

Gas Hydrates Formation for High – Efficiency Waste Water Treatment: Experimental Removal of NH_4^+ from Water via CO_2 Hydrates Formation

Alberto Maria Gambelli^{a,*}, Federico Rossi^a, Giovanni Gigliotti^b

^aUniversity of Perugia, Engineering Department, Via G. Duranti 93, 06125, Perugia, Italy

^bUniversity of Perugia, Department of Civil and Environmental Engineering, Via G. Duranti 93, 06125, Perugia, Italy
albertomaria.gambelli@unipg.it

Waste water treatment is an essential and mandatory step for most of the industrial processes involving water. It has been widely proved that the overconsumption of this source, together with the exponential growth of anthropogenic damaging processed, lowered the quality of groundwater and, more in general, water resources, at an alarming pace. The removal of salts, ions dissolved in water and other effluents, can be carried out through several methods. Membrane separation, evaporation and crystallization are the most applied for water recovery, while membrane, chemical precipitation, adsorption, ion exchange and freezing/thawing are the most effective techniques for heavy metal ion solutions. When applying these procedures, some critical aspects must be considered, mainly associated to removal efficiency, costs, availability and non-toxicity of the raw materials, environmental concerning and other. In this context, gas hydrates can be considered an alternative solution for water treatment, capable to overcome all the critical issues related to the traditional strategies.

In particular, the formation of gas hydrates for ion removal from waste water, was proved to reach extremely high efficiencies; moreover, the removal efficiency was found to be proportional to the size of ions and to decrease with their charge. Based on these experimental considerations, this study deals with preliminary research on the removal of NH_4^+ from water. This species consists of one of the most affecting pollutants in bio – refineries and its removal is often energy intensive, with consequent high costs. Experiments were carried out in a lab – scale apparatus, where water was initially threatened with ammonium chloride at specific concentration. Carbon dioxide was finally chosen for the formation of hydrates.

1. Introduction

Gas hydrates are ice – like crystalline compounds, composed by water molecules, commonly referred as “hosts”, which form solid cavities where gaseous molecules, defined as “guests”, are physically but not chemically trapped (Galloway et al., 1970). To form the hydrate lattice, water molecules are linked through hydrogen bonding. Between water and gas molecules, only van der Waals forces are established and, being this kind of interaction extremely weaker than hydrogen bonds, the chemical interaction between the two compounds is neglected. The formation of hydrates requires the presence of suitable thermodynamic conditions, which change as a function of the guest species involved in the process (Englezos, 1993). The hydrate phase allows to liquid water to reach a more stable configuration at the local conditions: at certain conditions, the formation of ice is unfeasible while the production of hydrates is possible. In natural hydrate structure originate from three different unit cells: the cubic Structure I and Structure II and the hexagonal Structure H. The formation of a specific structure depends on the guest species (Makogon et al., 2010). The unit cells differ among each other for the typology and the number of basilar cavities they include. These cavities are indicated with the nomenclature “ n_i^{mi} ”, where “ n_i ” is the number of edges in face “ i ”, while “ mi ” is the number of faces having n_i edges. The five naturally occurring cavities are: pentagonal dodecahedron (5^{12}), tetrakaidecahedron ($5^{12}6^2$), hexakaidecahedron ($5^{12}6^4$), irregular dodecahedron ($4^35^66^3$) and icosahedron ($5^{12}6^8$). In nature, the most widespread structure is the cubic SI, whose unit cell consists of two pentagonal dodecahedrons and six tetrakaidecahedrons, because it characterizes methane and carbon dioxide hydrates (Gambelli et al., 2021).

The natural reservoirs of hydrates are considered the most abundant resource of methane; it has been estimated that such quantity, approximately equal $10^{15} - 10^{17} \text{ m}^3$, is enough to produce an amount of energy more than two times higher than the energy still obtainable from all the known and available conventional energy sources (Li et al., 2016). Approximately 97% of natural deposits are sited in deep oceans and continental margins, while the remaining 3% was discovered in permafrost regions (Kvenvolden, 1993).

Apart the energy – production field, the hydrates formation and dissociation processes can be advantageously applied in numerous key sectors, such as for seawater desalination and, more in general, ions removal from waste water (Kang et al., 2014). The so – called hydrate – based desalination technologies (HBD) (Bradshaw et al., 2006), are based on the formation of hydrate structure in the contaminated water. Ions dissolved in water cannot participate to the formation of hydrates (Lv et al., 2017). The following removal and dissociation of hydrates allows to obtain pure water, while ions remain in the aqueous phase (Rogers et al., 2007). The effect of salts and ions on the hydrates formation and dissociation processes explains the feasibility of HBD technologies and will be described in the following section. This study deals with carbon dioxide hydrate formation in presence of ammonium chloride (NH_4Cl). Different aqueous solutions of NH_4Cl were tested, in order to verify the role of ions concentration in water.

2. Effect of salts and ions on the formation and dissociation processes

The presence of salts dissolved in the aqueous solution, lowers the activity of water (Bavoh et al., 2017). The competition between columbic forces between water and salt molecules and the hydrogen bond forces between water molecules, inhibits the production of hydrates (Cha and Seol, 2013). At decreasing temperatures, the formation of hydrogen bonds is predominant and the consequent production of hydrates allows to recover pure water. The removal efficiency can be calculated according to (Montazeri and Koliopoulos, 2022):

$$\text{Removal eff.} = \frac{(C_{A0} - C_A)}{C_{A0}} * 100 [\%] \quad (1)$$

In the equation, C_{A0} is the concentration of ion A in the feed saline solution and C_A is its concentration in the produced fresh water. However, only the formation of hydrates is affected by the presence of ions, while the dissociation phase is only function of the crystalline structure of hydrates (Sahu et al., 2018). The removal efficiency of ions from water mainly depends on the size and charge: smaller sizes and higher charge numbers reduce the removal efficiency. It was proved that the removal efficiency increases with the decreasing of temperature and is also proportional to the initial concentration of salts in water. Ions with high charges are capable to form stronger bonds with water molecules and, as a consequence of it, their removal from water is more difficult. Conversely, the diffusion of ions is reverse proportional to their size (Lu et al., 2021) and their removal is consequently easier (Englezos et al., 1987). Thus, the removal efficiency for anion and cations is similar: anions have a stronger interaction in the electrolyte solution but, on the other side, cations have on average larger size. It is expected to obtain high removal efficiency of ammonium ion from water.

3. Materials and Methods

3.1 Experimental apparatus

The experiments were carried out in a small – scale (volume equal to 1000 cm^3) unstirred reactor, inserted in a cooling room to control temperature and equipped with pressure and temperature sensors. A deepened description of the reactor can be found in (Rossi et al., 2021); here only some relevant details are provided. The cooling room allows to lowers the internal temperature up to $-10 \text{ }^\circ\text{C}$, with accuracy equal to $\pm 10 \text{ }^\circ\text{C}$. The decreasing of temperature can be defined manually, or it can be programmed. With this latter option, it is possible to have the same evolution of temperature in all the experiments, thus favouring the reproducibility of results. The temperature was measured with Type K thermocouples, having class accuracy 1. Six devices were inserted in the reactor, in order to detect any internal gradient. However, during this study, none gradient was observed and only one temperature value (for each measure) was shown in the experimental section, consisting of a mean of the values measured by each thermocouple. The internal pressure was measured with a digital manometer, model MAN-SD, having accuracy equal to $\pm 0.5\%$ of full scale. All the sensors were connected to a data acquisition system (provided by National Instrument) and managed in LabView.

3.2 Materials

The reactor was filled with 0.27 L of demineralized water and 0.8 L of porous silica sand. Before being inserted in the reactor, water was mixed with NH_4Cl . Four different concentrations were tested: expressed as percentage of weight, in the various systems, the quantity of salt dissolved in the aqueous solution was equal to 1.35%, 4.05%, 9.46% and 13.51%. This percentage mean a related concentration of NH_4^+ equal to 1.35, 9.46 and 13.51 wt%. Sand was inserted exclusively to favour the growth of hydrates and make the process diffused along the

whole reactor and not exclusively limited to the gas – liquid interface. The porous medium consists of spherical grains, having size in the range of 150 – 250 μm . The porosity of the medium is equal to 34%. Finally, Ultra High Purity (UHP) carbon dioxide was used. The purity degree was equal to 99.997%.

3.3 Experimental procedure

The methodology followed for the production and dissociation of hydrates, is the same described in previous studies (Gambelli and Rossi, 2023). The reactor was filled with sand and with the aqueous solution selected. Then the reactor was closed and CO_2 was fluxed within it. The injection phase occurred at high temperatures, enough elevated to avoid the formation of hydrates during such phase. CO_2 was fluxed until reaching the desired internal pressure. The cooling room was set at 0 $^\circ\text{C}$. With the growth of hydrates, the enclathration of gas molecules led to the lowering of pressure. In correspondence of the lowest temperature, as soon the pressure stabilized, the formation phase ended. The cooling room was switched off and the gradual increase of temperature led to the complete dissociation of hydrates previously formed. Pressure and temperature values were constantly measured and sampled every 30 s; with these values, it was possible to perfectly define the thermodynamic evolution of the experiments. With these data and also considering the properties of the guest involved (mainly its solubility), it is possible to define the quantity of hydrates formed. The results obtained were then compared with an experimental phase boundary equilibrium line for CO_2 hydrates, defined with values collected from literature and available elsewhere.

4. Results and Discussion

Figures 1 – 2 show the pressure – temperature profile of CO_2 hydrates formation and dissociation in presence of 0.5 wt% NH_4^+ .

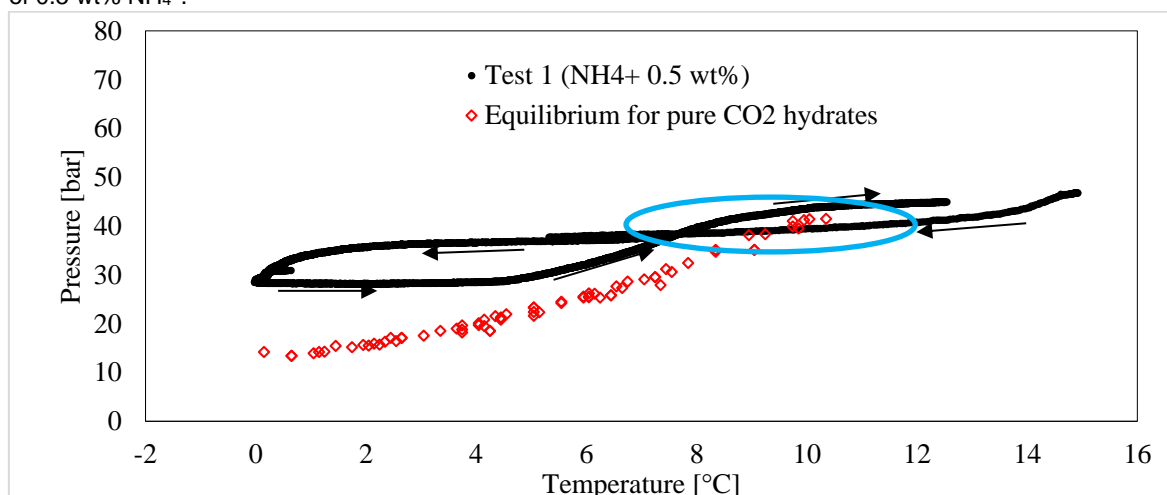


Figure 1: CO_2 hydrates formation and dissociation in Test 1 (NH_4^+ 0.5 wt%).

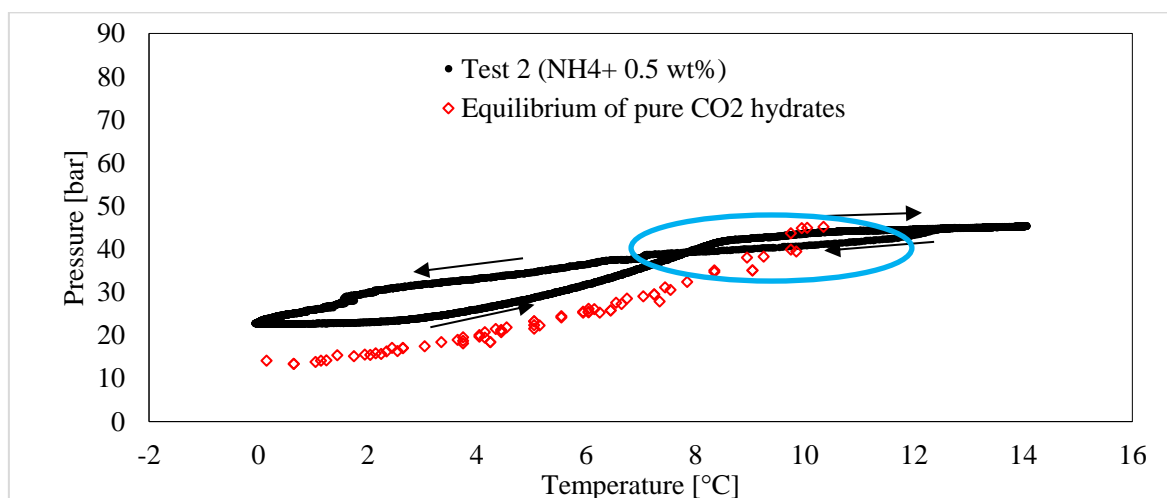


Figure 2: CO_2 hydrates formation and dissociation in Test 2 (NH_4^+ 0.5 wt%).

About dissociation, the curve did not vary significantly between the tests and its trend was comparable with the phase boundary equilibrium curve for pure carbon dioxide hydrates. The difference mainly depended on the porous medium inserted in the reactor and on the process conditions (Ghaedi et al., 2016). Silica sand, as clay, zeolite and others, may alter the hydrate formation/dissociation mechanisms, due to their physical (mainly) and chemical properties. The main relevant properties in this sense are particle size, porosity of the whole medium, permeability, thermal conductivity and water saturation (Yang et al., 2016). It was found that a larger surface area of media favours the production of hydrate structures. Conversely, the trend observed during hydrates formation is function of the stochastic nature of the process. This latter contribution is clearly visible in the horizontal pressure trend, occurred in each test immediately after hydrates formation. Once the production of clathrates ended, the internal temperature was increased again to obtain their dissociation. However, the dissolution of water cages occurred with a certain delay and pressure remained constant. As previously asserted, ions intervened on the formation, by shifting it at more severe thermodynamic conditions, while the dissociation was not altered. As a consequence of it, the distance between the two curves increased. The role of memory effect on this portion of tests, is clearly visible in Test 1. In this first experiments, the usage of fresh water made, the conditions required for hydrate formation, still more severe than in other tests. Therefore, pressure remained constant for a higher temperature interval than in the other tests. In particular for Test 1, the formation phase ended at 0.07 °C, while the dissociation started only when the internal temperature reached 4.53 °C. Finally, the lower kinetics of the first experiment can be also verified with the pressure established at the end of hydrates formation. In Test 1, 28.48 bar were reached, while in the other tests better results were reached in terms of hydrate production and the pressure dropped to 20.55 bar. A further aspect of interest consists of the overlapping between formation and dissociation curves, which appeared in each test and has been highlighted with a blue circle in figures 3 – 5. Theoretically, the two curves should converge before the system exits from the hydrate stability zone, because the difference between them is only related to hydrates, whose presence is excluded outside from such region. However, the so – called “anomalous self – preservation”, or the capability of the hydrate system to preserve itself, for a certain time period, even at conditions unfeasible for the permanence of hydrates, often deviates the dissociation curve and shifts the convergency point slightly outside from the stability region. Therefore, the phenomenon observed in the tests cannot be related to the anomalous self – preservation effect. In the following diagrams, the formation and dissociation of carbon dioxide hydrates is shown in presence of NH_4^+ concentrations, in the aqueous solution, respectively equal to 3.5 (Figure 3) and 5 wt% (Figure 4).

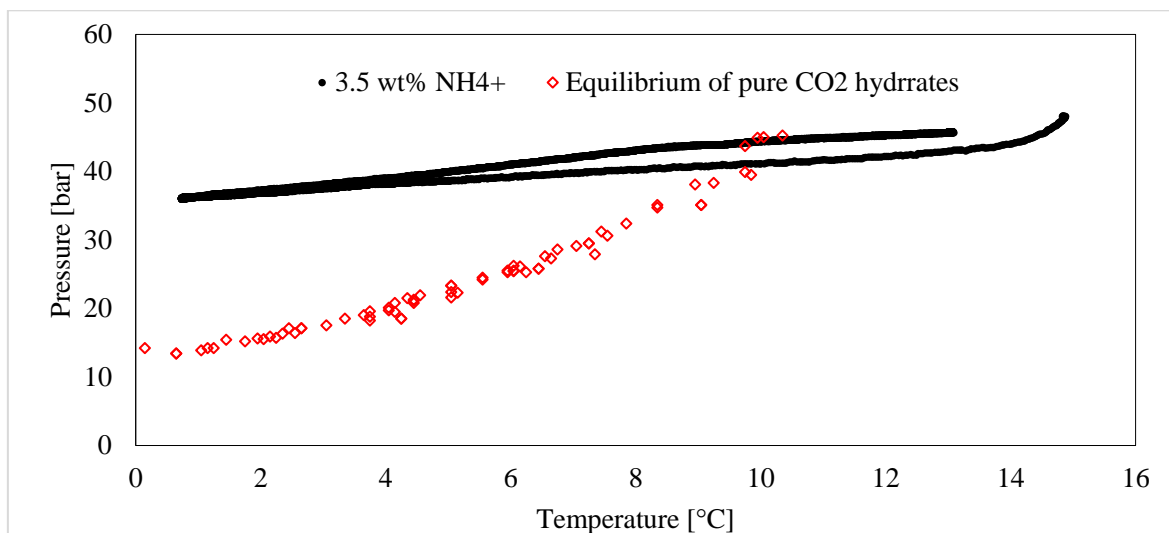


Figure 3. CO_2 hydrates formation and dissociation in presence of 3.5 wt% NH_4^+ in the aqueous solution.

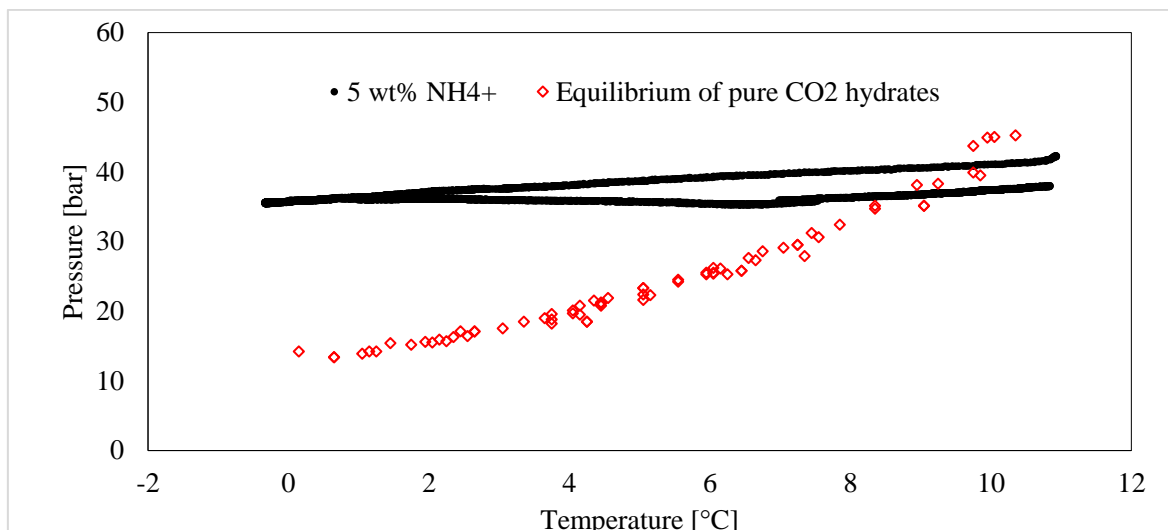


Figure 4. CO₂ hydrates formation and dissociation in presence of 5 wt% NH₄⁺ in the aqueous solution.

The increase of NH₄Cl concentration in water, made the formation of hydrates negligible or completely absent. The pressure varied exclusively with temperature, while none relevant change of it was found due to the formation of hydrates. The only sign of a minor production of hydrates can be found in the lowest value of pressure reached from the system at the end of the hydrates formation phase, which was respectively equal to 33.79 bar at 1.5 wt% NH₄⁺, 36.24 bar at 3.5 wt% NH₄⁺ and 36.41 bar at 5 wt% NH₄⁺. Differently, the trend of pressure observed during the temperature decrease and the one observed during its increase, showed a weak proportionality with the salt concentration in water.

Based on these results, it can be asserted that NH₄Cl is an inhibitor for hydrates. According to the current literature, the inhibition interests exclusively the formation phase, while it does not affect the dissociation process. Moreover, the effect is proportional to the concentration of salt in the aqueous phase. However, such proportionality is not linear: at 0.5 wt% NH₄⁺, a massive production of hydrates was achieved, while at the higher concentrations tested, the growth of hydrates was weak or completely absent. It suggests that the linear proportion between salt concentration and inhibiting effect, exists only within a narrow range, which needs of further experiments to be definitively identified. Therefore, at low concentrations, the formation of hydrates can be exploited as techniques for NH₄⁺ removal from waste water. Further steps of the present research will consist of the accurate definition of the proportionality between concentration and inhibiting effect at low NH₄⁺ concentrations and the definition of the NH₄⁺ removal efficiency, via hydrates formation, via analyses of water composition before the formation of hydrates and after their production and removal from the aqueous phase.

5. Conclusions

This study deals with carbon dioxide hydrates formation and dissociation in an aqueous solution containing NH₄Cl at different concentrations, or 0.5, 3.5 and 5 wt%. According to the literature, the dissolution of salt and the consequent release of ions in water, affect the process and inhibits the production of hydrates. Scope of this research was to detect the inhibiting action produced by NH₄Cl and to describe it under a thermodynamic point of view. If this additive intervenes on the process, it could be possible to apply the formation of hydrates as strategy for NH₄⁺ removal from water. The experimental results allowed to reach the following conclusions:

- 1) As expected, NH₄Cl acted as inhibitor for CO₂ hydrates formation;
- 2) Differently, none relevant change was observed during the dissociation of hydrates;
- 3) The inhibiting action increased with concentration; however, the proportionality was not linear. In particular, at NH₄⁺ concentrations equal or higher than 3.5 wt%, the production of hydrates was negligible or completely absent. It suggests that a linear correlation can be found only at lower concentration of the additive in the aqueous solution.
- 4) At these concentrations, the massive formation of hydrates is possible and, because the process is highly sensible to the additive, the removal of NH₄⁺ from water via hydrates formation was definitively proved.

Further developments of this study will consist of the definition of the range in which the inhibiting effect is linearly proportional to the concentration. Then, the NH₄⁺ removal efficiency will be experimentally measured,

with appropriate analyses of the water composition before the formation of hydrates and after their production and removal from the aqueous phase.

References

- Bavoh C.B., Partoon B., Lal B., Gonfa G., Foo Khor S., Sharif A.M., 2017, Inhibition effect of amino acids on carbon dioxide hydrate. *Chem. Eng. Sci.*, 171, 331 – 339.
- Bradshaw R.W., Simmons B.A., Majzoub E.H., Clift W.M., Dedrick D.E., 2006, Clathrate hydrates for production of potable water. *Mater. Res. Soc. Symp. Proc.*, 930, 14 – 19.
- Cha J.H., Seol Y., 2013, Increasing gas hydrate formation temperature for desalination of high salinity produced water with secondary guests. *ACS Sustain. Chem. Eng.*, 1, 1218 – 1224.
- Englezos P., Kalogerakis N., Dholabhai P.D., Bishnoi P.R., 1987, Kinetics of formation of methane and ethane gas hydrates. *Chem. Eng. Sci.*, 42, 2647 – 2658.
- Englezos P., 1993, Clathrate hydrates. *Ind. Eng. Chem. Res.*, 32, 1251 – 1274.
- Galloway T.J., Ruska W., Chappellear P.S., Kobayashi R., 1970, Experimental measurement of hydrate numbers for methane and ethane and comparison with theoretical values. *Ind. Eng. Chem. Fundam.*, 9, 237 – 243.
- Gambeli A.M., Stornelli G., Di Schino A., Rossi F., 2021, Methane and carbon dioxide hydrates properties in presence of Inconel 718 particles: Analyses on its potential application in gas separation processes to perform efficiency improvement. *Journal of Environmental Chemical Engineering*, 9, 106571.
- Gambelli A.M., Li Y., Rossi F., 2022, Influence of different proportion of CO₂/N₂ binary gas mixture on methane recovery through replacement processes in natural gas hydrates. *Chemical Engineering and Processing – Process Intensification*, 175, 108932.
- Ghaedi H., Ayoub M., Bhat A.H., Mahmood S.M., Akbari S., Murshid G., 2016, The effects of salt, particle and pore size on the process of carbon dioxide hydrate formation: a critical review. *AIP Conference Proceedings*, 1787, 060001.
- Li X.S., Xu C.G., Zhang Y., Ruan X.K., Li G., Wang Y., 2016, Investigation into gas production from natural gas hydrate: a review. *Applied Energy*, 172, 286 – 322.
- Lu H., Matsumoto R., Tsuji Y., Oda H., 2001, Anion plays a more important role than cation in affecting gas hydrate stability in electrolyte solutions? – a recognition from experimental results. *Fluid Phase Equilibr.*, 178, 225 – 232.
- Lv Y.N., Wang S.S., Sun C.Y., Gong J., Chen G.J., 2017, Desalination by forming hydrate from brine in cyclopentane dispersion system. *Desalination*, 413, 217 – 222.
- Kang K.C., Linga P., Nam Park K., Choi S.J., Lee J.D., 2014, Seawater desalination by gas hydrate process and removal characteristics of dissolved ions (Na⁺, K⁺, Mg²⁺, Ca²⁺, B³⁺, Cl⁻, SO₄²⁻). *Desalination*, 353, 84 – 90.
- Kvenvolden K.A., 1993, Gas hydrates – geological perspective and global change. *Rev. Geophys.*, 31, 173 – 187.
- Makogon Y.F., Holditch S.A., Makogo T.Y., 2007, Natural gas-hydrates – a potential energy source for the 21st Century. *J. Petrol. Sci. Eng.*, 56, 14 – 31.
- Montazeri S.M., Koliopoulos G., 2022, Hydrate based desalination for sustainable water treatment: A review. *Desalination*, 537, 115855.
- Rogers R., Zhang G., Dearman J., Woods C., 2007, investigations into surfactant/gas hydrate relationship. *J. Pet. Sci. Eng.*, 56, 82 – 88.
- Rossi F., Li Y., Gambelli A.M., 2021, Thermodynamic and kinetic description of the main effects related to the memory effect during carbon dioxide hydrates formation in a confined environment. *Sustainability*, 13, 13797.
- Sahu P., Krishnaswamy K., Ponnani N.K., Pande A., 2018, A thermodynamic approach to selection of suitable hydrate formers for seawater desalination. *Desalination*, 436, 144 – 151.
- Yang S., Babu H., Sam F., Linga P., 2016, Carbon dioxide hydrate kinetics in porous media with and without salts. *Applied Energy*, 162, 1131 – 1140.