



ISSUES UNDERLYING THE FEASIBILITY OF STORING CO₂ AS HYDRATE DEPOSITS

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Background to the Study

The IEA Greenhouse Gas R&D programme (IEA GHG) is systematically evaluating the cost and potential of measures for reducing emissions of greenhouse gases arising from anthropogenic activities, especially the use of carbon dioxide capture and storage. The captured CO₂ can be stored in geological reservoirs rather than being emitted to the atmosphere. Geological reservoirs that can be considered include: deep saline aquifers and depleted oil and gas fields. CO₂ can also be injected into oil fields to enhance oil recovery (CO₂-EOR) and into coal seams to enhance the release of methane (CO₂-ECBM). In these the costs of storage are offset by product sales, making these storage options commercially attractive.

Another option that can be considered is the formation of CO₂ hydrates. Analogous compounds, methane hydrates, are known to have existed for thousands of years in many parts of the world. If CO₂ can be stored in a similar manner, considerable quantities of CO₂ could be sequestered, which could have a major influence on the degree of future climate change. Initial scientific evidence suggests that CO₂ hydrates form similar stable molecules to methane hydrates. There are two options for CO₂ storage as hydrates. The first is the direct formation of CO₂ hydrates, perhaps on the ocean floor, whilst the second, and possibly more attractive, option is to combine CO₂ storage with release of methane from hydrate deposits. If this approach could be achieved in practice, the storage option could be more attractive, in the same way as CO₂-EOR or CO₂-ECBM.

Compared to the other storage options, knowledge on hydrate chemistry and the potential for storage of CO₂ as hydrates is at an early stage of development. Hydrates are attracting considerable interest internationally and studies on the fundamental science of hydrates are now underway in many research laboratories throughout the world. To assist the international community in assessing this potential CO₂ storage option, IEA GHG commissioned a small study to review the current state of knowledge about hydrates and determine where further information about CO₂ storage as hydrates is needed (for example, information which could be obtained by appropriate research). A more extensive study is currently underway to investigate in detail the potential for combining methane extraction from natural gas hydrates with CO₂ storage. This second study also focuses on natural gas hydrate deposits in permafrost regions rather than sub sea hydrate deposits.

Dr Mark Rodger of the University of Warwick, UK, undertook the study

Results and Discussion

The following areas are described in the report

- A review of hydrate chemistry
- The potential for CO₂ storage as hydrates

- The potential for extraction of methane from natural gas hydrates combined with CO₂ storage
- Issues that need to be addressed

A review of hydrate chemistry

A hydrate is a general class of crystalline host/guest compound. A tetrahedral hydrogen-bonding network of water forms the host. This network is sufficiently open to create pores (or cavities) that are large enough to contain a variety of other small molecules (the guests). Guest molecules can include CH₄ and CO₂. The pressure and temperature of the system largely determine the stability of the hydrate. For natural gas components, the required conditions are comparable to those found in and around the sea floor along the continental margins. Other factors that affect the stability of gas hydrates include: the presence of other chemicals, non-equilibrium conditions, and the environment in which the hydrates are being formed. One important property of hydrates in this context is permeability. The hydrate forms a "skin" at a water/guest interface, which acts as an impervious seal, preventing escape of guest species from within the lattice.

Methane hydrates occur naturally throughout the world existing as either particles finely dispersed in the sea floor sediment or as hydrate capped gas reservoirs. Sea floor hydrates are the most common form of naturally occurring hydrates. Where hydrates are associated with reservoirs, they form an impervious seal above a porous rock stratum, thereby creating an effective gas trap. Hydrate reservoirs are found in permafrost regions of Alaska and Canada, but sub-sea reservoirs have also been found.

The potential for CO₂ storage as hydrates

CO₂ storage as CO₂ hydrates is most likely to be technically feasible if the CO₂ is injected into a porous rock or mud deposit on the ocean floor that then becomes sealed by growing a layer of CO₂ hydrate at its boundary. This situation is analogous to the conditions found in many hydrate-capped CH₄ reservoirs. Thermodynamic considerations indicate that CO₂ and CH₄ hydrate have similar conditions for stability. CO₂ hydrate can form at shallower depths than CH₄ hydrate, while the latter will generally persist to greater depths; in most cases there is a substantial region where both forms of hydrate may be stable. The different range of stability for CO₂ hydrate indicates that there could be new sites for CO₂ storage that are unsuitable for CH₄, and so would provide a completely new storage resource. Using existing data on seafloor geology and correlating these with the physical requirements (temperature and pressure) for stable CO₂ hydrate formation could be a method for identifying regions where hydrate storage can be considered. In assessing viability of this storage option a number of factors still need to be considered, which are:

- There are indications that CO₂ hydrate behaves unusually at high pressures, giving volumes that are much larger than expected, and this may place the integrity of a potential store at risk. It is not known currently why such behaviour occurs.
- It is known from studies on methane hydrate formation in porous substrates, such as sandstones, that the substrate modifies both the kinetic and thermodynamic properties of the hydrate. The same must be anticipated for CO₂. Both experimental and theoretical studies are needed of the effect of the composition and character of any potential substrate before predictions can be made on the long-term viability of a potential storage site.

The ecological consequences also need to be investigated. Hydrates tend to form in regions where methanogenic bacteria can be found and, thus, storing large amounts of CO₂ could be expected to affect the local ecology. The consequences are likely to be site-specific, and so will necessitate suitable ecological surveys once potential sites are found.

The potential for extraction of methane from natural gas hydrates combined with CO₂ storage

Since much of the natural methane hydrates occur in low concentrations on the sea floor, it is very doubtful whether there is any potential (not even technical potential) for injecting CO₂ and extracting methane in this situation. Methane hydrate-capped gas reservoirs, therefore, offer the most potential for CO₂ storage combined with methane extraction. This preliminary study has concluded that it is unlikely that CO₂ injection into a methane hydrate-capped subsea reservoir will enhance methane extraction whilst storing CO₂. A number of reasons for this conclusion arose, which include:

- If CO₂ is injected near the surface of the hydrate capped gas reservoir, the impervious skin formed by the hydrate will act as a transport barrier. The kinetics for the displacement of CH₄ will be very slow, which will limit the scope for replacing CH₄ with CO₂. Experiments performed in Japan indicated that the process was very slow. About 16% of the methane hydrate decomposed, to be replaced by CO₂ hydrate, in 800 hours.
- Enhanced methane recovery will involve pumping CO₂ into the gas reservoir, which must in turn lie below the stable hydrate zone as defined in Figure 3. In such circumstances, the CO₂ will be trapped (either as a free gas or most likely as a fluid) at too great a depth for CO₂ hydrate to form. The presence of the methane hydrate associated with a natural gas reservoir will, therefore, inhibit the formation of CO₂ hydrate.
- The density of CO₂ is greater than that of CH₄ so, potentially the CO₂ would collect in the bottom of the gas trap and force the CH₄ out the top. However, methane and CO₂ are miscible fluids, indeed supercritical CO₂ is an excellent solvent for most organic compounds (which would probably be the case given likely injection pressures). Thus one would expect the CH₄ in the reservoir and the CO₂ to mix, rather than maintain the phase separation required for this form of enhanced methane recovery.

In addition, injection of CO₂ could preferentially produce a mixed hydrate rather than a pure hydrate. CO₂ will occupy only the large cavities in the hydrate lattice, whereas methane can occupy both the large and the small ones. This means that up to twice as much methane as carbon dioxide could be incorporated into a mixed hydrate. The methane incorporated into such a mixed hydrate will be trapped for as long as the CO₂ hydrate is stable; by design, this should be for in excess of 100 years if acceptable reductions in atmospheric levels of CO₂ are to result. Thus the formation of CO₂ hydrate could actually reduce the yield of methane from a natural gas reservoir.

The results, therefore, suggest that storage of CO₂ as the hydrate in hydrate capped gas reservoirs will not occur. If gaseous storage is adequate, both a CH₄ and a mixed CH₄/CO₂ hydrate cap will still provide an adequate seal for the CO₂ storage. This will, however, reduce the yield of methane from a natural gas reservoir, and will hinder the recovery of methane from CH₄ hydrate deposits. Thus, coupling methane exploitation and CO₂ storage may have some adverse economic consequences. Also, contamination of the gas reserve in the reservoir would not be commercially acceptable to the field operator. It is possible that these difficulties can be alleviated by careful design of the CO₂ injection technology, although extensive further research would be needed to determine whether this could be achieved in practise.

Issues that need to be addressed

Further research is needed to address a number of the scientific and technical unknowns concerning the feasibility of this method of storing CO₂ either as CO₂ hydrates or in CH₄ hydrate reservoirs.

Research associated with the following areas is considered to be particularly necessary (not in order of priority):

1. Mapping of possible sites for sub-sea CO₂ storage should be undertaken to identify which of the known methane hydrate sites would be suitable for CO₂ storage and also search more widely for potential new sites.
2. Experiments are needed to define the hydrate stability curves for CO₂ hydrate in the presence of the full range of impurities likely to be encountered, including variations in the pH of the aqueous phase and the effect of the carbonate equilibrium. This data should then be used to re-calibrate existing models for predicting hydrate stability.
3. The kinetics and thermodynamics of hydrate formation in porous materials needs to be characterised to assess the influence of pore size and of the chemical composition of the rocks.
4. The diffusion of CO₂ through thin hydrate films, and through hydrates that form in porous rocks needs to be considered. These results then need to be combined with existing percolation/diffusion theories to predict the diffusive loss rates for CO₂ from hydrate-capped gas traps to allow the maximum storage times to be estimated.
5. Comprehensive simulations (which combine the kinetic/thermodynamic developments and diffusive studies itemised above) with existing reservoir and fluid flow modelling schemes are needed to estimate the efficiency with which a CO₂ store can be created.
6. The existence of sub-sea CO₂ stores needs to be incorporated into global climate simulations so that the effects of future climate changes on the stability of these stores can be estimated.
7. Ecological surveys and environmental impact studies will be needed for any potential storage sites identified. These surveys should catalogue the bacterial species present, and identify their nutrients and waste products and consider the effect of any pH changes due to dissolution of CO₂.

Expert Group Comments

The comments drawn from the experts were generally complimentary of the study. Most of the reviewers agreed with the general conclusions of the report. Many of the comments received were editorial. A number of experts requested more technical detail (on specific subjects such as the biological consequences), but this was not within the scope of the study.

It was notable that many of the experts responded with different theories on aspects of the study and opinions varied about which references were more appropriate to explain the conclusions drawn. Also opinions differed on the availability of data in certain cases. It is felt that these points reflect the current state of knowledge relating to hydrates, as it is new science with extensive laboratory work underway worldwide. All the reviewers agreed that more research on the subject was needed.

Major Conclusions

The major conclusions of the report are:

1. That CO₂ storage beneath the deep ocean, through the formation of CO₂ hydrate capped reservoirs, is scientifically feasible. However, extensive research would be needed to demonstrate the integrity of this storage option; the environmental/ecological consequences also must be carefully considered.
2. The enhancement of the extraction of methane from natural gas hydrates whilst storing CO₂ does not appear to be feasible. The hydrate will form an impervious barrier, which will limit the scope for replacing CH₄ hydrate with CO₂ hydrate, because the kinetics of the displacement will be very slow.

3. Injected CO₂ can be stored in a hydrate-capped gas reservoir. In such circumstances, the CO₂ can be trapped (either as a free gas or most likely as a fluid) by the methane hydrate or by the formation of a combined CO₂/CH₄ hydrate. The CO₂ could be stored for hundred of years provided exploitation of the methane hydrate resource is not considered in the future.

Recommendations

It is clear from the study that extensive further research is needed to determine the technical feasibility of CO₂ storage either as discrete hydrate deposits on the sea floor or in methane hydrate capped reservoirs. IEA GHG would, therefore, recommend to the international research community that the key research topics identified in this study be included in future research plans and programmes to assisting in developing the state of knowledge of hydrate chemistry and their potential as a CO₂ storage option.

One of the key findings of this preliminary study was that storage of CO₂ as hydrates combined with methane extraction did not look immediately promising in subsea situations. It must be noted at this stage that this review was based on available theoretical reference data and no consideration to the physical engineering of CO₂ injection into methane hydrates was given, because it was outside the contractors remit. However, the contractor noted that it is possible that to overcome, through careful design of the CO₂ injection technology, some of the objections raised about combined CO₂ injection and methane extraction could well be overcome. A second more extensive study is now underway that will evaluate in more detail the issue of CO₂ injection into CH₄ hydrates. This second study will include consideration of the engineering aspects of CO₂ injection and methane extraction, as well as considering the environmental issues associated with this storage technology. The study will focus on the permafrost natural gas hydrates which are considered to be more suitable for combined methane extraction and CO₂ storage than subsea hydrate deposits.

Issues Underlying the Feasibility of Storing CO₂ Using Sub-Sea Hydrate Deposits

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1 The Scope of this Report

Concern about the effect on climate of releasing large volumes of CO₂ is increasing and is set to become a major consideration in the global economy. As a result of various scientific studies, and particularly arising out of the Kyoto protocol, there is now a major interest in devising strategies for either reducing CO₂ emissions, or failing that, for producing safe methods for long-term CO₂ storage.

The purpose of this report is to consider what is known about storing CO₂ as sub-sea deposits, and to identify what still needs to be known before the viability of such a scheme can be assessed. Within this report the term “sub-sea deposit” is taken specifically to mean storage *below* the sea floor, *i.e.* geological sequestration. There has also been considerable discussion of deep-sea storage, *i.e.* by dumping CO₂ at depths for which the density of CO₂ exceeds that of sea water so that “lakes” of CO₂ will form on the sea floor. Some of the issues surrounding the feasibility of these two methods are similar, particularly relating to the possibility and desirability of forming CO₂ hydrate. However there are also many differences between the two storage mechanisms, and these are sufficiently great to warrant separate studies into the viability of deep-sea and sub-sea storage. This report focuses on issues for sub-sea CO₂ storage and on the role that CO₂ hydrate formation may play.

The possibility of geological sequestration is not limited to sub-sea storage. Analogous storage mechanisms involving hydrate formation may also be possible in permafrost regions. On-shore sites would provide some simplifications for implementing any storage scheme. However, the important scientific issues underlying the feasibility of geological storage are likely to be more restrictive for storage in permafrost regions. In particular, the factors that control the long term stability, the rate of CO₂ leakage, and the subsequent environmental consequences of any leaks are likely to be less restrictive for sub-sea storage. Thus assessing the feasibility of sub-sea storage is a useful starting point for determining whether geological sequestration of CO₂ is viable.

Given that natural gas hydrate deposits have existed over geological timescales, the idea of storing CO₂ in sub-sea reservoirs is not unreasonable at first sight. Indeed, the factors that lead to trapping of natural gas are similar to those that could lead to stable CO₂ reservoirs. There are differences—for example, biodegradation pathways for CO₂- and CH₄-hydrate are different—but the similarities are sufficiently strong that there may be advantages in coupling CO₂ storage with natural gas recovery. This report also seeks to identify some of the scientific and technological issues that may arise in this context.

Please note that within this report references are indicated by superscript numbers that refer to the numbered list given in section 6. Footnotes are denoted by superscripted symbols, and appear at the bottom of that page.

2 Introduction

In discussions of how to alleviate global warming problems created by the ever-increasing release of anthropogenic CO₂ into the atmosphere, there are several ways in which the vast resources of the world's oceans have been considered. Three in particular warrant mention: ocean fertilisation to increase the oceanic biomass; dumping of CO₂ to form “deep sea lakes” on the sea floor; and storing CO₂ below the sea floor in geological deposits. The purpose of this report is to identify the questions that need to be answered before the feasibility of the last option—sub-sea CO₂ reservoirs—can be assessed.

Although there has been some discussion of all the main oceanic CO₂ storage methods,¹ the literature on sub-sea storage is rather sparse. Most of the attention for physical storage methods has instead focussed on deep-sea storage. Some information is available from analogies with studies on methane and natural gas. Indeed, CO₂ is a component of natural gas, and its physical properties show many similarities with those of CH₄. There is also a great deal of information about the physical and chemical properties of CO₂ in non-geological environments. Much of the knowledge base for current discussions on sub-sea natural gas storage comes from these sources. Very recently there has been increased interest in CO₂ / water systems.² These have largely been motivated by the idea of deep-sea CO₂ storage, and have therefore focussed on CO₂ / H₂O liquid/liquid interfaces; the additional presence of soil or rock in sub-sea environments will substantially alter both the thermodynamics and kinetics of hydrate formation, and so some of this work may have only indirect relevance to sub-sea storage.

In sub-sea disposal, the CO₂ can either be stored in fluid form, creating the analogue of a natural gas well, or in the form of a *clathrate hydrate* (also called a *gas hydrate*, or simply *hydrate*). The latter is a crystalline mixture of water with CO₂. In reality, it is likely that both forms will be present in any useful CO₂ reservoir. Indeed, even though the greater volume of CO₂ is likely to be stored as a fluid, the whole viability of such reservoirs could well depend on the concurrent formation of CO₂ hydrate. The reason for this stems from geological conditions that are often associated with sub-sea gas reservoirs. Such reservoirs may form where layers of porous rock are surmounted by some impervious layer: leakage of gas from the porous rock will be prevented by the impervious layer so that over time a gas reservoir will build up. This is explained schematically in Figure 1.

Gas hydrates may provide a self-generating impervious cap. Where the porous strata are also water-rich, and provided suitable temperature and pressure conditions prevail (see section 2.1), the gas and water will combine to form a layer of gas hydrate. The gas hydrate is itself impervious to both the gas and water, and so provides a barrier to escape of any further gas. Of course, in real systems the CO₂ layer is unlikely to be complete, and so some leakage is to be expected. However if the leakage is sufficiently slow and occurs into a suitable CO₂ sink (*e.g.* dissolution in the ocean) then effective CO₂ sequestration could still be accomplished in this manner. Thus effective sub-sea CO₂ storage is likely to involve both hydrate and fluid phases.

This report begins with a sufficient summary of the physical properties of these two phases to allow an appreciation of the issues surrounding sub-sea CO₂ disposal. More detailed information is available elsewhere.³ The remainder of the report (sections 3–5) is structured

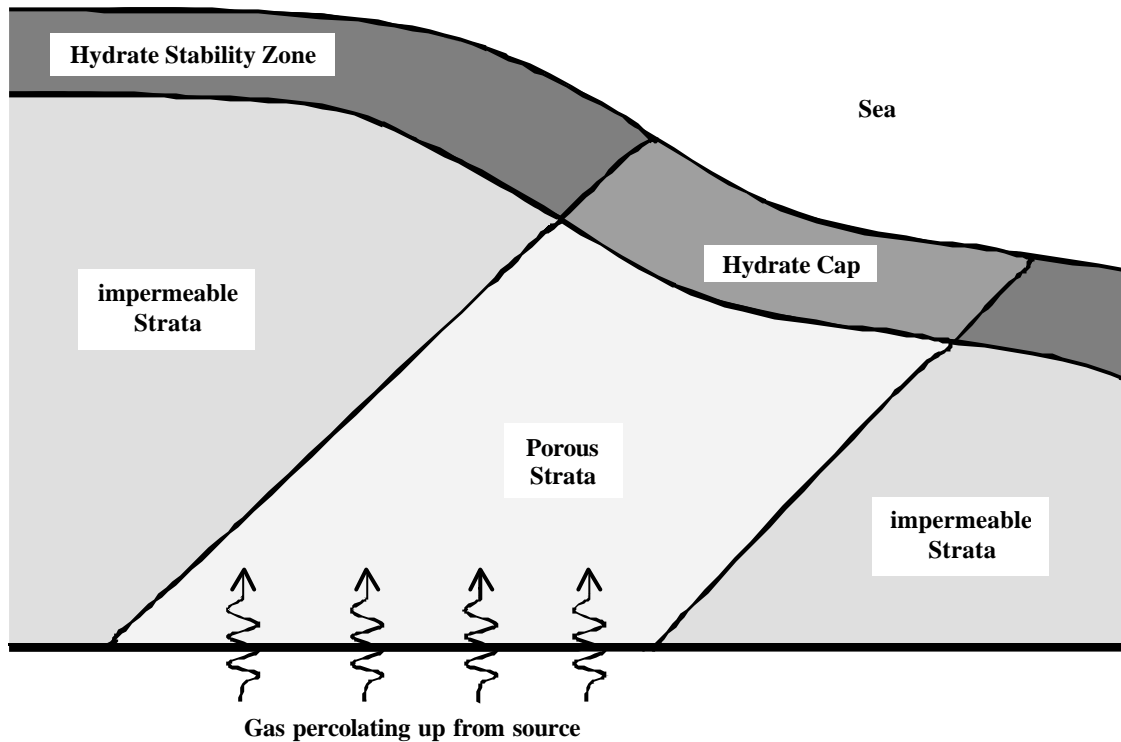


Figure 1: Schematic representation of how a hydrate capped gas trap can form. The darkened layer below the sea floor indicates the zone in which hydrates are thermodynamically stable, provided enough gas and water are available. Hydrates are likely to form when gas and water are mixed within this zone (e.g. by gas percolating up through the porous strata). The resulting layer of hydrate is impermeable to the gas, and so its formation seals off the gas trap.

around a series of questions that must be addressed before the viability of sub-sea storage can be assessed:

1. Is it possible to identify sub-sea sites that could be used to store CO₂?
2. What would be the viable timescale on which the CO₂ could be stored?
3. What would be the environmental impact of such storage?
4. What are the practical and technical issues involved in implementing such a storage strategy?
5. Are there any advantages in combining CO₂ storage with natural gas exploitation?

2.1 Summary of the Physical Properties of CO₂ Hydrate

Clathrate hydrates are a general class of crystalline host/guest compound. A tetrahedral hydrogen bonding network of water forms the host. This network is sufficiently open to create pores (or cavities) that are about 4–5 Å in radius, *i.e.* large enough to contain a variety of other small molecules (the guests). In general the guest molecules should be nonpolar, or perhaps weakly polar, so that they do not disturb the water hydrogen bonding network; but

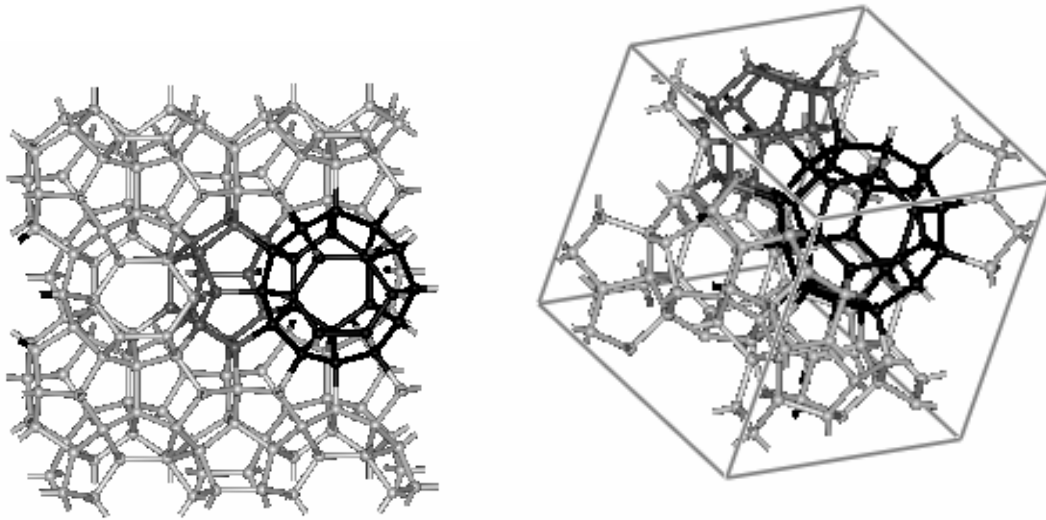


Figure 2: structures for type I (left) and type II (right) clathrate hydrates. Both structures are formed by packing together polyhedra of two different sizes. For each structure, one example of the larger polyhedron has been coloured black, and one adjacent smaller (dodecahedral) cavity in dark grey. Another possible structure, structure H, is not depicted as it is unlikely to be important for CO₂ storage.

thereafter the main constraint is merely that they should be of an appropriate size to fit into the cavities in the water lattice. These criteria are well satisfied by most of the principal components of natural gas, including CH₄ and CO₂.

There are several different hydrate crystal structures, depending on which guest molecules are present. Diagrams of two of these are given in Figure 2. Both CO₂ and CH₄ will generally form the type I hydrate structure, although only small amounts of ethane or propane are required to form type II hydrates containing a mixture of the guest molecules. This means that the structure adopted in natural deposits depends on the origin of the gas: biogenic gas is primarily methane and so likely to generate type I hydrates, while thermogenic gases contain a mixture of higher hydrocarbons and so are likely to generate type II hydrates. The thermodynamic stability of the different hydrate structures is slightly different, and so the details of which guest molecules are present can affect the precise details of the conditions under which the hydrates may be expected to form, although qualitatively they exhibit very similar behaviour.

The composition of a hydrate is determined by the number and type of cages found within the water lattice and by the thermodynamic conditions under which it was formed. For type I hydrates the unit cell contains two smaller cavities (radius 3.9 Å) and six larger elliptical cavities (radius 4.0–4.6 Å) along with 46 water molecules. Thus an ideal composition of (Small)₂(Large)₆ · 46 H₂O may be anticipated, although not all cavities need be occupied by guest molecules and so the factors 2 and 6 may be smaller (and non-integral). For a type II hydrate there are 16 small cages (radius 3.9 Å) and 8 large cages (radius 4.7 Å) along with 136 water molecules in the unit cell, giving an ideal composition of (Small)₁₆(Large)₈ · 136 H₂O. Methane is a suitable size to fill any of the cavities, but CO₂ is too large to occupy the smaller cavities. Thus the ideal composition for pure methane hydrate (type I) is CH₄ · 5.75

Hydrate Stability Curves

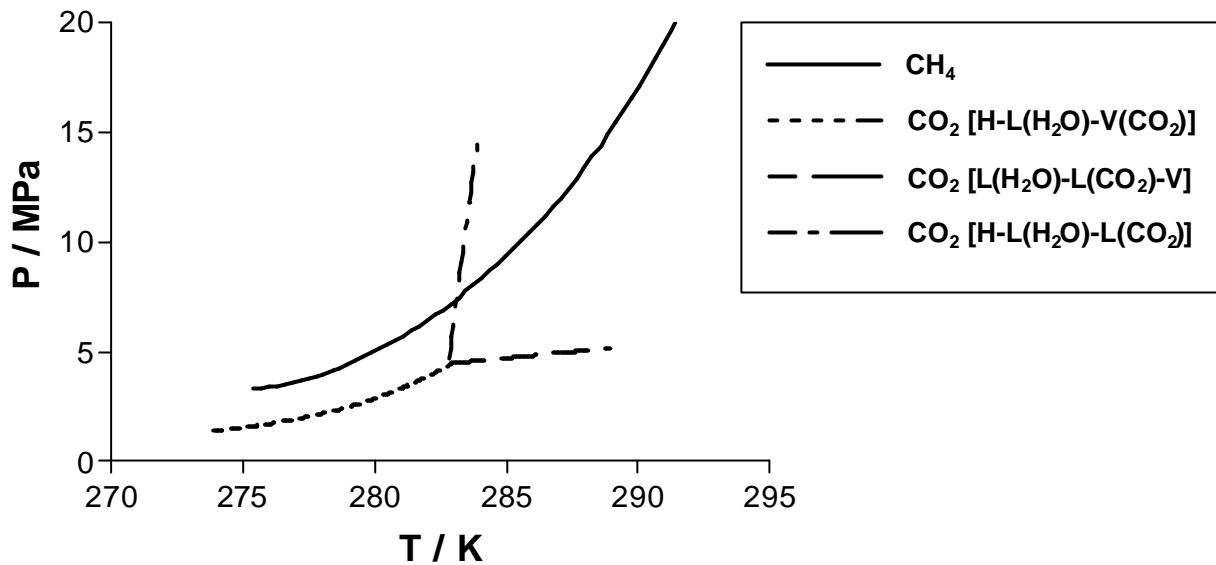


Figure 3: three-phase equilibrium lines for CO₂ and CH₄ hydrate. Hydrates will be stable for pressure-temperature combinations that lie above the respective lines. The cusp in the CO₂ curve at about 283 K arises because the hydrate curve overlaps the CO₂ liquid/vapour coexistence curve at this point. Thus, below 283 K hydrate forms from the CO₂ vapour, while above 283 K it must form from liquid (or dense fluid) CO₂. Since the liquid is far less compressible than the gas, much greater pressure changes are required to affect equilibrium.

H₂O (i.e. 8 methane for every 46 water molecules), whereas the ideal composition for pure CO₂ hydrate is CO₂ · 7.67 H₂O. This difference is sufficient to ensure that hydrate formation from a saturated water solution leads to a contraction with CH₄, but an expansion with CO₂. Much larger differences in composition are found when enough ethane or propane is present to cause type II hydrates to form. Both ethane and propane are also too large to occupy the small cages, and so only CH₄ can enter the small cages in the type II structure. Given a sufficient pressure of CH₄, there may be as much as one methane for every 8.5 waters in the mixed type II hydrate, whereas CO₂ will have to compete with both ethane and propane to occupy only one cavity for every 17 water molecules. Thus the presence of small amounts of ethane and propane can reduce the density of methane in a hydrate by about 30%, but will more than halve the density of CO₂.

The stability of the hydrate is largely determined by the pressure and temperature of the system: at sufficiently low temperatures and high pressures the hydrate becomes the thermodynamically stable form for a water/guest mixture. The actual temperatures and pressures depend on the nature of the guest compound involved, but for natural gas components they are comparable with those found in and around the sea floor along the continental margins. A convenient method of depicting the conditions for stability is via the three-phase equilibrium line that defines the conditions under which the hydrate, water-rich and guest-rich phases can all coexist. The three-phase lines (or hydrate stability curves) for CH₄ and CO₂ are given in Figure 3. One may anticipate that hydrates will form for temperature-pressure combinations that lie above these lines, but not for temperatures and pressures below the line.

The behaviour of CO₂ is not simple for the temperatures and pressures of interest. At about 283 K the conditions for forming CO₂ hydrate overlap the conditions for CO₂ liquid-vapour coexistence. Thus above 283 K CO₂ hydrate forms from liquid CO₂ while below 283 K it forms from CO₂ gas. The result is a much steeper hydrate curve above 283 K, and with a consequent cross-over with the CH₄ hydrate curve at 283.1 K and 7.4 MPa.

The implications of this for sub-sea CO₂ storage, and for enhanced methane recovery, are important. A more complete discussion is given later (see especially section 3.2), but it is useful to foreshadow these discussions at this stage. In essence, the data in Figure 3 indicates that the physical conditions required for stability of CH₄ and CO₂ hydrate overlap, but that neither is subsumed by the other. Thus one might expect to find regions where both CH₄ and CO₂ hydrate are stable, but also regions where only CH₄ hydrate can be stable, and still other regions where only CO₂ hydrate is stable. Where both are stable, it turns out that the two zones of stability usually start at the sea floor, but that the zone of stability for CH₄ hydrate extends deeper below the sea floor than that for CO₂ hydrate.

There are a number of factors other than temperature and pressure that will affect the stability of gas hydrates, and so will change the shape and position of the hydrate stability lines in Figure 3. In the context of CO₂ storage, the most important of these are probably the presence of other chemicals, non-equilibrium conditions, and the environment in which the hydrates are being formed. An obvious example of the first is that the presence of salt will lower the hydrate melting point. This is precisely the same effect that leads to salt water freezing at lower temperatures than pure water. Another example is the presence of alternative guest species. Gas hydrates are not specific chemical compounds with well-defined combining ratios. Instead, they can form from a mixture of guest molecules, and the composition of that mixture can vary continuously according to the conditions of formation. Thus in the presence of a mixture of CO₂ and CH₄, one will form a mixed CO₂/CH₄ hydrate rather than separate CH₄ and CO₂ hydrates. The resulting hydrate stability curve can therefore vary between the extremes presented in Figure 3 as the composition of the guest-rich phase varies from pure CO₂ to pure CH₄. The presence of small amounts of other hydrate-forming species, such as ethane or H₂S will likewise shift the position of the stability curves, and in particular will lower both the CH₄ and CO₂ hydrate curves.

The theory for calculating such shifts is well developed, and good discussions can be found elsewhere.⁴ For this review it is sufficient to know that such calculations can be made, but that they require a knowledge of a number of parameters that can not be obtained from independent experiments and so the parameters are normally derived by fitting the theory to extensive experimental data on hydrate stability. The resulting methods are very good for systematising well studied systems, but are sometimes of limited use in making predictions on new systems.

Non-equilibrium considerations can be important when determining whether hydrates will form and remain stable. The curves in Figure 3 are for a three-phase equilibrium, and thus delineate conditions for long-term stability. However, conditions in nature are usually not in equilibrium, particularly where large amounts of material are present. For example, where the liquid water is not saturated in the guest species, hydrate may not form even though the temperature and pressure is suitable; on the other hand, once hydrates do form, metastability effects could mean they will take millions of years to decompose, even when the temperatures and pressures are unsuitable.⁵ Thus the hydrate stability curves are a useful guide to hydrate formation, but should not be taken as the definitive guide to when and where hydrates will form.

The third factor—environmental effects—arises where hydrates are formed in porous media. In such cases a very large percentage of the hydrate formed can be near the interface with the surrounding rock, and so factors such as pore size distribution and composition of the porous medium will affect the properties of the hydrate.⁶ The theory of porous medium influences on hydrate formation is just beginning to be developed.⁷

One other property of hydrates is particularly important for any discussion of CO₂ storage, and that is its permeability. To a very good approximation, hydrates are impervious to both the host (water) and guest (CO₂, CH₄, *etc.*) molecules on any reasonable timescale. There have been very few measurements of diffusion in bulk hydrate samples, but those that do exist suggest that diffusion of water is at least 100 times slower than it is in ice,⁸ and there are no reports of diffusion of the guest in such systems. In the case of CO₂ hydrate there does appear to be some diffusion of CO₂ through the initial hydrate “skin” that forms at a water / CO₂ interface, but this is probably related to fractures of the interfacial skin or to undersaturation of one phase, and does not appear to be seen through the hydrate bulk.⁹ The significance of these observations for CO₂ storage is that the formation of CO₂ hydrate in sub-sea sediments can be expected to form an impervious seal, preventing escape of CO₂ from deeper sediments. Of course a perfect seal is unlikely to form in any real system, but substantially reduced permeability and self-sealing of some escape conduits may be expected to result from hydrate formation. This mass transport barrier is also likely limit the scope for replacing CH₄ hydrate with CO₂ hydrate, simply because the kinetics for the displacement will be very slow.

2.2 Relevant Fluid Properties

The description of fluid phases is a mature technology and this report assumes reasonable familiarity with fluid phase behaviour. The main point to note is that the prevailing conditions for which sub-sea storage is likely to be feasible are above the critical pressure for the main natural gas components. In particular, the critical pressures for methane and CO₂ are 4.6 MPa and 74 MPa, respectively. Thus for storage below ocean depths of about 750 meters, both CO₂ and CH₄ will exhibit supercritical[†] behaviour, and liquid/vapour phase changes will not occur *in situ*.

2.3 Initial Statement of Feasibility

From the information given above, one must conclude that the scientific viability of storing CO₂ as hydrate-capped sub-sea gas reservoirs warrants investigation. The very fact that hydrate-capped methane reservoirs do occur and have existed on geological timescales provides a proof-of-concept. CO₂ hydrates show similar physical properties to those of methane hydrates—particularly the fact that they form an impermeable barrier—and can form under similar pressures to those required for CH₄ hydrate. Thus, at first sight, it must be reasonable to suggest that CO₂ storage could be effected by creating hydrate-capped CO₂ reservoirs analogous to the existing natural gas reservoirs, or by replacing the CH₄ in naturally occurring methane hydrate. Another possibility, which might be easier to achieve, would be to introduce CO₂ into natural gas reservoirs which already have a methane hydrate

[†] In the context of this report, “supercritical” is taken to describe a system the remains *either* above its critical temperature *or* above its critical pressure at all times. In either case, the density of the system will vary continuously with any imposed changes, and no fluid-fluid phase transition will occur.

cap. Detailed examination of these ideas is required before any of them could be considered as a practical path to alleviate atmospheric CO₂ release. The purpose of this report is to identify some of those issues that require more detailed examination.

3 CO₂ Storage

3.1 Naturally Occurring Hydrates

THE ANALOGY WITH METHANE HYDRATE

The idea of sub-sea CO₂ storage involving hydrates has gained a great deal of credence from the facts that vast amounts of methane have already been stored in this way on geological timescales, and that the conditions for which CO₂ hydrate is stable can subsume the equivalent conditions for methane (see section 2.1). There are at least two major limitations that are overlooked by this analogy. The first is one of quantities. If one merely replaces methane with CO₂ then one is left with the question of what to do with the methane—an even more potent greenhouse gas than CO₂. Presumably the point of extracting methane is to use it as an energy source, in which case it will just regenerate CO₂ and one has made no net difference to the carbon cycle. While this would provide a source of energy—methane—without further exacerbating the global warming problem, it would be preferable to provide a net sink in the carbon cycle. In reality, since there would be an energy cost involved in replacing sub-sea methane hydrate with CO₂ hydrate and that energy resource is likely to come from carbon-based fuels, a replacement strategy would still be a net source of CO₂, albeit at reduced emission rates. The point at issue here is that in assessing the viability of any sequestration method, it will be important to determine the quantity of CO₂ that can be stored, and the efficiency (in terms of the overall CO₂ cycle) with which the storage can be effected.

The second limitation is probably more fundamental. While the current estimates of the amount of naturally occurring methane hydrate are very large (to within an order of magnitude, they constitute more than half the world's organic carbon content¹⁰), they are not necessarily in a form that would permit replacement by CO₂. The question of how naturally occurring hydrates form is still subject to some discussion, but it is likely that most of the methane is biogenic in origin, and thus involves the release of small amounts of methane over a large area. This in turn leads to small hydrate particles that are finely dispersed through the sea-floor sediment. The technology required to replicate a similar supply of CO₂ on the same scale as found in nature is not achievable at present. Smaller, more concentrated deposits may be viable provided sufficient volumes of CO₂ can be deposited as hydrates with acceptable efficiency; the knowledge-base needed to predict this is discussed in sections 3.2 and 3.3.

There is one class of methane hydrate deposit that is likely to provide a reasonable blue-print for CO₂ storage. These are the systems in which hydrate itself forms an impervious seal above a porous rock stratum, thereby creating an effective gas trap¹⁰. Probably the best-known example—the Messoyakha field¹¹—is actually in a permafrost region, but numerous sub-sea examples are also found. In many cases this can be a self-trapping mechanism: hydrates may form if the junction between the free gas zone and a water-rich zone above it, occurs at temperatures and pressures that are within the hydrate stability zone. In such cases, release of CO₂ deep in the porous strata could generate a CO₂ hydrate layer above the release point that would prevent the CO₂ from escaping. It would thus generate an effective store for CO₂ in both hydrate and fluid forms. Given the different range of stability for CO₂ hydrate compared with CH₄ hydrate, CO₂ storage in this manner would not be limited to places where methane hydrate is already found, and so might provide a real sink in the carbon cycle.

This association of CO₂ hydrate formation with geological gas traps is not essential. Existing natural traps that are not associated with hydrates could also be used, and indeed are already used to some extent by the oil industry. However existing traps usually contain some other fluid such as oil or thermogenic gas already, and so raise the complexities associated with fluid replacement strategies. The singular advantage of coupling gas traps with CO₂ hydrate formation is that the seal, and hence the trap, would not exist prior to the CO₂ injection: the resulting traps would represent a *new* storage resource. Further, since the seal is self-generated, one might expect that any leaks that form—say due to weak seismic activity—could be plugged by the crystallisation of more CO₂ hydrate. This is clearly a best-case scenario, and is useful for establishing whether the idea is worth pursuing. As outlined below, there are a number of practical and technical difficulties that will limit the efficiency of such storage, and these will need to be understood better before the feasibility of sub-sea CO₂ sequestration can realistically be assessed.

CO₂ HYDRATES

Another source of guidance on the feasibility of sub-sea CO₂ storage might seem to be found in naturally occurring CO₂ hydrate deposits. Unfortunately, the literature on these is very sparse. Those reports of which the author is aware are perhaps best characterised as representing the incidental formation of CO₂ hydrates, or CO₂-containing hydrates. For example, CO₂ hydrates have been reported in Okinawa trough, but they appear where CO₂-hydrocarbon fluid inclusions leak through fissures.¹² CO₂ has also been found in hydrates recovered from the Gulf of Mexico,¹³ but in this case the samples were predominantly methane hydrate with the methane being of thermogenic origin: thermogenic natural gases may contain as little as 20% methane,¹⁴ and so a mixed hydrate is to be expected. There are some calculations to suggest that CO₂ hydrates could form in various marine areas of South East Asia¹⁵, but there has not been any experimental confirmation of this. In summary, there are no reports in the literature of concentrations of natural CO₂ hydrate.

The absence of reports of natural CO₂ hydrates could occur for various reasons. Apart from the obvious explanation (*i.e.* there are no natural CO₂ hydrates), it must be recognised that there has not been any financial incentive to search for CO₂ hydrates. There have been considerable technical difficulties in recovering methane hydrates from sub-sea core samples, due to the difficulties in maintaining internal pressures during core recovery, and it is likely that recovering samples of CO₂ hydrates would be just as difficult. This, coupled with the lack of economic incentive to search for CO₂ hydrate, may explain why such hydrates have not been found. Another, more fundamental explanation might also exist. Kvenvolden reports that, with the exception of the Gulf of Mexico and Caspian Sea, the methane in sub-sea hydrate deposits is biogenic in origin, deriving originally from the microbial reduction of CO₂.¹⁴ Thus it is entirely possible that, over geological timescales, microbial activity has converted potential CO₂ hydrate deposits into methane hydrate deposits. If this were the case, it would suggest that sub-sea sequestration of CO₂ is plausible and could even have spin-offs in replenishing methane reserves, although substantial enhancement of the microbial activity would be needed to make this advantageous on human timescales.

CHARACTERISTICS OF A POTENTIAL HYDRATE-RELATED CO₂ STORE

From the above discussion, it appears that sub-sea sequestration is most likely to be associated with CO₂ hydrate formation. Ideally, the storage site would be formed by using CO₂ hydrate formation to cap a potential gas reservoir. The technical feasibility of creating

such a store will depend on the amount of CO₂ that would be stored as hydrate, the amount of CO₂ stored as fluid in or below the hydrate-forming region, the rate at which the CO₂ can be deposited, and the percentage of CO₂ lost while creating the store. Sequestration is likely to be most efficient when an effective hydrate seal can be formed and the ratio of trapped gas to hydrate is large; however detailed calculations of the amount and efficiency of CO₂ storage might show that hydrate formation alone is sufficient to alleviate global warming. A number of the factors to be addressed in making such calculations are discussed in the following sections. The discussion will be focussed around hydrate-capped reservoirs as this subsumes the simpler hydrate-only system.

3.2 Identification of Potential Sites

Potential CO₂ storage sites must satisfy a combination of suitable physical, chemical and geological properties. In many cases these properties are well understood, although the relevant data may not have been compiled with CO₂ hydrate in mind. Thus locating at least some potential sites is likely to be achievable with the current knowledge-base. The following discussion identifies some of the questions that must be addressed in identifying potential sites, should they exist. The demarcation between the different topics is not always clear-cut, and so the headings are meant as a guide rather than as a rigorous categorisation.

EXISTING HYDRATE-CAPPED METHANE TRAPS

The obvious starting point for identifying possible storage sites is the analogous natural gas sites that already exist. Since CO₂ hydrate can form under similar conditions to CH₄ hydrate, replacement of CH₄ with CO₂ could create CO₂ storage sites that are stable on geological timescales. By ensuring that the pressure of the CO₂ matches that of the CH₄, it might also be possible to ensure that there is little change to the geological stability of the region. There is an underlying assumption that CO₂ hydrate formation is entirely analogous to CH₄ hydrate formation, and this is not always the case (see GEOCHEMICAL CONSTRAINTS, below). Nonetheless, the existing CH₄ hydrate reservoirs should provide a good starting point for any feasibility study.

As identified in the introduction, it is desirable to extend the scope of this search beyond the existing methane sites. The following sections enumerate some of the factors that should be considered in identifying *both* existing methane reservoirs and potential new carbon reservoirs.

PHYSICAL CONDITIONS

The starting point in locating suitable sites is to map out the regions below the sea floor in which the physical conditions (primarily temperature and pressure) would allow the formation of CO₂ hydrate. The methods for doing this are already well established in connection with methane hydrate.¹⁶ An example of how to do this is presented in Figure 4. In this figure the depth below sea level has been used as a measure of the ambient pressure: for example, for every 10 m of water below sea level, the pressure will increase by about 1 atm. A knowledge of the thermal gradient, both in the sea and then below the sea floor, can be used to calculate the temperature at each depth. Note that the comparatively rapid loss of heat through convection in liquid water means that there is an inversion of the temperature gradient at the sea floor. By comparing this information with the stability conditions for hydrate formation (see Figure 3) it is possible to see whether there is a suitable overlap, and

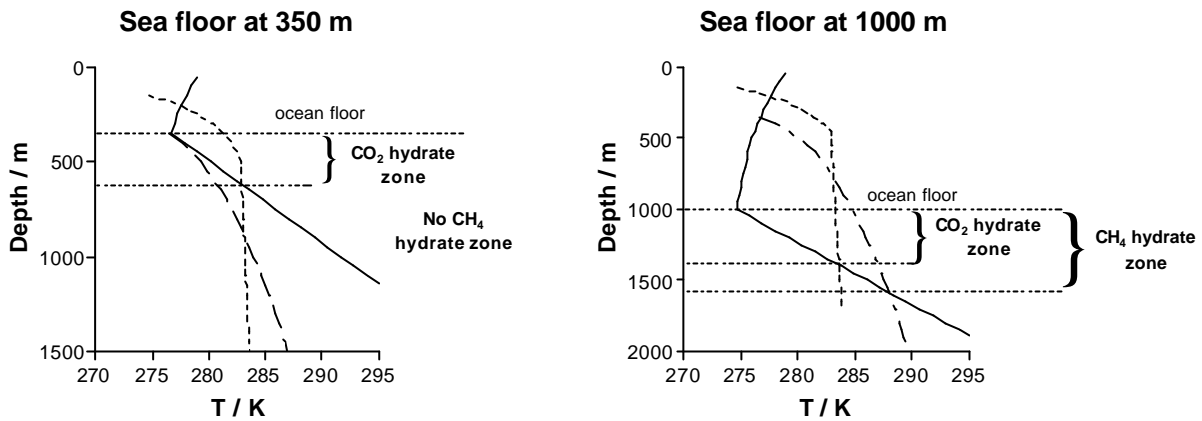


Figure 4: an example of how to calculate the zone of hydrate stability. The solid line indicates the temperature at different depths (calculated using typical thermal gradients and a sea-floor depth of either 350 m or 1000 m). The other two lines are the hydrate stability curves for CO₂ (---) and CH₄ (- · - · -) at the pressure and temperature associated with that depth. In principle, hydrates can form over the whole range of depths for which the hydrate stability curve lies to the right of the depth-temperature profile. In practice, hydrates will not form above the sea floor as sea water is not saturated in either CO₂ or CH₄

hence whether there is any chance that stable hydrate deposits will form. Hydrate formation may theoretically occur above the sea floor, but only if the sea were saturated in the hydrate forming gas (CH₄ or CO₂) and this is not usually the case. Thus hydrate formation should be limited to those regions below the sea floor for which the hydrate line lies to the right of the ambient temperature (as indicated in Figure 4). Note also that given the gradients of the various curves in Figure 4, the thickness of the hydrate forming zone will not change much with depth of the sea floor, so that the base of the hydrate zone has the same shape as the sea floor.

There is a good understanding of how to calculate geothermal temperature and pressure gradients and hydrate stability lines under normal conditions, and suitable computer programs exist that will give quite accurate calculations using standard personal computers. Such methods are well established for methane.¹⁷ There is no obvious reason why similar calculations can not be repeated, with reasonable accuracy, for carbon dioxide. Where high accuracy is needed, some modification of these calculations will be required to account for porosity and chemical impurities (as described under *GEOCHEMICAL CONSTRAINTS*), but calculations based on pure CO₂ hydrate should provide a reasonable first estimate of viable locations.

Two useful observations emerge from Figure 4. The first is that there are regions in which only CO₂ hydrate will form, but these are limited to fairly shallow ocean floors. The second is that where both hydrates can form it is almost always the case that both stability zones will commence at the sea floor, but that the CH₄ hydrate zone will go deeper than that for CO₂ hydrate; this will always be the case where the sea floor is below about 750 m. It is theoretically possible in shallower waters to find regions in which the CH₄ hydrate stability zone starts below the CO₂ hydrate stability zone, but this would require substantially greater geothermal gradients than shown in Figure 4, and could occur only in shallower waters.

GEOPHYSICAL REQUIREMENTS

As identified above, a potential sub-sea CO₂ storage site is likely to be characterised by a porous region that is suitably bounded by impermeable strata. In some cases it may be feasible that the entire impermeable region could be provided by hydrate formation. This is illustrated in Figure 5 and arises because the thickness of the hydrate-stable zone depends only weakly on depth, so that the base of the hydrate zone tends to mimic the shape of the sea floor. The feasibility of forming such a trap without significant loss of CO₂ would depend crucially on there being a suitable match between the rate of gas diffusion through the porous region and the corresponding rate of hydrate formation on its boundaries, and this may not be easy to ensure. Without such a match there will be either escape of CO₂ or incomplete filling of the gas trap. Detailed modelling of the reservoir fluid dynamics and hydrate formation kinetics in porous media, integrated with global warming simulations, would be needed to determine whether the resulting CO₂ storage would be sufficiently efficient. A more favourable scenario is where the sides of the gas trap are provided by existing impermeable layers (Figure 1).

Current sources of information, such as the Ocean Drilling Programme (ODP) and various oil exploration projects, provide a reasonably comprehensive knowledge of the seafloor geology in a number of regions of the world. In particular, there is data on a small number of methane hydrate sites.¹⁸ It is likely that these existing sources will provide a suitable data base for an initial estimate of the likelihood of finding sites that match the criteria outlined above and the possible volumes of CO₂ that could be stored in such sites. A considerable amount of analysis of the existing data would be needed, but the database itself should be adequate for an initial assessment of the feasibility of sub-sea CO₂ storage, and to identify some possible sites.

Another factor that would need to be considered is the mechanical strength of the sea floor. The absorption of appreciable amounts of gas into hydrate deposits could, in principle, lead to lower pressure in the porous region below the hydrate layer. At the same time, formation of CO₂ hydrates in water-filled pores would lead to an expansion of the water-phase and could cause fracturing of the microscopic rock structure. Both effects would generate new stresses in the sea floor, and could thereby weaken the geological stability of a region.

In order to assess the degree of risk this poses, it is necessary to know the mechanical properties of both the porous and impermeable strata, the degree to which water fills the pores in the porous media, and the extent to which this is affected by pore size. It is also necessary to be able to predict the distribution of hydrate formation in such a system. Some of the formalism required to make such predictions is available. Many of the same problems have already been tackled in the context of enhanced oil recovery from older oil reservoirs and so there are models for simulating the diffusion of gases through porous media, and reasonable information about pore size distributions in many regions of the sea floor. There is also an understanding of how water is distributed through different types of porous rock, and the degree to which the different pore sizes are filled by water. Some uncertainties have recently arisen about the expansion of the water phase when CO₂ hydrates form,¹⁹ and these will need to be resolved before risks to geological stability can be assessed with confidence; this point is discussed under GEOCHEMICAL CONSTRAINTS below.

GEOCHEMICAL CONSTRAINTS

The geochemical constraints on locating a suitable sub-sea CO₂ storage site are probably the least well understood, and a great deal of theoretical and experimental work is still needed

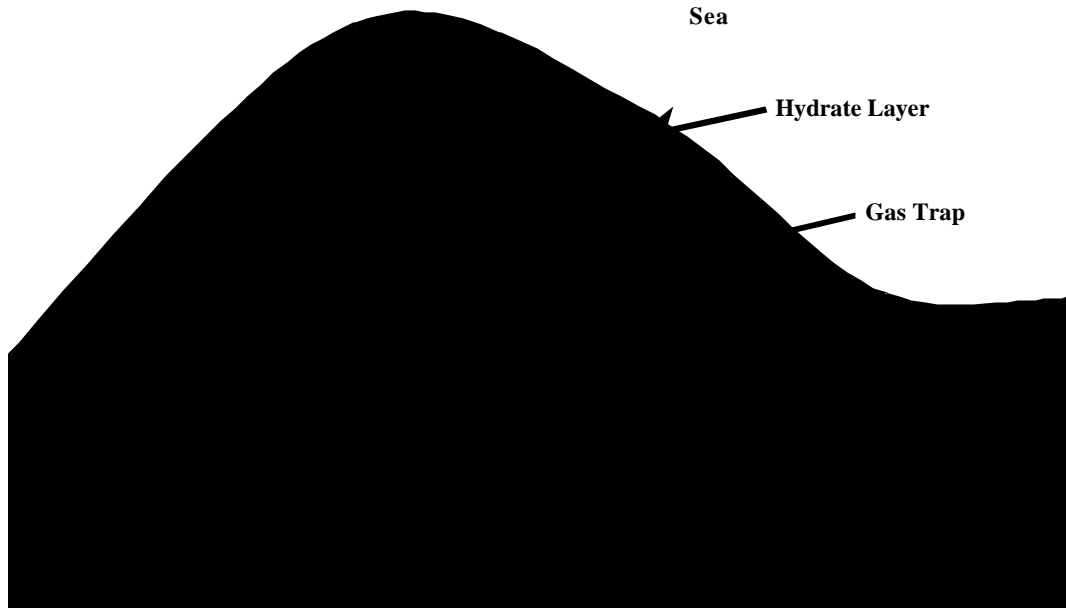


Figure 5: Illustration of how hydrate formation could generate an entire gas trap. Due to low and relatively uniform temperatures on the deep sea floor, the hydrate stability zone tends to follow the shape of the sea floor. Thus a mound formed from porous rock could become encased in a layer of clathrate, thereby trapping a pocket of gas at its centre

before one can hope to enumerate the ideal properties of a sub-sea CO₂ storage site. Broadly speaking, the geochemical issues fall into three categories: possible chemical reactions; hydrate formation kinetics; and hydrate stability.

Chemical Reactions

There is one very significant difference between CO₂ and CH₄: CO₂ can react with water. In particular, introducing CO₂ into water will lead to the formation of HCO₃⁻, CO₃²⁻ and H₂CO₃ species, and will in the process alter the pH of the system. The consequences of this have not been well established in connection with CO₂ hydrate formation, nor have the possible interactions with carbonate species present in the sea-floor sediment. Indeed, the experiments on CO₂ hydrate formation do show some abnormalities that need further investigation. Perhaps the most striking of these has come from the work of Brewer¹⁹ who found that liquid CO₂ left on the sea floor at depths of more than 3000 m did form a solid, but that the volume expansion involved in this process was many times greater than it would have been if CO₂ hydrate were to form. It has been suggested that the large volume arises from rapid hydrate growth giving rise to cavities which occlude sea water, *i.e.* a solid foam of CO₂ hydrate is formed; however there have been no molecular structural studies to confirm this and so the ramifications for sub-sea CO₂ storage can not be enumerated with any confidence. A volume expansion of this magnitude could also raise the possibility that the solid has a different structure or morphology from the known hydrates—possibly induced by impurities found on the sea floor—and that in turn implies that the permeability of such a solid is unknown. Further, expansions of this magnitude may not be possible in porous media, and so the self-capping process either may not occur, or if it did occur, could threaten geological integrity in the vicinity of the storage site. At worst such a phenomena could undermine the whole concept of sub-sea CO₂ storage. A much better understanding of how factors such as pH, the

carbonate equilibria and high pressure influence CO₂ hydrate formation is therefore an essential pre-requisite for establishing the feasibility of sub-sea, or indeed deep-sea, CO₂ storage.

Kinetics of Hydrate Formation

The rate at which CO₂ hydrate will form is likely to be a major determinant of the feasibility of sub-sea CO₂ storage. Since hydrate formation is essential for trapping the CO₂, if the kinetics are too slow then significant leakage of CO₂ must be anticipated prior to forming an adequate hydrate seal. Alternatively, if the kinetics are too rapid then hydrate formation may occur too close to the point of release, and the potential storage volume will be reduced. In part, the kinetics of hydrate formation can be modified by controlling factors such as the rate, pressure and location of CO₂ release, however the scope for exerting such control may be limited. Factors such as the porosity, pore size distribution, chemical composition and heat-flow characteristics of the sediment must also play a role. The chemical composition is likely to be particularly important for silicate- and carbonate-rich sediments, since these substances will have a strong ordering effect on any water they contain.

A closely related question is the volume of hydrate that will form, and the consequent permeability of the hydrate layer. If hydrate formation occurs slowly compared with the dissolution of CO₂ in the pore water, then some continued hydrate formation may be expected subsequent to initial hydrate formation. On the other hand, if the initial hydrate formation occurs rapidly at the CO₂ / water interface compared with dissolution, then hydrates may form in only a thin layer on any sensible time scale. Subsequent geological disturbances would then be likely to cause CO₂ leaks, and in extreme cases there would be an increased risk of a CO₂ blow-out. This issue is coupled to hydrate kinetics in that both the kinetics and thermodynamics of hydrate formation are dependent on pore size. Thus different CO₂ percolation channels will seal at different rates. A suitable match between the percolation rate for CO₂ and the hydrate formation rate will allow mixing of CO₂ and water over a wide band, and hence could generate a thick hydrate layer in a reasonable time.

At present the theory for how the character and size of pores affects the kinetics of hydrate formation is in its infancy. There are some theoretical developments aimed at predicting the effect of pore size on the stability of hydrates,⁷ but these do not account for the chemical composition of the sediment. Some experiments have been performed on the formation of methane hydrate in sandstone, and these do indicate significant differences in hydrate stability and kinetics from that found in simple gas/water mixtures.²⁰ Analogous experiments for CO₂ hydrate formation in a variety of soil and rock types is needed to provide the data from which a suitable theory can be developed and validated.

Nucleation of hydrates is typically rapid in heterogeneous environments, and so is unlikely to be a factor in determining hydrate formation kinetics.

Hydrate Stability

While a good first estimate of the possible hydrate-forming regions can be obtained from calculations on pure CO₂ hydrate formation, more accurate calculations may be needed if and when a potential site is identified. Two factors in sub-sea environments will complicate the process. The first—the porous medium—has been discussed above. The second is the presence of chemical impurities *in situ*.

It is well known that many chemicals will shift the location of the hydrate stability line in Figure 3. For example, the presence of dissolved salts will shift the curves to lower temperatures (*i.e.* destabilise the hydrate) whereas the presence of other potential guests such as propane or H₂S will tend to shift the curves to higher temperatures (*i.e.* stabilise the hydrates). These shifts can be calculated using established hydrate stability computer programs²¹ provided that one has suitable parameters for the impurities. Parameters are well known for natural gas formation in the presence of most of the common impurities found in sub-sea environments natural gas hydrates. However, the parameters were not developed from an extensive range of mixtures in which CO₂ was the major component and so may not be sufficiently accurate for sub-sea CO₂ storage predictions. They also are not parameterised for *pH* variations at present. Some systematic experiments may be needed to develop more appropriate parameters.

3.3 Long-Term Storage

An important factor in assessing the viability of any CO₂ storage strategy is the time-scale over which storage can be effected. The issues relating to the short-term stability of a storage site have been discussed in section 3.2. These involved identifying the rate at which a CO₂ trap would be sealed, the thickness of that seal, the changes to the geological stability caused by introducing CO₂ fluid and subsequently forming CO₂ hydrates, and the influence of the local chemistry on the impermeability of the seal. For long-term storage there are a number of additional factors to consider, and these are outlined below.

LEAKAGE MECHANISMS

Consequences of Leakage

Loss of CO₂ is to be expected both while laying down a CO₂ store, and during its subsequent lifetime. Such leakage may be acceptable for one of several reasons:

- (i) leakage may occur into another CO₂ sink, *e.g.* dissolution into the ocean;
- (ii) a reduction in CO₂ emissions, rather than complete abeyance, is probably adequate to avoid global warming; or
- (iii) it may be economically and technically feasible to capture and redeposit the CO₂ that leaks out.

In order to determine whether or not the leakage is acceptable, one will need to predict the rate of CO₂ loss from all possible mechanisms, and then feed this data into larger global warming simulations. The following discussion addresses some of the more important leakage mechanisms that would need to be characterised in order to do this.

Diffusion Pathways

It could be said that there is no such thing as an impermeable barrier—it just depends on how long one is willing to wait. The rate of diffusion for CO₂ through a single crystal of CO₂ hydrate may be extremely small, but it will not be zero. When the hydrate is formed in a porous medium, with no guarantee that the hydrate actually fills all the pores, then the rate of diffusion is likely to be considerably greater than for the single crystal. Hence the possibility of diffusive loss of CO₂ must be considered, particularly if storage is required for a period of centuries. The same processes will also lead to continued growth of CO₂ hydrate over time,

and consequent blocking of some of the longer-lived diffusion pathways. It will be important to be able to estimate the speed of this diffusion, so that the safe lifetime of the CO₂ storage can be estimated.

There is already a great deal of expertise for describing the flow of liquids and gases through porous materials, and diffusion of solutes within these fluids. This comes in part from the petroleum industry, where much work has been done on reservoir modelling, and geological modelling of aquifers, but also from quite different applications such as predicting the lifetime of radioactive waste dumps. The possibility of hydrate formation within the porous substrate adds a new dimension to these problems.

To understand what is still needed it is useful to consider the microscopic nature of a porous material. For typical rock systems such as sandstones, the solid rock actually contains a network of pores that may be only about 10^{-6} m in radius; in some cases they will be even smaller. These pores will overlap to provide a network of tiny channels through the material. When water is present, surface tension effects ensure that the hydrostatic pressure within each pore is slightly different, and so the porous medium actually represents a distribution of thermodynamic states. The situation is even more complicated when another fluid such as CO₂ or methane is present, since this will often lead to partial filling of the pores by water. For hydrophilic surfaces such as silicates, the water will coat the surface of the pore, but for hydrophobic surfaces it would be more likely to be found as a small droplet at the centre of the pore.

When CO₂ is forced through this system under conditions favourable to hydrate formation, it will form hydrate with the available water. However, because of the distribution of pore size and composition, hydrate formation will not necessarily occur in all pores just because the overall temperature and pressure are within the hydrate stable region. Further, partial filling of pores with water would lead to only partial filling with hydrate.⁷ The consequence for hydrate formation is uncertain. The formation of methane hydrate from saturated water would lead to a contraction of the aqueous phase,¹⁸ and so would leave the pores partly empty; for CO₂ hydrate, however, the opposite is true and an expansion of the aqueous phase results. On the other hand, if the CO₂ hydrate formation proceeds in the manner found by Brewer¹⁹, then an incomplete filling of the pore by the hydrate phase is again to be expected. For all these reasons it is likely that significant diffusion of CO₂ will continue after hydrate formation, and this will lead to both loss of CO₂ and to a gradual thickening of the CO₂ hydrate layer.

In order to predict the rate of CO₂ escape, it is therefore essential to know the thickness and distribution of hydrate in the hydrate zone, the rate of diffusion through the various pores (including pores blocked by only thin hydrate films), the rate of CO₂ diffusion through pore water, and the number, length and radius of available diffusion channels. Some of this information is available. In particular, there has been considerable discussion of the diffusion of CO₂ through the hydrate skin that forms at a CO₂ / water interface; however, there is currently no agreement on a theoretical treatment to predict these diffusion rates.²² Further, these discussions have been in the context of deep-sea CO₂ storage, and so there has been no consideration given to the effect of pore size and composition on this process. Experimental and theoretical studies of the diffusion of CO₂ through porous rocks are therefore needed to estimate the maximum time over which sub-sea CO₂ storage is likely to be feasible.

Biological Influences

Biological interaction with hydrates is well known for methane hydrate. In part this may be microbial, with different types of bacteria either oxidising the methane or reducing the carbon dioxide. However, higher life forms have also been found to disrupt methane hydrate formations, as in the polychaete worms found associated with methane hydrate plumes at a depth of more than 500 m in the Gulf of Mexico.²³

The greater stability of CO₂ hydrate in shallow waters does create possibilities for both animal and plant life forms to have an impact on sub-sea CO₂ storage. The stability zone for CO₂ hydrate could extend to sea floor depths of only about 200–300 m, and this overlaps significantly with the primary biosphere for higher organisms. While it is unlikely that any animal life forms would actively consume CO₂ from hydrates, it is conceivable that their activities could indirectly affect the integrity of a hydrate layer (*e.g.* burrowing through it).

It is unlikely that biological interactions will determine the scientific feasibility of sub-sea CO₂ storage. It is far more likely that the creation of a CO₂ store will affect the surrounding ecosystem, and so environmental impact studies will be needed if sub-sea CO₂ sequestration is shown to be feasible from a technical perspective. These issues are discussed briefly in section 3.4, but more complete studies will be the subject of future reports from the IEA Greenhouse Gas programme.

HYDRATE DECOMPOSITION

There are risks to the long-term viability of hydrate-related CO₂ storage arising from possible drifts in global climate. These arise mainly from possible changes in ambient temperature and can be understood by referring back to Figure 4. Global warming is likely to lead to an increase in the ambient temperature at storage sites, and this would tend to destabilise the hydrate deposits. For sub-sea deposits, the timescale for warming is likely to lag behind that for terrestrial changes, and can in any case be masked by shifts in tidal patterns. Small changes in temperature will shift the hydrate stability zone in Figure 4 upwards, and thus will lead to a narrower zone in which CO₂ hydrates can form. If the temperature changes are sufficiently large, this could lead to the disappearance of a stability zone, or to a hydrate zone that is too thin to provide an effective barrier to escape of underlying CO₂ fluids. An estimate of the maximum safe temperature increase should be included as part of the thermodynamic modelling that will be needed to identify potential storage sites (section 3.2: PHYSICAL CONDITIONS).

Reference to Figure 4 would seem to indicate that changes in the sea level should also affect the long term stability of hydrate deposits. The extent to which this will happen in the context of global warming is unclear. While melting of the polar ice caps will lead to an increase in sea level, it is only the melting of land-based ice mass that will alter the hydrostatic pressure on the existing sea floor. (The ocean is already supporting the weight of the sea-based ice mass, and melting this will merely redistribute that weight.) There may also be some effect due to subsequent changes in ocean salinity, but these will almost certainly be negligible over a span of 10² years. An increase in pressure will tend to offset any effect of increasing temperature, but the base of the hydrate stability zone is much more sensitive to temperature changes than to pressure changes (see Figure 4), and so this is likely to be negligible.

EARTHQUAKES, LAND SLIPPAGE ETC.

The most obvious risk to long-term storage is probably from geological instabilities: for example, geothermal or seismic activity in the vicinity of a CO₂ store will clearly introduce a risk of catastrophic CO₂ leaks developing. A number of such factors have already been catalogued in connection natural gas hydrates,²⁴ and these are likely to be relevant for CO₂ hydrate as well. It will be necessary to establish what is an acceptable level of risk in this context, and that will, in turn, depend on the size, number and distribution of CO₂ storage sites that is envisaged. The occasional rupture of a small site, with consequent release of relatively small amounts of CO₂ may have negligible consequences for global warming. In turn, the scale of sub-sea CO₂ storage can not be assessed until its initial viability has been considered. Thus, assuming appropriate sites in regions of stable geology can be identified, the effect of tectonic movement can probably be left to a later stage in the development cycle.

3.4 Environmental Impact

The possible impact on the environment can be grouped into three main classes: the impact on geological stability; the introduction of contaminants; and the effect on the biosphere. The issue of geological stability has already been addressed in connection with identifying a suitable site (section 3.2) and will not be considered further here. The possibility of contaminants depends largely on the technology used to produce the CO₂ prior to storage. If the CO₂ is produced in a highly purified state, then the only question is what effect does the CO₂ itself have on its environment; again, this has already been addressed in section 3.2. If impurities are present in the CO₂ then their impact will have to be considered. This will depend upon the technology used to capture CO₂. This technology is dealt with in other reports by the IEA Greenhouse Gas Programme; this report has not examined the consequent implications for environmental impact of hydrate storage.

Biological Impact

The nature of any biological impact will be very specific to the location of the storage site, and specific ecological impact studies will be needed once possible sites have been identified. In generic terms, the introduction of large amounts of CO₂ into an ecosystem must be expected to have some impact on the local ecology. Under the sea floor there are regions in which microbial reduction of CO₂ to CH₄ occurs;²⁵ indeed, this is probably one of the more significant sources of biogenic methane for methane hydrate formation. Thus shifts in the bacterial population of sub-sea sediments are likely to follow from attempts to store CO₂, with consequent changes in the concentration of compounds used or generated by these bacteria. The extent to which such methanogens could utilise CO₂ from CO₂ hydrates does not appear to be known, and so there is the possibility that bacterial activity could threaten the viability of the self-generating hydrate seal for a CO₂ gas trap. Alternatively, introducing large amounts of CO₂ will substantially lower the pH of water in the region, and this could adversely affect any bacteria present. Before a reasonable assessment of the biological impact is possible, work is needed to identify the relevant bacterial species present at each potential site, examine their tolerance to pH changes, analyse for the abundance of their other nutrients (is CO₂ the limiting compound?) and catalogue the compounds they produce. Knock-on effects for higher organisms must also be assessed.

3.5 Summary

In summary, sub-sea CO₂ storage is most likely to be technically feasible using a porous rock or mud deposit that is sealed by growing a layer of CO₂ hydrate at its boundary (Figure 1). A strategy for locating such regions would be to correlate the geological requirements (*e.g.* suitable porosity) with physical requirements (temperature and pressure) for stable CO₂ hydrate. This is entirely analogous to conditions found in many natural gas reservoirs, which are themselves gas traps that result when methane hydrate crystallises to create an impermeable barrier at the top of the porous deposit.

There is already an extensive data base on the sea floor geology, and suitable methods exist to calculate the zone of hydrate stability for different parts of the sea floor. These should be sufficient to identify at least some likely locations and estimate a probable CO₂ capacity as part of a feasibility study. Indeed, an analogous exercise has already been carried out for natural gas hydrates, and should be straightforward to repeat with CO₂ instead of CH₄ as the principal component of the gas.

Thermodynamic considerations indicate that CO₂ and CH₄ hydrate have similar, but not identical, conditions for stability. In particular, CO₂ hydrate can form at shallower depths than CH₄ hydrate, while the latter will generally persist to greater depths; in most cases there is a substantial region where both forms of hydrate may be stable. This suggests that existing natural gas reservoirs could be used for CO₂ storage, providing a source of energy that is almost neutral with respect to greenhouse gas emissions. While most of the natural methane hydrate occurs as finely dispersed crystals at concentrations that are too small for artificial storage to be economically viable, there are hydrate-capped natural gas traps that could be used as the basis for an initial feasibility study. The different range of stability for CO₂ hydrate also indicates that there could be new sites for CO₂ storage that are unsuitable for natural gas, and so would provide a completely new storage resource.

A number of other factors still need to be considered in assessing the viability of such stores. There are indications that CO₂ hydrate behaves unusually at high pressures, giving volumes that are much larger than expected, and this may place the integrity of a potential store at risk. It is not known why such behaviour occurs. It may arise from pressure effects on the carbon dioxide/carbonate/water equilibrium, from consequent *pH* changes, from the occlusion of water within the growing hydrate mass, or may be specific to the hydrate/liquid carbon dioxide/liquid water equilibrium. In any case, a fundamental understanding of the phenomenon will be an essential goal for any feasibility study.

Probably the other major factor that needs to be clarified before potential sites can be identified is the interaction between the medium in which hydrates will form and the properties of the hydrates themselves. It is known from studies on methane hydrate formation in sandstones that the sandstone modifies both the kinetic and thermodynamic properties of methane hydrate. The same must be anticipated for CO₂. Both experimental and theoretical studies into the effect of the composition and character of a porous substrate on the hydrate that forms within it will be needed before one can hope to predict the long-term viability of a potential storage site. These studies will need to address the diffusion of CO₂, the permeability of the hydrate in microscopic pores, the conditions for thermodynamic stability and the kinetics of formation.

Some ecological consequences also need to be investigated. Hydrates tend to form in regions where methanogenic bacteria can be found, and so dumping large amounts of CO₂ could be

expected to change the local ecology. The consequences are likely to be site-specific, and so will necessitate suitable ecological surveys once potential sites are found. Some generic work on the availability of CO₂ in CO₂ hydrates to various methanogens is also needed.

4 Enhanced Methane Recovery from Sub-Sea Reservoirs?

The possibility of using existing CH₄ reservoirs to store CO₂ has a number of practical and technical ramifications. There could be advantages from coupling the recovery of methane with the storage of CO₂, and certainly there will be economic benefits once a real cost accrues from generating CO₂. There are also some technical issues that may affect the viability of injecting CO₂. Some of these factors are elucidated in the remainder of this section.

4.1 Enhanced Methane Recovery?

There are situations in which injecting CO₂ can be used to enhance the recovery of methane from a fossil fuel reserve. A good example is with coalbed methane, where injecting CO₂ can enhance the rate of methane recovery substantially.²⁶ If the same could be achieved from sub-sea natural gas reservoirs, then sequestering CO₂ in sub-sea reservoirs would result in the double benefit of reducing CO₂ emissions and making CH₄ extraction more efficient.

Unfortunately, this is unlikely to prove possible. Enhanced methane recovery from coalbeds using CO₂ works through competitive adsorption. Methane is trapped in coalbeds because the methane molecules adsorb onto the surface of the coal particles; this is due to an attraction between the methane and the aromatic compounds and graphitic particles found in coal. However, CO₂ molecules adsorb even more strongly. So by injecting CO₂ one displaces the methane off the coal surface and into the gas phase, thereby freeing it for subsequent extraction. No similar adsorption process is encountered in sub-sea natural gas reservoirs and hydrate deposits. (Note that the inclusion of CO₂ into the clathrate cages is a bulk, rather than surface, phenomenon and therefore occurs by a very different mechanism. The inclusion mechanism is addressed later in this report.) There have also been suggestions of physical enhancement of the methane recovery rate from sub-sea reservoirs: because the density of CO₂ is greater than that of CH₄, the CO₂ would collect in the bottom of the gas trap and force the methane out the top. Again, this is unlikely to occur. Methane and CO₂ are miscible fluids, and so rather than effecting a separation, they will mix. Indeed supercritical CO₂ is an excellent solvent for most organic compounds, and the pressures at which CO₂ injection is likely to occur are typically above the critical pressure for CO₂ (74 MPa). Thus one must expect the CH₄ and CO₂ to mix, rather than maintain the phase separation required for this form of enhanced methane recovery. Inertial effects could give rise to some displacement of CH₄ before mixing is complete, but even this is likely to be mitigated by the relatively high compressibilities of both CO₂ and CH₄ fluids under likely operating conditions.

There is a third way in which CO₂ could enhance the recovery of CH₄: by competing for inclusion in the hydrate phase. While this suggestion is better founded than the previous two, the effect is still likely to be small. CO₂ will replace CH₄ in hydrates given suitable conditions (principally high CO₂ partial pressures and low CH₄ partial pressures). However existing laboratory experiments indicate that this is a very slow process even when conditions are optimal for CH₄ replacement. Experiments have been performed in which methane hydrate and liquid water were immersed in liquid CO₂ to determine whether CO₂ would displace the CH₄.²⁷ Some displacement was seen, provided CH₄ fugacities were kept below those required for methane hydrate formation, but the process was very slow. About 16% of the methane hydrate decomposed to be replaced by CO₂ hydrate in 800 hours; this compares

with 20 hours for complete decomposition of the methane hydrate when the CO₂ was replaced by N₂ at a comparable fugacity. In sub-sea environments, the hydrate is likely to be dispersed through porous strata, and mass transport limitations will ensure only limited access of injected CO₂ to the existing methane hydrate deposits. Thus any displacement is likely to be extremely slow, and even then will only commence once the partial pressure of methane falls below its equilibrium hydrate pressure. It should be stressed that the number of experiments on the kinetics of methane displacement by CO₂ in a hydrate is limited. It may be that operating at different water cuts, using CO₂ vapour instead of liquid, operating at different temperatures or using smaller hydrate particles could enhance the rate of CH₄ substitution. However the initial experimental data indicates that the kinetics of displacement is very slow, and involves decomposition then reformation of hydrate, rather than a simple displacement of the guest species. In most cases it is likely that the presence of CO₂ will hinder, rather than enhance, the recovery of methane from methane hydrate.

Thus it is unlikely that CO₂ injection can be used to induce a more rapid, or more complete, extraction of methane from sub-sea gas reservoirs, nor is it likely to facilitate the extraction of methane from any methane hydrate associated with such reservoirs.

4.2 General Considerations

CO₂ HYDRATE FORMATION

While much of the feasibility of creating sub-sea CO₂ storage wells arises from self-capping by hydrate formation, the formation of CO₂ hydrate may well interfere with the extraction of methane. Conversely, the presence of methane hydrate associated with a natural gas reservoir will inhibit the formation of CO₂ hydrate. There are two major reasons for this.

- (1) *Hydrate stability zones:* the steep slope of the CO₂ hydrate stability curve above 283 K (see Figure 3 and Figure 4) ensures that the base of the methane hydrate stability zone will actually lie *below* that for CO₂ hydrate. Enhanced methane recovery will involve pumping CO₂ into the gas reservoir, which must in turn lie below the hydrate zone. In such circumstances, the CO₂ will be trapped by methane hydrate at too great a depth for CO₂ hydrate to form. Thus formation of CO₂ hydrate will be possible only once the pressure of methane in the gas reservoir has been reduced sufficiently to decompose much of the CH₄ hydrate and thereby allow CO₂ to percolate into the CO₂ hydrate stability zone. This is only likely to happen very late in the lifetime of a gas reservoir.
- (2) *Help gas effects:* CO₂ will act as a help gas for CH₄ hydrate formation, and so will allow a mixed hydrate to form under conditions that are less extreme than those required for pure methane hydrate formation. Introduction of CO₂ will therefore enlarge the methane hydrate stability zone, thereby trapping more of the methane in hydrate deposits. This effect could be quite large. CO₂ will occupy only the large cavities in the hydrate lattice, whereas methane can occupy both the large and the small cavities (*cf.* Figure 2 and the discussion thereof). This means that up to twice[‡] as much methane as carbon dioxide could be incorporated into a mixed

[‡] The factor of 2 would be for type II hydrates, since 70% of the cavities in this structure are too small to incorporate CO₂. The factor would be smaller if type I hydrate were to form. Type II formation could be induced by the presence of small amounts of, *e.g.*, ethane or propane.

hydrate. The methane incorporated into such a mixed hydrate will be trapped for as long as the CO₂ hydrate is stable; by design, this should be for in excess of 100 years if acceptable reductions in atmospheric levels of CO₂ are to result. Thus the formation of CO₂ hydrate could actually reduce the yield of methane from a natural gas reservoir.

These effects are probably not adverse for CO₂ sequestration unless the long-term stability of the storage requires CO₂ to be in the hydrate form. If gaseous storage is adequate, both a CH₄ and a mixed CH₄/CO₂ hydrate cap will still provide an adequate seal for the CO₂ storage. They will, however, reduce the yield of methane from a natural gas reservoir, and will hinder the recovery of methane from CH₄ hydrate deposits. Thus coupling methane exploitation and CO₂ sequestration may have some adverse economic consequences. It is probable that these difficulties can be alleviated by careful design of the CO₂ injection technology. By controlling factors such as the depth and location of CO₂ injection (and perhaps changing this as the gas well matures), and the pressure and flow rate of the injected CO₂, it should be possible to control when and where hydrate formation will occur, and thereby minimise some of the undesirable side effects of CO₂ incorporation into hydrates.

GEOLOGICAL STABILITY

Recovery of natural gas from underground gas pockets inevitably leads to some loss of pressure in those regions. This can, in turn, lead to subsidence along the sea floor. However, if the methane is replaced by some other species, then the methane can be extracted without loss of pressure, and hence without subsidence.²⁸ Thus, by combining CH₄ extraction with CO₂ sequestration, it is possible to realise the methane reserves with minimal disruption to the local geological environment. Replacement of the CH₄ hydrate with CO₂ hydrate will similarly ensure that there is minimal change in the geological characteristics of the region, since CO₂ and CH₄ hydrates have very similar physical characteristics. Once again, however, it must be remembered that where CH₄ hydrate does exist, it will usually have a deeper zone of stability than will CO₂ hydrate, and so complete replacement of the CH₄ hydrate zone with CO₂ hydrate is not feasible.

DRILLING ADDITIVES

One final consideration to arise from combining natural gas exploitation with CO₂ sequestration is that the former operations make use of a number of chemical additives that will affect the efficacy of CO₂ storage. For example, it is common to add a number of inhibitors to the drilling mud, and to the oil and gas pipelines, in order to prevent blockages. Perhaps the most significant in the current context is that hydrate blockages are a major concern, and the well head is one of the major risk-points for hydrate formation since this is the region where pressure and temperature gradients tend to be greatest. Thus there is a risk that hydrate inhibitors could be introduced into the local environment, which could then destabilise the CO₂ hydrate and threaten the integrity of the storage site. Drilling muds will, by their very nature, come into contact with the local environment. On the other hand, pipeline additives should normally be well segregated from the environment. In either case, however, there will be the possibility of equipment failure, and accidental release of the chemical additives. If sub-sea CO₂ storage is found to be feasible in principle, and if it is deemed to be desirable to utilise existing natural gas sites for this purpose, then it will be important that a careful assessment is made of the risk and consequence of chemical releases

at the well head. At the same time, it will be important to devise effective strategies for mitigating the effects of any chemical releases that do take place.

4.3 Summary

It is unlikely that CO₂ injection can be used to enhance either the efficiency or the rate of CH₄ recovery from sub-sea methane reservoirs. Indeed it is quite possible that some loss of the methane capacity would result, due to stable mixed CO₂ / CH₄ hydrates forming. There may, however, be other advantages to combining CH₄ exploitation with CO₂ storage, with reduced greenhouse gas emissions and enhanced geological stability following methane extraction being two important examples.

5 Recommendations

The idea of storing CO₂ in hydrate-related sub-sea reservoirs does deserve closer inspection. It is possible that large volumes of CO₂ could be stored for very long timescales in this way. The method could also be combined with exploitation of natural gas reserves, yielding some economic and technical advantages in the process. Before the feasibility of this strategy can be assessed with confidence, more research is needed into a number of the scientific and technical unknowns surrounding sub-sea storage. Research associated with the following areas is particularly to be encouraged.

1. A concerted effort is needed to map out possible sites for sub-sea CO₂ storage. This process should identify which of the known methane hydrate sites would be suitable for CO₂ storage, but it should also search more widely for potential new sites that do not already contain a significant hydrocarbon reservoir. This project should involve a number of different tasks, including:
 - calculation of the pressure-temperature regions of the sea floor that are compatible with forming CO₂ hydrates;
 - a search of the existing geological maps to identify regions with the right geology to form gas traps, and that are consistent with the pressure-temperature conditions outlined above; the “right geology” should have regard to both the combination of porous and impermeable rock strata, and to the seismic and geothermal stability of the region;
 - an estimate of the volumes of CO₂ that could be stored in these sites.
2. Careful and systematic experiments should be performed to identify the hydrate stability curves for CO₂ hydrate in the presence of a range of impurities and including variations in the *pH* of the aqueous phase. This data should then be used to re-parameterise existing programs for predicting hydrate stability so that they will be accurate for systems in which CO₂ is the major constituent, rather than just a minor component.
3. New studies should be commissioned to characterise the effect of the carbonate equilibria (H₂O / CO₂ / CO₃²⁻ / HCO₃⁻ / H₂CO₃), *pH* and pressure on the stability, structure and permeability of CO₂ hydrate.
4. Research is needed to characterise the kinetics and thermodynamics of hydrate formation in porous materials, and particularly to assess the influence of pore size and of the chemical composition of the rocks.
5. Work is needed to characterise the diffusion of CO₂ through thin hydrate films, and through hydrates that form in porous rocks. The results of these studies then need to be combined with existing percolation/diffusion theories to predict the diffusive loss rates for CO₂ from hydrate-capped gas traps, and thereby estimate the maximum storage times for which sub-sea sequestration is likely to be useful.
6. Comprehensive simulations which combine the kinetic/thermodynamic developments of recommendation 4 and diffusive studies of recommendation 5 with existing reservoir and

fluid flow modelling schemes are needed to estimate the efficiency with which a CO₂ store can be created, and the amount of CO₂ that would be lost while creating the store. The consequences of such loss will also need to be evaluated.

7. The existence of sub-sea CO₂ dumps needs to be incorporated into global climate simulations so that the effects of future climate changes on the stability of these stores can be estimated.
8. Ecological surveys and environmental impact studies will be needed for the potential storage sites identified under point 1. Amongst other things, these should catalogue the bacterial species present, and identify their nutrients and waste products. Consideration should also be given to changes in geological stability that could arise from CO₂ hydrate formation and to the effect of any pH changes due to dissolution of CO₂.
9. It is unlikely that CO₂ injection can be used to enhance the efficiency with which CH₄ is extracted from existing natural gas wells. Indeed, CO₂ hydrate formation may well result in some loss of the methane reserve. CO₂ sequestration in old gas reservoirs may prove to be a viable long-term storage strategy, but if it is hoped to use CO₂ storage to increase the economic life-time of nearly-depleted reservoirs then careful consideration should be given to the methodology for injecting CO₂. The viability of such a scheme may depend on the ability to control the rate and location at which CO₂ hydrates will form.

It is important that recommendations 3–5 incorporate both experimental and theoretical elements. Ultimately it is essential that there is a capacity to predict these effects reliably and quantitatively. Thus suitable theories must be developed. At present, however, there is insufficient experimental data with which to develop and verify any theory, and so both systematic experiments and theoretical studies will be needed on these topics.

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