Carbon dioxide capture and geological storage

BY SAM HOLLOWAY*

British Geological Survey, Keyworth, Nottingham NG12 5GG, UK

Carbon dioxide capture and geological storage is a technology that could be used to reduce carbon dioxide emissions to the atmosphere from large industrial installations such as fossil fuel-fired power stations by 80–90%. It involves the capture of carbon dioxide at a large industrial plant, its transport to a geological storage site and its long-term isolation in a geological storage reservoir. The technology has aroused considerable interest because it can help reduce emissions from fossil fuels which are likely to remain the dominant source of primary energy for decades to come. The main issues for the technology are cost and its implications for financing new or retrofitted plants, and the security of underground storage.

Keywords: carbon dioxide; geological storage; storage capacity; leakage

1. Introduction

Carbon dioxide capture and storage (CCS) is a technology that could be used to reduce carbon dioxide (CO₂) emissions to the atmosphere from large stationary point sources such as new and existing fossil fuel-fired power stations by 80–90%. At its simplest, the CCS process is a chain consisting of three major steps: the capture and compression of CO₂; its transport to a storage location; and its long-term isolation from the atmosphere (figure 1).

Geological storage is generally regarded as the most mature option for isolating the captured CO₂ from the atmosphere (IPCC 2005). Pilot-scale (Wong & Gunter 1999; Hovorka 2005; Kikuta et al. 2005; van der Meer 2005; Pagnier et al. 2005; Yamaguchi et al. 2005) and industrial-scale (Korbul & Kaddour 1995; Wilson & Monea 2004; Chadwick et al. 2005; Riddiford et al. 2005) geological CO₂ storage projects have already been established; the Sleipner project (North Sea), which stores approximately 1 million tonnes of CO₂ annually, has been in operation since 1996. Geological CO₂ storage may take place either in reservoirs where the sole purpose is CO₂ storage, e.g. in saline water-bearing reservoir rocks, sometimes known as saline formations or saline aquifers, or in oil and gas fields or coal seams, where it may contribute to enhanced oil recovery (Klusman 2003; Wilson & Monea 2004), enhanced gas recovery (van der Burgt et al. 1992) or enhanced coalbed methane recovery (Reeves 2005), EOR, EGR and ECBM, respectively.

CCS has become the focus of significant interest because fossil fuels are likely to remain a major source of primary energy for decades to come (IEA 2005); decades in which it will be necessary to reduce carbon emissions to the Earth’s

*shol@bgs.ac.uk

One contribution of 13 to a Discussion Meeting Issue ‘Energy for the future’.
atmosphere if serious climate change and ocean acidification are to be avoided. As well as having the potential to reduce emissions from large stationary point sources, in the longer term CCS may be able to contribute to CO₂ emission reductions in the transport sector by providing a low-carbon route to hydrogen production from fossil fuels.

IPCC (2005) provides an excellent review of CCS technology. Consequently, this paper gives only a brief outline of the technology and focuses on the main issues concerning its wide-scale deployment.

2. Capture

Fossil fuel-fired power plants are the dominant industrial point sources of CO₂ in most countries (Rubin et al. 2005). CO₂ may be captured from these by the following.

— Pre-combustion techniques, which process fuel in a reactor with steam and air or oxygen to produce a gas mixture consisting mainly of carbon monoxide and hydrogen. Additional hydrogen and CO₂ are produced by reacting the carbon monoxide with steam in a shift reactor. The CO₂ is then separated at high pressure, usually using a physical or chemical absorption process.

— Oxyfuel combustion in which the fossil fuel is combusted in an O₂/CO₂ atmosphere, which results in a very CO₂-rich flue gas suitable for transport and storage. This technology is at the demonstration stage, with pilot plants under construction at present. A CO₂ separation unit is not required, but an air separation unit is required at the front end of the process to obtain the oxygen.
— Post-combustion techniques in which the CO\textsubscript{2} is extracted from the flue gases of the plant. These systems normally use a liquid solvent to capture the small fraction of CO\textsubscript{2} (typically 3–15\% by volume) present in a flue gas stream.

Capture is energy-intensive. The increase in fuel consumption per kilowatt hour for plants capturing 90\% of CO\textsubscript{2} using best current technology ranges from 11 to 40\%, depending mainly on the type of plant. Given that a small percentage of the CO\textsubscript{2} emitted by the modified plant is not captured, this results in the ‘net CO\textsubscript{2} avoided’ being around 80–90\% of the emissions of an equivalent base-case plant that has not been modified for CO\textsubscript{2} capture (Rubin et al. 2005).

The main issues for capture are cost and its implications in terms of financing new or retrofitted plant. Driving down the cost of capture (Thomas 2005) is likely to continue to be a goal for CCS technology. However, no operator will be competitive when deploying CCS unless the correct fiscal incentives are in place. These incentives would have to include a price for the CO\textsubscript{2} abated, whether through an emissions trading scheme or another mechanism. Some kind of guarantee of the long-term stability of such a support mechanism would likely be required to enable investment in new power plant or retrofits to take place (Gough et al. 2006). Meanwhile, the continued building of conventional (non-CCS) fossil fuel-fired power plants presents a challenge in terms of CO\textsubscript{2} emissions lock-in during the next three or four critical decades, hence the promotion of the concept of building capture-ready plants that could be converted economically to CCS (Gibbins et al. 2006). A further issue for capture is the vast volumes of CO\textsubscript{2} that have to be handled. Although some capture technologies are well known, they have not been demonstrated at the scale that would be required at a large power plant.

3. Transport

Owing to the large volumes involved, the most likely means of transport for CO\textsubscript{2} between a large point source and a storage site would be by pipeline. Existing CO\textsubscript{2} pipelines operate at pressures above 8 MPa (commonly 10–16 MPa) to avoid two-phase flow. However, it would be possible to use ships to transport CO\textsubscript{2} across seas (Berger et al. 2005) and this might be desirable for offshore enhanced oil recovery operations because it would allow intermittent CO\textsubscript{2} supply.

The main issues for CO\textsubscript{2} transport to a potential storage site are cost and safety, neither of which have proved significant obstacles in the construction of more than 2500 km of CO\textsubscript{2} pipelines in operation in (largely rural) areas of North America since the 1970s (Doctor et al. 2005).

4. Geological storage

There are many natural underground CO\textsubscript{2} fields around the world (Studlick et al. 1990; Pearce et al. 1996; Stevens 2005). These are identical to natural gas fields in every respect apart from their gas composition. Furthermore, many oil and natural gas fields contain varying quantities of CO\textsubscript{2} mixed with the hydrocarbon gases (Baines & Worden 2004). Many of these fields of both pure CO\textsubscript{2} and CO\textsubscript{2}–hydrocarbon mixtures have existed for hundreds of thousands to tens of millions of years. This proves that under favourable circumstances large
quantities of CO$_2$ can be retained underground for appropriate timescales: the aim of CO$_2$ storage is to identify places where such favourable geological circumstances are present, and imitate nature by storing CO$_2$ in them.

Rocks suitable for CO$_2$ storage commonly occur in major accumulations of sedimentary rocks known as sedimentary basins that may be up to a few kilometres thick and cover thousands of square kilometres. However, although very common, sedimentary basins do not occur in every country in the world. Nor are all sedimentary basins suitable for CO$_2$ storage.

(a) Typical physical conditions for geological CO$_2$ storage

The average temperature in many sedimentary basins increases by approximately 25–30°C km$^{-1}$ below the ground surface or sea bed, as a result of heat flow from the inside to the outside of the Earth. However, there is considerable variation in such geothermal gradients, both locally within basins and between basins worldwide (Tissot & Welte 1978). Pressure also increases downwards within the subsurface. Pressure in the pore spaces of sedimentary rocks is commonly close to hydrostatic pressure, which is the pressure generated by a column of water of equal height to the depth of the pore space. This is because the pore space is commonly filled with water and is connected, albeit tortuously, to the ground surface. However, under conditions where the pore space is not connected to, or not in equilibrium with, the surface, pressure may be greater than hydrostatic, when it is known as overpressure. The converse, underpressure, may also exist, either naturally, or as the result of abstraction of fluids such as oil and gas from a reservoir. When CO$_2$ is stored underground, there is a sharp increase in its density and corresponding decrease in volume at depths between approximately 600 and 1000 m depending on the precise geothermal conditions and pressure (Ennis-King & Paterson 2001, figure 2). This is associated with the phase change from a gas to a dense supercritical fluid.
Consequently, CO$_2$ occupies much less space in the subsurface than at the surface. One tonne of CO$_2$ at a density of 700 kg m$^{-3}$ occupies 1.43 m$^3$, but at 0°C and 1 atmosphere, 1 tonne of CO$_2$ occupies approximately 509 m$^3$.

Under the pressure–temperature conditions commonly found in the subsurface, supercritical CO$_2$ is less dense than, and only slightly miscible with, the water or brine that is most commonly found within the void spaces in sedimentary rocks. It is fully miscible with, but denser than, natural gas and can be fully miscible with oil, both of which are also buoyant relative to water or brine. Gaseous CO$_2$ is considerably less dense than water or oil and fully miscible with natural gas.

(b) Storage mechanisms

The main mechanisms that trap CO$_2$ in the subsurface are the following:

— trapping as a result of the buoyancy of CO$_2$ compared with water or brine, in structural or stratigraphic traps beneath cap rocks,
— trapping as a residual saturation along the CO$_2$ migration path within the reservoir rock,
— dissolution into the native pore fluid (most commonly brine),
— reaction of acidified groundwaters with mineral components of the reservoir rock, and
— adsorption onto surfaces within the reservoir rock, e.g. onto the carbonaceous macerals that are the principal components of coal.

Geological storage of gaseous or supercritical CO$_2$ in structural or stratigraphic traps requires a combination of a porous and permeable reservoir rock that will act as the storage reservoir and, in most cases, a low-permeability geological barrier such as beds of mudstone or halite in a configuration that will isolate the CO$_2$ from the atmosphere (certain permeable rocks, most pertinently coal, may adsorb CO$_2$ and theoretically do not require a low-permeability geological barrier to retain it). Low-permeability barriers can be divided into two classes: aquicludes, which are rocks such as halite that are essentially impermeable if not fractured; and aquitards, rocks such as shales and mudstones that have significant porosity but, owing to their very small pore throat size, very low permeability. If they are water-wet and have some permeability, water can pass through the latter, albeit very slowly, in response to a pressure gradient.

Most saline water-bearing reservoir rocks and oil and gas reservoirs are clastic and carbonate sedimentary rocks. Fluids can flow through them via connected, commonly intergranular, porosity and/or fractures. CO$_2$ sent for storage would be injected into them via a well or wells, at sufficient pressure to displace some of the pore fluid already present in the pore spaces and fractures. However, many reservoir formations are subdivided into compartments by faults, which may prevent, inhibit or allow the transmission of fluids. If the compartments are small and the faults are sealing, or only transmit fluids when large pressure differences develop across them (Gaarenstroom et al. 1993), it could become dangerous to pump CO$_2$ into them. There would be a rapid pore fluid pressure rise within the compartment into which injection was taking place, and the fracture pressure of the reservoir rock or cap rock could be exceeded. Thus, the CO$_2$ storage capacity...
of reservoirs is a function not only of their intrinsic rock properties (e.g. porosity, permeability and heterogeneity), but also of their size and the nature of their boundaries: at least some part of the boundary of the reservoir must be able to transmit the pore fluid displaced by the injected CO$_2$. Ultimately, the displaced fluid would be accommodated by fluid movement to the seabed or water table or, perhaps, by a slight expansion of the geological system into which injection was taking place (van der Meer 1992).

The rate of trapping by dissolution into brine will depend on how well the CO$_2$ mixes with the formation water once it is injected into the reservoir. Once a CO$_2$ accumulation has reached a stable position within the reservoir, diffusion of CO$_2$ into the water will be faster if it is a thin but widespread accumulation, with a high surface area to volume ratio. However, for many accumulations, dissolution could be slow; of the order of a few thousand years for typical injection scenarios (Ennis-King & Paterson 2001), unless there is some form of active mixing induced by fluid convection within the reservoir (Lindeberg & Wessel-Berg 1997).

Dissolution results in acidification of the brine into which the CO$_2$ dissolves, which can enable water/rock reactions, particularly the dissolution of carbonate minerals such as calcite and, at much slower rates, basic aluminosilicate minerals. The reaction of acidified brines with basic aluminosilicate minerals could lead to the precipitation of carbonates; so-called mineral trapping of carbon as a solid phase. However, the kinetics of such reactions is very slow; time spans of the order of hundreds to thousands of years may be necessary for significant storage by this mechanism (Xu et al. 2003).

Residual saturation trapping occurs because a small proportion of the injected CO$_2$ remains behind when a plume of injected CO$_2$ sweeps through the reservoir rock. This is trapped by capillary forces and in very small-scale structural or stratigraphic traps. Residual saturation may be of the order of 5–30% (Ennis-King & Paterson 2001) and thus it could be an important trapping mechanism, particularly if CO$_2$ is injected near the base of heterogeneous reservoir formations (Flett et al. 2005).

Coal seams can be reservoirs for gases. Coal contains a natural system of orthogonal fractures known as cleats, which impart some permeability to it, and although the solid coal between the cleats does not contain significant conventional porosity, it contains micropores in which a natural gas known as coalbed methane (CBM) can occur. This usually consists of more than 90% methane plus small amounts of higher hydrocarbons, CO$_2$ and N$_2$. The gas molecules are adsorbed onto the surfaces of the micropores. CO$_2$ has a greater affinity to be adsorbed onto coal than methane. Thus, if CO$_2$ is pumped into a coal seam, it may be stored by becoming adsorbed onto the coal, and displace methane from the adsorption sites. Any methane recovered could have an economic value and offset some of the costs of CO$_2$ sequestration. Experimental injection of over 100 000 tonnes CO$_2$ into the Fruitland coal seams in the San Juan Basin, USA, has enhanced coalbed methane production (Reeves et al. 2004). However, coalbed methane production (and probably CO$_2$ injection) can only be established in a minority of coalfields with exceptional permeability. Moreover, the methane in coal represents only a small proportion of the energy value of the coal, and the remaining energy would be sterilized if the coal were used as a CO$_2$ storage reservoir, i.e. the coal could not be mined or gasified underground without releasing the CO$_2$. 

Phil. Trans. R. Soc. A (2007)
Storage capacity

The available storage capacity is one of the critical parameters that could decide whether geological storage of CO₂ can be a major contributor to solving this century’s greenhouse problem. Unfortunately, the CO₂ storage capacity of saline water-bearing reservoir rocks is difficult to estimate. They are highly variable, and have little or no economic value so they are not usually well characterized, particularly outside the major oil and gas provinces. Thus, it is difficult to construct representative geological models and make meaningful numerical simulations of CO₂ injection and flow within them. Moreover, there are no accepted, simple, top-down methods of estimating their CO₂ storage capacity based on commonly available public domain data (Holloway et al. 2006, in press). Much further work is required to make realistic estimates of the storage capacity of saline water-bearing reservoir rocks. The CO₂ storage capacity of oil and gas fields is much more closely constrained because it is based on the principle that a proportion of the space occupied by the recoverable hydrocarbon reserves can be occupied by injected CO₂ (Bachu & Shaw 2003). Current estimates of global CO₂ storage capacity are shown in table 1.

In the UK, the majority of the storage capacity lies offshore. The storage capacity of the offshore oilfields resulting from EOR may be of the order of 1.2 Gt. The storage capacity of the southern North Sea gas fields may be between 3 and 4 Gt, and the storage capacity of the saline water-bearing reservoir formations is not known, but may be up to approximately 14 Gt in the southern North Sea alone (Holloway et al. 2006, in press).

Although they do not take account of issues of timing (i.e. whether oil and gas fields will be available for storage when needed) and location relative to the sources of CO₂, the estimates suggest that there is sufficient storage capacity in the oil and gas fields alone to make a significant impact on global (approx. 24 Gt CO₂ yr⁻¹) and UK national (approx. 0.56 Gt CO₂ yr⁻¹) emissions to the atmosphere.

5. Will geological storage sites leak?

This is a key question for carbon dioxide capture and geological storage. It has to be considered on a site-by-site basis because it depends on the nature of the highly variable natural geological barriers that confine the gaseous, supercritical or dissolved CO₂ and the integrity of any wells in or around the storage site.

Considering the natural system first, CO₂ dissolved in brine is able to pass from a reservoir rock into, and through, the porosity of aquitards, albeit extremely slowly, if the reservoir pore fluid is overpressured relative to the aquitard. Conversely, if the

Table 1. Global CO₂ storage capacity estimates (IPCC 2005).

<table>
<thead>
<tr>
<th>reservoir type</th>
<th>lower estimate of storage capacity (Gt CO₂)</th>
<th>upper estimate of storage capacity (Gt CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>oil and gas fields</td>
<td>675ᵃ</td>
<td>900ᵃ</td>
</tr>
<tr>
<td>coal seams (ECBM)</td>
<td>3–15</td>
<td>200</td>
</tr>
<tr>
<td>deep saline formations</td>
<td>1000</td>
<td>uncertain but possibly 10⁴</td>
</tr>
</tbody>
</table>

ᵃExcludes undiscovered reserves.
pressure in the reservoir lies on the hydrostatic pressure gradient, there is no driving force for vertical migration of CO₂-saturated brine and CO₂ transport into the overlying strata will only occur by diffusion, e.g. Lindeberg & Bergmo (2003). In some reservoir formations, there is (slow) natural fluid flow towards the basin margins, caused by compaction of the reservoir and surrounding strata under the weight of overlying sediments. This could transport dissolved CO₂ from the storage site, though at many sites rates could be negligible, e.g. Cawley et al. (2005). Dissolved CO₂ may also be transported vertically downwards because CO₂-saturated brine is denser than CO₂-free brine, and will tend to sink through the reservoir and accumulate at the base of reservoir formations, providing very secure storage (Lindeberg & Wessel-Berg 1997). These transport mechanisms can be modelled (Cawley et al. 2005) and therefore their effects can be predicted in storage site performance assessments.

Gaseous or supercritical CO₂ trapped as a residual saturation along the migration path is trapped by capillary forces and therefore will not be released unless or until it dissolves into the surrounding brine over time, when it becomes subject to the transport processes outlined above.

Free gaseous or supercritical CO₂ trapped in structural or stratigraphic traps may leak if

— the capillary entry pressure of the cap rock to CO₂ is exceeded,
— faults or other fractures in the confining strata exist, or are enhanced or created in response to changes in pore fluid pressure in the reservoir,
— there are gaps in the confining strata, or
— wells in the trap leak.

The capillary entry pressure of cap rocks can be measured, so in pore fluid pressure thresholds can be calculated that will prevent capillary leakage of free CO₂ into cap rocks—assuming that any heterogeneity in the cap rock can be neglected. In oil and gas fields, greater assurance can be achieved because the minimum capillary entry pressure of the cap rock can be determined empirically, from the overpressure in the hydrocarbon column.

Unidentified open fractures in the confining strata could form migration pathways for CO₂. In addition, it is possible that depressurization of oil or gas fields during production of their hydrocarbons could enhance or induce microfractures in the confining strata (Jimenez & Chalaturnyk 2003), although if there is little or no compaction of the reservoir during production, this is less probable. Moreover, an increase in pore fluid pressure during CO₂ injection could open or lubricate closed fractures or even induce new fractures and allow fluids to escape (Streit & Hillis 2003).

The long-term integrity of wells in and around the storage site (Celia & Bachu 2003; Benson 2005) is potentially a significant issue. A gas-tight cement bond is required between any wells and surrounding strata, and the wells themselves must be effectively plugged. The potential for leakage via abandoned wells may be poorly known, e.g. Cawley et al. (2005), and will be site-specific. Moreno et al. (2005) give a methodology for assessing the integrity of wells over time, which they have applied to CO₂ storage at the Weyburn oilfield, Saskatchewan. The maximum cumulative leakage from an estimated 1000 wells in the Weyburn field over a 5000 year time frame is estimated to be 0.03 Mt CO₂, i.e. an average...

Phil. Trans. R. Soc. A (2007)
release rate of 6 tonnes yr\(^{-1}\) (Wilson & Monea 2004). In many onshore storage sites, wells can be remediated (Benson & Hepple 2005). In offshore settings, wells drilled from oil and gas production platforms can be repaired while the platform is still in place, but it may be less practical to re-enter and re-complete abandoned exploration and appraisal wells. More research on long-term well integrity and the remediation of abandoned wells is needed.

6. Potential impacts of CO\(_2\) leaking from a geological storage reservoir

Impacts of leaks on humans and the natural environment depend more on the concentration of CO\(_2\) in the environment than its flux through the ground surface or seabed. Most of the potential leakage pathways described above are considered likely to lead to relatively low flux emissions. In onshore areas, low flux emissions of natural CO\(_2\) from the ground are well known and relatively common in volcanic provinces around the world (Holloway et al. in press). In most cases, they do not form major hazards, although dangerous or environmentally damaging CO\(_2\) concentrations can build up locally. The rapid release of CO\(_2\) from a highly pressured, highly permeable reservoir via a well or natural fracture could produce a high-flux emission, although the initially high velocity of such an emission in an onshore area would likely result in significant mixing with the ambient air. Moreover, techniques exist to remediate CO\(_2\) well blowouts (Lynch et al. 1985). Nevertheless, such an event could form a hazard to humans and other organisms. Emissions of CO\(_2\) into the base of a lake, resulting in a build-up of dissolved CO\(_2\) and subsequent sudden emission via a ‘limnic eruption’, such as occurred at Lake Nyos in 1986 (Kanari 1989) could be a major hazard, although CO\(_2\) build-up in lake waters can be monitored and remediated (Kling et al. 2005, http://www.biology.lsa.umich.edu/~gwk/research/nyos.html).

Much less is known about the environmental damage that potentially could be caused by CO\(_2\) persistently leaking from a sub-seabed storage site. This would likely form a plume of acidified seawater downcurrent of the leakage site and could be associated with a plume of CO\(_2\)-rich water emerging onto the sea floor. It may be appropriate to consider the risk and impacts of such leakage against the background of the unavoidable impacts of ocean acidification by unabated emissions of CO\(_2\) to the atmosphere (Turley et al. 2004; Royal Society 2005).

7. Discussion

The safe and secure geological storage of CO\(_2\) by humans for millennia or longer cannot be directly demonstrated because the underground storage of gases has not been taking place for long enough. However, experience from natural gas storage operations (Perry 2005) suggests that fluxes to the biosphere might be expected from a proportion of human-made CO\(_2\) storage sites. Therefore, assessing the risks and potential impacts of CO\(_2\) leaking out of a storage structure is critically important for the implementation of CCS technology. Consequently, it might be appropriate for engineered CO\(_2\) storage sites to be subject to a regulatory process that, prior to injection of any CO\(_2\), could include the following:

Phil. Trans. R. Soc. A (2007)
— thorough geological and hydrogeological characterization of the storage site and surrounding area,
— the construction of geological and reservoir models of the storage site and surrounding area,
— simulation of CO₂ injection into the storage reservoir,
— simulation of the long-term fate of the injected CO₂,
— risk assessment based on the site characterization, models and simulation,
— acquisition of baseline monitoring surveys, and
— assessment of mitigation options if the CO₂ should migrate out of the storage reservoir.

During CO₂ injection, monitoring of the subsurface and ground surface or seabed could be combined with history matching of the monitoring results with the models, to provide feedback to improve the understanding of the site. After injection has ceased, monitoring could continue for some time, although it may be appropriate to decrease its frequency. Agreement between the modelled and the observed results, allowing reliable extrapolation of CO₂ distribution into the future, could be required before the site is closed and monitoring discontinued.

8. Conclusions

Globally, we are deeply committed to the continued use of fossil fuels for decades to come. Carbon dioxide capture and geological storage is a technology with the potential to reduce net CO₂ emissions to the atmosphere from existing electricity, heat and industrial production facilities by 80–90%—or more if biomass is co-fired with the fossil fuels. There are clear advantages to near-term deployment of this technology, which requires a stable long-term policy framework including incentives that allow investment. The key issue for the technology is the site-specific question of whether the risk of leakage and any resulting adverse impacts on humans and the natural environment is acceptable. Careful and thorough site characterization is the key to assessing these risks.

This paper is published with the permission of the Director of the British Geological Survey (NERC). The author thanks Michelle Bentham and Erik Lindeberg for their permission to show figures 1 and 2, respectively.

References


*Phil. Trans. R. Soc. A* (2007)


Klusman, R. W. 2003 Rate measurements and detection of gas microseepage to the atmosphere from an enhanced oil recovery/sequestration project, Rangely, Colorado, USA. Appl. Geochem. 18, 1825–1838. (doi:10.1016/S0883-2927(03)00108-2)


Phil. Trans. R. Soc. A (2007)


