Capillarity

Vol. 15, No. 3, p. 53-57, 2025

Perspective

Experimental techniques for studying interfacial dynamics and sediment response during CH_4-CO_2 hydrate replacement

Shuang Cindy Cao[1], Xianglong Li[1], Jongwon Jung[2], Xiaoshuang Li[1]*

[1]*School of Urban Construction, Changzhou University, Changzhou 213000, China*
[2]*School of Civil Engineering, Chungbuk National University, Chungbuk 28644, Korea*

Keywords:
Carbon sequestration
CH_4-CO_2 replacement
hydrate-bearing sediments

Cited as:
Cao, S. C., Li, X., Jung, J., Li, X. Experimental techniques for studying interfacial dynamics and sediment response during CH_4-CO_2 hydrate replacement. Capillarity, 2025, 15(3): 53-57.
https://doi.org/10.46690/capi.2025.06.01

Abstract:
Methane hydrates are a largely untapped energy resource with the potential to support carbon sequestration through CH_4-CO_2 exchange. However, large-scale methane recovery from hydrate-bearing sediments remains constrained by key uncertainties related to sediment stability, multiphase fluid dynamics, and geomechanical responses during gas production. One of the key scientific challenges is to understand the transient interface dynamics and mechanical weakening of hydrate deposits during CH_4-CO_2 displacement, especially the unexplained effects of pore water meniscus surface evolution and its influence on sediment stability. This study reviews CH_4-CO_2 replacement methods, including microscale piezoelectric sensing, triaxial testing, and real-time resistivity monitoring. It quantifies displacement efficiency and hydrate dissociation geomechanics while analyzing interfacial dynamics and sediment behavior during exchange process.

1. Introduction

Methane hydrate is considered a clean energy resource, with global reserves estimated at between 500 and 10,000 gigatons of carbon (Collett et al., 2002). Methane gas hydrates are found in marine continental margins and permafrost sediments worldwide under low-temperature, high-pressure conditions. Traditional methane extraction methods such as depressurization and thermal stimulation face technical and environmental challenges. However, the CH_4-CO_2 replacement technique presents an alternative. This method not only enables methane recovery but also supports carbon sequestration, offering a dual benefit supported by thermodynamic feasibility and experimental validation. Under moderate conditions (e.g., 2 MPa, 2 °C), CO_2 can displace CH_4 in the hydrate by leveraging their chemical potential difference while maintaining the structural integrity of the surrounding sediments (Jung et al., 2010). The extent of the reaction and its efficiency in real systems are determined by multiple factors and coexisting processes, including pressure- and temperature-dependent solubility, interfacial properties, permeability, and density differences between water and CO_2, as well as invasion patterns, the specific surface area of the hydrate phase, fluid expansion after replacement, and changes in effective stress (Jung et al., 2010; Espinoza et al., 2011; Cai et al., 2025). These coupled phenomena ultimately dictate replacement efficiency. Given these phenomena and considerations, this work primarily focuses on current experimental insights into CH_4-CO_2 replacement efficiency and its effects on the strength of hydrate-bearing sediments, with particular emphasis on quantifying geomechanical impacts of hydrate dissociation and elucidating interfacial dynamics and sediment behavior during CH_4-CO_2 hydrate exchange. The latest experimental techniques and results associated with the CH_4-CO_2 replacement

Yandy Scientific Press

---

*Corresponding author.

E-mail address: scaocindy@cczu.edu.cn (S. C. Cao); S24210814007@smail.cczu.edu.cn (X. Li); jjung@chungbuk.ac.kr (J. Jung); xsli2011@126.com (X. Li).

Received April 23, 2025; revised May 12, 2025; accepted May 22, 2025; available online May 24, 2025.

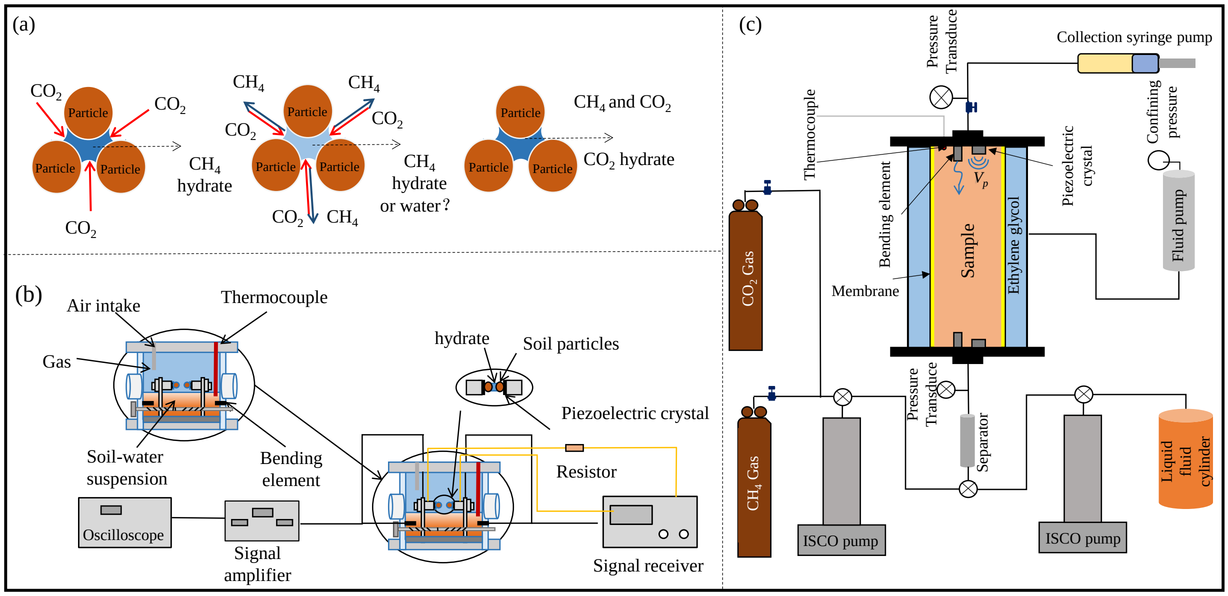

Fig. 1. Innovative mechanism and experimental apparatus for interfacial dynamics and mechanical response in CH_4-CO_2 hydrate replacement. (a) CH_4-CO_2 replacement in isolated hydrate between particles: CO_2 invasion into CH_4 hydrate-bearing sediments; CH_4-CO_2 replacement process; and replacement completion, (b) microscale mechanical changes during hydrate replacement measured using a piezoelectric crystal adapted for high-pressure reactor applications and (c) macroscopic mechanical changes during hydrate replacement measured by a triaxial apparatus.

process are compiled in (Table. 1).

2. Replacement efficiency and electromechanical response characteristics of hydrates in porous media

CH_4-CO_2 replacement rate primarily means how fast CH_4 hydrate changes to CO_2 hydrate without considering of CH_4 hydrate dissociation (Fig. 1(a)). To replace CH_4 in hydrate with invading CO_2, the structure of hydrate must be broken. This will cause the water meniscus to remain between particles (Fig. 1(a)) and affect the stability of sediments due to the additional pore-water pressure. However, there is still no consideration of how long the water meniscus remains between particles during CH_4-CO_2 replacement before CO_2 hydrate forms. Thus, the fundamental question remains poorly understood "How rapidly does CH_4-CO_2 replacement occur, and how does it affect the strength of hydrate-bearing sediments?". This critical knowledge gap impedes advancements in intelligent methane production from hydrate-bearing sediments via CH_4-CO_2 replacement technology. Therefore, this section will systematically analyze existing experimental methodologies for assessing the stability of hydrate-bearing sediments during CH_4-CO_2 replacement and provide forward-looking perspectives.

Conventional geomechanical testing systems typically analyze single variables and phase responses, in contrast to reservoir conditions where hydrate dissociation and reformation involve coupled thermal-hydraulic-mechanical-chemical (THMC) processes. This complexity exceeds traditional testing capabilities, particularly in quantifying mechanical-seepage coupling. Therefore, sensing systems integrating high-resolution monitoring are essential for correlating microstructural hydrate evolution with macro-scale mechanical behavior, and real-time monitoring of replacement efficiency has emerged as a critical factor for process optimization. Given their real-time capability and non-invasive features, conductivity-based measurement techniques could serve as a core methodology. These conductivity-based techniques are particularly effective for capturing the dynamic changes during CH_4-CO_2 replacement. Resistivity, as a key parameter for assessing the abundance and spatial distribution of natural gas hydrates, is closely related to the dynamic evolution mechanism and multiphysics coupling. The resistivity can link medium resistance to voltage parameters via series resistors, enabling dynamic monitoring (Jung et al., 2010).

The theoretical framework has been validated by numerous experimental studies using multiscale methods. For example, particle-scale simulations that integrate resistivity and shear wave stiffness measurements elucidate the coupled evolution of displacement dynamics and mechanical strengthening (Espinoza et al., 2011). Columnar experiments show that hydrate cementation has a dual regulatory effect on acoustic and electrical properties, with CO_2 hydrates significantly increasing P-wave velocity and resistivity (Ren et al., 2010; Jung et al., 2011). Additionally, the diffusion coefficient of water molecules increases with increasing of pore size and temperature (Liu et al., 2023). These findings collectively underscore the importance of balancing thermodynamic control and multiphysics monitoring for optimizing hydrate replacement strategies. On the other hand, in clayey silt hydrate reservoirs, fracture conductivity demonstrates a linear decrease under

Table 1. Recent experimental methods and results of the CH_4-CO_2 replacement.

Method	State	Temp. (K)	Pres. (MPa)	Findings	References
Replacement in sediments	Quartz; Kaolin; Montmorillonite; Silt	274.15	3.3	Minor effects in quartz with kaolin; Promoting CH_4 extraction but inhibits CO_2 in Montmorillonite; Compression in water-bearing silty.	Mu et al. (2023, 2024); Gambelli et al. (2021); Luo et al. (2022)
		274.15	8.5		
		275.45	6.6		
		274.15	5.0		
Depressurization-assisted replacement	CO_2	274.2	3.3	Significantly improves the replacement efficiency.	Chaturvedi et al. (2023); Choi et al. (2022); Choi et al. (2024)
	CO_2	274.2	3.1		
	CO_2	274.2	3.1		
Mixed-gas replacement	Mixed CO_2/N_2	283.8	11	Methane hydrate dissociation rate is higher; CH_4 recovery is higher; CO_2 storage rate is increased.	Niu et al. (2023); Cao et al. (2024a)
		284.0	9.4		
		275.0	3.7		
Thermal-assisted replacement	CO_2	273.6-303.1;	4.10	Improves the CH_4 recovery rate.	Xu et al. (2019); Zhang et al. (2017)
	CO_2	273.6-279.1	3.70		

increasing closure pressure, whereas thermal conductivity variations emerge between gas-dominant and water-dominant systems, with saturation-dependent patterns revealing phase distribution dominance (Wang et al., 2025). During hydrate phase transitions, nonlinear coupling emerges among thermal conductivity, temperature, porosity, and saturation, modulated by effective stress and kinetic constraints (Wang et al., 2024a; Tang et al., 2025). Furthermore, at the microscale, the distribution pattern of hydrates (contact, suspension, or cemented) significantly affects conductivity by reconstructing the pore network (including throat contraction and increased path tortuosity). The salt exclusion effect reduces resistivity in contact-dominated hydrate distributions, whereas CO_2 hydrates induce sustained resistivity increases through continuous nucleation mechanisms (Cao et al., 2024b). Cross-hole resistivity tomography reveals that methane hydrate formation alters pore water conductivity via salt ion exclusion, with resistivity evolution strongly linked to pore water salinity dynamics. Moreover, the formation of CO_2 hydrates can cause a continuous increase in resistivity, while methane hydrate generation leads to increased pore water salinity and local resistivity decreases through salt ion exclusion mechanisms (Liu et al., 2024).

Taken together, the evidence suggests that the hydrate accumulation process is accompanied by heat release, ion migration, and multi-component consumption, resulting in complex thermal-flow-fluid coupling effects that cause resistivity to exhibit non-monotonic changes (Jung et al., 2015). Existing models still have systematic biases regarding the coupling effects of salt redistribution, thermodynamic constraints, and stress fields, necessitating the establishment of a comprehensive evaluation system that includes multi-component consumption rates, phase-state intermixing characteristics, and dynamic responses in resistivity. In summary, the quantitative characterization and mechanism model of resistivity evolution in the replacement process still need to be further improved.

3. Mechanical stability and experimental methods for hydrate replacement

Hydrates within sediment pores increase stiffness and strength of sediments. However, dissociation during replacement may weaken the sediment skeleton and change its permeability. Thus, real-time monitoring of hydrate saturation and mechanical effects is important. Comparable compressibility and expansion behaviors characterize CH_4 and CO_2 hydrate-bearing silty sediments, with CO_2 systems demonstrating attenuated volumetric contraction during phase transitions (Luo et al., 2020). Enhanced sediment strength through crystal bridging effects has been documented in CO_2-dominated environments, yet critical knowledge gaps persist regarding coupled phase interaction dynamics and long-term stability thresholds during multicomponent gas replacement processes. Furthermore, CH_4 and CO_2 hydrates exhibit similar shear strength and comparable compression-expansion characteristics in sandy sediments, but CO_2 hydrates in silty sediments show weaker shrinkage (Hyodo et al., 2014). Triaxial studies of hydrate-bearing sediments (silty-clay and sandy) under isotropic/deviatoric stresses have quantified their mechanical responses and temperature/confining pressure dependencies. While triaxial systems are capable of simulating THM-coupled environments, direct mechanical assessment during gas replacement remains limited by the stringent thermodynamic stability required during phase transitions. On the other hand, fine-grained hydrate-bearing sand exhibits brittle failure under low confining pressure but transitions to plastic deformation at high pressure (Zhou et al., 2021). Hydrate saturation and confining pressure jointly influence shear strength and modulus, though excessive saturation (> 30%) may induce cementation brittleness (Li et al., 2021; Liu et al., 2022).

Particle-scale monitoring techniques have been employed in prior investigations to elucidate the micro-scale mechanisms governing these mechanical behaviors. P-wave (compressional wave) propagation characteristics (velocity, amplitude), directly related to elastic modulus and density, serve as effective stiffness indicators. For example, sand grains, acting as Hertzian stiffness sensors, can sensitively capture contact condition changes. Piezoelectric crystal testing generates P-waves and measures signal amplitudes, offering high-resolution stiffness tracking during replacement (Fig. 1(b)). Minor variations in hydrate saturation substantially enhance P- and S-wave velocities (Espinoza et al., 2011). Combined cantilever beam strain gauges and full-bridge circuit-oscilloscope systems dynamically quantify shear stress evolution in silicate minerals, with results directly correlating to hydrate cementation effects on particulate assemblies. (Jung et al., 2011).

Based on previous findings, it is imperative to develop novel experimental apparatuses. Piezoelectric crystals and bender elements generate and receive P- and S-waves, while thermocouples and pressure sensors monitor temperature and pore pressure. Integrating these components with signal generators, oscilloscopes, and data loggers in a customized triaxial apparatus (Fig. 1(c)) enables real-time detection of mechanical changes. The system dynamically couples gas (CH_4/CO_2) and liquid (pore water/brine) seepage fields with stress-temperature fields, simulating transient phase transitions during reservoir exploitation. This approach not only elucidates multiphase seepage effects on shear strength, volumetric strain, and permeability anisotropy but also establishes coupled constitutive equations for reservoir stability prediction and process optimization.

4. Challenges and perspectives

The research on CH_4-CO_2 hydrate replacement still faces critical challenges. Current experimental techniques mainly focus on replacement rates but overlook CH_4 hydrate dissociation and fail to monitor real-time coupled processes such as pore-pressure buildup and effective stress reduction. Unresolved water meniscus dynamics during hydrate breakdown, combined with unquantified pore-volume expansion effects, critically impact sediment stability and may induce shear failure or fracture formation. Additionally, replicating reservoir-scale dynamics in laboratory settings remains difficult, and standardized protocols for quantifying volume expansion are lacking.

Future advancements should prioritize integrated approaches, combining microfluidic-nanoCT imaging to track meniscus lifetime and methane migration with coupled THMC monitoring (acoustic emission, Raman spectroscopy, and PIV) to resolve interfacial dynamics and sediment response. Machine learning-assisted systems could optimize CO_2 injection ratios and predict failure thresholds, while standardized multiscale testing protocols must bridge molecular-scale thermodynamics with sediment-scale stability (Wang et al., 2024b). Key priorities include developing in situ techniques to quantify time-dependent meniscus effects and pore-pressure dissipation. Addressing these challenges will enable intelligent methane production while ensuring geomechanical stability during CO_2 sequestration.

5. Conclusions

This paper systematically reviews the experimental research methods of interfacial dynamics and sediment response in CH_4-CO_2 hydrate replacement technology, and discusses the technology's potential and challenges in the synergistic integration of methane extraction and carbon sequestration. The principal conclusions of this investigation are summarized as follows. An integrated multi-scale experimental method, combining microscale piezoelectric sensing, triaxial mechanical testing, and real-time resistivity monitoring can achieve coupled observation spanning molecular hydration phase transitions. It reveals the critical role of pore water surfaces during CH_4-CO_2 replacement, where quantifiable pore pressure fluctuations influence sediment strength - a parameter frequently neglected in conventional systems. Future research should integrate traditional experiments with THMC monitoring to characterize meniscus dynamics and sediment response through a multi-scale platform linking molecular thermodynamics with reservoir stability. Such advancements will deepen the understanding of CH_4-CO_2 displacement processes while ensuring geological integrity during CO_2 storage and promoting sustainable energy-carbon synergies.

Acknowledgements

This work was supported by the National Natural Science Foundation of China Youth Project (NO. 42306234), the Jiangsu Basic Research Program Natural Science Foundation Youth Fund (NO. SBK2023044900). Acknowledgments also go to the Changzhou University High-level Talent Introduction Program.

Conflict of interest

The authors declare no competing interest.

References

Cai, J., Qin, X., Wang, H., et al. Pore-scale investigation of forced imbibition in porous rocks through interface curvature and pore topology analysis. Journal of Rock Mechanics and Geotechnical Engineering, 2025, 17(1): 245-257.

Cao, B. -J., Sun, Y. -F., Chen, H. -N., et al. Self-adaptive gas flow and phase change behaviors during hydrate exploitation by alternate injection of N_2 and CO_2. Petroleum Science, 2024, 21(3): 2120-2129.

Cao, S. C., Yuan, Y., Jung, J., et al. Effects of end-member sediments on CO_2 hydrate formation: Implications for geological carbon storage. Advances in Geo-Energy Research, 2024, 14(3): 224-237.

Chaturvedi, K. R., Sharma, T., Trivedi, J., et al. Experimental investigation for comparative effectiveness of CO_2+N_2 and CO_2+N_2+H_2 on integrated methane production and carbon storage from natural hydrate media. Journal of Environmental Chemical Engineering, 2023, 11(2): 109388.

Choi, W., Mok, J., Lee, J., et al. Effective CH_4 production and novel CO_2 storage through depressurization-assisted replacement in natural gas hydrate-bearing sediment. Applied Energy, 2022, 326: 119971.

Choi, W., Mok, J., Lee, J., et al. Influence of CO_2 injection rate and memory water on depressurization-assisted replacement in natural gas hydrates and the implications for effective CO_2 sequestration and CH_4 exploitation. Energy, 2024, 309: 133130.

Collett, T. S. Energy resource potential of natural gas hydrates. AAPG Bulletin, 2002, 86(11): 1971-1992.

Espinoza, D. N., Santamarina, J. C. P-wave monitoring of hydrate-bearing sand during CH_4–CO_2 replacement. International Journal of Greenhouse Gas Control 2011, 5 (4): 1031-1038.

Gambelli, A. M. Analyses on CH_4 and CO_2 hydrate formation to define the optimal pressure for CO_2 injection to maximize the replacement efficiency into natural gas hydrate in presence of a silica-based natural porous medium, via depressurization techniques. Chemical Engineering and Processing-Process Intensification, 2021, 167: 108512.

Hyodo, M., Li, Y., Yoneda, J., et al. Effects of dissociation on the shear strength and deformation behavior of methane hydrate-bearing sediments. Marine and Petroleum Geology, 2014, 51: 52-62.

Jung, J. W., Espinoza, D. N., Santamarina, J. C. Properties and phenomena relevant to CH_4–CO_2 replacement in hydrate-bearing sediments. Journal of Geophysical Research: Solid Earth, 2010, 115: B10102.

Jung, J. W., Santamarina, J. C. CH_4–CO_2 replacement in hydrate-bearing sediments: A pore-scale study. Geochemistry Geophysics Geosystems, 2010, 11: Q0AA13.

Jung, J. W., Santamarina, J. C. Hydrate adhesive and tensile strengths. Geochemistry, Geophysics, Geosystems, 2011, 12(8): Q08003.

Jung, J. Y., Lee, J. M., Hong, S. K., et al. Catalyzed transesterification kinetics in early stage of polycarbonate melt polymerization. Polymer-Korea, 2015, 39(2): 235-239.

Li, Y., Wu, D., Wu, P., et al. Mechanical characteristics of the hydrate-Bearing sediments in the South China Sea using a multistage triaxial loading test. Energy & Fuels, 2021, 35(5): 4127-4137.

Liu, J., Kong, L., Zhao, Y., et al. Test research progress on mechanical and physical properties of hydrate-bearing sediments. International Journal of Hydrogen Energy, 2024, 53: 562-581.

Liu, J., Zhao, Y., Sang, S., et al. Triaxial Tests of Hydrate-Bearing Clayey-Silty Sediments Under Different Hydrate Saturations and Effective Confining Pressures. Energy & Fuels, 2022, 36(23): 14042-14054.

Liu, S., A, H., Tang, S., et al. Molecular insights into structural and dynamic properties of water molecules in calcium silicate hydrate nanopores: The roles of pore size and temperature. Capillarity, 2023, 8(2): 23-33.

Luo, T., Han, T., Zhang, T., et al. Deformation behaviors of hydrate-bearing silty sediments during CH_4–CO_2 replacement. Journal of Petroleum Science and Engineering, 2022, 211: 110225.

Luo, T., Li, Y., Madhusudhan, B. N., et al. Comparative analysis of the consolidation and shear behaviors of CH_4 and CO_2 hydrate-bearing silty sediments. Journal of Natural Gas Science and Engineering, 2020, 75: 103157.

Mu, L., Li, X., Zhao, H., et al. Experimental study on the CH_4/CO_2 replacement in the sand-clay systems with a high water content. Geoenergy Science and Engineering, 2023, 231: 212412.

Mu, L., Zhao, H., Li, X., et al. Experimental investigation on the depressurization-assisted CH_4/CO_2 replacement behavior in the muddy silt slurries. Gas Science and Engineering, 2024, 126: 205345.

Niu, M., Yao, Y., Yin, Z., et al. Synergistic CH_4 hydrate recovery and CO_2 storage by coupling depressurization with CO_2/N_2 injection: A pilot-scale investigation. Chemical Engineering Journal, 2023, 475: 141129.

Ren, S. R., Liu, Y., Liu, Y., et al. Acoustic velocity and electrical resistance of hydrate bearing sediments. Journal of Petroleum Science and Engineering, 2010, 70(1-2): 52-56.

Tang, J., Lei, G., Shang, Y. Theoretical analysis of effective thermal conductivity for clayey hydrate-bearing sediments during hydrate dissociation and reformation processes. International Journal of Heat and Mass Transfer, 2025, 236: 126386.

Wang, C., Li, X., Ge, Y., et al. Experimental study of effective thermal conductivity of methane hydrate-bearing sediments in gas-rich and water-rich systems. Fuel, 2025, 381: 133537.

Wang, C., Li, X., Li, Q., et al. Thermal conductivity of hydrate and effective thermal conductivity of hydrate-bearing sediment. Chinese Journal of Chemical Engineering, 2024, 73: 176-188.

Wang, H., Zhang, M., Xia, X., et al. Lattice Boltzmann prediction of CO_2 and CH_4 competitive adsorption in shale porous media accelerated by machine learning for CO_2 sequestration and enhanced CH_4 recovery. Applied Energy, 2024, 370: 123638.

Xu, C. -G., Yan, R., Fu, J., et al. Insight into micro-mechanism of hydrate-based methane recovery and carbon dioxide capture from methane-carbon dioxide gas mixtures with thermal characterization. Applied Energy, 2019, 239: 57-69.

Zhang, L., Yang, L., Wang, J., et al. Enhanced CH_4 recovery and CO_2 storage via thermal stimulation in the CH_4/CO_2 replacement of methane hydrate. Chemical Engineering Journal, 2017, 308: 40-49.

Zhou, J., Yang, Z., Wei, C., et al. Mechanical behavior of hydrate-bearing sands with fine particles under isotropic and triaxial compression. Journal of Natural Gas Science and Engineering, 2021, 92: 103991.