025.162936.
- [160] J. Kihm, J. Kim, S. Wang, and T. Xu, “Hydrogeochemical numerical simulation of impacts of mineralogical compositions and convective fluid flow on trapping mechanisms and efficiency of carbon dioxide injected into deep saline sandstone aquifers,” *J. Geophys. Res. Solid Earth*, vol. 117, no. B6, Jun. 2012, doi: 10.1029/2011JB008906.

- [161] T. J. W. Postma, K. W. Bandilla, C. A. Peters, and M. A. Celia, “Field-Scale Modeling of CO₂ Mineral Trapping in Reactive Rocks: A Vertically Integrated Approach,” *Water Resour. Res.*, vol. 58, no. 1, Jan. 2022, doi: 10.1029/2021WR030626.
- [162] M. Uddin, F. Wright, S. Dallimore, and D. Coombe, “Gas hydrate dissociations in Mallik hydrate bearing zones A, B, and C by depressurization: Effect of salinity and hydration number in hydrate dissociation,” *J. Nat. Gas Sci. Eng.*, vol. 21, pp. 40–63, Nov. 2014, doi: 10.1016/j.jngse.2014.07.027.
- [163] J. Rutqvist, G. J. Moridis, T. Grover, and T. Collett, “Geomechanical response of permafrost-associated hydrate deposits to depressurization-induced gas production,” *J. Pet. Sci. Eng.*, vol. 67, no. 1–2, pp. 1–12, Jul. 2009, doi: 10.1016/j.petrol.2009.02.013.
- [164] R. Boswell *et al.*, “Occurrence of gas hydrate in Oligocene Frio sand: Alaminos Canyon Block 818: Northern Gulf of Mexico,” *Mar. Pet. Geol.*, vol. 26, no. 8, pp. 1499–1512, Sep. 2009, doi: 10.1016/j.marpetgeo.2009.03.005.
- [165] K. Midttomme and E. Roaldset, “The effect of grain size on thermal conductivity of quartz sands and silts,” *Petroleum Geoscience*, vol. 4, no. 2, pp. 165–172, May 1998, doi: 10.1144/petgeo.4.2.165.
- [166] J. Sun *et al.*, “Numerical simulation on gas production from hydrate reservoir at the 1st offshore test site in the eastern Nankai Trough,” *J. Nat. Gas Sci. Eng.*, vol. 30, pp. 64–76, Mar. 2016, doi: 10.1016/j.jngse.2016.01.036.