Chemical inhibitors as potential allied for CO_2 replacement in gas hydrates reservoirs: sodium chloride case study.

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Abstract - In previous experimental works we proved how the presence of sodium chloride may influence the replacement of methane contained into hydrate with carbon dioxide. Even if its chemical inhibitor effect is well known and documented in literature, the possibility of having different behaviours in function of the gaseous species involved in hydrate formation has not been explored. The first step of our research proved how NaCl inhibitor effect is more pronounced in methane hydrate formation rather than carbon dioxide one. That leads to a higher difference between temperature-pressure conditions describing the two species equilibrium curves and, thus, to greater possibilities of intervening in the replacement process in order to perform it and increasing both the amount of methane recovered and the quantity of carbon dioxide permanently stored. Two replacement tests were carried out in presence of 40 g/l of salt dissolved in water; then results were compared with two other tests previously realized with the same experimental apparatus but using pure demineralised water. The inhibitor effect of sodium chloride is well visible in the significantly lower quantity of methane hydrate formed in the first phase of tests. The same effect was observed during the carbon dioxide formation step, but its intensity was lower. In conclusion the use of NaCl led to a higher percentage of methane recovered and carbon dioxide stored, even if both quantities are lower than the respective value reached in tests carried out using demineralised water.

Keywords: Natural gas hydrate, CO_2 replacement strategies, Chemical inhibitors injection, Coupled methods, Sodium chloride effect.

1. Introduction

Gas hydrate are solid crystalline compounds that form when non-polar gaseous molecules having a proper size are entrapped in cages of water molecules in presence of relatively high pressure and low temperature conditions [1, 2]. In particular, in that structure, as in normal ice, each water molecule is hydrogen-bonded to for other water molecules. The main difference between these compounds stays in the formation of polyhedral water cages, that provide in clathrate structures more space for hosting the non-polar guest molecules [3]. Hydrate are widely distributed in deep oceans and in permafrost regions, where the local thermodynamic conditions guarantee their formation and stability [4]. Several different gaseous molecules can play the role of "hosts", the most interesting of them for human activities are hydrocarbons, such as methane, ethane (C_2H_6) and propane (C_3H_8) and carbon dioxide (CO_2) [2]. In presence of standard conditions of pressure and temperature, 1 m^3 of NGH hydrate can release at least 164 m^3 of methane [5]. For that reason, it is considered a high – density energy source. Moreover, the carbon content in the already known naturally – occurred hydrate sediments, is at least twice as that contained in all conventional energy sources [6], making NGH one of the most promising answers to the increasing energy demand. In the past decades, several estimations of the quantity of hydrate present worldwide were made. In 1973, considering that hydrates were uniformly distributed in the sediments, the whole amount was estimated to be in the range 3.021 – 3.085 $*10^{18}$ m^3 [7]. A more cautionary valuation was made by Mac–Donald: considering a constant hydrate saturation of 10%, he calculated the overall volume of that source to be 2.0 $* 10^{16}$ m^3[8]. Gornitz et al. calculated the amount of NGH using two different models: the in – situ microbial model (hydrate uniformly filled 5 – 10% of sediment pore spaces) and the pore fluid expulsion model (the hydrate saturation was linearly reduced from 50%, corresponding to the base of the gas hydrate stability zone, and 0%, corresponding to the top of that zone). In the first case the whole amount was estimated to be 26.4 – 139.1 $* 10^{15}$ m^3, while in the second one it corresponded to 114.5$*10^{15}$ m^3 [9]. With the aim of exploiting NGH reservoirs, several techniques for recover methane were performed; from these the most widely investigated and applied are: depressurization, thermal stimulation, chemical inhibitor injection and methane

replacement with other gaseous compounds. Depressurization consists in reducing the reservoirs pressure below the hydrate equilibrium value, keeping the temperature constant [10, 11]. In case of thermal stimulation, the opposite occurs: reservoir temperature is increased for moving the local thermodynamic conditions outside the NGH stability zone, without varying pressure [12, 13]. The use of chemical inhibitors permits to shift the hydrate equilibrium curve to higher pressure and/or lower temperature condition, making the reservoir local values inappropriate for their stability [14]. The most popular chemical inhibitors are alcohols and salts. In particular, inorganic salts are able to reduce the water activity in the surrounding liquid phase, making hydrate formation less likely than in pure demineralised water [15]. By the way, even if several studies proved the inhibitor effect of saline solutions on gas hydrate formation [16, 17], Farhang et al. and Nguyen et al. sustained that at low concentrations sodium halides may act as kinetic promoters for the formation process [18, 19]. Finally, gas replacement strategies consist in injecting other gases in water cages in order to get methane and, at the same time, trap the other compound, avoiding ice structures dissolution [20, 21]. The most common and useful gas used for carrying out that method is carbon dioxide. Thermodynamic equilibrium condition of hydrates are strongly related to the gaseous specie entrapped into water cages; carbon dioxide is able to form ice structure at lower pressure and/or higher temperature than methane. Thus the existence of a region between CH_4 and CO_2 hydrate equilibrium curves allow to realize the exchange process inside the already existing structures. By the way, reservoirs stability conditions are also affected by other physical, such as permeability, porosity, velocity of structures formation and their typology and so on [22]. All strategies just described may be combined and used together. The most adopted solution consists in combining depressurization and thermal stimulation [23].

Topic of the present work is combining chemical inhibitors injection method with CO_2 replacement. Sodium chloride is a chemical inhibitor for hydrate formation and its effect is widely documented in literature; however, as the best of our knowledge, there is lack of information about differences in behaviour of that inhibitor in function of the gaseous specie contained into water cages. The possible existence of it may play a key role in CH_4/CO_2 replacement strategies. If sodium chloride presence mainly affects methane hydrate formation rather than carbon dioxide, the thermodynamic area existing between their respective equilibrium curves might become wider, making the replacement process more feasible and efficient, in terms of quantity of methane recovered and carbon dioxide permanently stored. In previous works, we deepened the effect of N_aC_1 presence during CH_4 and CO_2 hydrate formation [24]; suddenly we also proposed a preliminary replacement test using a moderate amount of salt [25]. Results shown how salt presence mainly hinders methane hydrate formation, generating a greater distance between the two species equilibrium curves. As far as the CO_2 replacement process carried out in [25], it was noticed that gaseous composition of the mixture present into hydrate at the end of the whole process had a higher carbon dioxide concentration than tests carried out in pure demineralised water. In order to confirm the following thesis and for deepening the relation existing between saline concentration in water and replacement tests behaviour, the present work shows four replacement tests: two of them were carried out in pure demineralised water, while the other couple was performed in a saline solution having a concentration of 40 g/l. Some parameters were taken into account and compared, such as the quantity of methane hydrate formed before the replacement phase, the quantity of carbon dioxide involved in hydrate formation and the overall amount of CO_2/CH_4 hydrate formed during the whole tests, with the aim of verifying if sodium chloride brought benefits to the replacement phase.

2. Experimental apparatus

Tests described in the following sections were carried out adopting a lab – scale apparatus planned for simulate a classical hydrate seabed reservoir. A deepen description of its characteristic may be found elsewhere in literature [26, 27]. Here only the information useful for better understanding tests are reported.

Figure 1 describes a schematization of the whole experimental apparatus (at left) and shows a picture of the hydrate reactor (at right).
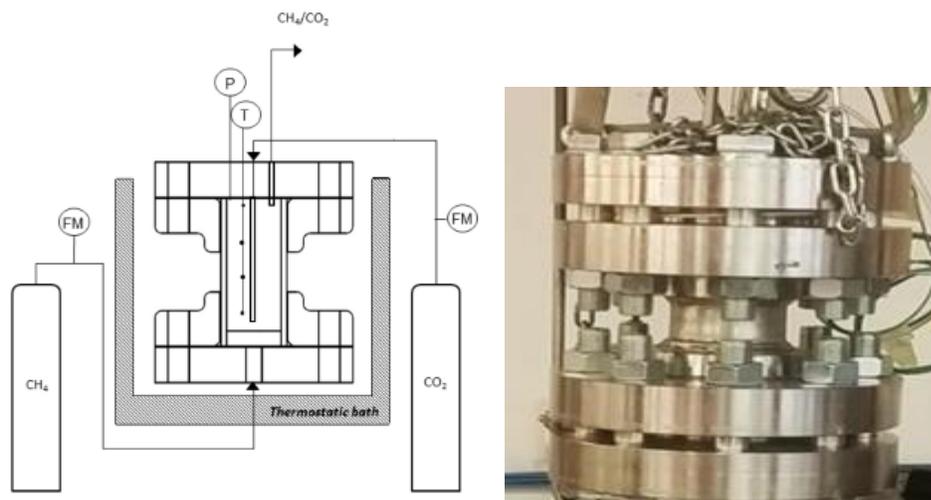
Fig. 1**:** Scheme of the experimental apparatus and image of the hydrate reactor.

The reactor is made of 316SS stainless steel and has an internal cylindrical volume of 949 cm^3 (internal diameter of 7.3 cm and height equal to 22.1 cm). The upper and lower surfaces are sealed with two flanges, both of them hosting channels for gases and instruments insertion. Methane is injected from the lower one, while carbon dioxide from the upper. Between reactor and cylinders, two flow – meters were positioned for measuring the amount of gas injected inside. Temperature and pressure are monitored using type K thermocouples (class accuracy 1) and a manometer. All these devices are inserted from the upper flange (see Figure 1). The reactor is immersed in a thermostatic bath filled with water. Thank to a double copper coil, water temperature is regulated with the use of a chiller, model GC – LT, and so indirectly the reactor temperature. The internal volume is filled with sand, composed by quartz spheres having 500 μm diameter. Sand porosity was measured using a porosimeter, model Thermo Scientific Pascal 140, and is equal to 34%.

3. Methods

Methane hydrate formation was carried out in the same way of previous works; thus it has not been described here [13, 26]. The replacement phase was performed via depressurization. As soon as CH_4 formation finished (the process can be considered concluded once pressure stops decreasing and stabilizes around a fixed value), the reactor was open for both injecting gaseous CO_2 and ejecting gaseous CH_4. In the same time, pressure was reduced from the local value to 31 – 33 bar, keeping as far as possible temperature constant. In this way the new thermodynamic configuration was suitable only for CO_2 hydrate formation, promoting methane hydrate dissociation. That operation led to an internal volume filled with a solid phase, which consists of CH_4 hydrate, and a gaseous one, composed by both species. The initial mixture concentration was measured via gas – chromatographic analysis. As in the previous case, CO_2 hydrate formation is related to an internal pressure decrease, which is lower than how registered during CH_4 hydrate formation properly for its partial dissociation (which caused an increase in pressure). At the end of the process a second gas – chromatographic analysis was made. Comparing the final gaseous composition with the initial and knowing pressure and temperature conditions both at the beginning and at the end of the process, the quantity of both species involved in the process was established. As far as results accuracy is concerned temperature was measured with type K thermocouples, having class accuracy 1, while pressure was measured with a manometer, model MAN-SD (by Kobold), with accuracy equal to ± 0.5% of full scale. The gas-chromatographic analysis was made with the use of two different columns: Molsieve 5A to detect methane and Poraplot PPU to detect carbon dioxide. In both cases, the measure uncertainty falls to the third decimal place of values produced.

4. Results and discussion

Four experimental tests are proposed; two of them were carried out in pure demineralised water, while the others were realized in presence of 40 g/l of sodium chloride. In all cases, the replacement process was performed via depressurization. For each test, a table showing all parameters of interest measured or calculated and two diagram describing pressure and temperature behaviour over time is provided. Data related to tests realized in pure demineralised water, now called Test 1 and Test 2, are provided in Table 1, while data concerning tests performed in a saline solution, called Test 3 and Test 4, are illustrated in table 2. Figures from 2 to 5 describes temperature (figures 2 and 4) and pressure (figures 3 and 5) trend over time. Figures 2 and 3 are related to tests that took place in demineralised water, while the others are described in figures 4 and 5.

Table 1: Main parameters describing Test 1 and Test 2, carried out in pure demineralised water.

Methane hydrate formation						Carbon dioxide replacement					
	Test 1	Test 2		Test 1	Test 2		Test 1	Test 2		Test 1	Test 2
P_i [bar]	58.99	43.37	P_f [bar]	52.62	31.89	P_i [bar]	38.57	21.56	P_f [bar]	34.39	16.05
T_i [°C]	2.83	1.75	T_f [°C]	2.15	2.43	T_i [°C]	5.38	3.44	T_f [°C]	1.59	2.47
Z_i	0.822	0.86	Z_f	0.84	0.90	Z_i	0.81	0.90	Z_f	0.83	0.925
n_{CH4INJ} [mol]	0.736	0.516	n_{CH4HYD} [mol]	0.091	0.153	% CO_{2i}	77.10	78.41	% CO_{2f}	69.81	70.24
						n_{CO2INJ} [mol]	0.598	0.320	n_{CO2HYD} [mol]	0.072	0.066
						$n_{CO2DISS}$ [mol]	0.231	0.131			

Both tables are divided in two sections: the first one describes methane hydrate formation (at left), while the second is related to the replacement process (at right). Letters P and T means pressure and temperature, while Z indicates the compressibility factor, calculated using the Peng – Robinson equation. Subscripts "i" and "f" mean respectively the beginning and ending of the process. Moles are described with letter "n" and subscript "INJ", "DISS" and "HYD" are related to the quantities injected inside the reactor, dissolved in water (that parameter need to be calculated only for CO_2, while is negligible for CH_4) and involved in hydrate formation. Finally, with "%CO_2" is indicated the volume concentration of carbon dioxide in the gaseous phase at the beginning of the replacement phase and immediately after its ending.
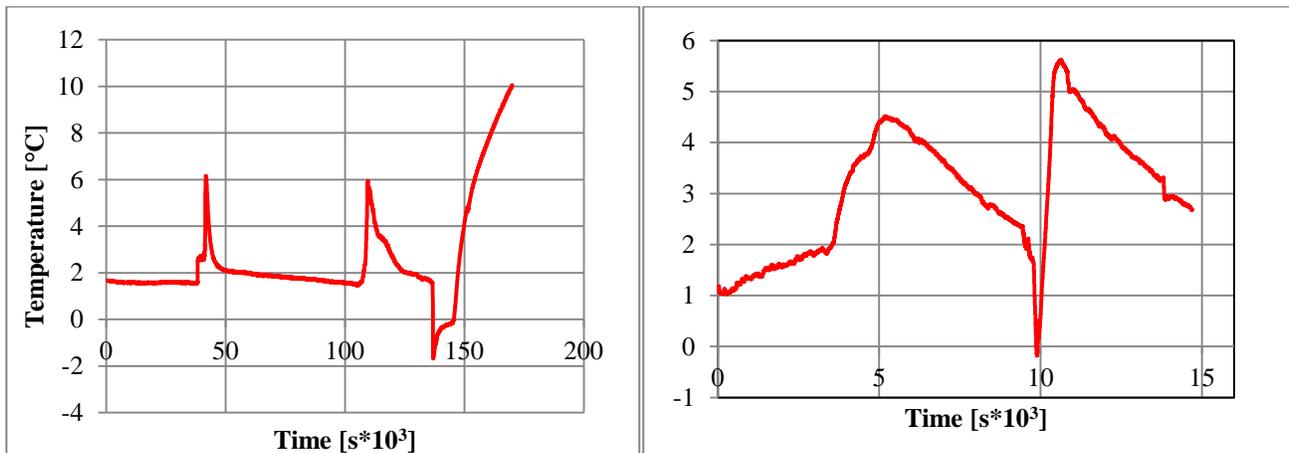

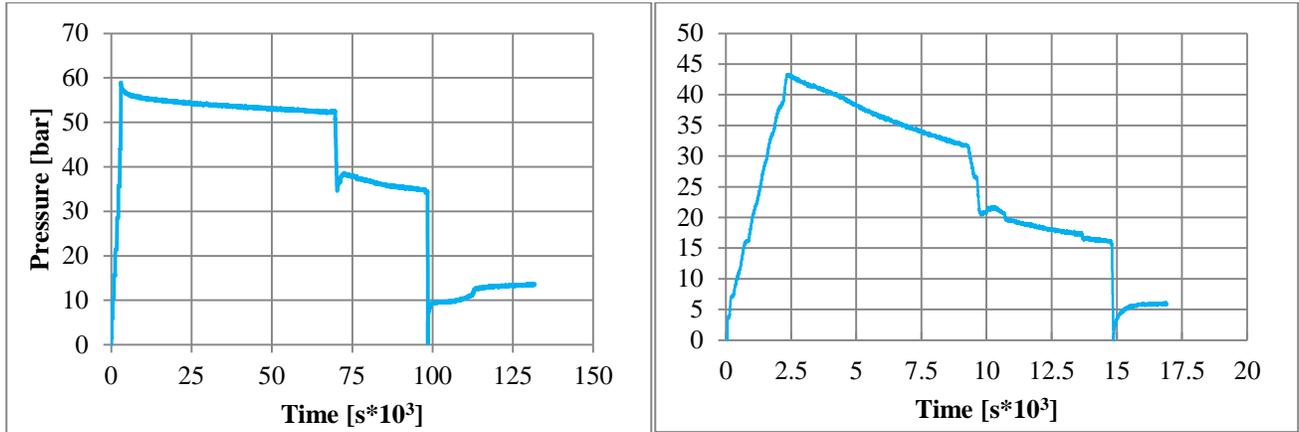Fig. 2: Temperature trend over time in Test 1 (at left) and Test 2 (at right).

Fig. 3: Pressure trend over time in Test 1 (at left) and Test 2 (at right).

Table 2: Main parameters describing Test 3 and Test 4, realized in presence of salt (40 g/l).

|		**Methane hydrate formation**						**Carbon dioxide replacement**				
	Test 1	Test 2		Test 1	Test 2		Test 1	Test 2		Test 1	Test 2
P_i [bar]	57.73	59.01	P_f [bar]	51.99	54.75	P_i [bar]	28.65	30.88	P_f [bar]	24.36	27.96
T_i [°C]	1.87	4.22	T_f [°C]	-0.15	-0.45	T_i [°C]	3.37	-0.05	T_f [°C]	0.19	-0.73
Z_i	0.82	0.82	Z_f	0.84	0.83	Z_i	0.86	0.84	Z_f	0.91	0.86
n_{CH4INJ} [mol]	0.701	0.730	n_{CH4HYD} [mol]	0.077	0.043	% CO_{2i}	85.15	94.09	% CO_{2f}	37.47	34.53
						n_{CO2INJ} [mol]	0.476	0.580	n_{CO2HYD} [mol]	0.183	0.238
						$n_{CO2DISS}$ [mol]	0.189	0.225			
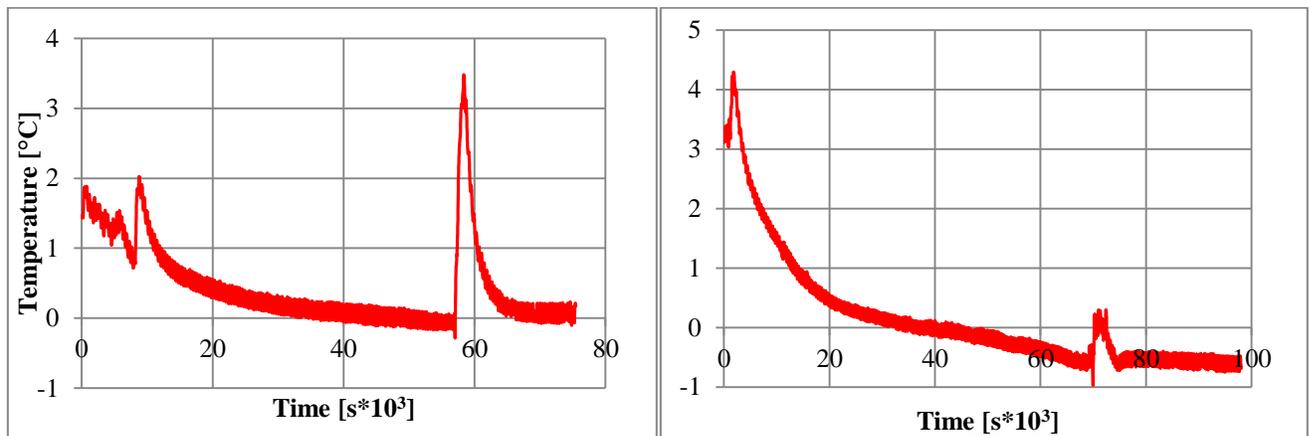
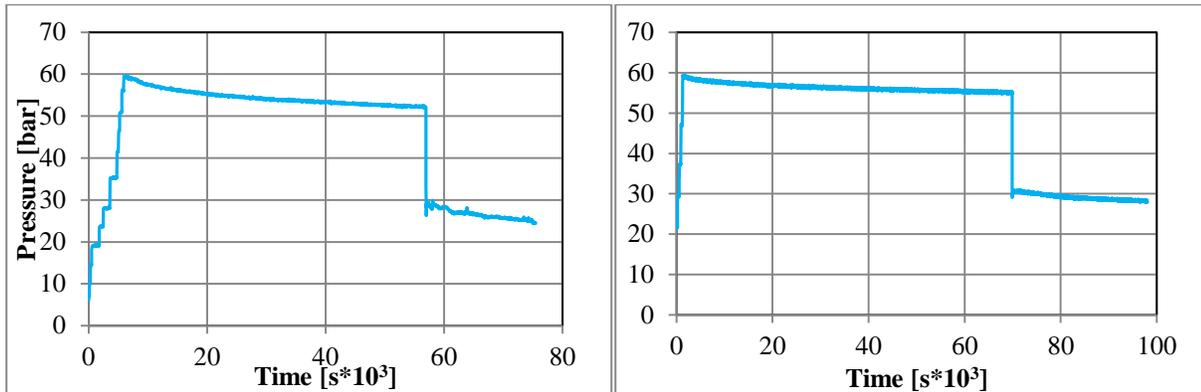Fig. 4: Temperature trend over time in Test 3 (at left) and Test 4 (at right).

Fig. 5: Pressure trend over time in Test 3 (at left) and Test 4 (at right).

The first difference that clearly appears comparing tests carried out with and without salt stays in the quantity of methane entrapped into hydrate in the process first phase. Tests 1 and 2 involved in hydrate formation respectively 0.091 and 0.153 moles of methane; on the contrary, in tests 3 and 4 only 0.077 and 0.043 moles were encaged. That confirms how present in literature: sodium chloride is a chemical inhibitor for hydrate and, even if the initial pressure of each test is similar (thus the respective quantities of gas injected inside the reactor) in test realized without methane hydrate formed in the first phase are at least double than other tests. Another difference of interest is the initial pressure of the replacement process. The lowest value registered in tests 3 and 4 is 28.65 bar, while in absence of salt the process was able to start also at 21.56 bar. That information needs to be considered for well understanding benefits of performing CH_4/CO_2 replacement in a saline environment. Advantages stay in increasing the distance existing between methane and carbon dioxide hydrate equilibrium curves and in both cases the presence of sodium chloride moved these curves to higher pressure and/or lower temperature. That permits to draw a primary conclusion: even if the distance between equilibrium curves remains the same, the presence of salt gives the possibility to inject in the hydrate reservoir a greater quantity of carbon dioxide (because all pressure values are shifted to higher values and so the respective quantities of gas), allowing the possibility of forming a more elevated amount of CO_2 hydrate. During the replacement phase, CO_2 hydrate occur in two different ways: i) the replacement of methane continued into already existing clathrates and ii) the formation of ex – novo hydrate. The possibility of injecting a grater quantity of CO_2 (per unit of volume) without reducing the distance between equilibrium curves than the classical configuration reached in demineralised water, allows to store a greater quantity of carbon dioxide. Thus the presence (or the insertion) of sodium chloride permits to improve one of the two most important topics that replacement strategies have: the maximization of carbon dioxide entrapped into water cages and so permanently stored. Finally, the most important aspect to analyse is the mole number of carbon dioxide involved into hydrate. In tests performed without salt that parameter was 0.072 (Test 1) and 0.066 (Test 2) moles; in both cases that value is widely lower than the respective obtained in experiments carried out with salt, that reached 0.183 moles in Test 3 and 0.238 moles in Test 4. That result may assume different meanings. Sodium chloride strongly hindered methane hydrate formation during the first phase of the process, providing more space for a sudden ex – novo hydrate formation. Clearly the higher distance between thermodynamic conditions suitable for CH_4 hydrate stability in presence of N_aC_l and pressure – temperature values present inside the reactor during the replacement phase, favoured a more pronounced exchange between the two gaseous species. In every case, results shown in the present work prove how the presence of sodium chloride increased the quantity of carbon dioxide permanently stored in form of hydrate. In literature the use of chemical inhibitors for intervening in natural gas hydrate reservoirs is mainly finalized to methane recovery; in this work the purpose of valuating that method also for improving CO_2 replacement strategies, has been carried on and strengthened with experimental evidence. Future works will be implemented for finding other chemical inhibitors able to improve the replacement process efficiency and for well comprehend how the exploitation of salt already present in the reservoir, or the adding of a further quantity from the external, may optimize the process.

5. Conclusion

The present work investigates and describes the possibility of increasing the CO_2 replacement process efficiency by exploiting sodium chloride and its properties. In literature is often reported the coupling of two different techniques for intervening on natural gas hydrate reservoirs; the most adopted solution consists in the contemporary use of depressurization and thermal stimulation. Here we proposed to couple the CO_2/CH_4 replacement with the use of chemical inhibitors. Four tests were carried out, two of them in presence of 40 g/l of sodium chloride, while the others in pure demineralised water. All tests were composed by two different phases: the primary formation of methane hydrate and then the replacement with carbon dioxide. Experiments highlighted how the presence of salt brought to a lower quantity methane hydrate formed (an obvious result considered the inhibitor properties of salt). Moreover, that led to a higher quantity of carbon dioxide stored in form of hydrate. The presence of a wider space due a lower CH_4 hydrate presence favoured a more intensive formation of ex – novo hydrate containing CO_2. Combining pressure values imposed for the replacement phase and the modified equilibrium conditions for CH_4 hydrate due to salt presence, also the exchange phase between the two gaseous specie was improved. A method for well making a distinction between ex – novo and already existing CO_2 hydrate need to be elaborated; in every case, experimental results proposed in this work clearly show how sodium chloride can be defined as a potential allied for increasing both the efficiency of replacement strategies and the quantity of CO_2 permanently stored in form of hydrate.

References

[1]   Sloan Jr. ED, Koh C. Clathrate hydrates of natural gases. CRC Press; 2007.

[2]   Sloan Jr. ED. Fundamental principles and applications of natural gas hydrates. Nature 2003;426(6964):353.

[3]   Moridis G, Reagan M, Kim SJ, Seol Y, Zhang K. Evaluation of the gas production potential of marine hydrate deposits in the Ulleung Basin of the Korean East Sea. SPE J. 14, 2009, PP. 759–781.

[4]   Mori YH. Recent advances in hydrate-based technologies for natural gas storage—a review. J Chem Ind Eng (China) vol. 54, no.1, 2003.

[5]   Boswell R, Collett TS. Current perspectives on gas hydrate resources. Energ Environ Sci 4, 2011, pp. 1206–15.

[6]   Gambelli AM. Natural gas recovery from hydrate compounds using CO2 replacement strategies: experimental study on thermal stimulation. Energy Procedia, vol. 148, 2018, pp. 647–654.

[7]   Trofimuk AA, Cherskiy NV, Tsarev VP. Accumulation of natural gases in zones of hydrate formation in the hydrosphere. Doklady Akademii Nauk SSSR 212, 1973, pp. 931–4.

[8]   Macdonald GJ. The future of methane as an energy resource. Annu Rev Energy 15, 1990, pp. 53–83.

[9]   Milkov AV. Global estimates of hydrate-bound gas in marine sediments: how much is really out there? Earth Sci Rev 66, 2004, pp. 183–97.

[10]   Li B, Liang YP, Li XS, Wu HJ. Numerical analysis of methane hydrate decomposition experiments by depressurization around freezing point in porous media. Fuel, vol. 159, 2015, pp. 925–34.

[11]   Myshakin EM, Ajayi T, Anderson BJ, Seol Y, Boswell R. Numerical simulations of depressurization-induced gas production from gas hydrates using 3-D heterogeneous models of L-Pad, Prudhoe Bay Unit, North Slope Alaska. Journal of Natural Gas Science and Engineering, vol. 35, 2016, pp. 1336–52.

[12]   Lee Y, Choi W, Seo YJ, Lee JY, Lee J, Seo Y. Structural transition induced by cage dependent guest exchange in CH4 + C3H8 hydrates with CO2 injection for energy recovery and CO2 sequestration. Applied Energy, vol. 228, 2018, pp. 229–39.

[13]   Gambelli AM, Rossi F. Natural gas hydrate: Comparison between two different application of thermal stimulation for performing CO2 replacement. Energy, vol. 172, 2019, pp.423 – 434.

[14]   Liang YP, Liu S, Zhao WT, Li B, Wan QC, Li G. Effects of vertical center well and side well on hydrate exploitation by depressurization and combination method with wellbore heating. J Nat Gas Sci Eng. Vol. 55, 2018, pp. 154–64.

[15]   Xu C-G, Li X-S. Research progress of hydrate-based CO2 separation and capture from gas mixtures. RSC Adv 35 (2014) 18301–16.

[16] Masoudi R, Tohidi B, Danesh A, Todd AC, Anderson R, Burgass RW, Yang J. Measurement and prediction of gas hydrate and hydrated salt equilibria in aqueous ethylene glycol and electrolyte solutions. Chemical Engineering Science, vol. 60, no. 15, 2005, pp. 4213–24.

[17] Mohammadi AH, Kraouti I, Richon D. Methane hydrate phase equilibrium in the presence of NaBr, KBr, CaBr2, K2CO3, and MgCl2 aqueous solutions: experimental measurements and predictions of dissociation conditions. J Chem Thermodyn, vol. 41, no. 6, 2009, pp. 779–82.

[18] Farhang F, Nguyen AV, Sewell KB. Fundamental investigation of the effects of hydrophobic fumed silica on the formation of carbon dioxide gas hydrates. Energy Fuels, vol. 28, no. 11, 2014, pp.7025–37.

[19] Nguyen NN, Nguyen AV. The dual effect of sodium halides on the formation of methane gas hydrate. Fuel 156 (2015) pp. 87–95.

[20] Babu P, Linga P, Kumar R, Englezos P. A review of the hydrate based gas separation (HBGS) process for carbon dioxide pre-combustion capture. Energy, vol. 85 (2015), pp. 261–79.

[21] Linga P, Kumar R, Englezos P. The clathrate hydrate process for post and precombustion capture of carbon dioxide. J Hazard Mater, vol. 149, no.3, 2007, pp. 625–9.

[22] Gambelli AM, Catellani B, Nicolini A, Rossi F. Experimental study on natural gas hydrate exploitation: Optimization of methane recovery, carbon dioxide storage and deposit structure preservation. Journal of Petroleum Science & Engineering, vol. 177, 2019, pp. 594–601.

[23] Miyazaki K, Masui A, Sakamoto Y, Aoki K, Tenma N, Yamaguchi T. Triaxial compressive properties of artificial methane-hydrate-bearing sediment. J Geophys ResSol Ea (2011) 116.

[24] Gambelli AM, Rossi F. Investigation on effects produced by sodium chloride presence on the CO2 hydrate formation process. The 2nd Conference of the Arabian Journal of Geosciences, Sousse, Tunisia, 25 – 28 November 2019.

[25] Gambelli AM, Filipponi M, Nicolini A, Rossi F. International Multidisciplinary GeoConference: SGEM; Sofia Vol. 19, Fasc. 4.1 : 333 – 343. Sofia: Surveying Geology & Mining Ecology Managment (SGEM). (2019) DOI: 10.5593/sgem2019/4.1/S17.043.

[26] Rossi F, Gambelli AM, Sharma DK, Castellani B, Nicolini A, Castaldi MJ: Simulation of methane hydrates formation in seabed deposit and gas recovery adopting carbon dioxide replacement strategies. Applied Thermal Engineering 148, 2019, pp. 371–381.

[27] Gambelli AM, Castellani B, Nicolini A, Rossi F. Gas hydrate formation as a strategy for CH4/CO2 separation: experimental study on gaseous mixtures produced via Sabatier reaction. Journal of Natural Gas Science and Engineering 71 (2019) 102985.