Can CO_2 hydrate assist in the underground storage of carbon dioxide?

C. A. ROCHELLE[1*], A. P. CAMPS[1,2], D. LONG[3], A. MILODOWSKI[1], K. BATEMAN[1], D. GUNN[1], P. JACKSON[1], M. A. LOVELL[2] AND J. REES[1]

[1] *British Geological Survey, Keyworth, Nottingham NG12 5GG, UK*
[2] *Department of Geology, University of Leicester, Leicester LE1 7RH, UK*
[3] *British Geological Survey, Edinburgh EH9 3LA, UK*
* *Corresponding author, caro@bgs.ac.uk*

Abstract

The sequestration of CO_2 in the deep geosphere is one potential method for reducing anthropogenic emissions to the atmosphere without necessarily incurring a significant change in our energy-producing technologies. Containment of CO_2 as a liquid and an associated hydrate phase, under cool conditions, offer an alternative underground storage approach compared to conventional supercritical CO_2 storage at higher temperatures. We briefly describe conventional approaches to underground storage, review possible approaches for using CO_2 hydrate in CO_2 storage generally, and comment on the important role CO_2 hydrate could play in underground storage. Cool underground storage appears to offer certain advantages in terms of physical, chemical and mineralogical processes, which may usefully enhance trapping of the stored CO_2. This approach also appears to be potentially applicable to large areas of sub-seabed sediments offshore Western Europe.

8796 words, 73 references, 6 figures

Keywords: Carbon dioxide. CO_2, underground storage, sequestration, hydrate

It is now widely accepted the rising levels of carbon dioxide (CO_2) in the Earth's atmosphere are causing global climate change, and this is a subject of international concern (e.g. IPCC 1990, 2007). Furthermore, if something is not done to reduce emissions of greenhouse gases to the atmosphere, predictions suggest an unprecedented rate of future temperature increase, with unknown, but possibly rapid, consequences for the global climate. Measurements show that global temperatures rose by 0.3-0.6°C in the 20th century. If the trends in current emissions continue there are suggestions (Karl *et al*. 2000; RCEP 2000) that the global mean temperature is likely to be about 3°C higher than at present by the end of the 21st century. The main difficulty in attempting to combat climate change is the world population's high dependence on fossil fuels as an energy source. Alternatives such as solar energy and other renewables are making a useful contribution, and some countries presently rely heavily on nuclear power, nonetheless, the culture and lifestyle of many countries appear to be strongly linked to fossil fuel usage for many years to come.

Assuming that we continue to burn fossil fuels, yet wish to mitigate CO_2 emissions to the atmosphere, we are faced with a limited number of alternatives:

1. To reduce our CO_2 emissions by using lower carbon fuels (e.g. gas instead of coal);
2. To utilise the produced CO_2;
3. To dispose of the CO_2 in another domain of the planet, such as the geosphere, the terrestrial biosphere or the oceans.

In order to stabilise atmospheric CO_2 concentrations at current values, it may be necessary to reduce CO_2 emissions by 60% or more over the next 50 years (RCEP 2000). Although many countries are making strenuous efforts to reduce their CO_2 emissions, this is proving extremely difficult because all countries, and not just the developing ones, continue to strive for economic growth - which requires energy. Even those countries that have managed to make significant reductions in their energy intensity have struggled to reduce overall emissions. Almost the only exceptions are countries that have greatly reduced their use of coal or have developed a substantial nuclear energy base (e.g. Sweden). Therefore, it seems likely there will be no reduction in the production of CO_2, at least in the short term.

Although large-scale utilisation of waste CO_2 is initially attractive, it has major problems, as converting it into useful substances requires large energy inputs. In many cases, if these energy inputs are in the form of fossil fuels, a net saving of CO_2 emissions becomes impossible. Alternatively, we could prevent the CO_2 entering the atmosphere in the first place. At present we are disturbing the balance of the natural 'carbon cycle' where carbon is slowly cycled between atmosphere, biosphere, hydrosphere and geosphere, by rapidly transferring large amounts of carbon from the geosphere into the atmosphere. By storing (or sequestering) vast volumes of CO_2 securely without any land use or verification problems, we may be able to redress some of this imbalance. One possible location for such a store is within porous rocks underground (the geosphere). In essence, geological storage aims to put the carbon directly back into the place from which it originally came (in the form of fossil fuels), thereby avoiding the atmospheric part of the carbon cycle.

The underground storage of CO_2

Underground storage is a feasible means of sequestering very large quantities of CO_2 produced by point sources such as fossil fuel fired power plants (e.g. Freund & Ormerod

1996; Haugen & Eide 1996; Holloway 1996a,b; Baines & Worden 2004a and references therein). Currently this is already being demonstrated, with 1-2 Mtonnes of CO_2 injected annually at both the Sleipner gas field, North Sea (Baklid *et al.* 1996; IEA GHG 1998) and the Weyburn oil field, southern Saskatchewan, Canada (Moberg 2001; Malik & Islam 2000; Wilson & Monea, 2004).

The concept of underground sequestration (in its conventional form) involves first capturing the CO_2 at source to produce a pure CO_2 stream (e.g. via amine scrubbing of power plant flue gases). This is followed by compression to liquefy the CO_2 prior to transportation by pipeline to the injection site. Once at the injection site, the CO_2 can be injected via wells into deep reservoir rocks capped by very low permeability seals such as shales or clays. Injection could be into traps directly analogous to oil or natural gas fields (e.g. Bergman *et al.* 1996), or as at Sleipner into large aquifers.

If the CO_2 is injected at a depth of about 800 metres or more, and assuming average geological conditions in the world's sedimentary basins, pressure and temperature will increase beyond the point where CO_2 becomes *supercritical* (approximately 31°C, 74 bars) (Fig. 1). The density of supercritical CO_2 varies depending on pressure and temperature. However, for many currently-envisaged storage conditions it is likely to have a density in the order of 700 kg m^{-3} - far denser than gaseous CO_2 (approximately 2 kg m^{-3} at Earth surface conditions), but less dense than formation porewater (approximately just greater than 1000 kg m^{-3} depending on salinity). As a consequence, stored CO_2 will occupy much less volume than gaseous CO_2, effectively greatly increasing the storage potential of sedimentary basins.

After injection, the CO_2 will initially be stored in a free state as a buoyant 'pure' phase below an impermeable caprock (described as 'physical trapping' by Bachu *et al.* [1994]), in much the same way as methane in natural gas fields. However, over time it will dissolve in the formation water of the reservoir ('solubility trapping'). Once dissolved, it will no longer be buoyant, and hence its migration will only be driven by very slow regional-scale groundwater flow. The dissolved CO_2 will lower the pH of the formation water, and over even longer timescales (measurable in 100s or 1000s of years) this dissolved CO_2 will react with minerals within the rocks to precipitate calcite or other carbonate minerals (described as 'mineral trapping' by Bachu *et al.* [1994]). This will result in the immobilisation of at least a proportion of the carbon for geologically significant timescales (e.g. Baker *et al.* 1995; Czernichowski-Laurol *et al.* 1996a,b; Gunter *et al.* 1993, 1997; Rochelle *et al.* 1999, 2004). The extent of such reactions will depend upon various factors such as the composition of the porewater, the composition of the rocks and minerals it encounters, as well as the *in-situ* pressure and temperature.

If the underground storage of CO_2 is to be a practicable large-scale disposal method, there is a need to ensure it will remain safely underground, and not return to the atmosphere within relatively short geological timescales (i.e. thousands of years). This would allow natural buffering processes (e.g. oceanic and forestry sinks) to have sufficient time to reduce global atmospheric CO_2 levels to environmentally acceptable levels. Indeed, acceptable performance will need to be demonstrated in order to satisfy operational, regulatory and public acceptance criteria. The generally good track record of CO_2-assisted enhanced oil recovery operations and purpose-designed underground storage of natural gas shows underground storage can be

practicable and leakage minimised, at least over anthropogenic or 'industrial' decadal timescales.

With underground sequestration, it is possible that the CO_2 could be retained for timescales of tens of thousands to millions of years (e.g. Holloway 1997; Pearce *et al.* 1996). Indeed, many *natural* CO_2 fields have been discovered that are far older than this (e.g. Baines & Worden 2004b; Czernichowski-Lauriol *et al.* 1996a; Pearce *et al.* 1996, 2004; Zheng *et al.* 2001). For example, the CO_2 in the natural carbon dioxide field at Pisgah Anticline in Central Mississippi, USA is thought to have originated from thermal metamorphism of Jurassic carbonates by the Jackson Dome igneous intrusion during late Cretaceous times (Studlick *et al.* 1990), which ended some 65 million years ago. Thus, given appropriate geological structures, the underground storage of CO_2 appears to be a safe and practicable way of reducing anthropogenic emissions of CO_2 to the atmosphere.

How can hydrates help with CO_2 sequestration?

Until recently, the majority of hydrate studies within the natural environment have concentrated on methane hydrate (CH_4) an ice-like compound naturally stable in certain sea floor sediments. Many of these studies have focussed on the release of methane through natural processes, possibly linked to long-term changes in climate or through human activity (i.e. global warming or production of CH_4 as an energy source). Over the past few years however, there has been growing interest in hydrates as a store for anthropogenic CO_2, locking up CO_2 in an easily formed solid phase in domains of the planet where it will not be released to the atmosphere over relatively short timescales.

In addition to the current approaches to deep CO_2 storage described previously, there is another approach involving storage at cooler temperatures, but still at high-pressure conditions beneath permafrost regions or in sediments below the floor of deep oceans. This 'cool storage' approach has received relatively little attention even though it may offer certain advantages in terms of long-term containment of CO_2. In particular, under appropriate conditions (typically <10°C and with hydrostatic heads >400 m) CO_2 hydrate becomes stable, and this could help immobilize CO_2 for geologically-important timescales (e.g. Koide *et al.* 1996).

Trapping CO_2 as a hydrate phase on the ocean floor

Prior to discussing the benefits of immobilising CO_2 as a hydrate *within sediments*, it is first useful to summarise other proposed methodologies for storing CO_2 as a hydrate phase. Much research has focussed on releasing liquid CO_2 into the deep oceans, either as droplets within the water column, or as pools on the ocean floor (e.g. Austvik & Løken 1992; Brewer *et al.* 1999; Hirai *et al.* 1997; IPCC 2005; Warzinski *et al.* 2000). Interaction of the CO_2 with seawater under the *in-situ* pressure and temperature conditions would favour CO_2 hydrate formation, either as 'skins' around liquid CO_2 or as more solid masses over longer times. Although the CO_2 hydrate would eventually dissipate through equilibration with the seawater, the slow rate of reaction and slow turnover of the deep oceans may allow the CO_2 to be locked up in hydrate form for timescales measurable in at least hundreds of years (e.g. Wilson

1992; Herzog 1996). There are two main limitations in applying this approach. Firstly, there has been much concern about the impact that large quantities of CO_2 would have on marine, especially benthic, organisms. Secondly, the emplacement of large quantities of waste CO_2 into the deep oceans is currently prohibited under the terms of international agreements, such as the 'London Dumping Convention' (IMO 1997) and 'OSPAR Convention' (OSPAR 1992)

Other studies have also considered confining CO_2 hydrate directly to shallow sediments on the deep sea floor (e.g. IEA GHG 2004). This approach involves trapping CO_2 in pure hydrate form, transporting the CO_2 hydrate as large blocks on board ships, and then releasing them to fall to the deep sea floor, and possibly even into soft sediments. Again, this approach would not be permissible under the above international conventions.

These approaches involve storage of CO_2 hydrate on the ocean floor or within the top few metres of sediment. One consequence of this is a high potential that dissolution of CO_2 into the bottom waters will reduce seawater pH and adversely impact the marine ecosystem. Such impacts could be avoided if the CO_2 were stored in a stable form with minimum risk of release to the ocean floor. One possible approach would be to create CO_2 hydrate deeper within the sediment, far below the few 10s of cm of bioturbated sediment, and at a depth where it would not affect marine organisms. Indeed, the presence of significant accumulations of CH_4 hydrate in such sediments testifies to its potential as a long-term store of gas trapped in hydrate form.

Trapping CO_2 as a hydrate phase during methane extraction

One way to help offset the costs of CO_2 storage in sediments would be to combine it with the recovery of hydrocarbons. In the case of hydrates, several studies have investigated the use of injected CO_2 to liberate methane gas (CH_4) from hydrate in sediments, and in the process lock up CO_2 in CO_2 hydrate (e.g. IEA GHG 2000a,b; Nakano 1998). The methane gas could then be captured and marketed. Although initially attractive, this approach has some potential problems, notably the distributed nature of methane hydrate in marine sediments and the costs of working offshore may make this approach overly expensive. Although sub-permafrost hydrates may be less costly in terms of drilling compared to those below the seabed, the generally remote location of most permafrost areas may mean they are further away from large sources of CO_2, and hence CO_2 transportation or pipeline costs would be higher. Finally, the injected CO_2 and liberated methane would mingle within the sediment, and thus a mixed gas could be produced at the production well. This could necessitate expensive separation equipment to get the methane to saleable quality.

Direct trapping of CO_2 as a hydrate phase within sediments

Applications of CO_2 hydrate storage involve the direct geological disposal of CO_2, and two different scenarios can be envisaged:

1. As a secondary chemical containment mechanism, resulting from the (unintended) upward migration of CO_2 from a deep, warm storage reservoir (i.e. escape from a deep store of supercritical CO_2);

2. As a primary containment mechanism, where CO_2 hydrate forms an impermeable 'cap' over a larger quantity of liquid CO_2.

Firstly, secondary chemical containment provides a backup trapping mechanism, should deeper barriers be breached and effectively building 'redundancy' into the storage scheme. As mentioned earlier, the deep storage of CO_2 involves injection into warm rocks that are at least 800 m deep. Although detailed geological characterisation of deep storage facilities would be carried out, it is always possible that some CO_2 may migrate upwards at some time. This could occur along unidentified small faults/fractures below the resolution of geophysical imaging, or along poorly sealed boreholes. If the CO_2 store lay below a deep enough and cold enough body of water, or below a region of thick permafrost, then upward-migrating CO_2 could enter a zone of CO_2 hydrate stability within the sediments. The formation of CO_2 hydrate could then enhance any natural low permeability caprock, slowing the ascent of CO_2, or even possibly blocking flow pathways (such as can happen when methane hydrate completely blocks pipelines).

Other studies have suggested that CO_2 hydrate may also be able to form locally, within sediments seemingly too warm to form hydrate. A preliminary study by Pruess (2003) modelled what would happen if liquid CO_2, rising along a flow pathway, started to boil off as it depressurised. The latent heat of vapourisation required to boil off the CO_2 would cool the surrounding rocks, possibly to the point at which CO_2 hydrate, or even ice, would form. As a result, flow pathways could be reduced or even blocked. In the Pruess (2003) model, a cool zone several hundreds of metres thick was predicted to form, which could slow the ascent of the CO_2 and cause it to spread out laterally. Pruess (2003) also notes however, that the preliminary model was somewhat idealised, and needs to be improved by containing more realistic geological structures.

Secondly, using CO_2 hydrate as a primary containment mechanism for stored CO_2 has been considered in several studies (e.g. IEA GHG 2000a; Koide *et al.* 1997; Sasaki & Akibavashi 2000; Someya *et al.* 2006). This approach involves injecting (usually liquid) CO_2 into deep-water sediments or sub-permafrost sediments just below the CO_2 hydrate stability zone. As the slightly buoyant liquid CO_2 rises, it would enter cooler rocks lying within the hydrate stability zone. The precipitation of significant amounts of CO_2 hydrate within pore spaces could impede further upward migration of CO_2. On a larger-scale, the liquid CO_2 would spread out forming a 'pool' capped with an impermeable layer of CO_2 hydrate (Fig. 2) (together with any pre-existing natural low permeability caprock).

Any liquid CO_2 able to find a way through the cap of CO_2 hydrate or natural caprock would itself react to form CO_2 hydrate as long as it encountered water-rich sediment. With a sufficiently thick hydrate stability zone therefore, the hydrate cap would have a capacity to self-seal, building redundancy into the storage scheme. For CO_2, this self-sealing would be facilitated by the ability of CO_2 hydrate to form relatively rapidly (probably faster than for methane hydrate) under appropriate conditions (e.g. Brewer *et al.* 1999; Riestenberg *et al.* 2004; Sakai *et al.* 1990; Someya *et al.* 2006). However, this may not be immediately adjacent to the hydrate cap, previous studies have found methane transport along fractures through the lower parts of the hydrate stability zone (Gorman *et al.* 2002), for example. These fractures were hydrate-lined and prevented water reacting with the methane, though they could not be

maintained in the shallower, more plastic sediments, and gas migration was stopped here due to more extensive hydrate formation.

CO_2 hydrate stability within sediments

Whether CO_2 hydrate acted as a primary or secondary trapping phase (or even its formation during the liberation of methane from CH_4 hydrate), it is necessary to know over what conditions/depths CO_2 hydrate is stable and how CO_2 hydrate forms within sediments. The former is important for large-scale predictions to identify suitable regions with potential for CO_2 storage - assuming the underlying geology is suitable. Indeed, the IEA Greenhouse Gas R&D Programme has already identified the need for such work (IEA GHG 2000a). Large-scale predictions will also be necessary to identify regions where methane hydrate may also be stable (e.g. on one hand so as not to 'pollute' an exploitable CH_4 hydrate resource, or on the other hand, to explore areas for possible liberation of methane from CH_4 hydrate during CO_2 hydrate formation).

Mapping hydrate stability zones – the large scale

In an attempt to address the issue of where CO_2 hydrate may be stable on a regional scale, a preliminary theoretical study has been undertaken to estimate CO_2 (and CH_4) hydrate stability zones for sediments offshore western Europe (Rochelle & Camps 2006; Camps 2007). As a basis for the calculations, an empirical relationship between pure methane and pure water was used. This was presented in the JOIDES Pollution Prevention and Safety Panel report (JOIDES, 1992), where the equilibrium is described by the equation:

$$\ln P = A - B/T \qquad [1]$$

where A and B = constants determined by experimental hydrate stability data.

Using this relationship an algorithm was developed to enable calculation of CO_2 and CH_4 hydrate stability zones. An appropriate temperature reduction was included to account for the changes in equilibrium conditions due to the presence of seawater (salinity reducing hydrate stability). Constants were determined from data constructed using CSMHYD (Sloan, 1998), which calculates hydrate equilibrium formation conditions.

For each location (latitude and longitude), the program uses input of water depth (i.e. pressure), bottom water temperature and geothermal gradient. GEBCO global bathymetry data sets have been used to provide detailed bathymetry for offshore Europe (IOC *et al.* 2003). To determine bottom water temperatures CTD cast temperature data have been gathered from various sources, including ICES (the International Council for the Exploration of the Sea), BODC, the Coriolis Data Service, and IOS reports [e.g. Read *et al.* 1991, Saunders & Cooper, 1987]). Within the model, water depths are relatively well-constrained, and based upon high resolution, detailed datasets. Less information is available on bottom water temperatures, and the largest area of uncertainty is the resolution of geothermal gradient data because the available information is limited. A value of 30°C/km was used in the model, but it is acknowledged that in reality, certain areas may have higher or lower geothermal

gradients, and this would affect predicted hydrate stability, particularly at a local scale (see Camps *et al*. this volume). For example, a higher geothermal gradient would result in a thinner hydrate stability zone (and vice versa). For the data shown in Fig. 3 an increase in temperature of 1°C results in a decrease in CO_2 hydrate stability zone thickness of about 35-40 m.

The calculated CO_2 (and CH_4) hydrate stability zones were plotted using the contouring package SURFER and output as maps of hydrate thickness (Fig. 3). Calculations predict that CO_2 hydrate will be stable over large regions, with the base of the CO_2 hydrate stability zone reaching a depth of up to about 450 m below the ocean floor. Given that the distribution of the hydrate stability zone shown in Fig. 3 is largely controlled by the position of the continental slope, and given the scale of the map, the uncertainty over geothermal gradients mainly controls the thickness of the CO_2 hydrate zone rather than its spatial distribution. Nevertheless, the preliminary model does indicate that there is potential for the formation of a thick cap of CO_2 hydrate above a store of liquid CO_2.

The information in Fig. 3 is also useful when considering the most appropriate locations for this type of storage methodology. For example, the relatively shallow seas around most of the UK preclude the formation of CO_2 hydrate in near-shore sediments (for all but the very NW of Scotland). As a consequence, this approach would necessitate considerable investment in pipelines to enable access to the deep cold sediments necessary for this type of storage. Conversely, Portugal, northern Spain, SW France and parts of Norway, show greater potential where relatively deep waters lie close to shore. Although this does not identify whether suitable geological structures exist in these regions (or for that matter, whether large point sources of CO_2 exist close to these coastal regions), it can illustrate this approach to both industry and environmental policy makers this approach, and whether it is worthwhile considering for inclusion in their portfolio of possible CO_2 management and mitigation strategies.

Hydrate within pore spaces – the small scale

Assuming porous sediments of suitable extent exist within the CO_2 hydrate stability zone, there is a need to know what impact CO_2 hydrate formation will have on the sediments and which sediments are most suitable. This might include whether hydrate will form in the centre of pores or on grain surfaces, whether it will cement grains together and make the sediment stronger, and/or whether precipitation will create an effective impermeable barrier to upward CO_2 migration. It will also be important to consider whether the origin of the CO_2 influences hydrate precipitation. For example, there may be differences in the nature of the hydrate when formed purely from dissolved CO_2 (i.e. in water-saturated rock *adjacent* to any CO_2 'pool'), compared to that formed from within the CO_2-rich phase (i.e. within the CO_2 'pool').

Laboratory-based studies can provide useful insights into processes controlling the above, but although there have been various studies on CO_2 hydrate, very few of them bring together the sediments, water of appropriate salinity, and conditions appropriate to geological storage. As part of this study, CO_2 hydrate has been formed within synthetic sandy sediments under both seawater-saturated and seawater poor conditions (Camps 2007). These reflect the conditions which may exist adjacent to, and within an underground store of CO_2. Damp sediments were

used to represent CO_2-dominated conditions within the main storage region - it being assumed that most water would have been displaced from the pores except for a thin film on the grain surfaces. This provided an open pore network for CO_2 ingress. As a consequence of thin water films and of easy CO_2 ingress, hydrate formation was rapid and widespread throughout the sediment sample. The CO_2 hydrate replaced the water film completely and cemented the grains together (Fig. 4). In some pores larger hydrate crystals formed, reaching sizes of about 100 μm. Other parts of the pores remained open, and it is possible that CO_2 could still migrate through the sample – albeit in a restricted manner. The limiting factor for hydrate growth appears to have been the availability of water, which was all converted to hydrate (cf Gorman *et al.* 2002). An interesting consequence of this was halite precipitation (Camps 2007; Camps *et al.* this volume), which previous workers have predicted may form during hydrate growth in areas of restricted water availability (Harrison *et al.* 1995; Lorenz & Müller 2003).

Sediments saturated with water were used to represent conditions adjacent to the main storage area – it being assumed that CO_2 would either diffuse into the surrounding water, or CO_2-saturated porewater would migrate away from the CO_2-water interface. In the experiments only the upper part of the wet sediment was in contact with the CO_2. At the CO_2-water interface precipitation of CO_2 hydrate was rapid, and some evidence of halite precipitation was again observed (Camps 2007). Further into the sediment, though still relatively close to the CO_2-water interface (in these experiments a few mm), hydrate filled all the intergranular pore space and cemented sediment grains together. The formation of this hydrate appears to have greatly reduced the transport of CO_2 into the rest of the sediment, leaving the majority of the remaining sediment uncemented. However, observations of the zone between the cemented and uncemented sediment (both visual and by SEM) suggest that hydrate tends to be restricted to the centres of pore spaces.

Cementation of sediment grains by CO_2 hydrate is advantageous for underground CO_2 storage because:

1. It traps stored CO_2 as a solid phase;
2. It makes the sediment more stable; this could be particularly important given the sediments are expected to be relatively poorly consolidated;
3. CO_2 migration through the sediments is reduced or, with sufficient hydrate formation, possibly even stopped.

The latter point is particularly important as it relates to the thickness of the hydrate 'cap' needed to contain a 'pool' of stored CO_2. In several of our simple laboratory experiments it was found that only a very thin (approximately 2 mm) hydrate layer was enough to restrict CO_2-water reaction and prevent further hydrate formation (at least over timescales of days-weeks). Similar observations have been made by other workers, who studied the release of liquid CO_2 into the deep ocean (e.g. Aya *et al.* 2000). More relevant however, are observations from complex laboratory experiments, which show that a relatively thin layer of rapidly-formed CO_2 hydrate is capable of withstanding a significant differential pressure across it (Someya *et al.* 2006). Although more work is needed to ascertain the effects of other factors (such as hydrate strength, salinity, sediment mineralogy etc), the information currently available seems to suggest that a relatively thin 'cap' of CO_2 hydrate may be perfectly able to prevent a slightly buoyant 'pool' of stored liquid CO_2 from rising.

Other CO_2 trapping mechanisms operating near the hydrate stability zone

CO_2 hydrate will not be the only trapping mechanism for stored CO_2. In order to ascertain the overall potential for CO_2 storage it is important to consider the other mechanisms that will operate within, or close to the CO_2 hydrate stability zone.

Density and viscosity

Most of the schemes currently being considered for underground CO_2 storage involve *in-situ* conditions above the critical point of CO_2 (i.e. >31.1°C, >73.8 bar), where a supercritical phase is stable (Fig. 1). The density of this supercritical phase will vary with temperature and pressure, but may typically be of the order of 700 kg m^{-3}. As a consequence, a low permeability caprock (e.g. shale or evaporite) is needed to prevent the buoyant CO_2 rising towards the surface.

Within deep-water sediments or below permafrost regions, pressures may be as equally high as in a deep aquifer storage system, but temperatures may be much lower. Under these conditions the stable phase of CO_2 is likely to be a liquid, which is likely to have a higher density than that of supercritical CO_2 (e.g. Sasaki & Akibayashi 2000) (see Fig. 5). For example, at 10 MPa [100 bar] warm CO_2 at 30°C occupies more pore space than does cool CO_2 at 10°C (in this case by about 20%). Thus, for similarly sized reservoirs, significantly greater quantities of CO_2 could be stored under cooler conditions.

There are other benefits from cool storage. As well as requiring less volume for storing the same weight of CO_2, the increased density would reduce buoyancy forces driving vertical migration. This could mean that a thinner caprock may be sufficient to contain the stored CO_2. Cooler temperatures would also increase the viscosity of CO_2. For example, at a pressure of 10 MPa [100 bar], data in Vesovic *et al.* (1990) indicate that CO_2 viscosity at 30°C is approximately 70 μPa s^{-1}, but at 10°C this increases to approximately 110 μPa s^{-1} (an increase of nearly 60%). As a consequence, vertical migration of cool CO_2 is likely to be slower than warm CO_2. Both increased density and increased viscosity are advantageous, in reducing the potential for CO_2 to escape.

Solubility

Compared to many other gases, CO_2 is relatively soluble in water, and its dissolution into formation porewater will occur once it is injected underground. Indeed, previous studies have shown a significant amount (>10%) of stored CO_2 can be trapped as a dissolved phase over intermediate timescales (e.g. Johnson *et al.* 2001, 2004; Wilson & Monea 2004). Once dissolved, the CO_2 will no longer be subject to the same buoyancy-driven upward migration as supercritical CO_2. Consequently, enhancing the amount of dissolved CO_2 will aid long-term storage.

CO_2 solubility increases with decreasing temperature up to the point where CO_2 hydrate is stable (Fig. 6). Therefore, porewaters adjacent to areas of CO_2 hydrate formation (i.e. just outside the hydrate stability zone) may also be able to store significant amounts of CO_2. For example, for seawater salinities and 10 MPa [100 bar] pressure, the solubility of CO_2 is

approximately 25% greater at about 10°C compared to that at 30°C. In general terms therefore, given that liquid CO_2 is stable at temperatures below that of supercritical CO_2, the storage of liquid CO_2 favours solubility trapping (and at sufficiently low temperatures, mineral trapping as a hydrate). Consequently, it appears to offer some benefits in terms of long-term containment.

CO_2 solubility is however, also controlled by ionic strength (salinity), pressure and pH. It decreases with increasing ionic strength, increases with increasing pressure, and increases with increasing pH. Overall CO_2 solubility is also controlled by the pH of the groundwater through linked equilibria such as:

$$CO_{2\,(aq)} + H_2O \Leftrightarrow CO_{2\,(aq)} + H_2O \Leftrightarrow H_2CO_3^{\circ} \Leftrightarrow HCO_3^{-} + H^{+} \qquad [2]$$

As a consequence, mineral assemblages that allow fluid-rock reactions to buffer pH at higher values will facilitate higher CO_2 solubility (Gunter *et al.* [1993] and Rochelle *et al.* [2004]). Assessment of the amount of CO_2 held in dissolved form therefore needs to be made on an individual site-by-site basis using appropriate *in-situ* temperature, pressure and fluid compositions.

There is one final advantage to dissolved CO_2. Formation water enriched in CO_2 is denser than its CO_2-free equivalent. It is possible, therefore (given a thick enough reservoir rock), that 'plumes' of CO_2-rich water may descend *slowly* from the CO_2-water interfaces of a storage scheme. This process facilitates further CO_2 dissolution through increased CO_2-water mixing. It also makes the trapped CO_2 descend further underground, as opposed to ascending as would occur if CO_2 were in its buoyant free-phase.

Mineral trapping

Although CO_2 hydrate is likely to form relatively rapidly at low temperatures, it is not the only solid phase, which may form. CO_2-water-rock reactions may also produce a variety of secondary carbonate minerals that would enhance mineral trapping (e.g. Bachu *et al.* 1994; Baker *et al.* 1995; Gunter *et al.* 1993, 1997; Harrison *et al.* 1995; Rochelle *et al.* 2004). It is noted however, that the rate and extent of such reactions is likely to be much slower under cool conditions than under warm storage conditions. Nonetheless, limited precipitation of carbonate minerals could still occur under conditions close to the hydrate stability zone, helping to trap CO_2. For example, Gunter *et al.* (1997) suggested that detrital Ca-rich feldspar might react to form calcite:

$$\underset{\text{anorthite}}{CaAl_2Si_2O_8} + CO_{2\,(aq)} + 2\,H_2O \Rightarrow \underset{\text{calcite}}{CaCO_3} + \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} \qquad [3]$$

Similarly, Johnson *et al.* (2001, 2004) postulated that in saline solutions K-rich feldspar might react to form a different carbonate mineral, dawsonite:

$$\underset{\text{K-feldspar}}{KAlSi_3O_8} + Na^{+} + CO_{2\,(aq)} + H_2O \Rightarrow \underset{\text{dawsonite}}{NaAlCO_3(OH)_2} + \underset{\text{quartz/chalcedony/cristobalite}}{3\,SiO_2} + K^{+} \qquad [4]$$

Reactions such as these are likely to be relatively slow however, and be dependent upon the abundance and dissolution rates of the dissolving minerals. While they enhance the appeal of CO_2 sequestration through this approach, they are an added bonus, but may provide relatively little contribution in the short term compared to CO_2 hydrate formation.

Summary

The underground storage of CO_2 is increasingly seen as a possible method for reducing anthropogenic emissions of this greenhouse gas to the atmosphere without necessarily dramatically changing our energy-producing technologies. Most of the current approaches are aimed at storage within deep porous rocks below 800 m, where *in-situ* conditions of pressure and temperature are sufficient for injected CO_2 to exist as a buoyant *supercritical* phase. There is however, an alternative approach to underground storage – using liquid CO_2 and associated CO_2 hydrate. This requires similarly high pressures, but would operate at lower temperatures – such as might be found beneath the floors of cold, deep oceans, or permafrost regions. Although this concept of 'cool storage' has received much less attention compared to that of 'warm storage', it does appear to offer certain advantages in terms of the mechanisms that may trap the stored CO_2:

1. In terms of the free CO_2 phase, liquid CO_2 can have a significantly higher density compared to supercritical CO_2, so more of it can be stored in an equivalent volume of rock. Its lower buoyancy and higher viscosity would also help reduce the rate of vertical migration from the storage horizon;
2. In terms of dissolved CO_2, its solubility increases significantly at lower temperatures (up to the point where CO_2 hydrate precipitates);
3. In terms of storing CO_2 as solid phases, cool conditions would allow for the precipitation of CO_2 hydrate as well as carbonate minerals. CO_2 hydrate would be advantageous as it forms rapidly, only requiring the presence of water and CO_2. It could form via 2 routes; intentionally – as a primary storage mechanism, or unintentionally – as a secondary 'backup' storage mechanism (e.g. as a result of leakage of CO_2 from a deep, warm reservoir to shallower, cooler horizons). As a primary storage mechanism it may form an impermeable 'cap' above a 'pool' of liquid CO_2, enhancing the sealing properties of a natural caprock.

If CO_2 hydrate is to play a role in underground storage, we need to be able to predict where it will be stable on a regional scale. This has been done for offshore Western Europe and although this does not identify local geological structures suitable for CO_2 storage, it does show that large regions have the potential for CO_2 hydrate formation in deep-water sediments. We also need to know about smaller-scale processes, such as the relationship between CO_2 hydrate and sediment grains at a pore scale, and how this influences the overall physical properties of the sediment. Results from laboratory experiments show that hydrate formation is rapid and that it can act as a cement to the sediment grains, although its morphology may differ if grown in water-saturated or CO_2-saturated conditions. Experimental results also indicate that even a relatively thin layer of hydrate can be effective at greatly retarding CO_2 migration rates. This suggests that even a relatively thin 'cap' of CO_2 hydrate may be able to prevent a slightly buoyant 'pool' of stored liquid CO_2 from rising.

In conclusion, there could be a role for CO_2 storage under cool conditions, and CO_2 hydrate could have an important part to play in this. However, in assessing the overall storage potential of an individual storage scheme, it will be important to consider all possible trapping mechanisms, and not just those involving CO_2 hydrate. To achieve this fully will require the close co-operation of those with in-depth knowledge of both hydrate phases and underground CO_2 storage. Much work remains to be undertaken to fully understand how CO_2 hydrate can best contribute to underground storage and the complex inter-relationship it may have with sediments. Sequestration of CO_2 as hydrate could provide another technique to add to the portfolio of strategies that could help reduce emissions of anthropogenic CO_2 to the atmosphere.

Ameena Camps acknowledges the Natural Environment Research Council for funding under grant NER/S/A/2003/11923. Erik Lindberg is thanked for the use of the Sintef CO_2 density model. Peter Miles and Mark Rodger are thanked for their useful comments that helped improve this paper. This paper is published with the permission of the Executive Director of the British Geological Survey (NERC).

References

Atkins, P. W. 1982. Physical Chemistry (2nd ed.), Oxford University Press.

Austvik, T. & Løken, K. P. 1992. Deposition of CO_2 on the seabed in the form of hydrates. . Energy Conversion and management, 33(5-8), 659-666.

Aya, I., Yamane, K. & Kojima, R. 2001. Simulation experiment of CO_2 storage at 3600 m deep ocean floor. In (D. Williams, B. Durie, P. McMullan, C. Paulson & A. Smith eds) 'Proceedings of the 5th International Conference on Greenhouse Gas Control Technologies GHGT-5', CSIRO Publishing, Collingwood, Australia, 423-428.

Bachu, S., Gunter, W. D., & Perkins, E. H. 1994. Aquifer disposal of CO_2: hydrodynamic and mineral trapping. *Energy Conversion and Management*, 35, 269-279.

Baines, S. J. & Worden, R. H. 2004a. Geological Storage of Carbon Dioxide. Geological Society Special Publication number 233, 255p.

Baines, S. J. & Worden, R. H. 2004b. The long-term fate of CO_2 in the subsurface: natural analogues for CO_2 storage. In (S.J. Baines and R.H. Worden eds) 'Geological Storage of Carbon Dioxide', Geological Society Special Publication number 233, 59-85.

Baker, J. C., Bai, G. P., Hamilton, P. J., Golding, S. D. & Keene, J. B. 1995. Continental-scale magmatic carbon dioxide seepage recorded by dawsonite in the Bowen-Gunnedah-Sydney basin system, eastern Australia. *Journal of Sedimentary Research*, A65(3), 252-530.

Baklid, A., Korbø L. R. & Owren, G. 1996. Sleipner Vest CO_2 disposal, CO_2 injection into a shallow underground aquifer. *Society of Petroleum Engineers*, 36600, 269-277.

Bergman, P. D., Drummond, C. J., Winter, E. M. & Chen, Z-Y. 1996. Disposal of power plant CO_2 in depleted oil and gas reservoirs in Texas. Proceedings of the Third International Conference on Carbon Dioxide Removal, Massachusetts Institute of Technology, Cambridge, MA, USA, 9-11 September 1996.

Brewer, P. G., Friederich, G., Peltzer, E. T. & Orr, F. M. Jr (1999). Direct experiments on the ocean disposal of fossil fuel CO_2. Science, 284, 943-945.

Camps, A. P. 2007. Hydrate formation in near surface ocean sediments. Unpublished PhD thesis, Leicester University.

Camps, A. P., Long, D., Rochelle, C. A. & Lovell, M. A. 2009. Mapping Hydrate Stability Zones Offshore Scotland. In: Long, D., Lovell, M. A., Rees, J. G. & Rochele, C. A. (eds) Sediment-Hosted Gas Hydrates: New Insights on Natural and Synthetic Systems. Geological Society, London, Special Publications, 319, 81–91.

Czernichowski-Lauriol, I., Sanjuan, B., Rochelle, C., Bateman, K., Pearce, J. & Blackwell, P. 1996a. Inorganic geochemistry. Chapter 7 in *'The Underground Disposal of Carbon Dioxide'* (S. Holloway ed.), Final Report of Joule II Project Number CT92-0031.

Czernichowski-Lauriol, I., Sanjuan, B., Rochelle, C., Bateman, K., Pearce, J. & Blackwell, P. 1996b. Analysis of the geochemical aspects of the underground disposal of CO_2. In *'Deep Injection Disposal of Hazardous and Industrial Wastes, Scientific and Engineering Aspects'* (J.A. Apps and C.-F. Tsang eds), Academic Press, ISBN 0-12-060060-9, 565-583.

Enick, R. M. & Klara, S. M. 1990. CO_2 solubility in water and brine under reservoir conditions. Chemical Engineering Communications, 90, 23-33.

Freund, P. & Ormerod, W. 1996. Progress towards storage of CO_2. Proceedings of the Third International Conference on Carbon Dioxide Removal, Massachusetts Institute of Technology, Cambridge, MA, USA, 9-11 September, 1996.

Gorman, A. R., Holbrook, W. S., Hornbach, M. J., Hackwith, K. L., Lizarralde, D. & Pecher, I. 2002. Migration of methane gas through the hydrate stability zone in a low-flux hydrate province. Geology, 30(4), 327-330.

Gunter, W. D., Perkins, E. H. & McCann, T. J. 1993. Aquifer disposal of CO_2-rich gases: reaction design for added capacity. *Energy Conversion Management*, 34, 941-948.

Gunter, W. D., Wiwchar, B. & Perkins, E. H. 1997. Aquifer disposal of CO_2-rich greenhouse gases: extension of the time scale of experiment for CO_2-sequestering reactions by geochemical modelling. *Mineralogy and Petrology*, 59, 121-140.

Harrison, W. J., Wendlandt, R. F. & Sloan, E. D. 1995. Geochemical interactions resulting from carbon dioxide disposal on the seafloor. Applied Geochemistry, 10, 461-475.

Haugen, H. A. & Eide, L. I. 1996. CO_2 Capture and Disposal: The realism of large scale scenarios. Energy Conversion and Management, 37 (6-8), 1061-1066.

Herzog, H. J., Adams, E. E., Auerbach, D. & Caulfield, J. 1996. Environmental impacts of ocean disposal of CO_2. Energy Conversion and Management, 37(6-8), 999-1005.

Hirai, S., Okazaki, K., Tabe, Y. & Hijikata, Y. 1997. Numerical simulation for dissolution of liquid CO_2 droplets covered with clathrate film in intermediate depth of ocean. Energy Conversion and management, 38 (supplement) S313-S318.

Holloway, S. 1996a. An overview of the Joule II project 'The Underground Disposal of Carbon Dioxide', Energy Conversion and Management, 37 (6-8), 1149-1154.

Holloway, S. (ed.) 1996b. *The Underground Disposal of Carbon Dioxide, Final Report of Joulle II Project Number CT92-0031*. British geological Survey, 355p, ISBN 0 85272 280 X.

Holloway, S. 1997. An overview of the underground disposal of carbon dioxide. Energy Conversion and Management, 38 (supplement) S193-S198.

IEA GHG 1998. Sleipner aquifer storage of CO_2. *Greenhouse Issues*, 34, 4.

IEA GHG 2000a. Issues underlying the feasibility of storing CO_2 as hydrate deposits. IEA Greenhouse Gas R&D Programme Report PH3/25.

IEA GHG 2000b. Natural gas and methane hydrates. IEA Greenhouse Gas R&D Programme Report PH3/27.

IEA GHG 2004. Gas hydrates for deep ocean storage of CO_2. IEA Greenhouse Gas R&D Programme Report PH4/26.

IMO 1997. Convention on the prevention of marine pollution by dumping of wastes and other matter (London Convention 1972). Compilation of the full texts of the London Convention 1972 and of the 1996 Protocol thereto. LCo2/Circ.380, 63p, International Maritime Organisation, London.

IOC, IHO & BODC, 2003. Centenary Edition of the GEBCO Digital Atlas, published on CD-ROM on behalf of the Intergovernmental Oceanographic Commission and the International Hydrographic Organization as part of the General Bathymetric Chart of the Oceans, British Oceanographic Data Centre, Liverpool, U.K.

IPCC 1990. Scientific assessment of climate change. Working group 1 report of the Intergovernmental Panel on Climate Change, WNO, Geneva. World Wide Web Address: http://www.ipcc.ch/ipccreports/assessments-reports.htm

IPCC 2005. Carbon dioxide capture and storage. Working Group 3 report of the Intergovernmental Panel on Climate Change (B. Metz, O. Davidson, H. de Coninck, M. Loos & L. Meyer eds), Cambridge University press, New York, 431p.

IPCC 2007. Forth Assessment Report: Climate Change. Published by the IPCC. World Wide Web Address: http://www.ipcc.ch/ipccreports/assessments-reports.htm

Johnson, J. W., Nitao, J. J. & Knauss, K. G. 2004. Reactive transport modelling of CO_2 storage in saline aquifers to elucidate fundamental processes, trapping mechanisms and sequestration partitioning. In (S.J. Baines and R.H. Worden eds) 'Geological Storage of Carbon Dioxide', Geological Society Special Publication number 233, 87-106.

Johnson, J. W., Nitao, J. J., Steefel, C. I. & Knauss, K. G. 2001. Reactive transport modelling of geologic CO_2 sequestration in saline aquifers: the influence of intra-aquifer shales and the relative effectiveness of structural, solubility, and mineral trapping during prograde and retrograde sequestration. In *'Proceedings of the First National Conference on Carbon Sequestration, Washington, DC, May 14-17, 2001'*.

JOIDES, 1992. JOIDES Pollution Prevention and Safety Panel, Ocean Drilling Program Guidelines for Pollution Prevention and Safety. Joides Journal 18, Special Issue No7, 24pp.

Karl, T. R., Knight, R. W. & Baker, B. 2000. The record breaking global temperatures of 1997 and 1998: evidence for an increase in the rate of global warming? Geophysical research letters, 27, 719-722.

King, M. B., Mubarak, A., Kim, J. D. & Bott, T. R. 1992. The mutual solubilities of water with supercritical and liquid carbon dioxide. *Journal of Supercritical Fluids*, 5, 296-302.

Koide, H., Takahashi, M., Shindo, Y., Tazaki, Y., Ijiima, M., Ito, K., Kimura, N., & Omata, K. 1997. Hydrate formation in sediments in the sub-seabed disposal of CO_2. Energy Vol. 22, No. 273, 279-283.

Kojima, R. Yamane, K. & Aya, I. 2003. Dual nature of CO_2 solubility in hydrate forming region. In: *'Greenhouse gas Control Technologies'* (J. Gale & Y. Kaya eds), Elsevier Science.

Kuk, M. S. & Montagna, J. C. 1983. Solubility of oxygenated hydrocarbons in supercritical carbon dioxide. In: *'Chemical Engineering at Supercritical Fluid Conditions'*, 101-111, Ann Arbor Science, Ann Arbor, U.S.A.

Lorenz, S. & Müller, W. 2003. Modelling of halite formation in natural gas storage aquifers. Proceedings of the 'TOUGH Symposium 2003', Lawrence Berkeley National Laboratory, Berkeley, California, May 12-14, 2003.

Malik, Q. M. & Islam, M. R. 2000. CO_2 injection in the Weyburn field of Canada: Optimization of enhanced oil recovery and greenhouse gas storage with horizontal wells. *Society of Petroleum Engineers*, 59327, 16p.

Moberg, R. 2001. The Weyburn CO_2 monitoring and storage project. *Greenhouse Issues*, 57, 2-3.

Nakano, S., Yamamoto, K. & Ohgaki, K. 1998. Natural gas exploitation by carbon dioxide from gas hydrate fields – high-pressure phase equilibrium for an ethane hydrate system. Proceedings of the Institution of Mechanical Engineers, 212 Part A, 159-163.

OSPAR 1992. Convention for the protection of the marine environment of the north-east Atlantic, 32p, OSPAR Commission, London.

Pearce, J., Czernichowski-Lauriol, I., Lombardi, S., Brune, S., Nador, S., Baker, J., Pauwels, H., Hatziyannis, G., Beaubien, S. & Faber, E. 2004. A review of natural CO_2 accumulations in Europe as analogues for geological sequestration. In (S.J. Baines and R.H. Worden eds) 'Geological Storage of Carbon Dioxide', Geological Society Special Publication number 233, 29-41.

Pearce, J., Holloway, S., Wacker, H., Nelis, M. K., Rochelle, C. A. & Bateman, K. 1996. Natural occurrences as analogues for the geological disposal of carbon dioxide. *Energy Conversion and Management*, 37, 1123-1128.

Pruess, K. 2003. Numerical simulation of leakage from a geologic disposal reservoir for CO_2, with transitions between super- and sub-critical conditions. Proceedings of the 'TOUGH Symposium 2003', Lawrence Berkeley National Laboratory, Berkeley, California, May 12-14, 2003.

RCEP 2000. Energy – the changing climate. Twenty-second report of the Royal Commission On Environmental Polution, Cm 4749, 292pp.

Read, J. F., Pollard, R. T & Hirst, C. 1991. CTD data from the north east Atlantic, April 1989, collected on RSS *Discovery* Cruse 181. Institute of Oceanographic Sciences, Deacon Laboratory, Report no. 285, 157pp.

Riestenberg, D., Chiu, E., Gborigi, M., Liang, L., West, O. R. & Tsouris, C. 2004. Investigation of jet breakup and droplet size distribution of liquid CO_2 and water systems – implications for CO_2 hydrate formation for ocean carbon sequestration. American Mineralogist, 89, 1240-1246.

Rochelle, C. & Camps, A. 2006. Underground storage of CO_2 as a liquid and solid hydrate. Greenhouse Issues, 82, 8-9.

Rochelle, C. A., Czernichowski-Lauriol, I. & Milodowski, A. E. 2004. The impact of chemical reactions on CO_2 storage in geological formations, a brief review. In (S.J. Baines and R.H. Worden eds) 'Geological Storage of Carbon Dioxide', Geological Society Special Publication No. 233, 87-106.

Rochelle, C. A., Pearce, J. M. & Holloway, S. 1999. The underground sequestration of carbon dioxide: containment by chemical reactions. In *'Chemical Containment of Waste in the Geosphere'*, Geological Society Special Publication No. 157, 117-129.

Sakai, H., Gamo, T., Kim, E.-S., Tsutsumi, M., Tanaka, T., Ishibashi, J., Wakita, H., Yamano, M. & Oomori, T. 1990. Venting of carbon dioxide-rich fluid and hydrate formation in mid-Okinawa trough backarc basin. Science, 248, 1093-1096.

Sasaki, K. & Akibayashi, S. 2000. A calculation model for liquid CO_2 injection into shallow sub-seabed aquifer. In 'Gas Hydrates, challenges for the future' (G.D. Holder & P.R. Bishnoi eds), Annals of the New York Academy of Sciences, Volume 912, 211-225.

Saunders, P. M. & Cooper, S. 1987. CTD data on the Iberian Abyssal Plain. Institute of Oceanographic Sciences, Deacon Laboratory, Report no. 247, 70pp.

Sloan, E. D. Jr. 1998. Clathrate Hydrates of Natural Gases. Marcell Dekker Inc, 359pp.

Someya, S., Saito, K., Nishio, M. & Tsutsui, K. 2006. CO_2 sequestration under a sealed layer with clathrate hydrate in sediments. Proceedings of *'Sediment-hosted gas hydrates: New insights on natural and synthetic systems'*, 25-26 January 2006, London, p 34, Geological Society.

Studlick, J. R. J., Shew, R. D., Basye, G. L. & Ray, J. R. 1990. A giant carbon dioxide accumulation in the Norphlet Formation, Pisgah Anticline, Mississippi. In: 'Sandstone Petroleum Reservoirs', Barwis, J. H., McPherson, J. G. & Studlick, J. R. J. eds, 181-203, Springer Verlag, New York.

Vesovic, V., Wakeham, W. A., Olchowy, G. A., Sengers, J. V., Watson, J. T. R. & Millat, J. 1990. The transport properties of carbon dioxide. Journal of Physics and Chemistry Refference Data, 19(3), 763-808.

Warzinski, R. P., Lynn, R. J. & Holder, G. D. 2000. The impact of CO_2 clathrate hydrate on deep ocean sequestration of CO_2 – Experimental observations and modeling results. In 'Gas Hydrates, challenges for the future' (G. D. Holder and P. R. Bishnoi eds), Annals of the New York Academy of Sciences, Volume 912, 226-234.

Wiebe, R. 1941. The binary system carbon dioxide-water under pressure. Chemical Reviews, 29, 475-481.

Wiebe, R. & Gaddy, V. L. 1939. The solubility in water of carbon dioxide at 50, 75 and 100°, at pressures to 700 atmospheres. Journal of the American Chemical Society, 61, 315-318.

Wiebe, R. & Gaddy, V. L. 1940. The solubility of carbon dioxide in water at various temperatures from 12 to 40° and at pressures to 500 atmospheres. Critical phenomena. *Journal of the American Chemical Society*, 62, 815-817.

Wilson, M. & Monea, M. (eds) 2004. IEA GHG Weyburn CO_2 Monitoring & Storage project Summary Report 2000-2004. Volume 3 of the proceedings of the '7th International Conference on Greenhouse Gas Control Technologies', September 5-9, 2004, Vancouver, Canada, Petroleum Technology Research Centre, Regina, 273p.

Wilson, T. R. S. 1992. The deep ocean disposal of carbon dioxide. Energy Conversion and Management, 33(5-8), 627-633.

Zheng, L., Wang, S., Liao, Y. & Feng, Z. 2001. CO_2 gas pools in Jiyang sag, China. Applied Geochemistry, 16, 1033-1039.

Fig. 1. CO_2 phase diagram (modified after Atkins 1982).

Fig. 2. Schematic diagram showing the relative position of injected liquid CO_2 and associated 'cap' of CO_2 hydrate.

Fig. 3. Map of predicted thickness (m) of the CO_2 hydrate stability zone within seabed sediments for offshore Western Europe. Note that the Mediterranean Sea is not covered by this study.

Fig. 4. Cryogenic SEM photomicrograph of sand grains (light grey) coated with a film of CO_2 hydrate (dark grey) that has been partly removed from the grains in places. Note larger crystals of CO_2 hydrate in the larger pore spaces – a good example is just to the right of the centre of the image. (Experiment using sand and synthetic seawater).

Fig. 5. Variation in CO_2 density over a range of temperatures, for an assumed hydrostatic head of 1 km (10 MPa) (prepared using a density model courtesy of Sintef). CO_2 density is about 20% greater at 10°C compared to 30°C.

Fig. 6. Variation in CO_2 solubility over a range of temperatures, for an assumed hydrostatic head of 1 km (10 MPa) and for seawater-like salinities (prepared using data from Enick & Klara 1990; King *et al.* 1992; Kojima *et al.* 2003; Kuk & Montagna, 1983; Wiebe 1941; Wiebe & Gaddy 1939, 1940).

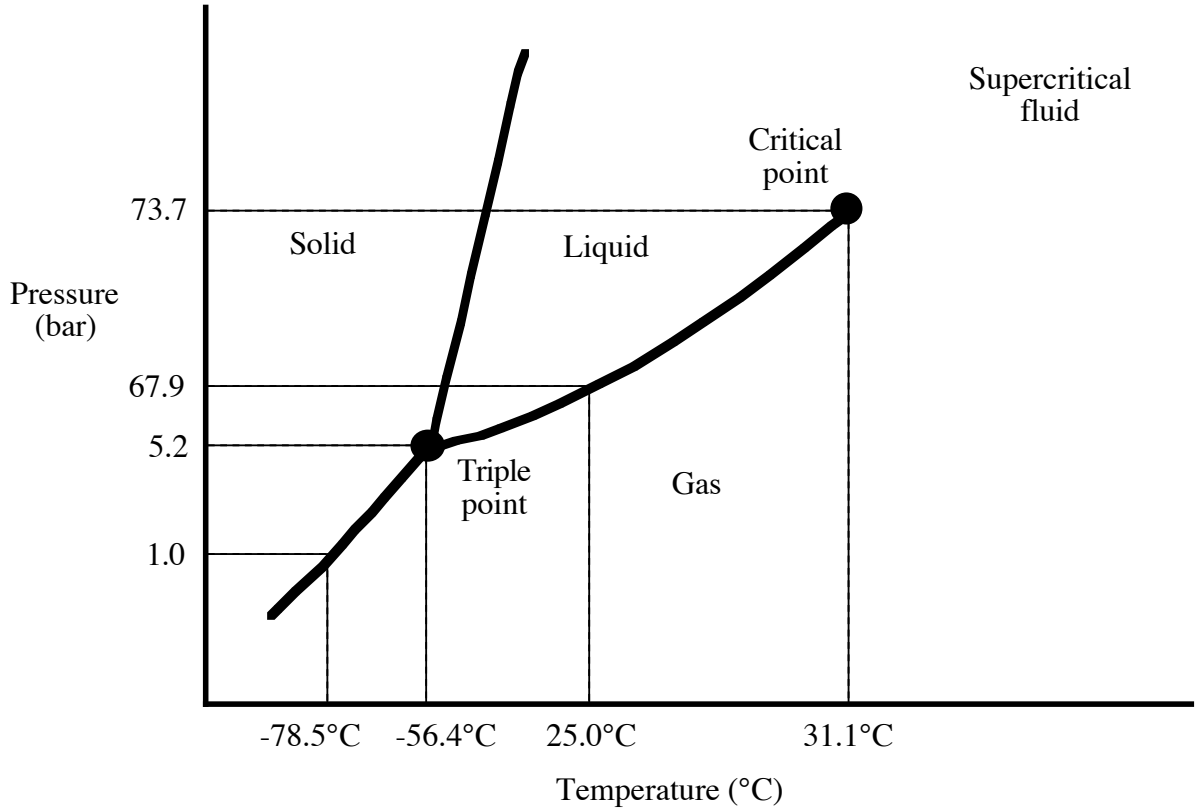

Fig. 1. CO_2 phase diagram (modified after Atkins 1982).

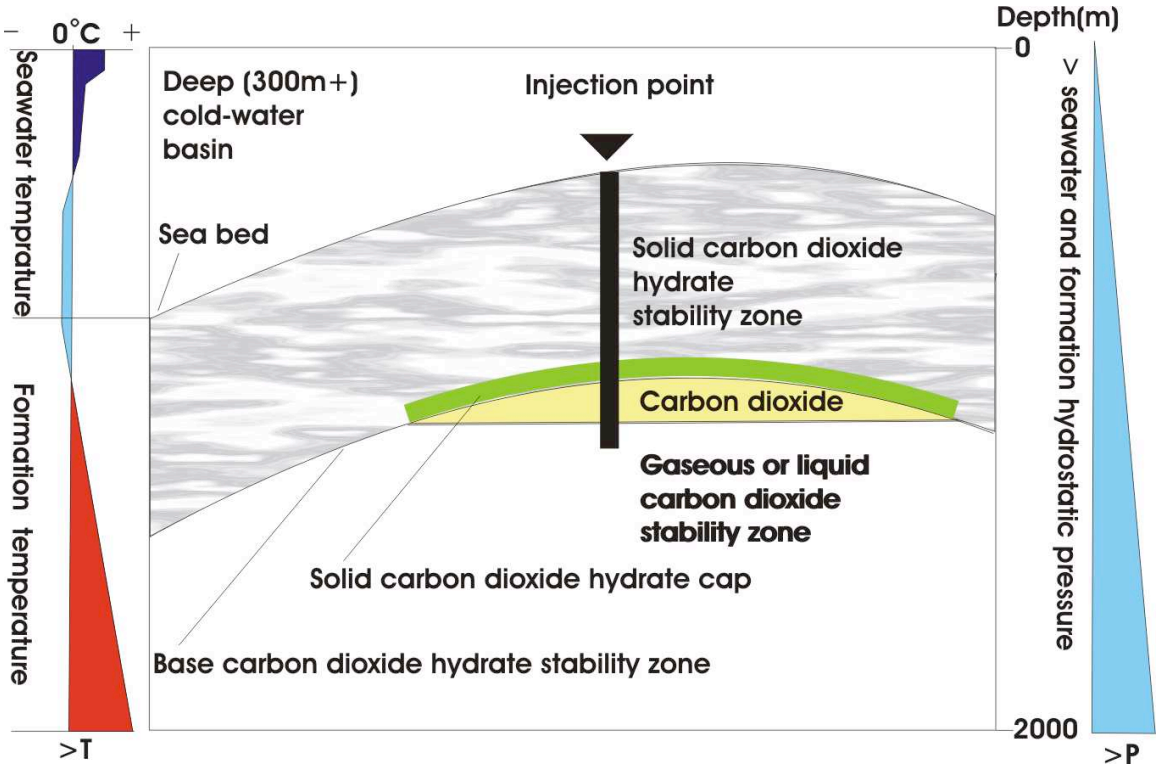

Fig. 2. Schematic diagram showing the relative position of injected liquid CO_2 and associated 'cap' of CO_2 hydrate.

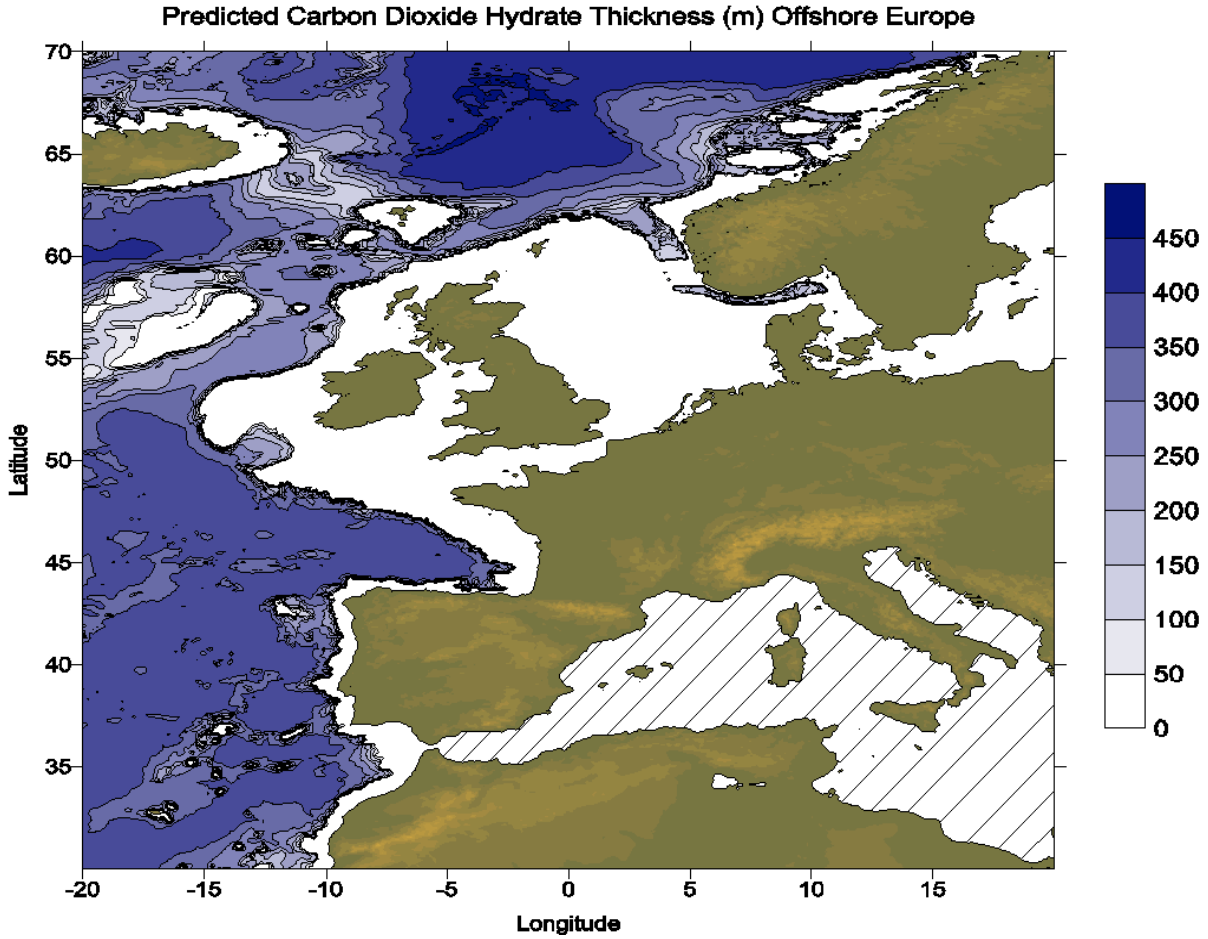

Fig. 3. Map of predicted thickness (m) of the CO_2 hydrate stability zone within seabed sediments for offshore Western Europe. Note that the Mediterranean Sea is not covered by this study.

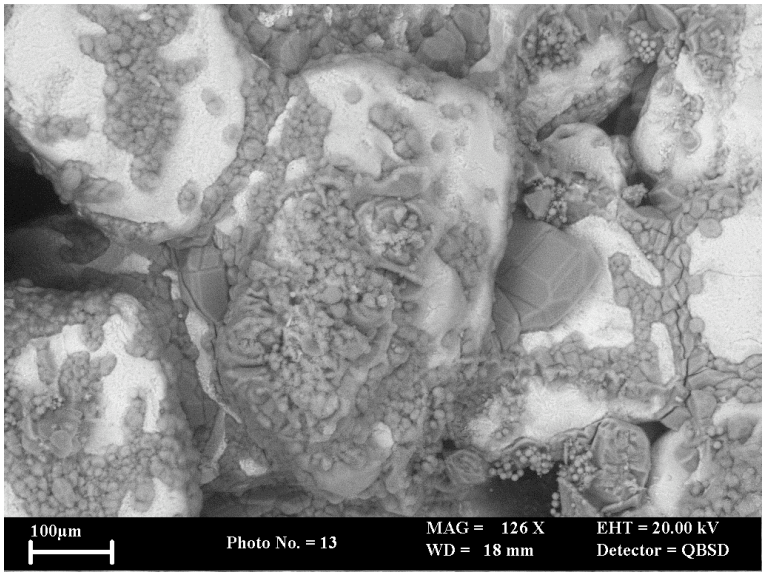

Fig. 4. Cryogenic SEM photomicrograph of sand grains (light grey) coated with a film of CO_2 hydrate (dark grey) that has been partly removed from the grains in places. Note larger crystals of CO_2 hydrate in the larger pore spaces – a good example is just to the right of the centre of the image. (Experiment using sand and synthetic seawater).

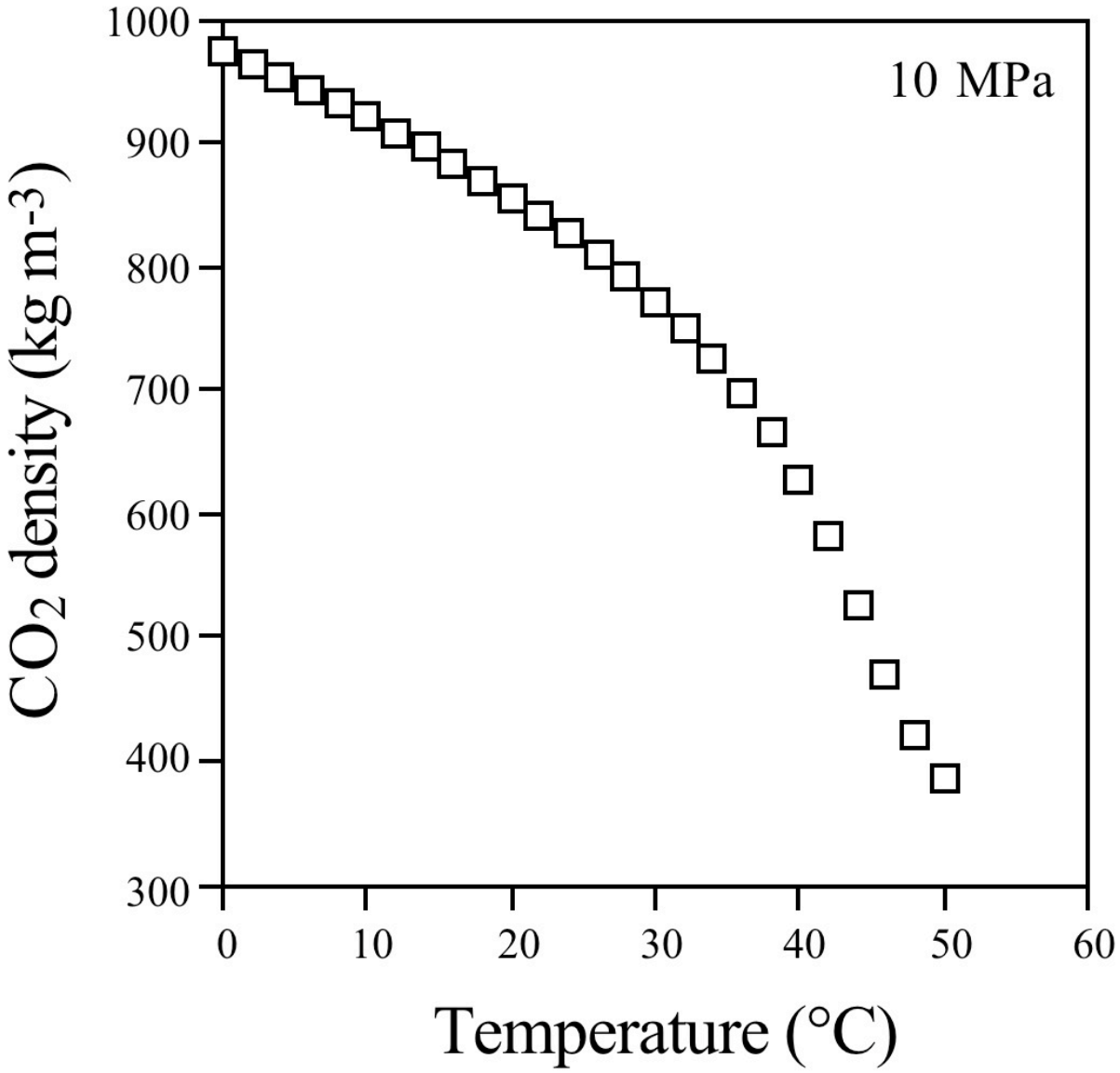

Fig. 5. Variation in CO_2 density over a range of temperatures, for an assumed hydrostatic head of 1 km (10 MPa) (prepared using a density model courtesy of Sintef). CO_2 density is about 20% greater at 10°C compared to 30°C.

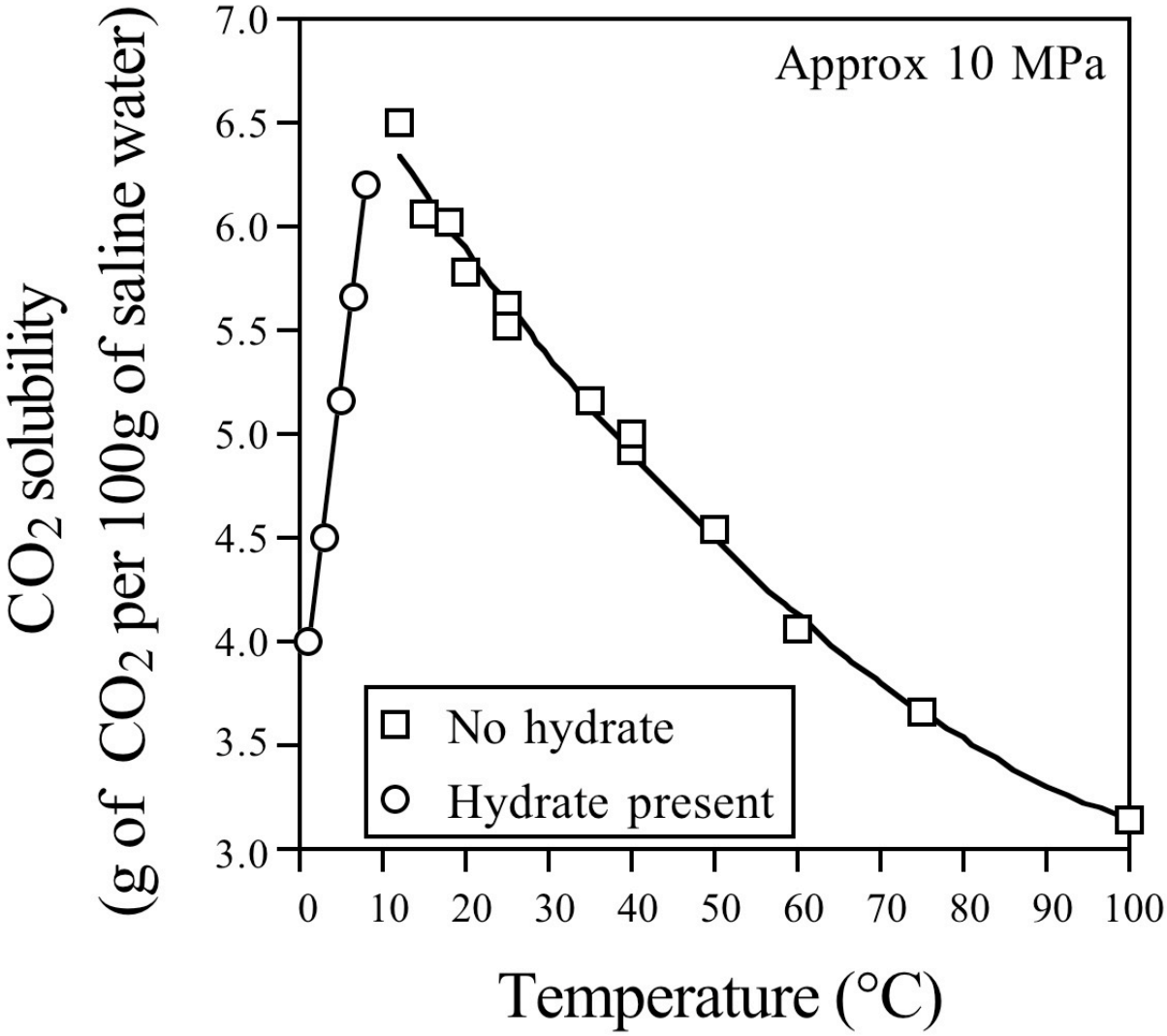

Fig. 6. Variation in CO_2 solubility over a range of temperatures, for an assumed hydrostatic head of 1 km (10 MPa) and for seawater-like salinities (prepared using data from Enick & Klara 1990; King *et al*. 1992; Kojima *et al*. 2003; Kuk & Montagna 1983; Wiebe 1941; Wiebe & Gaddy 1939, 1940).