

**INVESTIGATION OF CO<sub>2</sub> HYDRATE FORMATION KINETICS AND  
PORE-SCALE DYNAMICS FOR ENHANCED  
CARBON SEQUESTRATION**

**BY**

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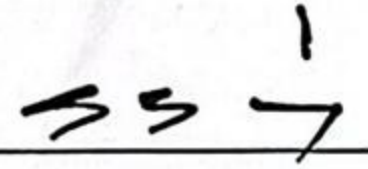
This thesis, written by **MUHAMMAD AUFA HABIBURRAHMAN** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN PETROLEUM ENGINEERING**.

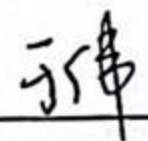
  
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*To my parents, whose unwavering love and support has guided me always and forever.*

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## LIST OF ABBREVIATIONS

|                 |                                                      |
|-----------------|------------------------------------------------------|
| <b>AOI</b>      | : Area of Interest                                   |
| <b>CBM</b>      | : Coalbed Methane                                    |
| <b>CCD</b>      | : Charged-Coupled Device                             |
| <b>CCS</b>      | : Carbon Capture and Storage                         |
| <b>CMC</b>      | : Critical Micelle Concentration                     |
| <b>CNT</b>      | : Classical Nucleation Theory                        |
| <b>CP</b>       | : Cyclopentane                                       |
| <b>CPA</b>      | : Cubic-Plus-Association                             |
| <b>DSLR</b>     | : Digital Single-Lens Reflex                         |
| <b>EOR</b>      | : Enhanced Oil Recovery                              |
| <b>EOS</b>      | : Equations of State                                 |
| <b>GS-12</b>    | : Ethoxylated Quaternary Ammonium Gemini Surfactant  |
| <b>HEN</b>      | : Heterogeneous Nucleation                           |
| <b>HON</b>      | : Homogeneous Nucleation                             |
| <b>HPS-ALTA</b> | : High-Pressure-Stirred Automatic Lag Time Apparatus |
| <b>IFT</b>      | : Interfacial Tension                                |
| <b>IW</b>       | : Ice Water                                          |
| <b>KHP</b>      | : Kinetic Hydrate Promoters                          |
| <b>LTHP</b>     | : Low-Temperature and High-Pressure                  |

|             |                                    |
|-------------|------------------------------------|
| <b>LW</b>   | : Liquid Water                     |
| <b>MCP</b>  | : Methylcyclopentane               |
| <b>MD</b>   | : Molecular Dynamics               |
| <b>MEG</b>  | : Monoethylene Glycol              |
| <b>MRI</b>  | : Magnetic Resonance Imaging       |
| <b>NGH</b>  | : Natural Gas Hydrates             |
| <b>NMR</b>  | : Nuclear Magnetic Resonance       |
| <b>PEG</b>  | : Polyethylene Glycol              |
| <b>PID</b>  | : Proportional-Integral-Derivative |
| <b>PTFE</b> | : Polytetrafluoroethylene          |
| <b>PV</b>   | : Pore Volume                      |
| <b>RPM</b>  | : Rotation Per Minute              |
| <b>RTD</b>  | : Resistance Temperature Detector  |
| <b>SDS</b>  | : Sodium Dodecyl Sulfate           |
| <b>SL</b>   | : Sulfonated Lignin                |
| <b>TBAB</b> | : Tetra-n-Butylammonium Bromide    |
| <b>TBAC</b> | : Tetra-n-Butylammonium Chloride   |
| <b>THF</b>  | : Tetrahydrofuran                  |
| <b>THP</b>  | : Thermodynamic Hydrate Promoter   |
| <b>WAG</b>  | : Water-Alternating-Gas            |

## ABSTRACT

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Thesis Title : INVESTIGATION OF CO<sub>2</sub> HYDRATE FORMATION KINETICS AND PORE-SCALE DYNAMICS FOR ENHANCED CARBON SEQUESTRATION

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The challenge of mitigating carbon emissions has driven interest in storing CO<sub>2</sub> as hydrates within cold subsurface environments, utilizing their potential for stable, long-term sequestration. This study explores the pore-scale and chip-scale behavior of CO<sub>2</sub> hydrates in microfluidic porous media, focusing on their formation, distribution, and propagation dynamics under controlled thermodynamic and kinetic conditions. A low-temperature, high-pressure (LTHP) microfluidic system combined with advanced imaging techniques was employed to characterize hydrate morphology and growth, while a High-Pressure Stirred Automated Lag Time Apparatus (HPS-ALTA) was used to evaluate the kinetics of chemical promoters under constant cooling conditions. At the pore scale, liquid CO<sub>2</sub> hydrates formed stable, pore-filling structures that drastically reduced permeability, while gaseous CO<sub>2</sub> hydrates underwent a two-stage transformation from porous, dark phases to non-porous, transparent phases. At the chip scale, CO<sub>2</sub> distribution and hydrate propagation were significantly influenced by injection rates and subcooling, with higher rates promoting shear-induced nucleation and greater subcooling accelerating growth through enhanced thermodynamic driving forces. The evaluation of novel chemical promoters, including a gemini surfactant (GS-12) and water-soluble organoclay (Laponite-RD),

revealed distinct mechanisms such as interfacial tension reduction, micelle formation, and modified water-CO<sub>2</sub> interactions. GS-12 and SDS demonstrated superior performance in accelerating hydrate formation and optimizing CO<sub>2</sub> storage capacity at both pore-scale and chip-scale levels, outperforming thermodynamic agents like tetrahydrofuran (THF). These findings provide critical insights into the mechanisms of hydrate formation and the strategic use of promoters to enhance cold subsurface carbon storage.

## ملخص الرسالة

الاسم الكامل: محمد عوفا حبيبور رحمن  
عنوان الرسالة: دراسة حركية تكوين هيدرات ثاني أكسيد الكربون وديناميكياتها على مستوى المسام لتحسين احتجاز الكربون  
التخصص: هندسة البترول  
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يعتبر تخزين ثاني أكسيد الكربون على شكل هيدرات في البيئات الجوفية الباردة إحدى الطرق البديلة للتغلب على تحدي الحد من انبعاثات الكربون نظرًا لقدرتها على الحبس المستقر طويل الأجل. تستكشف هذه الدراسة السلوك على مستوى المسام وعلى مستوى الرقائق لهيدرات ثاني أكسيد الكربون في الوسائط المسامية الدقيقة، مع التركيز على تكوينها وتوزيعها وديناميكيات انتشارها تحت ظروف ديناميكية حرارية وحركية محكمة. تم استخدام نظام ميكروفلويديك، مع تقنيات تصوير متقدمة لتوصيف شكل الهيدرات ونموها (LTHP) يعمل عند درجات حرارة منخفضة وضغط عالٍ، بينما تم استخدام جهاز الضغط العالي المزود بتقنية التحريك والتحليل الزمني المؤتمت (HPS-ALTA) لتقييم حركية المضافات الكيميائية تحت ظروف التبريد المستمر. على مستوى المسام، شكلت هيدرات ثاني أكسيد الكربون السائلة هياكل ثابتة تملأ المسام مما أدى إلى تقليل كبير في النفاذية، بينما مرت هيدرات ثاني أكسيد الكربون الغازية بمرحلتين من التحول من مراحل داكنة مسامية إلى مراحل شفافة غير مسامية. على مستوى الرقائق، تأثر توزيع ثاني أكسيد الكربون وانتشار الهيدرات بشكل كبير بمعدلات الحقن ودرجات التبريد الفائق، حيث عززت المعدلات العالية التولد النواتجي الناتج عن القص، وسرعت درجات التبريد الفائق النمو عبر تعزيز القوى الدافعة الديناميكية الحرارية. كشف والطين العضوي القابل للذوبان (GS-12) تقييم المضافات الكيميائية المبتكرة، بما في ذلك الفاعل السطحي المزوج عن آليات مميزة مثل تقليل التوتر السطحي، وتكوين المذيلات، وتعديل تفاعلات الماء، (Laponite-RD) في الماء أداءً متفوقًا في تسريع تكوين الهيدرات وتحسين سعة تخزين ثاني أكسيد الكربون و SDS و GS-12 مع ثاني أكسيد الكربون. أظهر أكسيد الكربون على المستويين المجهرى والرقائقي، متفوقين على العوامل الديناميكية الحرارية مثل التتراهيدروفوران تقدم هذه النتائج رؤية حاسمة حول آليات تكوين الهيدرات والاستخدام الاستراتيجي للمضافات لتعزيز تخزين (THF) الكربون في البيئات الجوفية الباردة.



# CHAPTER 1

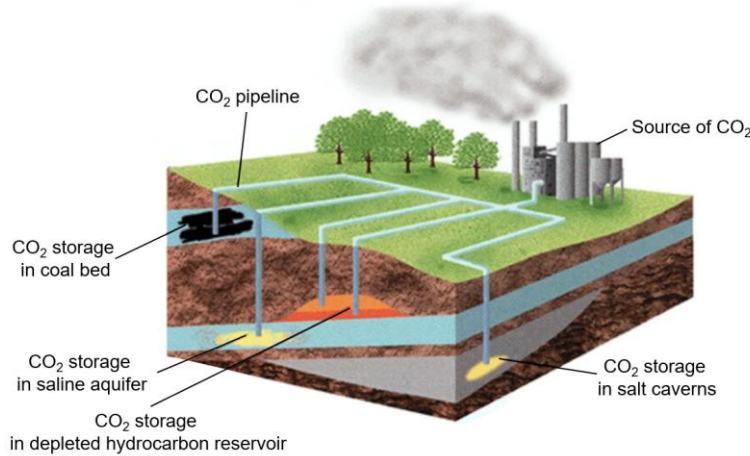
## INTRODUCTION

### 1.1 Background and Motivation

Carbon dioxide (CO<sub>2</sub>) emissions have reached critical levels, with severe implications for the planet. Since the Industrial Revolution, the earth's surface temperature has risen at an average rate of approximately 0.0034 °C per year [1]. This rate far exceeds previous geological warming events, intensifying the risks of natural disasters and severely impacting ecosystems and human life. Carbon capture and storage (CCS) has emerged as one of the most effective solutions to mitigate CO<sub>2</sub> emissions. This technique involves the capture of CO<sub>2</sub> from industrial and energy production sources and its secure storage in deep geological formations underground. It is projected that these geological formations will adequately sequester the retained CO<sub>2</sub> for millions of years, preventing any upward migration induced by buoyancy and the limitations of the overlying caprock [2].

Underground carbon sequestration in subsurface systems is a promising strategy leveraging natural geological formations like depleted hydrocarbon fields, deep saline aquifers, salt caverns, and unmined coal seams for CO<sub>2</sub> storage [3]. **Figure 1.1** outlines these primary methods of geological storage. A more recent approach involves storing CO<sub>2</sub> as hydrates within marine seabed or permafrost regions [4]. CO<sub>2</sub> hydrates are crystalline compounds that trap CO<sub>2</sub> molecules in water-based lattice structures under high-pressure, low-temperature conditions common in deep-sea or sub-permafrost settings [5]. These hydrates offer remarkable stability and high storage density, holding up to 164 m<sup>3</sup> of CO<sub>2</sub> gas per m<sup>3</sup> of hydrate, ensuring secure and efficient containment [5]. Unlike other methods,

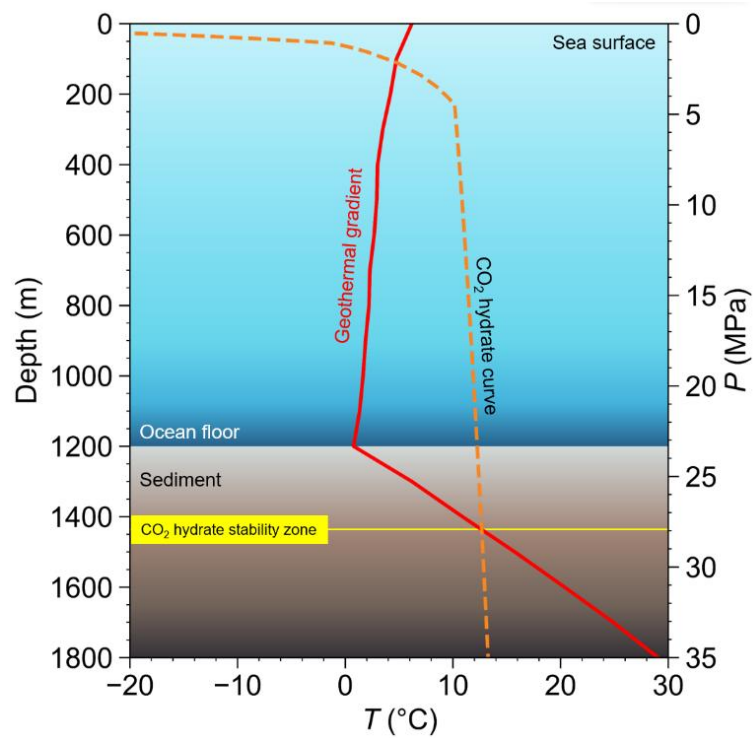
CO<sub>2</sub> hydrates naturally form self-sealing barriers within sediments, reducing gas migration, slowing CO<sub>2</sub> diffusion, and enhancing containment integrity [6]. Controlled CO<sub>2</sub> hydrate formation is a promising carbon capture and storage (CCS) solution, combining safe, long-term containment with minimized leakage risks through hydrate-induced barriers.



**Figure 1.1.** Schematic representation of geological CO<sub>2</sub> storage methods. Various subsurface formations include: depleted hydrocarbon reservoirs, deep saline aquifers, unmined coal seams, and salt caverns (<https://petrolessons.com/carbon-capture-utilization-and-storage/>).

Natural gas hydrates are commonly found in oceanic and permafrost regions where pressure and temperature conditions favor their thermodynamic stability [4]. **Figure 1.2** illustrates the stability conditions for CO<sub>2</sub> hydrates. These hydrates form based on thermodynamic principles, and phase diagrams for gas hydrates allow us to predict the depth, pressure, and temperature conditions that maintain hydrate stability within a specific layer thickness in subsurface formations. However, factors such as water column height, local geothermal gradients, and natural gas composition can influence the thickness of hydrate-bearing sediments [7]. In general, the phase diagram of CO<sub>2</sub> hydrates is influenced by thermodynamic properties such as molecular size and interactions [8]. CO<sub>2</sub> has higher solubility in water and forms hydrates at lower temperatures and pressures. Additionally, CO<sub>2</sub> transitions from gas to liquid above 4.45 MPa, influencing its hydrate phase behavior.

The yellow horizontal line in **Figure 1.2** indicate the base zones for CO<sub>2</sub> hydrates, where the local geothermal gradient intersects with their respective hydrate equilibrium curves.



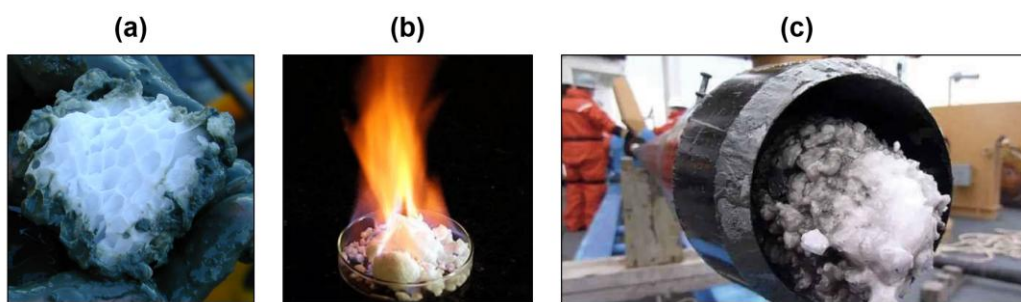
**Figure 1.2.** Depth-pressure-temperature phase diagram illustrating the stability zones for CO<sub>2</sub> hydrates in marine environments, adapted from Xie et al. (2020)[9]. The red line represents the geothermal gradient, while the dashed lines denote the stability curves for CO<sub>2</sub> hydrates. The yellow horizontal line indicate the base stability zones for CO<sub>2</sub> hydrates.

With CO<sub>2</sub> hydrates showing significant promise for environmental sustainability, particularly in sub-seabed storage, this study focuses on their behavior in subsurface porous media. While the scientific feasibility of CO<sub>2</sub> hydrates has been explored, engineering aspects like CO<sub>2</sub> injectivity and the impact of chemical promoters remain crucial. Controlled experiments are conducted using artificial microfluidic porous media to investigate CO<sub>2</sub> hydrate behavior under hydrate-forming conditions. The study also evaluates the role of promoters in enhancing hydrate formation, advancing CCS technologies for a more sustainable future.

## 1.2. CO<sub>2</sub> Hydrates

### 1.2.1. Definition

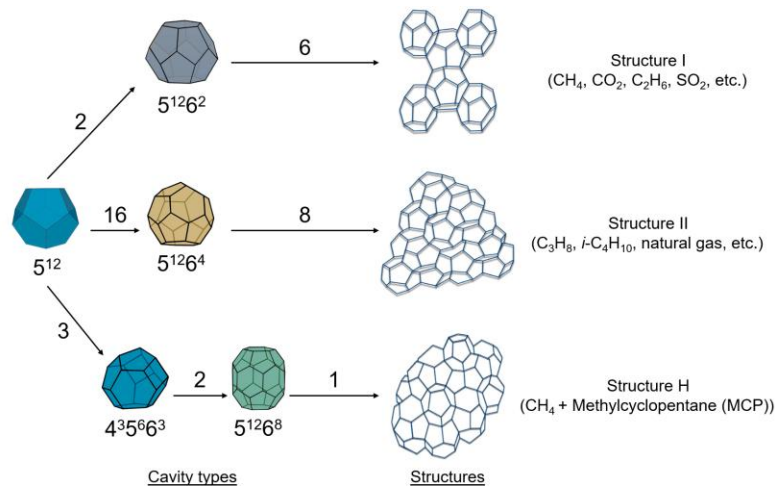
CO<sub>2</sub> hydrates are nonstoichiometric, ice-like crystalline compounds that form under high-pressure and low-temperature conditions, where water molecules arrange into cage-like structures (cavities) around CO<sub>2</sub> molecules[5]. The physical appearance of natural gas hydrates is depicted in **Figure 1.3**. The phenomenon of hydrates was first documented in 1810 by Sir Humphrey Davy, who observed that a chlorine-water mixture froze at a higher temperature than pure water[10]. In 1934, Hammerschmidt[11] studied hydrate formation in natural gas pipelines, discovering that methane and other hydrocarbons form solid, ice-like blockages with water at high pressures and low temperatures. His work revealed that hydrates could form above freezing temperatures, influenced by factors such as gas composition, pressure changes, and flow velocities.



**Figure 1.3.** (a) A methane hydrate block embedded in sediment at Hydrate Ridge, off the coast of Oregon, USA ([https://en.wikipedia.org/wiki/Clathrate\\_hydrate](https://en.wikipedia.org/wiki/Clathrate_hydrate)). (b) Burning methane hydrate (Siażik and Malcho, 2017)[12]. (c) Gas hydrate blockage in a submarine pipeline (Lv et al., 2023)[13].

In 1951, Claussen[14] proposed the first structural model of gas hydrates, distinguishing them from ice by the presence of void spaces large enough to enclose gas molecules. This model hypothesized a pentagonal dodecahedral structure fitting into a diamond lattice framework. These cubic cells accommodate both small and large gas molecules in different cavities, explaining variations in gas-to-water ratios among hydrates.

Von Stackelberg and Müller (1951)[15] confirmed this hypothesis, identifying two distinct hydrate structures: structure I (s-I) and structure II (s-II). Structure I accommodates smaller guest molecules such as CO<sub>2</sub> and SO<sub>2</sub> and consists of a cubic unit cell containing 48 water molecules and 8 cavities. Structure II is suited for larger molecules like propane and butane, with a cubic unit cell comprising 136 water molecules. In 1987, Ripmeester and colleagues[16] identified a new hydrate structure, termed "structure H" (s-H), using advanced NMR and diffraction techniques. Unlike earlier hydrate structures that housed single-sized guest molecules, s-H requires both large and small guest molecules for stability. **Figure 1.4** illustrates the three types of clathrate hydrate cages.



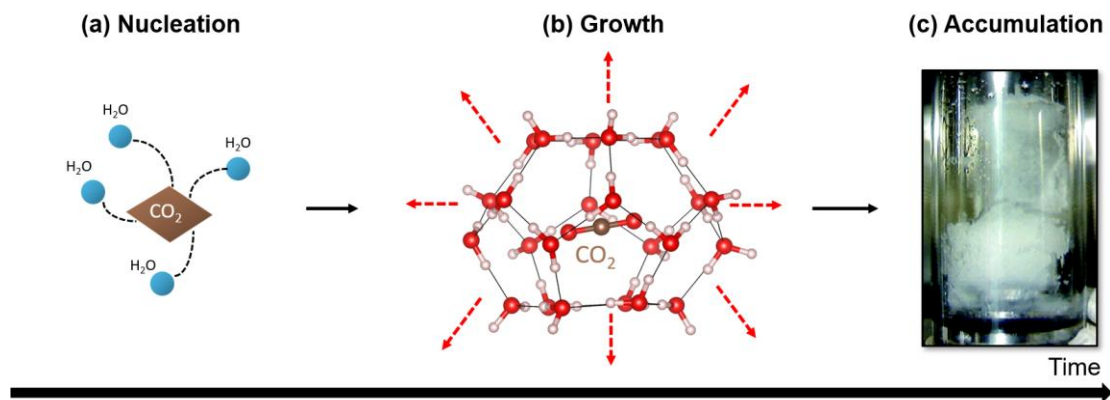
**Figure 1.4.** Types of cavities and common clathrate hydrate structures (Aminnaji et al., 2024)[17].

### 1.2.2. Hydrate Formation

Hydrate formation occurs through the sequential processes of nucleation and growth, essential for understanding gas hydrate formation, stabilization, and accumulation. In the nucleation stage, water molecules cluster around gas molecules to form amorphous crystals, which may evolve into structured hydrate-like formations[18]. This stage is highly sensitive to local fluctuations in mass, temperature, and pressure, affecting the growth and

dissolution of early crystals. Critical factors like energy barriers, critical nucleus size, and nucleation rate are central to hydrate science, though the precise mechanisms remain incompletely understood [19].

Once nuclei reach a critical size, they transition to the growth phase, during which stable hydrate crystals increase in both size and quantity. This phase represents a rapid progression toward substantial, detectable hydrate formation (**Figure 1.5**). While the transition from nucleation to growth is often indistinguishable at the macroscopic level, the visible onset of hydrate accumulation marks the dominance of the growth process. This phase is governed by intrinsic kinetics, as well as mass and heat transfer mechanisms, each described by theoretical models that elucidate their specific roles in hydrate crystallization[20].



**Figure 1.5.** Stages of hydrate formation: (a) Nucleation[21], where initial molecular clusters form, (b) Growth[22], where stable hydrate structures expand, and (c) Accumulation[23], where visible hydrate crystals aggregate over time.

### 1.2.3. Hydrate Nucleation

Hydrate nucleation occurs via either homogeneous nucleation (HON) or heterogeneous nucleation (HEN). HON, involving only solute and nuclei in pure systems, is rarely observed due to the absence of impurities. Instead, HEN dominates in real systems, where

impurities and foreign surfaces, such as container walls, act as nucleation sites. Nucleation is inherently challenging to study due to its molecular scale and stochastic nature, requiring multiple trials to obtain statistically reliable nucleation rates [19].

Hydrate nucleation is driven by a balance between surface and volume free energy within forming hydrate clusters [24]. Assuming spherical nuclei, the excess Gibbs free energy ( $\Delta G$ ) is expressed as:

$$\Delta G = \Delta G_s + \Delta G_v = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \Delta G_v \quad (1.1)$$

where  $\Delta G_v$  is the free energy change per unit volume, and  $\gamma$  is the interfacial tension between the crystalline surface and the liquid phase. In **Equation (1.1)**,  $\Delta G$  represents the sum of surface excess free energy ( $\Delta G_s$ ) and volume excess free energy ( $\Delta G_v$ ), both dependent on the nuclei radius ( $r$ ). During cluster formation, the positive surface energy resists nucleation by favoring smaller clusters, while the negative volume energy promotes growth by incorporating solute molecules into the cluster interior[24].

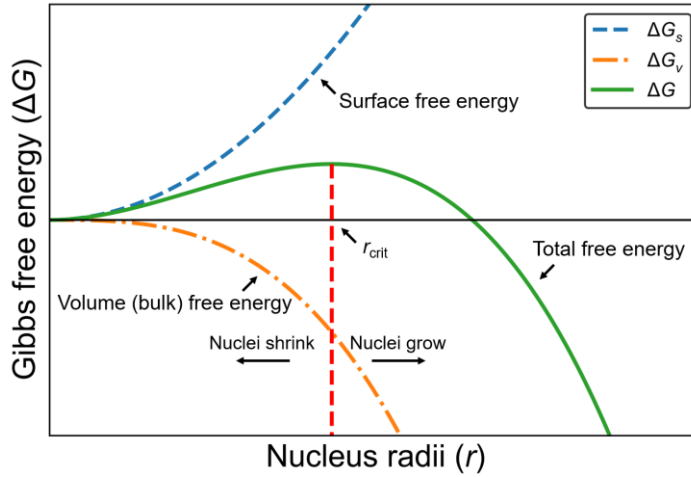
The critical size and energy barrier for nucleation can be derived by setting the derivative of **Equation (1.1)** with respect to cluster radius ( $r$ ) to zero:

$$r_{\text{crit}} = -\frac{2\gamma}{\Delta g_v} \quad (1.2)$$

$$\Delta G_{\text{crit}} = \frac{4}{3}\pi \gamma r_{\text{crit}}^2 \quad (1.3)$$

As illustrated in **Figure 1.6**, the total free energy ( $\Delta G$ ) varies with cluster radius, reaching a maximum energy barrier ( $\Delta G_{\text{crit}}$ ) at a critical radius ( $r_{\text{crit}}$ ), indicated by the vertical, red-dashed line. This critical size represents the threshold beyond which clusters stabilize and grow into macroscopically detectable hydrates. According to Mullin's

theory[24], the critical size increases with rising temperature and decreasing subcooling, making nucleation less favorable near equilibrium conditions. In these regions, surface energy dominates, preventing the system from overcoming the energy barrier required for cluster growth.



**Figure 1.6.** Relationship between Gibbs free energy ( $\Delta G$ ) and nucleus radius ( $r$ ) during hydrate nucleation. The critical nucleus radius is marked by the vertical, red-dashed line, where the total free energy reaches its maximum, representing the energy barrier for stable hydrate growth.

#### 1.2.4. Nucleation Rate

Nucleation, as a thermally activated process, involves overcoming an energy barrier for nuclei to form. The nucleation rate ( $J$ ), representing the number of nuclei per unit volume per unit time ( $\text{m}^{-3} \cdot \text{s}^{-1}$ ), is described by an Arrhenius-type equation[25]:

$$J = A \exp\left(-\frac{\Delta G_{\text{crit}}}{k_B T}\right) \quad (1.4)$$

where  $A$  is the pre-exponential factor or reaction frequency,  $\Delta G_{\text{crit}}$  is the Gibbs free energy barrier for forming critical nuclei,  $k_B$  is the Boltzmann constant ( $1.3805 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$ ), and  $T$  is the absolute temperature.

Classical Nucleation Theory (CNT) provides the expression for the free energy barrier of nucleation for spherical, non-electrolytic systems, as derived by Mullin (2001)[24]:

$$\Delta G_{\text{crit}} = \frac{16\pi\gamma^3 v^2}{3(k_B T \ln S)^2} \quad (1.5)$$

where  $\gamma$  is the surface tension between the crystal and solution,  $v$  is the molecular volume,  $S$  is the supersaturation level.

Combining **Equations (1.4) and (1.5)**, the nucleation rate becomes:

$$J = A \exp\left(-\frac{16\pi\gamma^3 v^2}{3k_B^3 T^3 (\ln S)^2}\right) \quad (1.6)$$

These equations show that the nucleation rate and free energy barrier depend on temperature, supersaturation, and surface tension.

Roelands et al. (2006)[26] expanded the pre-factor  $A$  as:

$$A = Z f^* C_{\text{ns}} \quad (1.7)$$

where  $Z$  is the Zeldovich factor, ( $\approx 0.01-1$ ) representing the probability that a critical nucleus will grow rather than dissolve,  $f^*$  is the attachment frequency ( $\text{s}^{-1}$ ), the rate at which molecules attach to a nucleus to promote growth, and  $C_{\text{ns}}$  is the concentration of nucleation sites ( $\text{m}^{-3}$ ).

Substituting  $A$  back into the nucleation rate equation yields:

$$J = Z f^* C_{\text{ns}} \exp\left(-\frac{\Delta G_{\text{crit}}}{k_B T}\right) \quad (1.8)$$

Taking the natural logarithms of both sides results in:

$$\ln J = \ln(Z f^* C_{\text{ns}}) - \left(\frac{\Delta G_{\text{crit}}}{T}\right) \left(\frac{1}{T}\right) \quad (1.9)$$

**Equation (1.9)** suggests that a plot of  $\ln J$  versus  $1/T$  should yield a straight line with a slope of  $\Delta G_{\text{crit}}/k_B$ . By multiplying the slope by  $k_B$ , the free energy barrier can be estimated.

This approach also allows for the determination of critical nucleus size, provided that the surface tension ( $\gamma$ ) is known. Mullin (2001)[24] notes that  $\Delta G_{\text{crit}}$  and the critical radius vary with temperature, resulting in a slightly curved  $\ln J$  versus  $1/T$  plot rather than a perfect straight line. As  $1/T$  decreases or  $T$  increases, the slope becomes steeper, reflecting temperature-dependent changes in the energy barrier.

### 1.2.5. Hydrate Growth

The growth kinetics of CO<sub>2</sub> hydrate are influenced by various factors, including CO<sub>2</sub> concentration in water, temperature, pressure, and the diffusion rates of water and gas molecules[20]. Experimental studies reveal that higher dissolved CO<sub>2</sub> concentrations accelerate hydrate growth rates, transitioning the process from being diffusion-controlled to interfacial reaction-controlled. This shift is supported by high-pressure in-situ measurements, which highlight increased mass transfer flux to the hydrate crystal surface[27]. To better understand these processes, models focusing on intrinsic kinetics, mass transfer, and heat transfer mechanisms have been developed.

Intrinsic kinetics can be isolated by minimizing mass and heat transfer effects, often using stirred tank reactors. Under these conditions, the growth rate depends on the fugacity difference between dissolved CO<sub>2</sub> and its equilibrium state. Clarke and Bishnoi (2005)[28] modeled intrinsic kinetics using the equation:

$$R(t) = \pi K^* \mu_2 (f - f_{\text{eq}}) \quad (1.10)$$

where  $R(t)$  is the reaction rate,  $K^*$  is the intrinsic rate constant near the hydrate particle,  $\mu_2$  is the second moment of the particle size distribution, and  $f - f_{\text{eq}}$  is the fugacity difference.

When mass and heat transfer resistance are negligible,  $K^*$  approximates the intrinsic rate constant.

In mass transfer-controlled growth,  $\text{CO}_2$  dissolution primarily governs the hydrate growth rate. Zhou and Ferreira (2017) [29] expressed the growth rate  $G$  as:

$$G = k_l \rho_{\text{sol}} A_h \left( x_b^{(\text{CO}_2)} - X_{\text{int}}^{(\text{CO}_2)} \right) \quad (1.11)$$

where  $k_l$  is the mass transfer coefficient of  $\text{CO}_2$  from bulk liquid to crystal,  $\rho_{\text{sol}}$  is solution density,  $A_h$  is hydrate layer area, and  $x_b^{\text{CO}_2}$  and  $X_{\text{int}}^{\text{CO}_2}$  are the  $\text{CO}_2$  mole fractions in the bulk liquid and the liquid-crystal interface, respectively.

For heat transfer-dominated models, temperature plays a critical role in controlling the growth rate, which is influenced by conductive and convective heat transfer. Uchida et al. (1999) [30] proposed a model for  $\text{CO}_2$  hydrate film growth based on the temperature gradients:

$$\vartheta = \frac{\lambda}{L \rho_c r_c} \Delta T \quad (1.12)$$

where  $\vartheta$  is the  $\text{CO}_2$  hydrate film growth rate,  $\lambda$  is thermal conductivity,  $L$  is the latent heat of hydrate formation,  $\rho_c$  is hydrate density,  $r_c$  is the curvature radius of the hydrate front, and  $\Delta T$  is temperature difference.

### 1.2.6. $\text{CO}_2$ Hydrate Phase Equilibria

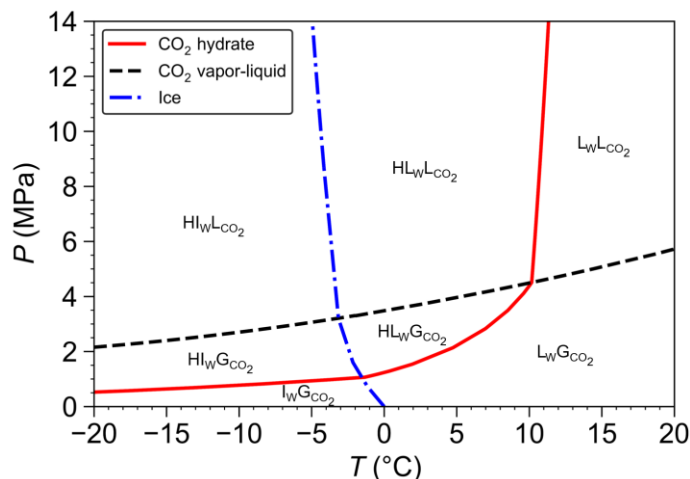
Determining the equilibrium conditions of  $\text{CO}_2$  hydrates is crucial for understanding their behavior under varying temperature and pressure, particularly for applications in carbon sequestration. Experimental methods for identifying hydrate dissociation points include visual observation and graphical analyses through isochoric, isothermal, or isobaric

processes, utilizing a variety of experimental setups. Among these, nonvisual methods combined with stepwise heating for hydrate dissociation are recommended for their accuracy and time efficiency [31]. However, in multicomponent systems, variations in heating curve slopes can complicate the precise identification of dissociation points, introducing potential inaccuracies [32].

Numerical modeling, particularly through equations of state (EOS) such as the Cubic-Plus-Association (CPA) and Peng-Robinson EOS, has proven highly effective in analyzing CO<sub>2</sub> hydrate phase equilibria. The CPA EOS is particularly suited for mixtures containing non-polar hydrocarbons, self-associating polar water, and cross-associating molecules like CO<sub>2</sub>, making it indispensable for geological CO<sub>2</sub> sequestration and CO<sub>2</sub>-enhanced oil recovery applications [33]. When integrated with the van der Waals–Platteeuw theory, the CPA EOS provides precise predictions for hydrate phase equilibria across various gases, including CO<sub>2</sub> and its mixtures [34]. Furthermore, extending the CPA EOS to incorporate aqueous components using Peng-Robinson principles enhances its utility in flow assurance and process simulations involving water and hydrate inhibitors [35].

Experimental phase diagrams and simulations delineate the hydrate phase boundaries for CO<sub>2</sub> in water systems over a range of pressures, capturing critical features such as the CO<sub>2</sub> liquid-gas equilibrium line and the ice melting line. For example, **Figure 1.7** presents a typical CO<sub>2</sub> hydrate phase diagram, highlighting these boundaries. However, the presence of electrolytes significantly alters phase behavior. Zheng et al. (2020) [36] studied CO<sub>2</sub> hydrates in NaCl solutions and observed that phase boundary pressures increased to 61.99 MPa and temperatures to 295.09 K. This effect occurs because higher NaCl concentrations

reduce water activity, which stabilizes the hydrate phase. Such findings provide valuable data for understanding hydrate behavior under high-pressure, high-temperature conditions.

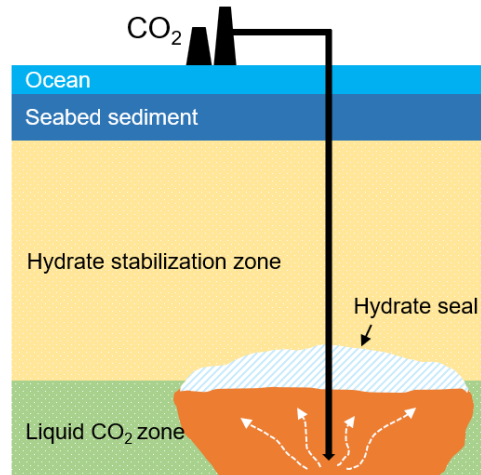


**Figure 1.7.** Hydrate phase boundary and phase equilibrium for the CO<sub>2</sub> + water system up to 14 MPa. The red and black dashed lines represent the CO<sub>2</sub> hydrate phase boundary and the CO<sub>2</sub> liquid-vapor equilibrium, as predicted by the Multiflash 7.0 software package. The blue dashed line indicates the ice melting equilibrium for water saturated with CO<sub>2</sub>[37]. Labels: H = CO<sub>2</sub> hydrate, LCO<sub>2</sub> = liquid CO<sub>2</sub>, GCO<sub>2</sub> = gaseous CO<sub>2</sub>, L<sub>w</sub> = liquid water, I<sub>w</sub> = ice.

### 1.3. Hydrate-Based CO<sub>2</sub> Storage

#### 1.3.1. CO<sub>2</sub> Hydrate Storage in Subsurface Porous Media

CO<sub>2</sub> sequestration in subsurface porous media via hydrates is a promising but underexplored technology. In cold, high-pressure pore water aquifers, CO<sub>2</sub> can form stable hydrates, providing dense storage in deep-sea environments [38]. However, direct injection into these aquifers may lead to immediate hydrate formation, reducing injectivity. To mitigate this, CO<sub>2</sub> should be injected into regions outside the hydrate stability zone, allowing migration to areas where hydrate formation is favorable. Once formed, CO<sub>2</sub> hydrates act as secondary seals, creating pore-filling barriers that significantly reduce permeability. These barriers effectively prevent CO<sub>2</sub> escape, even in formations with minimal initial water content[4,6]. A schematic representation of this sequestration method is shown in **Figure 1.8**.



**Figure 1.8.** Schematic of CO<sub>2</sub> sequestration in subsea porous media with self-sealing via hydrate formation, adapted from Gauteplass et al. (2020)[39].

Extensive laboratory experiments have been conducted to simulate subsurface conditions and better understand CO<sub>2</sub> hydrate behavior in porous media. For example, Qureshi et al. (2022)[40] conducted experiments using artificial sediment composed of silica sand and 3.5 wt% NaCl brine. Their findings revealed that CO<sub>2</sub> hydrates remained stable within brine-saturated sediments due to a protective layer formed by the silica sand. This layer limited direct brine exposure, reducing dissociation rates. Additionally, the salinity of the brine enhanced phase equilibrium, stabilizing hydrates under high-pressure conditions. A follow-up study confirmed that the protective effect of the sand bed minimized hydrate dissociation by reducing fluid dynamics and direct water exposure, supporting long-term CO<sub>2</sub> sequestration [41].

In related research, Dhamu et al. (2023) [42] explored the role of liquid CO<sub>2</sub> as a guest molecule in hydrate formation. They observed that liquid CO<sub>2</sub> significantly accelerated hydrate formation compared to gaseous CO<sub>2</sub>. This enhanced performance was attributed to the higher density of liquid CO<sub>2</sub>, which promotes rapid interactions with water in sediments, resulting in faster kinetics and a higher conversion rate. These findings highlight

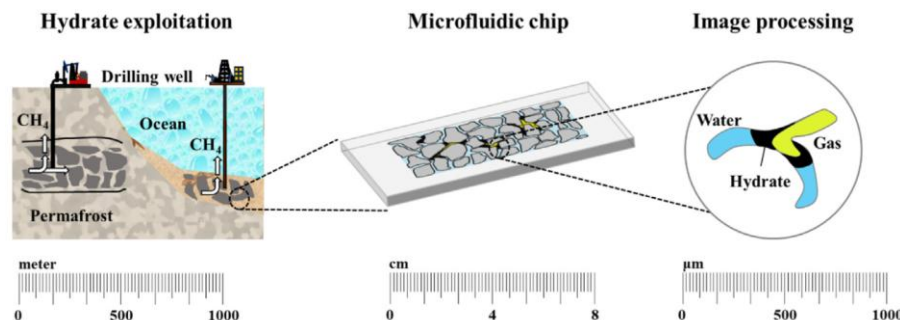
liquid CO<sub>2</sub>'s potential to improve the efficiency of hydrate formation for CO<sub>2</sub> storage applications, further advancing the feasibility of this technology for large-scale implementation.

### **1.3.2. In-Situ Experiments of CO<sub>2</sub> Hydrate Formation in Porous Media**

Advanced technologies have been instrumental in studying CO<sub>2</sub> hydrate formation and behavior in situ within porous media. Cheng et al. (2013) [43] utilized MRI to detect hydrogen nuclei signals from water molecules, enabling the visualization and quantification of CO<sub>2</sub> hydrate growth, saturation, and distribution over time. As hydrates form, water signal intensity decreases due to the transition of water into hydrate, offering a direct method to monitor hydrate dynamics. Similarly, low-field NMR (LNMR) has provided insights into the spatial and temporal evolution of CO<sub>2</sub> hydrate formation, capturing saturation levels across various pore sizes and tracking growth and dissociation processes within the sample [44]. Micro-CT, employed by Ta et al. (2015) [45], offers pore-scale resolution for analyzing CO<sub>2</sub> hydrate growth in brine-saturated porous media. This technique reveals that CO<sub>2</sub> hydrates initially form at grain contacts and extend dendritically into pore spaces. The mechanical stress induced by volume expansion during hydrate growth often results in cracks and imperfections, providing a clearer understanding of hydrate formation mechanisms in porous environments.

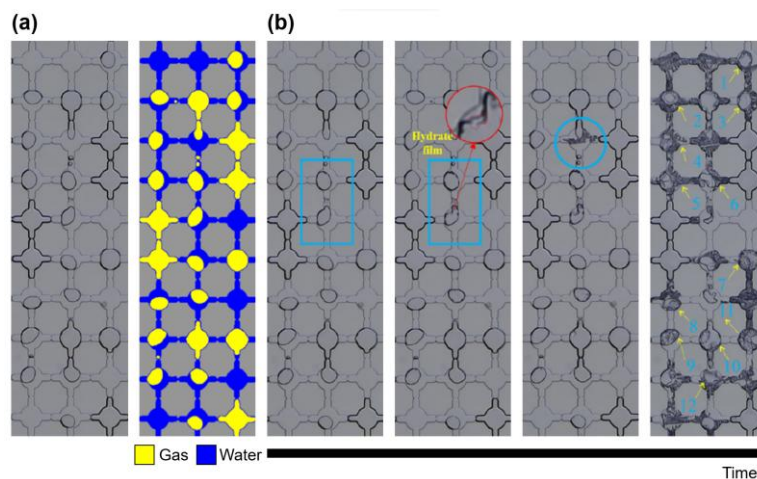
In recent years, microfluidics has become a leading method for investigating hydrate phase transitions and behavior at the microscale. By replicating flow geometry within a 2D porous medium model, microfluidics allows precise observation of fluid interactions and hydrate behavior [46]. Over the past two decades, microfluidics has emerged as a central tool in hydrate research, particularly in studies of porous media [47–49]. **Figure 1.9**

illustrates the application of microfluidics and image analysis in studying methane hydrate sediments, demonstrating common methodologies employed in this field[50].



**Figure 1.9.** Schematic of methane hydrate exploitation and microfluidic observation. Hydrate deposits in oceanic and permafrost settings are simulated in a microfluidic chip (center), with image processing (right) used to distinguish water, gas, and hydrate phases for studying formation and dissociation[50].

While most microfluidic studies focus on methane as the primary guest molecule, limited research has explored CO<sub>2</sub>. Observations of methane hydrate formation demonstrate nucleation at the gas-water interface near pore walls, forming small crystals that expand radially as a thin film along the gas-liquid boundary. Over time, hydrate nuclei consume surrounding methane and water, expanding into the gas phase within pores until reaching a stable three-phase equilibrium of gas, water, and solid hydrate[51] (**Figure 1.10**).



**Figure 1.10.** Progression of methane hydrate formation in a microfluidics porous medium over time[51]. (a) Initial gas (yellow) and water (blue) distribution in the porous network. (b) Sequential stages of hydrate formation, beginning with hydrate film emergence (highlighted in red) and continued nucleation at gas-water interfaces within the porous structure.

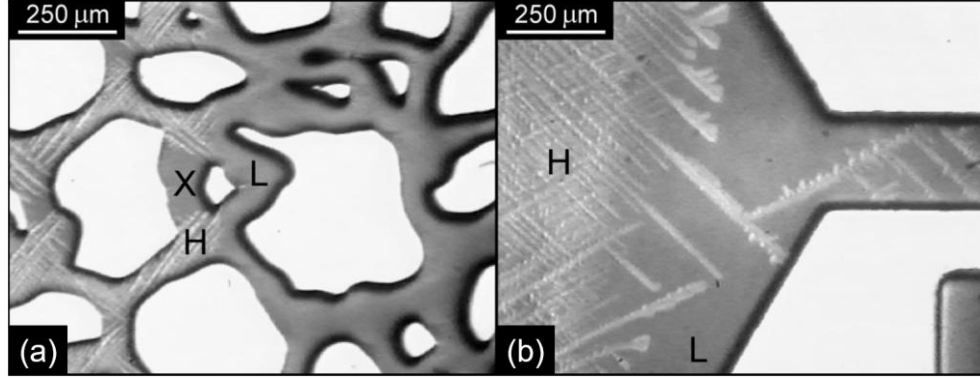
Further studies emphasize the influence of porous media properties on hydrate behavior in confined micro-environments. Ouyang et al. (2023) [52] investigated methane hydrate nucleation in microfluidics, finding that surface wettability significantly affects nucleation dynamics. In hydrophilic channels, hydrate nuclei grow uniformly from gas-water interfaces toward the gas phase, while in hydrophobic channels, nucleation is sporadic, forming around isolated gas bubbles attracted to hydrophobic surfaces. Hydrophilic surfaces promote continuous gas-water interfaces through enhanced water diffusion, whereas hydrophobic surfaces limit water diffusion, resulting in dispersed gas distribution. Permeability also plays a critical role in hydrate behavior, as shown by Chen et al. (2019) [53], who observed that hydrate saturation drastically reduces permeability by obstructing pore throats, restricting fluid flow. This reduction occurs as hydrate particles occupy pore spaces, significantly hindering fluid transfer.

Microfluidics has also facilitated the quantification of hydrate growth rates. Almenningen et al. (2021) [54]. examined methane hydrate growth in sandstone-like micromodels under high-pressure, low-temperature conditions, discovering that hydrate growth occurs more rapidly along pore walls than at pore centers due to higher subcooling near the walls. Morphological studies using microfluidics provide further insights into hydrate growth. Wang et al. (2021) [55] identified two primary morphologies of methane hydrate at the pore scale: (1) smooth, continuous crystals formed from dissolved gas and water, and (2) honeycomb structures with rough surfaces formed at the gas-water interface. Smooth crystals grow rapidly as solution gas migrates directly to the hydrate front, while honeycomb structures form more slowly, with water permeating through a hydrate crust that limits gas transfer.

This body of research underscores the importance of microfluidic techniques in advancing the understanding of hydrate behavior in porous media. These studies provide critical insights into the factors influencing hydrate phase behavior, serving as benchmarks for numerical simulations and informing field-scale applications. The following section will focus specifically on studies of CO<sub>2</sub> hydrates in microfluidic systems, addressing the current gap in research for this context.

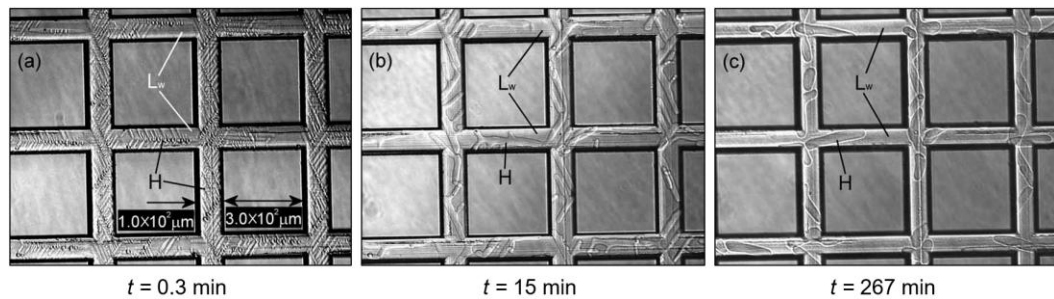
### **1.3.3. CO<sub>2</sub> Hydrates in Microfluidics**

CO<sub>2</sub> hydrates were among the first gas hydrates studied using microfluidics, with Tohidi et al. (2001) [49] pioneering this approach. They utilized glass micromodels to study CO<sub>2</sub> alongside other guest molecules like CH<sub>4</sub> and tetrahydrofuran (THF). Their objective was to visually observe hydrate formation and dissociation within synthetic porous media, capturing pore-scale distribution and morphology. These studies focused on understanding how hydrates grow within pore spaces and along grain surfaces, as well as potential cementation effects in sedimentary systems. Their findings suggested that CO<sub>2</sub> hydrates could form directly from dissolved gas, supporting the hypothesis that hydrates may precipitate from solution in marine sediments [56]. Additionally, they noted that hydrate masses tended to concentrate in pore centers rather than on surfaces, indicating that substantial sediment cementation would require significant hydrate volumes. This observation suggested that sediment permeability remains largely unaffected at low hydrate saturations, although more recent research has shown that hydrate formation can reduce permeability, warranting further investigation [53,57].



**Figure 1.11.** CO<sub>2</sub> hydrate formation in a microfluidic micromodel, as demonstrated by Tohidi et al. (2001)[49]. (a) Shows the advancing hydrate front (H) and liquid water phase (L), with a bypassed region (X) where hydrate has not formed within the pore network. (b) Displays a transparent layer of hydrate along the liquid phase, with distinct parallel ridges intersecting at an angle of 105–110°. White regions represent the grains in the micromodel structure.

Katsuki et al. (2006) [48] extended this work by exploring the formation, growth, and aging of CO<sub>2</sub> hydrate crystals in glass micromodels composed of square-shaped, homogeneous grains (**Figure 1.12**). Using CO<sub>2</sub>-saturated water and gaseous CO<sub>2</sub> under varying subcooling conditions, they observed significant differences in hydrate morphology. At higher subcooling levels (e.g., 7.3 °C), rapid, fine dendritic hydrates formed, which later transitioned into particulate crystals with limited bonding to the glass surface. In contrast, lower subcooling levels (e.g., 1.7 °C) produced faceted hydrate crystals with stronger physical bonds to the glass. These findings highlighted that reduced driving forces enhance sediment stabilization through hydrate formation, as bond variability influences the mechanical and fluid transport properties of hydrate-bearing sediments.



**Figure 1.12.** Temporal images showing the morphological evolution of CO<sub>2</sub> hydrate crystals from fine dendritic structures to particulate crystals at 3.3 MPa and 0.5 °C, with a subcooling of 7.3 °C[48]. 'L<sub>w</sub>' denotes the liquid water, while 'H' represents CO<sub>2</sub> hydrate crystals. The images capture the progression at (a) 0.3 min, (b) 15 min, and (c) 267 min after the onset of hydrate formation.

Despite these advancements, studies on CO<sub>2</sub> hydrates using microfluidics to replicate porous rock media in geological storage remain limited. Furthermore, many microfluidic designs do not fully capture the complexity of geological formations (e.g., serpentine structures). Nevertheless, these systems provide valuable insights into the potential of CO<sub>2</sub> storage via hydrate formation. **Table 1.1** summarizes CO<sub>2</sub> hydrate studies conducted with microfluidics, categorized by year, and highlights their contributions to understanding CO<sub>2</sub> hydrate nucleation, growth, and stability. These studies also shed light on the effects of pore structure, pressure, and salinity on CO<sub>2</sub> storage potential and sealing efficiency, advancing techniques for long-term, stable carbon sequestration across diverse geological conditions.

**Table 1.1.** Literature summary on microfluidics studies of CO<sub>2</sub> hydrate formation.

| Reference                    | Microfluidics setup                                                                                                 | Condition                                   | Result                                                                                                                    |
|------------------------------|---------------------------------------------------------------------------------------------------------------------|---------------------------------------------|---------------------------------------------------------------------------------------------------------------------------|
| Tohidi et al. (2001)[49]     | Glass micromodel with sediment-like pores; methyl blue dye excluded from hydrate phase; digital camera observation. | $P = 6.2$ MPa, $\Delta T = 9$ °C.           | CO <sub>2</sub> hydrates formed in pore centers with crystalline structures, avoiding grain binding.                      |
| Katsuki et al. (2006)[48]    | Grid-patterned glass micromodel in a temperature-controlled jacket; CCD camera observation.                         | $P = 3.3$ MPa, $\Delta T = 1.7 - 7.3$ °C.   | Higher subcooling formed non-cementing crystals; lower subcooling created robust, faceted crystals bridging pores.        |
| Hauge et al. (2016)[58]      | Silicon wafer micromodel with sandstone-like pores; digital microscope used for hydrate growth visualization.       | $P = 5.8$ MPa, $T = 0.5$ °C.                | Hydrates initiated at gas-water interfaces, forming crystalline structures in connected water-filled pores.               |
| Almenning et al. (2018)[59]  | Silicon micromodel with sandstone-like pores; steady CO <sub>2</sub> and water injection under a microscope.        | $P = 7$ MPa, $T = 1.3$ °C.                  | Hydrates reduced permeability by sealing pore throats, supporting CO <sub>2</sub> immobilization in sandstone.            |
| Gauteplass et al. (2020)[39] | Glass micromodel in a high-pressure chamber; Methylene Blue dye visualized water phases.                            | $P = 7$ MPa, $T = 4$ °C.                    | Hydrates sealed pores, reducing leakage; sandstone sealed faster than limestone due to mineral dissolution.               |
| Wells et al. (2021)[60]      | Silicon reactor with spiral channels; Raman spectroscopy tracked hydrate formation.                                 | $P = 1.4 - 3.4$ MPa, $\Delta T$ up to 2 °C. | Hydrates propagated faster at higher pressure; 47% water converted to hydrates in 1 hour.                                 |
| Pandey et al. (2021)[61]     | High-pressure micromodel with sandstone-like pores; phase transitions monitored via microscope.                     | $P = 6.7$ MPa, $T = 3.5$ °C.                | Hydrates encapsulated CO <sub>2</sub> , restricting flow; pressure drop caused dissociation and self-sealing reformation. |

|                             |                                                                                                      |                                                 |                                                                                                                            |
|-----------------------------|------------------------------------------------------------------------------------------------------|-------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------|
| Pandey et al. (2022)[62]    | Micromodel mimicking Berea sandstone; pore-scale transitions observed with a microscope.             | $P = 5.9 - 6.9$ MPa, $T = 3.3 - 4.5$ °C.        | Dense hydrates formed, fully filling pores and stabilizing; higher injection rates accelerated crystallization.            |
| Le Goff et al. (2022)[63]   | Silicon micromodel with thermoelectric cooling; reflected light microscopy used.                     | $P$ up to 8 MPa, $T$ as low as $-17.5$ °C.      | Mixed hydrates formed with rapid growth, especially in high salinity; dissociation temperatures were lower than predicted. |
| Wadsworth et al. (2024)[64] | Borosilicate channels in a serpentine pattern; Raman spectroscopy measured hydrate growth.           | $P = 2.5 - 3.1$ MPa, $\Delta T = 0.5 - 1.5$ °C. | Hydrates formed dense crystalline layers, with higher CO <sub>2</sub> flow increasing film thickness.                      |
| Zhang et al. (2024)[65]     | High-pressure chip mimicking seafloor sediments; Raman spectroscopy tracked mixed hydrate formation. | $P = 10$ MPa, $T = 2$ °C.                       | Mixed hydrates filled pores faster than pure CO <sub>2</sub> hydrates, enhancing stability and reducing permeability.      |

This study uses a high-pressure, low-temperature microfluidic setup to explore CO<sub>2</sub> hydrate behavior in porous media. The system features a  $45 \times 30$  mm glass micromodel chip, etched to a 20  $\mu\text{m}$  depth, with homogeneous pore sizes (75–90  $\mu\text{m}$ ) and throat sizes (30–50  $\mu\text{m}$ ). The micromodel, with 53% porosity and a 14.3  $\mu\text{L}$  pore volume, replicates porous media for hydrate studies. Two high-resolution cameras capture chip- and pore-scale views at 3.45  $\mu\text{m}/\text{pixel}$  resolution.

Housed in a water-filled chamber functioning as a high-pressure reservoir, the micromodel is cooled by a water-MEG mixture circulated by a chiller to simulate hydrate-zone temperatures. Desktop software maintains pressures near 10 MPa and monitors temperature variations to assess CO<sub>2</sub> hydrate behavior. The system logs pressure, temperature, and timestamps while capturing one frame per second. Post-experiment image analysis is performed using ImageJ Fiji, enhanced with Python scripts for improved efficiency and accuracy.

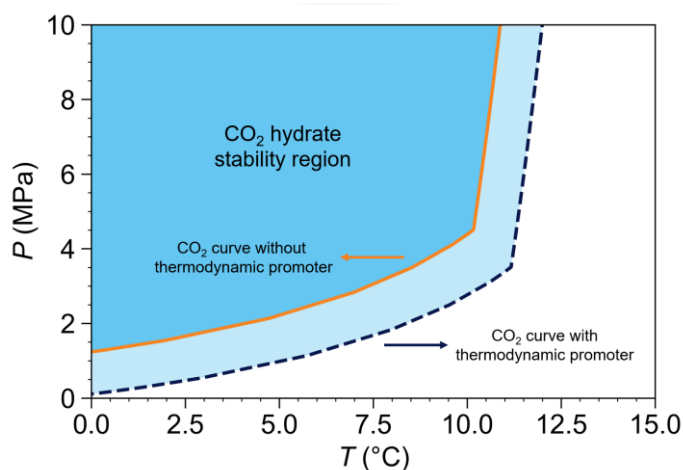
## **1.4. Enhancing CO<sub>2</sub> Hydrate Formation Using Promoters**

To maximize the potential of CO<sub>2</sub> hydrates in CCS, it is essential to address the challenges inherent in gas hydrate formation. Among these challenges are the complexities of nucleation and the development of a hydrate film at the gas–liquid interface, which inhibits gas transfer into the liquid phase [58]. This phenomenon limits both the hydrate formation process and the conversion rate of water to hydrate, resulting in extended induction times, substantial subcooling requirements, slow formation rates, and low gas storage efficiency. Physical methods have been proposed to overcome these limitations by enhancing mass transfer [59,60]. These methods focus on increasing the gas-liquid contact area, improving heat and mass transfer, and optimizing molecular orientation to reduce induction times and support stable hydrate growth.

An alternative approach to addressing these challenges involves the use of chemical promoters. These additives enhance hydrate formation by reducing surface tension, increasing gas diffusion, altering the liquid's microstructure, and improving heat dissipation during the exothermic formation process[61]. Compared to physical methods, chemical promoters are more energy-efficient, require less equipment, and are generally more practical. Promoters are classified into two main types: kinetic promoters, which accelerate the rate of hydrate formation by reducing induction times, and thermodynamic promoters, which stabilize the hydrate structure under milder pressure and temperature conditions [61,62]. The use of these promoters significantly improves the overall efficiency and viability of CO<sub>2</sub> hydrate-based CCS, making it a promising solution for mitigating climate change.

### 1.4.1. Thermodynamic Hydrate Promoters (THP)

Thermodynamic hydrate promoters (THPs) enhance the stability and formation of hydrates by shifting the equilibrium curve to milder conditions, such as lower pressures and higher temperatures, thereby expanding the hydrate stability zone (**Figure 1.13**). Common THPs include tetrahydrofuran (THF), cyclopentane (CP), propane ( $C_3H_8$ ), and quaternary ammonium salts like tetra-n-butylammonium bromide (TBAB) and chloride (TBAC) [61]. While THF, CP, and  $C_3H_8$  form hydrates without altering the water cavity structure, TBAB and TBAC form semi-clathrates by chemically bonding with water molecules [63].



**Figure 1.13.** Phase diagram showing the CO<sub>2</sub> hydrate stability region with and without a thermodynamic promoter. The solid orange line represents the CO<sub>2</sub> hydrate stability curve without a promoter, while the dashed navy blue line shows the stability curve with a thermodynamic promoter.

THPs promote hydrate stability by occupying hydrate cages, strengthening the thermodynamic driving force and fostering favorable conditions for hydrate formation. For example, THF forms structure II (s-II) hydrates by filling large  $5^{12}6^4$  cages, while CO<sub>2</sub> occupies smaller cages within the same structure [5]. This dual occupancy creates stable CO<sub>2</sub> hydrates under milder conditions, with THF acting as a "seed" that reduces the amount of CO<sub>2</sub> needed for cage occupancy [62]. However, excessive THF concentrations (above

5.56 mol%) may counteract its promoting effect by over-occupying lattice sites, potentially destabilizing the hydrate network [64].

The ability of THPs to shift the CO<sub>2</sub> hydrate equilibrium phase diagram stems from their molecular-level interactions, particularly cage occupancy. THPs generally form s-II hydrate structures, which are more complex than s-I structures due to their capacity to accommodate larger molecules[65]. When both CO<sub>2</sub> and a THP act as guest molecules, the resultant hydrate structure exhibits increased stability due to maximized cage occupancy. This thermodynamic effect is particularly beneficial for hydrate-based CO<sub>2</sub> capture and separation processes conducted under ambient or mild conditions, making THPs instrumental in advancing practical applications of CO<sub>2</sub> hydrate technology

#### **1.4.2. Kinetic Hydrate Promoters (KHP)**

Kinetic Hydrate Promoters (KHPs) enhance hydrate formation by reducing induction time and accelerating growth rates without altering the hydrate structure or equilibrium [62]. Instead, they stimulate nucleation and promote rapid growth, making them highly advantageous for applications in energy storage, transport, and carbon capture. As previously discussed, hydrate nucleation involves microscopic clustering of water and gas molecules that must reach a critical size for self-sustaining crystal growth. Because direct observation of nucleation is challenging, induction time is often used as a proxy in kinetic studies. Induction time refers to the interval between the system entering the hydrate stability region and the first detectable signs of hydrate formation, typically evidenced by gas consumption or temperature spikes resulting from exothermic reactions[66]. Another important metric is the hydrate formation rate, which reflects the speed at which gas

molecules are incorporated into hydrate cages. Faster rates indicate the effectiveness of a KHP in enhancing hydrate formation kinetics.

KHPs can be categorized into three main classes: surfactants, amino acids, and nanoparticles, each with distinct mechanisms to promote hydrate formation by reducing induction time or accelerating growth rates. **Table 1.2** summarizes representative examples from each class, focusing on their effects and underlying mechanisms in promoting CO<sub>2</sub> hydrate formation. While many of these KHPs have been extensively studied for methane hydrates, this review also highlights their relevance to CO<sub>2</sub> hydrates. As detailed in **Table 1.2**, each KHP class exhibits unique mechanisms that influence hydrate formation. Together, these insights into KHP mechanisms provide a foundation for advancing hydrate-based CO<sub>2</sub> storage technologies.

**Table 1.2.** A summary of various types of kinetic hydrate promoters (KHPs) along with their effects and mechanisms in promoting CO<sub>2</sub> hydrate formation.

| Kinetic hydrate promoters            | Result                                                                                             | Mechanism                                                                                                                                | Reference                     |
|--------------------------------------|----------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------|
| SDS (sodium dodecyl sulfate)         | 43.05% conversion, 80.06 L/L gas storage at 240 ppm.                                               | Reduces interfacial tension, stabilizes quasi-liquid layer, enhances gas dissolution and nucleation; excess SDS restricts gas diffusion. | Zhang et al. (2022)[67]       |
| Gemini surfactant (C8, C12 variants) | C8 boosts methane hydrate formation and storage; C12 less effective due to higher surface tension. | Dual hydrophilic heads and hydrophobic tails lower surface tension, enhance diffusion, stabilize hydrate crystals.                       | Kwon et al. (2011)[68]        |
| DOWFAX 8390                          | Matches SDS promotion with only 25% of the concentration.                                          | Hydrophobic micro-domains increase methane concentration, reduce surface tension, and support stable gas transfer.                       | Verrett and Servio (2012)[69] |
| DOWFAX C6L, 2A1                      | Higher adsorption efficiency than SDS; C6L achieves maximum interface adsorption.                  | Reduces gas-water surface tension, forms stabilizing pseudo-monolayers and hemimicelles for continuous growth.                           | Salako et al. (2013)[70]      |
| SL (sulfonated lignin)               | Enhances CO <sub>2</sub> recovery to 63.5%, but with longer induction time.                        | Increases CO <sub>2</sub> solubility via sulfonic group interactions and hydrogen-bond strengthening.                                    | Yi et al. (2019)[71]          |
| L-tryptophan                         | Increases CO <sub>2</sub> uptake 3.6x in deionized water, but only 1.5x in brine.                  | Aligns indole side chain with CO <sub>2</sub> , enhancing solubility, nucleation, and hydrate growth.                                    | Jeenmuang et al. (2024)[72]   |

|                        |                                                                                                       |                                                                                                        |                        |
|------------------------|-------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|------------------------|
| Graphite nanoparticles | Cuts induction time by 80.8%, boosts gas consumption by 12.8%, 98.8% reaction completion in 400 mins. | High surface area aids nucleation, enhances CO <sub>2</sub> adsorption, and improves heat dissipation. | Zhou et al. (2014)[73] |
|------------------------|-------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|------------------------|

This study explores the potential of a novel gemini surfactant, an ethoxylated quaternary ammonium salt synthesized in-house at KFUPM, for promoting CO<sub>2</sub> hydrate formation. This surfactant effectively reduces surface tension in saline and freshwater environments at low concentrations, yet its application to CO<sub>2</sub> hydrates remains unstudied. Previous research on methane hydrates highlights the superior performance of gemini surfactants over SDS. For example, Kwon et al. (2011) [68] showed shorter-chain variants like C8DS enhance hydrate formation due to their lower critical micelle concentration (CMC). Similarly, Verrett and Servio (2012) [69] and Salako et al. (2013) [70] demonstrated the efficiency of gemini surfactants like DOWFAX 8390 and C6L in promoting methane hydrates at significantly lower concentrations.

In addition to the gemini surfactant, this study investigates Laponite-RD, a water-soluble organoclay known for its rheological properties. While Laponite-RD has been primarily studied for its role in drilling fluids, Wang et al. (2023) [75] found it promotes hydrate formation at higher concentrations by reducing induction time. Examining these materials may provide deeper insights into CO<sub>2</sub> hydrate formation with kinetic hydrate promoters (KHPs).

To assess the effectiveness of these promoters, experiments will utilize the high-pressure stirred lag time apparatus (HPS-ALTA), which enables precise, reproducible measurements through constant cooling cycles. This method generates statistical

distributions of subcooling temperatures for hydrate nucleation events, offering insights into the predictability and efficiency of each promoter. The results, analyzed within the framework of nucleation theory, will compare the gemini surfactant and Laponite-RD against SDS, a standard KHP, at equivalent concentrations to ensure meaningful benchmarks. Narrower subcooling distributions will indicate improved nucleation control, contributing to a better understanding of hydrate formation mechanisms.

### **1.5. Research Gaps and Objectives**

The literature review reveals a significant gap in the study of CO<sub>2</sub> hydrate formation within microporous environments, in contrast to the extensive research available on methane hydrates. Current research provides limited insights into the spatial and temporal dynamics of CO<sub>2</sub> hydrate formation across interconnected pore networks, leaving cross-pore hydrate behavior insufficiently understood. This restricts the ability to capture hydrate growth patterns at a scale relevant for real-world applications. Additionally, the influence of CO<sub>2</sub> injection rates on hydrate nucleation, growth, and propagation remains largely unexplored, despite its importance for optimizing carbon capture and storage (CCS) strategies.

Another critical gap exists in the evaluation of chemical promoters for CO<sub>2</sub> hydrate formation. While certain surfactants have been investigated, the performance and mechanisms of advanced kinetic promoters, such as gemini surfactants and water-soluble organoclays, in porous media remain largely unstudied. This lack of understanding hinders the development of efficient methods for enhancing hydrate formation kinetics, critical for improving CO<sub>2</sub> sequestration technologies. Furthermore, strategies to stabilize and enhance CO<sub>2</sub> hydrates using novel additives, particularly within pore- and chip-scale systems, remain underdeveloped.

The objectives of this thesis are:

1. To provide detailed observations of CO<sub>2</sub> hydrate behavior at both pore and chip scales, enabling an understanding of formation patterns, growth kinetics, and hydrate interactions across interconnected porous media.
2. To investigate how varying CO<sub>2</sub> injection rates affect hydrate nucleation, distribution, and propagation following the induction period, establishing benchmarks for hydrate-based CCS applications.
3. To evaluate the effectiveness and mechanisms of novel kinetic promoters, specifically Gemini surfactants and water-soluble organoclays, in enhancing CO<sub>2</sub> hydrate formation under controlled cooling conditions.
4. To develop optimized strategies for CO<sub>2</sub> hydrate formation and stabilization by integrating insights from both pore-scale and chip-scale studies with promoter evaluations, advancing the practicality and scalability of CCS technologies.

## **1.6. Thesis Structure**

The following is the structure of this thesis:

### **CHAPTER TWO: Dynamics and Morphology of CO<sub>2</sub> Hydrates Formation in Microfluidic Porous Media**

This chapter investigates CO<sub>2</sub> hydrate formation in porous media using a low-temperature, high-pressure microfluidic system. Liquid CO<sub>2</sub> hydrates formed stable, swelling, pore-filling structures, while gaseous CO<sub>2</sub> hydrates underwent a two-stage transformation from porous to transparent phases. Key findings include differences in induction time,

subcooling, and saturation between phases, with liquid CO<sub>2</sub> hydrates demonstrating superior pore-filling efficiency. Advanced imaging revealed hydrate propagation driven by heat and mass transfer, highlighting phenomena such as crustal fingering and pore blockage. These insights contribute to optimizing carbon capture and storage strategies by understanding phase-dependent hydrate behaviors and their impact on permeability.

### **CHAPTER THREE: Injection Strategies and Growth Kinetics of CO<sub>2</sub> Hydrates in Porous Media**

This chapter examines the impact of CO<sub>2</sub> injection rates and subcooling on hydrate formation, growth kinetics, and storage in porous media. Higher injection rates reduced hydrate induction times via shear-induced nucleation, while slower rates limited pore utilization and CO<sub>2</sub> storage capacity. Subcooling significantly enhanced growth rates, demonstrating its critical role as a thermodynamic driving force. Growth kinetics were found to depend more on temperature than injection rates, with larger subcooling promoting faster hydrate formation. To address risks of hydrate-induced blockages, an alternating CO<sub>2</sub>–water injection strategy is proposed, improving injectivity and storage efficiency in marine sediments. These findings provide insights for optimizing hydrate-based carbon sequestration strategies.

### **CHAPTER FOUR: Performance Evaluation of Kinetic Hydrate Promoters for CO<sub>2</sub> Hydrate Formation**

This chapter evaluates the kinetics of CO<sub>2</sub> hydrate formation using the HPS-ALTA system and three chemical promoters: sodium dodecyl sulfate (SDS), a gemini surfactant (GS-12), and Laponite-RD. SDS exhibited the highest nucleation rates ( $12.1 \text{ s}^{-1}$ ) at 0.5 wt%,

facilitated by adsorption and micelle formation. GS-12 reduced interfacial tension and achieved optimal rates ( $8.9 \text{ s}^{-1}$ ) at 1 wt%, while Laponite improved CO<sub>2</sub>-water interactions, peaking at  $4.0 \text{ s}^{-1}$  at 0.1 wt%. The study identified distinct promotive mechanisms for each compound, emphasizing the importance of tailoring promoter type and concentration for enhancing CO<sub>2</sub> hydrate formation.

## **CHAPTER FIVE: Influence of Promoters on CO<sub>2</sub> Hydrate Formation Dynamics in Porous Media**

This chapter investigates the performance of kinetic (SDS, GS) and thermodynamic (THF) hydrate promoters in microfluidic porous media, focusing on induction time, CO<sub>2</sub> storage capacity, and growth rates. SDS excelled in maximizing CO<sub>2</sub> storage and growth rates, achieving a capacity of  $0.91 \pm 0.02$  and a growth rate of  $2.85 \pm 0.36 \text{ mm/s}$ , attributed to bubble stabilization and enhanced gas-liquid interactions. GS significantly reduced induction time (10 s at 5  $\mu\text{L/min}$ ) by minimizing interfacial tension, though its rapid nucleation limited CO<sub>2</sub> mobility at lower flow rates. THF facilitated hydrate formation under milder conditions ( $\Delta T \approx 1.8 \text{ }^\circ\text{C}$ ) but had limited effects on growth rate or storage. These findings emphasize the tailored use of promoters to optimize CO<sub>2</sub> hydrate formation, advancing carbon sequestration in porous environments.

## **CHAPTER SIX**

This chapter summarizes the key findings from this research and provides recommendations for future studies aimed at advancing the field of CO<sub>2</sub> hydrate-based carbon sequestration.

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## **CHAPTER 2**

# **DYNAMICS AND MORPHOLOGY OF CO<sub>2</sub> HYDRATES FORMATION IN MICROFLUIDIC POROUS MEDIA**

### **Abstract**

This chapter investigates the phase transitions of CO<sub>2</sub> hydrates in porous media, focusing on their dynamics, morphology, and implications for carbon capture and storage (CCS). A low-temperature, high-pressure (LTHP) microfluidic system, featuring a precision-engineered micromodel, was employed to simulate natural porous media. Experiments were conducted under varied conditions, using both liquid and gaseous CO<sub>2</sub>. Results revealed distinct phase transition behaviors, with liquid CO<sub>2</sub> hydrates forming stable, pore-filling structures that significantly reduced permeability. In contrast, gaseous CO<sub>2</sub> hydrates underwent a two-stage transformation, transitioning from dark, porous hydrates to transparent, non-porous phases. Key parameters such as induction time, subcooling, and saturation were quantified. Conceptual models and quantitative analyses, including volume variation indices and hydrate saturation profiles, highlight the contrasting behaviors of hydrates formed from different CO<sub>2</sub> phases.

### **2.1. Introduction**

The formation and behavior of CO<sub>2</sub> hydrates in porous media are fundamental to advancing carbon capture and storage (CCS) technologies. These hydrates, which develop in natural or artificial porous environments such as sediments and microfluidic chips, are shaped by various factors, including pore geometry, pressure-temperature conditions, and fluid flow dynamics[1,2]. Despite their potential, significant knowledge gaps persist in understanding

their growth patterns, spatial distribution, and saturation levels. These elements are crucial for evaluating hydrate stability, fluid transport properties, and the overall efficiency of hydrate-based CO<sub>2</sub> sequestration processes[3–5]. Furthermore, investigating CO<sub>2</sub> hydrate formation extends beyond CCS, offering insights into the geo-mechanical properties of marine sediments. These properties influence the stability of subsea infrastructure and natural gas hydrate reservoirs[6,7], highlighting the broader implications of hydrate studies.

This research addresses these challenges through the use of a low-temperature, high-pressure (LTHP) microfluidic system, enabling detailed visualization of hydrate phase transitions at both pore and chip scales. This innovative methodology captures the intricate dynamics of CO<sub>2</sub> hydrate morphology and propagation under controlled experimental conditions. The microfluidic chip facilitates high-resolution imaging, providing critical insights into hydrate interactions within porous media. A series of experiments were conducted across a range of conditions, with temperatures varying between 0.9 °C and 6.6 °C and pressures ranging from 3.1 MPa to 11.3 MPa. This research tackles key challenges in CO<sub>2</sub> hydrate dynamics, advancing carbon capture strategies for sustainable climate mitigation and environmental stability.

## **2.2. Methodology**

### **2.2.1. Materials**

The hydrate formation experiments utilized CO<sub>2</sub> gas with 99.9% purity, supplied by Saudi Industrial Gas Company Ltd., as the primary guest molecule. Deionized (DI) water from Milli-Q® (Sigma-Aldrich) served as the hydrate-forming medium. These experiments

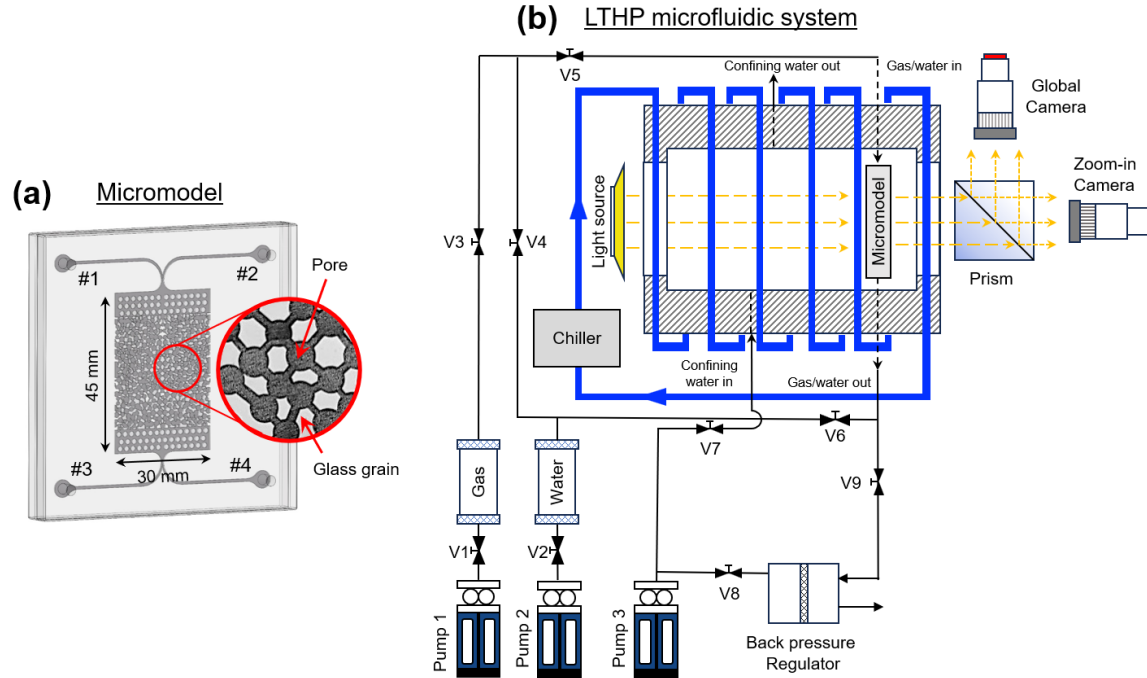
were conducted using a precision-engineered glass microfluidic chip, or micromodel, custom-designed by LightFab GmbH. The micromodel's symmetrical inlet and outlet channels facilitated controlled fluid flow, creating an ideal environment for observing hydrate behavior under realistic experimental conditions.

The micromodel's porous structure covers an effective area of  $45\text{ mm} \times 30\text{ mm}$  with a depth of  $20\text{ }\mu\text{m}$ , containing over 18,000 randomly interconnected circular pores. These pores, featuring radii between  $75\text{ }\mu\text{m}$  and  $90\text{ }\mu\text{m}$  and throat sizes ranging from  $30\text{ }\mu\text{m}$  to  $50\text{ }\mu\text{m}$ , closely mimic the properties of natural porous media. With a permeability of  $400\text{ mD}$ , a porosity of  $53\%$ , and a total pore volume of  $14.3\text{ }\mu\text{L}$ , the micromodel provides a controlled yet realistic high-permeability platform for studying hydrate propagation and interactions in subsurface porous media. **Figure 2.1(a)** provides a detailed schematic and microscopic image of the porous structure.

### **2.2.2. Low-Temperature and High-Pressure (LTHP) Microfluidic System**

The micromodel is securely housed within an insulated cylindrical vessel designed to maintain precise confining pressure, as depicted in **Figure 2.1(b)**. The vessel, filled with water, is pressurized using a high-pressure pump (VP-250 K, Vindum Pump), ensuring controlled experimental conditions. Sapphire windows are installed at both ends of the vessel, enabling light transmission, with the micromodel meticulously aligned between them. Uniform illumination is achieved using an edge-lit collimated backlight (Advanced Illumination), which enhances the clarity and quality of visual observations. A prism cube directs the transmitted light into two separate paths, feeding high-resolution cameras (Allied Vision) configured for distinct imaging perspectives. One camera captures chip-

scale images to provide an overall view of hydrate formation, while the other focuses on pore-scale imaging, achieving a resolution of 3.45  $\mu\text{m}/\text{pixel}$ .



**Figure 2.1.** Schematic of the experimental setup for CO<sub>2</sub> hydrate formation. (a) Micromodel design and porous structure, with the inset highlights the pore and glass grain structure. (b) Low-Temperature and High-Pressure (LTHP) microfluidic system.

Gas and water are injected into the micromodel using two high-pressure pumps (VP-200 K, Vindum Pump), which allow precise flow control with increments as small as 0.1  $\mu\text{L}/\text{min}$ . A back-pressure regulator ensures consistent pore pressure is maintained during the experiment. Temperature control is provided by a chiller (HAAKE A25, Thermo Fisher Scientific), which circulates an ethylene glycol-water coolant through a hose around the vessel. The vessel's large volume (1.5 L) serves as a constant-temperature reservoir, ensuring thermal stability relative to the micromodel's small pore volume (14.3  $\mu\text{L}$ ). During each experiment, CO<sub>2</sub> pressure, liquid pressure, back pressure, temperature, and high-resolution images are continuously recorded using the setup's programmed built-in software.

### 2.2.3. Experimental Procedures

To initiate hydrate formation, the micromodel was first saturated with deionized (DI) water under stabilized temperature and back-pressure conditions tailored for hydrate formation. CO<sub>2</sub> was then injected at a flow rate of 50  $\mu\text{L}/\text{min}$  to establish the initial CO<sub>2</sub> saturation ( $S_{\text{CO}_2}$ ). Once the system stabilized, gas injection was stopped, and images, along with pressure and temperature data, were recorded at one-second intervals. Hydrate formation was triggered by reducing the temperature by approximately 2 °C from the stabilized conditions. Conversely, hydrate dissociation was induced by either increasing the temperature or depressurizing the system using the back-pressure regulator.

The experimental conditions for hydrate formation are outlined in **Table 2.1** and depicted in **Figure 2.2(a)**. Most experiments were conducted at high pressures where CO<sub>2</sub> exists in liquid form, replicating conditions typical of natural hydrate-bearing environments. Additional tests were performed at lower pressures where CO<sub>2</sub> remains in its gaseous state, allowing for a comparative analysis of hydrate behavior across different CO<sub>2</sub> phases. The equilibrium temperature ( $T_{eq}$ ) for hydrate formation was calculated using the cubic-plus-association (CPA) model in Multiflash 7.0 software. Subcooling ( $\Delta T$ ) was defined as the temperature difference between  $T_{eq}$  and the formation temperature ( $T_f$ ). The induction time ( $t_{ind}$ ), representing the interval between the cessation of gas injection and the onset of hydrate formation, was identified by the appearance of darker regions in the micromodel, signifying the development of solid hydrate structures.

**Table 2.1.** Experimental conditions for CO<sub>2</sub> hydrate formation in the micromodel.

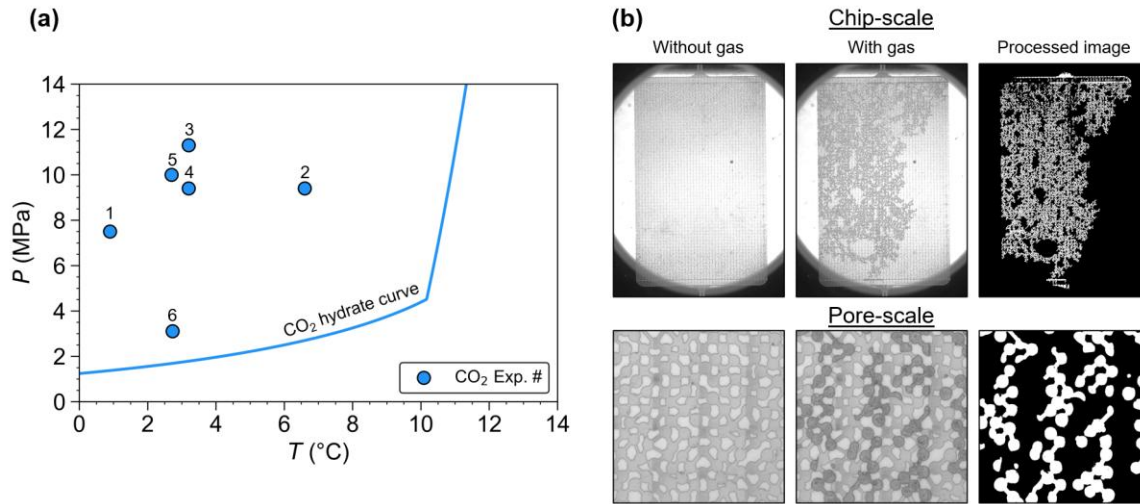
|        | $P$ (MPa) | $T_f$ (°C) | $T_{eq}$ (°C) | $\Delta T$ (°C) | $t_{ind}$ (s) | $S_{\text{CO}_2}$ |
|--------|-----------|------------|---------------|-----------------|---------------|-------------------|
| Exp. 1 | 7.5       | 0.9        | 10.6          | 9.7             | 8640          | 0.75              |
| Exp. 2 | 9.4       | 6.6        | 10.8          | 4.2             | 282           | 0.78              |
| Exp. 3 | 11.3      | 3.2        | 11            | 7.8             | 42            | 0.85              |

|                     |     |     |      |     |      |      |
|---------------------|-----|-----|------|-----|------|------|
| Exp. 4              | 9.4 | 3.2 | 10.8 | 7.6 | 14   | 0.73 |
| Exp. 5              | 10  | 2.7 | 10.9 | 8.2 | 66   | 0.78 |
| Exp. 6 <sup>g</sup> | 3.1 | 2.7 | 7.7  | 5   | 2786 | 0.8  |

<sup>g</sup>Gaseous CO<sub>2</sub> experiment.

## 2.2.4. Image Processing Methods

Both chip-scale and pore-scale images were analyzed using the ImageJ FIJI software package. Variations in light transmission across the micromodel allowed for the differentiation of gas, water, and hydrate phases based on pixel grayscale values: water appeared as the lightest phase, gas as intermediate, and hydrate as the darkest. Phase saturation was quantified by subtracting reference images of DI water-filled micromodels, taken before gas injection, from the experimental result images. The processed images were then binarized using a specific threshold to distinguish between phases and calculate saturation values. This image processing workflow ensured accurate phase identification and quantification. An example of this procedure is shown in **Figure 2.2(b)**.

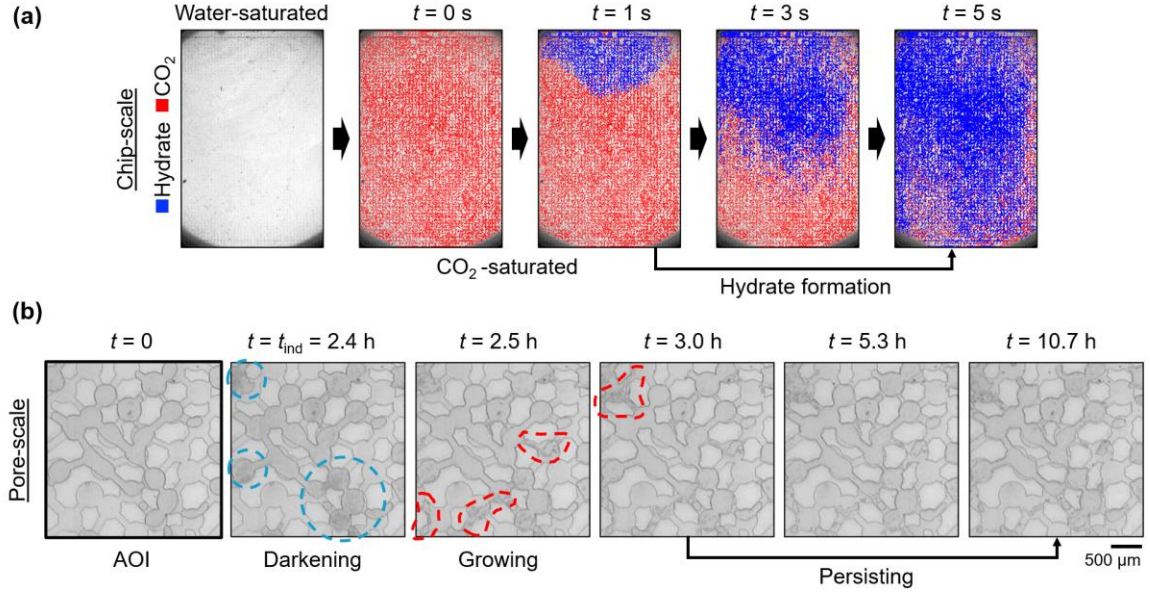


**Figure 2.2.** (a) P-T conditions for CO<sub>2</sub> hydrate formation in seven experiments (blue circles) relative to the CO<sub>2</sub> hydrate equilibrium curve, with numbers indicating experiment IDs. (b) Chip- and pore-scale imaging analysis: chip-scale images illustrate the porous medium without gas, with gas, and the binary-processed gas distribution, while pore-scale images detail the porous structure, gas presence, and binary processing.

## 2.3. Results and Discussion

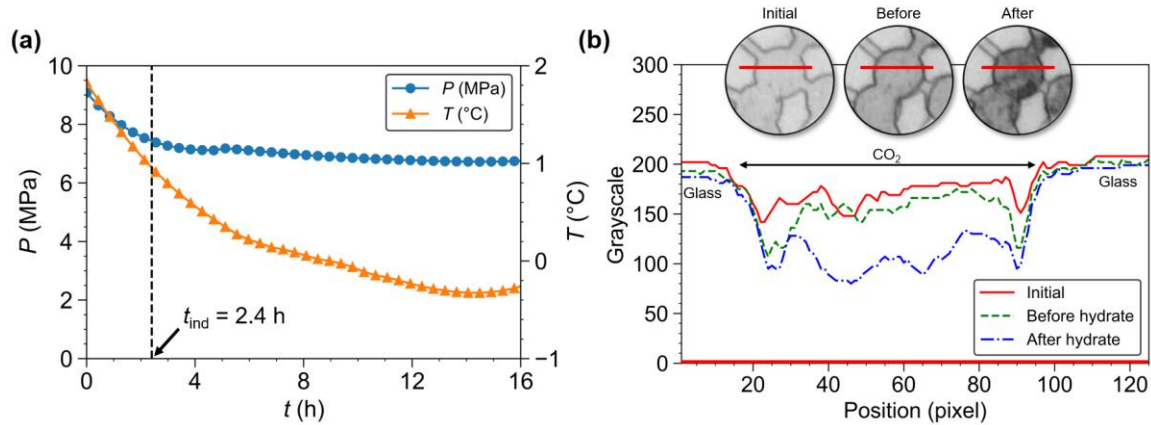
### 2.3.1. CO<sub>2</sub> Hydrate Formation Dynamics in Porous Media

The characteristics of CO<sub>2</sub> hydrate formation under suitable conditions were demonstrated using Experiment 1. Following CO<sub>2</sub> injection, hydrate formation was visually identified, as highlighted in **Figure 2.3(a)**. The phase transition from liquid CO<sub>2</sub> to hydrate, did not cause significant macro-scale changes within the micromodel during the 16.6-hour experiment. Initially, CO<sub>2</sub> appeared as clustered bubbles, which darkened rapidly upon reaching the induction time (**Figure 2.3(b)**). This transformation coincided with a pressure drop of approximately 1.5 MPa from the initial system pressure of 9 MPa (**Figure 2.4(a)**), confirming the initiation of hydrate formation as CO<sub>2</sub> was consumed[8]. The hydrates formed under conditions of 7.5 MPa pressure and a temperature of 0.9 °C.



**Figure 2.3.** Illustration of CO<sub>2</sub> hydrate formation and phase transition in a micromodel experiment at  $P = 7.5$  MPa and  $t = 0.9$  °C. (a) Temporal chip-scale images of CO<sub>2</sub> hydrate formation, with the area of interest (AOI) highlighted by a black square. (b) Pore-scale images of the AOI capturing hydrate formation at  $t = t_{ind} = 2.4$  h, growth until  $t = 3$  h, and persistence of morphology up to 10.7 h.

Pore-scale imaging of the area of interest (AOI) (**Figure 2.3(b)**) revealed that the observed darkening in the dashed-blue region resulted from lateral growth of hydrate crystals along the CO<sub>2</sub>-water interface. This growth formed a thin hydrate shell that reduced light transmission[9]. As the process progressed, hydrate crystals extended into the water phase, a phenomenon commonly reported in hydrate-visualization studies[10–12] (highlighted by the red dashed area in **Figure 2.3(b)**). The initially curved CO<sub>2</sub>-water interfaces gradually transformed into angular, solid edges. Over 10.7 hours, the liquid-formed CO<sub>2</sub> hydrates retained their morphological structure, with only minor shrinkage observed across all hydrates.



**Figure 2.4.** (a) Pressure and temperature profiles recorded throughout the hydrate formation process. (b) Grayscale profile differentiating phases within the micromodel, including glass, liquid CO<sub>2</sub> prior to hydrate formation and CO<sub>2</sub> hydrate.

Grayscale analysis provided additional insights into the transformation. Initially, the liquid CO<sub>2</sub> phase exhibited a lighter grayscale value, which progressively decreased as hydrates formed (**Figure 2.4(b)**). This change facilitated the calculation of CO<sub>2</sub> hydrate saturations using the method described in **Figure 2.2(b)**. Additionally, pore-filling behaviors, such as crustal fingering, were observed during the early stages of hydrate

formation[13]. These findings highlight the intricate dynamics of hydrate formation and serve as a valuable reference for future experimental studies and analyses.

### 2.3.2. CO<sub>2</sub> Hydrate Thickening and Its Pore-Filling Effect

To investigate broader aspects of CO<sub>2</sub> hydrate behavior in porous media, an additional experiment using gaseous CO<sub>2</sub> (Exp. 6: 3.1 MPa and 2.7°C) was conducted and compared with the liquid CO<sub>2</sub> experiment (Exp. 1) discussed earlier. In the gaseous CO<sub>2</sub> experiment, hydrates initially formed as darkened regions, transitioning into a transparent phase over 80 hours. This phenomenon was observed both at the chip scale (**Figure 2.5(a)**) and pore scale (**Figure 2.5(b)**). The transparent phase is hypothesized to result from the extended dissolution of CO<sub>2</sub> gas into the water phase, making the gas appear to vanish[14]. However, further observations suggest a different mechanism.

A two-stage process was identified for gaseous CO<sub>2</sub> hydrates: the initial darkening of the hydrates was followed by a gradual transition into a transparent phase. It is hypothesized that gaseous CO<sub>2</sub> forms non-porous hydrates instead of dissolving completely[15]. This hypothesis is supported by the rapid pressure build-up observed when gas was reinjected into the micromodel after hydrate formation. This response indicates that the micromodel remained blocked by the formed hydrates even after hours of experimentation. This phase transition behavior contrasts with liquid CO<sub>2</sub> hydrates, likely due to the density difference between gaseous and liquid CO<sub>2</sub>. Gaseous CO<sub>2</sub> hydrates, being thinner, appear more transparent than those formed by liquid CO<sub>2</sub>.

To verify this hypothesis, a volume variation index,  $I_v$ , was introduced to analyze hydrate thickness variation relative to the original gas phase, as defined by **Equation (2.1)**:

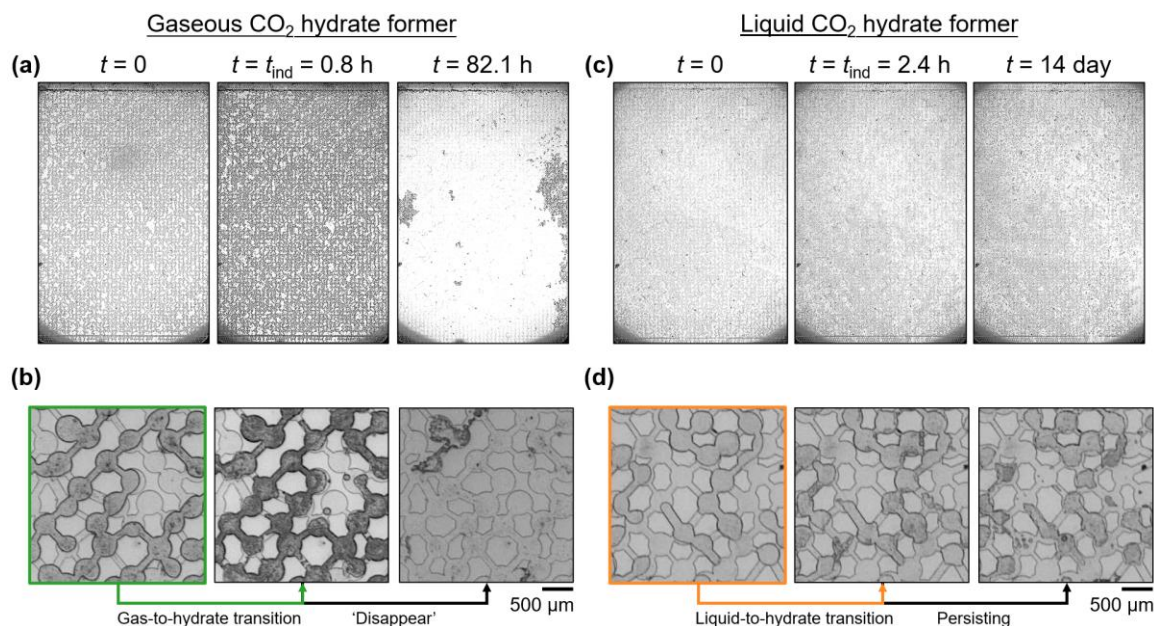
$$I_v = \frac{\rho_g M_h}{\rho_h M_g} \quad (2.1)$$

where  $\rho_g$  and  $\rho_h$  are the densities of the gas and hydrate, respectively, and  $M_g$  and  $M_h$  are their molar masses. If  $I_v < 1$ , it indicates hydrate shrinkage; if  $I_v > 1$ , it suggests swelling. Since the guest gas and hydrates are confined by pore walls, swelling hydrates will match the pore depth, while shrinking hydrates will only partially fill the pores. The hydrate thickness,  $\delta_h$ , was estimated using **Equation (2.2)**:

$$\delta_h = I_v \delta_p; (I_v < 1) \quad (2.2)$$

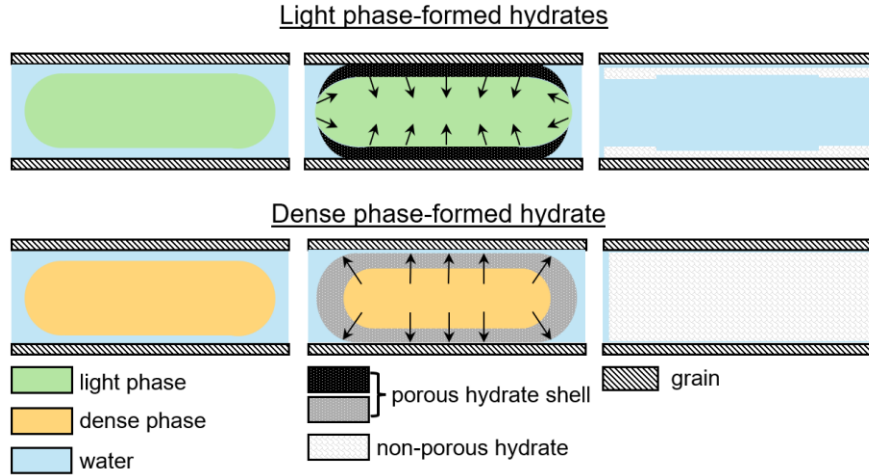
where  $\delta_p$  is the pore depth, set to 20  $\mu\text{m}$  in this study. The densities of gaseous and liquid  $\text{CO}_2$  are 78.2  $\text{kg/m}^3$  and 953.2  $\text{kg/m}^3$ , respectively[16]. Calculations yielded volume variation indices of 0.27 for gaseous  $\text{CO}_2$  and 3.61 for liquid  $\text{CO}_2$ , indicating shrinkage and swelling behaviors, respectively.

For liquid  $\text{CO}_2$ , hydrates darkened slightly during the early formation stages and maintained their morphology throughout the 14-day observation period without transitioning to a transparent phase (**Figure 2.5(c)**). The liquid  $\text{CO}_2$  hydrates swelled, filling the pores and forming persistent sheet-like structures. Pore-scale images (**Figure 2.5(d)**) confirmed this pore-filling effect, showing limited shrinkage and slight growth into the water phase, which stabilized over time.



**Figure 2.5.** Comparison of CO<sub>2</sub> hydrate behavior in micromodel experiments using gaseous CO<sub>2</sub> (a, b) and liquid CO<sub>2</sub> (c, d). (a) Chip-scale images for gaseous CO<sub>2</sub> showing hydrate formation at  $t = 0$ , darkening at  $t = t_{ind} = 0.8$  h, and transition to a transparent phase at  $t = 82.1$  h. (b) Pore-scale images for gaseous CO<sub>2</sub> depicting the gas-to-hydrate transition and hydrate transparency. (c) Chip-scale images for liquid CO<sub>2</sub> showing hydrate formation at  $t = 0$ , initial darkening at  $t = t_{ind} = 2.4$ , and persistence of morphology up to 14 days. (d) Pore-scale images for liquid CO<sub>2</sub> illustrating the liquid-to-hydrate transition and hydrate persistence.

A conceptual model (**Figure 2.6**) was developed to illustrate pore-filling behaviors during hydrate phase transitions. Initially, guest molecule bubbles occupy the pores, separated by water films at the gas-liquid interfaces. In the early stages of hydrate formation, porous hydrate shells form at these interfaces, eventually transitioning into non-porous, annealed hydrates[15,17]. For gaseous CO<sub>2</sub>, volume decreases as gas converts into hydrates, forming thin films that partially fill the pores, a phenomenon referred to as grain-coating[18]. Conversely, liquid CO<sub>2</sub> hydrates expand in volume, rapidly filling the pores and transitioning into non-porous hydrates that cement the pores, significantly reducing permeability. Similar behaviors have been observed in cyclopentane and tetrahydrofuran hydrates, where high-density liquid guest molecules exhibit comparable pore-filling and cementation effects[19–21].



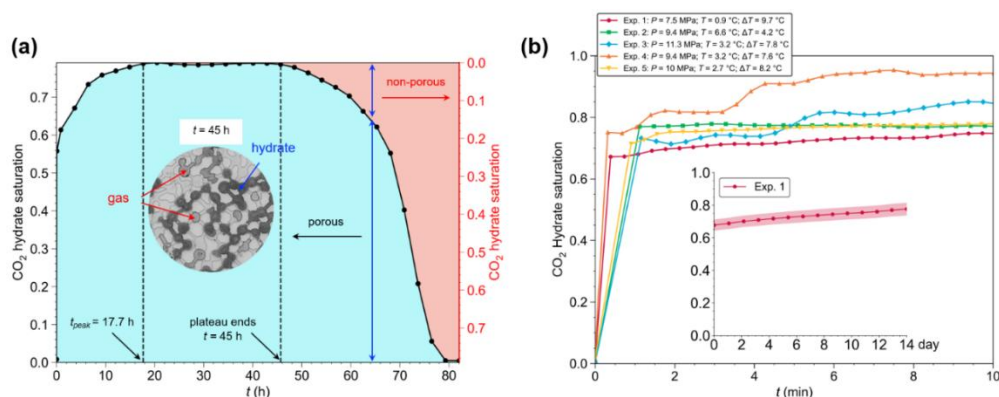
**Figure 2.6.** Conceptual model illustrating pore-filling behaviors during hydrate phase transitions for light phase-formed (gaseous CO<sub>2</sub>) and dense phase-formed (liquid CO<sub>2</sub>) hydrates.

### 2.3.3. CO<sub>2</sub> Hydrate Formation Kinetics

The formation kinetics of CO<sub>2</sub> hydrates from both gaseous and liquid phases were analyzed under various conditions by plotting hydrate saturations over time, calculated from grayscale contrasts in the captured images. For gaseous-phase CO<sub>2</sub> hydrates (Exp. 6), the saturation of dark hydrates initially increased, as shown in **Figure 2.7(a)**, peaking at  $t = 17.7$  h. This was followed by a stable plateau lasting 28 hours. After the plateau, dark hydrate saturation decreased to zero by  $t = 82$  h, indicating a transition to denser, non-porous hydrates as previously discussed. The kinetics can be divided into two stages: the initial lateral growth of hydrates and subsequent thickening in a perpendicular direction. A pore-scale image at  $t = 45$  h (inset of **Figure 2.7(a)**) reveals the presence of free gas bubbles during hydrate formation, which did not immediately transition into hydrates. This behavior suggests a localized drop in pore pressure near the hydrate interface, likely due to experimental conditions being close to the equilibrium curve (**Figure 2.2(a)**), creating a metastable hydrate formation condition[22,23]. The extended plateau likely represents a

balance between hydrate formation and dissociation. Once a new equilibrium is reached, the phase transition to non-porous hydrates resumes.

In contrast, as depicted in **Figure 2.7(b)**, liquid CO<sub>2</sub>-formed hydrates exhibit rapid saturation increases within approximately one minute, reaching plateaus with minor fluctuations. Unlike gaseous-phase hydrates, no transition into a transparent phase was observed, attributed to the density differences between liquid and gaseous CO<sub>2</sub>. Although a higher subcooling degree promotes hydrate formation, its effect on liquid-phase CO<sub>2</sub> is less pronounced than on gaseous CO<sub>2</sub>, likely due to the stronger mass transfer driving forces of liquid CO<sub>2</sub>[24]. Experiment 1 was used to investigate the long-term stability of liquid CO<sub>2</sub> hydrates, and over a 14-day period, hydrate saturation remained nearly constant. No significant dissolution or Ostwald ripening[25] was observed during this period (inset of **Figure 2.7(b)**).



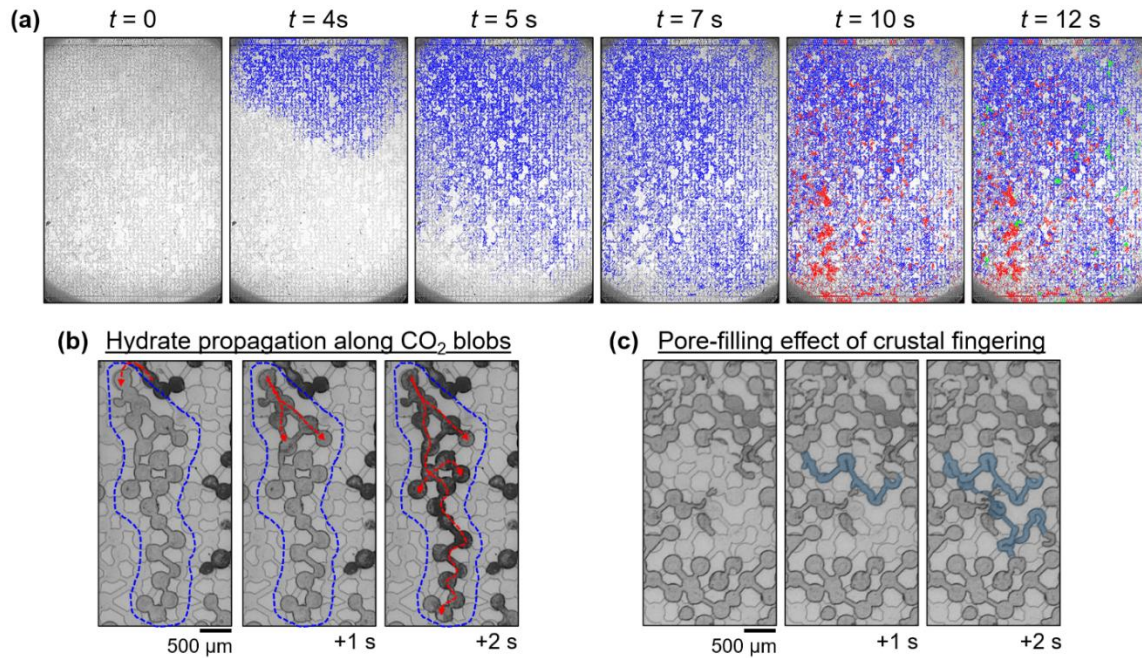
**Figure 2.7.** CO<sub>2</sub> hydrate saturation profiles over time for gaseous and liquid CO<sub>2</sub> hydrates. Gaseous CO<sub>2</sub> hydrates show peak saturation at  $t_{peak} = 17.7$  h, plateauing until  $t = 45$  h, and transitioning to non-porous hydrates by  $t = 82$  h. (b) Liquid CO<sub>2</sub> hydrates exhibit rapid saturation within one minute, remaining stable over 14 days.

### 2.3.4. Hydrate Propagation Across Pores

Compared to other microfluidic studies, the large viewing area of our system ( $45 \times 30$  mm, containing over 18,000 pores) enables the observation of collective behaviors in hydrate

formation and propagation across pore spaces in porous media. In a quasi-static, closed-system experiment with minimal fluid flow, we observed distinct phenomena during early hydrate formation and growth. Liquid CO<sub>2</sub> was injected at a constant rate of 10  $\mu\text{L}/\text{min}$  under controlled conditions (Exp. 5: 10 MPa and 2.7°C), revealing specific patterns of hydrate formation and propagation.

As shown in **Figure 2.8(a)**, hydrates formed after an induction time of 66 seconds, propagating along the flow direction (indicated in blue) and sweeping through all CO<sub>2</sub> clusters in the micromodel. Following this, hydrate growth extended beyond the CO<sub>2</sub> clusters into the surrounding water phase (indicated in red and green). This behavior can be divided into two processes: primary growth, which involves the initial propagation of hydrates across the CO<sub>2</sub> clusters within the micromodel, and secondary growth, characterized by the intrusion of hydrates into the water phase within the pore spaces.



**Figure 2.8.** Observation of CO<sub>2</sub> hydrate formation and propagation in a micromodel experiment (Exp. 5: 10 MPa, 2.7 °C). (a) Chip-scale images show hydrates forming and propagating along CO<sub>2</sub> clusters (blue regions) and extending into the surrounding water phase (red and green regions). (b) Pore-scale images depict hydrate propagation along CO<sub>2</sub> blobs. (c) The crustal fingering phenomenon highlights the pore-filling effect.

During primary growth, hydrate nucleation triggered rapid propagation across the pores, starting from the inlet. Hydrate formation in one CO<sub>2</sub> blob induced growth in adjacent, disconnected blobs by increasing the CO<sub>2</sub>-water interfacial area. This "chain reaction" effect occurred as hydrate shells formed on one blob, altering local pressure and temperature conditions, which promoted nucleation in nearby blobs[26]. This process, illustrated in **Figure 2.8(b)**, occurred rapidly within seconds. The hydrate formation within individual gas blobs was likely driven by coupled mass and heat transfer kinetics. As shown in **Figure 2.6**, a thin water film initially separated the glass and the CO<sub>2</sub>. During mass transfer, CO<sub>2</sub> molecules diffused from the bulk gas phase into the surrounding water, creating a concentration gradient that drove nucleation and the initial growth of hydrates at the thin water film[27]. Simultaneously, the exothermic nature of hydrate formation generated thermal gradients. Localized heat dissipation created regions of subcooling, enhancing hydrate stability and promoting growth[28].

Secondary growth occurred after hydrate propagation reached the micromodel outlet. This stage involved hydrates expanding into the water phase, as seen in the red and green regions of **Figure 2.8(a)**. The growth was primarily influenced by mass transfer mechanisms. As CO<sub>2</sub> diffused from the CO<sub>2</sub> phase into the water, a concentration gradient formed at the gas-liquid interface[27]. The higher CO<sub>2</sub> concentration in the gas phase compared to the water phase drove CO<sub>2</sub> dissolution, leading to the formation of a dissolved gas layer near the interface. This dissolved gas interacted with water molecules to form hydrate nuclei, further enhanced by subcooling effects.

At the pore scale, a crustal fingering phenomenon was observed, further influencing hydrate growth kinetics. Vacant water-filled pores were quickly occupied by expanding

intestine-like hydrate structures emerging from the CO<sub>2</sub> blobs **Figure 2.8 (c)**. This process, as studied by Fu et al. (2020)[13] is driven by localized pressure drops, causing gas to burst through weak points in the hydrate shells. The dynamics of crustal fingering are controlled by the competition between gas flow and hydrate growth. When gas flow surpasses the rate of hydrate formation, gas propagates through the crust, forming fingers. The resulting intestine-like morphology is shaped by wall confinement and the growth of hydrate shells.

Over time, the pressure differential between the injection and outflow points increased, ultimately leading to complete blockage of the micromodel due to hydrate formation. This pore-filling effect, including the thickening and swelling of hydrates and specific phenomena such as crustal fingering, significantly impacts CO<sub>2</sub> injectivity and overall storage capacity. While previous studies suggest that increasing hydrate saturation reduces CO<sub>2</sub> permeability[29–31], our findings show that permeability can drop to zero if hydrates form at the injection point, regardless of the overall saturation level. These results highlight the importance of operational parameters, such as injection rates and system conditions, as potential areas for further research.

## **2.4. Conclusion**

This chapter examined the dynamics and phase transitions of CO<sub>2</sub> hydrates in porous media under controlled experimental conditions, providing critical insights into their formation, morphology, and implications for CCS. By employing a low-temperature, high-pressure microfluidic system, the study revealed distinct behaviors of hydrates formed from liquid and gaseous CO<sub>2</sub>, with significant differences in morphology, pore-filling effects, and stability.

Liquid CO<sub>2</sub> hydrates demonstrated swelling behavior, characterized by a volume variation index of 3.61, and efficiently filled pore spaces, forming stable, persistent structures over extended periods. This swelling nature highlights their potential for pore-filling and cementation, effectively immobilizing fluid flow and maintaining structural integrity. Such attributes make liquid CO<sub>2</sub> hydrates suitable for long-term carbon sequestration in deep reservoirs. In contrast, gaseous CO<sub>2</sub> hydrates exhibited a two-stage formation process, transitioning from porous to non-porous, transparent structures. With a volume variation index of 0.27, these hydrates showed significant shrinkage during the phase transition. This difference in behavior, driven by lower CO<sub>2</sub> density and distinct mass transfer limitations, highlights the challenges of using gaseous CO<sub>2</sub> hydrates for efficient pore utilization.

Hydrate propagation across the porous medium revealed a cascading effect. Primary growth was initiated at the CO<sub>2</sub>-water interface and extended rapidly to adjacent regions, followed by secondary growth into the water phase. These processes were driven by coupled heat and mass transfer mechanisms, with localized thermal gradients and concentration differences enhancing hydrate formation. Pore-scale imaging captured crustal fingering, an intricate growth phenomenon where hydrates expanded into water-filled pores, forming intestine-like structures that reduced permeability and ultimately led to complete pore blockage. The study also highlighted the unique kinetics of hydrate growth. Liquid CO<sub>2</sub> hydrates displayed rapid and stable growth, while gaseous CO<sub>2</sub> hydrates were subject to prolonged transitions influenced by experimental conditions near the equilibrium curve. These observations underscore the significant role of operational

parameters such as pressure, temperature, and subcooling in controlling hydrate formation dynamics.

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# **CHAPTER 3**

## **INJECTION STRATEGIES AND GROWTH KINETICS OF CO<sub>2</sub> HYDRATES IN POROUS MEDIA**

### **Abstract**

This chapter investigates the role of CO<sub>2</sub> injection rates and subcooling on hydrate formation dynamics, storage capacity, and propagation within microfluidic porous media. Using a low-temperature, high-pressure (LTHP) system, liquid CO<sub>2</sub> was injected at varying flow rates (5–100 µL/min) to simulate seabed sediment conditions. Results revealed that higher injection rates reduced hydrate induction time due to shear-induced nucleation, while lower rates resulted in incomplete pore space utilization, limiting CO<sub>2</sub> storage capacity. Subcooling emerged as a critical factor in hydrate growth, with greater degrees of subcooling significantly enhancing growth rates. The findings suggest that while injection rate influences hydrate nucleation and storage efficiency, growth rates are primarily governed by thermodynamic driving forces. To address risks such as pipeline blockages from premature hydrate formation, an alternating CO<sub>2</sub>–water injection strategy is proposed, enhancing injectivity and capacity for hydrate-based carbon storage. These insights advance the understanding of CO<sub>2</sub> hydrate behavior under controlled conditions and provide practical implications for optimizing storage in marine sediments.

### **3.1. Introduction**

Sequestering carbon dioxide (CO<sub>2</sub>) as hydrates within seabed sediments presents a promising solution for carbon capture and storage (CCS), providing both extensive storage capacity and environmental stability in deep ocean conditions. Field-scale tests in the deep

ocean have demonstrated that CO<sub>2</sub> can indeed form stable hydrates under certain conditions, supported by studies in various marine settings where CO<sub>2</sub> injection has led to rapid hydrate formation and dissolution in seawater[1–5]. Early tests by Brewer et al. (1997–1999)[3–5] observed methane hydrate formation in deep waters and CO<sub>2</sub> hydrate formation in sediments, with notable findings on CO<sub>2</sub> dissolution rates and stability at depths up to 3600 meters. More recently, Qureshi et al. (2022–2024)[1,6–9] provided experimental evidence of CO<sub>2</sub> hydrate stability in sediments under simulated oceanic conditions, showing that hydrates formed with liquid CO<sub>2</sub> are particularly stable. These field-scale and laboratory studies have demonstrated the feasibility of CO<sub>2</sub> storage as gas hydrates and highlighted the potential of hydrate-based CCS in oceanic sediments.

Despite these promising field results, significant gaps remain in understanding how to control and optimize CO<sub>2</sub> hydrate formation, especially at injection rates suitable for long-term storage in marine sediments. Our study addresses this gap by focusing on the role of injection rates in CO<sub>2</sub> hydrate formation within porous media, exploring how these rates influence key factors such as induction time, storage capacity, and hydrate growth rates. Induction time, defined as the time required for hydrate nucleation, is a crucial metric for assessing the practicality of hydrate-based CO<sub>2</sub> storage, while storage capacity represents the ultimate sequestration potential. This study also investigates the impact of subcooling degree ( $\Delta T$ ) on hydrate growth rates, with the hypothesis that higher  $\Delta T$  accelerates formation. By examining these factors, our research aims to bridge the understanding between controlled laboratory results and potential field applications, contributing insights to advance CO<sub>2</sub> storage in marine sediments.

## 3.2. Methodology

### 3.2.1. Experimental Setup and Materials

The experimental setup in this chapter is identical to that described in **Chapter 2**, with a specific focus on chip-scale observation phenomena. Chip-scale imaging provides a broader perspective on hydrate propagation within porous media, allowing for a comprehensive understanding of the overall behavior of hydrates. The materials used include pure CO<sub>2</sub> (99.9% purity) supplied by Saudi Industrial Gas Company Ltd. and deionized (DI) water from Milli-Q® (Sigma-Aldrich).

### 3.2.2. Experimental Procedures

Initially, the micromodel chip was saturated with deionized (DI) water, and we allowed both the temperature and back pressure to stabilize at 10 MPa for all experiments. Subsequently, liquid CO<sub>2</sub> was injected at varying flow rates of 5, 10, 20, 50, and 100 µL/min, while images were captured at a rate of one frame per second. The use of liquid CO<sub>2</sub> was intended to replicate the conditions found in seabed sediments, where high pressure maintains CO<sub>2</sub> in a liquid state.

During the injection process, we monitored the moment when CO<sub>2</sub> first appeared at the micromodel inlet, which was recorded as  $t_0$ . Following this, we observed the formation of hydrates, which was indicated by a darker appearance in the captured images, as discussed in **Chapter 2**. The time at which hydrate formation commenced was recorded as  $t_{ind}$ , marking the induction time for hydrate formation. It is important to note that complete saturation was not always achieved; at lower flow rates, early hydrate formation occasionally occurred before full CO<sub>2</sub> saturation could be attained within the pores.

Once hydrates had formed, the micromodel exhibited darker regions, and pressure began to build at the inlet due to pore blockage. We allowed this pressure to increase until it reached 14 MPa, at which point the pump automatically ceased operation to ensure that the system was fully stabilized and blocked by hydrates. To dissociate the hydrates, we reduced the back pressure to near atmospheric levels and flushed the micromodel with DI water at a rate of approximately 0.3 mL/min. After confirming the absence of hydrates and residual CO<sub>2</sub>, we proceeded to repeat the experiment with different parameter variations.

### **3.2.3. Data Processing and Analysis**

The data processing and analysis methods are detailed in the Results and Discussion section. These include measuring induction time, calculating gas saturation through image analysis (primarily using ImageJ), and performing various image processing tasks. Python was also used, particularly for analyzing hydrate growth rate, accompanied by a workflow diagram for clarity. Additional workflow diagrams and written explanations will outline the overall data processing steps, providing a clear overview of the analytical process.

## **3.3. Results and Discussion**

### **3.3.1. Effect of Injection Rate on Induction Time**

To measure induction time, we recorded the moment gas first began flowing into the micromodel, as illustrated in **Figure 3.1(a)**, using the image processing methods for gas and hydrate phase identification detailed in **Chapter 2**. Initially, at  $t = 0$ , the micromodel was filled with DI water only. At  $t = 1$  s, the gas became visible entering from the inlet, marked in red. The gas continued to flow, and the moment of hydrate formation was noted

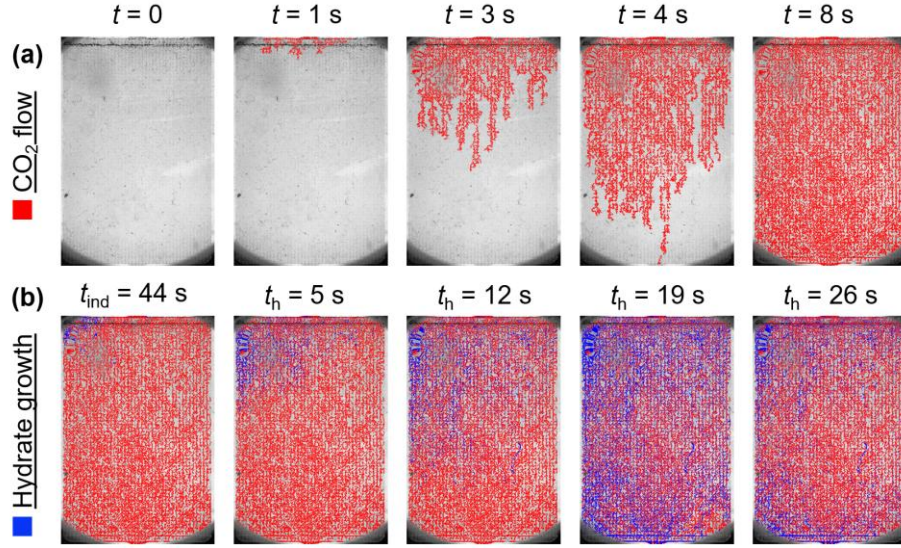
as the induction time ( $t_{ind}$ ) as shown in **Figure 3.1(b)**, where hydrates are represented in blue. Following induction, the hydrates grew and propagated throughout the micromodel.

**Table 3.1.** Hydrate formation induction times ( $t_{ind}$ ), CO<sub>2</sub> saturation ( $S_{CO_2}$ ), and average growth rate ( $v_h$ ) at varying flow rates ( $Q$ ).

| $Q$ ( $\mu\text{L}/\text{min}$ ) | $t_{ind}$ (s) <sup>a</sup> | $S_{CO_2}$ <sup>b</sup> | $v_h$ (mm/s) <sup>a</sup> |
|----------------------------------|----------------------------|-------------------------|---------------------------|
| 100                              | $90 \pm 87$                | $0.81 \pm 0.03$         | $3.98 \pm 0.38$           |
| 50                               | $87 \pm 25$                | $0.77 \pm 0.02$         | $3.41 \pm 0.33$           |
| 20                               | $422 \pm 61$               | $0.71 \pm 0.05$         | $3.41 \pm 0.08$           |
| 10                               | $703 \pm 348$              | $0.65 \pm 0.09$         | $3.33 \pm 0.72$           |
| 5                                | $673 \pm 125$              | $0.56 \pm 0.07$         | $3.70 \pm 0.92$           |
| 1                                | -                          | $0.49 \pm 0.05$         | -                         |

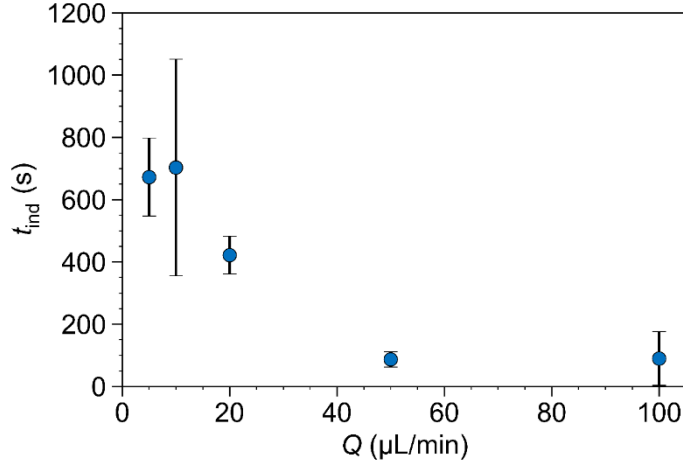
<sup>a</sup>Conducted at  $\Delta T = 7.3$  °C. <sup>b</sup>Conducted at  $\Delta T = 8.1$  °C.

Previous studies have indicated that shear-induced systems are more effective at triggering hydrate formation compared to quiescent systems [10–13]. In quiescent systems, mass transfer is limited because the water layer impedes gas molecules from escaping into the gas phase, reducing gas-water contact [14]. To simulate this effect, we set a  $\Delta T$  of 7.3 °C and varied the CO<sub>2</sub> injection rate, akin to a sensitivity study where only one parameter changes at a time. Here, the injection rate acts as the primary shear-inducing factor in the CO<sub>2</sub>-water system, promoting hydrate formation. By varying the injection rates and repeating each rate at least three times, we aimed to validate our findings, recognizing that hydrate formation is inherently stochastic. Even with identical system and operational parameters, induction times can vary significantly, as reported in multiple studies [13,15].



**Figure 3.1.** Temporal evolution of CO<sub>2</sub> flow and hydrate growth within microfluidic porous media at specified time intervals. (a) CO<sub>2</sub> flow initiation and progression. (b) CO<sub>2</sub> hydrate formation stages observed post-induction time ( $t_{ind} = 44$  s).

**Figure 3.2** illustrates the relationship between flow rate and induction time, with error bars showing variability across different rates, while **Table 3.1** provides detailed rate and induction time values. The data reveals a clear trend: higher flow rates are associated with shorter induction times, supporting the concept of shear-induced hydrate formation. In shear-induced systems, higher flow rates increase the driving force for nucleation, intensify mixing, and create a more dynamic environment, reducing mass-transfer limitations [13]. This dynamic environment facilitates gas supersaturation in the aqueous phase, promoting the formation of critically sized nuclei [13]. However, the results also show considerable variability in induction times, particularly at a flow rate of 10  $\mu\text{L}/\text{min}$ , which had the largest error margin at  $703 \pm 348$  s. In contrast, the smallest error was seen at a flow rate of 50  $\mu\text{L}/\text{min}$ , with an induction time of  $87 \pm 25$  s. This variability highlights the stochastic nature of hydrate formation, an important consideration for practical applications, such as CO<sub>2</sub> storage in hydrate-bearing seabed sediments.



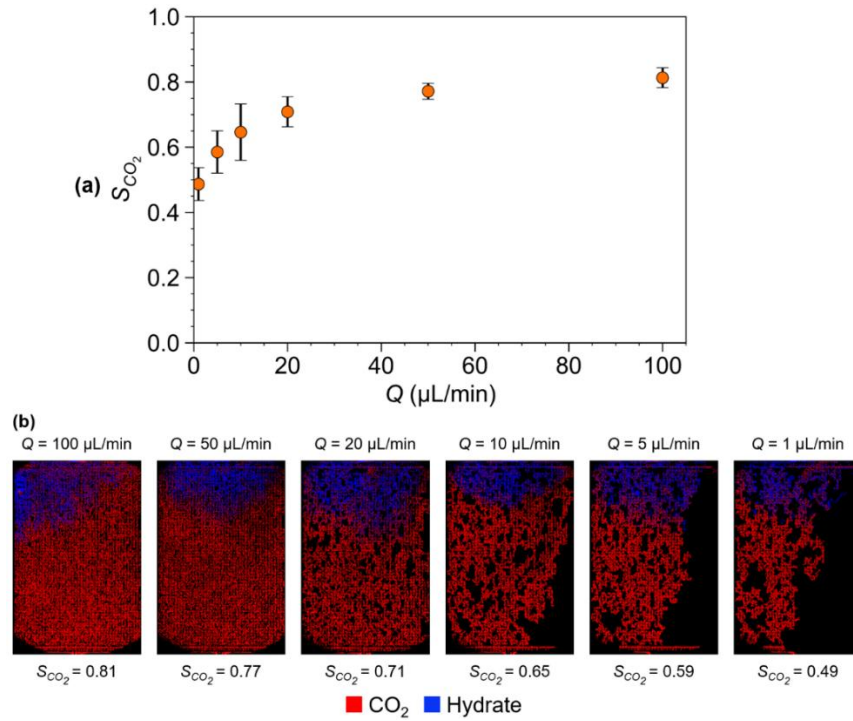
**Figure 3.2.** Relationship between CO<sub>2</sub> injection flow rate ( $Q$ ) and CO<sub>2</sub> hydrate induction time ( $t_{ind}$ ) observed in experiments conducted at  $\bar{P} = 10.1$  MPa and  $\Delta\bar{T} = 7.3$  °C.

### 3.3.2. Effect of Injection Rate on CO<sub>2</sub> Storage Capacity

Maximizing CO<sub>2</sub> storage capacity in porous media involves ensuring that pore spaces are filled with CO<sub>2</sub>, though complete saturation is limited by the presence of water and other fluids. Another approach to maximize storage capacity is through CO<sub>2</sub> injection, where continuous injection aims to occupy all available pore spaces. In this study, we varied injection rates to observe their impact on CO<sub>2</sub> hydrate storage capacity by measuring for the CO<sub>2</sub> saturation ( $S_{CO_2}$ ) using image analysis. This process involved subtracting the background image from the image with CO<sub>2</sub> immediately before hydrate formation, then cropping to isolate only the porous media area for accurate CO<sub>2</sub> saturation calculation. A binarization step followed, with CO<sub>2</sub> shown as white pixels by applying a specific threshold and noise removal procedure. After binarization, we measured the ratio of white pixels to the total area and, knowing the porosity of the porous media is 53%, divided the white pixel area by the porosity to determine CO<sub>2</sub> saturation for each image.

For this experiment series,  $\Delta T$  was maintained at 8.1 °C for all rates, with injection rates as low as 1 μL/min to examine effects. The results, shown in **Figure 3.3(a)**, indicate

that different flow rates produce distinct outcomes. Error bars in **Figure 3.3(a)** reveal relatively low variability, indicating a predictable trend, with detailed values provided in **Table 3.1**. The data shows a decrease in storage capacity at lower injection rates, as slower flows require more time to reach maximum capacity. As CO<sub>2</sub> flow slows, hydrates (in blue) begin to form within the micromodel, as illustrated in **Figure 3.3(b)**.

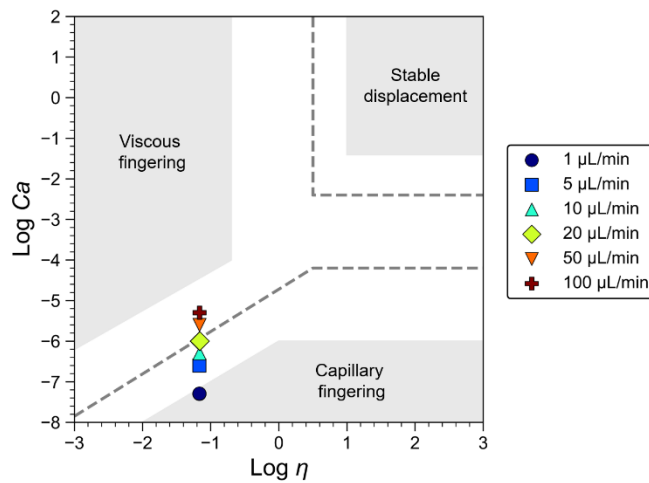


**Figure 3.3.** (a) Relationship between CO<sub>2</sub> injection flow rate ( $Q$ ) and CO<sub>2</sub> storage capacity ( $S_{\text{CO}_2}$ ) observed in experiments conducted at  $\bar{P} = 10.1$  MPa and  $\Delta\bar{T} = 8.1$  °C. (b) Visual representation of CO<sub>2</sub> and hydrate distribution within the porous media, showing hydrates (in blue) forming before complete CO<sub>2</sub> saturation of the pore spaces (in red) at lower injection rates.

At injection rates of 20  $\mu\text{L}/\text{min}$  and lower, **Figure 3.3(b)** highlights that CO<sub>2</sub> (in red) fails to completely occupy the porous spaces. Inadequate displacement of water results in premature hydrate formation, which impedes achieving maximum storage capacity. This finding underscores the dependence of water displacement efficiency on injection force. This phenomenon can be analyzed using flow regime analysis through the capillary number ( $\text{Ca} = \frac{v\mu}{\sigma}$ ) and its relationship with viscosity ratio ( $\eta = \frac{\mu_{\text{CO}_2}}{\mu_w}$ ), as defined by Lenormand et

al. (1988)[16]. The capillary number, calculated from the injection flow rate, uses the following parameters: CO<sub>2</sub> viscosity is 0.115 cP[17] at 10 MPa and 2.7 °C, water viscosity of approximately 1.67 cP[18] under the same conditions, and liquid CO<sub>2</sub>-water interfacial tension of 38 mN/m[19].

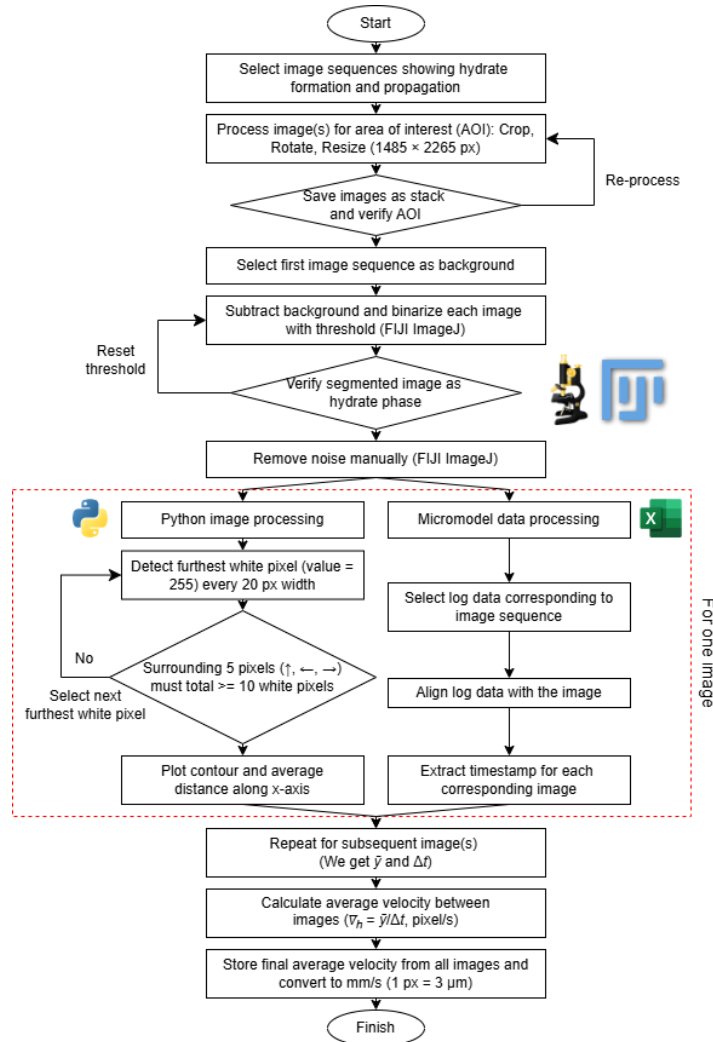
**Figure 3.4** shows that data points from varying flow rates lie in the transition zone between capillary fingering and viscous fingering. At the lowest rate (1  $\mu\text{L}/\text{min}$ ), the flow regime is in the capillary fingering zone. As the injection rate increases, the regime shifts toward viscous fingering. In a liquid CO<sub>2</sub>-water system under hydrate stability conditions, low flow rates promote capillary fingering, which hinders CO<sub>2</sub> distribution across the porous media. Conversely, an optimal injection rate generates a more favorable flow regime, though it does not approach fully stable displacement. To minimize fingering effects, excessively low or high rates should be avoided. These findings underscore the critical need to optimize injection rates to enhance CO<sub>2</sub> storage efficiency.



**Figure 3.4.** Log Ca-log  $\eta$  stability diagram highlighting three regions: viscous fingering, capillary fingering, and stable displacement. Experimental CO<sub>2</sub>-water displacement data at varying injection rates illustrate flow behavior under hydrate stability.

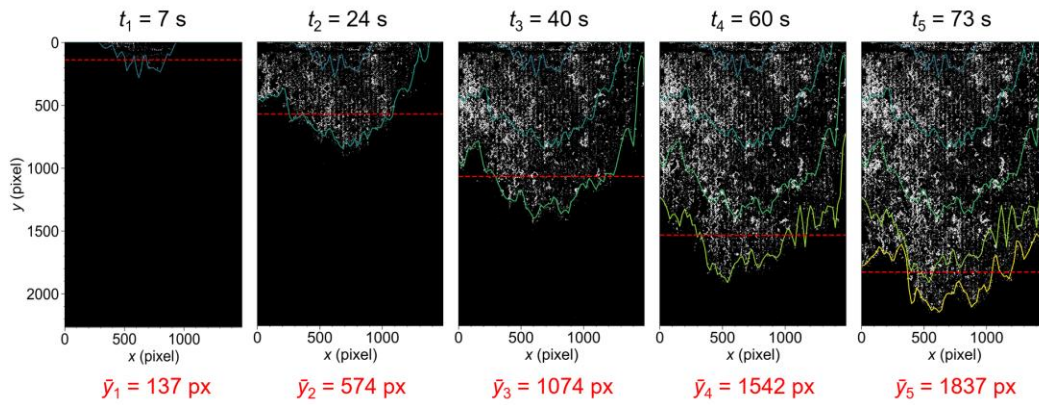
### 3.3.3. Effect of Injection Rate and Subcooling on CO<sub>2</sub> Hydrate Propagation Rate

Hydrate growth rate is a key focus in hydrate-related studies due to its implications for control strategies in practical applications[20]. **Figures 3.1(b)** and **3.3(b)** illustrate the propagation of hydrates (shown in blue) moving toward the outlet at the bottom of the micromodel chip. To determine the rate of hydrate growth, we employ a combined image processing technique using Python. The workflow is detailed in **Figure 3.5**.



**Figure 3.5.** Workflow for analyzing CO<sub>2</sub> hydrate growth rate through image sequence and micromodel data processing.

Initially, each image sequence is cropped to isolate the micromodel, excluding unnecessary areas. The initial image, taken just before hydrate formation, serves as the background. As hydrates form, each subsequent image is subtracted from this background to highlight only the hydrate phase. Using a consistent threshold value, the images from each experiment are binarized, resulting in binary images where hydrates appear in white against a black background.



**Figure 3.6.** Temporal progression of CO<sub>2</sub> hydrate front in the micromodel, showing the y-position) of the furthest extent of hydrate formation over time. Each panel represents a snapshot at distinct timestamps, with corresponding average y-positions ( $\bar{y}$ ) indicated in red.

A Python algorithm tracks the farthest white pixel along the y-axis every 20 pixels across the x-axis in the cropped micromodel image ( $1485 \times 2265$  pixels). To address noise, ImageJ is used for manual image cleaning by selecting and removing unwanted pixels. After noise removal, the algorithm identifies the y-position of the farthest white pixel and scans the left, right, and above this pixel. If the surrounding area includes at least 10 contiguous white pixels, it marks this position as the furthest extent of the hydrate front. If this condition is not met, the algorithm proceeds to the next farthest white pixel along the y-axis for that x position and repeats the scanning process. This method generates a contour-like curve representing hydrate coverage, as shown in **Figure 3.6**.

To calculate growth rate, we measure the average distance traveled by the hydrate front between consecutive images using timestamp data from the microfluidic system. The red dashed line in **Figure 3.6** indicates this average distance over time. Applying a standard velocity formula, we determine growth rate in pixels per second, then convert it to mm/s (considering each pixel represents 20  $\mu\text{m}$ ). This process produces a detailed series of velocity data across all image sequences, resulting in a final calculated CO<sub>2</sub> hydrate growth rate.

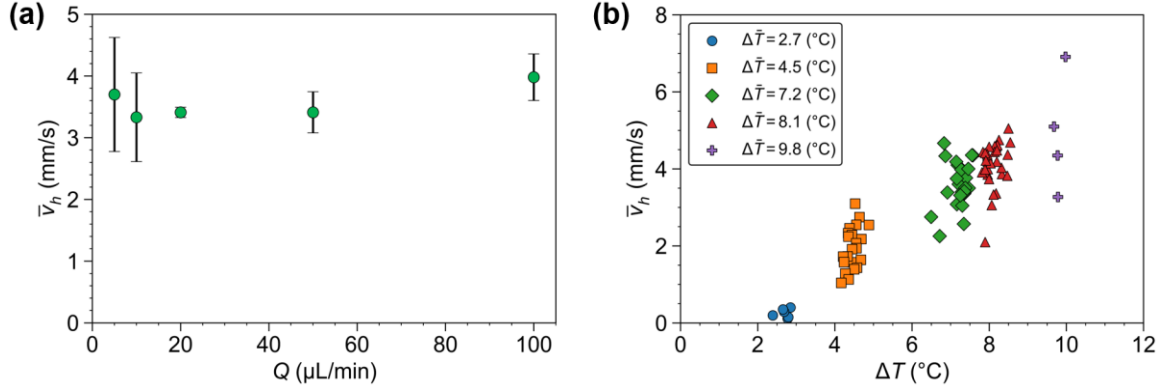
To examine the effect of injection rate on CO<sub>2</sub> hydrate growth rate ( $\bar{v}_h$ ), experiments were conducted under conditions of  $\Delta T = 7.3$  °C, with each injection rate repeated three times for validation. As shown in **Figure 3.7(a)** and **Table 3.1**, there is no consistent correlation between flow rate and CO<sub>2</sub> hydrate growth rate. This suggests that growth rate is predominantly influenced by the intrinsic properties of guest molecule of hydrates—primarily pressure and temperature—as supported by existing literature[21–23]. Factors such as molecular interactions and CO<sub>2</sub> solubility[24] may play a more significant role than the operational parameter of injection rate.

Subsequent experiments varying  $\Delta T$ , as shown in **Figure 3.7(b)**, reveal that higher  $\Delta T$  values correlate with increased growth rates, suggesting that reduced formation temperature enhances CO<sub>2</sub> hydrate growth. Detailed mean growth rates with corresponding  $\Delta T$  values are provided in **Table 3.2**. Greater subcooling provides the thermodynamic driving force necessary for the water-to-hydrate phase transition, reducing the nucleation energy barrier and accelerating overall growth by increasing nucleation sites[25]. These findings indicate that while flow rate does not affect CO<sub>2</sub> hydrate growth, lowering system temperature and increasing  $\Delta T$  significantly enhances growth.

**Table 3.2.** Average subcooling and corresponding average CO<sub>2</sub> hydrate growth rates, showing an increasing trend with higher subcooling.

| $\Delta\bar{T}$ (°C) | $\bar{v}_h$ (mm/s) |
|----------------------|--------------------|
| 2.7                  | $0.25 \pm 0.11$    |
| 4.5                  | $1.95 \pm 0.55$    |
| 7.2                  | $3.59 \pm 0.59$    |
| 8.1                  | $4.12 \pm 0.59$    |
| 9.8                  | $4.91 \pm 1.53$    |

However, relying solely on  $\Delta T$  as a driving force may underestimate the growth rate, as it is also influenced by intrinsic kinetics, mass transfer, and heat transfer[20]. Modeling these mechanisms could provide further insights but would require more advanced experimental setups beyond the scope of this study. Additionally, previous hydrate studies predominantly used bulk systems like stirred-batch reactors[26–28], and the models derived from them may not accurately represent microfluidic systems. To the author’s knowledge, no studies have yet combined microfluidic experiments with data-driven modeling of hydrate growth kinetics. The type of porous media—such as sandy media, silica gel, glass beads, or nanoparticles[29]—also significantly impacts hydrate formation kinetics by altering mass transfer and fluid flow rates[20]. Therefore, more controlled parameter settings in microfluidic porous media setups are essential for accurately capturing these influences and enabling reliable modeling of hydrate growth kinetics.



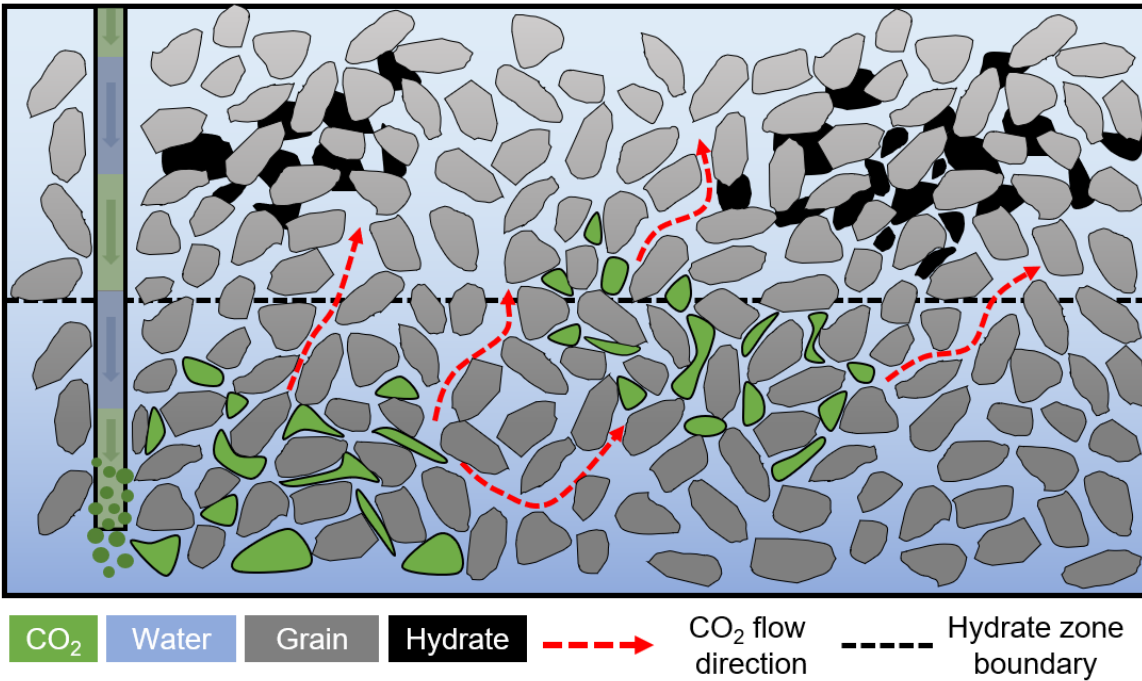
**Figure 3.7.** (a) Relationship between CO<sub>2</sub> injection flow rate ( $Q$ ) and average hydrate growth rate ( $\bar{v}_h$ ) under a constant subcooling ( $\Delta T = 7.3$  °C). (b) Influence of varying subcooling levels ( $\Delta T$ ) on hydrate growth rate.

### 3.3.4. Proposed Mechanism for Storing CO<sub>2</sub> as Hydrates in Seabed Sediments

Observations indicate that injection rate does not influence hydrate growth rate. Instead, higher subcooling ( $\Delta T$ ) correlates with increased hydrate growth rates, meaning lower system temperatures enhance hydrate formation. From a practical perspective, seabed sediment sites with low temperatures suitable for CO<sub>2</sub> storage as hydrates also pose a risk of premature hydrate formation, potentially leading to pipeline blockages near the pipeline's end due to the stronger driving force at these low temperatures[1]. Continuous CO<sub>2</sub> injection could further increase this risk, as CO<sub>2</sub> hydrate growth may outpace the injection rate, resulting in hydrate plugging within the pipeline, with hydrates propagating from formations already present in the reservoir.

In response to these risks, we propose an alternating CO<sub>2</sub>–water injection strategy to improve injectivity for CO<sub>2</sub> storage as hydrates in shallow seabed sediments. This method is analogous to the water-alternating-gas (WAG) technique used in enhanced oil recovery[30]. In this approach, CO<sub>2</sub> and warmer-than-ambient water are injected alternately below the hydrate stability zone, as shown in **Figure 3.8**. This technique allows CO<sub>2</sub> plumes to migrate laterally and rise due to gravity and buoyancy. Subsequent water

injection breaks up large CO<sub>2</sub> clusters into smaller ones, creating buffer zones between CO<sub>2</sub> aggregations and preventing continuous CO<sub>2</sub> clusters that could block the pipeline. Once hydrate formation begins, the water phase between CO<sub>2</sub> clusters helps reduce hydrate-induced cementation of sediment grains and diverts CO<sub>2</sub> flow into other regions, thereby enhancing both injectivity and capacity for CO<sub>2</sub> storage.



**Figure 3.8.** Illustration of the alternating CO<sub>2</sub>–water injection strategy proposed for CO<sub>2</sub> storage as hydrates in shallow seabed sediments.

### 3.4 Conclusions

This chapter explored the quantitative effects of injection rates and subcooling on CO<sub>2</sub> hydrate dynamics, with key findings providing a detailed understanding of hydrate nucleation, growth, and storage behavior in porous media. It was demonstrated that higher injection rates led to faster hydrate nucleation, with induction times as low as 90 seconds at high rates, while slower rates extended induction times to over 700 seconds. CO<sub>2</sub> saturation exhibited a similar dependency on flow rates, with maximum saturations

reaching 0.81, compared to 0.49 at the lowest rates. These results highlight the significant influence of injection velocity on hydrate nucleation and storage efficiency, underscoring the need for precise rate control in field applications.

Hydrate growth rates were found to be largely independent of injection rates, with values remaining within a narrow range of 3.7 to 4.0 mm/s. However, subcooling emerged as a critical factor, with growth rates increasing from 0.04 mm/s at a subcooling degree of 2.7 °C to 0.74 mm/s at 9.8 °C. These findings reveal that thermodynamic driving forces, rather than operational parameters like injection velocity, govern the kinetics of hydrate formation, making temperature control essential for maximizing growth efficiency.

The study also proposed a practical alternating CO<sub>2</sub>–water injection strategy to address risks associated with premature hydrate-induced blockages. This approach ensures better lateral distribution of CO<sub>2</sub> and prevents the formation of continuous clusters, enhancing both injectivity and capacity. By optimizing conditions to maintain stable hydrate formation while minimizing plugging risks, this strategy provides a viable path forward for efficient carbon sequestration.

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## **CHAPTER 4**

# **PERFORMANCE EVALUATION OF KINETIC HYDRATE PROMOTERS FOR CO<sub>2</sub> HYDRATE FORMATION**

### **Abstract**

This chapter investigates the kinetics of CO<sub>2</sub> hydrate formation using a second-generation High-Pressure Stirred Automated Lag Time Apparatus (HPS-ALTA) and evaluates the efficiency of three chemical promoters: sodium dodecyl sulfate (SDS), a gemini surfactant (GS-12), and Laponite-RD (a water-soluble organoclay). These promoters were tested across various concentrations to assess their influence on nucleation rates and subcooling behavior. Results showed that SDS achieved the highest nucleation rates ( $12.1 \text{ s}^{-1}$ ) at 0.5 wt%, while GS-12 and Laponite exhibited optimal rates of  $8.9 \text{ s}^{-1}$  and  $4.0 \text{ s}^{-1}$  at 1 wt% and 0.1 wt%, respectively. Mechanistic studies revealed distinct promotive effects, with SDS enhancing hydrate nucleation through adsorption and micelle formation, GS-12 reducing interfacial tension, and Laponite modifying water-CO<sub>2</sub> interactions via its hydration layer. This research demonstrates that careful optimization of promoter type and concentration can significantly enhance the kinetics of CO<sub>2</sub> hydrate formation, providing valuable insights for advancing carbon capture and storage technologies.

### **4.1. Introduction**

The utilization of CO<sub>2</sub> hydrates presents a promising approach for Carbon Capture and Storage (CCS) due to their ability to store significant volumes of gas in compact crystalline structures. Under high-pressure and low-temperature conditions, CO<sub>2</sub> hydrates can sequester up to  $164 \text{ m}^3$  of gas per  $1 \text{ m}^3$  of solid hydrate, offering an efficient solution for

large-scale carbon storage[1]. This method leverages the unique properties of hydrates to provide stable and efficient sequestration, making it an attractive alternative to conventional CCS techniques[2]. However, practical implementation faces notable challenges, including long induction times and slow hydrate growth rates, which increase operational costs and limit scalability.

To address these challenges, researchers have focused on chemical promoters that accelerate hydrate nucleation and growth. Promoters are broadly categorized into thermodynamic hydrate promoters (THPs), which enable hydrate formation under milder conditions, and kinetic hydrate promoters (KHPs), which enhance growth rates and reduce induction times[3]. This study aims to advance the understanding of CO<sub>2</sub> hydrate formation kinetics and the role of these promoters by utilizing the second-generation HPS-ALTA system[4]. This state-of-the-art apparatus captures high-resolution data on hydrate formation with a statistically significant number of data points.

The promoters tested in this research include a novel gemini surfactant (GS), derived from quaternary ammonium salts, and Laponite-RD, an organoclay known for its unique colloidal properties. Both are compared against sodium dodecyl sulfate (SDS), a commonly used KHP. Using constant cooling experiments, the study evaluates hydrate nucleation kinetics through Classical Nucleation Theory (CNT) and statistical models, analyzing induction times and subcooling-dependent nucleation rates. These insights aim to address the existing limitations of CO<sub>2</sub> hydrate-based CCS and contribute to the development of more efficient and scalable carbon sequestration strategies.

## 4.2. Methodology

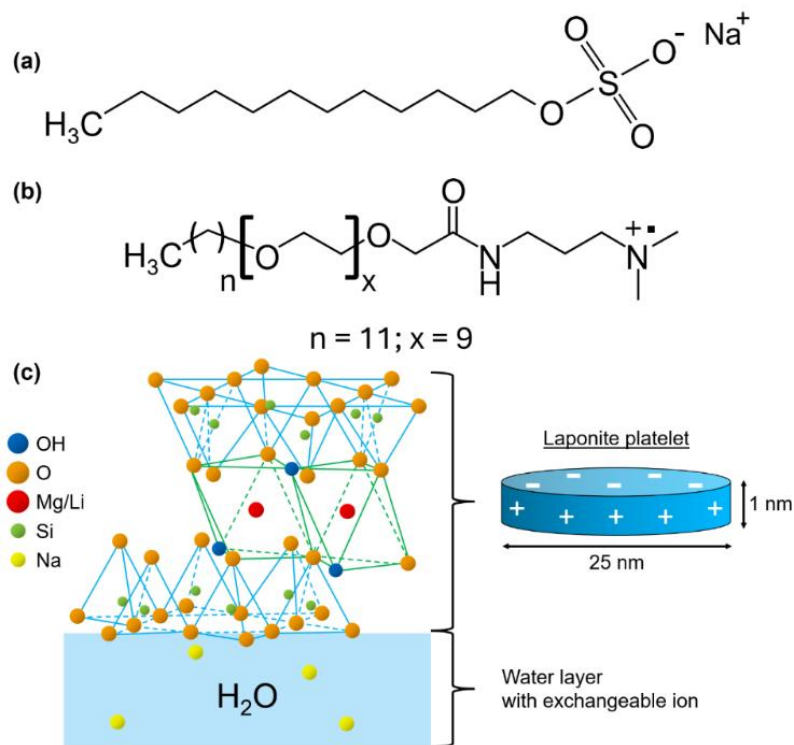
### 4.2.1. Materials

The ethoxylated quaternary ammonium gemini surfactant (GS-12) was synthesized in-house at King Fahd University of Petroleum & Minerals using the method described by Hussain et al. (2019)[5]. The synthesis process involved reacting glycolic acid ethoxylate lauryl ether with 3-(dimethylamino)-1-propylamine, followed by the addition of dibromoalkane to form the quaternary ammonium gemini structure with a C12 spacer. GS-12 was chosen for this study due to its surface-active properties, including ethoxy units that enhance solubility in brine and seawater, as well as its ability to form micelles[6]. The molecular structure of GS-12 is illustrated in **Figure 4.1(b)**. The final product was purified through column chromatography to ensure high purity.

Laponite-RD, sourced from BYK Additives & Instruments, was included in this study to assess its potential as a promoter for CO<sub>2</sub> hydrate formation. Laponite is a layered silicate mineral comprising alternating layers of silica tetrahedra and magnesia octahedra in a 2:1 ratio along the Z-axis. Its disk-like crystals have a diameter of 25 nm and a thickness of 1 nm. Laponite is widely used in water-based drilling fluids due to its stability and rheological properties at elevated temperatures[7,8]. However, in this research, the focus is on its role in CO<sub>2</sub> hydrate formation kinetics. The structure of Laponite is illustrated in **Figure 4.1(c)**.

For benchmarking, sodium dodecyl sulfate (SDS, 99% pure, ACS reagent-grade) obtained from Sigma-Aldrich was selected as the reference kinetic hydrate promoter (KHP) due to its well-documented efficacy in enhancing hydrate formation[9]. The molecular

structure of SDS is shown in **Figure 4.1(a)**. The concentrations tested for all additives were 0, 0.05, 0.1, 0.5, 1, and 2 wt%. High-purity CO<sub>2</sub> gas (99.9%) was supplied by Saudi Industrial Gas Company Ltd., and deionized water (Milli-Q® Plus 185) was used to minimize impurities and ensure consistency during the hydrate formation experiments.



**Figure 4.1.** Molecular structures and schematic representations of additives used in this study. (a) Sodium dodecyl sulfate (SDS). (b) Ethoxylated quaternary ammonium gemini surfactant (GS-12). (c) Laponite-RD, a layered silicate mineral with a disk-like structure (25 nm diameter, 1 nm thickness).

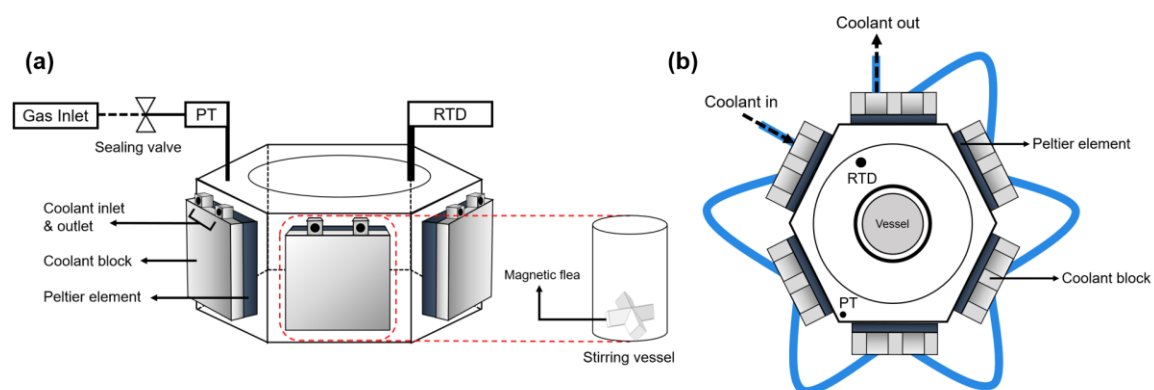
#### 4.2.2. HPS-ALTA System

The experimental setup employs the second-generation High-Pressure Stirred Automated Lag Time Apparatus (HPS-ALTA), developed by Metaxas et al. (2019) [4] (**Figure 4.2(a) & (b)**). The apparatus features four stainless-steel high-pressure cells, each independently controlling temperature and pressure. Each cell, with a hexagonal outer cross-section and a 2.4 cm diameter cylindrical well, holds 10.9 mL and includes a PTFE-

encapsulated stir bar (0.9 mL) for continuous mixing, agitated by a magnetic stirrer to ensure homogeneity and enhance gas dissolution.

Temperature control is managed by thermoelectric Peltier elements (Custom Thermoelectric, LLC), regulated through a PID loop in LabVIEW. Internal temperatures are measured using 100  $\Omega$  platinum RTDs (Omega Engineering Inc.), while a water-MEG coolant mixture circulates through coolant blocks driven by a chiller system (MC 600, LAUDA-Brinkmann, LP). Pressure monitoring is handled by an in-line transducer (DJ Instruments) positioned between the cell and sealing valve.

The system offers precise thermal control, capable of cooling at 1  $^{\circ}\text{C}/\text{min}$  and heating at 8.5  $^{\circ}\text{C}/\text{min}$ , crucial for hydrate formation and dissociation cycles. Data acquisition and control are managed by a National Instruments CompactDAQ system, recording temperature and pressure data at a frequency of 1 Hz, ensuring accurate monitoring throughout the experiments.



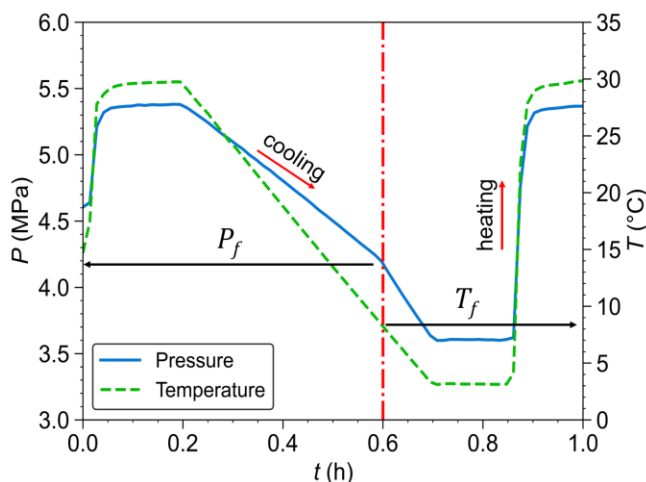
**Figure 4.2.** Schematic representation of the High-Pressure Stirred Automated Lag Time Apparatus (HPS-ALTA) system. (a) Detailed view of the HPS-ALTA cell. (b) Top view of the HPS-ALTA cell.

### 4.2.3. Experimental Procedures

In each experiment, 4 mL of degassed, deionized water was loaded into a 10.9 mL high-pressure cell, followed by the injection of 6 mL of CO<sub>2</sub> gas. A PTFE-encapsulated stir bar (0.9 mL) was employed to ensure continuous stirring at 700 RPM, promoting effective gas-liquid mixing and minimizing mass-transfer limitations—a design specifically tailored for this apparatus. Each cell was purged three times with CO<sub>2</sub> gas to eliminate residual air before the experiment began. The system was then pressurized to 5 MPa at 30 °C and held until pressure and temperature stabilized. Once stabilized, the cell was cooled at a constant rate of 1 °C/min until reaching a target temperature of 0 °C. Hydrate formation was identified through pressure drops, signifying CO<sub>2</sub> consumption during hydrate growth. Upon reaching 0 °C, the system was maintained at this temperature for 10 minutes to allow the hydrate phase to stabilize fully. The cell was then reheated at 8.5 °C/min back to 30 °C and held for 10 minutes to ensure complete dissociation of any formed hydrates, eliminating residual "memory effects" that could influence subsequent cycles.

This cooling-heating cycle was repeated until at least 100 hydrate formation events were recorded for each tested chemical concentration, providing high-resolution data for statistical analysis. An example of one cycle is shown in **Figure 4.3**. For each cooling cycle, the onset temperature ( $T_f$ ) and pressure ( $P_f$ ) of hydrate formation were recorded at the point where a sudden pressure decrease occurred, as indicated by the vertical dashed red line in **Figure 4.3**. The subcooling ( $\Delta T$ ) for each formation event was calculated using the equilibrium dissociation temperature ( $T_{eq}$ ) of CO<sub>2</sub> hydrates, calculated via the Cubic-Plus-Association (CPA) model implemented in MultiFlash 7.0. Subcooling data were then binned using Knuth's optimal binning method[10], a data-driven approach to determine

the ideal bin count, allowing an accurate representation of nucleation probability without assuming a specific distribution. These binned data were used to generate cumulative formation probability distributions, which were subsequently applied to analyze general  $\Delta T$  behavior and construct a nucleation rate model.



**Figure 4.3.** Example of a cooling-heating cycle used in CO<sub>2</sub> hydrate formation experiments within the HPS-ALTA system. Vertical dashed red line marked the onset of hydrate formation.

## 4.3. Results and Discussion

### 4.3.1. Subcooling Temperature Distribution Between Promoters

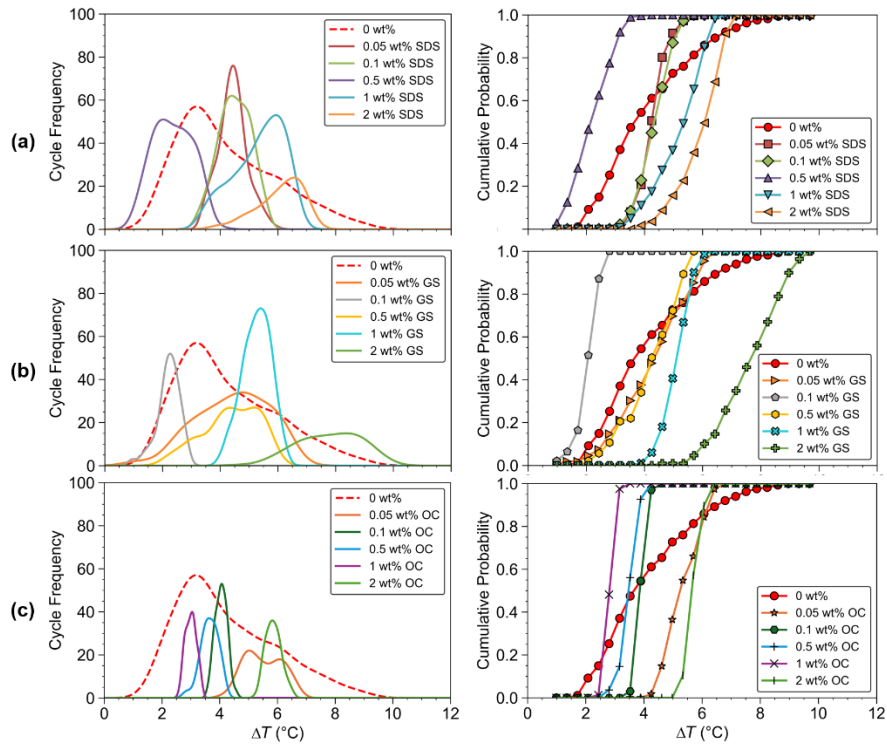
Each cell in an experiment can produce over 100 cyclic hydrate formation-dissociation events, with the pressure and temperature data for hydrate formation recorded and analyzed for distribution patterns. **Figure 4.4** presents both the histogram and cumulative probability function for each chemical promoter. Detailed statistical measurements for all data are summarized in **Table 4.1**. This analysis focuses on variations in subcooling across different concentrations of chemical promoters, emphasizing the stochastic nature of hydrate formation through distribution analysis.

**Table 4.1.** Statistical data for each tested promoter. The table includes the number of hydrate formation events recorded ( $N$ ), average formation pressure ( $\bar{P}_f$ ), average formation temperature ( $\bar{T}_f$ ), average subcooling temperature ( $\Delta\bar{T}$ ), standard deviation of subcooling temperature ( $\sigma$ ), and the minimum and maximum subcooling temperatures ( $\Delta T$ ) for each recorded hydrate formation event.

| Concentration (wt.%) | $N$ | $\bar{P}_f$ (MPa) | $\bar{T}_f$ (°C) | $\Delta\bar{T}$ (°C) | $\sigma$ (°C) | Max $\Delta T$ (°C) | Min $\Delta T$ (°C) | Max $J$ (s <sup>-1</sup> ) |
|----------------------|-----|-------------------|------------------|----------------------|---------------|---------------------|---------------------|----------------------------|
| 0                    | 455 | 3.85              | 5                | 4.25                 | 1.67          | 9.08                | 1.85                | 7.58                       |
| 0.05 SDS             | 247 | 3.95              | 5                | 4.43                 | 0.49          | 5.94                | 3.4                 | 11.53                      |
| 0.1 SDS              | 285 | 4.01              | 5.04             | 4.5                  | 0.56          | 5.71                | 3.1                 | 7.12                       |
| 0.5 SDS              | 288 | 4                 | 7.16             | 2.36                 | 0.69          | 4.14                | 0.81                | 12.8                       |
| 1 SDS                | 280 | 3.89              | 3.97             | 5.35                 | 0.87          | 6.79                | 3.2                 | 9.56                       |
| 2 SDS                | 115 | 3.75              | 3                | 6.08                 | 0.78          | 7.3                 | 3.77                | 4.13                       |
| 0.05 GS              | 109 | 3.95              | 5                | 4.43                 | 1.24          | 6.57                | 1.05                | 1.93                       |
| 0.1 GS               | 140 | 4.13              | 7.53             | 2.2                  | 0.4           | 2.91                | 0.91                | 3.07                       |
| 0.5 GS               | 141 | 3.59              | 4.4              | 4.37                 | 0.96          | 5.85                | 2.18                | 3.39                       |
| 1 GS                 | 283 | 3.85              | 4                | 5.26                 | 0.5           | 6.31                | 3.96                | 7.07                       |
| 2 GS                 | 109 | 3.49              | 0.8              | 7.78                 | 1.09          | 9.87                | 4.76                | 4.04                       |
| 0.05 OC              | 115 | 3.52              | 3.14             | 5.51                 | 0.64          | 6.72                | 4.1                 | 2.93                       |
| 0.1 OC               | 109 | 3.33              | 4.21             | 4.05                 | 0.2           | 4.59                | 3.59                | 3.96                       |
| 0.5 OC               | 122 | 3.75              | 5.44             | 3.65                 | 0.3           | 4.21                | 2.76                | 2.51                       |
| 1 OC                 | 112 | 3.65              | 5.9              | 3                    | 0.18          | 3.37                | 2.61                | 1.93                       |
| 2 OC                 | 110 | 3.5               | 2.75             | 5.86                 | 0.27          | 6.52                | 5.28                | 2.14                       |

In the control system (0 wt% concentration, CO<sub>2</sub> with pure water), over 450 data points were collected. As expected, this pure system exhibited the widest subcooling distribution, reflecting the inherent variability in hydrate formation without additives[11]. In contrast, systems containing chemical promoters demonstrated narrower subcooling distributions across all cases, indicating reduced stochasticity and a more predictable formation process. This significant reduction in stochasticity aligns with nucleation theory, where additives influence both thermodynamic and kinetic parameters. Similar trends were reported by May et al. (2018)[12] in studies on kinetic hydrate inhibitors (KHI) using the first-generation HPS-ALTA, where correlations with thermodynamic and kinetic nucleation parameters were examined.

Optimal subcooling suppression was observed at specific concentrations for each promoter: 0.5 wt% for SDS, 0.1 wt% for GS-12, and 1 wt% for Laponite. Beyond these concentrations, the effectiveness of each promoter decreased. For SDS, higher concentrations reduced promotive effects due to micelle formation, which limits the availability of free water necessary for hydrate nucleation and growth[13]. GS-12 was most effective at low concentrations, where its ability to significantly reduce interfacial tension was maximized [5,9]; increasing the concentration beyond the optimal level led to CO<sub>2</sub> hydrate inhibition. Laponite exhibited minimal promotive effects at 0.05 wt% and showed similar performance at 0.1, 0.5, and 1 wt%, with inhibition occurring at higher concentrations. This inhibition is likely due to gel formation inherent to clay [14], which can alter the bulk properties of the experimental system.



**Figure 4.4.** Histogram (left) and cumulative probability function (right) of subcooling ( $\Delta T$ ) for CO<sub>2</sub> hydrate formation with (a) SDS, (b) GS-12, and (c) Laponite as chemical promoters at varying concentrations (0–2 wt%).

### 4.3.2. Nucleation Rates Derived from the Hazard Rate Function

According to CNT, the probability of induction time follows an exponential distribution:

$$F(t) = 1 - \exp(-Jt) \quad (4.1)$$

where  $J$  is the nucleation rate and  $t$  is the elapsed time. This theoretical framework has been validated across various experimental setups[4,15–17].

In constant cooling experiments, Barwood et al. (2022)[17] emphasized the importance of accounting for the system's exposure to increasing subcooling over time, requiring specific adjustments to the  $t$  term in **Equation (4.1)**. They addressed this using the hazard function, which incorporates the system's history by defining the probability of hydrate formation at a given time, conditional on it not having occurred earlier. The hazard function is expressed as:

$$h(\Delta T) = \frac{f(\Delta T)}{1-F(\Delta T)} \quad (4.2)$$

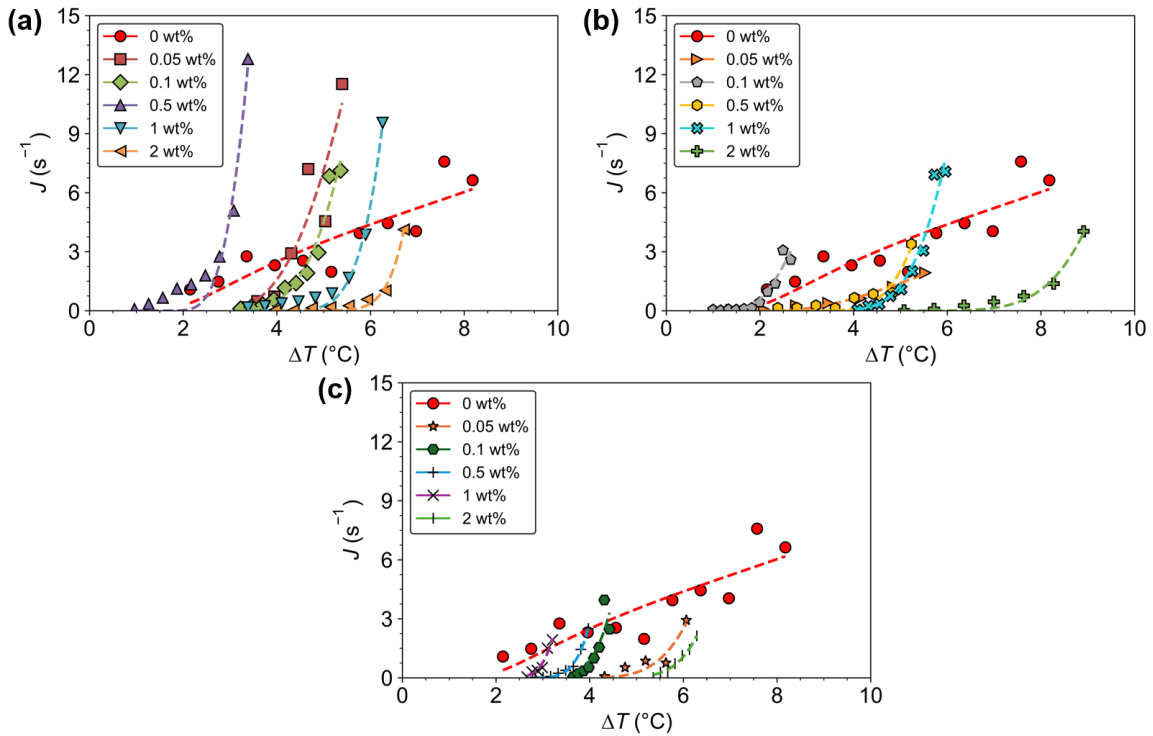
where  $f(\Delta T)$  is the probability density function and  $F(\Delta T)$  is the cumulative probability function of subcooling. For ramped temperature experiments, where  $J$  varies, the hazard function provides the conditional probability of hydrate formation at each subcooling level.

Subcooling-dependent nucleation rates are then calculated by multiplying the hazard rate function  $h(\Delta T)$  by the cooling rate  $\beta$ , as shown:

$$J(\Delta T) = h(\Delta T)\beta \quad (4.3)$$

This approach, validated by Al-Mukadam et al. (2021)[18] in constant cooling experiments on lithium disilicate crystallization, provides a more accurate assessment of subcooling distributions, reducing overestimation and enhancing analytical precision.

By adapting the hazard rate function, nucleation rates can be derived directly from raw data. **Figure 4.5** plots  $J$  versus  $\Delta T$  for all tested promoters, with **Table 4.1** summarizing the maximum  $J$  values for each case. In the control sample (0 wt%), the nucleation rate increases steadily with subcooling, indicating a higher probability of CO<sub>2</sub> hydrate formation at higher  $\Delta T$ . This hazard-based interpretation provides greater physical context than standalone probability distributions, offering qualitative insights into nucleation rates. Across all promoters and concentrations, nucleation rates exhibit an exponential increase beyond specific subcooling thresholds, highlighting the importance of optimizing promoter concentrations and subcooling conditions.



**Figure 4.5.** Subcooling-dependent nucleation rates ( $J$ ) for CO<sub>2</sub> hydrate formation with varying concentrations of (a) SDS, (b) GS-12, and (c) Laponite.

As shown in **Table 4.1**, SDS demonstrated superior performance across all concentrations, followed by GS-12 and Laponite. SDS's superior nucleation rate, peaking at  $12.1 \pm 0.6 \text{ s}^{-1}$  at 0.5 wt% and 0.05 wt%, reflects its strong kinetic promoting effects. This

performance at low concentrations supports its use in applications requiring environmentally friendly chemicals[19]. GS-12 exhibited an optimal nucleation rate of  $8.9 \text{ s}^{-1}$  at 1 wt%, while Laponite reached a maximum of  $4 \text{ s}^{-1}$  at 0.1 wt%, demonstrating lower effectiveness.

The distinct performance of GS-12 and Laponite reflects their differing functionalities. GS-12's ability to reduce interfacial tension at low concentrations suggests its suitability for enhanced oil recovery (EOR) applications[5,20], which operate under relatively higher temperature conditions. Conversely, Laponite's primary role as an inhibitor in drilling fluids[7], where it increases induction times at low concentrations[8], likely limits its promotive effects. These findings emphasize SDS as the most effective promoter for  $\text{CO}_2$  hydrate formation, even at low concentrations, with significant implications for reducing environmental impact. Further experimental studies are recommended to fully understand Laponite's potential roles in  $\text{CO}_2$  hydrate processes, whether as a promoter or an inhibitor.

### **4.3.3. Mechanisms of the Promoters in $\text{CO}_2$ Hydrate Formation**

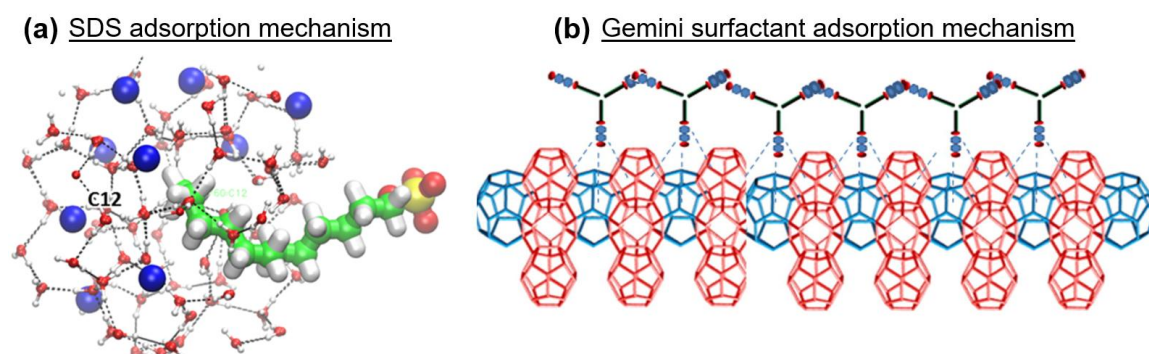
To deepen the understanding of how the tested promoters facilitate hydrate formation, this study explores their underlying mechanisms based on existing literature and proposes models or schematics to elucidate these processes. This approach complements the primary focus on pressure and temperature trends fitted with nucleation theory, which alone does not provide a comprehensive view of the mechanisms involved.

#### **4.3.3.1. SDS Mechanism**

SDS has been extensively studied for its role in enhancing  $\text{CO}_2$  hydrate nucleation. Some studies suggest that SDS promotes hydrate formation through micelle formation, which

provides nucleation sites[21–23]. However, micelle formation occurs only above the Krafft point (8–16 °C at atmospheric pressure)[9], while hydrate formation typically requires high pressure and lower temperatures, often below this threshold. This indicates that micellar mechanisms alone cannot fully explain SDS’s promotive effect under hydrate-forming conditions.

A more widely accepted mechanism involves SDS adsorption onto the hydrate surface at the molecular level. Molecular dynamics simulations by Choudhary et al. (2018)[24] suggest that SDS molecules orient their hydrophobic tails toward the growing hydrate surface, allowing partial occupation of hydrate cages while the hydrophilic head remains exposed to water. This configuration stabilizes nascent hydrate nuclei and reduces nucleation barriers by modifying the hydrate structure (**Figure 4.6 (a)**). The increased porosity resulting from this adsorption mechanism enhances the mass transfer of guest molecules, accelerating hydrate growth[25].



**Figure 4.6.** Adsorption mechanisms of surfactants promoting CO<sub>2</sub> hydrate formation. (a) SDS adsorption mechanism, where hydrophobic tails orient toward the hydrate surface (Choudhary et al., 2018)[24]. (b) Gemini surfactant adsorption mechanism, with one hydrophilic head binding to the surface and hydrophobic tails forming micelle-like structures (Salako et al., 2013)[26].

#### 4.3.3.2. *GS-12 Mechanism*

The gemini surfactant GS-12, which consists of two quaternary ammonium head groups connected by a spacer and a 12-carbon hydrophobic tail, exhibits a similar molecular

configuration to SDS. Despite this similarity, GS-12 is kinetically less efficient than SDS. This difference may arise from additional structural components in GS-12, such as polyethylene glycol (PEG) and an amide linker, which stabilize the surfactant structure but introduce inhibitory effects. PEG, for example, is known to hinder methane hydrate formation, which could explain GS-12's reduced kinetic efficiency compared to SDS[27].

For GS-12, adsorption likely follows a mechanism similar to that observed in other gemini surfactants. Salako et al. (2013)[26] suggest that only one hydrophilic head group of GS-12 binds to the clathrate hydrate surface, while its hydrophobic tail aligns toward the surface. This configuration alters surface energy, thereby promoting nucleation (**Figure 4.6 (b)**). As additional surfactant molecules adsorb onto the hydrate surface, interactions between the hydrophobic tails of the adsorbed surfactants and those of the surfactants in solution could lead to the formation of micelle-like structures. These structures may further enhance nucleation by creating additional nucleation sites.

However, the PEG group in GS-12 could reduce its efficiency by introducing steric hindrance, limiting its ability to interact effectively with the hydrate surface. To better understand GS-12's role as a CO<sub>2</sub> hydrate promoter, adsorption isotherm analysis or molecular dynamics simulations tailored to its specific molecular structure would provide valuable insights into its adsorption behavior and nucleation-promoting mechanisms.

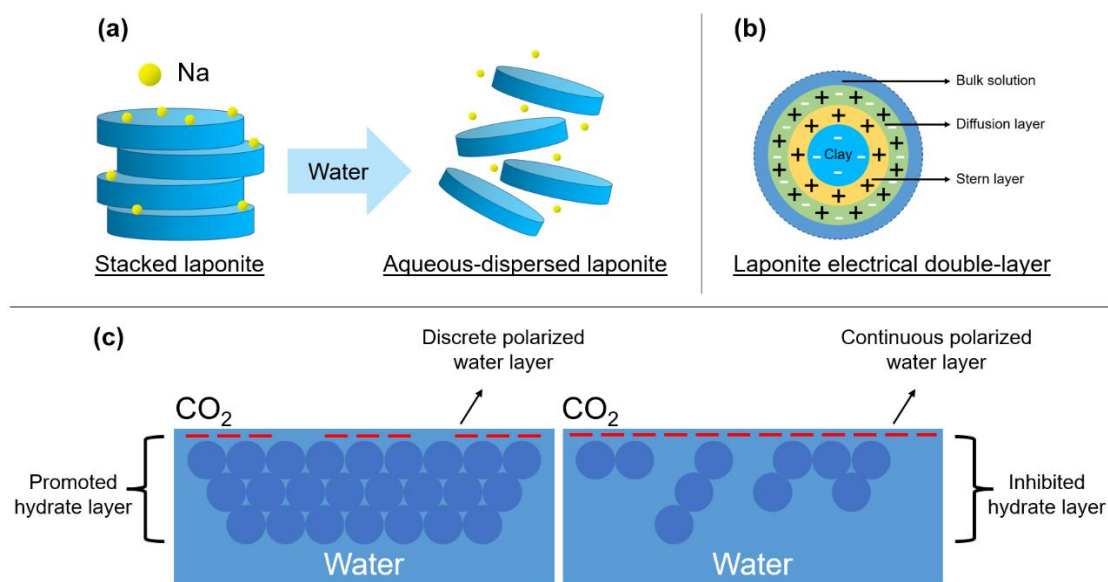
#### ***4.3.3.3. Laponite (Organoclay) Mechanism***

Laponite, a synthetic clay with a lattice structure similar to bentonite, promotes hydrate formation through mechanisms comparable to those observed in natural clays. Kumar et al. (2024)[28] demonstrated that bentonite enhances CO<sub>2</sub> hydrate formation, likely due to

its layered structure. Laponite differs from bentonite in its composition and particle size; its octahedral layer contains magnesium or lithium instead of magnesium or aluminum, and it exfoliates into individual nanoplatelets when dispersed in water (**Figure 4.7 (a)**).

Exfoliation exposes Laponite's hydration layer, influencing water-CO<sub>2</sub> interactions. The sodium content in the clay determines the mobility of water molecules within this layer. Laponite's dispersed sodium ions create an open hydration layer, which attracts positive ions from the environment to form a Stern layer (**Figure 4.7 (b)**). At optimal concentrations (0.05–1 wt%), this configuration promotes hydrate formation by forming a discrete polarized water layer at the CO<sub>2</sub>-liquid boundary, without impeding gas transfer. However, concentrations above 2 wt% result in the formation of a continuous polarized layer, which becomes excessively thick, reducing gas transfer rates and hindering hydrate formation (**Figure 4.7 (c)**).

Additionally, Laponite's smaller particle diameter (approximately 25 nm) compared to bentonite (100 nm) may influence its promotive effect. Kumar et al. (2024)[28] suggest that bentonite's larger size enhances its effectiveness, potentially due to differences in surface area or structural properties. Further comparative studies of Laponite and bentonite in CO<sub>2</sub> hydrate formation could clarify the factors driving their effectiveness.



**Figure 4.7.** Laponite mechanisms promoting CO<sub>2</sub> hydrate formation. (a) Transformation of stacked Laponite into aqueous-dispersed nanoplatelets upon water exposure. (b) Schematic of Laponite's electrical double layer. (c) Conceptual model of hydrate layer formation in a clay system.

## 4.4. Conclusion

This chapter presented a comprehensive evaluation of the kinetics of CO<sub>2</sub> hydrate formation facilitated by SDS, GS-12, and Laponite-RD as chemical promoters. Utilizing the second-generation HPS-ALTA system, the study analyzed nucleation rates, subcooling behavior, and the mechanisms underlying promoter performance, providing key findings relevant to the advancement of hydrate-based carbon sequestration strategies.

SDS demonstrated the highest kinetic efficiency, achieving nucleation rates of up to  $12.1 \text{ s}^{-1}$  at 0.5 wt%, attributed to its ability to stabilize nascent hydrate nuclei through adsorption and micelle-like behavior. Its promotive effects were sustained across a wide range of concentrations, making SDS a robust candidate for applications requiring efficient hydrate formation. Conversely, GS-12 exhibited its optimal nucleation rate of  $8.9 \text{ s}^{-1}$  at 1 wt%, leveraging its ability to reduce interfacial tension. However, structural components

such as polyethylene glycol within GS-12 introduced inhibitory effects at higher concentrations, reducing its overall efficiency compared to SDS.

Laponite-RD, although less effective than SDS and GS-12, provided unique insights into hydrate formation in systems incorporating clay minerals. With nucleation rates peaking at  $4.0 \text{ s}^{-1}$  at 0.1 wt%, Laponite promoted hydrate formation by creating polarized hydration layers that enhanced  $\text{CO}_2$ -water interactions. However, at concentrations exceeding 2 wt%, its promotive effects diminished due to gel formation, which inhibited gas transfer and slowed hydrate growth.

Mechanistic analyses further elucidated the role of each promoter in hydrate formation. SDS and GS-12 primarily enhanced nucleation through adsorption-driven stabilization, while Laponite influenced water structure and interfacial dynamics. These findings highlight the diverse pathways through which chemical promoters facilitate hydrate formation, emphasizing the importance of tailoring promoter selection and concentration to specific operational needs.

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## **CHAPTER 5**

# **INFLUENCE OF PROMOTERS ON CO<sub>2</sub> HYDRATE FORMATION DYNAMICS IN POROUS MEDIA**

### **Abstract**

This chapter explores the efficacy of kinetic and thermodynamic promoters in enhancing CO<sub>2</sub> hydrate formation within microfluidic porous media. Using a borosilicate glass microfluidic model, the performance of two kinetic hydrate promoters (Gemini surfactant, GS; sodium dodecyl sulfate, SDS) and a thermodynamic hydrate promoter (tetrahydrofuran, THF) was evaluated across key metrics, including induction time, CO<sub>2</sub> storage capacity, and hydrate growth rate. Experiments were conducted under controlled subcooling and flow rate conditions, capturing chip-scale and pore-scale dynamics through advanced imaging techniques. Results demonstrated that GS significantly reduced induction time by minimizing interfacial tension, while SDS excelled in maximizing CO<sub>2</sub> storage capacity and hydrate growth rate through bubble stabilization and enhanced gas-liquid interfacial interactions. THF enabled hydrate formation under milder conditions but was less effective in accelerating growth or improving storage. These findings provide critical insights into the mechanisms governing hydrate formation, informing the design of efficient and sustainable CO<sub>2</sub> sequestration technologies in porous environments.

### **5.1. Introduction**

In **Chapter 4**, we investigated how promoters enhance CO<sub>2</sub> hydrate formation by reducing mean subcooling and accelerating nucleation rates through statistical analysis of hundreds of hydrate formation cycles. Building on these findings, this chapter examines the effects

of promoters in microfluidic porous media, focusing on metrics such as induction time, CO<sub>2</sub> storage capacity, and hydrate growth rate. By analyzing CO<sub>2</sub> hydrate behavior from both pore-scale and chip-scale perspectives, this study provides a detailed understanding of how promoters influence hydrate formation in microfluidic environments. To the best of our knowledge, research on the pore-scale behavior of CO<sub>2</sub> hydrates in porous media with promoters remains limited. Most studies have concentrated on bulk experiments and macro-scale analyses, exploring the overall morphology of hydrates rather than their detailed pore-scale dynamics [1–3].

This study employs a borosilicate glass microfluidic porous medium to investigate CO<sub>2</sub> hydrate behavior with two kinetic hydrate promoters (KHPs): a novel Gemini surfactant (GS) and sodium dodecyl sulfate (SDS). Their performance is compared based on the three key metrics identified earlier. Unlike **Chapter 4**, which explored the potential of water-soluble organoclay (Laponite-RD) to enhance hydrate formation[4], this chapter focuses exclusively on GS and SDS. Organoclay was found to obstruct the porous medium by forming a gel network, which impeded fluid flow and reduced water-gas contact, suggesting its suitability for other porous media where gelation does not hinder fluid dynamics. Additionally, tetrahydrofuran (THF), a thermodynamic hydrate promoter (THP), was tested to investigate CO<sub>2</sub> hydrate formation at higher temperatures near the hydrate equilibrium curve. The results for THF are evaluated alongside GS and SDS to offer deeper insights into the influence of different promoter types on hydrate formation within microfluidic porous media.

## 5.2. Methodology

### 5.2.1. Experimental Setup and Materials

The experimental setup in this chapter is identical to that described in **Chapter 3**, focusing on both chip-scale and pore-scale phenomena. Chip-scale observations provide a broad overview of hydrate behavior across pores, while pore-scale analysis examines specific phenomena, such as bubble formation induced by surfactant effects.

The gemini surfactant (GS) used in this study was synthesized in-house at King Fahd University of Petroleum and Minerals by Dr. Hussain and colleagues. Details of its synthesis and properties are documented in their published work[5]. A concentration of 0.1 wt% GS was selected based on findings from **Chapter 4**, where this concentration effectively reduced the subcooling degree. Sodium dodecyl sulfate (SDS, Sigma-Aldrich) was used at a concentration of 0.15 wt%. Although **Chapter 4** identified 0.5 wt% as the optimal concentration, this higher concentration caused precipitation in the micromodel chip, obstructing fluid flow.

Tetrahydrofuran (THF, Thermo Fisher Scientific) was used at a concentration of 5.56 mol%, determined to be optimal for promoting hydrates by shifting the hydrate equilibrium curve[6]. Higher concentrations were avoided, as excess THF saturates the clathrate cages, preventing guest molecules from being encapsulated. Pure CO<sub>2</sub> (99.9% purity, Saudi Industrial Gas Company Ltd.) and deionized (DI) water (Milli-Q®, Sigma-Aldrich) were used as base materials for the experiments.

### 5.2.2. Experimental Procedure

The experiments were conducted similarly to those in **Chapter 3**, with the addition of promoters. Promoter solutions were prepared by stirring for approximately 30 minutes to ensure homogeneity. The solution was then injected into the micromodel, ensuring full saturation of the porous medium. The system was subsequently pressurized to 10 MPa and allowed to stabilize. For KHP studies using surfactants (GS and SDS), the system temperature was maintained at approximately 6 °C, ensuring a consistent subcooling ( $\Delta T$ ) of about 4.5 °C to evaluate the promoters' effectiveness under moderate temperature conditions within the phase equilibria. For THF studies using THF, the temperature was set to 9.1 °C to investigate CO<sub>2</sub> hydrate formation near the hydrate equilibrium curve, with a  $\Delta T$  value of approximately 1.8 °C. Preliminary tests with THF at 10 °C and without a promoter at 9.1 °C were unsuccessful, as no hydrates formed under these conditions. However, THF experiments at 9.1 °C provided valuable data, making it the chosen temperature for this study.

After confirming full saturation and stabilization of the system, liquid CO<sub>2</sub> was injected at varying flow rates of 5, 10, 20, 50, and 100  $\mu\text{L}/\text{min}$ , consistent with the approach in **Chapter 3**. Images were captured at a rate of one frame per second using a programmed software on a desktop, which also controlled two cameras—one for chip-scale views and the other for pore-scale observations. The cameras operated simultaneously, pairing each chip-scale image with a corresponding pore-scale image, although the pore-scale view covered only a portion of the larger chip-scale area. Following the experiments, image processing and analysis were performed using ImageJ and Python, adhering to the methodology established in **Chapter 3**.

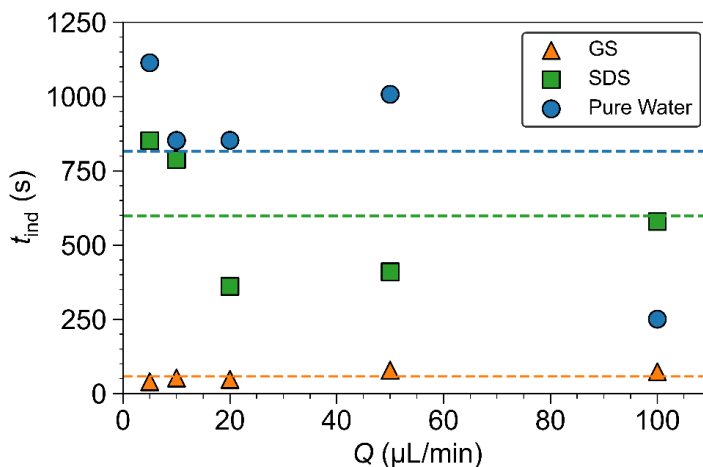
## 5.3. Results and Discussion

### 5.3.1. Effect of KHPs on Induction Time

The same method for calculating induction time described in **Chapter 3** was applied in this study. Induction time was defined as the interval between the initial visibility of CO<sub>2</sub> at the micromodel inlet and the formation of hydrates, signaled by a darker visual appearance. Multiple experiments were conducted for each flow rate and each condition (with and without promoters) to ensure robust confirmation of the results. The calculated induction times for all datasets and flow rates are presented in **Figure 5.1** and **Table 5.1**. A noteworthy observation was made for GS at a flow rate of 5  $\mu\text{L}/\text{min}$ , where the induction time was exceptionally short. This anomaly is likely due to premature hydrate formation during CO<sub>2</sub> injection, potentially occurring in the injection line before entering the micromodel. Such early hydrate formation adversely impacted CO<sub>2</sub> storage capacity at this low flow rate, resulting in near-zero saturation. The slow movement of CO<sub>2</sub>, combined with rapid hydrate formation, hindered its effective utilization within the porous medium; this issue is explored in more detail in the following section.

As observed in **Chapter 3**, induction time generally increases as flow rate decreases, due to lower shear effects at reduced rates[7,8]. However, significant variability persists, as evidenced by large error margins. In this study, results for pure water were consistent with the findings in **Chapter 3**, but the surfactants demonstrated more complex behavior. For instance, SDS did not exhibit a clear trend across flow rates, which can be attributed to the inherently stochastic nature of hydrate nucleation and growth[9]. Conversely, GS showed a relatively consistent trend in induction times across different flow rates.

Nevertheless, this consistency does not eliminate the inherent randomness of hydrate formation, as stochasticity remains a fundamental characteristic of the process.



**Figure 5.1.** Induction time ( $t_{\text{ind}}$ ) as a function of flow rate ( $Q$ ) for  $\text{CO}_2$  hydrate formation in microfluidic porous media with and without promoters. The dashed horizontal lines represent the overall average induction times for each system across all flow rates.

When the overall average induction times across all flow rates were plotted as dashed horizontal lines in Figure 5.1, GS outperformed both SDS and pure water. This superior performance is likely due to GS's ability to significantly reduce interfacial tension, facilitating greater  $\text{CO}_2$  dissolution and accelerating hydrate formation under identical conditions[10]. The effectiveness of gemini surfactants in reducing interfacial tension is well-documented, particularly in oilfield applications such as enhanced oil recovery (EOR), where they are known to substantially improve production efficiency[11,12].

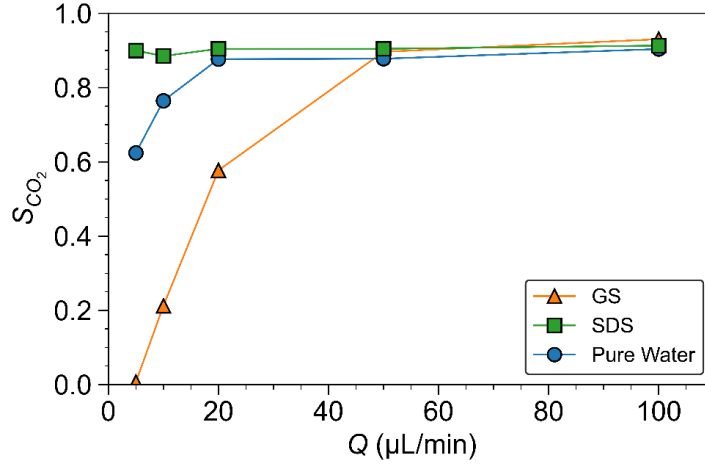
**Table 5.1.** Summary of induction times ( $t_{ind}$ ) and CO<sub>2</sub> storage capacities ( $S_{CO_2}$ ) at various flow rates ( $Q$ ) for GS, SDS, and pure water in microfluidic porous media. Data is presented as mean  $\pm$  standard deviation for multiple experimental runs.

| $Q$<br>( $\mu\text{L}/\text{min}$ ) | GS              |                 | SDS               |                 | Water              |                 |
|-------------------------------------|-----------------|-----------------|-------------------|-----------------|--------------------|-----------------|
|                                     | $t_{ind}$ (s)   | $S_{CO_2}$      | $t_{ind}$ (s)     | $S_{CO_2}$      | $t_{ind}$ (s)      | $S_{CO_2}$      |
| 5                                   | 10              | 0.01            | $851.7 \pm 828.5$ | $0.90 \pm 0.02$ | $1114.0 \pm 970.2$ | $0.62 \pm 0.13$ |
| 10                                  | $52.5 \pm 19.1$ | $0.21 \pm 0.11$ | $788.3 \pm 694.3$ | $0.88 \pm 0.02$ | $852.3 \pm 736.7$  | $0.76 \pm 0.14$ |
| 20                                  | $47.7 \pm 32.5$ | $0.58 \pm 0.34$ | $361.0 \pm 276.6$ | $0.90 \pm 0.03$ | $853.0 \pm 615.2$  | $0.88 \pm 0.01$ |
| 50                                  | $78.5 \pm 47.4$ | $0.90 \pm 0.12$ | $410.2 \pm 686.2$ | $0.90 \pm 0.03$ | $1007.8 \pm 914.8$ | $0.88 \pm 0.02$ |
| 100                                 | $73.0 \pm 51.0$ | $0.93 \pm 0.21$ | $579.5 \pm 650.3$ | $0.91 \pm 0.02$ | $250.5 \pm 347.5$  | $0.90 \pm 0.01$ |

These findings underscore the importance of macro-scale interfacial tension reduction in promoting CO<sub>2</sub> hydrate formation in microfluidic porous media. However, understanding the molecular-level mechanisms behind these observations requires alternative experimental approaches. Techniques such as adsorption isotherm measurements and zeta potential analysis[13] and molecular dynamics (MD) simulations[14,15] could provide deeper insights into the interactions between surfactants, CO<sub>2</sub>, and water at the pore scale.

### 5.3.2. Effect of KHPs on CO<sub>2</sub> Storage Capacity

**Chapter 3** demonstrated that flow rates significantly influence CO<sub>2</sub> storage capacity, as they are closely tied to the mobility and capillary effects of fluid flow in porous media[16]. In this chapter, the influence of promoters on storage capacity is also evident. **Figure 5.2** illustrates the relationship between flow rate and CO<sub>2</sub> storage capacity for each system tested. For pure water, the trend aligns with previous findings, where lower flow rates result in reduced CO<sub>2</sub> occupancy in the micromodel. However, SDS maintains higher CO<sub>2</sub> occupancy even at low flow rates, achieving levels comparable to those observed at higher flow rates.



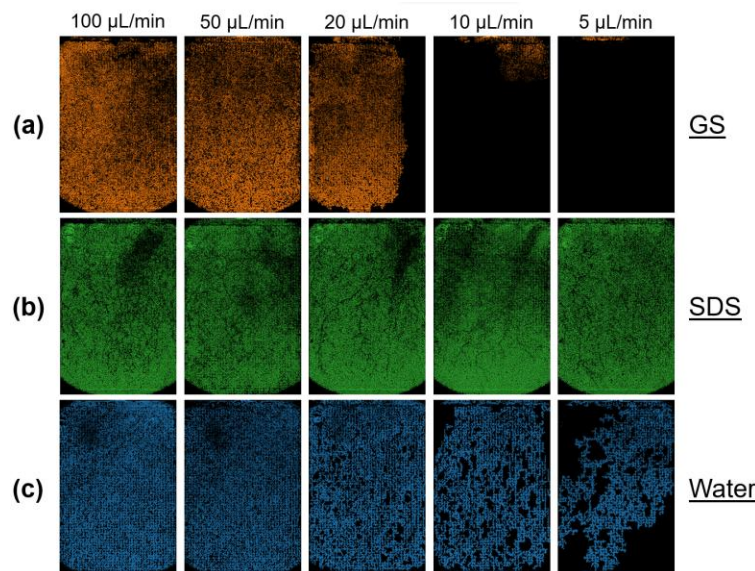
**Figure 5.2.**  $\text{CO}_2$  storage capacity ( $S_{\text{CO}_2}$ ) versus flow rate ( $Q$ ) for pure water (blue), SDS (green), and GS (orange) in microfluidic porous media.

This behavior is consistent with findings by Parra et al. (2019)[17], who performed molecular dynamics (MD) simulations of  $\text{CO}_2$  in water in the presence of SDS. Their results indicated that SDS reduces the  $\text{CO}_2$ -water interfacial tension, stabilizing  $\text{CO}_2$ -in-water bubbles by forming a compact surfactant monolayer. This monolayer enhances  $\text{CO}_2$  displacement of water and limits  $\text{CO}_2$  diffusion into the water phase. These stabilized bubbles further reduce  $\text{CO}_2$  mobility, allowing  $\text{CO}_2$  to access all areas of the porous medium and enhancing storage capacity[18]. In our experiments, bubble generation occurred due to friction or shear between the injected  $\text{CO}_2$  and the SDS solution. This phenomenon was evident in the chip-scale observations, as shown in **Figure 5.3**. The resulting bubble appeared as a denser color intensity in the micromodel compared to pure water, necessitating adjustments to the threshold settings during image binarization. The general observation is that surfactants, such as SDS and GS, reduced the black (water) areas in the micromodel compared to pure water, indicating improved  $\text{CO}_2$  occupancy.

Although GS generates fewer bubbles or foam than SDS, its superior interfacial tension reduction ensures  $\text{CO}_2$  occupancy levels comparable to those achieved with SDS.

However, GS's rapid reduction of induction time inhibits the effective utilization of this property. The ability of GS to maximize CO<sub>2</sub> occupancy becomes more apparent in pore-scale phenomena, which will be discussed in the upcoming section. At low flow rates, such as 5  $\mu\text{L}/\text{min}$ , the primary limitation of GS becomes evident. CO<sub>2</sub> barely enters the micromodel before hydrate formation begins, significantly reducing storage capacity. At higher flow rates (above 50  $\mu\text{L}/\text{min}$ ), all systems demonstrate improved CO<sub>2</sub> storage capacity, but differences persist. Pure water exhibits lower capacity at low flow rates due to limited mobility and capillary effects[19], while GS's faster hydrate nucleation restricts CO<sub>2</sub> movement, leading to incomplete saturation.

Among the tested systems, SDS proves to be the most effective at enhancing CO<sub>2</sub> storage capacity, outperforming both GS and pure water. However, considering environmental implications, SDS may not be ideal for practical applications of CO<sub>2</sub> hydrate storage in seabed sediments due to potential ecological concerns. As a more sustainable alternative, bio-surfactants have been extensively studied and are recommended for future research[20–22]. The development and application of environmentally friendly promoters could play a critical role in advancing the practical implementation of CO<sub>2</sub> hydrate storage in porous seabed sediments.



**Figure 5.3.** CO<sub>2</sub> hydrate occupancy in microfluidic porous media at flow rates of 100, 50, 20, 10, and 5  $\mu\text{L}/\text{min}$  for (a) gemini surfactant (GS), (b) sodium dodecyl sulfate (SDS), and (c) pure water. The denser color intensity observed with SDS indicates bubble generation, while GS shows lesser bubble formation. Detailed  $S_{\text{CO}_2}$  value are presented in **Table 5.1**.

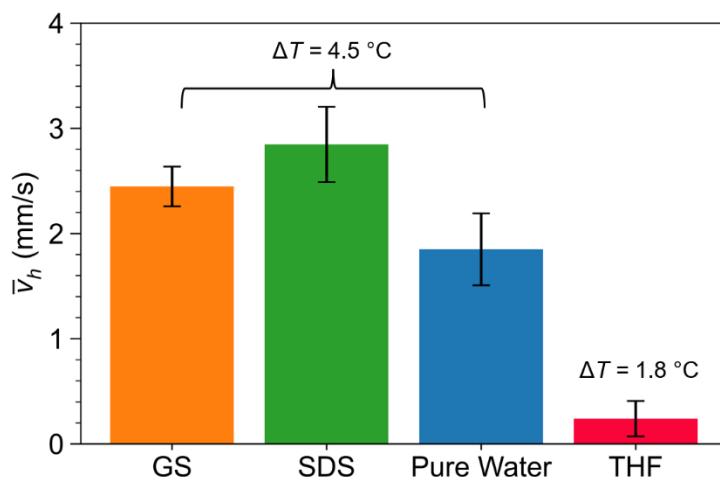
### 5.3.3. Effect of KHPs on CO<sub>2</sub> Hydrate Growth Rate

Using the same method for calculating CO<sub>2</sub> hydrate growth rate described in **Chapter 3**, this chapter examines the growth rate in the presence of KHPs. Since injection rate does not influence hydrate growth rate, this study focuses exclusively on the effect of each KHP at a constant  $\Delta T = 4.5\text{ }^\circ\text{C}$ . **Figure 5.4** illustrates the impact of surfactants on hydrate growth rate, showing that SDS achieves the highest growth rate, with an average of  $2.85 \pm 0.36\text{ mm/s}$ , followed by GS at  $2.45 \pm 0.19\text{ mm/s}$ , and water at  $1.85 \pm 0.34\text{ mm/s}$ . The results for water are consistent with **Chapter 3**, where an average growth rate of  $1.95 \pm 0.55\text{ mm/s}$  was observed, validating the reliability of the experimental setup and methodology.

The superior growth rate observed with SDS can be attributed to the increased presence of bubbles and significant changes in their morphology and behavior under the influence of SDS. Du et al. (2018)[23] demonstrated that SDS generates smaller bubbles, thereby increasing the gas-liquid interfacial area, which facilitates efficient gas diffusion and

hydrate nucleation. Similarly, Tajima et al. (2010)[24] observed that SDS adsorbs at the gas-liquid interface, altering the rigidity and morphology of hydrate films on bubble surfaces. The hydrate films formed in the presence of SDS are less rigid, rougher, and more heterogeneous, allowing for continuous breaking and reformation cycles. This dynamic restructuring promotes gas transfer into the aqueous phase, sustaining rapid hydrate growth. Thus, the generation of smaller bubbles, increased interfacial area, and dynamic hydrate film restructuring are the primary mechanisms through which SDS facilitate superior hydrate formation rates.

The role of bubbles in hydrate formation, regardless of the presence of surfactants, has been well-documented in prior studies. Uchida et al. (2021)[25] demonstrated that ultra-fine bubbles (UFBs) enhance CO<sub>2</sub> hydrate formation by providing additional nucleation sites. These bubbles, characterized by high internal pressure and surface free energy, promote nucleation and growth. Similarly, Kuang et al. (2019)[26] reported that bubbles facilitate gas-liquid interactions, accelerate gas dissolution, and enhance hydrate growth. The pronounced effect of SDS over GS in promoting CO<sub>2</sub> hydrate growth rate can be attributed to the higher prevalence of bubbles in the SDS system. These bubbles not only maximize CO<sub>2</sub> storage but also significantly enhance hydrate growth by providing additional pathways for gas transport and nucleation.



**Figure 5.4.** Average CO<sub>2</sub> hydrate growth rate ( $\bar{v}_h$ ) in the presence of promoters (GS, SDS, and THF) and pure water at a constant subcooling ( $\Delta T = 4.5$  °C for GS, SDS, and water, and  $\Delta T = 1.8$  °C for THF). Error bars represent standard deviations from multiple experimental runs.

#### 5.3.4. Effect of THF on CO<sub>2</sub> Hydrate Growth Rate

The effect of THF on hydrate growth rate was investigated through experiments conducted at higher temperatures ( $T = 9.1$  °C) with an average  $\Delta T$  of 1.8 °C. The THF concentration was maintained at the optimal value of 5.56 mol%, as identified by Babu et al. (2016)[6]. Concentrations above this threshold result in an excess of THF molecules occupying the s-II hydrate structure, preventing CO<sub>2</sub> molecules from being encapsulated within clathrate cages. The results, presented in **Figure 5.4**, indicate a hydrate growth rate of  $0.24 \pm 0.17$  mm/s, which is significantly lower than rates observed in other systems. This reduced growth rate is primarily attributed to the lower  $\Delta T$ , despite the promotional effect of THF. These findings suggest that while THF facilitates hydrate formation under milder pressure and temperature conditions, it does not enhance the growth rate, which remains strongly dependent on the  $\Delta T$  value. Although some studies suggest that THF kinetically promotes CO<sub>2</sub> hydrate formation[27,28], its primary role in this context appears to be enabling hydrate formation under less stringent conditions rather than accelerating growth.

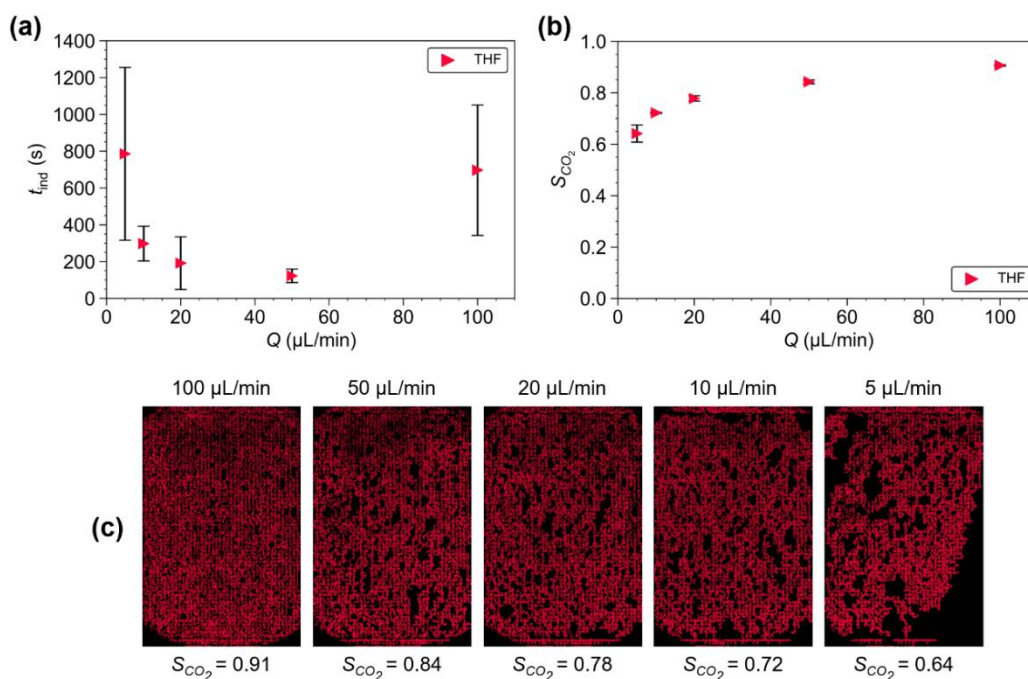
**Figure 5.5(a)** illustrates the relationship between CO<sub>2</sub> injection rate and induction time. Lower injection rates generally correspond to longer induction times; however, the induction time at 100  $\mu\text{L}/\text{min}$  is also relatively high, reflecting the inherent stochasticity of hydrate formation[7]. Across all rates, large error bars further underscore this variability. These results, combined with findings from **Chapters 3 and 5**, indicate that flow rate alone is insufficient to reliably reduce induction time. Instead, the use of kinetic promoters proves more effective, though significant variability persists even with their application.

**Table 5.2.** Summary of induction times ( $t_{ind}$ ) and CO<sub>2</sub> storage capacities ( $S_{\text{CO}_2}$ ) at various flow rates ( $Q$ ) for THF system in microfluidic porous media.

| $Q$<br>( $\mu\text{L}/\text{min}$ ) | THF               |                   |
|-------------------------------------|-------------------|-------------------|
|                                     | $t_{ind}$ (s)     | $S_{\text{CO}_2}$ |
| 5                                   | $785.7 \pm 469.6$ | $0.64 \pm 0.03$   |
| 10                                  | $298.0 \pm 94.6$  | $0.72 \pm 0.01$   |
| 20                                  | $191.7 \pm 143.1$ | $0.78 \pm 0.01$   |
| 50                                  | $122.7 \pm 36.9$  | $0.84 \pm 0.01$   |
| 100                                 | $697.0 \pm 354.6$ | $0.91 \pm 0.02$   |

In contrast, **Figure 5.5(b)** shows a consistent trend where lower flow rates result in reduced CO<sub>2</sub> saturation. **Figure 5.5(c)** depicts the occupied pore spaces of CO<sub>2</sub> in the presence of the THF system. Although the pore spaces in **Figure 5.5(c)** appear visually similar at first glance, the overall trend confirms that lower flow rates lead to lower CO<sub>2</sub> saturation. This outcome can be attributed to THF's inherent inability to significantly reduce interfacial tension under fixed pressure conditions. Garrido et al. (2017) [29] suggests that CO<sub>2</sub> in a THF system can reduce interfacial tension at elevated pressures due to enhanced CO<sub>2</sub> surface activity, but this effect is pressure-dependent. In contrast, surfactants like SDS are inherently designed to reduce interfacial tension[30], making them more effective for such applications. As a result, THF's capacity to maximize CO<sub>2</sub>

occupancy within pore spaces is inherently limited. For applications aiming to maximize CO<sub>2</sub> saturation in porous media, higher injection rates are therefore preferable. THF's role remains valuable for facilitating hydrate formation at milder conditions, but its effectiveness is constrained when considering CO<sub>2</sub> saturation and occupancy. Detailed data for induction time and CO<sub>2</sub> saturation for the THF system are presented in **Table 5.2**.



**Figure 5.5.** Influence of CO<sub>2</sub> injection rate on hydrate induction time, CO<sub>2</sub> saturation, and pore occupancy in the presence of THF (5.56 mol%). (a) Relationship between injection rate and induction time. (b) Relationship between injection rate and CO<sub>2</sub> saturation. (c) Visual representation of chip-scale CO<sub>2</sub> hydrate occupancy across various flow rates.

### 5.3.5. Effect of Promoters on CO<sub>2</sub> Hydrate: Pore Scale Phenomena

In the presence of promoters, the pore-scale behavior of CO<sub>2</sub> hydrate formation differs significantly from that in systems containing only water. Notably, surfactants generate bubbles that influence the growth mechanism of CO<sub>2</sub> hydrates. **Figure 5.6** illustrates the pore-scale formation of CO<sub>2</sub> hydrates under different systems. **Figure 5.6(a)** depicts the system with CO<sub>2</sub> in pure water without additives, a phenomenon consistent with observations discussed in **Chapter 2**. Under the given pressure conditions (~10 MPa), CO<sub>2</sub>

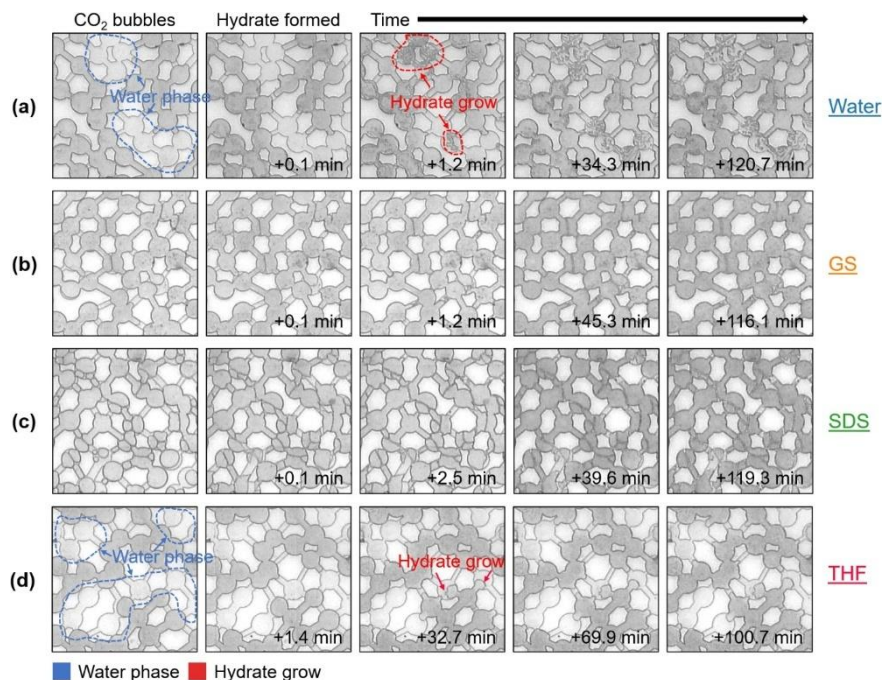
remains in the liquid phase and appears lighter in grayscale (compared to gaseous CO<sub>2</sub>, which appears darker as demonstrated in **Chapter 2**) due to its higher density. Within approximately 0.1 minutes, CO<sub>2</sub> bubbles transition to a darker color, indicating the formation of a thin solid hydrate shell that reduces light transmission. After 1.2 minutes, hydrate growth is observed (highlighted by the red dashed area) extending from the CO<sub>2</sub> phase into the water phase (blue dashed area). This behavior, where hydrates grow into the water phase, is a typical phenomenon widely documented in previous studies [31–33]. Over time, up to 2 hours, the parent hydrates within the large, connected CO<sub>2</sub> cluster phase darken further, while hydrates in the water phase shrink due to CO<sub>2</sub> consumption.

The behavior observed in the water system contrasts sharply with that in systems containing surfactants, such as GS and SDS, as shown in **Figures 5.6(b) and 5.6(c)**. In these cases, minimal or no visible water phase remains, indicating that CO<sub>2</sub> occupies nearly all pore spaces. This is evidenced by the darker appearance in pore throats and spaces from the beginning of the image series. This observation aligns with previous chip-scale results. Although GS generates fewer bubbles than SDS, its ability to reduce interfacial tension enables significant CO<sub>2</sub> occupancy in pore spaces. This supports our previous claim that GS can maximize CO<sub>2</sub> occupancy through its superior interfacial tension reduction without heavily relying on bubble presence. However, while GS can achieve CO<sub>2</sub> occupancy similar to SDS, previous discussions have highlighted that GS's greater efficiency in reducing induction time for hydrate formation makes it slightly less effective than SDS in maximizing CO<sub>2</sub> saturation within the pores.

These findings suggest that surfactants with interfacial tension-reducing properties have considerable potential to enhance CO<sub>2</sub> occupancy in porous media. Studies by Kim

and Santamarina (2014) [34] demonstrate that surfactant molecules align at the CO<sub>2</sub>-water interface, weakening the local electric field and reducing surface tension. This reduction in interfacial tension, combined with increased contact angles and decreased capillary forces, facilitates CO<sub>2</sub> displacement into smaller pores and reduces residual water saturation. However, it is essential to note that the capillary forces driving hydrate formation differ from those involved in CO<sub>2</sub> displacement, as hydrate growth relies on higher capillary forces, as previously discussed [3]. By lowering interfacial tension, surfactants overcome resistance observed in pure water systems, achieving maximum CO<sub>2</sub> occupancy in porous media.

In contrast, THF exhibits behavior similar to the water system, as shown in **Figure 5.6(d)**. A substantial water phase remains visible, and the hydrate growth extending from the CO<sub>2</sub> phase into the water phase is smaller than the growth observed within the water phase itself, even after 2 hours. This behavior may be influenced by the  $\Delta T$ , as lower  $\Delta T$  values typically result in less prominent hydrate formation and growth compared to higher  $\Delta T$  conditions [35]. THF primarily facilitates hydrate formation under milder pressure and temperature conditions but does not significantly enhance hydrate growth or the structural strength of the formed hydrates unless supported by additional kinetic promoters, such as surfactants [2].



**Figure 5.6.** Pore-scale CO<sub>2</sub> hydrate formation in microfluidic porous media under different systems: (a) pure water, (b) GS, (c) SDS, and (d) THF. The blue-dashed area represents the water phase, while the red-dashed area highlights hydrate growth into the water phase.

## 5.4. Conclusions

This chapter provides a detailed examination of how kinetic and thermodynamic hydrate promoters (KHPs and THPs) influence CO<sub>2</sub> hydrate formation in microfluidic porous media. The results highlight the unique strengths of Gemini surfactant (GS), sodium dodecyl sulfate (SDS), and tetrahydrofuran (THF) in enhancing key performance metrics, including induction time, CO<sub>2</sub> storage capacity, and hydrate growth rate. Each promoter exhibited distinct advantages, emphasizing the versatility of these additives in addressing specific operational objectives.

Among the tested promoters, GS emerged as the most effective in reducing induction time, achieving values as low as 10 seconds at 5  $\mu\text{L}/\text{min}$ . This performance starkly contrasts with SDS, which required  $851.7 \pm 828.5$  seconds, and pure water, which exhibited an even longer induction time of  $1114.0 \pm 970.2$  seconds under similar conditions. The remarkable

efficiency of GS stems from its superior ability to reduce interfacial tension, enabling rapid nucleation of hydrates. However, at lower flow rates, GS's rapid nucleation limited CO<sub>2</sub> storage capacity, as premature hydrate formation restricted gas mobility within the porous medium.

In terms of CO<sub>2</sub> storage capacity, SDS consistently outperformed all other systems. At higher flow rates, such as 100  $\mu\text{L}/\text{min}$ , SDS achieved a CO<sub>2</sub> storage capacity ( $S_{\text{CO}_2}$ ) of  $0.91 \pm 0.02$ , matching GS's performance but surpassing pure water at  $0.90 \pm 0.01$ . Even at low flow rates (5  $\mu\text{L}/\text{min}$ ), SDS retained its effectiveness, maintaining an  $S_{\text{CO}_2}$  of  $0.90 \pm 0.02$ , far exceeding GS's 0.01 and pure water's  $0.62 \pm 0.13$ . This consistent performance is attributed to SDS's ability to stabilize bubbles, reduce CO<sub>2</sub>-water interfacial tension, and ensure effective CO<sub>2</sub> displacement into the porous medium. These properties allowed SDS to achieve higher CO<sub>2</sub> occupancy even under conditions where other systems struggled.

The hydrate growth rate further reinforced SDS's superior performance, achieving an average rate of  $2.85 \pm 0.36$  mm/s compared to GS at  $2.45 \pm 0.19$  mm/s and pure water at  $1.85 \pm 0.34$  mm/s. This difference is largely attributed to SDS's ability to create a larger gas-liquid interfacial area through bubble generation and stabilization, which facilitated efficient gas diffusion and rapid hydrate nucleation. THF, on the other hand, demonstrated limited effectiveness in accelerating hydrate growth, with a growth rate of only  $0.24 \pm 0.17$  mm/s. However, THF's strength lies in enabling hydrate formation under milder pressure and temperature conditions ( $\Delta T \approx 1.8$  °C,  $T = 9.1$  °C), where other promoters may require more stringent conditions to initiate formation.

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## **CHAPTER 6**

### **CONCLUSIONS AND RECOMMENDATIONS**

#### **6.1. Conclusions**

1. Liquid CO<sub>2</sub> hydrates demonstrated significant swelling (volume variation index of 3.61), efficiently filling pore spaces and forming stable structures, effectively immobilizing fluid flow. This makes them highly suitable for long-term sequestration. Conversely, gaseous CO<sub>2</sub> hydrates underwent a two-stage transition with substantial shrinkage (volume variation index of 0.27) and limited pore utilization, attributed to the lower density of gaseous CO<sub>2</sub>.
2. Injection rates and subcooling were key factors in hydrate nucleation and CO<sub>2</sub> distribution within porous media. Higher injection rates reduced induction times to as low as 90 seconds and increased CO<sub>2</sub> saturations up to 0.81, while lower rates resulted in extended induction times and incomplete pore utilization. While hydrate growth rates were independent of injection velocity, they were strongly influenced by subcooling, increasing from 0.25 mm/s at 2.7 °C subcooling to 4.91 mm/s at 9.8 °C.
3. Among the tested promoters, SDS achieved the highest nucleation rates (12.1 s<sup>-1</sup> at 0.5 wt%) by stabilizing hydrate nuclei through adsorption and micelle formation, making it a robust candidate for efficient hydrate formation. GS-12 performed optimally at 1 wt% (8.9 s<sup>-1</sup>), effectively reducing interfacial tension, though higher concentrations showed inhibitory effects due to structural components like polyethylene glycol. Laponite-RD enhanced CO<sub>2</sub>-water interactions via polarized

hydration layers, achieving peak nucleation rates of  $4.0 \text{ s}^{-1}$  at 0.1 wt%, with reduced efficiency at higher concentrations due to gel formation.

4. The Gemini surfactant (GS) significantly reduced induction times (as low as 10 seconds at  $5 \text{ }\mu\text{L/min}$ ) by lowering interfacial tension, enabling rapid nucleation. However, premature hydrate formation at low flow rates limited  $\text{CO}_2$  storage capacity. SDS excelled in maximizing  $\text{CO}_2$  storage capacity ( $0.91 \pm 0.02$ ) and hydrate growth rates ( $2.85 \pm 0.36 \text{ mm/s}$ ) by stabilizing bubbles and enhancing interfacial interactions across various flow conditions. Tetrahydrofuran (THF) facilitated hydrate formation under mild conditions but showed limited ability to accelerate growth rates, highlighting its niche application in low-pressure, low-temperature scenarios.

## 6.2. Recommendations

Based on the findings of this study, several future recommendations are proposed to advance the research and application of hydrate-based  $\text{CO}_2$  storage in cold subsurface formations:

1. Assess the scalability of laboratory-derived parameters for upscaling to field-scale applications, incorporating dimensional analysis and sensitivity studies to ensure reliable extrapolation across scales.
2. Conduct advanced flow loop experiments to investigate  $\text{CO}_2$  phase behavior and multiphase transport dynamics during migration from the surface to subsurface hydrate zones, with a focus on thermodynamic and kinetic constraints.

3. Evaluate the thermophysical effects of impurities, including multi-component gas mixtures, saline environments, and ionic species, on the nucleation and growth of hydrates in marine sediment matrices.
4. Utilize a range of porous media, particularly those with complex heterogeneity in permeability and porosity distributions, to simulate realistic subsurface conditions.
5. Examine the coupled geo-mechanical response of hydrate-bearing formations, with emphasis on  $\text{CO}_2\text{-CH}_4$  exchange mechanisms, fracture propagation, and implications for seabed structural integrity and stability.
6. Develop mechanistic growth models for hydrates within porous media, addressing discrepancies with bulk-phase reactor data by incorporating pore-scale physics and interfacial phenomena.
7. Investigate the stochastic and probabilistic nature of hydrate nucleation, leveraging nucleation kinetics and molecular dynamics simulations to elucidate energy pathways and entropy changes during hydrate formation.
8. Explore sustainable and eco-compatible promoters, such as bio-surfactants, amino acids, and naturally derived amphiphilic compounds, to enhance  $\text{CO}_2$  hydrate formation efficiency while mitigating adverse environmental effects.

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### Scientific Journals (Thesis-Related):

- Habiburrahman, M., Yu, W., Kun, G., Wang, J., Sultan, A. (2024) Density-dependent pore-filling behaviors and lateral propagation of CH<sub>4</sub> and CO<sub>2</sub> hydrates forming in microfluidic porous media. Chemical Engineering Journal. **Under review.**
- Habiburrahman, M., Yu, W., Sultan, A. Enhancing CO<sub>2</sub> storage capacity in seabed sediments using surfactant-induced hydrate formation. **Draft finished.**
- Yu, W., Habiburrahman, M., Sultan, A. Microfluidic Study of Hydrate Formation and Propagation in Porous Media during CO<sub>2</sub> Injection into Cold Aquifers for Carbon Sequestration. **Draft finished.**

### Scientific Journals (Non Thesis-Related):

- Astsauri, T., Habiburrahman, M., Ibrahim, A.F., and Wang, Y. (2024). Utilizing machine learning for flow zone indicators prediction and hydraulic flow unit classification. Sci Rep 14, 4223. <https://doi.org/10.1038/s41598-024-54893-1>.

#### **Conferences and Symposiums:**

- Microfluidic Study of the Phase Transition Behaviors of CH<sub>4</sub> and CO<sub>2</sub> Hydrates in Porous Media, 6<sup>th</sup> International Gas Conference. Doha, Qatar, December 2024.
- Habiburrahman, M., Yu, W., Sultan, A. Advancing CO<sub>2</sub> Sequestration Efficiency via Surfactant-Assisted Hydrate Dynamics in Cold Aquifer. **Abstract submitted** for MEOS GEO (2025).