

Research Article

Natural Gas Production from Methane Hydrate Deposits Using CO₂ Clathrate Sequestration: State-of-the-Art Review and New Technical Approaches

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This paper focuses on reviewing the currently available solutions for natural gas production from methane hydrate deposits using CO₂ sequestration. Methane hydrates are ice-like materials, which form at low temperature and high pressure and are located in permafrost areas and oceanic environments. They represent a huge hydrocarbon resource, which could supply the entire world for centuries. Fossil-fuel-based energy is still a major source of carbon dioxide emissions which contribute greatly to the issue of global warming and climate change. Geological sequestration of carbon dioxide appears as the safest and most stable way to reduce such emissions for it involves the trapping of CO₂ into hydrocarbon reservoirs and aquifers. Indeed, CO₂ can also be sequestered as hydrates while helping dissociate the in situ methane hydrates. The studies presented here investigate the molecular exchange between CO₂ and CH₄ that occurs when methane hydrates are exposed to CO₂, thus generating the release of natural gas and the trapping of carbon dioxide as gas clathrate. These projects include laboratory studies on the synthesis, thermodynamics, phase equilibrium, kinetics, cage occupancy, and the methane recovery potential of the mixed CO₂-CH₄ hydrate. An experimental and numerical evaluation of the effect of porous media on the gas exchange is described. Finally, a few field studies on the potential of this new gas hydrate recovery technique are presented.

1. Introduction

Since their initial discovery by Sir Davy Humphrey in 1810, natural gas hydrates have graduated from a laboratory oddity to a hydrocarbon production nuisance as seen forming inside the chamber bell used to cap the spill in the deep water horizon oil well, and so forth, before being considered as a potential energy resource for the future. For many decades, countries such as the USA, Canada, Japan, India, and China have funded major research projects to get a better understanding and knowledge of natural gas hydrates [1]. Resource assessment studies have demonstrated the huge potential of gas hydrate accumulations as a future energy resource [2].

World energy demand is steadily rising due to global population and economic growth. World energy consumption is expected to increase from 472 quadrillion Btu to 678

quadrillion Btu in 2030, that a total increase of 44% from 2006 to 2030 [3]. China and India are currently the fastest growing non-OECD economies, and their combined energy consumption is expected to represent 28% of the world energy consumption in 2030 [4]. Despite recent progress in obtaining energy from nonfossil fuels, nearly 80% of the world energy supply will still be generated from oil, natural gas, and coal. The combustion of these fuels is a major source of carbon dioxide emissions. Unfortunately, a perceived change in the global climate has been attributed to the increasing concentration of Green House Gases such as CO₂ in the atmosphere. Geological sequestration of CO₂ is a potential solution to this problem. Typical geological sequestration consists in capturing and storing the gas in a geological setting such as active and depleted oil/gas reservoir, deep brine formations, deep coal seams, and coal-bed methane formation [5]. Sequestration of CO₂ in marine

and arctic hydrates is considered as an advanced geologic sequestration concept, which needs further investigation [6].

Gas hydrates are found in nature, in permafrost and marine environments. They contain mixtures of gases such as methane and ethane, with carbon dioxide and hydrogen sulfide as trace. Methane is the predominant component of natural gas hydrates, which is the reason they are simply called methane hydrates. Gas hydrates form under specific conditions: (1) the right combination of pressure and temperature (high pressure and low temperature), (2) the presence of hydrate-forming gas in sufficient amounts, and (3) the presence of water. CO₂ and CH₄ hydrates are of interest with CO₂ being a preferential hydrate guest former when compared to CH₄. In addition, CO₂ hydrates are more stable than CH₄ hydrates, and the exposition CH₄ hydrates to carbon dioxide has resulted in the release of methane, while carbon dioxide remained trapped. Thus, the use of carbon dioxide to recover natural gas from hydrate deposits has gained more and more relevance in the industry.

Other techniques are being explored in the area of production from hydrate deposits. However, the resource is still not commercially viable due to technical, environmental, and economic issues. Any further investigation of the mixed CO₂-CH₄ gas hydrate properties could lead to major breakthroughs in the fields of unconventional resource production and carbon sequestration.

2. What Are Methane Hydrates?

Natural gas hydrates, commonly called methane hydrates, are crystalline compounds, which are constituted of gas and water molecules. The water molecules or host molecules form a hydrogen-bonded lattice, in which gas molecules or guest molecules are entrapped. The presence of guest molecules stabilizes the lattice due to the sum of the attractive or repulsive forces between molecules known as the Van der Waals forces. There is no bonding between the host molecules and the guest molecules, that is, the gas molecules are free to rotate inside the lattice [2, 7-9]. Gas hydrate formation and dissociation are described by the following equations:

$$G + N_H H_2O \rightarrow G \cdot N_H H_2O \text{ and } G \cdot N_H H_2O \rightarrow G + N_H H_2O,$$

where N_H is the hydration number and G is the guest molecule. Gas hydrate formation is an exothermic process while gas hydrate dissociation is endothermic.

Gas hydrates come under three distinguishable structures: type I, type II, and type H. All structures involve a network of interconnected cages. Structure I (sI) hydrates display unit cells that are constituted of 46 water molecules organized into 2 small cavities and 6 large cavities. The small cavities are dodecahedral cages with 12 pentagonal faces. They are usually denoted as 5¹² cages. The large cavities are 14-sided polyhedra (tetrakaidecahedron), which are usually denoted as 5¹²6². The unit cells of Type II hydrates (sII) contain 136 water molecules. They are organized into 16 small cavities and 8 large cavities. The small cavities are of the same kind as the small cavities in sI hydrates. However, the large cavities are hexacaidecahedra (5¹²6⁴) with

12 pentagonal faces and 4 hexagonal faces [9]. In 1987, a new hydrate structure was discovered and called structure H (sH). This structure contains 34 water molecules in its unit cell, forming a hexagonal lattice. Type H hydrates display three types of cavities: three 5¹² cages, two 4³5⁶6³ cages, and one large 5¹²6⁸ [9, 10].

Because of the size difference between the cages, the three types of hydrates tend to trap different kinds of molecules. Type I hydrates are usually formed with smaller molecules such as ethane and hydrogen sulfide. Type II clathrates are formed by larger molecules such as propane and isobutane. Type H hydrates require the presence of a small molecule such as methane and a type H gas former like 2-methylbutane and cycloheptane to be created. They are less common in nature than the other types of gas hydrates [9, 10]. Figure 1 illustrates the different sorts of hydrate structures and some of their gas-forming molecules. These structures have been observed with X-ray diffraction.

Methane and carbon dioxide both form type I hydrates. The comparison of their hydrate phase equilibrium conditions suggests the occurrence of a transition zone between both hydrate equilibrium curves where CO₂ hydrates can exist while CH₄ hydrates dissociate into methane gas and water. The hydrate phase diagrams of both compounds are presented in Figure 2. In addition, the heat of formation of carbon dioxide hydrate (-57.98 kJ/mole) is greater than the heat of dissociation of methane hydrate (54.49 kJ/mole). The heat released from the formation of carbon dioxide hydrate in the presence of methane hydrate should be sufficient to dissociate the methane hydrate and recover methane gas [11]. Thirdly, it has been experimentally proven that carbon dioxide is preferentially trapped over methane in the hydrate phase [12]. These observations fuel the growing interest in the use of carbon dioxide for natural gas recovery from gas hydrate deposits.

Gas hydrates can be naturally found in permafrost areas and subsea environments. The temperature and pressure gradients which are at play underneath the Earth help define specific hydrate occurring zones, when associated to the thermodynamic hydrate equilibrium conditions. These zones are called hydrate stability zones [8]. Figure 3 displays the hydrate stability zones in permafrost and marine environments.

Assessment methods for gas hydrates include seismic studies (bottom simulating reflectors), pore water salinity measurements, well-logging, and direct observations from core samples [13]. So far, 89 hydrate locations have been discovered all over the world [14]. These locations are presented in Figure 4.

3. Current Research Status

Three main production methods have so far been explored for the recovery of natural gas from hydrate deposits: depressurization, thermal stimulation, and inhibitor injection [8, 15, 16]. These methods aim at thermodynamically destabilizing the reservoir environment to provoke the release of the entrapped gas [17, 18]. They have been investigated

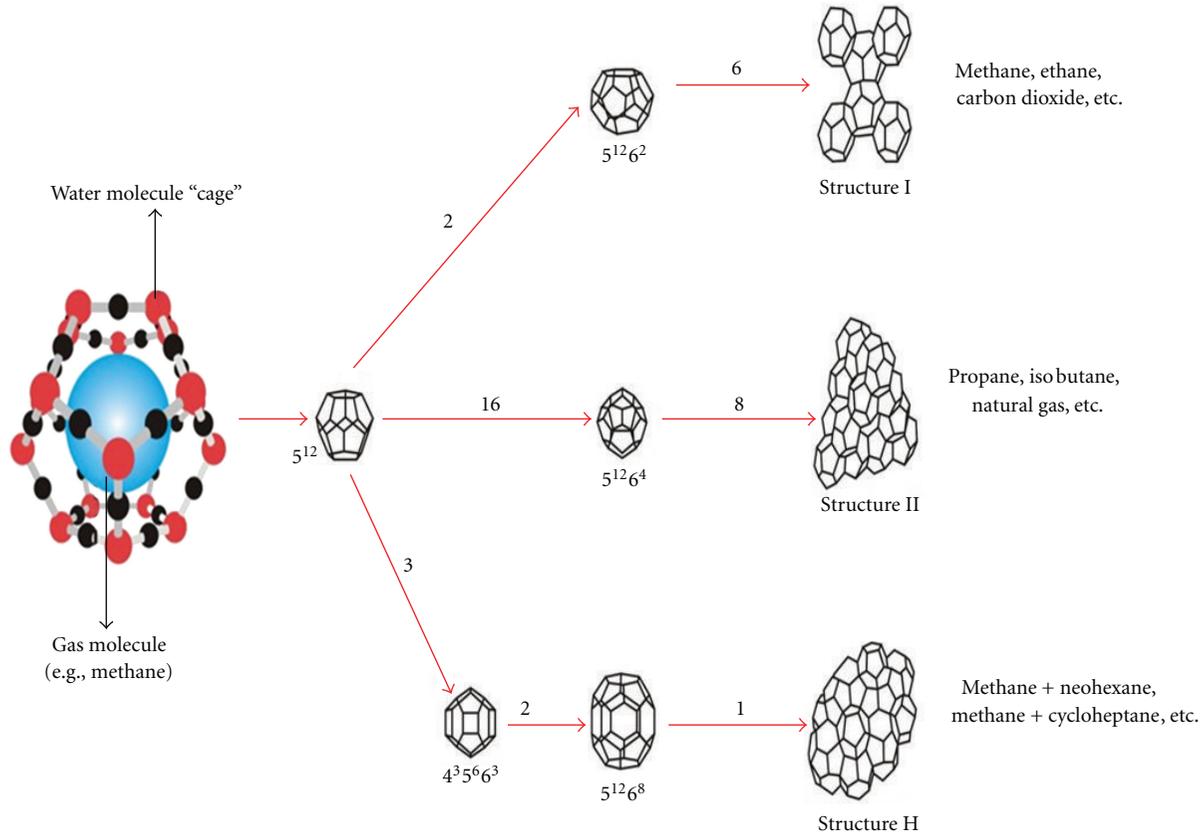


FIGURE 1: Different types of clathrate hydrates [9].

experimentally, numerically, and in the field. However, they have not yet been used for commercial production of natural gas hydrates due to remaining technical and economic issues. A fourth method was introduced a few years ago and is based on the concept of hydrate guest molecule exchange between methane and carbon dioxide in the hydrate phase.

In 1996, Ohgaki et al. [12] examined the possible interactions between these two hydrates by injecting carbon dioxide (gas) into an aqueous-gas hydrate system containing methane. CO_2 displays a higher chemical affinity than CH_4 in the hydrate structure since it has a higher heat of formation and equilibrium temperature; that is, at 1000 psi, the equilibrium temperature of CH_4 hydrate is approximately 283.15 K while the equilibrium temperature of CO_2 hydrate is around 286.15 K. Ohgaki et al.'s experiments resulted in the synthesis of a mixed CO_2 - CH_4 hydrate. The equilibrium concentrations obtained for CO_2 were greater in the hydrate phase than those of CH_4 and less than the concentrations of CH_4 in the gas phase. Nakano et al. (1998) [19] performed a similar study using carbon dioxide and ethane and obtained comparable results. Smith et al. (2001) [20] inquired the feasibility of exchanging carbon dioxide with methane in geologic accumulations of natural gas hydrates. They numerically investigated the effect of the pore size distribution on the conversion of CH_4 hydrate to CO_2 hydrate. It was demonstrated that the guest molecule exchange between CO_2 and CH_4 , in porous media was less thermodynamically favored, as the pore size decreased. They recommended these

numerical results be validated by laboratory experiments. Seo et al. (2001) [21] experimentally investigated hydrate phase equilibrium processes for mixtures of CO_2 and CH_4 . They determined the existing conditions of quadruple points ($\text{H-L}_w\text{-L}_{\text{CO}_2}\text{-V}$) in order to examine the hydrate stability. It was noted that the equilibrium curves of the mixed hydrates lied between those of simple carbon dioxide and methane hydrates. For a given mixture, the concentration of CO_2 in the hydrate phase decreased as the pressure was lowered. In 2003, Lee et al. [22] published the results of their study on the thermodynamics and kinetics of the conversion of CH_4 hydrate to CO_2 hydrate. They analyzed the distribution of guest molecules over different cavities for pure methane hydrates and different mixtures of CO_2 - CH_4 hydrates, using solid state NMR methods. It was observed that the cage occupancy ratio of CH_4 in the pure methane hydrate decreased as the concentration of CO_2 in the mixture increased. This was explained by the fact that CO_2 preferentially occupied large $5^{12}6^2$ cages in the mixed hydrate. In terms of kinetics, it was noticed that the conversion of CH_4 hydrate to CO_2 hydrate happened much more quickly than the formations of pure CO_2 and CH_4 hydrates. The amount of CH_4 that could be recovered from the gas hydrate of composition $\text{CH}_4 \cdot 6.05\text{H}_2\text{O}$ was limited to 64% of the original entrapped gas, even with a CO_2 concentration of 100 mol%. Ota et al. (2004) [23] focused on the gas exchange process using liquid CO_2 . They performed laboratory measurements using the Raman spectroscopy and

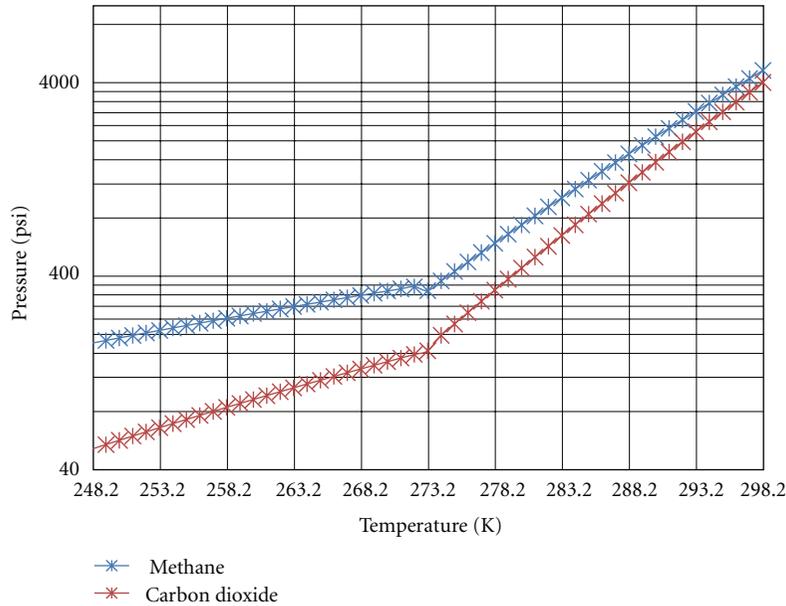


FIGURE 2: CH₄ and CO₂ hydrate phase diagrams [2].

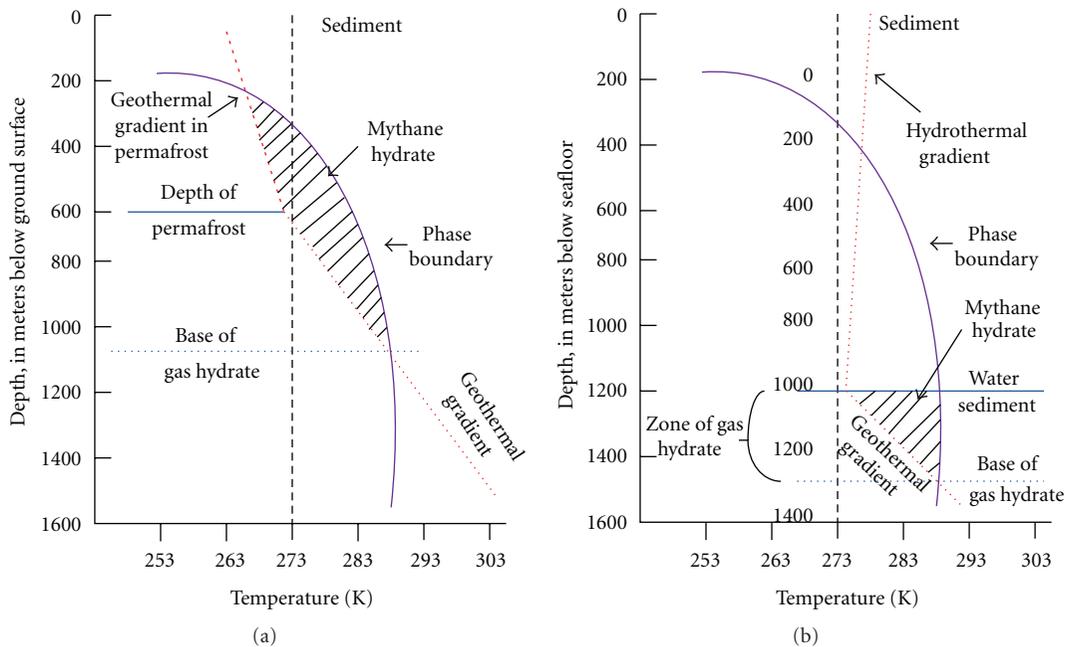


FIGURE 3: Hydrate stability zones in permafrost and marine environments [2].

numerical simulations, and they found similar results in terms of feasibility of the molecular gas exchange. Stevens et al. (2008) [24] took the studies on this topic one step further by publishing his work on the gas exchange between CO₂ and CH₄ in hydrates formed within sandstone core samples. He used a MRI to analyze the samples and realized there was formation of CO₂ hydrate at the expense of the initial CH₄ hydrate. Diffusion seemed to be the main driving force behind the conversion from CH₄ hydrate to CO₂ hydrate. A considerable amount of CH₄ was released during the process, which was judged as rapid and efficient. There

was no free water present. The permeability of the core was reduced during CH₄ hydrate formation. This reduced permeability was maintained constant during the CH₄-CO₂ exchange, and the permeability levels were considered sufficient for gas transportation. In 2008, Youngjune et al. [25] made a major discovery while they were inquiring the effect of the injection of a binary mixture of N₂ and CO₂ on methane hydrate recovery. They found out that the injection of a binary mixture of N₂ and CO₂, instead of the traditional pure CO₂, increased the percentage of methane recovered from 64% to 85% for type I gas hydrates. They

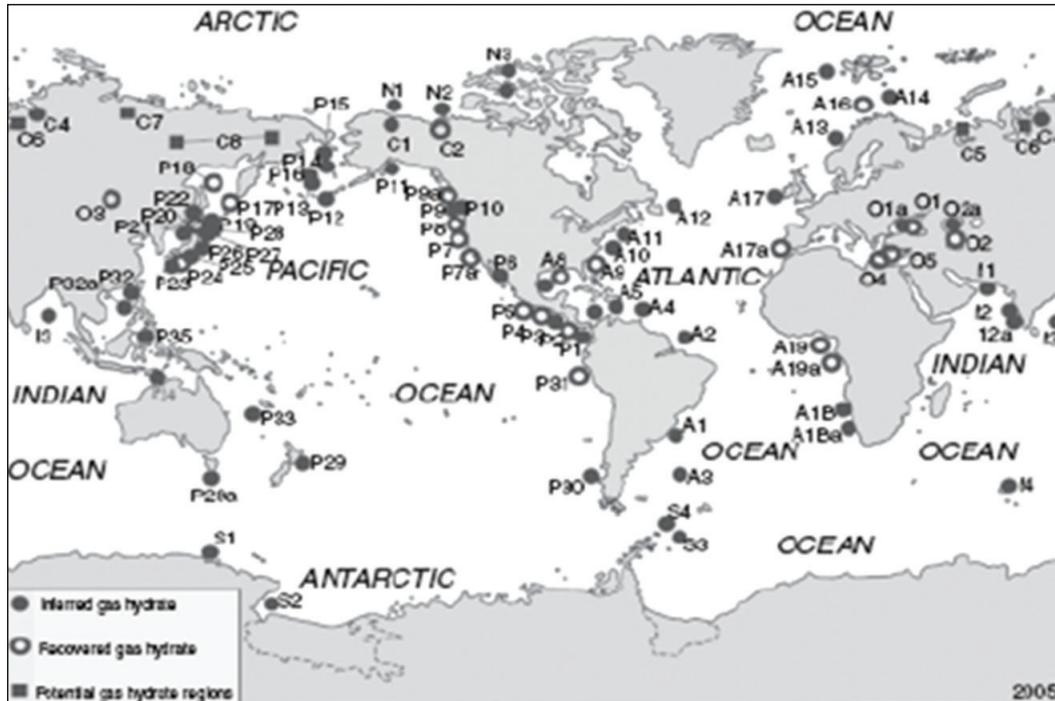


FIGURE 4: World gas hydrate locations [13].

also looked at the potential influence of structural transition by forming a type II $\text{CH}_4\text{-C}_2\text{H}_6$ hydrate and injecting CO_2 and a mixture of CO_2 with N_2 . It was determined that the hydrate structure changed from type II to type I during the gas injection, thus increasing the gas recovery to more than 90% for CH_4 . Besides these major thermodynamically related numerical and laboratory investigations, several studies were conducted to evaluate the potential of this new concept as a field scale production method for methane hydrate deposits. In 2003, Rice [26] proposed a scheme for methane recovery from marine hydrate accumulations. In this scheme, the produced methane would be converted into hydrogen and carbon dioxide; then, the carbon dioxide would be reinjected into the ocean to be converted into CO_2 hydrates and finally the produced hydrogen would be used as fuel. Methane would be recovered from hydrates using depressurization combined with thermal stimulation. No direct molecular gas exchange between CH_4 and CO_2 was inferred in this production scheme. In 2004, McGrail et al. [27] investigated Ohgaki et al.'s method to determine the rate of CO_2 gas penetration in the bulk methane hydrate, using the Raman spectroscopy. They discovered that the rates of CO_2 gas penetration were too low for this method to be useful for gas hydrate production. Then, they performed a preliminary study on a new enhanced gas hydrate recovery concept based on the injection of a microemulsion of CO_2 and water in the methane hydrate core samples. The technique was validated through laboratory experiments and numerical simulation, using a custom model based on STOMP- CO_2 . Finally, Castaldi et al. (2006) [28] examined the technical feasibility of applying a down-hole combustion method for gas recovery from hydrate accumulations, while

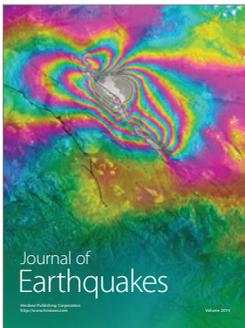
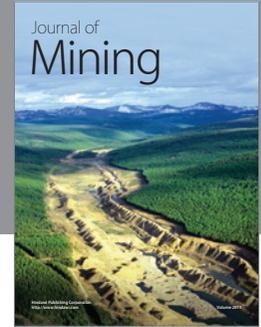
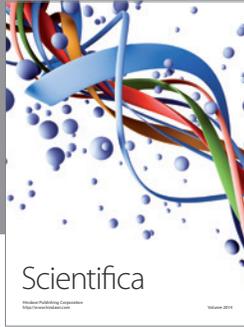
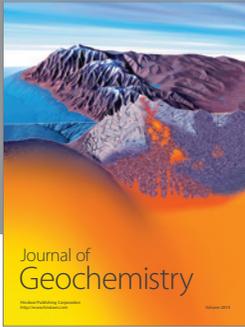
sequestering CO_2 as hydrates. The gas molecular exchange between CH_4 and CO_2 was not directly mentioned, but they suggested there should be equality between the rates of CO_2 hydrate formation and CH_4 hydrate dissociation, during the process. In 2006, Goel [11] released a review of the status of research projects and issues related to methane hydrate production with carbon dioxide sequestration. It was concluded that although several studies had been performed on the topic, additional experimental data was needed on the topic of $\text{CH}_4\text{-CO}_2$ molecular gas exchange in hydrate-bearing sediments. He emphasized the importance of fully knowing the thermodynamics and kinetics of the formation and dissociation of this mixed hydrate and of the conversion process, in porous media. He also pointed out the essence of understanding the equilibrium conditions of the mixed hydrate in sediments as a function of pressure, temperature, mole fraction of CO_2 and CH_4 in the mixture, pore size, porous material, and flow properties.

4. Conclusions

This paper is a brief review of the studies that have been performed on the gas molecular exchange between CO_2 and CH_4 within the hydrate phase. As this paper highlights, such studies are even more essential in this day and age, as we need to quickly discover and exploit new sources of energy in a sustainable and energy-efficient manner. An emphasis is put here on experimental, numerical, and field investigations of the gas hydrate recovery process using CO_2 , clathrate sequestration. All studies present positive outcomes and further research on the topic is encouraged to make this new recovery technique commercially viable.

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