Experimental analysis of the CO$_2$/CH$_4$ Replacement Efficiency due to Sodium Chloride Presence in Natural Gas Hydrates Reservoirs

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Abstract. Nowadays natural gas hydrates represent a promising opportunity for counteracting several crucial issues of the 21$^{th}$ century. They are a valid answer to the continuously increasing energy demand, moved by the global population growth; moreover, considering their conformation and the possibility of using them for carbon dioxide permanently storage, gas hydrates may become a carbon neutral energy source, where for each methane molecule recovered, another carbon dioxide molecule is entrapped in solid form. Considering that the combustion of one methane molecule for energy production leads to the formation of one CO$_2$ molecule, the hydrates exploitation can be considered a clean process in terms of impact on the climate change. This work shows how the presence of sodium chloride affects the CO$_2$/CH$_4$ replacement process into a gas hydrates reservoir. Replacement experimental results carried out in pure demineralised water were compared with the same values performed in a mixture of water and salt, having a concentration of 37 g/l. Some parameters of interest were discussed, such us methane hydrates formed before the replacement process, total amount of hydrates (composed by both species) reached at the end of the whole process, CO$_2$ moles that formed hydrate, quantity of hydrate present before the replacement process which were actually involved in the CO$_2$/CH$_4$ exchange and carbon dioxide amount which led to the formation of new hydrates structures.

Keywords: natural gas hydrate; CO$_2$/CH$_4$ exchange; Chemical inhibitors injection; Sodium chloride effect.

1 Introduction

From literature data, natural gas hydrates are emerging as one of the most promising alternatives to conventional resources of natural gas [1, 2]. The main strategies for methane recovery consist in generating a pressure drop inside the reservoir or/and heating it, in order
to move the local thermodynamic conditions outside from the equilibrium area for methane hydrates and so cause their dissociation [3]. However, in most cases the energy necessary for carrying out these strategies is very similar to the amount which is recovered; thus the necessity of promoting different solution than the simple depressurization or thermal stimulation. Here is proposed a short summary of the main techniques adopted for intervening on hydrates reservoirs, with their most important characteristics. Depressurization strategies shift the reservoirs thermodynamic conditions outside from the hydrate stability zone (HSZ) by reducing pressure, while maintaining temperature constant. That method was successfully applied in both offshores and onshore field tests [4]; in both cases reservoirs had high porosity, high permeability and high hydrate saturation. In situation different from these (or in the majority of cases), depressurization methods become inefficient [5]. Thermal stimulation consists in bringing heat into the reservoirs with several different techniques, such as steam injection, hot brine injection, in-situ combustion and electromagnetic heating [6]. Here hydrates were moved away from their stability zone by increasing temperature and keeping pressure constant. Several research articles affirm the low efficiency of thermal stimulation, due to the huge quantity of heat loss to porous media in the hydrate layers [7]. As depressurization, even this method is less effective in reservoirs with a low hydrate saturation degree [8]. The injection of chemical inhibitors permits to move the local condition far from the stability zone without varying pressure and temperature [9]. The most popular chemical inhibitors are methanol, monoethylene glycol and diethylene glycol. The elevated quantities necessary for water treatment in hydrate reservoirs make that process unfeasible under an economic point of view. Moreover, the release of these substances inside deposits may represent a not tolerable impact on the external environment. Nowadays the most actual problem it to define a new solution able to minimize energy costs for methane recovery. In this direction is the replacement technology, which consists in extracting methane from hydrates by replace it with other gas molecules [10, 11]. The most investigated solution for the replacement process is carbon dioxide. Using it, two different goals can be reached together: methane recovery for energy production and CO₂ storage, in order to avoid its diffusion in atmosphere. The possibility of carrying out the replacement between these two species is possible thank to the higher stability of CO₂ hydrates, that need of lower pressure and/or higher temperature values for their formation and stability [12]. Several researches proved that the replacement process does not require external energy [13, 14]. Moreover, the process is not accompanied by the release of free water [15]. One obstacle for CO₂/CH₄ exchange consists in the new CO₂ hydrates formation, which is able to clog sediment pores and isolate CH₄ hydrates from carbon dioxide, hindering the replacement process [16]. Similar conclusions were reached in further experimental works available in literature [17]. In the following pages, the possibility of improving the carbon dioxide replacement process by exploiting sodium chloride characteristics was explored. Salt is a chemical inhibitor for hydrates formation; thus its presence moves pressure-temperature conditions to higher values of the first parameter and/or lower values of the second. However, previous work proved how its behaviour as inhibitor for the process may change in function of the gaseous compound involved in hydrates formation [18, 19]. The negative impact previously described affect both CH₄ and CO₂ hydrate formation, but with different intensity. In particular, methane hydrate formation is more penalized than carbon dioxide. This difference leads to a greater distance between the two species equilibrium curves, that means a wider pressure-temperature range for performing the replacement process and consequent greater possibilities to improve its efficiency. Efficiency is strongly affected by the process kinetics [20]; sodium chloride permits to perform thermodynamic conditions feasible for CO₂ hydrate formation and, at the same time, make the distance from methane hydrate stability zone higher than in case of pure demineralized water. In the present paper
ten CO₂ replacement tests carried out in absence of salt were compared with many other tests realized in a mixture of demineralised water and salt, with a concentration of 37 g/l. Different methods for comparing them were proposed. Firstly, the methane amount involved in hydrates formation at the beginning of each test was evaluated, in order to well understand how salt presence hinders the process in case of methane as host molecule. Hydrates quantity produced at the end of the whole experiment was taken into account for monitoring water cages preservation, which may be considered a key factor during operations in natural gas hydrate reservoirs. Finally, carbon dioxide moles involved into hydrates was evaluated in both its contribution: the part which took the place of methane in already existing hydrates and the part that contributed to new hydrates formation.

2 Experimental apparatus

Experiments here proposed were carried out in a laboratory scale apparatus able to well simulate a classical hydrate seabed reservoir. A deepen description of its characteristic may be found elsewhere in literature [21, 22]. In Figure 1, a scheme of the completely assembled experimental apparatus (at left) and an image of the reactor (at right) are provided.

![Fig. 1. Scheme of the completely assembled experimental apparatus and image of the reactor.](image)

The reactor is made with 316SS stainless steel; it has a cylindrical internal volume of 949 cm³, with a diameter equal to 7.3 cm and 22.1 cm height. While the lateral surface consists in a 0.7 cm thick wall, the upper and lower sections are sealed with two flanges. Both of them host channels used for gas flowing and for measure devices disposal inside the reactor. As explained in the scheme of Figure 1, methane is flushed from the lower flange, while carbon dioxide from the upper. Between gas cylinders and the reactor, two flowmeters are present for measuring quantities injected inside the internal volume. Temperature is constantly controlled using four type K thermocouples, having class accuracy 1 and positioned at different depths. Black points in the scheme indicate thermocouples positioning: they are located respectively at 2, 7, 11 and 16 cm depth from the upper flange. Pressure is monitoring with a digital manometer, model MAN-SD, having accuracy equal to ± 0.5 of the full scale. Even in this case, the device communicates with the reactor internal environment from the upper flange. If thermocouples are used to control
temperature, a thermostatic bath was planned to regulate it. The vessel contains a mixture of water a glycol and exchanges heat with coolant contained in a double copper coil, which is directly connected to a chiller, model GC-LT. Finally, the internal volume is filled with 0.74 l of sand composed by quartz spheres with 500 μm diameter. Sand porosity is equal to 34% and was measured with a porosimeter, model Thermo Scientific Pascal 140.

3 Experimental procedure

The experimental section consists in 20 carbon dioxide replacement tests, divided in two equal groups, whose difference is the use of sodium chloride or its absence. Methodology used for carrying out tests without salt has been widely described in previous works [23]. The second group of tests was realized in a mixture of pure demineralised water and sodium chloride, having a concentration of 37 g/l. The first phase, or the methane hydrates formation, was performed in the same way of first group tests: once temperature reached 1÷3 °C inside the reactor, methane was gradually injected until reaching the desired value. Considering temperature interval previously indicated and the presence of salt, the value decided for the internal pressure was in the range 60÷62 bar. The following spontaneous pressure decrease proved hydrate formation. The process was considered ended as soon as pressure stopped decreasing and stabilized around a constant value.

On the contrary, the CO₂ replacement process was performed in a different manner. In all cases, the strategy adopted was depressurization. Immediately after the CH₄ hydrates formation, the communication between reactor and CO₂ cylinder was opened for promoting the gas flow; at the same time, also the reactor ejection valve was opened. Thus guaranteed an inlet gas flow of pure carbon dioxide and an outlet flow composed by a mixture of carbon dioxide and methane. At the same time pressure was reduced from the value reached at the end of methane hydrates formation to 31÷33 bar, keeping as far as possible temperature constant. That depressurization led to internal thermodynamic conditions feasible for CO₂ hydrates formation and stability. The contrary occurred for CH₄ hydrates.

At the beginning of the CO₂ replacement phase, the internal volume was thus composed by a solid phase of CH₄ hydrates and a gaseous one containing both species. The next step consisted in closing the ejection valve while maintaining opened the connection with the CO₂ cylinder. This is the main difference with methodology adopted for tests belonging to the first group. In the first group of tests, as soon as the desired composition was reached, the connection between the reactor and the CO₂ cylinder was interrupted. The continuous supply of CO₂ was not realized for maintaining the gaseous phase composition constant; in fact, the release of part of methane contained into hydrates and the constant pressure value led to a variation of that composition in favour of methane presence. By adopting this strategy, pressure was kept constant and so the distance between local pressure and the equilibrium value for CO₂ hydrates did not reduced over time, avoiding the consequent hydrates formation rate decrease. Moreover, an unlimited availability of carbon dioxide was provided. Obviously, the classical pressure decrease due to hydrates formation was not visible in this case, therefore the process duration was fixed at 23 h (that value was fixed in function of experience reached in previous experimental works). Finally, the reactor was opened for completely remove the gaseous phase, then it was immediately closed again for favouring hydrates dissociation. The quantity of hydrates produced was determined by measuring the dissociation pressure and temperature. A gas-chromatographic analysis permitted to define the percentage of hydrates involving both species used during tests. That analysis was made using two different columns: Molsieve 5A to detect methane and Poraplot PPU to detect carbon dioxide. In both cases, measures uncertainty falls to the third decimal place of values produced.
4 Results and Discussion

Results are shown in two different tables: the first one is related to tests carried out in pure demineralized water, while the second describes tests realized in presence of sodium chloride.

**Table 1.** Main parameters measured and calculated in tests carried out in pure demineralized water.

| Test n° | H(CH₄)ₚᵢᵣₑ [mol] | H(TOT)ₚᵢᵣₑ [mol] | H(CO₂)ₚᵢᵣₑ [mol] | H(CH₄)ₚᵢᵣₑ [mol] | ΔH(CH₄) [mol] | ε [%] | ΔH [mol] |
|---------|-------------------|-------------------|-------------------|-------------------|---------------|-------|----------|
| 1       | 0.082             | 0.163             | 0.056             | 0.107             | -0.025        | -30.49| 0.081    |
| 2       | 0.27              | 0.073             | 0.011             | 0.062             | 0.208         | 77.04 | -0.197   |
| 3       | 0.21              | 0.151             | 0.021             | 0.13              | 0.08          | 38.1  | -0.059   |
| 4       | 0.24              | 0.092             | 0.02              | 0.072             | 0.168         | 70    | -0.148   |
| 5       | 0.09              | 0.077             | 0.026             | 0.051             | 0.039         | 43.33 | -0.013   |
| 6       | 0.11              | 0.07              | 0.015             | 0.055             | 0.055         | 50    | -0.04    |
| 7       | 0.26              | 0.073             | 0.017             | 0.056             | 0.204         | 78.46 | -0.187   |
| 8       | 0.2               | 0.086             | 0.012             | 0.074             | 0.126         | 63    | -0.114   |
| 9       | 0.22              | 0.193             | 0.027             | 0.166             | 0.054         | 24.55 | -0.027   |
| 10      | 0.23              | 0.081             | 0.026             | 0.055             | 0.175         | 76.09 | -0.149   |

**Table 2.** Main parameters measured and calculated in tests carried out in sealed water (37 g/l).

| Test n° | H(CH₄)ₚᵢᵣₑ [mol] | H(TOT)ₚᵢᵣₑ [mol] | H(CO₂)ₚᵢᵣₑ [mol] | H(CH₄)ₚᵢᵣₑ [mol] | ΔH(CH₄) [mol] | ε [%] | ΔH [mol] |
|---------|-------------------|-------------------|-------------------|-------------------|---------------|-------|----------|
| 11      | 0.056             | 0.113             | 0.065             | 0.048             | 0.008         | 14.29 | 0.057    |
| 12      | 0.065             | 0.116             | 0.064             | 0.052             | 0.013         | 20    | 0.051    |
| 13      | 0.051             | 0.096             | 0.073             | 0.023             | 0.028         | 54.9  | 0.045    |
| 14      | 0.06              | 0.136             | 0.117             | 0.019             | 0.041         | 68.33 | 0.076    |
| 15      | 0.064             | 0.043             | 0.025             | 0.018             | 0.046         | 71.86 | -0.021   |
| 16      | 0.061             | 0.126             | 0.103             | 0.023             | 0.038         | 62.3  | 0.065    |
| 17      | 0.07              | 0.133             | 0.105             | 0.028             | 0.042         | 60    | 0.063    |
| 18      | 0.08              | 0.152             | 0.11              | 0.042             | 0.038         | 47.5  | 0.072    |
| 19      | 0.059             | 0.247             | 0.206             | 0.041             | 0.018         | 30.51 | 0.188    |
| 20      | 0.103             | 0.121             | 0.085             | 0.036             | 0.067         | 35.19 | 0.018    |

In the following lines, parameters shown in tables 1 and 2 are described. H(CH₄)ₚᵢᵣₑ is the quantity of methane involved into hydrates formation before the replacement phase, while H(CO₂)ₚᵢᵣₑ and H(CH₄)ₚᵢᵣₑ are the quantities of respective species measured after hydrates dissociation after the replacement process. Their sum gives H(TOT)ₚᵢᵣₑ. With ΔH(CH₄) is indicated the difference between methane moles contained into hydrate before and after the replacement phase; this parameter represents the quantity of methane released and is directly linked to the process efficiency. In an ideal process its value would be always equal to 0, because the total amount of methane would be recovered and replaced with carbon dioxide. For a higher comprehension of the process efficiency, the previous parameter is also provided under form of percentage (ε). The last parameter, ΔH, consists in the difference between hydrates formed at the end of the replacement process (composed by both species) and methane hydrates present inside the reactor immediately before. The sum of H(CO₂)ₚᵢᵣₑ and H(CH₄)ₚᵢᵣₑ clearly gives H(TOT)ₚᵢᵣₑ; the same results can be reached by adding ΔH to H(CH₄)ₚᵢᵣₑ. As it is possible to see, parameter ΔH often assumes negative values, especially in tests carried out without salt. Thus the quantity of carbon dioxide hydrates formed during the replacement is lower than dissociated methane.
hydrates. The following hypothesis was made: CO$_2$ hydrates covered as much as possible dissociated CH$_4$ hydrates. If H(CO$_2$)$_{\text{post}}$ is lower than ΔH(CH$_4$), all formed CO$_2$ hydrates took part in the replacement process; on the contrary, if the relation between these parameters is inverted, CO$_2$ hydrates may be considered as sum of two different contribution: the first one took origin from the replacement process and replaced all methane released, while the second describes the formation of new CO$_2$ hydrates, which used the free water and free space again present inside the reactor after methane formation phase and immediately before the replacement process. A further consideration for tests having a negative value of ΔH(CH$_4$). This is the case of Test 1, realized in pure demineralised water. That value gives the idea of a new formation of methane hydrates during the replacement process: the final quantity of CH$_4$ hydrate is in fact higher than the same value measured before. Considering pressure-temperature conditions during that phase, a new methane hydrates formation cannot be considered feasible. The reason of that particular values stays in how experimentally proved in previous works [17]: the fast formation of new carbon dioxide hydrates (which usually occurs immediately after CO$_2$ injection inside the reactor) is capable to form a shell around the methane hydrates core, which hinders existing hydrates dissociation and is also able to entrap CH$_4$ molecules present in gaseous phase. For that reason, after the replacement phase, a higher quantity of methane inside the reactor may be measured. In Table 2, considering how expressed among, an evaluation of CO$_2$ hydrates formed through methane replacement in already existing water cages and new CO$_2$ hydrates formed in the available free space was made.

Table 3. Carbon dioxide hydrates which came from the replacement of methane (left columns) and which formed in the available free space (right columns).

| Test n° | H(CO$_2$)$_{\text{rep}}$ | H(CO$_2$)$_{\text{new}}$ | Test n° | H(CO$_2$)$_{\text{rep}}$ | H(CO$_2$)$_{\text{new}}$ |
|---------|--------------------------|--------------------------|---------|--------------------------|--------------------------|
| 1       | 0                        | 0.056                    | 11      | 0.008                    | 0.057                    |
| 2       | 0.011                    | 0                        | 12      | 0.013                    | 0.051                    |
| 3       | 0.021                    | 0                        | 13      | 0.028                    | 0.045                    |
| 4       | 0.02                     | 0                        | 14      | 0.041                    | 0.076                    |
| 5       | 0.026                    | 0                        | 15      | 0.025                    | 0                        |
| 6       | 0.015                    | 0                        | 16      | 0.038                    | 0.065                    |
| 7       | 0.017                    | 0                        | 17      | 0.042                    | 0.063                    |
| 8       | 0.012                    | 0                        | 18      | 0.038                    | 0.072                    |
| 9       | 0.027                    | 0                        | 19      | 0.018                    | 0.188                    |
| 10      | 0.026                    | 0                        | 20      | 0.067                    | 0.018                    |

Table 3 provides all further data necessary for a deepen comparison between tests carried out in simple demineralised water and tests realized in presence of salt. First of all, parameter H(CH$_4$)$_{\text{pre}}$ clearly proves the inhibitor effect of sodium chloride: even if thermodynamic conditions are similar in both groups of tests, the initial quantity of methane hydrates formed is significantly higher in tests carried out without salt. In tests 11-20, that parameter assumes values in the range 0.051 – 0.103 mol, while in absence of salt the range 0.082 – 0.27. Thus, a saline solution with concentration of 37 g/l strongly affects hydrate formation, drastically reducing the quantity of gas entrapped into water cages. That parameter does not constitute a novelty, but completely corresponds to how present in literature about the effect of sodium chloride on the process. Comparing parameter H(TOT)$_{\text{post}}$, values concerning the two types of tests are quite similar: the overall amount of hydrates, present after the replacement process ending, is similar in both cases. In theory, that number should have been lower in tests belonging to the second group. From results, the main reason to explain it properly stays in the lower inhibitor effect that salt exercises.
on CO₂ hydrates. Its presence led to a lower presence of CH₄ hydrates, providing a considerably greater free space and free water for CO₂ hydrate formation. Adding a higher availability of sources with a less pronounced inhibitor effect, CO₂ hydrate production was more massive than tests carried out in absence of salt. Another parameter which assumes similar values in both groups is ε, or the reduction of methane present inside the reactor due to the replacement process, expressed in form of percentage. Even if values related to methane are significantly lower in tests with salt, the ratio between them remains similar to how observed in the first group tests. Without considering Test 1, were the final CH₄ hydrates amount value is overestimated for the presence of a shell composed by CO₂ hydrates, parameter ε stays in the range 38.1 – 78.46 for tests belonging to the first group (absence of salt) and in the range 14.29 – 71.86 for the second group. The most important difference visible in Table 1 and Table 2 is described with parameter H(CO₂)post. While in tests 1 – 10 values can vary from 0.011 to 0.056 mol, in tests 11 – 20 the range is considerably higher: from 0.025 to 0.206 mol. That explains why the presence of sodium chloride may improve the CO₂/CH₄ replacement process efficiency: the quantity of carbon dioxide involved in hydrates formation is extremely higher in presence of salt. As explained before, H(CO₂)post values do not show the real benefit of salt, but give an overestimation of it. The presence of more space and free water guaranteed more potentiality for hydrates formation, however that positive contribution cannot be considered when intervening in real seabed hydrates reservoirs. In future works, the difference of free space will be evaluated in order to exclude it for the replacement process efficiency evaluation. In each case, it influences only considerations about new CO₂ hydrates formation, while cannot intervenes on the real replacement phase. Seeing Table 3, the higher formation of new hydrate structures containing CO₂ clearly appears. At the same time, the table show how salt presence improves the carbon dioxide quantity involved in the replacement process. In tests realized in absence of salt the quantity of hydrates dissolved during the replacement phase was higher than hydrates formed in the same time; thus, all CO₂ moles involved in the formation process took part in the replacement of methane in already existing water cages. Nevertheless, moles of CO₂ which replaced methane into hydrates in tests carried out in presence of salt are greater. In tests 1 – 10 parameter H(CO₂)rep falls in the range 0.011 – 0.027 (even here, Test 1 was not taken into account for reasons previously explained), while in tests 11 – 20 the same parameter assumed values in the range 0.008 – 0.042. In the present work, the precise quantity of carbon dioxide injected inside the reactor for performing the replacement phase was not measured, mainly for difficulties found in its evaluation. In fact, the CO₂ injection starts with an initial gas flowing to (only CO₂) and from the reactor (a mixture of both species), in order to remove methane in gaseous phase which did not participate in hydrates formation. Even during this phase, CO₂ hydrate formation occurs. Moreover, that phase has a time duration variable from each test; thus, the exact evaluation of CO₂ injected which effectively contributed to the process (not only forming hydrates but also varying internal conditions, such as partial pressure, whose influence cannot be neglected [22]), was not performed and will be object of future works. Finally, in the last part of this paragraph one test for each group was describe by showing its temperature and pressure trend over time. Figures 2 and 3 are related to Test 6, carried out in pure demineralised water, while figures 4 and 5 are referred to Test 18, realized in presence of sodium chloride.
Fig. 2. Pressure trend over time in Test 6, carried out in absence of salt.

Fig. 3. Temperature trend over time in Test 6, carried out in absence of salt.
Fig. 4. Pressure trend over time in Test 18, carried out in presence of salt.

Fig. 5. Temperature trend over time in Test 18, carried out in presence of salt.

Seeing pressure diagrams, the first difference appears in correspondence of carbon dioxide injection. In test 6, methane hydrates formation continued until reaching 33 bar; considering CH$_4$ hydrates equilibrium conditions widely documented in literature and the temperature increase, which occurred in this test due to the injection of CO$_2$ and the immediate hydrates formation, a strong depressurization was not necessary. On the
contrary, in Test 18 the presence of salt led to a minor methane hydrates formation, thus to a higher final pressure, which made necessary a significant pressure reduction, in order to make thermodynamic condition feasible for CO₂ hydrates formation and stability. In pressure diagrams, this is the only difference of interest between the two typologies of tests: methane injection, methane hydrates formation and CO₂ replacement phase showed a very similar trend.

Temperature diagrams assume several differences from each other. In Test 6, the methane hydrates formation is accompanied by a pronounced temperature increase, due to exothermic nature of the process; that peak is not visible in Test 18. Motivation of it stays in the very reduced quantity of hydrates produces in this second case, which led to a heat production too small for generating a temperature increase similar to Test 6. Moreover, methane hydrates formation in Test 6 was enough massive to generate a second temperature peak, even if less massive than the first one. Temperature increase, at the beginning and during the replacement phase, is present in both tests, however with some differences. In Test 6 its increase is more pronounces, rapid and constant than Test 18. It means that no methane hydrates dissociation occurred during the injection phase. On the contrary, a partial dissociation can be observed in Test 18. Finally, once the injection phase finished, in Test 6 a balance between heat produced by CO₂ hydrates formation and heat absorbed by CH₄ hydrates dissociation was registered, while the temperature decrease in Test 18 proved that hydrates formation is more massive than their dissociation. That is clearly visible in Table 3, which explains how, in tests carried out in presence of sodium chloride, the contribution of new water cages formation (containing CO₂) was predominant.

5 Conclusions

Nowadays natural gas hydrates are considered a potential opportunity for responding to the continuously increasing energy demand and, at the same time, counteracting climate changes due to CO₂ emissions in atmosphere. In this paper the positive effect of sodium chloride on the CO₂/CH₄ exchange process was investigated. Ten replacement tests, carried out in pure demineralized water and already described in previous works, were compared with further ten tests realized with a solution of water and sodium chloride, with a concentration of 37 g/l. Result clearly prove the inhibitor effect of salt, which led to a minor methane hydrates formation during the first part of all tests. However, moles of carbon dioxide involved in hydrates formation is significantly higher in tests carried out with salt. Moles entrapped in water cages are in the range 0.011 – 0.056 in absence of salt, while the same range is 0.025 – 0.206 in presence of it. Furthermore, the two contributions which constitute moles of CO₂ entrapped were analysed, or the quantity which replaced methane into already existing water cages and quantity related to new structure formation. In presence of salt, a significant quantity of CO₂ participated to the formation of new hydrates (while it was not observed in absence of salt, where the whole amount of hydrates after the replacement process is lower than the same quantity measured immediately before). Moreover, also the CO₂ amount which replaced methane into already present hydrate is higher in tests carried out in presence of salt. In conclusion, the presence of a chemical inhibitor as sodium chloride provides the opportunity of improving the CO₂/CH₄ replacement process efficiency and, at the same time, increasing the quantity of carbon dioxide permanently stored in solid form into hydrates.

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