Energy Proceedings
Vol 57, 2025
ISSN 2004-2965

ECPA Module: An Advanced Compositional Model for Enhanced Gas Recovery and CO_2 Storage in Porous Media Using an Association Equation of State

Wei Xiong [1,2*], Yu-Long Zhao [1], Shao-Mu Wen [3], Li-Li Liu [4], Zheng-Lin Cao [5], Xin Huang [6], Lie-Hui Zhang [1]

1 National Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, China

2 National Key Laboratory of Natural Gas Hydrate, Southwest Petroleum University, Chengdu, 610500, China

3 PetroChina Southwest Oil & Gas Field Company, Chengdu, Sichuan 610051, China

4 Exploration and Development Research Institute, PetroChina Changqing Oilfield Company, Xi'an, Shaanxi 710018, China

5 PetroChina Research Institute of Petroleum Exploration and Development, Beijing 100083, China

6 Research Institute of Natural Gas Technology, PetroChina Southwest Oil & Gasfield Company, Chengdu 610100, Sichuan

(*Corresponding Author: 18328068580@163.com)

ABSTRACT

Compositional simulation plays a vital role in understanding the behavior of multiple components within the captured CO_2, such as impurities or various injection scenarios, helping optimize the storage process and ensure its long-term safety and effectiveness. A new *ecpa* module in MATLAB Reservoir Simulation Toolbox (MRST) has been developed based on the electrolyte cubic-plus-association equation of state (e-CPA) to simulate enhanced gas recovery and CO_2 storage with CO_2 injection. The *ecpa* module combines Fickian diffusion, Langmuir adsorption, and the e-CPA equation of state to accurately describe phase equilibria and transport phenomena in complex systems such as CO_2-CH_4-H_2O-NaCl system. The e-CPA equation of state demonstrates superior accuracy over conventional models (e.g., PR EoS) in predicting vapor-liquid equilibria and phase behavior across a wide range of pressures and temperatures. For the CO_2-H_2O system, the e-CPA model achieves lower average absolute relative deviations (AARD: 5.93% for CO_2 solubility, 9.54% for H_2O content in gas) compared to Tsivintzelis's model (AARD: 8.52% and 15.55%, respectively). In the Barnett shale case study, accounting for sorption and diffusion increases CH_4 mass flow rates by 15–20%, highlighting their critical role in unconventional reservoir simulations. Comparisons with ECLIPSE and CMG (GEM) reveal strong agreement in CO_2-CH_4 mixing behavior, recovery factors, and breakthrough times. MRST (e-CPA) matches CMG's predictions for CH_4 production and CO_2 storage, validating its matrix-fracture coupling and thermodynamic consistency. The *ecpa* module, consolidated into the MRST framework, provides an open-source, state-of-the-art tool for simulating multicomponent flow in geological carbon storage, shale gas recovery, and enhanced hydrocarbon extraction. Its release in MRST 2025a will enable broader academic and industrial adoption, fostering advancements in subsurface energy systems.

Keywords: CCUS, enhanced gas recovery, CO_2 storage, brine, dual-permeability, e-CPA equation of state

NONMENCLATURE

Abbreviations	
AARD	Average absolute relative deviation
AD-OO	Automatic differentiation-object-oriented
CCUS	Carbon Capture, Utilization, and Storage
e-CPA	Electrolyte cubic-plus-association equation of state
EoS	Equation of state
MRST	MATLAB Reservoir Simulation Toolbox
PR	Peng-Robinson

This is a paper for International CCUS Conference 2025 (ICCUSC 2025), May 28-29, 2025, Beijing, China.

TPFA	Two-point flux approximation
Symbols	
m	Molality
p	Pressure
x	Molar fraction in liquid phase
y	Molar fraction in vapor phase

1. INTRODUCTION

As a predominant greenhouse gas contributing to global climate change, carbon dioxide (CO_2) necessitates urgent development of innovative strategies to mitigate anthropogenic emissions. Carbon Capture, Utilization, and Storage (CCUS) has emerged as a critical technological pathway for achieving decarbonization targets. Within CCUS implementation, numerical simulation serves as a cornerstone for project feasibility assessment, enabling precise prediction of geological reservoir capacities through sophisticated modeling of multiphase flow dynamics and sequestration mechanisms across temporal scales. Particularly, compositional simulation provides indispensable insights into complex multicomponent interactions inherent in captured CO_2 streams-including impurity phase behavior under varying pressure-temperature regimes and differential migration patterns during miscible/non-miscible injection scenarios. This advanced modeling capability facilitates optimization of storage reservoir engineering parameters while ensuring rigorous evaluation of long-term containment security and environmental efficacy.

Accurate phase equilibrium modeling of CCUS-associated fluids in briny formations constitutes a persistent scientific challenge in reservoir characterization. Bian et al.[1] established a computational framework integrating the Cubic Plus Association (CPA) equation of state (EoS)[2] with Wong-Sandler mixing rules[3], achieving robust solubility predictions for CO_2 in NaCl aqueous solutions under extreme reservoir conditions: pressure regimes (0-350 MPa), thermal gradients (288.15-523.15 K), and salinity variations (0-6 mol/kg H_2O). Parallel methodological development by Xiong et al.[4] employed CPA EoS coupled with Huron-Vidal mixing rules[5] to characterize CH_4 solubility in saline systems across analogous thermodynamic conditions encountered in subsurface reservoirs (*P*: 0-140 MPa; *T*: 298.15-512.15 K; *m*: 0-6 mol/kg H_2O). Notwithstanding these advancements, critical limitations persist in both formulations[1,4]. The domain-restricted applicability confined to pure gas solubility in monovalent salt systems significantly compromises predictive accuracy for gas-phase water content—a crucial parameter in multiphase flow simulations. Addressing this knowledge gap, Xiong et al.[6] recently pioneered an electrolyte CPA (e-CPA) EoS specifically engineered for CCUS fluid systems. This next-generation thermodynamic model demonstrates versatility in predicting multicomponent gas solubility (including CH_4, CO_2, H_2S, N_2, O_2, Ar, and atmospheric mixtures) within complex brine chemistry environments. Comparative analyses reveal the e-CPA framework's superior performance metrics over conventional approaches (e-PR, e-P-LJ, e-ALS, e-PT, e-PC-SAFT, e-SAFT-LJ), particularly in capturing non-ideal solution behaviors and long-range ion interactions characteristic of hypersaline reservoirs. This methodological advancement enables more reliable quantification of gas-brine interfacial phenomena critical for CO_2 injectivity analysis and storage integrity assessments.

High-fidelity thermodynamic derivatives constitute an essential prerequisite for reliable numerical simulation of CO_2 geological storage systems employing the e-CPA equation of state. Nevertheless, the inherent mathematical complexity arising from cross-association interactions poses significant numerical challenges in determining precise site fraction derivatives for multi-component associating fluids—a process conventionally constrained by iterative computational intensity. In a seminal methodological advancement, Xiong et al.[7] developed a universal explicit parameterization framework for cross-association mechanisms across diverse bonding typologies. The proposed paradigm innovatively derives the non-bonded fraction of cross-associating species through analytical relationships governing self-association systems, thereby circumventing the conventional iterative convergence requirements. This algorithmic acceleration achieved remarkable computational economy, demonstrating 70% reduction in central processing unit (CPU) time for both flash calculations and compositional simulations—a critical enhancement for field-scale CCUS modeling. The generalized formulation extends e-CPA's predictive domain to complex multiphase systems involving H_2O-CO_2-H_2S-N_2-O_2-Ar-SO_2-CH_4-C_2H_6-C_3H_8 mixtures, encompassing typical contaminants encountered in industrial CCUS streams. Benchmark analyses demonstrate quantitative agreement between e-CPA predictions and experimental phase behavior data across gas-liquid-solid equilibria, particularly under high-salinity

reservoir conditions where traditional models exhibit significant deviations.

The open-source MATLAB Reservoir Simulation Toolbox (MRST)[8] provides a compositional module incorporating two complementary formulations: (1) an overall composition formulation with global mole fractions and pressure as primary variables, and (2) a natural-variable formulation employing pressure combined with phase-specific mole fractions and saturations[9]. Thermodynamic closure is achieved through *K*-value correlations and cubic equations of state. Built upon an object-oriented architecture with automatic differentiation (AD-OO framework), the simulator enables flexible implementation of novel physical models and numerical schemes through operator overloading and symbolic differentiation techniques[8,9]. This extensible framework supports multiple discretization paradigms, though our current investigation focuses specifically on fully implicit coupling with two-point flux approximation (TPFA) spatial discretization and single-point upstream weighting.

Conventional cubic equations of state (e.g., Peng-Robinson[10]) exhibit significant limitations in modeling the complex phase equilibria of CO_2-impurity-brine systems encountered in geological carbon storage. These multicomponent systems manifest multifaceted intermolecular interactions spanning short-range repulsive forces, dispersive attractions, chemical association phenomena, long-range electrostatic ion interactions, and aqueous hydration effects[11]. This inherent complexity necessitates the development of a next-generation electrolyte-based compositional simulator specifically tailored for CCUS applications in brine-saturated porous media. Such an advanced simulator integrate a thermodynamically rigorous electrolyte equation of state capable of explicitly resolving both Coulombic interactions and solvation thermodynamics.

Recent advancements in numerical simulation of CO_2-EGR processes have been systematically demonstrated through a series of studies by Xiong's research team. In their foundational work[12], the researchers constructed an advanced compositional simulator by integrating MRST platform capabilities with the e-CPA thermodynamic model. Their framework incorporates critical mechanisms such as molecular diffusion and competitive adsorption, with subsequent analysis[13] quantitatively revealing that while diffusive transport accelerates CO_2 breakthrough times, selective adsorption phenomena positively influence both enhanced gas recovery and long-term carbon sequestration outcomes. Building upon these findings, Xiong et al.[14] subsequently developed a novel dual-permeability compositional model employing the CPA equation of state. This enhanced formulation enables comprehensive investigation of multiphysics coupling effects. The model's reliability was rigorously validated through dual-methodology verification using natural variable formulations and overall composition approaches, with comparative benchmarking against commercial CMG simulator results demonstrating satisfactory consistency.

Building on the capabilities of MRST, we developed an *ecpa* module that accurately characterizes the behavior of CCUS fluids in both gas reservoirs and brine-filled formations. The thermodynamic framework of the novel e-CPA equation of state was seamlessly incorporated into MRST's AD-OO architecture, enabling the creation of an advanced compositional simulator capable of utilizing either overall molar composition or natural variable formulations as primary variables. To enhance density calculations, the Peneloux volume translation technique was applied to refine the EoS-predicted volumes, while a new viscosity model (e-CPA-FV [15]) was developed to achieve superior accuracy in CCUS fluid viscosity predictions compared to conventional LBS methods.

2. RESULTS AND DISCUSSION

2.1 Comparison with other equation of state models

Tsivintzelis et al.[19] investigated cross-association between CO_2 and water, evaluating CO_2 as inert or with 2B, 3B, and 4C association structures. Their study modeled CO_2-water interactions both with and without cross-association, employing either combining rules or spectroscopic cross-solvation energies. Results demonstrated superior correlation for CO_2-water mixtures when explicit solvation was included, whereas treating CO_2 as self-associating yielded less satisfactory outcomes. Table 1 presents parameters from Tsivintzelis et al.[19], which include one electron acceptor for CO_2 and a modified CR-1 combining rule.

Table 1 CPA parameters optimized by Tsivintzelis et al. for CO_2-H_2O system*[19]

Association sites	k_{ij}	ε_{cross}	β_{cross}	Reference
CO_2 (0ed-1ea)	$-0.15508+0.000877$	8328	0.1836	[19]

*ed, electron donor; ea, electron acceptor. k_{ij}, binary interaction parameters; ε_{cross}, β_{cross} cross-associating strength parameters.

For the CO_2-H_2O system, both models perform well at low pressures (Figure 1). However, Tsivintzelis's model becomes unreliable above 100 MPa, as only the k_{ij} parameter is temperature-dependent. In contrast, our model incorporates a temperature-dependent cross-association factor (s_{ij}), critical for high-pressure/temperature accuracy. The proposed CPA model achieves AARDs of 5.93% (CO_2 solubility) and 9.54% (H_2O in gas phase), outperforming Tsivintzelis's 8.52% and 15.55%, respectively.

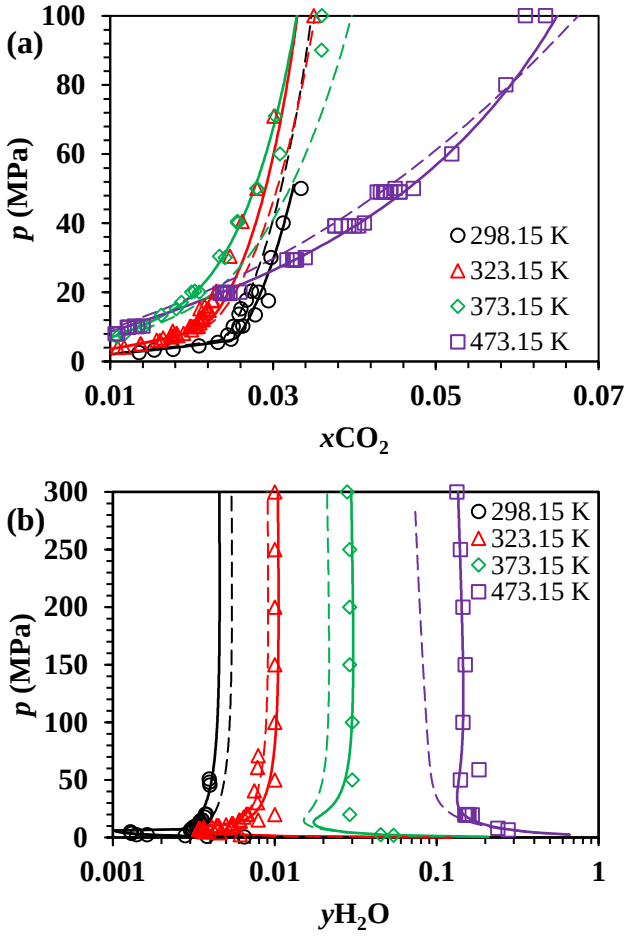

Fig. 1. Experimental and calculated (a) CO_2 solubility in the liquid phase and (b) H_2O content in the CO_2-rich phase for the H_2O-CO_2 system (298.15–473.15 K). Solid line: proposed model; dotted line: Tsivintzelis's model [19]. Data from Refs. [20–24]. (Following Figure S28 in [7])

2.2 Comparison with Olorode's model

Olorode et al.[25] developed an embedded discrete-fracture model (EDFM) using PR EoS for fractured reservoir simulations. We implemented a comparable MRST-based model substituting PR EoS with CPA EoS, validated against Barnett shale-gas reservoir data[25,26].

Case 1: Simulation parameters (Table 2) and domain geometry (Figure 2) were used to model 15 years of CH_4 production. The MRST framework integrates advanced modules, and our CPA-based CO_2 storage model (Zenodo: 10.5281/zenodo.10691505)[12] has been extended with a dual-porosity/dual-permeability model based on Xiong's work[12].

Table 2 Representative Barnett shale-gas model parameters[26]

Parameters	Values
Fracture half-length, x_f	91.4 m
Fracture width, w_f	3×10^{-3} m
Reservoir thickness, h	100.6 m
Matrix permeability, K_m	10^{-19} m^2
Fracture permeability, K_f	5×10^{-11} m^2
Matrix porosity, ϕ	0.04
Fracture porosity, ϕ_{frac}	0.33
Temperature, T	366.5 K
Well radius, r_w	0.1 m
Initial reservoir pressure, p_i	3.45×10^7 Pa
Initial mole fractions, z_i	[0.001 0.999]
Flowing bottom-hole pressure, p_{wf}	3.45×10^6 Pa
Tortuosity, τ	1
ρ_L of H_2O and CH_4	[0 2.99] kg/m^3
Langmuir pressure, p_L for H_2O and CH_4	[10.8 10.8]$\times10^6$ Pa
Diffusivity of H_2O and CH_4	[0, 2.5] $\times10^{-7}$ m^2/s

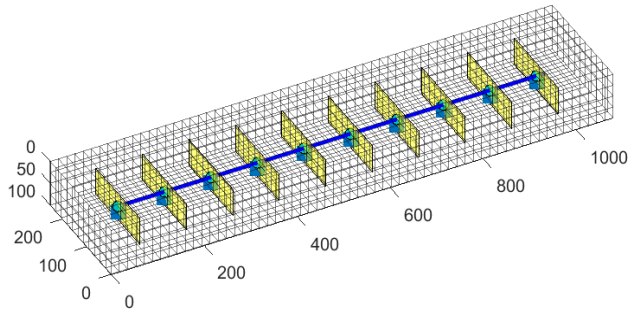

Fig. 2. Simple Barnett shale-gas simulation domain with 10 fractures. Dimensions are in meters[26]. (Following Figure 10.17 in [26])

Adsorption and diffusion significantly enhance CH_4 mass flow (Figure 3). Figure 3 demonstrates that adsorption and diffusion enhance the mass flow rate of CH_4 in shale gas reservoirs. MRST, a state-of-the-art simulator, incorporates advanced modules such as automatic differentiation, e-CPA, and EDFM. A CPA-EoS-based compositional model for CO_2 geological storage is accessible via the open-access Zenodo repository (doi: 10.5281/zenodo.10691505)[12]. However, this model

lacks dual-porosity or dual-permeability capabilities. To address this limitation, we developed a new dual-porosity/dual-permeability model by extending Xiong's framework[12] to incorporate multiple transport mechanisms. The self-contained source code for reproducing all simulations has been consolidated into the *ecpa* module and submitted to the Applied Computational Science group at SINTEF Digital for potential inclusion in the 2025a release.

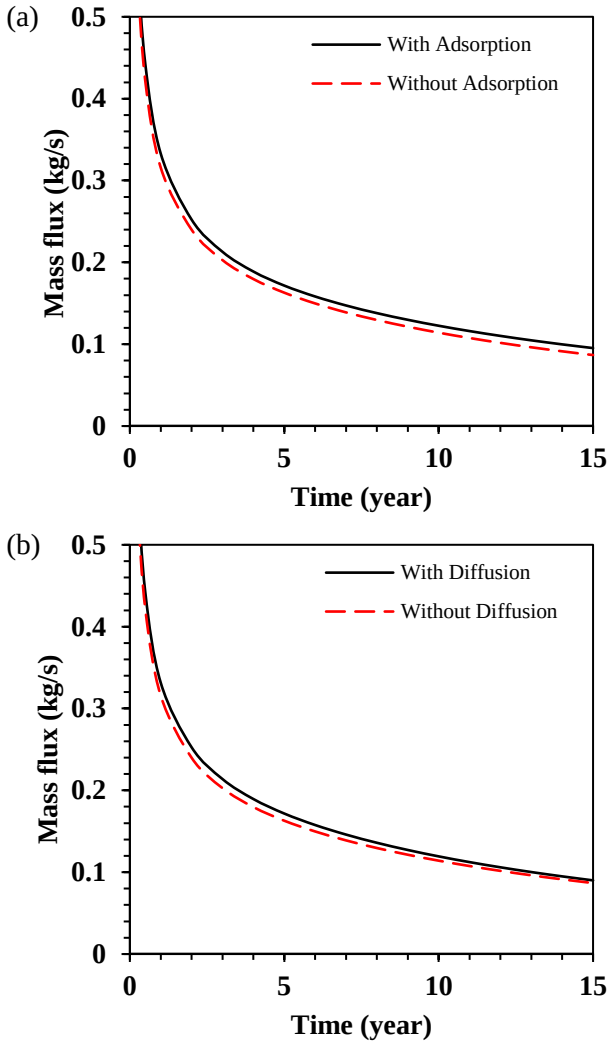

Fig. 3. Computed mass flow of CH_4 at extraction well. (a) with and without sorption; (b) with and without diffusion. (Following Figure S8 in [14])

2.3 Comparison with ECLIPSE

Case 2: Figure 4 illustrates a five-spot pattern representing a generic enhanced gas recovery scenario, comprising one injection well and four production wells. Due to symmetry, only a quarter of the domain is modeled. The discretization length is set to 4.572 m. Reservoir properties are detailed in Table 3. As depicted in Figure 4, CO_2 injection occurs in the lower left corner (spanning 4.572 m), while CH_4 production takes place in the upper right corner (also spanning 4.572 m).

Table 3 Reservoir properties and simulation parameters[27]

Property	
Quarter five-spot area	201.19 m × 201.19 m
Reservoir thickness	45.72 m
Porosity	0.23
Brine saturation	0
Reservoir temperature	66.7 ◦C
Initial pressure	35.5 bar
Coefficient of molecular diffusion	6e-7 m^2/s
Horizontal permeability	5e-14 m^2
Vertical permeability	5e-15 m^2

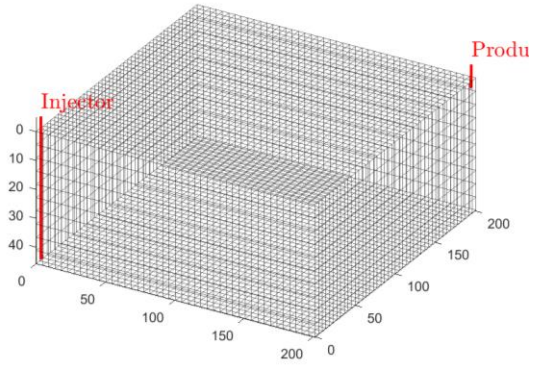

Fig. 4. Five-spot pattern depicting the CO_2 injection well and the CH_4 production wells (left). Reservoir geometry and well configuration used in this work (right). (Following Figure 7 in [13])

Two permeability fields were simulated: homogeneous (Table 3) and heterogeneous (Table 4). Notably, the mean horizontal permeability in Table 4 is 50 mD, with horizontal permeability being an order of magnitude greater than vertical permeability. The reservoir initially contains only CH_4, and all boundaries are no-flow. CO_2 is injected at 0.1 kg/s, while CH_4 production maintains a constant pressure of 35.5 bar. Table 5 present results from multiple compositional simulators. Heterogeneous permeability yields a marginally higher CH_4 recovery rate than homogeneous permeability, as CO_2 breakthrough at the production well is delayed. MRST (PR-LBC) and MRST (e-CPA-LBC) results align closely with ECLIPSE[27], whereas MRST (e-CPA-FV) shows earlier CO_2 breakthrough due to underestimated CO_2 viscosity in the e-CPA-FV model. Consequently, CH_4 recovery for MRST (e-CPA-FV) is lower than other models.

Table 4 Reservoir permeability from the bottommost layer 1 to the topmost layer 10[27]

Layer	Horizontal permeability (mD)	Vertical permeability (mD)
1	60	6
2	60	6
3	100	10
4	5	0.5
5	20	2
6	90	9
7	40	4
8	5	0.5
9	20	2
10	100	10

produced at the production well. This study focuses on investigating the mechanisms of EGR and CO_2 storage in depleted carbonate gas reservoirs, neglecting spatial heterogeneity observed in practical reservoir conditions. The reservoir temperature is 358.89 K. Both the matrix and fractures exhibit an initial pressure of 5.5 MPa, with H_2O saturation set to zero in both domains. The porosities of the matrix and fractures are 0.05 and 0.01, respectively. Matrix permeabilities in the *x*-, *y*-, and *z*-directions are 0.1, 0.1, and 0.01 mD, respectively, while fracture permeability is 5 mD. Fractures are spaced 10 m apart. Injection and production wells are positioned on the left and right boundaries of the model, respectively. The CO_2 injection rate is 2×10^5 m³/day (equivalent to 3.62×10^5 kg/day), and the production well maintains a bottom-hole pressure of 5.5 MPa. Initially, the reservoir contains pure CH_4 with a CO_2 molar fraction of zero. A 30-year CO_2 injection simulation is conducted using multiple simulators incorporating Kazemi's shape factor. The binary interaction parameter of 0.105 is applied to modify the phase behavior of the CO_2-CH_4 system, and the corresponding value for the CPA EoS is set to 0.1. For simplicity, diffusion and adsorption mechanisms are excluded from this analysis.

Table 5 Key results for the simulations[13]

Model	Homogeneous permeability			Heterogeneous permeability		
	Production well shut-in time (days)	CO_2 mass fraction in extraction well (%)	Recovery factor (%)	Production well shut-in time (days)	CO_2 mass fraction in extraction well (%)	Recovery factor (%)
MRST (PR-LBC)	1800	20.93	50.46	1890	20.54	57.28
MRST (e-CPA-LBC)	1800	23.13	52.51	1890	23.35	59.44
MRST (e-CPA-FV)	1260	22.14	36.07	1620	20.59	37.22
ECLIPSE	1727	20.00	50.00	1843	20.00	55.00

2.4 Comparison with CMG

Case 3: A three-dimensional reservoir geometry is depicted in Figure 5. The reservoir is discretized into 40 × 19 × 10 grid cells, with each cell measuring 2000 × 950 × 100 m in physical dimensions. Currently, the recovery rate in actual gas production reaches 85.15%, while the average formation pressure is maintained at 5.5 MPa. Due to reservoir energy depletion, CH_4 is no longer

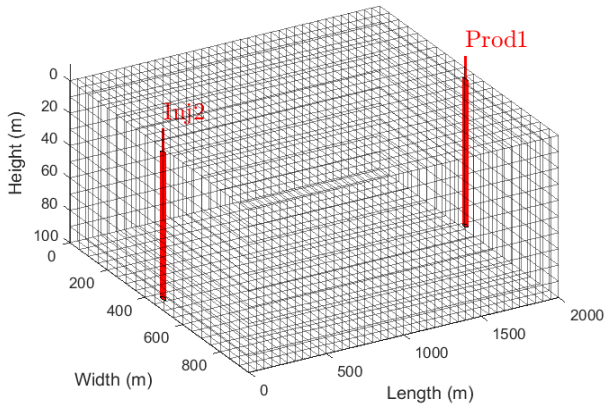

Fig. 5. Reservoir geometry and well configuration used in Case 3. (Following Figure 3 in [14])

The extended Langmuir model is implemented in CMG simulations. The maximum molar adsorption capacity for CH_4 and CO_2 is set to 0.33 mol/kg and 0.50 mol/kg per unit mass of rock, respectively (rock density = 3000 kg/m³). Corresponding Langmuir pressures are defined as 2.5 MPa for CH_4 and 2.0 MPa for CO_2. As shown in Figure 6, MRST simulations incorporating the adsorption mechanism exhibit good agreement with CMG results. However, the CH_4 mass rate predicted by CMG falls below that of MRST after 13 years, likely due to differences in mathematical formulations and numerical discretization methods. For instance, MRST employs a finite volume discretization scheme, whereas CMG utilizes a finite difference approach.

The diffusivity of CH_4/CO_2 in CMG is set to 0.00152 cm^2/s. The simulations of MRST for considering the diffusion mechanism agree with that of CMG in Figure 7, which indicates that the diffusion is correctly implemented in MRST.

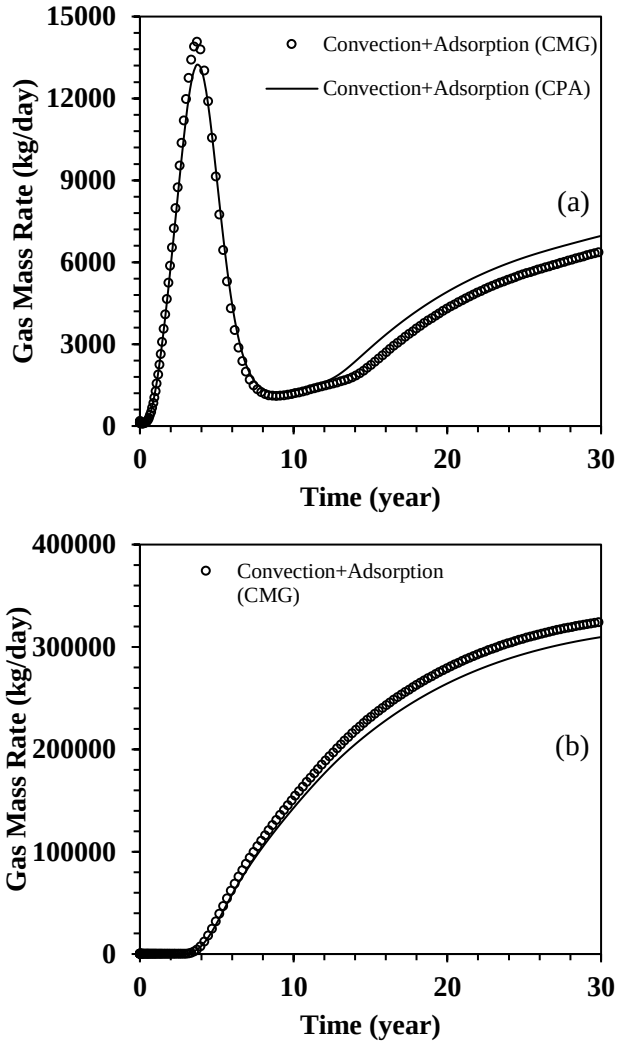

Fig. 6. Computed mass flow of CH_4 (a) and CO_2 (b) at extraction well using MRST and CMG simulators. Simulations consider the convection and adsorption mechanisms. The system is CO_2–CH_4 system. (Following Figure S1 in [14])

When the convection, diffusion, and adsorption mechanisms are taken into account, the CH_4 mass rate of CMG and MRST is almost the same in Figure 8(a). However, the CO_2 mass rate of CMG is significantly higher than that of MRST in Figure 8(b). The reason is that the mathematical model and numerical solution of MRST are fundamentally different from those of CMG.

2.5 Comparison with Hassanzadeh's model

Case 4: This example, adapted from Hassanzadeh[29], examines a setup more representative of potential carbon storage operations. Supercritical CO_2 is injected into a homogeneous saline aquifer at a constant volumetric rate via a single well over a two-year period.

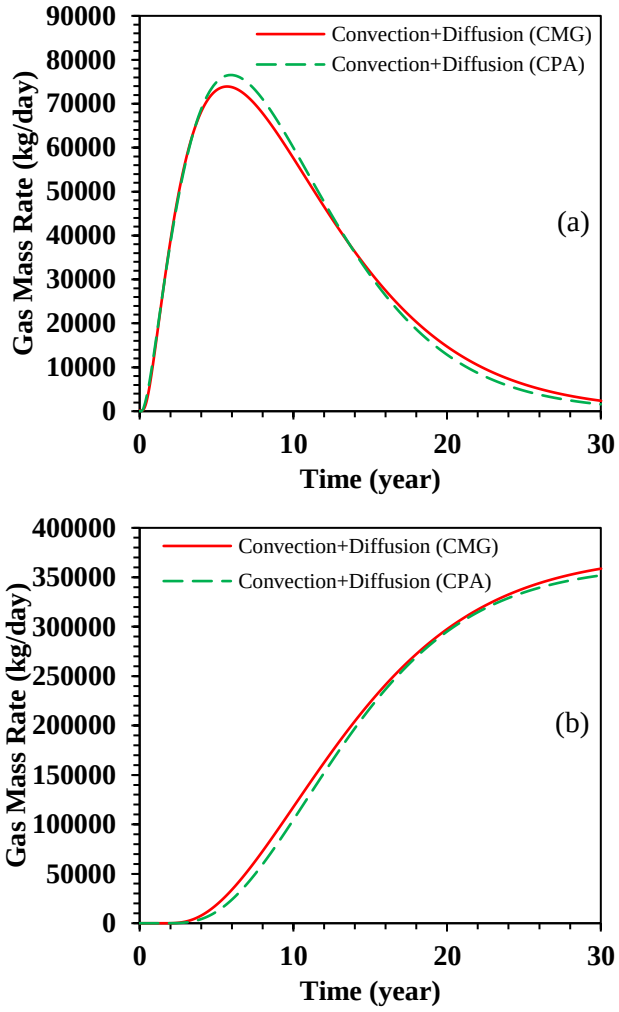

Fig. 7. Computed mass flow of CH_4 (a) and CO_2 (b) at extraction well using MRST and CMG simulators. Simulations consider the convection and diffusion mechanisms. The system is CO_2–CH_4 system. (Following Figure S2 in [14])

The injection well is positioned on the western boundary of the domain and perforated near the formation's base. Following injection cessation, the displaced CO_2 plume continues to migrate and dissolve into the resident brine. Key fluid and formation properties are summarized in Table 6.

The aquifer is assumed to be impermeable on all boundaries except the eastern boundary, where a constant pressure boundary condition is imposed to simulate outflow and mitigate overpressurization. The study domain comprises a $5000 \times 1 \times 39$ m^3 vertical cross-section discretized on a 99×39 rectilinear grid. The mesh

is refined laterally around the injection well, with a minimum grid spacing of 1 m adjacent to the well and a maximum spacing of 99 m at the domain's eastern boundary, located 5 km from the well.

Table 6 Parameters used for Case 4[12]

Fluid properties	
temperature	38 ℃
pressure	12 MPa
salinity	0.68 mol/kg
CO2 content	0
diffusivity	2e-9 m^2/s
Formation properties	
porosity	0.18
permeability	100 mD
rock compressibility	8e-5 bar^{-1}
Model domain	
height	39 m
width	1 m
length	5000 m

Hassanzadeh[29] employed an activity-based thermodynamic model incorporating both activity coefficients and fugacity coefficients. This asymmetric framework models the gas phase using an equation of state and the liquid phase with an activity coefficient approach. Under nonlinear relative permeability conditions, the vapor phase migrates upward, reaching saturation levels approaching 0.7 in the uppermost formation layer. This phenomenon aligns with previous observations by Miri and Hellevang[30], who identified a dry-out zone separated from the saturated brine by an unsaturated two-phase flow region (cf. Fig. 2 in their work). Consequently, future investigations will focus on salt precipitation dynamics under these conditions. CO_2 solubility trapping decreases by up to 74% as salt concentration increases from 0 to 6 mol/kg water. Notably, the PR equation of state underestimates CO_2 solubility in pure water compared to the experimental data.

3. CONCLUDING REMARKS

This study presents the *ecpa* module, which integrates advanced thermodynamic modeling with multicomponent transport mechanisms. The *ecpa* module combines Fickian diffusion, Langmuir adsorption, and the e-CPA equation of state to accurately describe phase equilibria and transport phenomena in complex systems such as CO_2-CH_4-H_2O-NaCl system. Key findings from the comparative analyses are summarized as follows:

Thermodynamic Modeling: The e-CPA equation of state demonstrates superior accuracy over conventional models (e.g., PR EoS) in predicting vapor-liquid equilibria and phase behavior across a wide range of pressures and temperatures. For the CO_2-H_2O system, the e-CPA model achieves lower average absolute relative deviations (AARD: 5.93% for CO_2 solubility, 9.54% for H_2O content in gas) compared to Tsivintzelis's model (AARD: 8.52% and 15.55%, respectively), particularly under high-pressure conditions (>100 MPa). The inclusion of temperature-dependent cross-association parameters in e-CPA further enhances its predictive capability for high-temperature reservoirs.

Adsorption and Diffusion Mechanisms: The integration of Langmuir adsorption and Fickian diffusion significantly impacts shale gas recovery. In the Barnett shale case study, accounting for sorption and diffusion

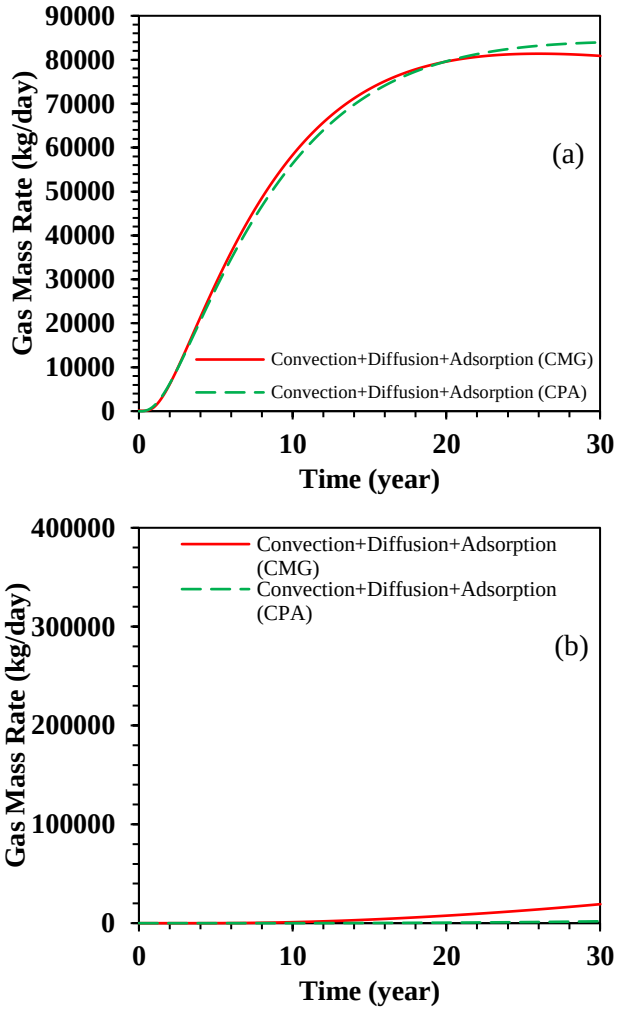

Fig. 8. Computed mass flow of CH_4 (a) and CO_2 (b) at extraction well using MRST and CMG simulators. Simulations consider the convection, diffusion, and adsorption mechanisms. The system is CO_2–CH_4 system. (Following Figure S3 in [14])

increases CH_4 mass flow rates by 15–20%, highlighting their critical role in unconventional reservoir simulations. The dual-porosity/dual-permeability implementation in MRST (e-CPA) successfully captures matrix-fracture interactions, aligning with results from Olorode's EDFM model and commercial simulators like CMG.

Validation Against Commercial Simulators: Comparisons with ECLIPSE and CMG (GEM) reveal strong agreement in CO_2-CH_4 mixing behavior, recovery factors, and breakthrough times.

Field-Scale Applicability: The 3D simulation of CO_2-enhanced gas recovery (EGR) in a fractured carbonate reservoir demonstrates the module's robustness in large-scale scenarios. MRST (e-CPA) matches CMG's predictions for CH_4 production and CO_2 storage, validating its matrix-fracture coupling and thermodynamic consistency. Adsorption and diffusion mechanisms, when activated, further align MRST with CMG's results, though differences in numerical solvers (finite volume vs. finite difference) lead to minor deviations in late-stage CO_2 breakthrough profiles.

Limitations and Future Work: While the *ecpa* module excels in high-pressure/temperature regimes, its current formulation does not account for salt precipitation effects, which may influence CO_2 solubility trapping in saline aquifers. Future extensions will incorporate salt precipitation dynamics and optimize computational efficiency for industrial-scale applications.

The *ecpa* module, consolidated into the MRST framework, provides an open-source, state-of-the-art tool for simulating multicomponent flow in geological carbon storage, shale gas recovery, and enhanced hydrocarbon extraction. Its release in MRST 2025a will enable broader academic and industrial adoption, fostering advancements in subsurface energy systems.

ACKNOWLEDGEMENT

This research is supported by the State Key Program of National Natural Science Foundation of China (No. U23A2022), State Key Program of National Natural Science Foundation of China (No. 52234003), National Science Fund for Excellent Young Scholars (No. 52222402), National Natural Science Foundation of China (No. 52474047), Sichuan Science and Technology Program (No. 2024JDRC0087), National Science and Technology Major Project (No. 2024ZD1406601), and Science and Technology Cooperation Project of the CNPC-SWPU Innovation Alliance (No. 2020CX020202 and 2020CX030202). We thank Dr. Knut-Andreas Lie, Olav Møyner, and Kai Bao, currently with SINTEF Digital, for helpful technical discussions.

DECLARATION OF INTEREST STATEMENT

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

REFERENCE

[1] Bian XQ, Xiong W, Kasthuriarachchi DTK, Liu YB. Phase equilibrium modeling for carbon dioxide solubility in aqueous sodium chloride solutions using an association equation of state. Ind Eng Chem Res 2019;58: 10570-10578.

[2] Kontogeorgis GM, Voutsas EC, Yakoumis IV, Tassios DP. An equation of state for associating fluids. Ind Eng Chem Res 1996;35: 4310-4318.

[3] Wong DSH, Sandler SI. A theoretically correct mixing rule for cubic equations of state. AIChE J 1992;38: 671-680.

[4] Xiong W, Bian XQ, Liu YB. Phase equilibrium modeling for methane solubility in aqueous sodium chloride solutions using an association equation of state. Fluid Phase Equilib 2020;506: 112416.

[5] Huron MJ, Vidal J. New mixing rules in simple equations of state for representing vapour-liquid equilibria of strongly non-ideal mixtures. Fluid Phase Equilib. 1979;3: 255-271.

[6] Xiong W, Zhang LH, Tian Y, Li LX, Zhao YL, Chen ZX. Phase equilibrium modeling for carbon dioxide capture and storage (CCS) fluids in brine using an electrolyte association equation of state. Chem Eng Sci 2023;275: 118723.

[7] Xiong W, Zhang LH, Zhao YL, Wen SM, Liu LL, Cao ZL, Jiang XY. Phase equilibrium modeling for CCUS fluids using a modified association equation of state. J Supercrit Fluids 2025;219: 106543.

[8] Lie KA. An introduction to reservoir simulation using MATLAB/GNU Octave: User guide for the MATLAB Reservoir Simulation Toolbox (MRST). Cambridge: Cambridge University Press; 2019.

[9] Møyner O. Compositional simulation with the AD-OO framework. In Lie KA, Møyner O, editors. Advanced Modeling with the MATLAB Reservoir Simulation Toolbox, Cambridge: Cambridge University Press; 2021, p. 324-374.

[10] Guo JJ, Xiong W, Hu QY, Tian Y, He X, Zhang LH, Zhang T. Stability Analysis and Two-Phase Flash Calculation for Confined Fluids in Nanopores Using a Novel Phase Equilibrium Calculation Framework. Ind Eng Chem Res 2022;61: 2306-2322.

[11] Ahmed S, Ferrando N, De Hemptinne JC, Simonin JP, Bernard O, Baudouin O. Modeling of mixed-solvent electrolyte systems. Fluid Phase Equilib 2018;459: 138-157.

[12] Xiong W, Zhang LH, Zhao YL, Wen SM, Bao K, Møyner O, Lie KA. Compositional simulation for carbon storage in porous

media using an electrolyte association equation of state. SPE J 2024;29: 3314-3336.
[13] Xiong W, Zhao YL, Wen SM, Zhang BN, Huang X, Wang YC, Zhang T. Influence of Diffusion, Adsorption, Connate Water, and Salinity on Enhanced Gas Recovery and Carbon Storage Reservoir Simulations. Energy Fuels 2024;38: 12645-12657.
[14] Xiong W, Zhao YL, Zhang LH, Wen SM, Liu LL, Cao ZL, Jiang XY. Mechanism study of enhanced gas recovery and CO_2 storage in naturally fractured carbonate reservoirs using a dual-permeability model coupled with association equation of state. Gas Sci Eng 2025;139: 205632.
[15] Xiong W, Zhang LH, Zhao YL, Hu QY, Tian Y, He X, Zhang T. Prediction of the viscosity of natural gas at high temperature and high pressure using free-volume theory and entropy scaling. Pet Sci 2023;20: 3210-3222.
[16] dos Santos PF, André L, Ducousso M, Contamine F, Cézac P. Experimental measurement of CO_2 solubility in aqueous Na_2SO_4 solution at temperatures between 303.15 and 423.15 K and pressures up to 20 MPa. J Chem Eng Data 2020;65: 3230-3239.
[17] Wiebe R, Gaddy VL. Vapor phase composition of carbon dioxide-water mixtures at various temperatures and at pressures to 700 atmospheres. J Am Chem Soc 1941;63: 475-477.
[18] NIST Chemistry WebBook. (2023, January 30). NIST Standard Reference Database Number 69. Retrieved from https://doi.org/10.18434/T4D303.
[19] Tsivintzelis I, Kontogeorgis GM, Michelsen ML, Stenby EH. Modeling phase equilibria for acid gas mixtures using the CPA equation of state. Part II: Binary mixtures with CO_2. Fluid Phase Equilib 2011;306: 38-56.
[20] Valtz A, Chapoy A, Coquelet C, Paricaud P, Richon D. Vapour–liquid equilibria in the carbon dioxide–water system, measurement and modelling from 278.2 to 318.2 K. Fluid phase equilib 2004;226: 333-344.
[21] Bamberger A, Sieder G, Maurer G. High-pressure (vapor+liquid) equilibrium in binary mixtures of (carbon dioxide+water or acetic acid) at temperatures from 313 to 353 K. J Supercrit Fluids 2000;17: 97-110.
[22] Briones JA, Mullins JC, Thies MC, Kim BU. Ternary phase equilibria for acetic acid-water mixtures with supercritical carbon dioxide. Fluid Phase Equilib 1987;36: 235-246.
[23] Guo H, Chen Y, Hu Q, Lu W, Ou W, Geng L. Quantitative Raman spectroscopic investigation of geo-fluids high-pressure phase equilibria: Part I. Accurate calibration and determination of CO_2 solubility in water from 273.15 to 573.15 K and from 10 to 120 MPa. Fluid Phase Equilib 2014;382: 70-79.
[24] Hou SX, Maitland GC, Trusler JM. Measurement and modeling of the phase behavior of the (carbon dioxide+ water) mixture at temperatures from 298.15 K to 448.15 K. J Supercrit Fluids 2013;73: 87-96.
[25] Olorode O, Wang B, Rashid HU. Three-dimensional projection-based embedded discrete-fracture model for compositional simulation of fractured reservoirs. SPE J 2020;25: 2143-2161.
[26] Lie KA, Møyner O. Advanced modelling with the MATLAB reservoir simulation toolbox. Cambridge: Cambridge University Press; 2021.
[27] Class H, Ebigbo A, Helmig R, Dahle HK, Nordbotten JM, Celia MA, Wei L. A benchmark study on problems related to CO_2 storage in geologic formations: summary and discussion of the results. Computat geosci 2009:13: 409-434.
[28] Computer Modelling Group. (2019.10). CMG GEM Manual. Retrieved from https://www.cmgl.ca/solutions/software/gem/.
[29] Hassanzadeh H. Mathematical Modeling of Convective Mixing in Porous Media for Geological CO_2 Storage. Canada: University of Calgary; 2006.
[30] Miri R, Hellevang H. Salt precipitation during CO_2 storage—A review. Int J Greenh Gas Con 2016;51: 136-147.