

Editorial

# Special Issue “Analysis and Experimental Study on Natural Gas Hydrate Exploitation Processes”

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Gas hydrates are crystalline structures formed by water molecule cages hosting gas molecules. Natural reservoirs of methane hydrates are found both in continental sedimentary rocks in polar areas and in marine sediments. Major deposits have been identified at the borders of the continental platforms, where the presence of organic material and the appropriate conditions of pressure and temperature favor hydrate formation. Natural gas hydrates (NGHs) are the largest reservoir of natural gas on earth; it is estimated that the organic carbon stored in NGHs is twice the amount of natural gas from all available fossil sources.

Research outcomes from theoretical studies, molecular simulations, and experimental tests in laboratory settings have revealed the possibility of natural gas recovery and energy production from NGHs. The proposed methods for natural gas release from NGHs are depressurization, thermal stimulation, in situ combustion, and injection of chemical inhibitors for the hydrate equilibrium curve shift. In addition, a novel technique based on the injection of carbon dioxide into NGH reservoirs was proposed to obtain methane and simultaneously store carbon dioxide; considering the ideal carbon ratio of 1, the obtained fuel is carbon neutral.

In fact, if CO<sub>2</sub> is injected into NGH sediments, it causes CH<sub>4</sub> release and CO<sub>2</sub> hydrate formation, with the so-called CO<sub>2</sub>–CH<sub>4</sub> replacement process.

There is a vast literature on the energy potential of NGHs, with studies in laboratory settings and some recent field trials. Nevertheless, several issues of hydrate science need further investigation, for example, the kinetic and thermodynamic aspects related to the CO<sub>2</sub>–CH<sub>4</sub> replacement process, but also the formation process of pure species for the application of hydrate-based technologies in several areas of the energy industry.

On the above-mentioned topics, this Special Issue has collected five research papers, with eighteen authors from two countries in Europe (Italy and Denmark), the United States, and China. The most relevant outcomes of each paper are here briefly described.

As far as CO<sub>2</sub>–CH<sub>4</sub> replacement in NGHs is concerned, scientific research aims to improve the efficiency of this process to make the exploitation of NGHs economically advantageous. In [1], the authors analyzed the effect of sodium chloride (NaCl) on the CO<sub>2</sub>–CH<sub>4</sub> replacement process in NGHs, carrying out 18 hydrate formation tests, involving pure CO<sub>2</sub> and methane hydrates, with three different salt concentrations (0, 30, and 37 g/L NaCl).

The results show that NaCl exerts a stronger inhibitor effect on methane hydrates than on CO<sub>2</sub> hydrates, resulting in a bigger area between the pressure–temperature profile of CO<sub>2</sub> hydrates and the pressure–temperature profile of methane hydrates. A bigger distance between the two p–T curves means that it is easier to move from the methane hydrate stability zone, inducing the release of gaseous methane and the formation of CO<sub>2</sub> hydrate. Therefore, the presence of salt water may increase the efficiency of the CO<sub>2</sub>–CH<sub>4</sub> replacement process.



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The exploitation of NGHs as an energy source requires the precise prediction of the NGH formation conditions, as proposed in [2]. The authors proposed a novel hybrid genetic algorithm–support vector machine (GA–SVM) model, where the input variables are the relative molecular weight of natural gas and the hydrate formation pressure, while the output variable is the hydrate formation temperature. The GA–SVM model is a new hybrid model, where a neural network with genetic algorithms is used to optimize the process parameters of a support vector machine model. The new model is compared with nine other models, revealing that the GA–SVM model has the smallest average absolute relative deviation (0.04%). The paper proposed a new approach for an accurate prediction of the gas hydrate formation conditions for gas molecular weights in the range of 15.64–28.97 g/mol and natural gas pressures in the range of 367.65–33,948.90 kPa.

A computational approach is also used in [3] to investigate the hydrogen storage capacity in the sII hydrate structure. Hydrate science is here applied to hydrogen storage as an alternative sustainable pathway. The authors applied density functional theory and molecular dynamic simulations to investigate the stability of sII hydrogen hydrates. Calculations show that the best cage occupancy configuration is formed by two hydrogen molecules for the small cages and five hydrogen molecules for the large cages. The calculated hydrogen storage capacity is about 5.6 wt%. Molecular dynamic simulations enable the discovery that hydrogen hydrate can occur at mild pressures (>20 MPa) and low temperatures (<250 K). The results of such simulations highlight that clathrate hydrates could also be applied as a method for hydrogen storage.

Finally, two papers of this Special Issue are devoted to improving the kinetics of hydrate formation, which is a crucial aspect for the development of the hydrate-based technologies on industrial scales.

In [4], the authors studied the kinetics of methane hydrates in the presence of sodium dodecyl sulfate (SDS) and investigated the effect of SDS concentration on the nucleation temperature, induction time, gas uptake, and hydrate saturation. The authors also applied a rocking cell, traditionally used to study hydrate inhibitors, to evaluate the effect of hydrate promoters on methane hydrate formation, varying the concentration in the range of 500–3000 ppm.

The experimental results suggest that the concentration of SDS is a critical factor for the kinetics of methane hydrates. High concentrations of SDS lead to low induction times, while low concentrations lead to high gas uptakes and high hydrate saturations. Finally, the absorption and surface tension are both affected by the critical micelle concentration of SDS; the absorption modifies the gas uptake, while the surface tension influences the induction time below the critical micelle concentration. Such results contribute to the understanding of methane hydrate formation and storage with SDS as a kinetic promoter, leading towards an industrial application of this technology.

In [5], the kinetics of hydrate formation from flue gas in the presence of selected amino acids and surfactants as promoters are investigated. Four amino acids with a concentration of 3000 ppm are selected, considering different hydropathy indexes. Their hydrate promotion capabilities are evaluated through constant ramping and isothermal experiments at 120 bar pressure and 1 °C, and compared with those of SDS (500–3000 ppm) and water. The results show the correlation between the hydrate promotion capability of amino acids and their hydrophobicity. In particular, hydrophobic amino acids have a stronger hydrate promotion capability than water and hydrophilic amino acids. Considering the concentration, hydrophobic amino acid concentrations between 2000 and 3000 ppm result in a similar promotion capability to SDS. This research proves the potential use of amino acids as kinetic additives (promoters or inhibitors) of clathrate hydrates. They may be a non-toxic and eco-friendly alternative to traditional thermodynamic and kinetic promoters.

The five papers published in this Special Issue present new, important findings on hydrate science, contributing significantly to the development of hydrate-based technologies for energy applications. The Guest Editors suggest the submission of further articles in the Special Issue “Green Processes for Sustainable Fuel Production”.

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