Impact of CO₂ hydrates on injectivity during CO₂ storage in depleted gas fields
A literature review

Aghajanloo, Mahnaz; Yan, Lifei; Berg, Steffen; Voskov, Denis; Farajzadeh, Rouhi

DOI 10.1016/j.jgsce.2024.205250
Publication date 2024
Document Version Final published version
Published in Gas Science and Engineering

Citation (APA)

Important note
To cite this publication, please use the final published version (if applicable). Please check the document version above.
Impact of CO\textsubscript{2} hydrates on injectivity during CO\textsubscript{2} storage in depleted gas fields: A literature review

Mahnaz Aghajanloo\textsuperscript{a,}\textsuperscript{*}, Lifei Yan\textsuperscript{a}, Steffen Berg\textsuperscript{b}, Denis Voskov\textsuperscript{a,}\textsuperscript{c}, Rouhi Farajzadeh\textsuperscript{a,}\textsuperscript{b}

\textsuperscript{a} Delft University of Technology, Department of Geoscience and Engineering, Stevinweg 1, 2628 CN, Delft, the Netherlands
\textsuperscript{b} Shell Global Solutions International B.V., Grasweg 31, 1031 HW, Amsterdam, the Netherlands
\textsuperscript{c} Energy, Science and Engineering, Stanford University, USA

1. Introduction

According to the newest report from the Intergovernmental Panel on Climate Change (IPCC), carbon dioxide (CO\textsubscript{2}), the predominant greenhouse gas released from anthropogenic activities, contributed to 80% of the total greenhouse gas emissions (Levin et al., 2022; Parmesan et al., 2022). Recent research indicates that Carbon Capture and Storage (CCS) technologies offer an effective approach to mitigating the adverse effects resulting from excessive CO\textsubscript{2} emissions (Davoodi et al., 2023). Among various geological formations, CO\textsubscript{2} storage in depleted gas fields has significant benefits compared to other subsurface storage options such as aquifers and depleted oil fields (Pan et al., 2021; Peter et al., 2022; Tamaskovics et al., 2023). The risks and uncertainties associated with the depleted gas fields are comparatively lower because of their extended production history, proven sealing capacity, and (partial) availability of infrastructure and equipment required to store CO\textsubscript{2}. However, injection of CO\textsubscript{2} into these reservoirs poses some potential challenges for CO\textsubscript{2} injectivity, containment and well/facility integrity due to low temperatures caused by isenthalpic expansion of CO\textsubscript{2}. A key injectivity risk is due to possible formation of hydrates at the low expected temperatures. This study aims to address main causes of CO\textsubscript{2} hydrate formation and its impact on permeability of porous media. This review highlights the current state of knowledge in the literature while emphasizing the need to bridge existing gaps in derisking CO\textsubscript{2} injection into (depleted) low-pressure gas reservoirs. In summary, according to the existing literature, the potential for hydrate formation is assessed to be credible. Current industry solutions exist to manage this risk; however, they are costly and energy intensive. Future research will be needed to provide capabilities to manage this risk more efficiently.

\textsuperscript{*} Corresponding author.
E-mail address: m.aghajanloo@tudelft.nl (M. Aghajanloo).

https://doi.org/10.1016/j.jgsce.2024.205250

Received 23 December 2023; Received in revised form 3 February 2024; Accepted 19 February 2024
Available online 24 February 2024

2949-9089/© 2024 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).
of CO₂ wells. Injectivity impairment might be caused, for example, by the evaporation of water into dry or undersaturated CO₂ which can lead to the precipitation of salt (mainly halite) and thus plugging of the reservoir pores (Ott et al., 2021).

For CCS in low-pressure or depleted reservoirs, thermodynamic properties of CO₂ play a major role. CO₂ is usually transported to site location in liquid or supercritical state and injection is conducted in the state of high mass density to achieve sequestration targets (Shotton et al., 2022). The injection of high-pressure CO₂ into low pressure reservoirs leads to isenthalpic expansion of CO₂ which then causes a decrease in temperature (Chesnokov et al., 2023; Loewe et al., 2014). The magnitude of the temperature reduction depends on CO₂ flowrate, reservoir permeability, thickness and thermal properties of the rock and the in-situ brine, and well radius and completion (Mathias et al., 2010). For typical CO₂ injection rates (∼1Mtpa), the temperature is expected to be very low (Almenningen et al., 2021). If the temperature is below the hydrate phase boundary inside stability zone (see Fig. 1) and enough water is available in the porous medium, solid hydrates can form, which can reduce the porosity and eventually the permeability.

While hydrate formation has always played an important role in production, transportation and processing of hydrocarbons e.g., in pipelines (Sayani et al., 2020), and also methane hydrates at continental slopes are considered as a potential source of hydrocarbons (Demirbas, 2010; Englezos and Lee, 2005), there is a concrete case of relevance of CO₂ hydrates when CO₂ sequestration (CCS) in depleted gas fields is considered (Bui et al., 2018). Hydrate formation is considered as one of the major potential risks for the implementation of CO₂ storage in ultra-depleted reservoirs (<50 bar) (Sloan and Fleyfel, 1991). Formation of hydrates in porous media, apart from pressure and temperature, is influenced by several parameters related to properties of the rock (permeability, porosity, mineralogy), water (saturation, composition, salinity, type of salt) and gas (type, composition, or purity). To quantify and/or to design strategies to prevent or mitigate the impact of CO₂ hydrate on the injectivity, it is necessary to understand the impact of different factors on hydrate formation in porous media.

Over the past decades, much research has been conducted on CO₂ hydrate inside the bulk under various conditions and materials (Yang et al., 2013; Zheng et al., 2020). However, to the best of our knowledge, no review has been done on CO₂ hydrate formation/elimination in the context of CCS projects, especially on the topic of CO₂ injectivity in depleted gas fields. There are only a few precedence cases from the literature for CO₂ hydrate formation at field scale or field-related processes or projects. Most field examples (Gauteplass et al., 2020b; Jadhawar et al., 2006) are scattered and not at conditions relevant for CO₂ injection in depleted gas fields. Nevertheless, these examples demonstrate that in principle CO₂ hydrates or ice can form (Li et al., 2023; Semenov et al., 2023) and, if hydrates or ice formed (by different processes) (Sloan and Fleyfel, 1991; Zhang and Guo, 2017), they can significantly impair injectivity. However, there is no demonstrated case where CO₂ hydrates form due to the isenthalpic expansion cooling effect during CO₂ injection. In a field containing mainly CO₂, solids were formed which were identified as hydrates and/or ice (Xu et al., 2007); this demonstrates that hydrates or ice can indeed form in the field. Notice that in these cases, the solids were observed during production downstream of the separator and not during injection into the porous medium. Provision had been made for methanol injection to suppress hydrates, but this proved ineffective. In a water-alternating-gas (WAG) pilot, hydrogen carbonate gas was injected, and due to expansion of the hydrocarbon gases the temperature dropped, and hydrates formed. Consequently, gas injection rates dropped to zero in a matter of hours (Jensen et al., 2000). However, in this example, gas was injected in a well that had injected water for an extended period (44 million barrels). Consequently, the temperature in the near wellbore had dropped to 285K from the initial 403K (12°C, 130°C) at a reservoir depth of approximately 3000 m. This occurred in an area where the surrounding seawater temperatures are low, and the pressure is about 300 bar (Adeniyi and Ezeagu, 2020). These conditions fall within the hydrate window for hydrocarbon gas. Note that these are different conditions than the injection of CO₂ in depleted gas fields. The low temperature was most likely not due to isenthalpic expansion but to prolonged cold sea water injection.

Besides the above-mentioned cases, an injectivity impairment was demonstrated in an integrated experiment where the cooling effects from injection led to a complete blockage (Maloney and Briceno, 2009). All these examples show that the formation of hydrates in an injection scenario is not just hypothetical. There are concrete precedent cases of hydrate formation in the near-well region due to gas injection, although the conditions and chemical composition of reservoir fluids varied and none of them were close to the conditions expected for CO₂ injection in ultra-depleted gas fields.

The aim of this review is to provide an overview of the conditions and factors that facilitate or hinder the potential of large-scale CCS in depleted gas fields to support the assessment of the overall risk of hydrate formation for CCS in depleted gas reservoirs. Besides a set of actions that can be affordable and implemented to reduce the risk of CO₂ hydrate formation during injection will be assessed. It will be demonstrated that the kinetics of hydrate formation and propagation in porous media exhibit distinct behavior compared to a bulk environment. The properties of porous media, e.g., heterogeneous permeability, wettability, residual water saturation, gas impurity, and brine salinity, have varying degrees of impact on the hydrate formation and dissociation, which will be reviewed. The intrinsic factors of gas hydrate, e.g., memory effect (Rossi et al., 2021; Wen et al., 2021) and self-preservation effect (Vlasov, 2019) have a significant influence on the kinetic behavior of hydrate. Since, those factors compose a complicated system for tackling hydrate issues in the depleted gas field, their impact on CO₂ hydrate formation/dissociation process and its feasibility will be discussed. Furthermore, the likely simultaneous phenomenon of salt dry-out and gas hydrate is theoretically argued for the CO₂ injection. The interactions between the injection well and reservoir will be described for the corresponding thermodynamic conditions during hydrate formation and dissociation. Following that, feasible prevention approaches will be reviewed. Finally, we will discuss the scientific and engineering problems facing hydrate formation in porous reservoirs.
based on our current limited understanding.

2. Gas hydrate types and structure

Gas hydrates or clathrate hydrates are ice-like crystalline compounds composed of a low molecular weight gas (usually light hydrocarbons and water-soluble gases) and water molecules, combined under certain thermodynamic conditions (relatively high pressure and low temperature). In a clathrate hydrate network, water as a host forms a cage-like lattice structure through H-bonding surrounding the guest gas molecules (Sloan, 2003). Depending on the size and purity of the guest gas molecules, the number of water molecules participating in lattice clusters varies and determines the type of hydrate structure (Cai et al., 2022). In general, guest gas molecules have an important function in the stability of the hydrate structures in which the water molecules form a cage around the guest molecules. Because the structure of the clathrate hydrates is not based on covalent bonds but rather a hydrogen bonded framework, the process of their formation and dissociation is a first-order phase transition rather than chemical reactions (Sloan and Fleyfel, 1991). Hydrate nucleation is determined as an activated microscopic phenomenon in which many molecules (as auxiliary gas) such as those forming sI and larger molecule typically liquid hydrocarbons (0.75–0.9 nm).

In general, CO₂ forms the most common hydrate structure sI in the presence of free water under certain thermodynamic conditions depicted in Fig. 1 (Wroblewski, 1882). In Structure I, the hydrate nuclei are formed by connecting the large cages with pentagonal or hexagonal faces to the small cages. By joining these hydrate nuclei to each other, hydrate clusters are formed and adsorb the CO₂ molecule from the water phase to their surface. The upper part of the interconnected surfaces of the two cages is the favorable adsorption site for CO₂ molecules and can prepare two common pentagonal faces for further CO₂ hydrate formation. Next, the water molecules gradually and continually form cages around the CO₂ molecules and encage the CO₂ molecules into the clathrate structure. Theoretical and experimental evidence also supports the existence of metastable structures sII (Cabrera-Ramírez and Prosmiti, 2022; Fleyfel and Devlin, 1991; Lee et al., 2023; Staykova et al., 2003) and sH (Alavi and Woo, 2007; Cabrera-Ramírez and Prosmiti, 2022) of CO₂ hydrates under thermodynamic conditions approaching the ice melting point. Moreover, there is confirmation regarding the formation of CO₂ hydrate semi-clathrates with other guest components (Kumar et al., 2009; Torr et al., 2012; Zheng et al., 2017).

The following equation can be written for CO₂ hydrate formation/dissociation process (Nagashima et al., 2020):

\[
\text{H}_{2} \text{O} \rightleftharpoons \text{H}_{2} \text{O}^{+} + \text{e}^{-}
\]

In general, CO₂ forms the most common hydrate structure sI in the presence of free water under certain thermodynamic conditions depicted in Fig. 1 (Wroblewski, 1882). In Structure I, the hydrate nuclei are formed by connecting the large cages with pentagonal or hexagonal faces to the small cages. By joining these hydrate nuclei to each other, hydrate clusters are formed and adsorb the CO₂ molecule from the water phase to their surface. The upper part of the interconnected surfaces of the two cages is the favorable adsorption site for CO₂ molecules and can prepare two common pentagonal faces for further CO₂ hydrate formation. Next, the water molecules gradually and continually form cages around the CO₂ molecules and encage the CO₂ molecules into the clathrate structure. Theoretical and experimental evidence also supports the existence of metastable structures sII and sH (Cabrera-Ramírez and Prosmiti, 2022) of CO₂ hydrates under thermodynamic conditions approaching the ice melting point. Moreover, there is confirmation regarding the formation of CO₂ hydrate semi-clathrates with other guest components (Kumar et al., 2009; Torr et al., 2012; Zheng et al., 2017).

The following equation can be written for CO₂ hydrate formation/dissociation process (Nagashima et al., 2020):
where $n_0$ is the hydration number or the number of water molecules per guest gas molecule. $\Delta H$ represents the enthalpy of formation/dissociation of hydrate (exothermic heat released or endothermic heat absorbed) during phase transition, which causes the difference in the slope between $I_w$-$H$ and $L_w$-$H$ lines (see Fig. 1). Formation of gas hydrate is closely linked to the hydration number. In the case of CO$_2$ hydrate, which is mainly in the form of structure sI, the theoretical hydration number is approximately 5.75. However, achieving this value requires full occupancy of both small and large cavities.

3. Hydrate formation in porous media

In this section, we will review various aspects of affecting hydrate formation in porous media due to injection of CO$_2$. Formation and dissociation of CO$_2$ hydrate under bulk conditions (i.e., two-phase conditions in the absence of solid substrates) have been studied by many researchers (Dholabhai et al., 1993). The CO$_2$ concentration (CO$_2$ flow introduced into the bulk) in the bulk condition has a considerable impact on the properties of CO$_2$ hydrate formation and dissociation (Han et al., 2010). In the absence of flow, when the amount of CO$_2$ is inadequate to completely saturate the aqueous phase, pressure decreases considerably outside the hydrate stability zone and prevents the crystallization or breaking of the fragile hydrate crystals in their primary stages. In contrast, for high CO$_2$ concentrations, the aqueous phase is entirely saturated by CO$_2$ molecules and as a result, nucleation and crystallization of CO$_2$ hydrate take place (Hosseini Zadeh et al., 2021; Khurana et al., 2017). In addition, as the volumetric ratio of CO$_2$ increases, the time of decomposition and equilibration becomes longer and leads to creation of dense and relatively stable hydrate. Generally, hydrate formation in a bulk condition is influenced by the gas concentration, the gas–water interfacial area, mass transfer rate, and gas solubility in the aqueous phase, in addition to temperature and pressure conditions.

3.1. Impact of porous media on hydrate formation

There is a significant difference between formation of hydrate in the bulk fluids and within porous media (Wang et al., 2022). The nucleation mechanisms involve interfaces, either gas-liquid (hydrates form at the interface between connate water and gas) or liquid-liquid (hydrates in super-saturated brine form at the solid surface, mainly at clay minerals), which are significantly different in porous media than in bulk fluid experiments (Kvamme et al., 2020; Zhang et al., 2021).

Due to the exothermic nature of the hydrate formation, the nucleation and subsequent growth typically lead to an increase in the bulk temperature and a change in the bulk density of the phases (Yin et al., 2021). On the contrary, due to faster heat transfer in the porous medium, hydrate nucleation and growth do not have a noticeable effect on the pressure and temperature change inside porous medium (Zhang et al., 2021). Characteristics of porous media such as permeability (Xu et al., 2022), porosity, wettability (Li et al., 2022), mineral composition, pore size distribution (PSD) (Chong et al., 2016; Zhang et al., 2021), roughness, and water saturation (Bennamash et al., 2020; Jasamai et al., 2016) have a decisive role on hydrate nucleation and growth (crystallization). A porous medium has a vast specific surface area that can lead to an increase of the gas–water interface. Furthermore, the solid surface provides large area for water molecules to organize and promote nucleation sites (Yang et al., 2016; Zatsepina and Buffett, 2002). Nevertheless, when the pore sizes are too large, the thermodynamic conditions of hydrate formation are similar to the bulk conditions. This is because the gas molecules are present in the micro pores, where water molecules have minimum activity (Luo et al., 2022; Wang et al., 2022; Zhang et al., 2018). However, the inhibition impact of meso- and macro pores is relatively weaker (2 nm < meso < 50 nm < macro) (Chapter 2 - Structural Control of Nanoparticles, 2018). Therefore, as the pore size decreases, the risk of hydrate formation becomes lower (the hydrate phase boundary shown in Fig. 1 displaces to the left). This is attributed to the reduction of water activity in the porous medium owing to the dominant impact of capillary forces (Wu et al., 2021). Furthermore, the temperature of hydrate dissociation in porous media is lower than the decomposition temperatures in bulk due to existence of the capillary force (Geng et al., 2021; Nair et al., 2016). This indicates that hydrate formation is usually not a thermodynamically equilibrium step (it may not be repeatable) and depend on several factors, including agitation/turbulence, cooling rate, presence of additives, fluid composition, water memory, and degree of subcooling ( Gambelli et al., 2022).

Inside individual pores of porous media, hydrates can assume several different morphologies, which are sketched in Fig. 3. Pore filling hydrates nucleate within pore spaces or along grain surfaces without bridging grain particles. Contact cementing hydrates nucleate at the contact points between grains, serving as a cement, and grow around these points. Patchy hydrates nucleate and grow within pore spaces. Grain-coating hydrates nucleate on grain surfaces and coat their surface. Load-bearing hydrates nucleate in pores or grain surfaces, growing towards adjacent sands, while supporting matrix hydrates grow between grains, integrating into the sediment framework.

Furthermore, the presence of the porous medium significantly affects the bulk properties in addition to influencing the hydrate morphology at the pore level. This is because, apart from nucleation at the pore level, the growth requires capillary-driven transport, which limits the mass transfer (Handa and Ohsumi, 1995). One of the practical consequences is that CO$_2$ hydrates may preferentially form outside of the porous medium than inside (Ballard et al., 2001); however, this statement cannot be generalized because clay minerals have also been observed to act as nucleation seeds for hydrate formation.

3.1.1. Kinetics of CO$_2$ hydrate in porous media

The kinetics of CO$_2$ hydrate formation and dissociation plays an important role in assessing the injectivity of CO$_2$ injection wells. The regions with faster growth rates can lead to more severe hydrate plugging of the pores, potentially affecting the injectivity of CO$_2$ into the reservoir. Similarly, the rate of hydrate dissociation determines how fast or slow the injectivity of the wells are retrieved.

The nucleation of hydrates is a stochastic process that involves a substantial delay period lasting from hours to days, particularly in the absence of promoting agents (Bai et al., 2015; Ke et al., 2019). To accurately determine the nucleation process and growth pattern induction times, numerous individual experiments are required to gather relevant statistical data. (Talaghat and Khodaverdiloo, 2019). This is important when conducting laboratory experiments which need to be designed to last for several hours to reach a nucleation probability of 1 to provide reliable evidence for or against the occurrence of hydrates. Experiments that last only few minutes may miss the nucleation of hydrates. Also, in experiments, the conditions need to be kept stable for many hours. The induction time before hydrates form can vary from experiment to experiment even if conducted at nominally identical conditions (Natarajan et al., 1994).

The nucleating sites of the gas hydrates in pores directly determine the spatial occurrence and distribution of gas hydrates. Depending on the phase contact in the porous media, the nucleation may occur at the solid-water, and water-gas interfaces in the porous medium (Hawtin et al., 2008). Therefore, the interfacial tension of these interfaces can determine gas hydrate stability and formation region, which are classified as homogeneous nucleation of the spherical and heterogeneous nucleation of cap-shaped (solid-water), lens-shaped (gas-water), and film-shaped according to Fig. 4. Since the gas concentration at the gas-water interface is much higher than that in the bulk solution and due to rock presence as the third phase (foreign substance), gas hydrates mainly tend to be formed in pores, not on substrate surfaces, which indicates the heterogeneous nucleation of gas hydrates as lens-shaped.
The interactions between the main components of the hydrate, i.e., water and gas, are the basis of the three main proposed theories regarding (kinetics of) hydrate formation and dissociation (Lehmkuhler et al., 2009).

1. The cluster nucleation theory proposed by Sloan postulated that unstable clusters preferentially agglomerate near the water surface after the dissolution of the gas molecules in the aqueous phase (Sloan and Koh, 2008). When the cluster reaches a critical size, macroscopic nucleation begins.

2. Radhakrishnan and Trout proposed the local structuring theory based on the molecular dynamics (MD) simulation of the dense gas-water interface (Radhakrishnan and Trout, 2002). In this hypothesis, the water and gas molecules are placed stochastically to the point where a configuration like a hydrate phase is obtained which stabilizes after reaching a certain size and crystals begin to grow.

3. Surface-driven is the third theory introduced by Rodger, which states gas molecules are adsorbed on the water surface and are encapsulated in the middle of relatively constructed water cages (Rodger, 1990).

The physical and chemical characteristics of porous media such as particle size, roughness, wettability, and functional groups have a synergistic effect on the kinetics of CO$_2$ hydrate (Wang et al., 2022). For instance, surface roughness improves the nucleation sites (Wu et al., 2022). The wettability of surfaces is another property of the porous medium, which has different manifestations depending on the solubility of guest molecules (CO$_2$). It also impacts the mechanism and kinetics of the gas hydrate nucleation by altering the structure of water molecules.

Fig. 3. Morphology of the gas hydrates in porous media. Adapted from (Begum and Satyavani, 2022; Ma et al., 2019):

Fig. 4. Potential nucleation sites of the gas hydrates in porous media. Adapted from (Mirzaeifard et al., 2019):
and gas distribution near the connection surface (Bai et al., 2015; Ke et al., 2019). The activity of water confined in the pores could be depressed by the bonding of water molecules with the hydrophilic surfaces of pores, which inhibited hydrate formation (He et al., 2021; Wang et al., 2022). Moreover, a higher degree of wettability results in a shorter induction time for hydrate formation and a faster nucleation rate. Furthermore, the smallest rock particles increase the available specific surface area, provide more area for water distribution, and increase the interfacial contact between multiple points (water-gas-rock). Such a configuration promotes the proliferation of hydrate nucleation sites, giving rise to multiple simultaneous hydrate growth locations (Kvamme et al., 2009).

3.1.2. Impact of pore size on nucleation

The microscopic and macroscopic properties of porous media are strongly affected by the pore size distribution. For example, apart from connectivity of the pores, permeability of a porous medium has a direct relationship with its mean pore size. Therefore, pore size and distribution of pore size along the porous rock are expected to affect hydrate properties. Research has shown that the porous medium with small-diameter pores affects the phase conditions and shifts the hydrate equilibrium curve (Smith et al., 2002). As an example, porous medium with a 4 nm pore diameter displaces the hydrate phase equilibrium to lower temperatures by $-12 \, ^\circ\text{C}$ compared to $-0.5 \, ^\circ\text{C}$ for the porous medium of 100 nm (Uchida et al., 2002). These effects are mainly due to the additional resistance caused by capillary forces and surface tension between phases, which results in a decrease in the water activity, consequently affecting the hydrate phase boundary. Kang et al. (2008) investigated the hydrate phase equilibrium for CO$_2$/water systems in various porous media with three pore diameters of 6, 30, and 100 nm and concluded that the pores with 6 nm diameter improved the CO$_2$ hydrate thermodynamic stability, while the pores with diameter of 30 nm and 100 nm performed inhibition effect in the dissociation equilibria.

A decrease in the grain size potentially increases the rate of hydrate formation. Mekala et al. (2014) conducted CO$_2$ hydrate formation kinetic experiments in the presence of pure water and seawater (3.3 wt% salinity) using silica beds with three pore sizes. They observed that the CO$_2$ consumption in hydrate and the induction time of hydrate formation at the end of seawater experiment were both lower than those of the pure-water experiment. A smaller silica size exhibited an enhanced average rate of hydrate formation in the pure-water experiment.

3.1.3. Impact of minerals on hydrate formation

Reservoir rocks, generally sandstone and carbonates, consist of various minerals, such as quartz, kaolinite, bentonite, feldspar, calcite, dolomite, etc., which also play important role in formation and dissociation of hydrates in porous media (Rehman et al., 2021). Compared with sandy sediments, clay sediments are distinguished by an extensive specific surface area through small particle diameters, high capillary pressure, and massive content of bound water, influencing different features of hydrate-formation process (Nair et al., 2016). Mu and Cui investigated the hydrate equilibrium conditions under bulk and clay sediment with various salt content and showed that there is no coupling impact between the clay and salt (Mu and Cui, 2019). They also observed that the temperature changes in the clay and bulk phase were almost identical in the presence of salts. Consequently, due to the stronger interaction forces between the clay and water particles, as well as the strong absorption characteristics of the clay that reduce the effective porosity of the sediment through swelling, the coupling impact mostly occurs in the clay-containing systems (Geng et al., 2021). Therefore, the porosity reduction inhibits gas transmission and thus negatively impacts hydrate formation and dissociation (Kumar et al., 2015). Besides, there exist many exchangeable cations among the layered structure of the clays, particularly for bentonite as a lamellar aluminosilicate mineral (Bergaya et al., 2011). Therefore, this specific structure is characterized by its large water absorption capacity, where water can not only be uptaken into the inner part to bind water but also can create a hydrate structure (Jacobs et al., 2015). The water absorption indirectly increases the free water salinity, resulting in the hydrates formation under more stringent thermodynamic conditions (lower temperatures and higher pressures). A similar result is obtained by Ma et al. (2016) regarding the impact of the residual water on the hydrate dissociation conditions in the clays, indicating that actual salinity increases, especially when the water content is low owing to binding with clay (Ma et al., 2016).

3.2. Impact of water saturation on hydrate formation

In the bulk phase, when thermodynamic conditions are conducive to CO$_2$ hydrate formation, the limiting factor lies in the availability of sufficient amounts of water or CO$_2$. In the CCS projects, CO$_2$ is continuously supplied to the reservoir, and therefore, the final volume of the hydrate is determined by the water content of the porous formation or water saturation (Benneshab et al.). Consequently, the water degree affects the spatial availability of sites where hydrates can nucleate, growth and accumulate inside the pore. Moreover, water saturation retards the cold front, and slightly increases the minimum temperature (Chesnokov et al., 2023).

Fig. 5 shows the correlation between hydrate volume and water saturation. The calculations were performed using HydraFLASH software version 3.8 with Soave-Redlich-Kwong (SRK) Equation of State (EOS) for different water saturations at $P = 30 \, \text{bar}$. Hydrate saturation ($S_H$) was the calculated hydrate volume normalized to the pore volume of the porous medium according to the following equation:

$$m_H = \text{conv} \times n_{H_2O} \left( \frac{M_{H_2O} + M_{CO_2}}{M_{H_2O}} \right)$$

Where $m_H$ is the mass of hydrate, $\text{conv}$ is the water fraction that has converted to hydrate (%), $n_{H_2O}$, $M_{H_2O}$, and $M_{CO_2}$ are the total moles of water, the water and CO$_2$ molecular weight, respectively. Hydration number ($n_{H_2O}$) is the average number of water molecules per guest molecule in the hydrate. In equation (3), the term $\rho_H$ is density of hydrate and PV is the pore volume of the porous medium.

There is a linear relationship between hydrate volume (or hydrate saturation or hydrate volume fraction in the porous medium) and water saturation. Hydrate saturation refers to the volume fraction of pore space (containing water and hydrate) occupied by hydrate (You et al., 2019). High water saturation enables a more interconnected network of

![Fig. 5](image-url)
water molecules, facilitating the construction and accumulation of CO$_2$
hydrate lattice. However, the impact of $S_w$ on hydrate volume can vary
depending on the prevailing thermodynamic conditions of the system,
especially at low temperatures when hydrate coexists with the ice. The
simulation outcome suggests that when the reservoir conditions fall
within the hydrate stability region, the impact of temperature on the
volume of hydrate during CO$_2$ injection is relatively low. This limited
influence of temperature could stem from the fact that, when CO$_2$
concentrations are higher (due to CO$_2$ inflow), the water is rapidly saturated
with CO$_2$. Consequently, any additional temperature variations do not
substantially alter the solubility of CO$_2$ in water—an essential factor for
the formation of hydrates. This insight underscores the complex inter-
play between temperature, CO$_2$ concentrations, and water saturation in
determining hydrate volume within the porous system.

Furthermore, the temperature profile during cold CO$_2$ injection is
influenced by water saturation, which in turn affects the hydrate sta-
bility and phase transitions. The increase in water saturation results in
retardation of the cold front, and slight increase of the temperature in
the reservoir due to heat content of the water (Mathias et al., 2010).
Moreover, considering that the water in the reservoirs usually contains
high amounts of salt, hydrate formation has the potential to form con-
centration gradients and initiate the precipitation of salts or minerals
within the pore space of the rock formation, leading to a further reduction
in porosity (Zhang and Liu, 2016). The volume of the salt is
determined by the volume of the available water in the pores.

### 3.2.1. Memory effect on formation of hydrates

The water memory effect in the nucleation of gas hydrates refers to
the phenomenon that gas hydrates nucleate easier or faster in water that
has a history of gas hydrate formation compared to fresh water (water
without hydrate history) (Gao et al., 2023; Wei and Maeda, 2023). While
research on the water memory effect in bulk systems is relatively abund-
ant (Fandiño and Ruffine, 2014; Uchida et al., 2002; Zhao et al.,
2023), its influence on the behavior of CO$_2$ hydrate in porous media has
received less attention due to the complexity of the problem. Based on
the molecular hypothesis, the water memory effect can lead to changes
in the molecular structure and configuration of the water molecules after
dissociation of the CO$_2$ hydrate. The occurrence of the residual structure is
recognized by the difference in water viscosity before hydrate for-
mation and after hydrate dissociation. This altered water structure acts
as a kinetic promoter and influences the kinetics of CO$_2$ hydrate
nucleation and growth in the subsequent hydrate formation cycle. For
example, the remaining arrangements of the water molecules reinforce
the ability of the CO$_2$ molecules to incorporate into the hydrate lattice or
impact the nucleation of the hydrate crystals, when initiated by the
pre-existing clusters/structures in water. According to another hypo-
thesis, a significant number of nanobubbles, due to hydrate dissociation
in porous media, remain dispersed in the dissociated water for a long time
(more than one day). The CO$_2$–water interfaces of these nanobubbles
may act as nucleation sites for heterogeneous nucleation of the hydrate
in porous media and subsequently impact the history of distribution/-
accumulation and growth of the CO$_2$ hydrate (Hassanpourouzbund
et al., 2020; Khurana et al., 2017). Furthermore, the induction time (the
duration between the introduction of CO$_2$ into the system and the first
instance of CO$_2$ hydrate nucleation) is also influenced by the water
memory effect (Gauteplass et al., 2020a). This implies that the temporal
interval for the onset of the hydrate nucleation can be altered due to the
historical interactions of water with its surroundings (Fig. 6).

On the other hand, gas hydrate dissociation is an endothermic pro-
cess and requires an input of heat energy (depending on the occupancy
of the hydrate cage) to break the hydrate structure and release the gas
molecules. This energy can be sourced from the surrounding environ-
ment, leading to cooling of the system. During subsurface CO$_2$
storage, the cooling effect resulting from gas hydrate dissociation could establish
conditions conducive to the reformation of the new gas hydrates. This is
especially relevant if there are residual hydrate structures or memory of
previous hydrate formations in the porous medium. This process can
lead to a self-sustaining cycle, where dissociation of the existing hy-
drates triggers formation of new hydrates, especially if there is a
continuous supply of gas molecules. This phenomenon can have impli-
cations for the stability of the gas hydrates within the reservoir and their
potential to reform after dissociation. However, other parameters such
as the nature and purity of the guest compound, the mechanism and the
temperature of the dissociation, and the specific characteristics of the
porous medium all contribute to shaping these changes (Rossi and
Gambelli, 2021).

Another hypothesis for water memory effect is the reduced salinity of
water with every hydrate formation/dissociation cycle, which affects
both CO$_2$ dissociation and the phase diagram. This is schematically
shown in Fig. 7. As only water molecules enter the hydrate structure
(Shen et al., 2023), the salinity of the remaining brine increases to the
saturation point, such that eventually salt drop out or precipitation oc-
curs in the pores. During dissociation of the hydrate, water molecules
exit the lattice; however, due to the limiting mixing and relatively slow
rate of salt re-dissolution, for the following hydrate formation cycle the
brine salinity is effectively lower. Part of the salt could precipitate in
small corners and crevices making the dissolution process even slower.
The decrease in salinity increases the CO$_2$ solubility in brine and pro-
motes hydrate formation in the subsequent cycle.

### 3.2.2. Self-preservation effect on dissociation

Hydrate self-preservation is interrelated to the ice capping theory
(Falenty and Kuhls, 2009), which explains the process of development of
a thin liquid water layer on the hydrate surface and subsequently
freezing to create an ice cap. This phenomenon could pose another po-
tential challenge concerning the dissociation of CO$_2$ hydrates, when
favorable conditions for hydrate dissociation, such as pressure reduc-
tion, arise. Although regasification can be achieved by increasing the
temperature above the ice melting point, more extended stability of
hydrate within the self-preservation region has been experimentally
observed (Li et al., 2021). Due to limited available research, the exact
mechanism of self-preservation is obscure, and these knowledge gaps
must be comprehended especially for feasible CCS technologies. Under
normal conditions, the CO$_2$ molecules rupture from the hydrate struc-
ture, reducing the stability of the hydrate and allowing CO$_2$ to escape
into the gas phase (Kainai et al., 2023; Myshakin et al., 2009; Sum et al.,
1997). With self-preservation, the dissociated gas molecules are
prevented from leaving the hydrate lattice due to capillary forces that arise from the small pore size of the CO$_2$ hydrate structure, or a protective layer of the ice around the hydrate particles (Chen et al., 2021; Mestdagh and De Batist, 2015). In the context of subsurface CO$_2$ storage, this layer can be formed due to heat absorption during hydrate dissociation (endothermic reaction) (Pandey et al., 2021; Singh et al., 2020; Yang et al., 2021) or exposure to cold regions. Indeed, during the dissociation of CO$_2$ hydrate in the porous media, heat is absorbed by the rock and the in-situ fluids, leading to the formation of a cold or frozen layer in the surrounding layer. This layer acts as a thermal barrier, insulating the remaining CO$_2$ hydrate from further dissociation (Burla and Pinnelli, 2023; Majid and Koh, 2021). In addition, this cold zone can induce the nucleation of hydrate around the ice layer. This phenomenon is schematically shown in Fig. 8. This condition is more pronounced for higher dissociation rates due to limited time for heat exchange. On the other hand, pore size, geometry, and arrangement are interrelated factors that influence heat transfer in porous media.

3.3. Impact of impurities and mixing on hydrate formation

During CO$_2$ storage in a depleted gas field, the injected CO$_2$ will mix with the native gas (usually light hydrocarbons such as CH$_4$). Moreover, the injected CO$_2$ stream might contain small traces of other gases. The composition of gas affects both isenthalpic expansion cooling and hydrate properties (Chapoy et al., 2011; Kvamme, 2022). Depending on the specific conditions and the nature of the impurities, the presence of residual impurities can influence CO$_2$ phase behavior affecting its solubility and miscibility. Consequently, the stability conditions of hydrate can shift with these variations in pressure and temperature. Moreover, the magnitude of temperature reduction and the position of the cooling front caused by isenthalpic expansion effect is a function of gas composition (Ziabakhsh-Ganjii and Kooi, 2014). The macroscopic transport properties of the rock such as relative permeability and capillary pressure function can also be altered by presence of impurities in the gas phase (Anderson et al., 2009).

Fig. 9 compares the thermodynamic conditions of CO$_2$ hydrate in the presence of impurities with different concentrations inside the reservoir using HydraFLASH software and Cubic Plus Association (CPA) EoS. In the case of H$_2$S, its higher solubility results in a greater concentration of dissolved H$_2$S available for hydrate formation. The increased concentration of H$_2$S can enhance the likelihood of hydrate formation. In addition, H$_2$S can influence the thermodynamic conditions of the system, impacting the stability conditions for CO$_2$ hydrate formation, which favors the formation of hydrates at higher temperatures and lower pressures (Mohammadi and Richon, 2015). The presence of N$_2$ has minimal impact on CO$_2$ hydrate formation conditions compared to other impurities like CH$_4$ or H$_2$S. Since nitrogen does not strongly interact with water molecules or compete for hydrate cage occupancy, its presence has little effect on the stability or formation of CO$_2$ hydrate. The impact of gaseous impurities on CO$_2$ hydrate formation conditions tends to be more pronounced at higher pressures. At lower pressures, typically below 40 bar, the solubility of these impurities decreases in the solution, resulting in reduced interaction between the gas and water phases. Consequently, CO$_2$ hydrate formation is less affected by these gases, and the stability zone is closer to the pure CO$_2$ phase (the stability zone becomes wider).
3.4. Impact of capillary heterogeneity

For CO₂ storage applications, it is noteworthy to gain a better understanding of the impact of the geological heterogeneity on the multiphase flow properties of porous media, particularly in the CO₂/brine distribution during the long-term activity (Saadatpoor et al., 2010). The inherent heterogeneity of the sedimentary rocks gives rise to the issues in the variation of capillary pressure corresponding to local changes in porosity and permeability, for both perspectives of microscopic and macroscopic scenarios. The effect of heterogeneities can be commonly explained by the Leverett J-function and reflected on the Pₑ–S and kₑ–S relationship of a porous medium (Pini et al., 2012). This can be calculated by using the data of the measured capillary pressure. Leverett (1941) gave the scaling relationship of Leverett J-Function for characterizing rock sample capillary heterogeneity:

\[ P_r(S_w, k, \phi) = \sigma \cos \theta \sqrt{\frac{k_{eff}/\phi_{eff}}{k/\phi}} J(S_w) \]

where J is the dimensionless J-Function characteristic of a given rock type determined by the measured capillary pressure data, σ and θ are the interfacial tension and contact angle of the fluid systems, \( \phi_{eff} \) and \( k_{eff} \) are the reference porosity and permeability, and \( \phi \) and \( k \) are the porosity and permeability of the rock. Many studies of numerical modeling have revealed that heterogeneity plays a crucial role in CO₂ migration (or CO₂ trapping) and that the permeability dominates the plume migration distance and the sweep area (Han et al., 2010; Nghiem et al., 2009). Residual CO₂ trapping has an inverse function to the permeability, while a higher variance in \( ln k \) results in an increased residual trapping.

However, the impact of capillary heterogeneity on hydrate formation is still not well understood. When CO₂ flow encounters a rock, CO₂ displaces the in-situ brine, if the saturation is above the residual or connate water saturation. The non-uniform saturation of water leads to a capillary pressure gradient, that in turn results in back flow of water from the displacement front toward the injectors (Cui et al., 2018). The magnitude of the backflow depends on the shape of the capillary-pressure function, which is determined by the pore size distribution (heterogeneity), and permeability of the rock. The capillary-driven backflow accumulates water close to the injector, which in contact with the cold CO₂ converts to hydrates. As a result, with more water coming to near wellbore, the saturation of hydrate might increase resulting in more severe injectivity decline. This is similar to the halite precipitation or the dry-out process, which occurs due to the evaporation of water into the gas phase (Talman et al., 2020). Moreover, capillary crossflow can occur between the layers of different permeability, drawing more water from the low permeability layer to the high permeability layer (Roels et al., 2016). For the salt dry-out process, this phenomenon accumulates the brine (and eventually salt) inside the high permeability layer with the highest salt concentration at the interface of the two layers. The capillary pressure gradient is determined by the difference between the layers, the magnitude of the (horizontal and vertical) permeability, while the relative permeability and injection rate determine the magnitude of capillary-driven water backflow and crossflow. These effects are schematically shown in Fig. 10.

It should be noted that because of the key differences between the dynamics of the dry-out and hydrate formation processes, the impact of the capillary-pressure heterogeneity on the two processes could be different and needs further investigation.

3.5. Simultaneous salt dry-out and hydrate formation during CO₂ injection

Under favorable thermodynamic conditions, two processes of salt dry-out and hydrate formation can simultaneously occur in the reservoir during CO₂ injection. However, the interaction between the two competitive phenomena is not well-understood. Research is needed to investigate how the presence of simultaneous salt precipitation and CO₂ hydrate affects mass and heat transport in porous media.

During injection of cold CO₂, the saturations of water, salt, and hydrate vary continuously, at least near the wellbore area. When the temperature of CO₂ is above the hydrate equilibrium temperature, the near wellbore region has temperatures that are outside of the hydrate stability zone (the right region of diagram in Fig. 1). In this case, due to evaporation of water into the gas phase, a dry zone appears. The extent of this dry-out zone depends on reservoir properties, injection rate and salinity of brine. However, when the wellbore temperatures are below the hydrate stability zone, the appearance of the dry-out zone depends on the rates of water evaporation (salt precipitation) and hydrate formation. If evaporation rate is faster, a dry-out zone with high salt concentration might appear. However, the rate of water evaporation is very low at low temperatures, especially when the temperature drops below zero (see Fig. 11). If hydrate formation rate is larger, then hydrates will form first and the available water will be consumed in the hydrate structure. With departure of the water molecules, the brine salinity increases leading to salt precipitation occurring simultaneously in the potential hydrate zone (Liu and Flemings, 2007; Shen et al., 2023). The competition between water evaporation rate and hydrate formation rate needs to be discussed and requires more scientific investigation.

Hydrate formation rate is affected by multiple factors, e.g., temperature and pressure, surface active agents, salinity and ion types, pore size, water saturation, etc. (Zhao et al., 2016). This complexity makes it difficult to quantify the formation rate and to compare it with the loss rate of water. Wells et al. (2021) measured the CO₂ hydrate propagation in a microchannel at a rate over 1000 mm/s, under –2 °C and 400–500 psi. Additionally, the propagation rate increased with the increase in the subcooling temperature and pressure. In porous media, hydrate induction time in salt water is shorter than in pure water but the formation rate is the opposite (Yang et al., 2016). Gauteplass et al. (2018) performed a series of core flooding experiment on the Bentheimer sandstone for three cases of brine salinity, 3.5 wt%, 5 wt% and 7 wt%, under the experimental pressure of 70 bar and temperatures of 4 °C, 6 °C and 7 °C. They observed that after around 0.3 PV of CO₂ injection, the core samples were completely plugged due to hydrate formation. They also noticed that water saturation played an important role on the hydrate formation and pore blockage. In Zhang et al. (2019) experiments were
carried out in frozen sand and hydrates were forming from ice (Sice~13%). The formation rates were actually quite low (9.4 × 10^4 mol/h~17 mg/h, and the tests ran for ~140 h to reach a 66% conversion of ice to hydrates).

Furthermore, with evaporation of water, salinity of the reservoir brine starts to increase. The hydrate equilibrium temperature is shifted to lower temperatures. As a result, hydrate formation might be hindered when water evaporation is relatively high.

3.5.1. Impact of hydrate formation on rock permeability

A significant challenge in successful geological storage of CO₂ is the permeability impairment, and ultimately, injectivity loss due to CO₂ hydrate formation in the near-wellbore area. At the early stages of the injection, CO₂ density undergoes a substantial decline due to the dense-to-gas state transition, which subsequently impacts the wellhead pressure. Consequently, a prompt decrease of the pore space through the ongoing hydrate growth leads to a space blockage and a high-pressure gradient (White, 2011). To mitigate this issue, it is crucial to gain a thorough understanding of the relationship between the permeability and the geometrical features of the porous medium (porosity and permeability), and CO₂ hydrate saturation. Such understanding can provide insights into the mechanisms behind this challenge and aid in developing strategies to prevent or alleviate the adverse effects of CO₂ hydrate formation near the wellbore (Deng et al., 2021; Jianzhong Zhao et al., 2015).

Kneafsey et al. (2011) showed that the permeability of porous sediments appertains to porosity, pore geometry, hydrate morphology, as well as fluid characteristics. Priegnitz et al. (2015) proposed an empirical model, based on which the permeability of the porous medium is mainly influenced by porosity, pore size, and gas hydrate morphology. Hydrate formation in the pore space leads to a decrease in effective permeability, influenced by the hydrate morphology, its distribution and saturation (Sahoo and Best, 2021). In addition, the effective water permeability decreases with the decrease in the pore size, which is further affected by the rock heterogeneity. However, gas-hydrate morphologies that inhibit inner-pore connectivity (switch off pore network pathways) are more than the hydrate morphologies that only confine permeability within pores (reduce flow uniformly through the entire pores network) (see Fig. 3 for illustrations).

Verma and Pruess (1988) proposed a porosity-permeability relationship of the tube-in-series model, which is commonly used in numerical simulations. This model treats capillary as a 1-D tube consisting of wide and narrow segments. The value of the permeability is determined by the local radii of the narrowest part of the tube. Therefore, it can be used for correlating the changes in the permeability and the porosity induced by the clogging in the processes of mineral dissolution and precipitation, shown as

\[
\frac{k}{k_0} = \theta^2 \frac{1 - \Gamma + \Gamma/\theta^2}{1 - \Gamma + \Gamma \left( \frac{\theta}{\Gamma \theta_0 (\theta_0 - \theta_c)} \right)^2} \tag{4}
\]

\[
\theta = \frac{\theta_0 - \theta_c}{\phi_0 - \phi_c} \tag{5}
\]
Gas Science and Engineering 123 (2024) 205250

\[ \varphi_r = 2\pi \Gamma (r^2 - r^2) \]  

(6)

where, \( k_0 \) and \( \varphi_0 \) are the initial permeability and porosity, \( \theta \) is the normalized porosity, \( \varphi_r \) is a finite porosity, \( \Gamma \) is the fraction of the total length of a capillary tube has a \( r \) while the remainder \( 1 - \Gamma \) has a smaller radius \( r \), and \( \omega \) is the ratio of cross sectional areas of the tube segments \( (\tilde{r}/r)^2 \).

When \( \Gamma = 0.8 \) and \( \varphi_r = 0.9 \), is the porosity for the pore radius with \( r \), Equation (2) can be fit by a power law as below (Pruess and Müller, 2009), meaning that the permeability reduces to 0 while 10% of pore space is clogged. The relationship

\[ \frac{k}{k_0} = \left( \frac{\varphi - \varphi_r}{1 - \varphi_r} \right)^2 \]  

(7)

was proposed as a model in a numerical simulation (Liu et al., 2013). Here, the pore space is considered as cylindrical capillaries with a radii \( r \) and was either water-filled or completely dry. The capillary pressure had a relative change with pore volume due to mineral precipitation/dissolution. The permeability change can be described as follows (Le Gallo et al., 1998).

\[ \frac{k}{k_0} = \sqrt{\left(\frac{\delta - 1}{1 - \left(1 - \sqrt{S}\right)^n}\right) + 1} \]  

(8)

where \( \tau \) is the tortuosity factor, and \( \tau = 1 - S_0 + \delta S_p \), \( S_p \) is the effective brine saturation at the time when mineral reaction starts, \( \delta \) is the multiplied proportionality factor for calculating new pore-size distribution after reactions, and \( S \) is the effective water saturation during reactions.

Other correlations have been developed considering different pore shapes than the simple capillary model (e.g., capillary tube model and Kozeny grain model) and the location of hydrates in the pore space (e.g., surface coating and pore-filling), are presented in Table 1.

The permeability calculated by different models are shown in Fig. 12. The pore-filling models appear to allow for full blockage of the pores with formation of hydrates after a certain hydrate saturation.

Additionally, the porosity change with the hydrate formation and accumulation can be described as:

\[ \varphi_r = \varphi_r (1 - S_0) \]  

(9)

where \( \varphi_r \) and \( \varphi_0 \) are the total porosity of the porous domain with and without hydrate, respectively (Rempel and Buffett, 1997).

3.5.2. Impact of heterogeneity on permeability reduction

The hydrate nucleation pattern above pore scale level in combination with rock heterogeneity has a major impact on the permeability reduction as illustrated in Fig. 13. The largest permeability reduction is observed for a cross-sectional hydrate pattern (Pan et al., 2021). The lowest impact is observed in a layered system with layers parallel to flow direction where most of the hydrate is formed in the layers with smaller pores (which have the larger water contents due to higher capillary pressure).

Core flooding experiments imaged by MRI (Ji et al., 2019) suggest that it is possible that eventually the whole pore space of a large-scale rock sample is filled with hydrates, which is the worst case for permeability reduction.

It is important to mention that the larger scale spatial distribution of hydrates is not only a consequence of the rock heterogeneity but also a matter of the injection regime (Shagapov et al., 2015), in a similar way as the dissolution patterns in rock during reactive transport (frontal dissolution, homogeneous dissolution, wormholing etc. (Snippe et al., 2020). For gas hydrate formation, the dominant regimes are based on a conceptual mathematical model (Shagapov et al., 2015) considering volumetric zone, and frontal zone.

However, the initial distribution of the gas is not necessarily uniform. A similar observation was also made by CT scanning (Ji et al., 2019). Note that in the CT scanner, hydrates are identified via their lower density.

3.5.3. Dynamics of well-reservoir interaction

The temperature at the bottomhole depends on the back pressure induced by the porous medium connected to the well (Liu et al., 2016), which is largely determined by the permeability of the rock. The temperature at the sand face decreases with higher permeability. Therefore, for a heterogeneous reservoir with different permeability layers, the high permeability layers will be at higher risk for formation of hydrates due to combined effects of high CO₂ flowsrates in these layers and low temperature at the boundary. If the bottomhole temperature is already lower than equilibrium hydrate temperature (see Fig. 15A2), then CO₂ hydrate will form immediately starting from the sand face. Formation of hydrate reduces the rock permeability, resulting in increased pressure in the well (P₂ in Fig. 14), which in turn results in increase of temperature (T₁ in Fig. 14). The speed of pressure increase depends on the rate of hydrate formation and the magnitude of permeability reduction induced by the hydrate. The rock permeability can also be affected by other mechanisms such as salt precipitation, fines migration, dissolution of secondary mineral due to reduced pH, clay swelling, etc. If the temperature rises above the equilibrium hydrate temperature, hydrate will start to dissociate. With the dissociation of hydrate, the reservoir permeability increases, and thus the pressure starts to decline (P₂ in Fig. 14). Hydrate dissociation releases significant volume of CO₂ which can increase the pressure locally. The slope of P₁–P₂ line in Fig. 14 depends on the dissociation rate of the CO₂ hydrate. The rate of

Fig. 12. Rock permeability as a function of hydrate saturation – a compilation of analytical models provided in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Model</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capillary tube</td>
<td>( k_n = (1 - S_0)^2 )</td>
</tr>
<tr>
<td>Grain-coating</td>
<td></td>
</tr>
<tr>
<td>Pore-filling</td>
<td>( k_n = (1 - S_0)^2 / \ln(S_0) )</td>
</tr>
<tr>
<td>Kozeny grain</td>
<td>( k_n = (1 - S_0)^{n+1} )</td>
</tr>
<tr>
<td>Grain-coating</td>
<td>if 0 &lt; S₀ &lt; 0.8 then ( n = 0.5 )</td>
</tr>
<tr>
<td>Pore-filling</td>
<td>if S₀ &gt; 0.8 then ( n &gt; 1 )</td>
</tr>
<tr>
<td>Kozeny-Carman</td>
<td>( k_n = (1 - S_0)^{0.5} )</td>
</tr>
<tr>
<td>Carman</td>
<td>( n = 0.7 ) ( S_0 = 0.3 )</td>
</tr>
</tbody>
</table>

\( n \): saturation exponent.
dissociation is influenced by injection of hydrate inhibitors (HIs) and thermal stimulation. The extent of heat exchange between the surrounding formations and the hydrate-bearing formation can also affect the rate of dissociation. With the reduction of pressure, the well temperature also comes down. Because of the self-preservation effect, all the encaged CO₂ might not be released, which could result in higher pressure and temperature than those of the previous step. Moreover, with injection of more CO₂ the average reservoir pressure increases. Once again, if the temperature drops below the equilibrium hydrate temperature, hydrate starts to form. Because of the water memory effect, hydrate might form faster in the following cycles with potentially larger volumes or more compact structure.

This dynamic behavior in the boundary between the well and the reservoir continues until the average reservoir pressure increases above the HQP in Fig. 1. The value of the HQP is influenced by many parameters including brine salinity, composition, gas composition, concentration of chemical, etc. At this point, the well temperature stays above the hydrate equilibrium temperature and the situation becomes similar to Fig. 15. For this scenario, formation of hydrate inside the porous medium depends on the magnitude of the pressure drop (which eventually leads to low temperatures due to isenthalpic expansion cooling effect), largely influenced by rock permeability, thickness of the reservoir, injection rate, among other parameters (Mathias et al., 2010). The higher temperature of CO₂ near wellbore can result in faster evaporation of water into the CO₂ stream leading to zone with low water saturation and high salt concentrations.

3.5.4. Multi-scale visualization of hydrate formation in porous media

To detect the formation of hydrates in laboratory experiments, several experimental methods are available. They in general group into Pressure-drop measurements (indirect), and imaging of the hydrates (direct). Pressure-drop measurements utilize the effect of permeability reduction when hydrates form. Even though one of the key questions is the extent of the permeability reduction, the more basic question is whether hydrates are formed in the first place, and how much. Pressure drop is not only impacted by permeability reduction but also by changes in relative permeability, which also depend on an often-changing water saturation (Ott et al., 2011, 2021).

In addition, in certain types of pore geometries and heterogeneous settings, hydrates may form with hardly an impact on permeability (Ott et al., 2015; Pan et al., 2021). Therefore, pressure drop measurements alone are not considered a reliable method to detect hydrate formation. They provide indications and complementary information is required. To provide a clear and reliable indication of hydrate formation, in-situ monitoring methods are required. Several reliable in-situ imaging methods have been used in the literature including NMR (bulk) (Ji et al., 2019; Vaessen et al., 2000; Zuniga, 2020), MRI (imaging) (Haneda et al., 2002; Ji et al., 2019; Mooijer, 2004), CT (Meyer et al., 2018), micro-CT (Chaouachi et al., 2015), optical microscopy (2D only) (Lv et al., 2021), electrical resistance (Chen et al., 2020), and Raman spectroscopy (Ikeda et al., 1998, 2018; Nakano et al., 1998; Sun et al., 1997). NMR and MRI are considered very sensitive to the formation of hydrates because the water bound in hydrates is NMR silent (relaxation time is very short), which make hydrates easily and unambiguously detectable (Haneda et al., 2002).

2D-micromodels are usually applied to monitor the hydrate formation and kinetics under controllable observation domain and pore structure (Christiansen and Sloan Jr, 1994; Muraoka et al., 2020; Pandey et al., 2022). The formation of gas hydrates in the 2-D micromodels can be well explained (Wang et al., 2021). Some inside on interactions between wettability, supercooling and hydrate formations and dissociation can be discovered using pedant drop (Daniel-David et al., 2015) and capillary tubes experiments (Touil et al., 2019).

4. CO₂ hydrate prevention/remediation approaches

Gas hydrate controlling techniques (e.g. dehydration, thermal stimulation, and chemical additives, etc) rely on comprehending the mechanisms by which hydrates form and dissociate (Koh et al., 2002; Mooijer, 2004; Peters et al., 2012). In the context of CCS, the utilization of hydrate inhibitors (HIs) represents the most effective and practical chemical approach to control hydrate formation. This involves altering
hydrate phase boundaries, thereby situating the existing operating conditions outside the Hydrate Stability Zone (HSZ), which is useful in preventing injectivity decline due to the hydrate formation. HIs are segregated into three main groups based on the different inhibition mechanisms, thermodynamic hydrate inhibitors (THIs), kinetic hydrate inhibitors (KHIs), and anti-agglomerates (Ke et al., 2019).

4.1. Impact of thermodynamic hydrate inhibitors (THIs)

Under low water content, THIs is the best chemical to protect the system from hydrate formation by shifting the equilibrium boundary towards lower temperatures or higher pressure (Kelland, 2019; Koh et al., 2012). However, the amount of chemicals required to eliminate the hydrate formation condition may exceed half of the water content. Therefore, their utilization in the CCS project should be considered from two perspectives: (1) functional mechanism and antisolvent effect, (2) economic costs. The THIs can be predominantly classified into three distinct categories: glycols, alcohols, and salts.

4.1.1. Salts (mono and di-valent salts)

Salts or electrolytes are types of THIs that dissociate into cations and anions when dissolved in water and interact with water molecules through strong coulombic attractions which disrupt the hydrogen-bonding network of water and reduce its availability to participate in the hydrate network (Dholabhai et al., 1993; Javanmardi and Moshfeghian, 2006; Liu et al., 2021). Smaller ions with higher charge density have a stronger ability to interact and bond with water molecules, showing tendency to disrupt water structure, therefore, hinder hydrate cage formation (Holzammer et al., 2016; Zhang et al., 2018; Zuo and Stenby, 1997). The hydration of salt ions with water molecules in a saline solution enhances the ion charge, which leads to a decrease in the solubility of nonelectrolyte molecules (CO₂) so-called salting-out effect (Englezos and Bishnoi, 1988; Holzammer et al., 2016; Li et al., 2020). The effectiveness of the salting-out effect depends on the ionic radius of the salt ions, and as the ionic radius increases, the ability of the ions to induce the salting-out effect decreases. This is because larger ions have a weaker influence on water molecules, resulting in weaker solvation and a smaller impact on the solubility of nonelectrolyte molecules. Nevertheless, cations and anions can have distinct interactions with water molecules or may form complexes with CO₂ molecules. According to research studies, the inhibition impact of cations on CO₂ hydrate formation can be presented in the following order: Mg²⁺ > Ca²⁺ > Na⁺ > K⁺ (Falahieh et al., 2022; Pahlavanzadeh et al., 2023). However, the relative solubility and ionization properties of monovalent (NaCl and KCl) and divalent (CaCl₂ and MgCl₂) salts in water can indeed have different influences on kinetics, stability, and thermodynamic properties of CO₂ hydrate in distinct ways (Dholabhai et al., 1993; Zha et al., 2012).

Fig. 14 shows the formation conditions of CO₂ hydrate in the presence of single and binary salt solutions using HydraFLASH software. It is seen that increasing salinity of the solution enhances the inhibitory effect on CO₂ hydrate formation, which was observed at both high and low pressures in different saline solutions. However, at high pressures, increasing the solution salinity leads to a more pronounced inhibitory property, resulting in a larger decrease in the hydrate dissociation temperature. Regarding the information provided, at moderate pressures and concentrations below 5 wt%, MgCl₂ and CaCl₂ show a

Fig. 14. The continuous change of wellbore temperature and pressure during hydrate formation and dissociation.
comparable inhibitory effect on CO\(_2\) hydrate formation. However, at low pressures and concentrations above 10 wt%, MgCl\(_2\) demonstrates a greater capacity to decrease the equilibrium temperature of CO\(_2\) hydrate compared to CaCl\(_2\). In the binary combination of NaCl + MgCl\(_2\), MgCl\(_2\) has a stronger inhibitory impact compared to NaCl due to its smaller size and stronger interaction of Mg\(^{2+}\) ions with water molecules. On the other hand, in the NaCl + KCl mixture, Na\(^+\) and K\(^+\) ions, being even larger in size, exhibit a relatively lower inhibitory effect due to their weaker interaction with water molecules, however, NaCl exhibits a dominant inhibitory effect.

The presented data is a general trend observed in the laboratory and modeling studies, but the precise impacts can vary under reservoir conditions based on thermodynamic conditions and medium properties.

In the scenario where the reservoir experiences a significant drop in temperature, there is a possibility of salt precipitation occurrence. The cooling effect caused by the endothermic dissociation of CO\(_2\) hydrates is another problem that leads to further precipitation of salts, exacerbating the issue. This can lead to the salts losing their effectiveness, especially when operating below their eutectic temperature. In this regard, the maximum concentration of NaCl before precipitation is approximately 23.3 wt% at \(-21.1\) °C, while for a 30 wt% CaCl\(_2\) solution, precipitation begins at a lower temperature of \(-51.5\) °C. This parameter can also be impacted by the introduction of other chemicals like MeOH into the reservoir, which can be the subject of future research.

4.1.2. Glycols and alcohols

Research has revealed that reducing the molecular weight (MW) of alcohol or glycol compounds can lead to enhanced performance in suppressing hydrate formation. This effect is attributed to the ability of compounds to form more stable complexes with water or CO\(_2\) molecules. It’s noteworthy that, lower-MW inhibitors are generally more efficient as they yield higher molar/molal concentrations than higher-MW inhibitors at the same mass concentration. In this scenario, monoethylene glycol (MEG) exhibits more effective inhibition performance compared to diethylene glycol and triethylene glycol (TEG) due to its lower density and viscosity (Aminnaji et al., 2017; Gautepllass et al., 2020a; Munck et al., 1988; Nielsen and Bucklin, 1983). Moreover, methanol exhibits greater efficacy compared to ethanol. However, one significant drawback of these oxygenated inhibitors, like methanol, is their distribution/evaporation behavior (more volatile/lower boiling temperature), leading to a decrease in their concentration below the desired level compared to non-oxygenated inhibitors like MEG (Brustad et al., 2005). Fig. 17 compares the corresponding weight fraction of different glycols and alcohols as inhibitors for a 10 °C depression temperature of CO\(_2\) hydrate using HydraFLASH. According to the diagram, methanol is preferred due to its strong hydrate inhibition properties, and is often used as selective inhibitors in various applications. However, it should also be worth evaluating other factors such as antisolvent effect, solubility, potential side effects, safety, and economic feasibility when
selecting an appropriate inhibitor for CO$_2$ hydrate inhibition (Cao et al., 2020). The presence of MeOH at low temperature might result in precipitation of salt, that can adversely affect the rock permeability.

In addition, the thermodynamic conditions of CO$_2$ hydrate in the presence of effective alcohols and glycols have been obtained in a wide range of pressure and concentrations by utilizing HydraFLASH (Fig. 18). Accordingly, the effectiveness of MEG and Methanol can vary depending on their concentration in the system. At low concentrations, the differences in their ability to shift the phase diagram of CO$_2$ hydrate may be relatively small, and their inhibitory effects may be comparable, while as the concentration increases, the differences in their effectiveness become more pronounced.

Nevertheless, when considering the efficiency of MEG and MeOH as the most efficient and common THI in the context of CCS, the following points should be considered: (1) Due to dissociation of hydrate, the water content of the porous medium increases leading to dilution of MEG or MeOH solutions, which in turn reduces their effectiveness, (2) The temperature drop during CO$_2$ hydrate dissociation should be considered as part of the depression temperature to ensure that operation remains outside HSZ. (3) In terms of THIs selection, MEG is commonly used in gas-dominated systems due to its lower volatility or lower gas solubility compared to MeOH. (4) Due to the viscosity contrast between MEG and water, the mixture might be non-uniform, leading to less contact with the hydrate phase in porous media, which can affect its effectiveness. (5) The rate at which MeOH is injected needs to be aligned with the reservoir's salinity level, as MeOH is not compatible with high-salinity brines, particularly at lower temperatures. With precipitation of the salts, the inhibitory effect of electrolytes becomes less pronounced.
Moreover, the precipitation of salts can also impact the injectivity of CO₂ by reducing the reservoir’s porosity/permeability. (6) The compatibility of these chemicals with the reservoir minerals should also be evaluated.

4.2. Impact of kinetic hydrate inhibitors (KHIs)

One of the primary mechanisms of KHIs is the prolongation of the nucleation induction time by adsorption and forming a protective layer or altering the interfacial properties between water and gas phases (Aghajanloo et al., 2022; Bavoh et al., 2016; Li et al., 2019; Sun and Englezos, 2016). When it comes to large-scale subsurface CO₂ storage, the most superiority of KHIs is that they can be applied in relatively small concentrations, typically 0.1 wt% to 1 wt%. This can reduce the cost of materials and investment as well as minimize any potential side effects of inhibitors on the overall injectivity performance (Kelland, 2019). A major limitation of KHIs in the CCS context is the relatively low degree of subcooling; if subcooling is larger than a specific value (depending on the type of the KHI), the inhibitory property of these chemicals will be greatly diminished, and it may act as a promoter. At low subcooling temperatures pure KHIs are sufficiently effective, while under high subcooling, synergistic HIs may be appropriate (Clarke and Bishnoi, 2005).

The potential KHIs to be applied for CO₂ storage include: (1) Polymeric KHIs such as polyvinylcaprolactam (PVCap), polyvinylpyrrolidone (PVP), which are water-soluble polymers or oligomers that possess both hydrophobic and hydrophilic characteristics (Kolland et al., 2021). The hydrophobic portion of the KHI molecule inhibits hydrate formation by binding to the hydrate cages or occupying specific sites within the water structure (Yagasaki et al., 2015). KHIs reduce the availability of water molecules for hydrate nucleation and inhibit the growth of hydrate crystals. At the same time, the hydrophilic portion of the molecule interacts with water molecules, also reducing the contact surface area between water molecules and CO₂, thus limiting the opportunity for hydrate formation (Liu et al., 2020). However, from a chemical perspective, there are concerns regarding the KHI compounds, potentially adsorbing onto the surface of reservoir rocks. This adsorption could limit their effectiveness and result in increased costs for compensating for the adsorption phenomenon. (2) Biodegradable Inhibitors or environmentally friendly KHIs such as polyactic acid (PLA) and polyhydroxalkanoates (PHA) that can degrade over time, reducing the long-term impact on the reservoir and surrounding environment. (3) Synergistic combinations of KHIs with THIs such as methanol or MEG to enhance the efficiency and cost-effectiveness of KHIs that have the advantages of both types of inhibitors. The biodegradability and efficacy of the synergistic method can vary depending on the specific combination and the volume fraction of each inhibitor used. Furthermore, unlike THIs, the KHIs performance is time-dependent thus they are mainly applicable to dynamic flow systems, where the hydrate formation and dissociation rates are significant (Yang et al., 2018). The selection of the most suitable KHI for CO₂ storage requires a comprehensive evaluation of factors such as inhibitor performance, compatibility with the CO₂ stream and reservoir properties, cost-effectiveness, and large-scale availability, and operational considerations.

5. Discussion on gaps and future research

Formation of hydrates during injection of cold CO₂ poses potential challenges for low-carbon and cost-effective implementation of CO₂ storage in depleted gas fields. This paper provides a brief review of CO₂ hydrate and its impact on the rock permeability and well injectivity. There have been numerous experimental studies in the literature, which have focused mainly on CH₄ hydrate and more recently on CO₂ hydrate. However, the reported experimental data are not exactly representative of CCS in depleted gas fields. Most of the experiments are designed within the hydrate stability zone, i.e., hydrate formation is forced to form in the porous medium. There are only few reported precedent cases for hydrate formation at field scale or field-related processes or projects. Most of these examples from the field are scattered and not representative of the conditions of CO₂ injection in depleted gas fields. Nevertheless, these examples demonstrate that in principle CO₂ hydrates or ice can form and, if formed, can significantly impair injectivity. But there is no demonstrated experimental case where CO₂ hydrates form due to J-T cooling during CO₂ injection.

Under non-equilibrium conditions, the hydration number is usually slightly higher than 5.5, indicating that there is 5.5 times more water than CO₂ on a mole fraction basis. This value is influenced by the solubility of CO₂ in liquid water and various thermodynamic conditions. For instance, CO₂ solubility tends to increase significantly with a slight rise in temperature, but it slightly decreases with increasing pressure in the hydrate-water region. As such, the permeability impairment is water-saturation dependent. In the context of continuous CO₂ injection into depleted gas fields, water saturation serves as the limiting factor and prevents hydrate saturation from exceeding a certain threshold. For the water saturations representative of depleted gas fields, the formation of hydrate is expected to partially damage the injectivity. Nevertheless, it is important to note that the formation of CO₂ hydrates is not guaranteed and depends on a variety of factors.

There is a wealth of fundamental studies on many different aspects of hydrate formation where typically one or two parameters are varied at a time. These aspects range from the impact of pressure, temperature, rate, fluid composition, gas composition, impact of mineralogy in particular presence of clays, and the impact of heterogeneity on permeability impairment. Moreover, it is very unlikely that all field conditions can be reproduced in the laboratory to full extent. It is important to realize that pressure, temperature, and compositional gradients in the field are much larger than what can be realized in the laboratory within a single or a combination of experiments. That means that laboratory experiments need to focus on the window in terms of pressure, temperature and other parameters that bear the highest risk for hydrate formation.

Numerical simulations are required to estimate the magnitude of temperature reduction, pressure, and compositional gradients in the field, on which basis the window with the highest risk can be identified (for example by comparison to known bulk behavior for gas hydrates) and reproduced in experiments by active control. Currently, these simulations still have the drawback that they have difficulty with dealing with the continuous phase transitions (gas to liquid, gas to solid, etc). These simulations are still only an estimate of the gradients because these simulations require an input such as permeability reduction as a function of hydrate fraction, which is an outcome of an experimental program (for which these simulations are an input). That means that there is a feedback loop between field scale simulations to estimate the relevant parameter ranges, and the experimental program providing estimates of permeability reduction.

Identification of hydrates in situ experiments can pose a significant challenge. Identification on pressure drop alone may not be sufficient, since pressure drop is also influenced by saturation changes and other phenomena such as salt precipitation, thus masking the pressure response. Instead, utilizing imaging equipment such as MRI and CT scanner is recommended.

There is a significant likelihood of false positives and false negatives. This means that the impact of hydrates is not seen in the lab but plays an important role in the reservoir, or hydrate impact is established in the lab but plays no significant role in the reservoir. A field pilot is more likely to address the hydrates risk than laboratory experiments. However, such a pilot needs to have appropriate parameters in terms of temperature and pressure and for calibration of observations may need experimental information that is currently not available in literature.

In combination with the role that heterogeneity plays on the impact of hydrates on permeability reduction, it is not clear which factor in the end dominates with respect to formation and impact on injectivity. That makes the question of the hydrate formation risk very specific to the
actual field situation.

Capillary back flow and cross flow can be driven by the capillary pressure gradient in the process of hydrate formation or salt dry-out and by the capillary pressure difference between heterogeneous reservoir layers, respectively. Water saturation and distribution in the reservoir would have dynamic change that potentially causes the accumulation of hydrate formation near wellbore, which enhances the reduction of CO$_2$ injectivity. On the other hand, within the processes of hydrate formation or dissociation, reservoir heterogeneity improves the change of local capillary force where alters the thermodynamic conditions and affects hydrate stability. Unstable hydrate gives the uncertain water saturation and distribution and causes change of relative permeability of water. However, few studies have considered the role of heterogeneity in hydrate formation, or elucidated its influence on the wellbore impairment. It is critical to figure out the extent of heterogeneity effect and to tackle the potential problems in the wellbore integrity and injectivity reduction.

When CO$_2$ temperatures are above the hydrate equilibrium temperature, dry-out may be more pronounced due to increased water evaporation. In some cases, especially when wellbore temperatures are below the hydrate stability threshold, the competition between the water evaporation rate and hydrate formation rate may lead to the precipitation of salts in the reservoir. This can further complicate the dry-out challenges. It is therefore imperative to conduct further research to comprehensively explore the impacts of dry-out and hydrate formation on mass (effective permeability) and heat transport within porous media. Clarifying these interactions will not only advance our fundamental understanding of reservoir behavior during CO$_2$ injection but also contribute to the development of more effective mitigating strategies for subsurface carbon storage.

The dynamic behavior of hydrate formation and dissociation induces pressure and temperature changes. Hydrate formation near wellbore can cause permeability reduction and therefore pressure and temperature increase in the wellbore. Once the temperature is over the equilibrium hydrate level, hydrate starts to dissociate and release pressure and temperature.

Mitigation strategies (e.g., dehydration, thermal stimulation, and chemical additives, etc.) to eliminate the impact of CO$_2$ hydrate formation and dissociation are crucial in the context of CCS. Future research efforts should focus on various aspects of this challenge. For instance, the development of novel chemicals that can effectively prevent/inhibit CO$_2$ hydrate formation to maintain conditions outside of the hydrate stability zone, and to avoid injectivity decline caused by hydrate formation. These inhibitors should meet criteria such as effectiveness, safety, affordability, and biodegradability. Their correct selection is vital for maintaining the integrity of CCS systems during CO$_2$ injection and storage. Investigating the compatibility of these inhibitors with formation water and reservoir minerals is another key point. Understanding how these chemicals interact with different types of reservoir fluids is also critical for their effective use. Determining the optimal dosage of inhibitors required to effectively prevent CO$_2$ hydrate formation is essential, especially since recycling these inhibitors from formation water may not be feasible.

Numerical simulation of gas hydrates in porous media has historically faced limitations due to general complexity of the hydrate formation and dissociation processes. This problem requires consistent thermodynamics and chemistry incorporated into thermal-compositional modeling formulation and by construction represents interaction of several physical phenomena performed at different scales. The complexity of the existing models varies from a kinetic description with simplified thermodynamic interactions as in CMG STARS (CMG, 2007) and finishing with the most advanced simulation framework for modeling hydrate dynamics in porous media as in TOUGH-HYDRATE (Yin et al., 2018).

However, it’s crucial to acknowledge that the modern hydrate simulation models assume that hydrate formation and dissociation are driven by pressure differences relative to the hydrate equilibrium curve. This assumption is valid within specific regions of the thermodynamic space where three phases (vapor, liquid water, and hydrate) can coexist. In cases with limited brine or gas saturations, hydrate formation can still occur at pressures exceeding those predicted by the equilibrium curve. Furthermore, when modeling hydrate phase equilibria under equilibrium assumptions in TOUGH-HYDRATE, the simulator relies on tabulated equilibrium constants (Moridis, 2003). This approach simplifies the calculation of equilibria but may not capture the dynamic nuances of hydrate behavior under all conditions. Molecular dynamics simulations have also long been proven as a valuable tool, which not only provides insights into molecular phenomena, but is also useful for predicting the macroscopic mechanisms of hydrate formation, dissolution, and stability in porous media (Cheng et al., 2024; Ji et al., 2025).

Rock heterogeneity in combination with non-uniform fluid distribution affects hydrate behavior even at core scale. To deal with hydrate complexity, an effective inversion of core experiments should be performed first and then the modeling results should be regressed to the experimental observations. These observations include pressure measurements at different core locations and dynamic imaging, e.g., CT scans or MRI and allow to inverse the kinetic parameters of hydrate formation at different conditions and parameters. In addition, such model will allow an effective interpolation/extrapolation of experimental results in the parameter space of practical interest for hydrate formation and mitigation.

The developed model needs to be translated then to the reservoir scale. That is not an easy problem since upscaling of the compositional and thermal models are sensitive to the scale of representation. Problems of practical interest often require an effective representation at a coarse scale of almost every component in the governing equations. Several approaches have been proposed for a coarse-scale representation, but most of them are limited to the flow phenomena. In addition, the kinetic description of hydrate formation and dissociation requires to resolve the timescale of the problem when integrating conservation equations. All these time and space sensitivities pose serious challenges to gas hydrate upscaling process.

CRediT authorship contribution statement

Mahnaz Aghajanloo: Writing – original draft, Conceptualization.
Lifei Yan: Writing – original draft, Conceptualization. Steffen Berg: Writing – review & editing. Denis Voskov: Writing – review & editing, Supervision, Conceptualization. Rouhi Farajzadeh: Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Conceptualization.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Acknowledgement

Authors thank Shell Global Solutions International for granting permission to publish this work. Zaynetdinov, Timur is acknowledged for detailed review of the draft manuscript.
Nomenclature

AAs Anti Agglomerates
CCS Carbon Capture and Sequestration
Conv\(_w\) Water Conversion
CPA Cubic Plus Association
CT Computed Tomography
DEG diethylene glycol
EoS Equation of State
G Gas
GHSZ Gas Hydrate Stability Zone
H Hydrate
HB Hydrogen Bond
HSZ Hydrate Stability Zone
HQP High Quadruple Point
IL Ionic Liquid
I Ice
J dimensionless J-Function
k permeability
k\(_0\) initial permeability
k\(_{rw}\) relative permeability
k\(_{ref}\) reference permeability
KHIs Kinetic Hydrate Inhibitors
L Liquid water
LDHIs Low Dosage Hydrate Inhibitors
LQP Low Quadruple Point
m mass
MD Molecular Dynamics
MEG Mono-Ethylene Glycol
ME Memory Effect
MRI Magnetic Resonance Imaging
Mw Molecular Weight
NG Natural Gas
NMR Nuclear Magnetic Resonance
n mole
n\(_H\) hydration number
P Pressure
P\(_BH\) Borehole pressure
Pc Capillary pressure
PHA polyhydroxyalkanoates
PLA polylactic acid
PSD Pore Size Distribution
PV Pore Volume
r radius of capillary tube for the remainder 1-Γ
S effective water saturation
SRK Soave Redlich Kwong
S\(_h\) hydrate saturation
S\(_p\) effective brine saturation
S\(_w\) water saturation
T Temperature
T\(_BH\) Borehole temperature
T\(_{eq}\) Equilibrium temperature for hydrate
T\(_c\) critical temperature
TEG Triethylene Glycole
THIs Thermodynamic Hydrate Inhibitors
V vapor
WAG Water Alternating Gas
wt mass fraction

Greek Character
Δ\(_H\) enthalpy of hydrate formation/dissociation
φ porosity
φ\(_{ref}\) reference porosity
φ\(_0\) initial porosity
φ\(_c\) finite porosity
Porosity

$\psi_r$ porosity for the pore radius with $r$

$\psi_f$ total porosity of the porous domain with hydrate

$\psi_h$ total porosity of the porous domain without hydrate

$\theta_n$ normalized porosity

$\sigma$ surface tension

$\Gamma$ fraction of the total length of a capillary tube

$r$ radius of capillary tube

$\omega$ ratio of cross sectional areas of the tube segments $(r/r)^2$

$\tau$ tortuosity factor

$\delta$ a multiplied proportionality factor

References


Zuniga, A.R., 2020. NMR Studies of Natural Gas Hydrates Exposed to Thermally Controlled CO$_2$ Exchange. The University of Western Australia.