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Influence of water saturation and water memory on CO_2 hydrate formation/dissociation in porous media under flowing condition

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ABSTRACT

Injection of high-pressure CO_2 into depleted gas reservoirs can lead to low temperatures promoting formation of hydrate in the near wellbore area resulting in reduced injection rates. The design of effective mitigation methods requires an understanding of the impact of crucial parameters on the formation and dissociation of CO_2 hydrate within the porous medium under flowing conditions. This study investigates the influence of water saturation (ranging from 20 % to 40 %) on the saturation and kinetics of CO_2 hydrate during continuous CO_2 injection. The experiments were conducted under a medical X-ray computed tomography (CT) to monitor the dynamics of hydrate growth inside the core and to calculate the hydrate saturation profile. The experimental data reveal increase in CO_2 hydrate saturation with increasing water saturation levels. The extent of permeability reduction is strongly dependent on the initial water saturation: beyond a certain water saturation the core is fully blocked. For water saturations representative of the depleted gas fields, although the amount of generated hydrate is not sufficient to fully block the CO_2 flow path, a significant reduction in permeability (approximately 80 %) is measured. It is also observed that the volume of water + hydrate phases increases during hydrate formation, indicating a lower-than-water density for CO_2 hydrate. Having a history of hydrate at the same water saturation leads to an increase in CO_2 consumption compared to the primary formation of hydrate, confirming the existence of the water memory effect in porous media.

1. Introduction

Carbon dioxide (CO_2) emissions from anthropogenic sources are a major contributor to the rapid rise in global temperature and the subsequent effects of climate change, which will indeed have substantial implications for future life on Earth [1–3]. Considering the ongoing reliance on fossil fuels for energy generation, the adoption of carbon capture and storage (CCS) is increasingly acknowledged as a highly promising technology to mitigate the environmental impacts of CO_2 emissions [4,5].

Among the diverse geological formations applicable for CO_2 storage, gas-depleted fields hold distinct advantages and offer substantial secure and long-term storage capacity [6–10]. Nevertheless, in depleted low-pressure reservoirs, the introduction of high pressure condensed CO_2 during injection can lead to substantial adiabatic expansion, a phenomenon known as Joule-Thomson cooling (JTC), particularly within the well-tubing or the near wellbore region. This is mainly attributed to the establishment of significant pressure gradients [11]. A notable concern associated with this phenomenon is the potential for CO_2 hydrate generation when CO_2 interacts with the residual water during the injection phase [12,13]. This CO_2 hydrate formation pose flow assurance challenges and potentially compromise the functionality of the injection well Aghajanloo et al. [14], Chesnokov and a. F., Rouhi and Kahrobaei, Siavash and Snippe, Jeroen and Bedrikovetski, Pavel, [15].

Many publications on CO_2 injection in depleted gas reservoirs have addressed different aspects on the CO_2 phase transition (CO_2 hydrate formation) within the wellbore such as impact of CO_2 flow characteristic [12], CO_2 pretreatment [16], salinity of formation water [17,18], salt precipitation [19,20], and rock mineralogy and permeability [21], aiming to assess and mitigate this operational risk. Nevertheless, there has been no exploration into how reservoir water content (water saturation), and the water memory (refers to the phenomenon where previous hydrate formation experiences an impact on subsequent nucleation) impact the CO_2 hydrate formation and saturation under flowing conditions [22]. Research demonstrate that at high water

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Nomenclature

BP	Back Pressure
c	Chen model constant
CCS	Carbon Capture and Storage
CH	Core Holder
CP	Confining Pressure
CPA	Cubic-Plus-Association
CT	Computed Tomography
CT_{dry}	CT number of dry core [HU]
CT_{exp}	CT number during experiment [HU]
CT_{wet}	CT number of fully wet core [HU]
DP	Differential Pressure
E	Experiment
EoS	Equation of State
f_{conv}	water conversion [%]
JTC	Joule-Thomson Cooling
k	permeability [D]
MeOH	Methanol
MFC	Mass Flow Controller
m_H	mass of hydrate [g]
Mw	molecular weight [g/mol]
NH	hydration number
n	number of moles [mol]
n_t	moles of CO_2 at time t [mol]
n_{H_2O}	total mole of water [mol]
P	pressure
PT	Pressure Transducer
R	universal gas constant
r_{CO_2}	CO_2 consumption rate [mole/min]
S_H	hydrate saturation [%]
S_w	water saturation [%]
t	time [s]
T	Temperature
TC	Thermocouple
TJ	Thermal Jacket
V	Volume, [ml]
V_H	volume of hydrate [ml]
V_φ	volume of core porosity [ml]
z	compressibility factor

Greek Character

β	Pang-Sharma model constant
φ	porosity
ρ	density of hydrate [g/ml]
Δ	difference

Subscript & Superscript

H	hydrate
inj	injection
m	mole
t	time
w	water

saturations region, where the porous medium is predominantly filled with water (>90 %), the formation of gas hydrates can be constrained due to the limited availability of a gas phase Wang et al. [23]. Conversely, low water saturations with substantial gas content are more favorable for gas hydrate formation [24]. Furthermore, gas hydrate dissociation is an endothermic process, that requires heat to dissociate the hydrate structure to release gas molecules. This energy can be supplied from the surrounding pore area. This cooling effect may promote the reformation of the new gas hydrates, especially in the presence of water memory effect and continuous supply of gas moleculesAghajanloo et al. [14]. To assess the feasibility of CO_2 storage in depleted reservoirs, quantifying the impact of different water saturations in the presence/absence of water memory on CO_2 hydrate volume/saturation is required to identify under which condition hydrate is more stable and the effect of hydrate on injectivity becomes detrimental for CCS projects [25].

Hence, this study aims to present insights into the influence of water saturation levels on the volume of CO_2 hydrate and the resulting permeability changes in a Bentheimer core. The Bentheimer sandstone core is selected for the experimental investigations due to its homogeneity, consistent mineralogy, low clay content, and high permeability. The core flood experiments were conducted under isothermal condition of 273.65 K, with the initial pressure set at 3 MPa. This pressure is chosen as a representative value for the candidate depleted gas field in the North sea [26] while the temperature is assumed to be reached by the Joule-Thompson cooling happening due to the expansion of the cold liquid CO_2 injected into the reservoir. The study also provided an opportunity to assess whether the water memory can influence the kinetics of CO_2 hydrate such as CO_2 consumption rate and induction time within porous media. Furthermore, the study applied X-ray CT scanning to characterize and quantify water/hydrate saturation and distribution along the core during dynamic CO_2 injection, particularly at three initial water saturation levels.

2. Experimental section

2.1. Material

The CO_2 as hydrate former and N_2 had a certified purity respectively 99.7 % and 99.999 %, were sourced from Linde Co. gas supplier. The electrolyte (NaCl) was of certified 99.5-grade provided by Fisher Scientific. Deionized distilled water was used to prepare the brine solutions. Cylindrical outcrop Bentheimer core plugs were used as porous media in all the experiments. These core had dimensions of 3.8 cm in diameter, 17 cm in length, a porosity (φ) of 0.23, and permeability (K) ranging from 2.2 to 2.5 D.

2.2. Experimental setup

The schematic of the experimental setup applied for core-flood experiments is depicted in Fig. 1. This includes a Bentheimer sand rock coated with a 5 mm thick layer of epoxy resin to provide a protective barrier for the fluids. The sand core is located inside a polyetheretherketone (PEEK) core holder, which is designed to maintain containment at high pressure and low temperature. Four pressure transducers are employed to measure pressure changes at the: inlet, 2.25 cm from the inlet, 6.5 cm from the outlet, and outlet (GE UNIK 5000— Accuracy to ± 0.04 % Full Scale, ranges from 0.007 to 8 MPa). Two differential pressure devices (Endress and Hauser, Deltabar S, ranges: −0.03 to + 0.03 MPa) are utilized to acquire the pressure difference at the other two locations. Two thermocouples are placed inside the core and at the core outlet to measure local temperatures. A high-pressure control system, typically referred to as the back pressure system, is linked to the outlet of the core holder. The back pressure is adjusted with a large N_2 cylinder to sustain the specific pressure of the experiments (3 MPa). The effluent solution is accumulated in an adsorbent-equipped vessel. A data acquisition system is responsible for collecting and adjusting various parameters such as temperature and pressure within the system. This includes a pulse-free high-precision

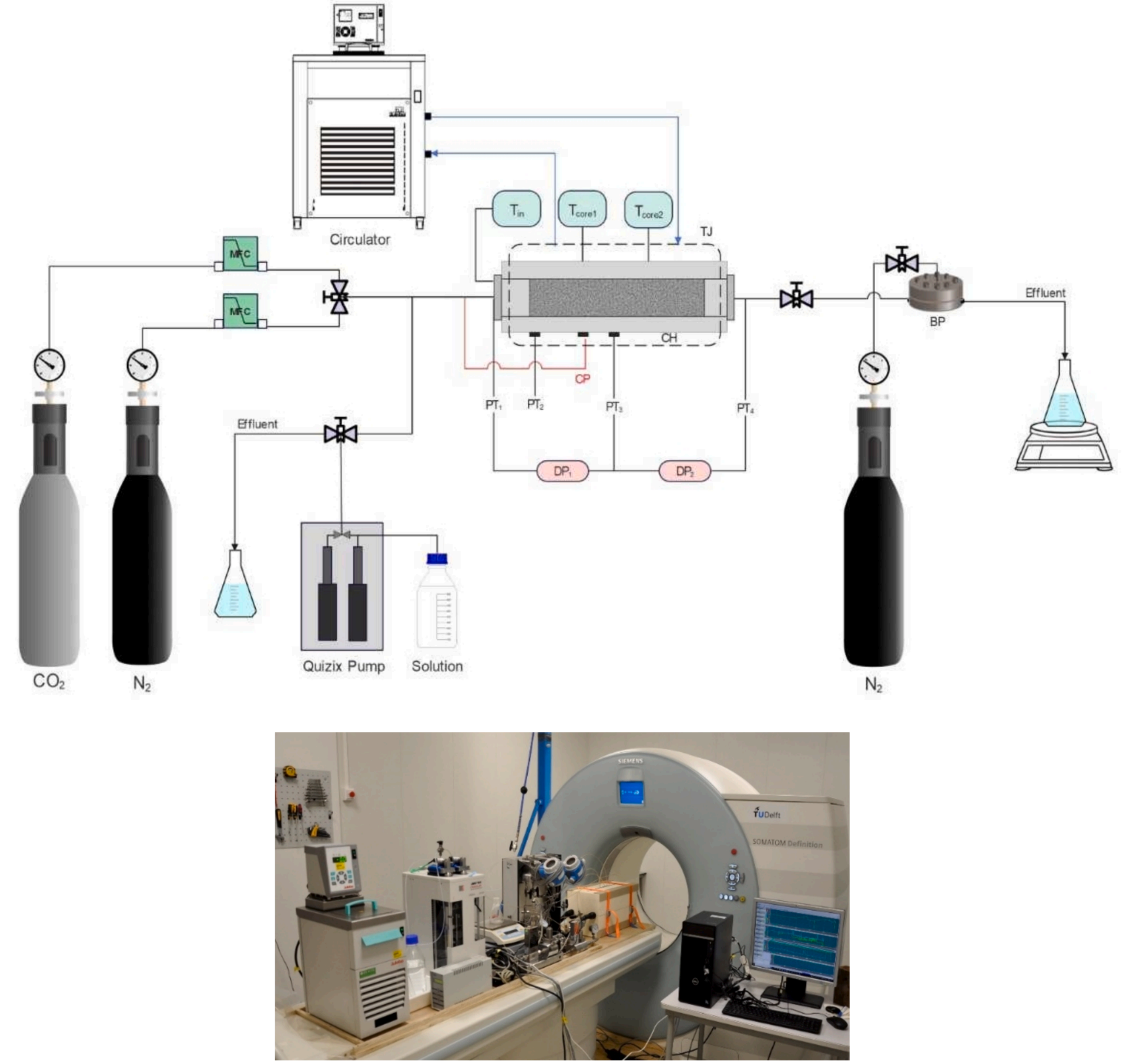

Fig. 1. Schematic diagram and photo of the laboratory apparatus. (BP) Back Pressure; (CH) Core Holder; (CP) Confining Pressure; (DP) Differential Pressure; (MFC) Mass Flow Controller; (PT) Pressure Transducer; (TC) Thermocouple; Thermal Jacket.

piston pump (Quizix QX-6000HC) for driving solutions from the vessel into the core holder and a high-pressure gas mass flow controller (Bronkhorst F-230 M) to manage the injection rate of gas flowrate. The inlet line between the pumps and the inlet end-cap is kept long to equilibrate the water and gas before entering the core. The effluent is collected in a 500 ml collection vessel. The core holder is enveloped by a cooling jacket where the cooling medium is continuously circulated through the jacket using a circulator (LAUDA Proline RP845). The precision of the circulator is within ± 0.1 K. A medical X-ray CT-scan instrument (Siemens Somatom Volume) is used to compute fluid saturation levels and hydrate volume during the formation/dissociation process. The slice thickness for each scan is 0.6 mm, while a resolution of 0.2 mm in the other two dimensions, leads to a voxel size of 0.2 * 0.2 * 0.6 mm^3. A voltage of 140 kV and a current of 250 mA is employed.

2.3. *Experimental procedure*

2.3.1. *Water saturation*

The experiments involved the measurement of water saturation, hydrate nucleation time and hydrate saturation by conducting coreflood tests on a homogenous Bentheim sandstone. To quantify the water/hydrate distribution within the rock core, a medical X-ray CT scanner was employed. To achieve a uninform water saturation below 40 % in the core, a modified gas/water co-injection technique was utilized [27]. In brief, the process began with the injection of N_2 into the system, gradually rising the pressure by 0.5 MPa increments up to a target pressure of 3 MPa. Confining pressure was set equal to the injection pressure. Subsequently, a degassed solution consisting of 1 wt% NaCl and deionized water with N_2 was simultaneously introduced into the vertical core using a specific fractional flow under constant temperature of 273.65 K. The total flow rate, which included both gas and liquid flow, was maintained at 6 ml/min. The ratio of brine to N_2 was regulated using a Quizix pump and a mass flow controller.

2.3.2. Hydrate formation/dissociation cycle

Following the establishment of the desired water saturation, CO_2 injection into the core commenced at a constant velocity of 1 ml/min. The initial pressures selected for hydrate formation in all experimental runs were set at 3 MPa, while the temperature was maintained at 273.65 ± 0.5 K (~6 degree of subcooling based on CO_2/water P-T phase diagram shown in Fig. 2). This consistent temperature and pressure were chosen to create a controlled environment closely resembling real-reservoir conditions where CO_2 hydrates can potentially form. This allowed for precise observations and measurements of CO_2 hydrate behavior under specific operating conditions. Cyclic tests were conducted to investigate whether the presence of water memory influences subsequent hydrate nucleation.

The experimental procedure encompassed CO_2 hydrate formation until a steady state was achieved, after which dissociation was initiated. The first three cycles involved thermal stimulation as a method for hydrate decomposition. This approach ensured the retention of the same solution for subsequent cycles. However, for some experiments, a solution containing methanol (MeOH) was introduced to assess the effectiveness of MeOH as a hydrate remediator to decompose the hydrate structure. Chemical solutions were prepared at loadings of 15 wt% MeOH with degassed deionized water containing 1 wt% NaCl. Considering that both temperature and duration of heating impact the water memory effect, surpassing a particular temperature threshold or exceeding a specific duration of heating can lead to a rapid decrease or complete disappearance of water memory [28]. In this study, during the hydrate dissociation process induced by thermal stimulation, the temperature remained below 293.15 K, and the dissociation process was limited to within a day to prevent the elimination of the water memory associated with hydrates.

- **CO_2 Consumption and Hydrate Formation Rate**

The data acquisition system recorded the pressures and temperatures inside the core sample every 10 s. The calculated CO_2 consumption (total moles of CO_2 consumed from the gas phase) at any given time (t) was determined as a function of the compressibility factor. The calculations were made based on an assumption regarding gas consumption (Δn), which was defined as the difference in the amount of CO_2 introduced into the core at time t (n_t) and the amount of CO_2 that exited the core at next time step ($n_t + \Delta t$). This estimation can be expressed as follows:

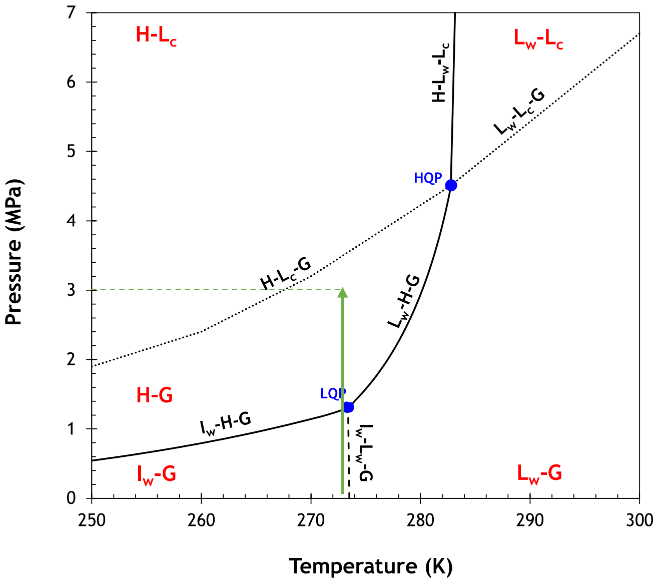

Fig. 2. Three-phase diagram of the CO_2-water mixture. The symbols I_w, L_c, L_w, H, and G represent ice water, liquid CO_2, liquid water, hydrate, and gas, respectively. HQP and LQP refer to high (L_wHL_CG) and low (I_wHL_WG) quadruple points. The smooth line represent the three-phase equilibrium line, the dotted line indicate the CO_2 condensed line, and the dashed line is ice line. (HydraFLASH version 3.8, CPA EoS).

$$n_t = \left(\frac{PV}{ZRT}\right)_t \tag{1}$$

$$\Delta n = \sum_0^t (n_t - n_{t-\Delta t}) \tag{2}$$

where P represents the pressure inside the core, V stands for gas volume, T is the temperature, and the universal gas constant is expressed as R. The compressibility factor (z) was calculated iteratively through the Cubic-Plus-Association (CPA) equation of state (EoS) using HydraFLASH software version 3.8. In equation (2), $t = 0$ denotes the initial condition (just before the CO_2 injection), and $t > 0$ represents time during CO_2 injection.

From kinetic perspective, the CO_2 hydrate formation process encompasses the diffusion of dissolved gas from the aqueous phase to the interface of the hydrate crystal and brine, where the CO_2 molecules are integrated into the clathrate structure. To quantify the rate of CO_2 hydrate formation in dynamic conditions, the moles of CO_2 consumed were utilized. The rate of change in CO_2 gas moles at each time yields the formation rate. This was computed using the following equation:

$$r_{CO_2} = \left(\frac{dn_t}{dt}\right)_{t-\Delta t,t} \tag{3}$$

Where r is the CO_2 hydrate formation rate. Δn is the difference in the number of moles of CO_2 gas. Δt is the time interval.

- **CO_2 Hydrate Saturation**

The total mass of hydrate formation [29]was obtained applying following equation:

$$m_H = f_{conv} \times n_{H_2O}\left[Mw^{H_2O} + \frac{Mw^{CO_2}}{NH}\right] \tag{4}$$

where f_{conv} denotes the fraction of water converted to hydrate, estimated from HydraFLASH software, considering water content (water saturation) and thermodynamic conditions specific to each experiment. The term n_{H_2O} is the total moles of water inside the core, and Mw^{H_2O} and Mw^{CO_2} are water and CO_2 molecular weight, respectively. Hydration number (NH) is the average number of water per gas molecule in an unit structure sI.

Hydrate saturation (S_H), was determined by calculating the volume of hydrate normalized to the pore volume of the core (V_φ). This calculation was carried out using the following equation:

$$S_H(\%) = \frac{V_H}{V_\varphi} = \frac{m_H}{V_\varphi \times \rho_H} \tag{5}$$

where V_H and ρ_H is the volume and density of hydrate defined by the following relationship:

$$\rho_H = \frac{m_H}{V_H} \tag{6}$$

To calculate water and hydrate saturations [30], CT images of the core were obtained under both fully brine-saturated (CT_{wet}) and dry (CT_{dry}) conditions. The saturation was calculated using the following equation [31]:

$$S_{w/H} = \frac{CT_{exp} - CT_{dry}}{CT_{wet} - CT_{dry}} \quad (7)$$

where, $CT_{\exp}$ represents the voxel level CT number for the core at various steps throughout the experiment, encompassing water saturation, CO_2 injection, CO_2 hydrate formation, and dissociation.

3. Results and discussion

3.1. *Impact of water saturation and water memory on CO_2 hydrate saturation*

A significant risk to injectivity during CO_2 storage is the potential for hydrate formation near wellbore area [16,21]. Consequently, when investigating the impact of hydrate, multiple factors need to be considered, including thermodynamic condition (T and P), salinity, and water saturation Wang et al. [32]. Depleted gas reservoir typically exhibit low water saturations; however, aquifer influx and water mobilized by capillary pressure can pull back water near wellbore area. Moreover, in a heterogeneous reservoir different layer may contain different levels of water saturation. Hence, it is essential to quantify impact of water saturation on extent of injectivity decline and dynamics of hydrate formation/dissociation.

To gain insight into the experimental findings, the initial step involved prediction of hydrate saturation (referring to the maximum water-to-hydrate conversion under given thermodynamic conditions) corresponding to water saturations ranging from 20 % to 60 % at 3 MPa using HydraFLASH software, applying the CPA EoS. Fig. 3 presents the linear correlation between hydrate volume/hydrate saturation and water saturation. The slope of the line in this figure is calculated to be 1.21, with $>$ 0.97 % water-to-hydrate conversion efficiency, indicating that CO_2 hydrate structure sI occupies 21 % more pore volume compared to water under assumed conditions. With hydration number of ~ 5.9 to 6.1, the estimated hydrate density is ~ 0.804 g/ml. This estimation assumes a uniform distribution of water and CO_2 and ignores the potential coexistence of ice due to nonuniformity, which may exist in a real system. Accordingly, in the studied range of water saturations (20 % – 60 %), when excess CO_2 is present, the efficiency of water-to-hydrate conversion remains constant across the specified water saturation levels. However, as depicted in Fig. 4, under a constant pressure of 3 MPa, the latent heat (enthalpy) of CO_2 hydrate formation decreasing from 396.7 kJ/kg with water saturation above 20 %. Additionally, the influence of water saturation on hydrate saturation is different when hydrate coexists with ice at lower temperatures. The simulation results also indicate that when the reservoir conditions are situated within the hydrate stability region, at a constant pressure the temperature has a relatively low impact on hydrate saturation during CO_2 injection. This limited influence of temperature can be attributed to the constant density of CO_2 in the gas phase (due to continuous CO_2 injection), leading to the saturation of water with CO_2. Consequently, the hydrate lattice stabilizes upon achieving maximum CO_2 filling. Consequently, additional temperature change does not significantly alter the encapsulation of CO_2, a crucial factor for hydrate stabilization. For these calculations, at $S_w = 0.81$, hydrate will fully occupy the porous medium. However, flow of CO_2 will be hindered if hydrate saturation reaches a specific value and therefore formation of hydrate will be limited due to inaccessibility of CO_2.

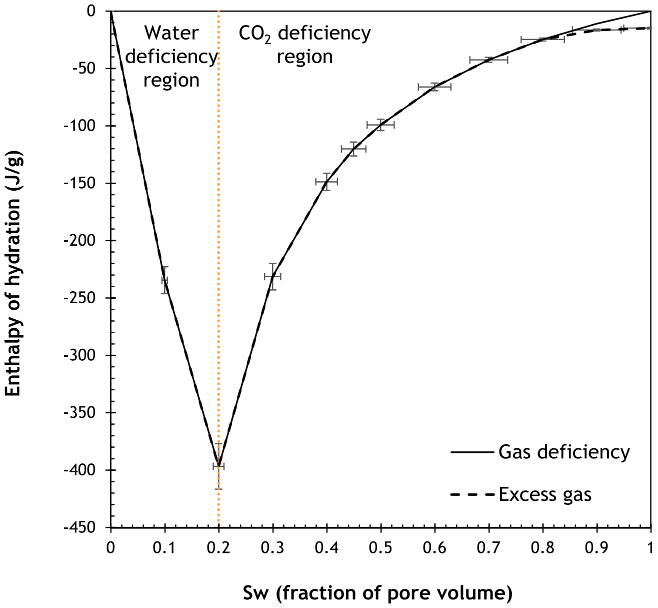

Fig. 4. Latent heat of hydrate formation in different water saturation at P = 3 MPa in presence/absence of excess CO_2. (HydraFLASH version 3.8, CPA EoS).

Fig. 5 **(a)** depicts the pressure and temperature data throughout four cycles of CO_2 hydrate formation and dissociation from a sample

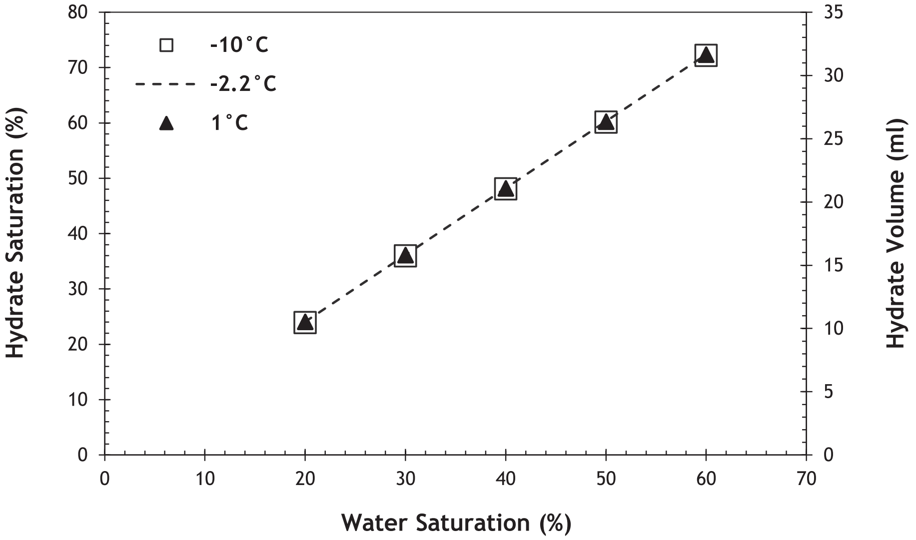

Fig. 3. Relation between water saturation, hydrate saturation and hydrate volume at P = 3 MPa for different temperatures. At T = 263.15 K, no ice formation was assumed. The density of the hydrate was calculated as 0.803 ± 0.0001 g/ml. (HydraFLASH version 3.8, CPA EoS).

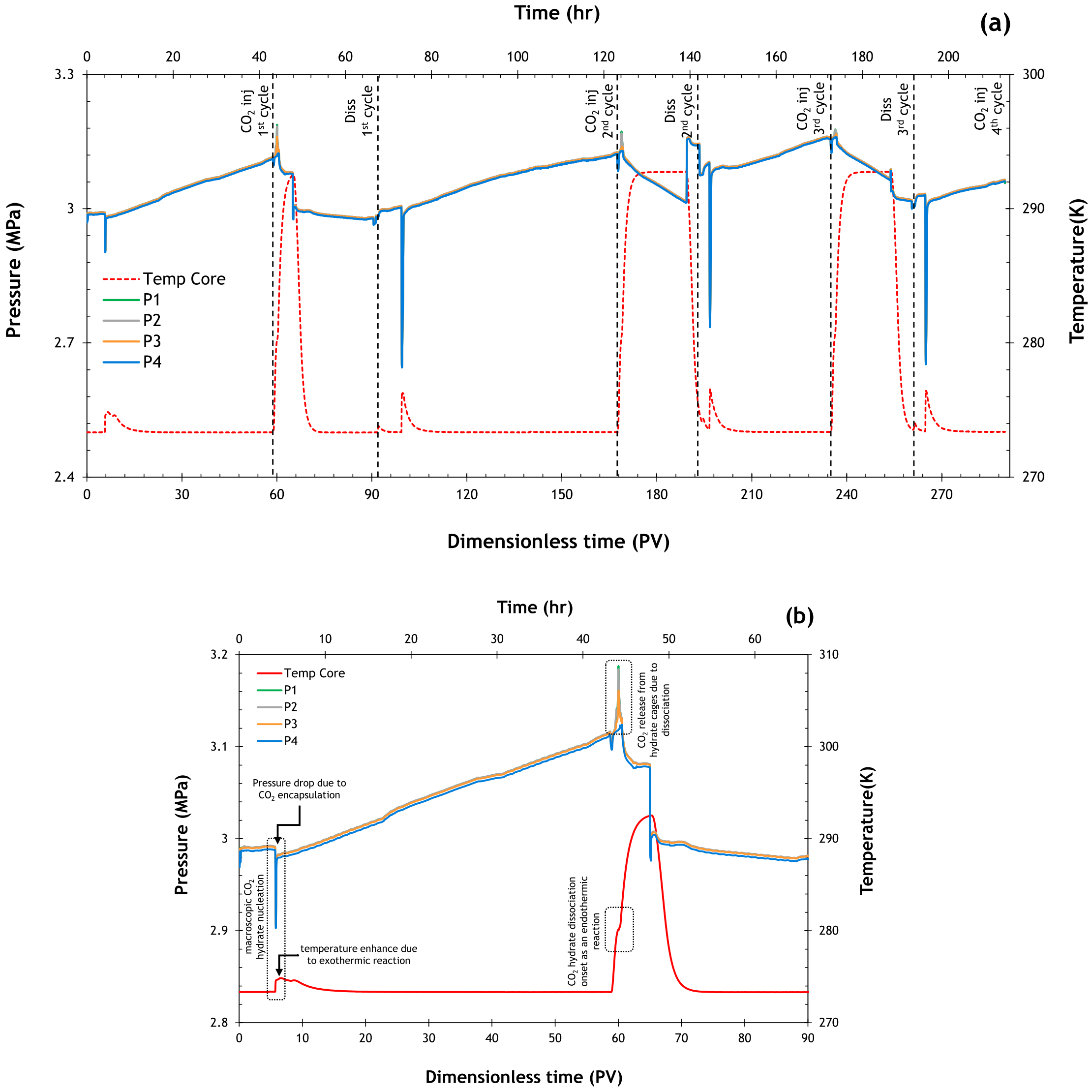

Fig. 5. Pressure and temperature profile during CO_2 hydrate formation and dissociation cycles (a), focused on the first cycle (b), for $S_w = 42.1$ % containing 1 wt% NaCl. Initial condition: 3 MPa; and 273.65 K. Pressure changes were monitored at the inlet (P_1), 2.25 cm from the inlet (P_2), 6.5 cm from the outlet (P_3), and the outlet (P_4).

experiment of 41.2 % water saturation (E8). CO_2 injection commenced in the first cycle following the saturation of the sand core with 1 wt% NaCl brine. The primary sign of hydrate formation was macroscopically detected at induction time, characterized by a simultaneous pressure drop due to CO_2 encapsulation within the hydrate cavities and a temperature increase resulting from the exothermic hydrate formation reaction (see Fig. 5 **(b)**). Following the induction period, pressures gradually increased, corresponding to the progress in hydrate growth during CO_2 injection. Despite this volume increase causing a reduction in porosity and permeability, leading to increased pressure, no blockage was recorded under these conditions. Moreover, this pressure increase also be attributed to the ongoing CO_2 injection, which resulted in hydrate cages trapping more CO_2 and thereby enhancing the stability of the hydrate structure. CO_2 injection persisted throughout each cycle until the thermodynamic conditions (P and T) reached a steady state. Thermal stimulation at 293.15 K was employed to dissociate the hydrate. Following the hydrate dissociation of the first cycle, water saturation decreased to 39.6 %, due to the production of 0.71 ml of water from the core (see Table 2). Subsequently, the system was cooled during N_2 injection, and the N_2 stream was replaced by the CO_2 upon reaching the desired subcooling (~6 degree of subcooling) to induce hydrate formation of the next cycle.

Analysis of data from the four cycles (details reported in Table 2) indicated that the first cycle exhibited a significantly lower pressure drop at induction time (0.09 MPa) compared to subsequent cycles (approximately 0.36 MPa). This difference was attributed to the water memory effect, arising from the extensive release of CO_2 encapsulated within hydrate cages during the first hydrate dissociation, leading to the generation of gas bubbles. These CO_2 bubbles contributed to the sharpest pressure drop during subsequent hydrate pore filling. However, despite these pressure variations, final hydrate volume calculations based on water saturation levels did not indicate substantial differences across cycles.

Table 1 provides relevant data from four cycles of hydrate formation for five different distinct water saturations. The most significant pressure drop arising from the onset of hydrate formation (macroscopic induction time) was observed in the fourth cycle of E1, characterized by the lowest water saturation. The result implies that within the studied range of water saturation, the water saturation level of 22 % forms a more stable structure of CO_2 hydrate. This criticality might be attributed to a more uniform water distribution at this specific water saturation level, resulting in an improved water–gas interface and an increased

Table 1
Summary of phase saturations and hydrate formation results from five distinct water saturation at 273.65 K and initial pressure of 3 MPa.

Water saturation (%)	Water conversion[a] (%)	Induction Time (hr)	Temp change with hydrate formation	CO_2 hydrate saturation[b] (%)	Blockage due to hydrate formation	CO_2 hydrate volume (ml)
E1,1 (22.1)	74.4	0.8	1.97	19.8	–	8.80
E1,2 (19.9)	87.2	1.4	2.11	21.0	observed	9.25
E1,3 (19.9)	89.7	1.3	2.53	21.6	–	9.53
E1,4 (19.9)	95.5	3.1	3.06	23.0	–	10.12
E2,1 (25.9)	58.7	1.7	1.65	18.4	–	8.11
E2,2 (25.9)	76.9	1.3	1.38	24.1	–	10.64
E2,3 (25.9)	83.3	2.2	2.37	26.1	–	11.52
E2,4 (25.9)	77.9	1.1	2.01	24.4	–	10.74
E3,1 (30.1)	61.8	2.7	1.26	22.5	–	9.91
E3,2 (30.1)	90.6	5.9	3.07	33.0	–	14.56
E3,3 (30.1)	90.9	5.5	3.06	33.1	–	14.59
E3,4 (30.1)	91.4	11.2	2.27	33.3	–	14.70
E4,1 (32.2)	70.8	0.4	1.56	27.6	–	12.16
E4,2 (32.2)	87.5	1.3	2.45	34.1	–	15.04
E4,3 (32.2)	86.5	0.9	2.30	33.7	–	14.86
E4,4 (32.2)	92.7	6.8	3.08	36.1	–	15.9
E5,1 (35.1)	61.0	0.9	1.12	25.9	–	11.41
E5,2 (35.1)	85.9	0.5	3.11	36.5	observed	16.08
E5,3 (35.1)	63.3	0.3	2.78	26.9	observed	11.85
E5,4 (35.1)	89.9	1.7	3.32	38.2	–	16.83

[a] hydration number = 6.2
[b] hydrate density ~ 0.803 g/ml

dissolution of CO_2. From another perspective, under the specified conditions (273.65 K and an initial pressure of 3 MPa, in the presence of water memory), the higher-pressure reduction observed in the fourth cycle contributes to the generation of a more stable hydrate, filled with the highest amount of CO_2. In this context, E3 with 30.1 % water saturation, demonstrated the longest induction time across all cycles. This observation suggests that at this specific water saturation level, the hydrate nucleation process took the longest time compared to other saturation levels. Moreover, a positive correlation between the induction times (whether fresh or from memory) and the hydrate saturation

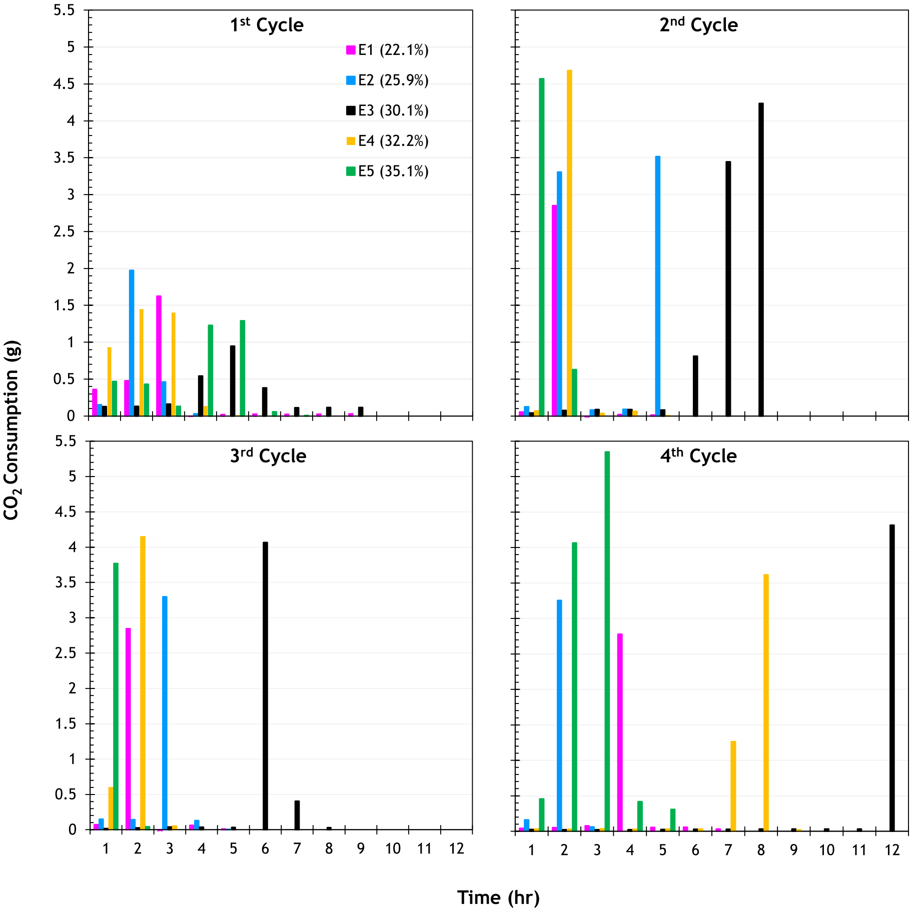

Fig. 6. Impact of water saturation and water memory on CO_2 consumption includes both CO_2 dissolution and hydrate formation during CO_2 injection. The data presented shows the CO_2 consumption rate per hour of CO_2 injection.

was evident in the obtained data. However, with an increase in water saturation, blockages in flow channels became apparent in certain secondary cycles, such as the second and third cycles in E5. This phenomenon led to a decline in permeability, confirming that the likelihood of blockage increases with hydrate re-formation. This could be attributed to the redistribution of water following hydrate dissociation. The pressure data recorded along the core length revealed that the blockage occurred in the end section of the core rock, which is likely associated with higher water saturation in that section due to displacement of water by CO_2. Based on the data provided in Table 1, slight variations in hydrate saturation (water-to-hydrate conversion) were observed among cases. However, across all water saturations, there was a consistent increase in conversion from the first cycle, which can be related to the memory effect. This implies that water memory not only accelerates hydrate nucleation but also influences hydrate density, possibly due to the residual structure hypothesis [33] and the guest supersaturation hypothesis [34]. Furthermore, findings show that during the primary hydrate formation, the synthesized CO_2 hydrate mainly occupies small pores, while in the secondary synthesis, it enters both small and large pores [35]. As a result, the CO_2 hydrate previously formed in the larger pores can impede the water in smaller pores from participating in the CO_2 hydrate formation process, creating a pore-blocking effect that was not observed in the second synthesis. Consequently, the calculated hydrate density was lower for the first cycle compared to the subsequent cycles.

As depicted in Fig. 6, it was observed that for cycles with identical initial water saturation, the average rate of secondary CO_2 consumption due to CO_2 dissolution and hydrate formation was 2.5 to 4 times greater than that observed in the primary formation. This trend was particularly pronounced at higher water saturations. To clarify, except for water saturations at 22 % and 25 %, in all cycles, the moles of CO_2 consumed were 1.5 times greater than in freshwater (the first cycle with no hydrate history). These findings suggest the presence of water memory during multicycle synthesis processes. Moreover, the findings reveal that during the primary synthesis, CO_2 predominantly occupies small pores, while in the secondary synthesis, it enters both small and large pores [35]. As a result, the CO_2 hydrate formed in the first cycle could exhibit a slightly lower density compared to the hydrate formed in the secondary synthesis. This difference in pore occupancy and distribution contributes to the observed density difference between the two synthesis cycles. The memory effect of hydrates has been elucidated through the proposal of various mechanistic hypotheses, including the residual structure hypothesis [36,37] and the guest supersaturation hypothesis [34]. Based on the residual structure hypothesis, it is assumed that after a cycle of formation and dissociation, the remaining structure retains the structural features of the hydrate phase. These residual cage structures serve as nucleation sites for the subsequent hydrate synthesis. However, the supersaturation hypothesis refers that by hydrate dissociation, dissolved gas molecules have a sufficiently small size, and the local pressure is sufficient to support gas bubble generation. The presence of these gas

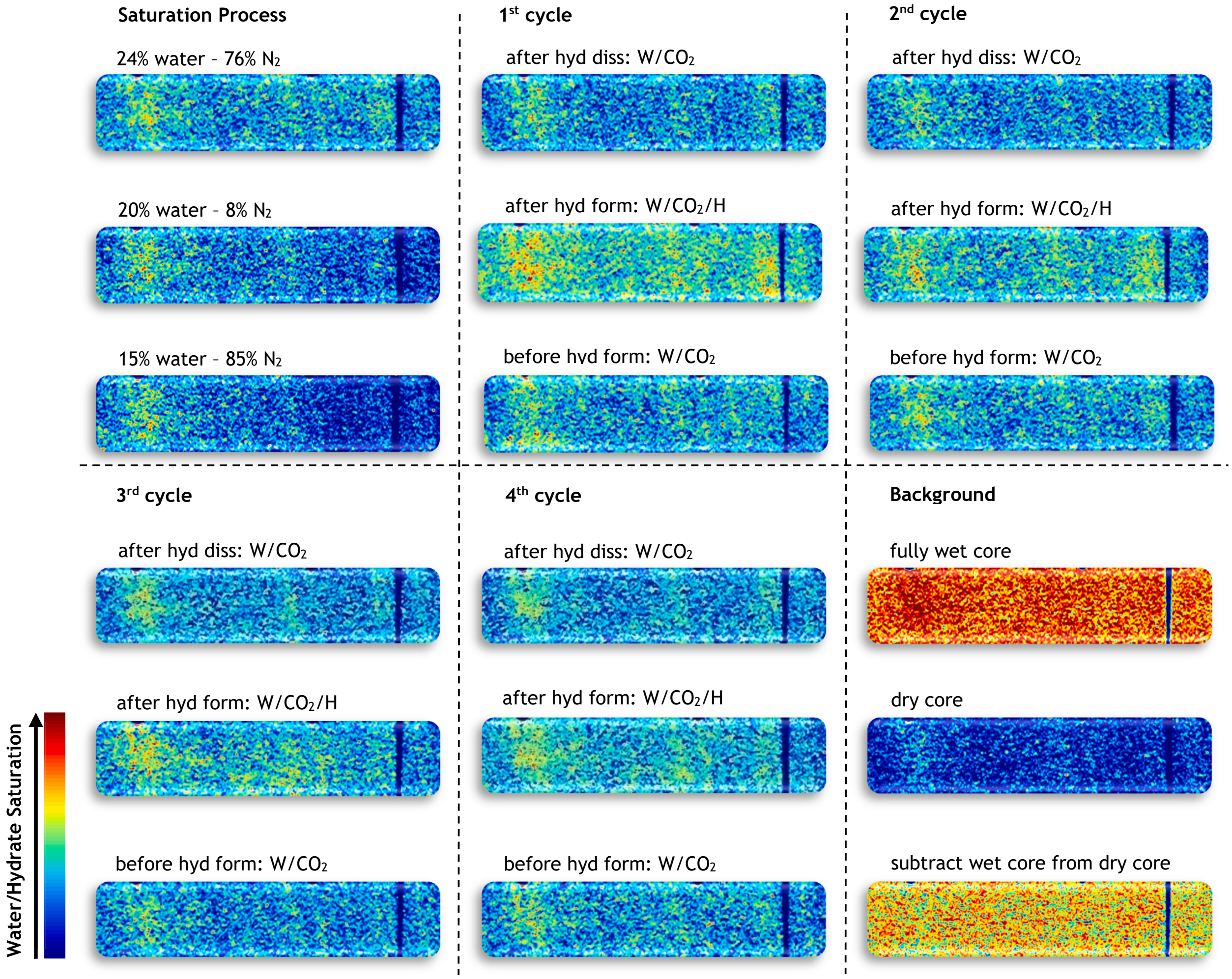

Fig. 7. Dynamic CT images of water/hydrate saturation maps during the water saturation process of a horizontal Bentheimer rock sample as well as during hydrate formation/dissociation cycles in E6. Flow direction is from left to right. (Colors qualitatively indicate water + hydrate saturation. red: high water/hydrate saturation; green/yellow: intermediate saturation; blue: low water/hydrate saturation).

bubbles facilitates the nucleation process for the subsequence hydrate formation [35].

Although the gas consumption rates increased with increasing water memory, E3 exhibited the highest CO_2 hydrate nucleation time among the studied cases.

3.2. Determination of Water/Hydrate saturations using CT-Scan

Medical X-ray CT scans were employed for three selected water saturation (24 %, 35 %, and 41 %) to evaluate water/hydrate distribution and quantify saturation throughout the core length during the hydrate formation/dissociation process. Given the resolution of medical CT images, and considering the similarity in density of water and CO_2 hydrate, it is very difficult to distinguish between these two phases through CT scanning.

Fig. 7 displays the CT scans from 24.3 % water saturation (E6), where the first section shows the fully saturated and dry core (background section). The three images located at the top left illustrate water saturation progress (water saturation change within the core sections during the water/N_2 co-injection). The remaining set of images in this figure depicts the pattern of water + hydrate saturation in three stages, including the conditions before and after hydrate formation, and after hydrate dissociation. In this figure, two high porosity zones are situated around 2.25 cm and 14.5 cm from the inlet, which are the locations of the pressure transducer (P_1) and the thermocouple (T_{core}), respectively. This increased porosity and permeability results in an accumulation of more water, leading to a higher saturation of hydrate within these core sections.

Moreover, the CT images (Fig. 7) and the graph obtained from image analysis (Fig. 8) indicated a redistribution of water and hydrate along the core sections throughout hydrate growth, particularly in the third cycleSeol and Kneafsey [38]. Furthermore, a comparison of water distribution across cycles confirmed that the hydrate dissociation process also altered the water distribution pattern. Based on Fig. 7, it is apparent that the hydrate saturation in the first cycle was slightly higher than the hydrate saturation observed in subsequent cycles. The observed slight decrease in hydrate saturation from the first cycle can be attributed to the influence of pore water redistribution on the rock surfaces [39] and the possible evaporation of water into the gas phase. This redistribution impacts the likelihood of hydrate nucleation, particularly in areas where the local water saturation on the rock surface is higher [40]. Another notable observation concluded from the cyclic tests on the Bentheimer core emphasizes the importance of the stochastic aspect of hydrate nucleation. Particularly under low subcooling conditions, serving as the hydrate driving force, hydrate nucleation is a stochastic process influenced by pore characteristics, salinity, and water history Lu et al. [33,41–43]. The experimental outcomes revealed that water level had the most significant impact on hydrate nucleation probability with 1 wt % salinity under consistent thermal history (water memory). However, in reservoir conditions where multiple conflicting aspects come into play, hydrate nucleation may be controlled by several factors [40].

To visualize the growth patterns of CO_2 hydrate in Bentheimer sandstone in the presence/absence of water memory, hydrate was repeatedly formed under a constant temperature of 273.65 K using

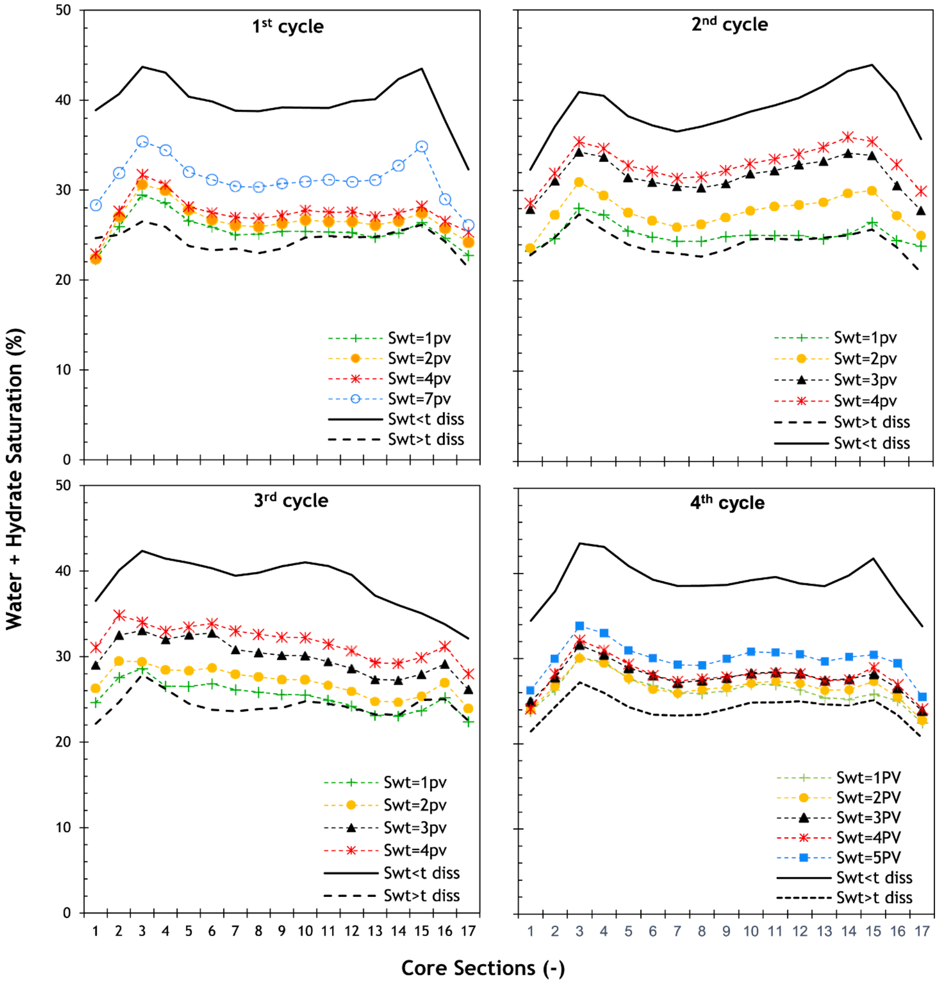

Fig. 8. Slice average saturations of water/hydrate along the length of the core during CO_2 injection and hydrate formation/dissociation across multiple cycles in E6. The time scale PV is equivalent to 44 min, based on the core pore volume and a CO_2 injection rate of 1 ml/min.

medical CT scan. Images were taken throughout the stages of hydrate formation, during stable hydrate conditions lasting up to one day, and following the decomposition step. Fig. 8 shows the slice-average saturation of water/hydrate along the 17 cm core during the four cycles of E6.

The data extracted from the CT scans of three selected water saturations are summarized in Table 2 and illustrated in Fig. 10. The results indicate an increase of approximately 10 %~15 % in final saturation of water + hydrate compared to the initial water saturation according to the flowchart represent in Fig. 9. This observation aligns well with the simulation results presented in Fig. 3.

Furthermore, considering the HydraFLASH conversion results and that the final stage reached a steady state without any further volume increase, it has been determined that the maximum water-to-hydrate conversion exceeded 98 %. Therefore, based on these findings, the density of hydrate emerged as a key factor. Under the specified experimental conditions, considering temperature, pressure, and excess CO_2 (due to the continuous CO_2 injection), HydraFLASH indicated a 21 % water-to-hydrate conversion and a hydrate density of 0.803 g/ml with a hydration number ranging from ~ 5.9 to 6.1 for structure sI. However, the CT experimental results suggest that to achieve this specific density (0.803 g/ml), a higher hydration number (>6.7) is required. Consequently, the CT results imply that the hydrate cavities are semi-filled with CO_2, which provides valuable insights into the hydrate composition under the dynamic CO_2 injection.

In Table 2, besides confirming the random process of hydrate nucleation, the observed variations in induction times between cycles attributed to the changing water history during dissociation [44,45]. For instance, in E7, hydrate was dissociated by thermal stimulation, and the core was kept at 293 K for a minimum of 40 h before fourth cycle of hydrate formation. These variations in thermal history are likely accountable for the discrepancies in induction time observed across the cycles. The results obtained indicate that induction times for CO_2 hydrate formation tend to increase with higher temperatures and longer dissociation durations.

The CO_2 injectivity index (*J*), calculated using Equation (8), which represents the ratio of the CO_2 injection rate (q_{CO_2}) to the differential pressure (*dp*), is depicted in Fig. 11 for different experiments (E1 to E8).

$$J = \frac{q_{CO_2}}{dp} \tag{8}$$

This data compares the impact of water saturation on the CO_2 injectivity index at the beginning of the growth phase, where a substantial amount of CO_2 is consumed during CO_2 dissolution and hydrate generation [46].

Table 2
Water saturation and CO_2 hydrate formation data with 1 ml/min CO_2 injection at 273.65 K and initial pressure of 3 MPa through the CT-scan.

water saturation (%)	Induction Time (hr)	Temp change with hydrate formation	Pressure drop by hydrate formation	CO_2 hydrate saturation[a] (%)	CO_2 hydrate volume (ml)
E6,1 (24.3)	3.9	1.42	0.85	38.7	12.88
E6,2 (24.4)	0.8	1.49	3.58	37.7	12.92
E6,3 (24.2)	0.3	1.54	3.66	37.4	12.83
E6,4 (24.3)	3.6	1.39	3.78	37.9	12.88
E7,1 (35.7)	0.7	1,85	0.16	48.5	18.80
E7,2 (31.4)	1.8	2.34	3.34	45.0	16.62
E7,3 (31.5)	2.3	2,90	4.47	46.8	16.73
E7,4 (31.4)	4.8	3.11	7.15	46.4	16.67
E8,1 (41.2)	5.0	1.48	56.4	54.7	21.89
E8,2 (39.6)	5.9	2.95	49.2	47.7	21.04
E8,3 (39.4)	2.1	2.99	49.9	48.4	20.93
E8,4 (39.5)	3.1	3,05	50.7	49.2	20.98

[a] based on HydraFLASH prediction > 97 % water-to-hydrate conversion was assumed.

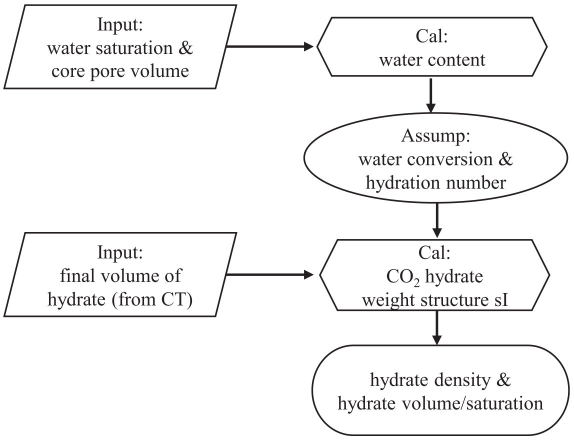

Fig. 9. Procedure of the estimation and calculation method for hydrate density and hydrate volume/saturation calculation based on the CT scan results.

Additionally, this figure highlights the effect of water hydrate memory on the injectivity of CO_2. The injectivity index in the first cycle of all experiments was higher than in the subsequent cycles due to the presence of water hydrate history in the secondary cycles. However, the experiment with an initial water saturation of 24.3 % (E6) was an exception, attributed to higher hydrate saturation compared to the other cycles, especially the third cycle. This finding indicates that hydrate saturation significantly impacts the injectivity index. According to the data reported in Table 2, in test E6, the hydrate saturation in the first cycle was substantially higher than in the subsequent cycles with the same water saturation level. Consequently, it was anticipated that the injectivity of the first cycle would be lower or comparable to that of the secondary cycles, even without considering water-memory effect [25]. Although the higher hydrate saturation in the first cycle of E7 and E8 compared to the secondary cycles was due to the higher initial water saturation of this cycle. Furthermore, in cycle 3 of experiment E6, the higher injectivity can be explained by the extended heating period for hydrate dissociation, which exceeded more than a day. This prolonged heating ensured the complete elimination of the hydrate history from the aqueous phase, thereby enhancing injectivity in the following cycles [47,48].

3.3. 3.Permeability change caused by hydrate formation

Two well-known Pang-Sharma [49] and Chen [50] models were used to predict the permeability reduction as a function of hydrate saturation. The purpose of selecting these two models was their inclusion of an adjustable parameter, which could be fine-tuned using the experimental data from this study to improve the accuracy of their predictions. The Pang-Sharma model includes a constant (β) that accounts for trapped particles deposit in the pores presented in equation (9):

$$\frac{k}{k_0} = \frac{1}{1 + \beta s_H} \tag{9}$$

The Chen model proposes a modified Corey model which includes a fitting parameter (*c*) that is depicted in equation (10):

$$\frac{k}{k_0} = (1 - s_H)e^{-cs_H} \tag{10}$$

In the above two equations, the brine permeability (*k*) values at each hydrate saturation were normalized by the initial permeability (k_0), the permeability before hydrate formation [51]. The obtained results indicated a decrease in normalized permeability with an increase in water or hydrate saturation, as shown in Fig. 12. The normalized permeability of the first cycle was compared with experimental data reported in the

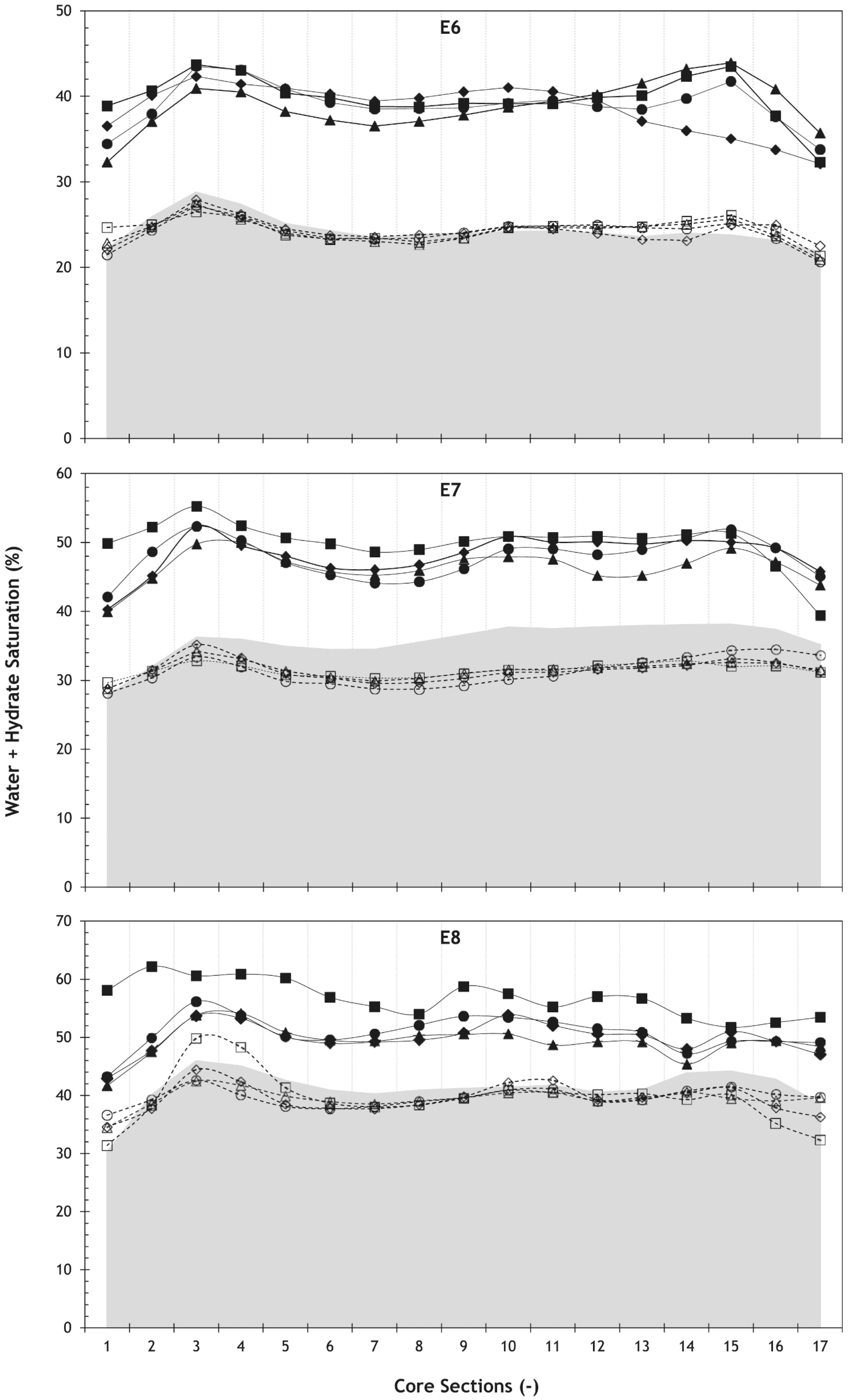

Fig. 10. Steady state water + hydrate saturation profiles along the length of the Bernheimer Sandrock core during four cycles of CO_2 hydrate formation/decomposition in E6, 7, and 8. The solid area shows the initial level of water saturation. ■: hydrate saturation of first cycle; ▲: hydrate saturation of second cycle; ◆: hydrate saturation of third cycle; ●: hydrate saturation of forth cycle; □; water saturation after CO_2 hydrate dissociation of first cycle; Δ: water saturation after CO_2 hydrate dissociation of second cycle ◇: water saturation after CO_2 hydrate dissociation of third cycle ○: water saturation after CO_2 hydrate dissociation of four cycle. (The solid line represents the CO_2 hydrate formation; The dashed line represents the CO_2 hydrate dissociation).

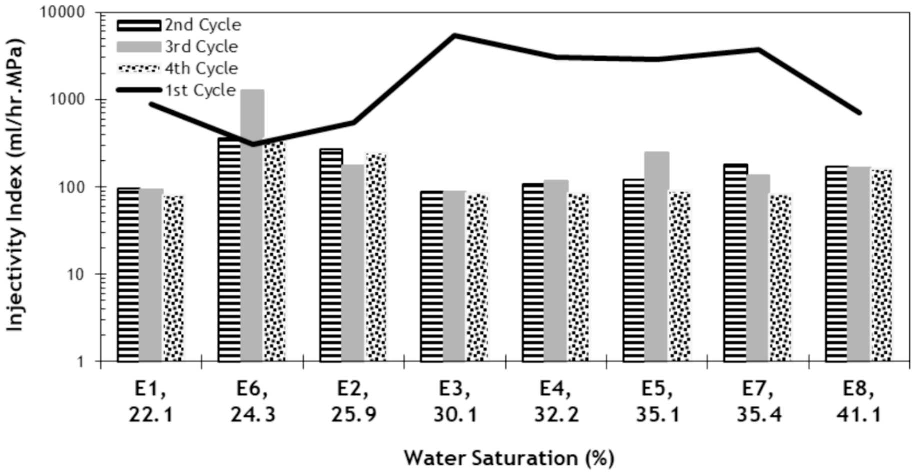

Fig. 11. Injectivity index at initial phase of rapid CO_2 consumption for different experiments.

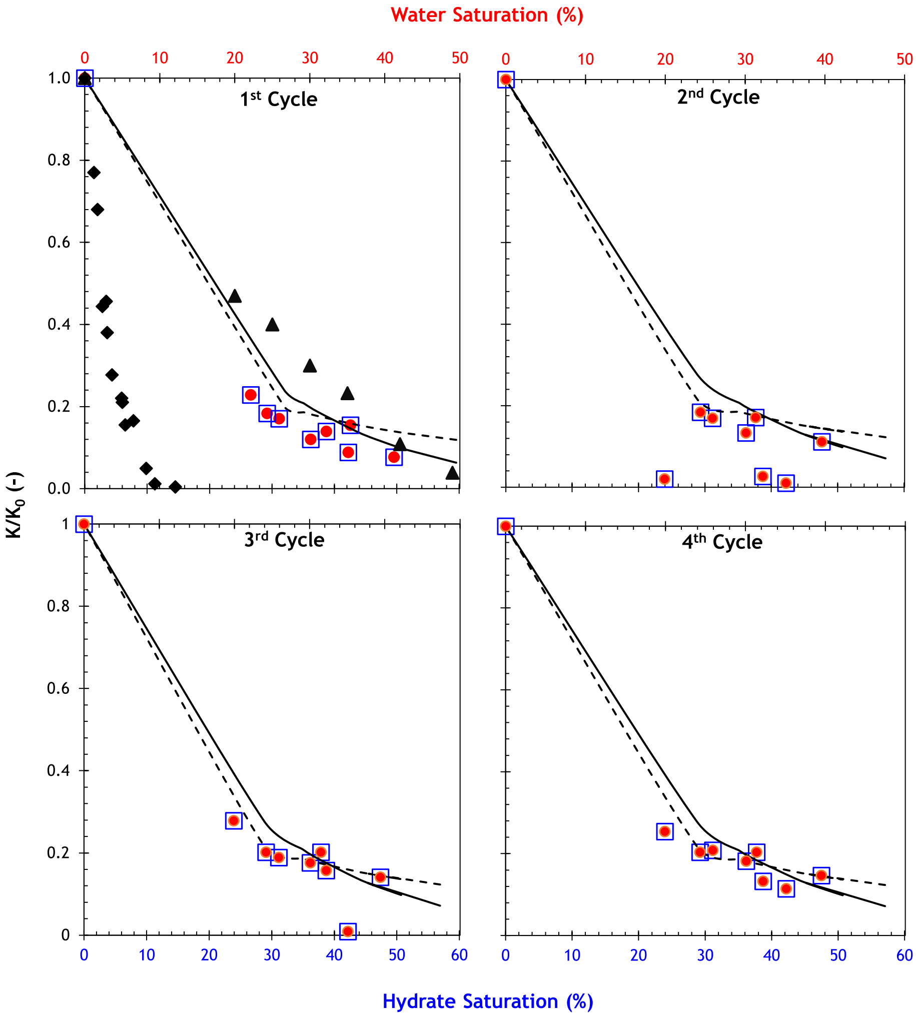

Fig. 12. Normalized permeability as a function of water/hydrate saturation – a compilation of experimental data compared to Pang Sharma and Chen models. (The blue hollow squares and red solid circles represent the normalized permeability as a function of hydrate saturation and water saturation, respectively (this study); solid triangles [52]) and solid rhombus [53]depict experimental data; The dashed and solid lines correspond to the Pang-Sharma and Chen models respectively, adjusted using experimental data from this study).

literature and this trend showed good agreement with the literature [52,53]. Moreover, the experimental results for the studied range of water saturations demonstrate a close alignment with the predicted values by the Pang-Sharma model, include a tuning parameter ($\beta = 0.15$) with a < 0.03 mean deviation from the experimental data.

As illustrated in Fig. 12, the experimental results indicate a notable reduction in normalized permeability, approximately 80 %, after hydrate formation across all water saturation levels. This permeability reduction was more pronounced at higher water saturation (up to 90 %). However, the normalized permeability reduction resulting from CO_2 hydrate formation in porosity, driven by the memory effect, did not exhibit a significant change compared to the primary hydrate formation (first cycle without the memory effect). Furthermore, at some specific water saturations, e.g. 35 % (second and third cycle) and 22.1 % (second cycle), the primary flow channels were completely obstructed during some cycles. This blockage is attributed to alterations in water/hydrate distribution following previous hydrate dissociation. The observed significant decline in permeability highlights the profound impact of CO_2 hydrate formation on flow characteristics within porous media. This underscores the potential challenges and considerations inherent in CO_2 injection processes, especially when confronting the occurrence of complete blockage in flow channels during CO_2 injection. After conducting permeability tests with brine (1 wt% NaCl) following CO_2 hydrate dissociation, a slight reduction in permeability was observed compared to the initial permeability (around ~ 2.5 D). This reduction was attributed to salt dropout in some experiments, highlighting the influence of water memory on the salinity of brine during each hydrate formation/dissociation cycle. The observation arises from the fact that only water molecules enter the hydrate structure during formation, causing an increase in the salinity of the remaining brine. During hydrate dissociation, water molecules exit the lattice. However, due to limited mixing and a relatively slow rate of salt re-dissolution, the salinity of brine is effectively reduced during the following hydrate formation cycle. This reduction eventually leads to salt dropout or precipitation in the pores, impacting the pore permeability of sandstone [54]. Moreover, the decrease in salinity enhances CO_2 solubility in brine, promoting hydrate formation in subsequent cycles.

4. Conclusions

This research focuses on investigating the impact of water saturation and water memory on saturation and kinetics of CO_2 hydrate in porous media under dynamic CO_2 injection conditions. The study employs five distinct water saturations ranging from 20 % to 40 % each of which contains four cycles of hydrate formation/dissociation. The core flood experiments are conducted at 273.65 K and an initial pressure of 3 MPa, under a medical CT scan to monitor the onset of hydrate formation and dynamics of hydrate growth inside the core, allowing for the calculation of hydrate saturation profiles. The key findings include:

- The water-to-hydrate conversion ratio is unaffected by the level of water saturation within the examined range. This is due to continuous CO_2 injection, which maximizes the saturation of water with CO_2.
- There is a direct correlation between CO_2 hydrate saturation and water saturation levels, with a ratio of 1.21.
- The rate and total amount of water-to-hydrate conversion increases in the presence of water memory, confirming the existence of the water memory effect in porous media.
- Permeability is substantially reduced (approximately 80 %), as a result of hydrate formation at each water saturation. This reduction depends on the initial water saturation. However, the generated hydrate is insufficient to completely block the CO_2 flow path.
- The volume of water + hydrate phases increases during hydrate formation by 10–15 %, indicating a lower density for CO_2 hydrate ~ 0.9–0.8 g/ml) as compared to water. The estimated CO_2 hydrate density is reasonably consistent with data obtained from the HydraFLASH software.

CRediT authorship contribution statement

Mahnaz Aghajanloo: Writing – original draft, Software, Methodology, Investigation. **Sadegh M. Taghinejad: . Denis Voskov:** Writing – review & editing, Supervision, Project administration, Conceptualization. **Rouhi Farajzadeh:** Writing – review & editing, Supervision, Project administration, Methodology, Investigation, Funding acquisition, 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.

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