

Perspective

Potential Pathway for Reliable Long-Term CO₂ Storage as Clathrate Hydrates in Marine Environments

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Abstract: A countermeasure to global warming is removing high CO₂ amounts from the atmosphere and locating the emitted CO₂ into long-term stable carbon storage sites. The sequestration technologies must be reliable, long-lasting, and environmentally friendly. An alternative and innovative approach that may meet the sequestration requirements is CO₂ storage as clathrate hydrates in marine environments. Extensive research has been devoted to CO₂-CH₄ replacement in natural gas hydrates. Another option is the direct formation of CO₂ hydrates into deep ocean water or into marine underfloor sediments. This article deals with the positioning of direct hydrate-based CO₂ storage among the other traditional geological options and the discussion of new, by-far, state-of-the-art knowledge required for the development of a hydrate-based CO₂ storage pathway that is reliable, stable, durable, efficient, and environmentally benign.

Keywords: clathrate hydrates; gas hydrate; carbon dioxide; carbon storage; sustainability

1. Introduction

The increase of greenhouse gas concentrations in the atmosphere, coming primarily from fossil fuel burning, causes global warming, which is the long-term heating of the Earth's surface, mainly observed in the pre-industrial era (between 1850 and 1900).

IPCC defines global warming as “an increase in the combined surface air and sea surface temperatures averaged over the globe and over a 30-year period” [1].

The rate and extent of global warming over the future decades are affected by the emission of several climate forcings [2].

Climate forcings are divided into two main groups: long-lived greenhouse gases (GHGs), such as carbon dioxide (CO₂), and short-lived climate forcings (SLCFs), such as methane [3].

Natural processes permanently removing CO₂ from the Earth system are very slow, and the reduction of global warming can be reached only through net zero global anthropogenic CO₂ emissions [4]. Then, anthropogenic CO₂ emissions must be compensated by a series of responses: mitigation, CO₂ removal, or solar radiation modification [1].

In particular, mitigation aims at reducing or preventing the emission of GHGs [5]. The development of CO₂ capture, utilization, and storage (CCUS) technologies may reduce the number of GHGs entering the atmosphere.

Carbon capture and storage (CCS) is the separation and capture of CO₂ from anthropogenic emissions and its permanent storage. The IPCC stated that to reach the 1.5 °C goal, in addition to CO₂ emission reduction, tens of Gt_{CO₂} per year must be removed from the atmosphere [1] and permanently stored. There are both biotic and abiotic CO₂ storage pathways. Biotic carbon storage is based on photosynthesis and CO₂ fixation in biota, soils, wetlands, and oceans [6]. Abiotic carbon storage includes, in addition to natural CO₂ dissolution in oceanic water, geological sequestration in saline formations, oil and natural gas reservoirs, deep coal seams, basalt formations, and organic-rich shales. For all the cited methods, there is a potential risk, which is the escape of CO₂ through permeable pathways,



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tectonic processes, faults, and rock fissures and their release into the atmosphere. More studies are needed to assess their long-term stability [7].

A novel idea with potential benefits is sequestering CO₂ as clathrate hydrates. Clathrate hydrates (CH) are non-stoichiometric solid compounds formed by crystalline water structures where a guest molecule is entrapped under low temperature (T) and high pressure (p) conditions [8]. One hydrate-forming guest molecule with a suitable size is CO₂.

Natural gas hydrates (NGH) exist in nature in suitable geological sites, with the presence of biogenic or thermogenic gas sources, cold and high pressure [9]. Such geological conditions occur both in polar continental rocks and in marine offshore sediments. Most NGH reservoirs have been found in porous media, such as unconsolidated marine underfloor sands, along the continental shelves and slopes, with water depths higher than 500 m.

Estimates of world NGH reservoirs, ranging from $2.5 \times 10^{15} \text{ m}^3$ to $3.0 \times 10^{18} \text{ m}^3$ [9], show that the amount of NGH organic carbon is twice the amount contained in all conventional hydrocarbon resources currently recoverable worldwide.

Natural gas production from oceanic NGH sediments is carried out through three main methods [10]: thermal stimulation, depressurization, and injection of chemical inhibitors. If CO₂ is injected into NGH sediments, it causes CH₄ release and CO₂ hydrate formation. Molecular dynamic simulations show that the CO₂-CH₄ replacement in hydrate cages is thermodynamically favored [11]. This indicates that the CH₄-CO₂ hydrate conversion is a spontaneous reaction, even if the extent of CO₂-CH₄ replacement is limited by differences in molecular diameter.

There is sound research work in the literature about the energy potential of NGH reservoirs, with laboratory studies and recent field trials. There are both several theoretical studies and molecular modeling on the NGH behavior and lab tests on the three methods of recovering gas from hydrate in laboratory settings.

Comprehensive reviews of the obtained results are given in [12]. According to a hydrate research roadmap published by the U.S. National Methane Hydrate R&D program [13], the key research topics to be investigated are the development of technologies for sampling, characterization, and production as well as the investigation of linkages between gas hydrate and global climate change.

As far as CO₂ replacement is concerned, various studies have shown the theoretical viability of the process in both the bulk phase and in porous media, also showing the rate of CH₄ production [14]. In situ combustion was also proposed to improve CO₂ injectivity and avoid premature CO₂ hydrate formation [15].

CO₂-CH₄ replacement in NGH is one of the hydrate-based options for storing CO₂. The other one is the direct CO₂ hydrate formation in water over the seabed or under the seafloor in sediments. The study of the CO₂-CH₄ replacement in NGH has involved the knowledge also on pure methane and CO₂ hydrates behavior. Therefore, the literature is rich in studies on this topic, but few papers are devoted to the application of pure CO₂ hydrates in marine environments as a pathway for long-term CO₂ storage.

This article deals with this topic and the possibility of developing reliable and long-term CO₂ storage as CH in the marine environment. So, in the following paragraphs, this promising option for CO₂ storage is proposed and discussed on the basis of literature evidence, starting from the wide research on CO₂-CH₄ replacement. The sound knowledge of hydrate science is a starting point for discussing the feasibility of direct CO₂ hydrate storage and the needed improvements to the state of the art to prove its potential competitiveness with the other CO₂ storage techniques.

2. CO₂ Storage as a Pathway against Global Warming

Secure and safe CO₂ storage is the second step after the capture of CO₂ from the atmosphere, and it is crucial to stabilize global temperatures.

The IEA's Net Zero Emissions by 2050 Scenario is based on the annual storage of 5.9 Gt of captured CO₂ [16]. By the same year, CCS will contribute to a 19% reduction in global CO₂ emissions.

Nevertheless, CO₂ removal from anthropic emissions or from the air requires CO₂ storage: without it, the potential for tackling global warming by CO₂ capture technologies cannot be realized.

Four main mechanisms in which CO₂ remains stored inside a reservoir are [17]:

- Structural Trapping (physical trapping in the rock with rocks as seals)
- Residual Trapping (CO₂ trapping in the pore space between the rock grains)
- Solubility Trapping (CO₂ dissolves into the brine water in the pore spaces)
- Mineral Trapping (when in the reservoir, the dissolved CO₂ reacts with the present minerals to form solid carbonate minerals)

Each one of the four mechanisms has specific storage performance and long-term security, as shown in Figure 1.

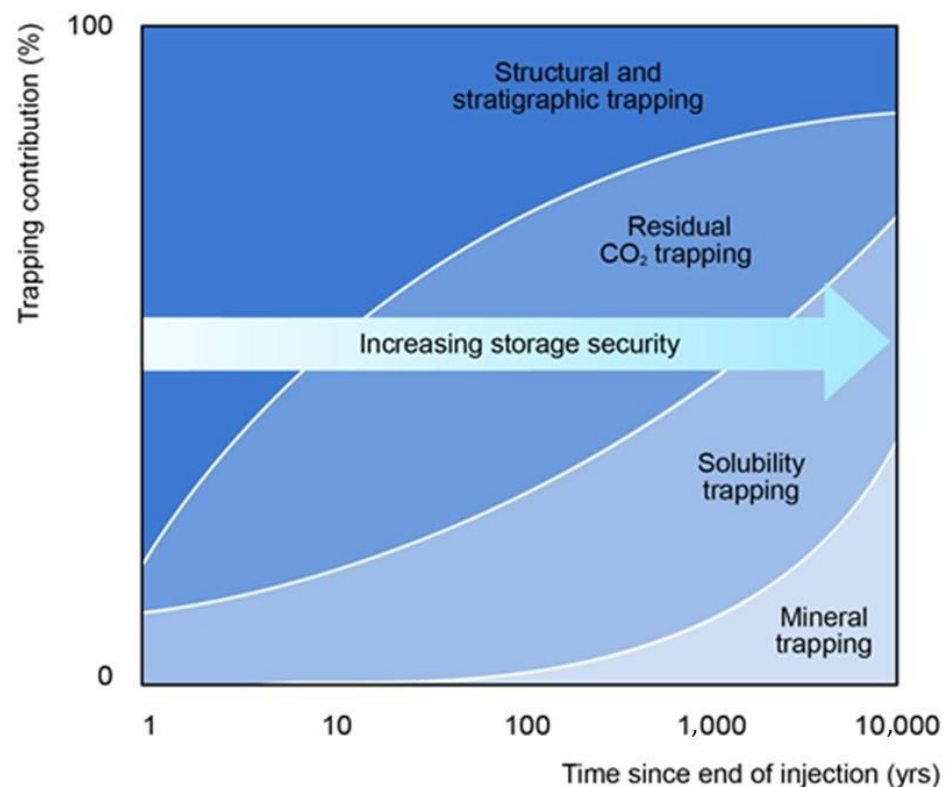


Figure 1. CO₂ trapping mechanisms: trapping times, contributions and storage security [18].

The main options for geological storage are oil/gas reservoirs, saline aquifers, coal bed reservoirs, caverns, and mines. An overview of these geological storage options is shown in Figure 2.

One significant parameter to be estimated is the capacity of the geological storage. During the past 10 years, a lot of work has been carried out on the evaluation of storage options capacities [19].

The IPCC information says that depleted oil/gas reservoirs can store 675–900 Gt of CO₂ [20]. Storage of CO₂ in depleted oil/gas reservoirs is based on enhanced oil/gas recovery (EOR), where CO₂ is used as a displacement agent for the recovery of additional fuel [21]. EOR is a mature technology, and many commercial projects have been carried out, driven more by the economics of oil production than by CO₂ storage purposes [22–24].

Saline aquifers are porous formations filled with brine, or salty water, used for all the trapping mechanisms [25]. They have 150–1500 Gt of estimated CO₂ storage capacity [19].

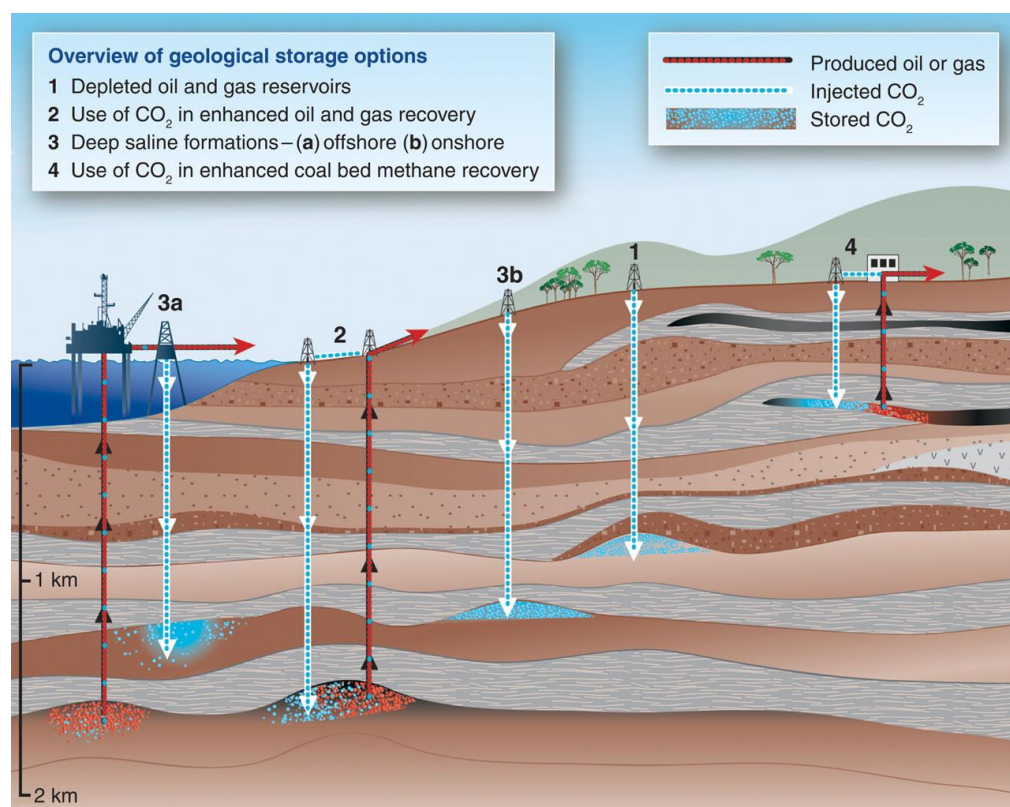


Figure 2. CO₂ storage options (taken from IPCC Special Report on Carbon Capture and Storage [26]).

CO₂ storage in coal seams is similar to EOR. CO₂ is injected into the coal beds for the application of enhanced coal bed CH₄ recovery [27]. In such reservoirs, CO₂ can exist in a pore matrix, both free and dissolved or adsorbed on the coal surface. Due to low permeability, not all porous media are suitable for permanent CO₂ storage. Structural trapping may create a free gas cap that does not ensure long-term storage [17]. The CO₂ storage potential of European coal seams is estimated to be about 6 Gt [19].

Caverns and abandoned mines are also an alternative as potential CO₂ storage structures, although the storage capacity is limited, and the suitable final use seems to be just temporary storage and not long-term CO₂ storage [19].

Basaltic rocks have been recently proposed for storing CO₂ in the mineralized form: a rapid chemical reaction is induced when CO₂ and water are injected together in basalt formations [28]. The research is at a very early stage, and the question of this storage technique's viability is still open [29].

Another option is the organic-rich shale permanently storing CO₂ in an adsorbed state within the distributed organic matter. There are some challenges, such as geologic heterogeneity, low permeability, and microscopic porosity, which make the matrix inaccessible. In addition, few geologic and petrophysical data are available, and this is a significant limitation in estimating their CO₂ storage potential [30].

To further develop CO₂ storage at a Gt scale, more storage resources should be assessed, tested, and developed. Storing CO₂ in marine environments in the form of hydrates is a novel but promising option, currently being proven at an early research stage. CH is used to trap CO₂ in a solid form under suitable conditions, occurring in high-pressure and low-temperature marine environments.

3. Clathrate Hydrates for CO₂ Storage

Gas hydrates are crystalline solids. They are called clathrate hydrates (CH) to distinguish them from stoichiometric hydrates in inorganic chemistry. The supramolecular crystalline structure is formed by polyhedra of hydrogen-bonded water molecules, in which

at most one guest molecule is contained. The cages are stabilized by van der Waals forces between the water molecules and the enclathrated guest molecule [31].

Intense research on clathrate hydrates started when they were identified as the responsible compounds for plugging natural gas pipelines. In fact, light gases present in petroleum fluids (methane, ethane) are hydrate-forming molecules. Beyond their role in pipeline plugs, however, clathrate hydrates have been studied in several areas of the energy field.

Because CH is a non-stoichiometric compound, the cages' filling depends on the formation conditions (temperature and pressure). There are different hydrate structures known as structure I (sI), structure II (sII), and structure H (sH), depending on the geometry and size of the guest molecule [31].

Methane forms sI hydrate occupying both large and small cages, but not sII because it is too small to stabilize the large cages in sII. CO₂ with intermediate molecule size forms sI hydrate, where the molecules enter the large cavities.

CH forms through nucleation and growth phases, for which gas accumulation is a crucial process. Nevertheless, there are some questions about how gas molecules aggregate. One theory proposed in [32] is that the CH₄ CH nucleation path occurs with a three-body aggregate pattern. This situation corresponds to the minimum free energy for the three-methane hydrophobic interaction.

CH exist in nature in ocean sediments and permafrost, entrapping CH₄ in large quantity safely for millennia [9]. They are widely studied for the full-scale development of the CH₄-CO₂ replacement process, which gives the opportunity to store CO₂ in existing NGH reservoirs while recovering methane for energy purposes. Hydrate reservoirs can be both CH₄ source and CO₂ storage sites, enhancing the idea of a carbon-neutral fuel source.

Figure 3 shows p-T equilibrium curves for CH₄ and CO₂ hydrates. Given a constant pressure, there is a region between the curves where gaseous CH₄ is released while CO₂ still forms hydrates. The corresponding equilibrium temperature for methane is much lower than that for CO₂. Operating within this region, we obtained the release of methane from the cages and the simultaneous formation and preservation of CO₂ hydrate.

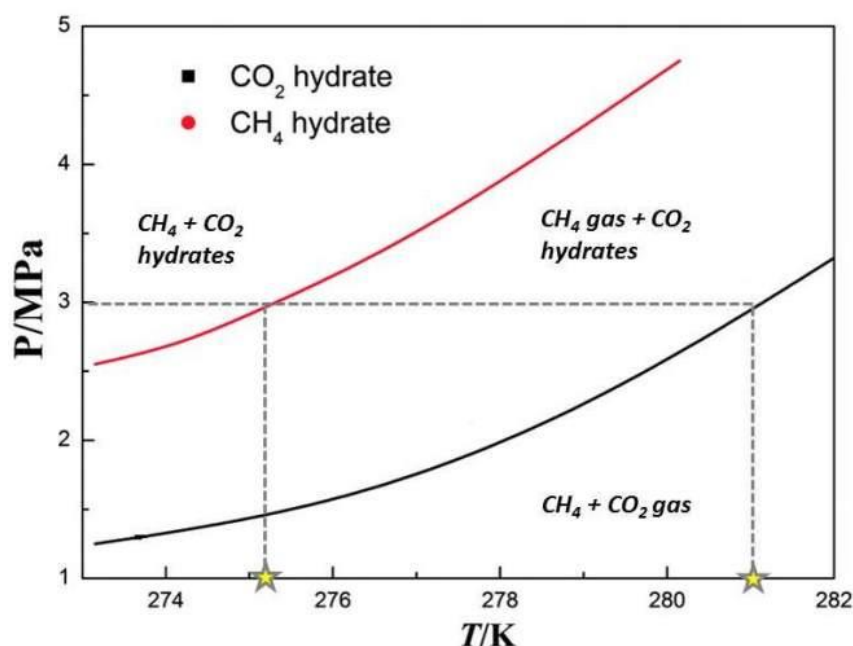


Figure 3. CH₄ and CO₂ CH equilibrium curves.

In the CO₂-CH₄ replacement process, CO₂ does not replace CH₄ in the 5¹² small cavities (CO₂ molecular diameter of 5.12 Å is larger than the diameter of 5¹² small cavities). This results in the highest CH₄ recovery from NGH by the replacement, equal to 75% [33].

This is the first limitation of the process since just methane in the middle cavities is replaced by CO₂. A solution to that could be the use of gaseous mixtures, such as CO₂/N₂. Studies have shown that the CH₄ replacement efficiency passes from about 73% with pure CO₂ to more than 90% with a CO₂/N₂ mixture [34].

Several reviews on the CO₂-CH₄ replacement process in NGH are available in the literature, presenting the key factors affecting the process and the efforts to improve the efficiency [35–38]: the use of secondary gases, pressure, CO₂ state, porous media, thermal stimulation, saturation.

The grain size of the sediment affects the stability of NGH, and in particular, sediment giving higher stability leads to a reduction in the replacement efficiency, thus favoring the preservation of NGH and reducing the exchange between the two gases. In [39], the recovered methane decreases by 10–15% passing from a grain size of 400–500 μm to 150–250 μm.

Inhibitors of methane hydrate formation, such as NaCl, instead, can improve CO₂ replacement by reducing the CH₄ hydrate stability zone and increasing the area between CO₂ and CH₄ equilibrium curves [40]. The number of CH₄ moles replaced passes from 32% to 55% in the presence of NaCl in the same experimental conditions [41].

The hydrate saturation is another parameter that has a great influence on methane recovery and CO₂-CH₄ replacement. In [14], for example, tests at 30% and 50% saturations, the injection of CO₂ increases the recovered methane and reduces the length of the process, while for a hydrate saturation value of 10%, this effect is negligible.

So, the CO₂-CH₄ replacement strictly depends on the local conditions of the sediment, and when reproduced in lab reactors, it also depends on the procedures and operating parameters, such as temperatures or the headspace volume above the porous medium in the reactors, resulting in inconsistencies among the experimental results [38].

For all these factors, when the replacement process occurs with thermal stimulation, a higher methane recovery is obtained. Thermal energy is necessary to break the bonds in the hydrate structure. In situ combustion was also proposed to improve CO₂ injectivity and avoid premature CO₂ CH formation [15].

Considering the energy consumption of the CO₂-CH₄ replacement in NGH, studies show that the energy cost due to the compression of the injected and recirculated CO₂ is almost 5% of the energy stored in the recovered methane, assuming a maximum value of the replacement efficiency equal to 56% [42]. Additional energy costs should be considered for thermal stimulation, resulting in an increase in the energy footprint.

There are further aspects highlighted by the cited reviews. The rate of replacement is low because of the low gas-water interfacial area in the sediment pore and the diffusivity factor. The release of methane is slow due also to a superficial layer formed by CO₂ CH which creates a transfer barrier.

Another issue is the not uniform distribution of the replacement inside the sediment together with the formation of new CO₂ hydrates, which causes a decrease in the replacement efficiency [14,43].

The discussed aspects make the development and the scale-up of the CO₂-CH₄ replacement at real scales challenging. An alternative pathway for CO₂ storage could be the direct formation of CO₂ hydrates in the marine environment. The sound body of knowledge on CH behavior is a significant starting point for the viability of the hydrate-based CO₂ storage solution. Nevertheless, in accordance with the literature, there are some issues to be addressed, as discussed in the following paragraph.

The abundant and wide distribution of NGH, stable reservoirs of methane for hundreds of years, suggests the potential of using CH for direct CO₂ storage, especially in marine environments where the appropriate pressure and temperature conditions occur.

The theoretical benefits of CO₂ CH for the CO₂ long-term sequestration are higher density with respect to seawater, causing a negative buoyancy effect; stability at moderate oceanic depth at T < 10 °C; storage in solid form, more resistant to perturbations than fluid flows; storage within cementing porous media (as the sediment of the seafloor); very low

CH dissolution and consequently lower CO_2 release into the surrounding water than that from liquid CO_2 .

Potential CO_2 CH storage sites include sub-seafloor sediments, deep oceanic basins, and depleted gas/oil reservoirs partially saturated with water. In direct CO_2 storage, CO_2 is injected into ocean water at a proper depth (100 m) or into sediment under the seafloor, as shown in Figure 4. Comparing the two options, CO_2 storage in sediments under the ocean floor is more stable.

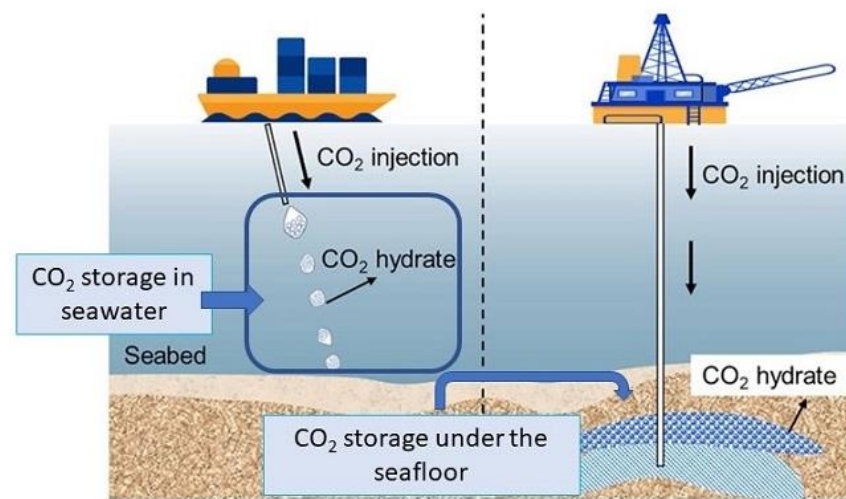


Figure 4. Approaches for CO_2 storage as CH in marine environment (adapted from [44]).

The conditions where CO_2 hydrates form and are stable can be determined using a pressure–temperature phase diagram, where the hydrothermal gradient of the ocean and the geothermal gradient of the seafloor are also considered. In Figure 5, taken from [45], the hydrate stability zone (HSZ) is limited by line AB over the seabed and by line BC under the seafloor.

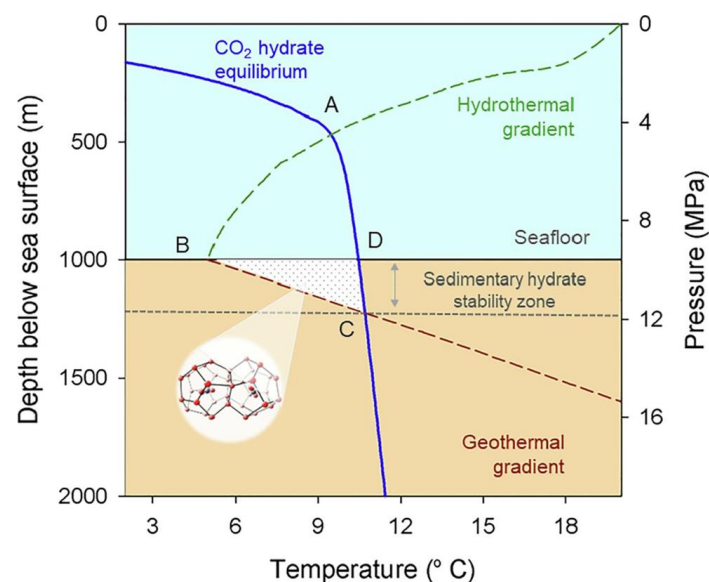


Figure 5. CO_2 hydrate stability zone [45].

Much research has assessed the potential sites for CO_2 storage as CH [42]. The Alberta area in western Canada, at a depth from 200 to 1000 m, has a potential of 256 Gt of CO_2 . The West European seabed sediments also have potential considering a depth of 450 m from the ocean floor. Based on the analogy to NGH, the potential CO_2 storage capacity of

CH is estimated to be unlimited over the seafloor and of about hundreds of thousands of Gt CO₂ under the seafloor [45].

4. Potential and Challenges for Direct CO₂ Storage as Clathrate Hydrates

There are significant aspects to be clarified by further research activities to define a potential pathway for direct CO₂ storage as clathrate hydrates; in particular, the following: (i) the proper approach of CO₂ storage as CH in the potential sites; (ii) key objectives of the laboratory investigations; (iii) identification of chemical compounds with an effect on CH; (iv) experimental tests on stability; (v) social acceptance studies.

The outcomes from the scientific research will constitute the knowledge needed to perform further economic studies and to set legal and regulatory frameworks. The IEA Report [18] confirms that there are limited cost studies for CO₂ storage projects, and it is possible to have just general conclusions from the few operating projects based on more developed technologies. For CO₂ CH, the economic evaluation is even more complex due to the limited scientific and technological experience.

The results of the scientific research will help in evaluating risks and site management requirements, which constitute key issues for the development of Legal and regulatory frameworks.

4.1. The Choice of the Approaches of CO₂ Storage as CH

The choice of potential sites depends on the equilibrium and kinetic characteristics of CO₂ hydrates in different water and/or sediment conditions. Some experiments were carried out in the ocean with a depth between 348–4500 m [46].

Results showed that, although CH density is higher than that of seawater, gaseous CO₂ could make the hydrate more buoyant and could rise up. There is also a dependency of the CH hydrate density with the formation mode [47].

The literature reviews agree that CO₂ CH storage in the ocean is theoretically feasible, but the formed CO₂ hydrate is unstable, and there are risks for the ocean environment and its ecosystems. CO₂ storage as CH in sediments under the seafloor is considered more reliable because the sediment constitutes a porous structure creating a good confining environment. However, performing real-size experiments in the ocean is challenging; for this reason, natural sediments are simulated or reproduced artificially in lab reactors.

CO₂ can be injected pure or in a mixture with other gases (coming from previous CCS processes on flue gas/biogas): the effect of such gases on the physical and chemical properties of the formed CH, especially density, should be deeply evaluated.

A detailed comprehension of the opportunities and disadvantages of the chosen approaches, with the geographical assessment of CH stability zones in marine locations, is necessary for the future.

4.2. Laboratory Investigations on CO₂ CH in Marine Environments

The thermodynamic stability of CO₂ CH in marine environments is determined by the water depth and the ocean thermal gradient. Some field tests were carried out and reported in the literature at several sea depths [46]. Nevertheless, there is a need for facilities to simulate the marine conditions in the laboratory, and more experimental work should be carried out to study procedures for CO₂ injection and CH formation.

In the case of CO₂ CH under the seafloor, a CH formation zone, where the density of liquid CO₂ is higher than pore water, typically exists within hundreds of meters. The experimental work to date refers to the effect of sediment characteristics, permeability variations, and the investigation of chemical reactions in the presence of other gases in addition to pure CO₂ at different depths [48,49]. There is a need for experimental studies to understand the dynamics of the CO₂ injection, the thermodynamics and kinetics of the hydrate formation/dissociation after CO₂ injection, the occurrence of chemical reactions between sediments/water/other gaseous components, which could come from previous CO₂ separation processes from flue gases [45].

One challenging aspect during the CO₂ injection is how to create a uniform and continuous CO₂ CH formation throughout the sediment, considering its decreasing permeability. Experimental tests but also technological solutions are needed to maintain CO₂ flow in the sediment during CH formation.

4.3. Identification of Major Chemical Compounds in Seawater and Pore Water in Seafloor Sediments

Salts in water are thermodynamic inhibitors of CH since they disturb the hydrogen bonds before the CH formation [50]. In addition, dissolved organic matter (DOM) is present in seawater [51], and its concentration is higher in the pore water of seafloor sediments. For this reason, their presence and their specific chemical structure could significantly affect the formation of CO₂ CH and their stability [52].

Sediments organic matters found at CH deposits consist of lignin compounds, lipids, proteins, carbohydrates, unsaturated hydrocarbons, and aromatics. Lignin-, amides-, and amine-based compounds can accelerate the formation of CO₂ CH, while lipids and unsaturated hydrocarbons show an inhibitory effect [53]. The presence of organic compounds may affect the local charges and therefore influence the arrangements of water or CO₂ molecules. In the presence of a weak alkaline environment, organic anions can produce, in pore water, coordination compounds with salt ions and strengthen the interchain interaction via hydrogen bonds [53]. In an acidified environment, the presence of protonated organic ions reduces the number of hydrogen bonds among the organic matter. The consequent decrease of negative charges may reduce the electrostatic interaction with the minerals' surface. This results in a redissolution of organic compounds in pore water, with a consequent great impact on the CO₂ sequestration in the CH [54].

So, the identification of the major ionic compounds to define their influence on CO₂ CH formation and stability is important to help the choice of a better natural site for CO₂ CH storage.

4.4. CO₂ CH Stability

The key question for the CO₂ geological storage is how much the sequestration is stable without CO₂ leakage. The crucial point for avoiding or at least considering CO₂ leakage an unlikely event is the proper site selection on the basis of the following criteria: lithology, permeability, injectivity, porosity, presence of impermeable sealing caps, seismicity, landslides, and volcanic activities [55].

The stability of CO₂ CH in sediments has been poorly investigated using fresh water and salt water; preliminary results show an adequate level of stability [56,57]. For strengthening experimental results, simulations on CO₂ CH formations and stability in porous media for a long time and spatial scales are surely useful. New insights and novel data are crucial to address the stability of CO₂ CH reproducing in the lab in the conditions occurring in nature.

4.5. Social Acceptance

Social acceptance is crucial in the development of any strategy or technology and should be carefully evaluated. There are several studies in the literature on the assessment of social acceptance of CO₂ storage options. In [58], results of a survey showed that citizens living near a potential CO₂ storage site have slightly negative attitudes towards CO₂ storage but also little knowledge and, most of all, little motivation to learn about CO₂ storage technologies and, therefore, they trust professional actors who instead show interest in storage projects.

In [59], 300 European citizens from several countries answered a questionnaire on CO₂ storage topics, and results showed that 70% of people do not think there are risks coming from the CCS technology and think that the CCS implementation is acceptable in Europe. Nevertheless, answers to other questions show a general lack of knowledge on the topic, and more scientific communication and dissemination seem to be necessary.

Considering the results of a recent review [60], the social acceptance issue seems to be a very complex subject to be investigated in terms of methodology and approaches, also because it is strictly dependent on the local conditions and communities and on the technology used. Technology can play an important role in the definition of practices and results of social acceptance studies. No specific studies on CO₂ storage as clathrate hydrates have been found in the literature, so great effort should be devoted to the assessment of impacts and acceptance of this technology in different social scenarios.

5. Conclusions

Currently, the risks of global warming caused by GHG emissions are an important social challenge. A countermeasure to global warming is removing CO₂ from the atmosphere and relocating it into safe, durable, and stable carbon storage sites.

As discussed in the state of the art, an alternative and innovative approach that may meet the sequestration requirements is marine CO₂ sequestration in the form of clathrate hydrates. The deep water or the sediments under the seafloor can create ideal conditions for CO₂ hydrate formation (low temperatures and high pressures), similar to how natural gas hydrates have naturally formed for millions of years.

Natural gas hydrates offer the opportunity to store CO₂ while recovering methane for energy purposes (CO₂-CH₄ replacement), which is one of the possible hydrate-based pathways for CO₂ storage.

The aspects discussed in the paper about the CO₂-CH₄ replacement make its development and the scale-up at real scales challenging. The other alternative is the direct formation of CO₂ hydrates in the marine environment.

The investigation of the direct CO₂ storage as clathrate hydrates have been chosen in accordance with their desirable properties if compared to other geological storage options: higher density than seawater, stability at moderate p-T conditions, solid storage, cementing effect in porous sediments, slower CO₂ dissolution in the surrounding water. These properties have been reported in literature reviews.

Nevertheless, the study of the direct CO₂ hydrate formation as a storage option is complex because clathrate hydrates, especially in sediments, may be influenced by many other parameters in addition to the variables that ensure the thermodynamic equilibrium.

For this reason, some technical challenges need to be investigated and hereunder summarized to make CO₂ storage via direct hydrate formation a viable pathway:

- Among the potential CO₂ storage sites, the geographical assessment of hydrate stability zones in marine locations with a detailed comprehension of the advantages/disadvantages of the chosen approaches;
- New knowledge of hydrodynamics and permeability, thermodynamics/kinetics of CO₂ hydrate formation/dissociation;
- New knowledge on the effect of salinity, of the dissolved organic matter, and of the presence of other gaseous components;
- New experimental data on the long-term stability of CO₂ hydrates;
- New technological solutions for CO₂ injection to obtain a high, continuous, and uniform formation of CO₂ hydrates;
- New specific social acceptance studies considering impacts, social communities, and hydrate technology peculiarities.

The scientific investigation will help in setting regulatory frameworks and economic evaluations.

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