

Investigating the Effect of Sodium Chloride on Methane Hydrate Equilibrium Conditions: Case Study of Caspian Sea Water Composition

Abstract

In this research, we conducted an experimental study on methane hydrate formation under various conditions, including the presence of salt and porous media. The effects of chamber stirring, mass transfer, and heat transfer on the formation and dissociation processes of methane hydrates were examined. Hydrate formation in water containing 1.5 wt% NaCl was investigated, along with a case study involving water from the southern region of the Caspian Sea. Two types of sand pack porous media, composed of glass beads with diameters of 3 mm and 5 mm, were used.

We analyzed temperature and pressure variations, the amount of hydrate formed in each experiment, and the kinetics of hydrate formation. Detailed observations and discussions on nucleation, induction time, and hydrate growth for each experimental condition are provided. The results highlight the influence of the tested parameters on methane gas absorption and the conversion rate of water to hydrate under different conditions.

Keywords: *Caspian Sea hydrate, gas hydrates, hydrate kinetic, induction time, Sodium Chloride.*

Introduction

Methane hydrate, also known as clathrate, is a solid, crystalline structure. In this structures, the water molecule (host) contains the methane molecule (guest). Guest molecules can include methane, ethane, propane, butane, nitrogen, oxygen, carbon dioxide, hydrogen sulfide, helium, neon, and argon[1]. Since methane comprises over 90% of natural gas, it is predominantly used in gas hydrate research.

In typical conditions, 1 m³ of solid methane hydrate at atmospheric temperature and pressure releases approximately 164 m³ of methane gas and 0.8 m³ of water upon conversion. The MH21 research project in Japan highlights the potential of methane hydrate resources in the Nankai Trough, estimating enough energy to sustain Japan's needs for over a decade [2]. Therefore, this amount of resources is very promising for countries that are highly dependent on energy imports.

The formation of methane hydrates involves several stages, beginning with nucleation where a primary nucleus forms in water, subsequently growing into a crystalline structure as it absorbs more gas. The time from the start of an experiment to the initial nucleation, known as the induction time (IT), varies significantly, ranging from minutes to several hours.

This study specifically examines the impact of sodium chloride (NaCl) on the kinetics of methane hydrate formation. Experiments were conducted using pure distilled water, a 1.5 wt.% NaCl aqueous solution, and water sourced from the Caspian Sea, aiming to draw meaningful comparisons and insights into the effects of NaCl on hydrate formation processes.

Gas hydrates have garnered significant attention due to their potential as a future energy resource and their impact on various industrial processes. In recent years, researchers have focused on understanding the influence of different factors, such as temperature, pressure, and salinity, on the formation and stability of gas hydrates. One such factor under investigation is the presence of sodium chloride (NaCl) salt, a common component in seawater, and its effect on the equilibrium conditions of methane hydrate. Studies in this area have revealed valuable insights into the complex interplay between salt concentration and hydrate formation. Daraboina et al. [3] investigated the impact of 5 wt.% sodium chloride on natural gas hydrate formation and dissociations in the presence of crude oil. Their study sought to understand the interplay of temperature in hydrate formation, utilizing temperature reduction for hydrate formation detection and temperature increase for dissociation detection.

Chong et al.[4] investigated the influence of sodium chloride (NaCl) at concentrations of 1.5 wt.% and 3 wt.% on methane hydrate kinetics formation under pressures ranging from 1 MPa to 4.2 MPa. Their results revealed a notable deceleration in the hydrate formation process attributable to the presence of salt. Their findings suggested that the presence of salt significantly altered the hydrate formation process, with higher salt concentrations leading to prolonged nucleation times and reduced hydrate formation rates.

Yu et al. [5] delved into the growth of hydrate nuclei in water with NaCl content, shedding light on the underlying mechanisms governing hydrate formation kinetics. They investigated the growth of hydrate nuclei in both pure water and water containing 3.5 wt.% NaCl, at varying flow rates of 0.8 m/s, 1.2 m/s, 1.6 m/s, and 1.9 m/s. the primary objective of their study was to investigate the factors contributing to hydrate formation in pipelines. Their study suggested that the presence of salt led to a decrease in the growth rate of hydrates, primarily attributed to dynamic factors rather than thermodynamic inhibition. On average, the growth rate of hydrates in salt's presence was 32% lower than that in pure water. Their analysis revealed that this reduction was attributable to factors related to the size of methane bubbles and dynamic aspects rather than the thermodynamic inhibitory effect of salt. Furthermore, the presence of salt resulted in smaller methane bubbles and diminished bubble coalescence.

Du et al. [6] investigated the thermodynamic inhibitory impact of NaCl, CaCl₂, and MgCl₂ on methane hydrate formation, aiming to prevent unintended hydrate formation in gas transmission pipelines. Their study revealed that NaCl exhibited a more pronounced inhibitory effect when considering equal mass fractions than the other two salts.

Chen et al. [7] investigated the influence of NaCl concentrations ranging from 0 wt.% to 5 wt.% in a methane-carbon dioxide hydrate mixture. In pure water, the total water conversion to hydrate exceeded 88%. Nevertheless, this percentage decreased with increasing salt concentration, reaching 79% for a 5 wt.% salt solution. Below a concentration of 1.5 wt.%, hydrate conversion occurred in a single stage, while at higher concentrations, it proceeded in two stages, displaying a significantly reduced rate.

In a related study, Prasad et al. [8] examined the equilibrium conditions of methane hydrate in NaCl solutions, focusing on the impact of varying salt concentrations on hydrate formation efficiency. Their research indicated a notable decrease in the total water conversion to hydrate with increasing NaCl concentrations, highlighting the inhibitory effect of salt on hydrate formation under specific environmental conditions.

While these studies provide valuable insights into the influence of NaCl salt on methane hydrate equilibrium conditions, there remains a need for further investigation, particularly in real-world scenarios such as those found in the South of the Caspian Sea. This region, characterized by unique environmental conditions and salinity levels, presents an intriguing case study for examining the interaction between salt content and methane hydrate formation.

Moreover, a geophysical data study was carried out to map gas hydrates in different regions of the Caspian Sea. The findings indicate a higher likelihood of gas hydrate presence in the northern part of the Caspian Sea, attributed to lower temperatures and greater depths when compared to the southern region [9].

Experimental materials

In this study, we utilized distilled water, Merck's NaCl salt, and nitrogen and methane gases with a purity of 99.99%. As part of the field investigation, a water sample was collected from the southeastern region of the Caspian Sea (Bandar Turkmen city, Golestan province, Iran). The water sample exhibited a total hardness of 8264.17 ppm and a Total Dissolved Solids (TDS) value of 29671.1 ppm.

The ion concentrations are provided in Table 1, revealing elevated levels of chloride and sodium ions compared to the other ions in the sample.

Table 1. Ion Concentrations in the Caspian Sea Water Sample

Component	Sodium	Chloride	Potassium	Magnesium	Calcium
Amount of (ppm)	6853.750	14367.850	153.550	1596.150	680.700

All the results mentioned were measured using a Metrohm Ion Chromatography instrument, model 850. Additionally, we used two types of porous media composed of glass beads with diameters of 3 mm and 5 mm. These beads were selected for their standard dimensions and lack of chemical influence on the formed hydrates.

Apparatus

All experiments were conducted within a high-pressure stainless steel crystallizer with an internal volume of 1000 ml was employed to contain the gas and liquid phases during the experiment. The reactor was capable of withstanding pressures up to 70 MPa. Temperature control was achieved using an incubator capable of reducing the temperature to 263.15 K. This provided a controlled environment for the formation and dissociation of methane hydrate. Test results were continually logged and recorded by a data logger at 20-second intervals, utilizing a combination of four pressure gauges and eleven thermometers which included 6 thermocouples in front of crystallizer and 5 thermocouples in back.

Additional equipment included a vacuum pump for evacuation and a syringe pump for fluid injection. Furthermore, a high-precision digital weight balance with an accuracy of 0.01 grams, connected to a personal computer interface, was utilized. Figure 1 shows the schematic of the experiment setup. For the hydrate dissociation process, a heater with a constant temperature increase rate was employed to induce dissociation through controlled heating.

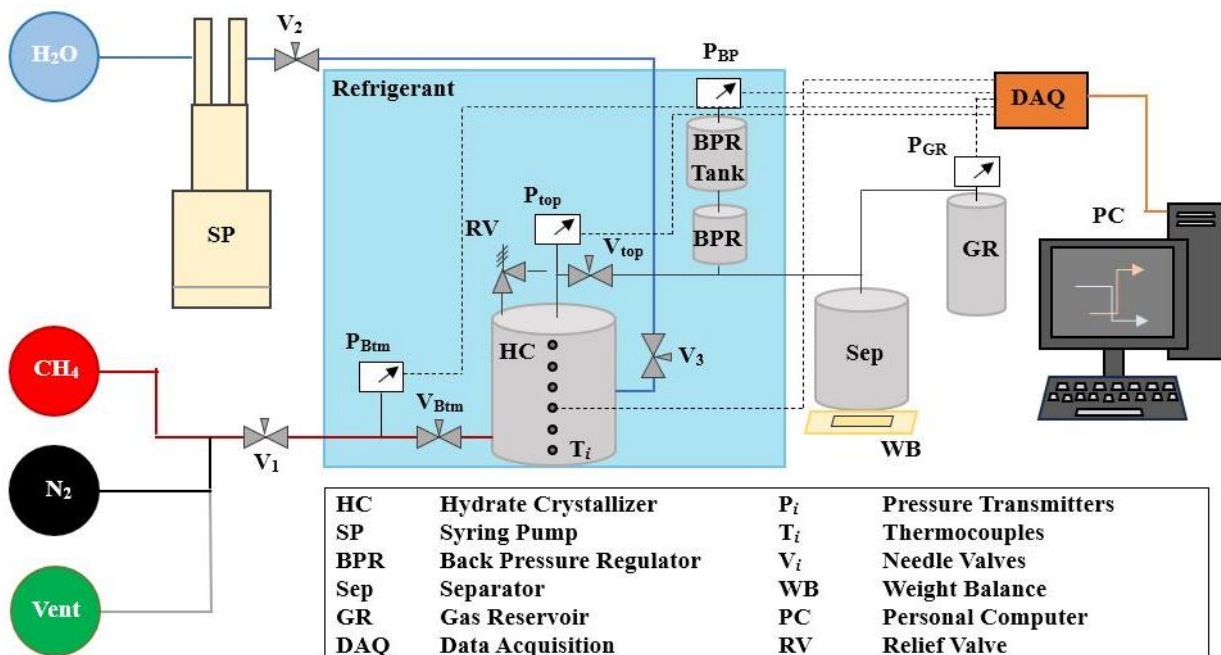


Fig. 1. Experimental apparatuses.

Procedure

At the beginning of each experiment, 50 ml of water, either distilled water with 1.5wt% sodium chloride added or water sourced from the Caspian Sea, was introduced into the cell. To ensure system integrity, all connections and valves were checked by injecting nitrogen gas. Methane gas was then injected and discharged three times to purge any residual air from the system. Methane was consistently introduced at a pressure of 9.3 MPa for all experiments.

A magnetic stirrer was utilized inside the crystallizer to maintain a consistent and continuous mixing of water and gas throughout the process. After the methane gas injection, the cooling device (incubator) was activated to commence the temperature reduction process.

The hydrate formation process is divided into several stages, starting with nucleation, where a primary nucleus forms in the water. This nucleus then absorbs more gas, leading to the growth of a crystalline hydrate structure. The period from the start of the experiment (t_0) to the onset

of primary hydrate nucleation ($t_{\text{stabilized}}$) is referred to as the induction time or IT. This time interval is random and can vary widely from minutes to several hours [10,11].

Upon successful hydrate formation, the dissociation process was initiated by gradually increasing the temperature. Temperature and pressure data were recorded and analyzed at 20-second intervals throughout the experiment.

During the experiment, the number of moles of methane converted to hydrate is calculated using the following simple molar balance equation:

$$(\Delta n_H)_t = V_{CR} \left(\frac{P_{CR}}{zRT} \right)_{t=0} - V_{CR} \left(\frac{P_{CR}}{zRT} \right)_t \quad (1)$$

The z-parameters, or the compressibility factor, were estimated using Pitzer's correlation, which was calculated using a written code in MATLAB software.

The amount of gas consumed, or the storage capacity, is typically stated during the hydrate growth process. In some articles, it is referred to as hydrate growth and is expressed as [11]:

$$\text{Gas Consumption or Hydrate Growth} = \frac{\text{mol of gas}}{\text{mol of water}} \quad (2)$$

Results and discussion

Two sets of experiments were conducted for methane hydrate formation using pure water. In the first set of experiments, the magnetic stirrer was turned off, while in the second set, the magnetic stirrer was operated at a constant speed. All experiments began with an increase in pressure followed by a cooling process. Data were recorded every twenty seconds throughout the experiments.

Each experiment was repeated five times. In the final repetition, after the hydrate formation process, the crystallizer was opened to observe and examine the formed hydrate. Figure 2 shows two samples of methane hydrates formed with (a) pure water and (b) Caspian Sea water, conducted by the student as part of this study. These hydrates were formed in a bulk volume environment, without the presence of a porous media, within the experimental crystallizer. After several hours from the start of the gas injection process, the pressure was reduced, and the crystallizer lid was quickly opened before the hydrate could dissociate.



(a)

(b)

Fig. 2. Methane hydrate formed in this research: (a) Methane+pure water hydrate, (b) Methane+Caspian Sea water hydrate

The gas hydrate formation process comprises two stages: nucleation and growth. Following the initial pressure drop and the initiation of the nucleation stage, the hydrate growth phase continues until completion [12-15].

In all conducted experiments, nucleation initiated with an abrupt change in pressure and temperature. From the moment temperature fluctuations commence, hydrate formation also begins and continues until further pressure reduction is nearly halted. Subsequently, the hydrate dissociation process was conducted by heating with a heater at a constant rate. Initially, the temperature rises without a change in pressure until the hydrate bonds begin to break and dissipate. Following this, the temperature increase process continues with an increase in pressure resulting from the release of gas trapped in the hydrate cages, until reaching approximately the initial pressure of the system at the onset of the formation process.

Figure 3 illustrates a complete cycle of methane hydrate formation and dissociation using pure water with the magnetic stirrer turned on. The induction time is marked by a relatively stable pressure and temperature. This phase indicates the period during which the system stabilizes and prepares for hydrate nucleation. The figure shows that during the induction period, there is minimal change in both temperature and pressure, suggesting that nucleation sites are forming but significant hydrate growth has not yet commenced.

The growth phase is indicated by a gradual decline in pressure and a corresponding decrease in temperature. This period signifies the active formation of methane hydrate, where methane gas is being absorbed into the hydrate structure, releasing heat and causing the observed temperature fluctuations. The pressure decreases steadily as gas molecules are incorporated into the hydrate lattice.

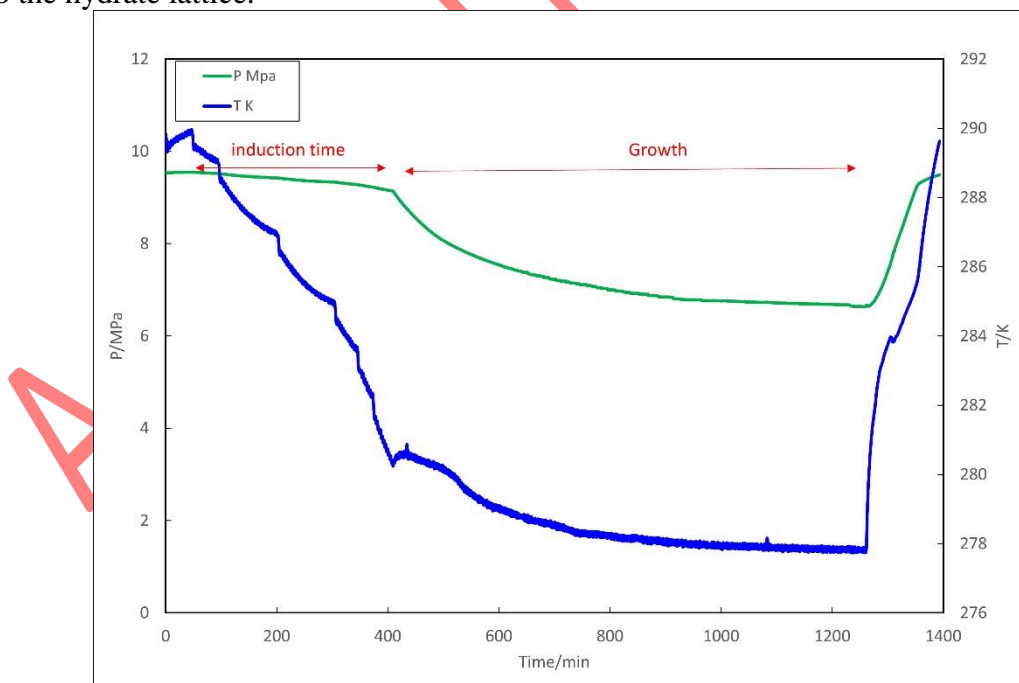


Fig. 3. The changes in pressure and temperature during an experiment on methane hydrate formation and dissociation.

The presence of salt as a chemical inhibitor resulted in a delay in gas absorption during the hydrate formation process. Figure 4 shows the temperature versus time profiles for pure water and water containing 1.5 wt% NaCl.

For pure water, indicated by the blue dotted line, the initial temperature is approximately 292 K and steadily decreases as the hydrate formation process begins, reaching a minimum of about 278 K. This decline is indicative of the endothermic nature of hydrate formation, where heat is absorbed from the surroundings. The small fluctuations observed during this phase suggest intermittent stages of nucleation and growth, reflecting the dynamic nature of hydrate formation.

For the 1.5% wt NaCl solution (gray dashed line), the initial temperature is also around 292 K, but the temperature decline is less steep, stabilizing around 282 K. This moderated decline indicates the inhibitory effect of NaCl on hydrate formation. The presence of salt reduces the activity of water molecules, thereby slowing down the hydrate formation process and resulting in a less pronounced temperature drop. The comparison between pure water and the NaCl solution highlights the significant impact of salt on methane hydrate behavior. Pure water facilitates a rapid and more dynamic hydrate formation and dissociation process. In contrast, the presence of NaCl inhibits these processes by reducing water activity and stabilizing the hydrate structure, leading to slower and more controlled formation and dissociation.

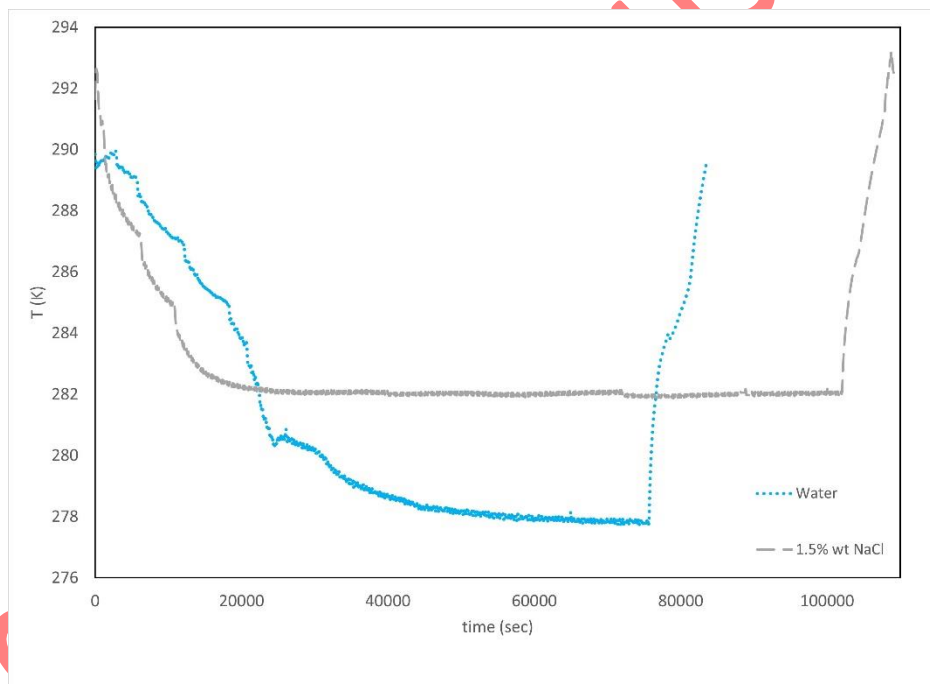


Fig. 4. Temperature vs. Time changes during the formation and dissociation of methane hydrate in pure water and 1.5% wt NaCl

Porous media with smaller grain sizes provide a larger surface area for hydrate formation relative to their volume. The increased number of nucleation sites enhances the rate of hydrate formation. Additionally, the increased interface area between gas and water molecules facilitates better contact, leading to improved nucleation and growth of hydrates. Figure 5 shows the temperature changes over time for the bulk volume without porous media and for two different sizes of glass beads.

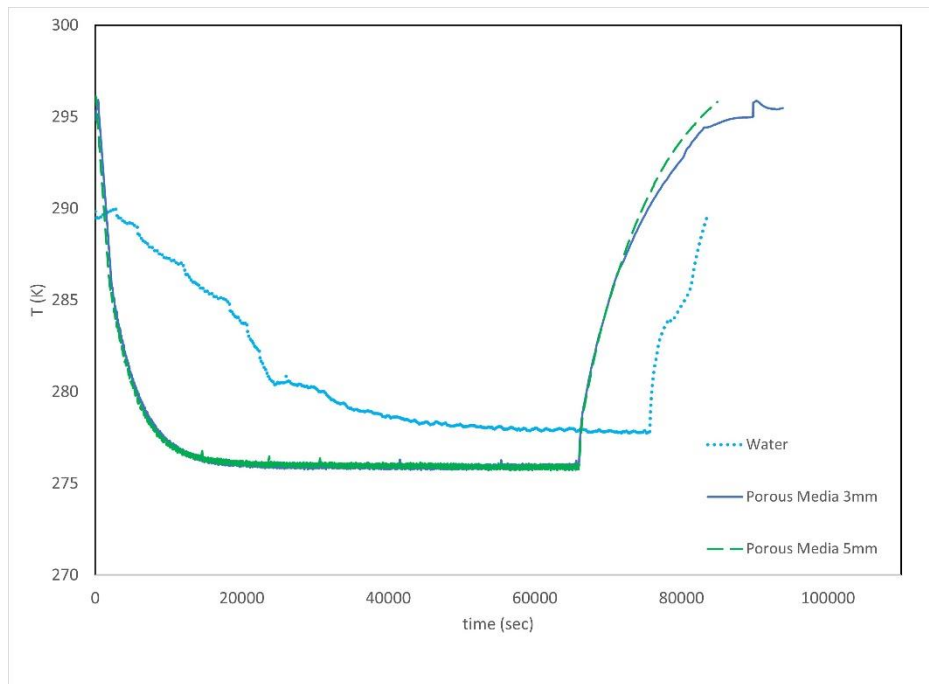


Fig. 5. Comparison of Temperature Changes Over Time for Porous Media of Different Sizes

In pure water (blue dotted line), the initial temperature is approximately 290 K and rapidly decreases to around 280 K as hydrate formation conditions are approached. This significant temperature drop indicates the endothermic nature of hydrate formation, where heat is absorbed from the surroundings. The small fluctuations observed during the temperature decrease reflect the dynamic process of nucleation and hydrate growth. In the 3 mm porous media (dark blue line), the initial temperature is also around 295 K, and the temperature begins to drop. Although small fluctuations are observed, they are less pronounced than in pure water, indicating that the porous media moderates the formation process, leading to more stable hydrate growth.

In the 5 mm porous media (green line), the initial temperature and temperature decrease are similar to the 3 mm medium, but the temperature stabilizes slightly higher, around 277 K. The hydrate formation process is slower, with a more stable temperature profile and fewer fluctuations.

Regarding the dissociation process, as illustrated in the figure, it progresses gradually after initiation in the porous media environments. The porous media effectively control the release of methane gas and the associated heat. In the 3 mm porous medium, the temperature increase occurs slightly faster compared to the 5 mm beads, indicating that smaller pores facilitate dissociation due to the increased surface area. The result of the hydrate formed in one of the experiments using porous media is shown in Figure 6.

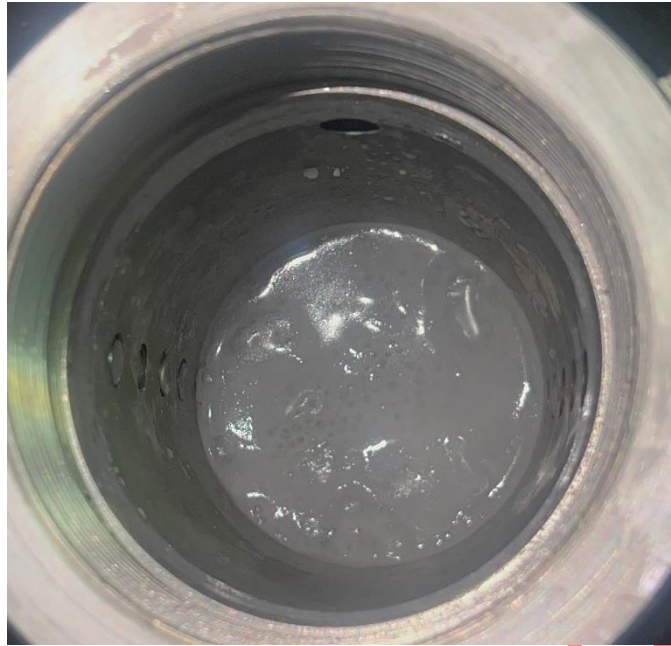


Fig. 6. The hydrate formed in the porous media during one of these experiments

As illustrated in the figure, the presence of porous media facilitated the formation of hydrate throughout the entire cell volume, rather than being limited to the interface between the water and gas or along the cell walls.

The results indicate that pure water exhibits the fastest and most significant temperature changes, reflecting dynamic behavior with pronounced fluctuations. The presence of salt and impurities in the NaCl solution and Caspian Sea water moderates the hydrate behavior, resulting in a more stable temperature profile. Porous media, by providing nucleation sites, influence the thermal behavior, leading to more controlled formation and dissociation processes.

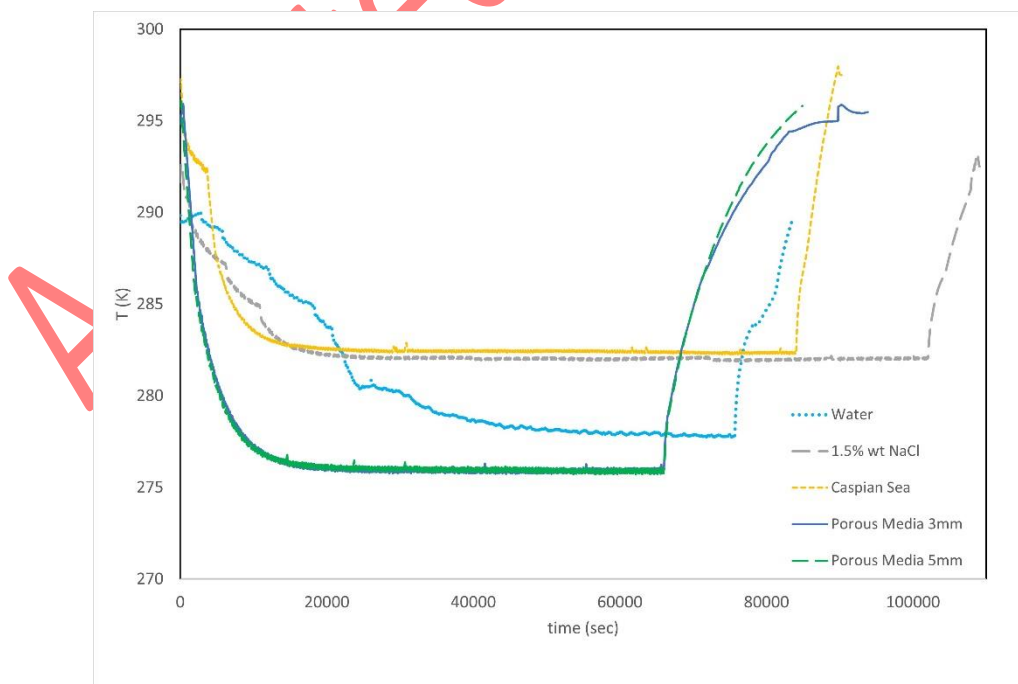


Fig. 7. Temperature changes over time for six different experiments

Using the calculations based on the provided equations, the amount of gas and water absorbed during the hydrate formation process was determined using a MATLAB code. These values were then divided to calculate the hydrate growth.

Figure 8 presents this data for methane hydrate experiments conducted with pure water under both stirred and non-stirred conditions, in 3 mm and 5 mm glass bead porous media, in water containing 1.5 wt% NaCl, and in Caspian Sea water.

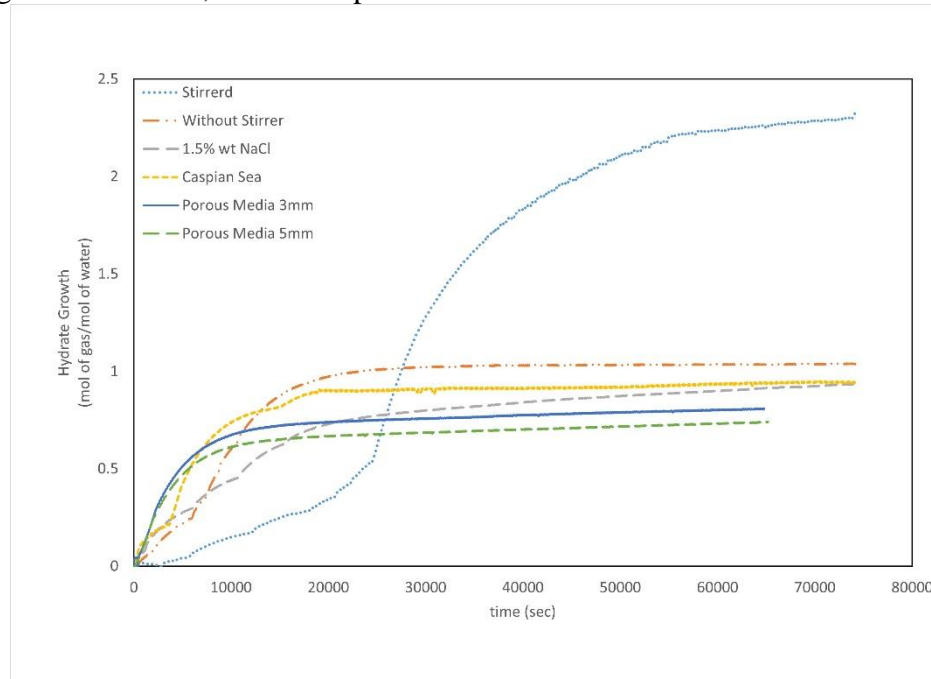


Fig. 8. Comparison of hydrate growth in the various experiments of this study

In the experiment with pure water and a constant-speed magnetic stirrer (blue dotted line), a peak in hydrate growth is observed at 40,000 seconds (~11 hours), reaching 2.3 mol gas/mol water. This indicates that stirring significantly enhances hydrate formation by improving mass and heat transfer, facilitating uniform methane distribution in water. The stirrer promotes nucleation sites throughout the water phase, facilitating growth. In contrast, without stirring (orange dashed line), hydrate growth is slower, reaching 1.2 mol gas/mol water due to less efficient gas distribution and heat transfer, resulting in slower kinetics and potential diffusion limitations.

In the 1.5 wt% NaCl solution experiment (gray line), hydrate growth reached 1.1 mol gas/mol water. Sodium chloride acts as a thermodynamic inhibitor, with salt ions interfering with hydrogen bonds essential for hydrate formation, raising the thermodynamic stability threshold and slowing nucleation and growth.

In the Caspian Sea water experiment (yellow dashed line), final hydrate growth was around 1 mol gas/mol water, similar to the NaCl solution. The presence of various salts and impurities in Caspian Sea water mimics the inhibitory effects of NaCl. This experiment is significant as it reflects real-world conditions, indicating that sea water composition can have inhibitory effects similar to those observed in natural marine sediments.

Experiments with 3 mm (blue line) and 5 mm (green dashed line) porous media show different growth rates. The 3 mm beads showed slightly better hydrate growth (0.8 mol gas/mol water compared to 0.7 mol gas/mol water for 5 mm beads). Porous media act as nucleation sites, enhancing hydrate formation. Smaller beads likely provide more nucleation sites, impacting growth rates, although they may also restrict gas flow.

Figure 9 illustrates the temperature changes over a period of 5 hours following the initial nucleation under various conditions.

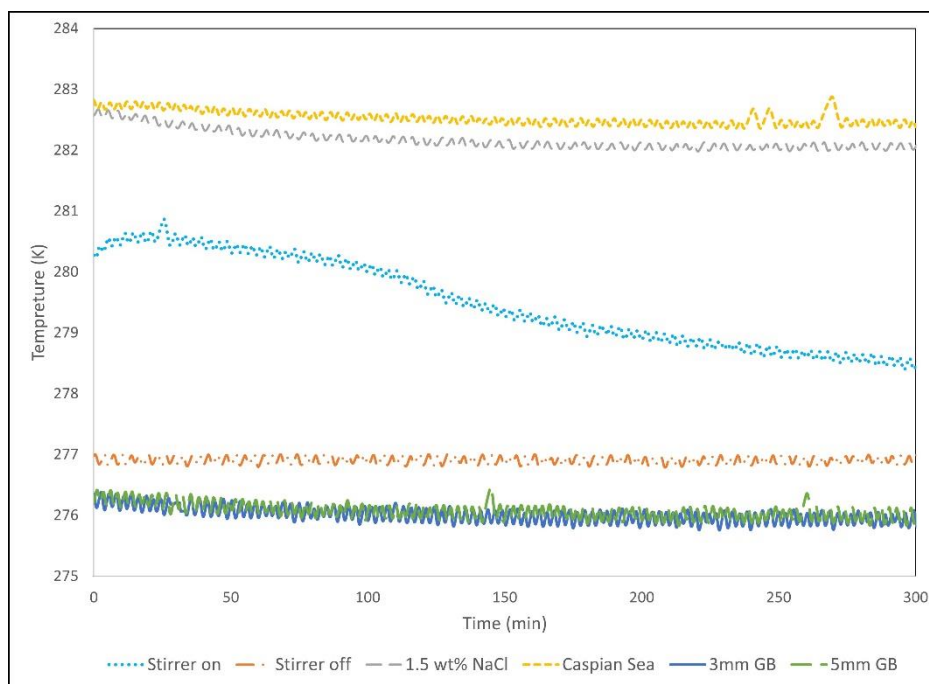


Fig. 9. Temperature changes during the first 5 hours after nucleation

After nucleation, temperature fluctuations increase, reflecting the stochastic nature of the process. In pure water with a magnetic stirrer (blue dotted line), the temperature decreases continuously from around 280 K, with fluctuations indicating dynamic nucleation and hydrate growth due to enhanced gas and water distribution. Without stirring (orange dashed line), nucleation starts at 277 K with slower temperature decrease and fewer fluctuations, suggesting a gradual process due to limited methane diffusion.

In the NaCl solution, nucleation begins at 282 K and stabilizes, with salt ions inhibiting hydrogen bonding and hydrate formation. In Caspian Sea water, nucleation starts at 283 K, with small fluctuations indicating continued dynamic formation despite the inhibitory effects of salts.

In porous media, nucleation occurs around 276 K in both 3 mm and 5 mm bead environments. The numerous nucleation sites provided by the pores enhance hydrate formation efficiency, with consistent small fluctuations indicating continuous nucleation and growth within the porous structure.

Conclusion

This study systematically investigated methane hydrate formation and dissociation under various conditions, including pure water, NaCl solution, Caspian Sea water, and different porous media. The results reveal that stirring significantly enhances hydrate growth due to improved mass and heat transfer, while the presence of salts and impurities in NaCl solution and Caspian Sea water stabilizes the system and slows hydrate formation. Porous media, particularly with smaller pore sizes, provide numerous nucleation sites, leading to more efficient hydrate formation and controlled dissociation. These findings have significant implications for industrial applications in methane hydrate production, storage, and transportation. Understanding the inhibitory effects of salts and the advantages of porous media can aid in designing more effective systems for hydrate management. Insights from natural water compositions highlight the importance of real-world environmental factors.

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