Carbon Dioxide Storage

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Transport of CO_2

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EXECUTIVE SUMMARY

Transport is that stage of carbon capture and storage that links sources and storage sites. The beginning and end of 'transport' may be defined administratively. 'Transport' is covered by the regulatory framework concerned for public safety that governs pipelines and shipping. In the context of long-distance movement of large quantities of carbon dioxide, pipeline transport is part of current practice. Pipelines routinely carry large volumes of natural gas, oil, condensate and water over distances of thousands of kilometres, both on land and in the sea. Pipelines are laid in deserts, mountain ranges, heavily-populated areas, farmland and the open range, in the Arctic and sub-Arctic, and in seas and oceans up to 2200 m deep.

Carbon dioxide pipelines are not new: they now extend over more than 2500 km in the western USA, where they carry 50 $MtCO_2$ yr^{-1} from natural sources to enhanced oil recovery projects in the west Texas and elsewhere. The carbon dioxide stream ought preferably to be dry and free of hydrogen sulphide, because corrosion is then minimal, and it would be desirable to establish a minimum specification for 'pipeline quality' carbon dioxide. However, it would be possible to design a corrosion-resistant pipeline that would operate safely with a gas that contained water, hydrogen sulphide and other contaminants. Pipeline transport of carbon dioxide through populated areas requires attention be paid to design factors, to overpressure protection, and to leak detection. There is no indication that the problems for carbon dioxide pipelines are any more challenging than those set by hydrocarbon pipelines in similar areas, or that they cannot be resolved.

Liquefied natural gas and petroleum gases such as propane and butane are routinely transported by marine tankers; this trade already takes place on a very large scale. Carbon dioxide is transported in the same way, but on a small scale because of limited demand. The properties of liquefied carbon dioxide are not greatly different from those of liquefied petroleum gases, and the technology can be scaled up to large carbon dioxide carriers. A design study discussed later has estimated costs for marine transport of 1 $MtCO_2$ yr^{-1} by one 22,000 m^3 marine tanker over a distance of 1100 km, along with the associated liquefaction, loading and unloading systems.

Liquefied gas can also be carried by rail and road tankers, but it is unlikely that they be considered attractive options for large-scale carbon dioxide capture and storage projects.

4.1 Introduction

CO_2 is transported in three states: gas, liquid and solid. Commercial-scale transport uses tanks, pipelines and ships for gaseous and liquid carbon dioxide.

Gas transported at close to atmospheric pressure occupies such a large volume that very large facilities are needed. Gas occupies less volume if it is compressed, and compressed gas is transported by pipeline. Volume can be further reduced by liquefaction, solidification or hydration. Liquefaction is an established technology for gas transport by ship as LPG (liquefied petroleum gas) and LNG (liquefied natural gas). This existing technology and experience can be transferred to liquid CO_2 transport. Solidification needs much more energy compared with other options, and is inferior from a cost and energy viewpoint. Each of the commercially viable technologies is currently used to transport carbon dioxide.

Research and development on a natural gas hydrate carrying system intended to replace LNG systems is in progress, and the results might be applied to CO_2 ship transport in the future. In pipeline transportation, the volume is reduced by transporting at a high pressure: this is routinely done in gas pipelines, where operating pressures are between 10 and 80 MPa.

A transportation infrastructure that carries carbon dioxide in large enough quantities to make a significant contribution to climate change mitigation will require a large network of pipelines. As growth continues it may become more difficult to secure rights-of-way for the pipelines, particularly in highly populated zones that produce large amounts of carbon dioxide. Existing experience has been in zones with low population densities, and safety issues will become more complex in populated areas.

The most economical carbon dioxide capture systems appear to favour CO_2 capture, first, from pure stream sources such as hydrogen reformers and chemical plants, and then from centralized power and synfuel plants: Chapter 2 discusses this issue in detail. The producers of natural gas speak of 'stranded' reserves from which transport to market is uneconomical. A movement towards a decentralized power supply grid may make CO_2 capture and transport much more costly, and it is easy to envision stranded CO_2 at sites where capture is uneconomic.

A regulatory framework will need to emerge for the low-greenhouse-gas-emissions power industry of the future to guide investment decisions. Future power plant owners may find the carbon dioxide transport component one of the leading issues in their decision-making.

4.2 Pipeline systems

4.2.1 Pipeline transportation systems

CO_2 pipeline operators have established minimum specifications for composition. Box 4.1 gives an example from the Canyon Reef project (Section 4.2.2.1). This specification is for gas for an enhanced oil recovery (EOR) project, and parts of it would not necessarily apply to a CO_2 storage project. A low nitrogen content is important for EOR, but would not be so significant for CCS. A CO_2 pipeline through populated areas might have a lower specified maximum H_2S content.

Dry carbon dioxide does not corrode the carbon-manganese steels generally used for pipelines, as long as the relative humidity is less than 60% (see, for example, Rogers and Mayhew, 1980); this conclusion continues to apply in the presence of N_2, NO_x and SO_x contaminants. Seiersten (2001) wrote:

"The corrosion rate of carbon steel in dry supercritical CO_2 is low. For AISI 1080 values around 0.01 mm yr^{-1} have been measured at 90–120 bar and 160°C–180°C for 200 days. Short-term tests confirm this. In a test conducted at 3ºC and 22°C at 140 bar CO_2, and 800 to 1000 ppm H_2S, the corrosion rate for X-60 carbon steel was measured at less than 0.5 μm yr^{-1} (0.0005 mm yr^{-1}). Field experience also indicates very few problems with transportation of high-pressure dry CO_2 in carbon steel pipelines. During 12 years, the corrosion rate in an operating pipeline amounts to 0.25-2.5 μm yr^{-1} (0.00025 to (0.0025 mm yr^{-1})".

The water solubility limit in high-pressure CO_2 (500 bar) is 5000 ppm at 75°C and 2000 ppm at 30°C. Methane lowers the solubility limit, and H_2S, O_2 and N_2 may have the same effect.

Corrosion rates are much higher if free water is present; hydrates might also form. Seiersten (2001) measured a corrosion rate of 0.7 mm yr^{-1} corrosion rate in 150 to 300 hours exposure at 40°C in water equilibrated with CO_2 at 95 bar, and higher rates at lower pressures. She found little difference between carbon-manganese steel (American Petroleum Institute grade X65) and 0.5 chromium corrosion-resistant alloy. It is unlikely to be practicable to transport wet CO_2 in low-alloy carbon steel pipelines because of this high corrosion rate. If the CO_2 cannot be dried, it may be necessary to build the pipeline of a corrosion-resistant alloy ('stainless steel'). This is an established technology. However the cost of steel has greatly increased recently and this may not be economical.

Once the CO_2 has been dried and meets the transportation criteria, the CO_2 is measured and transported to the final use site. All the pipelines have state-of-the-art metering systems that accurately account for sales and deliveries on to and out of each line, and SCADA (Supervisory Control and Data Acquisition) systems for measuring pressure drops, and redundancies built in to allow for emergencies. In the USA, these pipelines are governed by Department of Transportation regulations. Movement of CO_2 is best accomplished under high pressure: the choice of operating pressure is discussed in an example below, and the reader is referred to Annex I for a discussion of the physical properties of CO_2.

4.2.2 *Existing experience*

Table 4.1 lists existing long-distance CO_2 pipelines. Most of the projects listed below are described in greater detail in a report by the UK Department of Trade and Industry (2002). While there are CO_2 pipelines outside the USA, the Permian Basin contains over 90% of the active CO_2 floods in the world (O&GJ, April 15, 2002, EOR Survey). Since then, well over 1600 km of new CO_2 pipelines has been built to service enhanced oil recovery (EOR) in west Texas and nearby states.

4.2.2.1 Canyon Reef

The first large CO_2 pipeline in the USA was the Canyon Reef Carriers, built in 1970 by the SACROC Unit in Scurry County, Texas. Its 352 km moved 12,000 tonnes of anthropogenically produced CO_2 daily (4.4 Mt yr^{-1}) from Shell Oil Company gas processing plants in the Texas Val Verde basin.

4.2.2.2 Bravo Dome Pipeline

Oxy Permian constructed this 508 mm (20-inch) line connecting the Bravo Dome CO_2 field with other major pipelines. It is capable of carrying 7.3 $MtCO_2$ yr^{-1} and is operated by Kinder Morgan.

4.2.2.3 Cortez Pipeline

Built in 1982 to supply CO_2 from the McElmo Dome in S.E. Colorado, the 762 mm (30-inch), 803 km pipeline carries approximately 20 Mt CO_2 yr^{-1} to the CO_2 hub at Denver City, Texas. The line starts near Cortez, Colorado, and crosses the Rocky Mountains, where it interconnects with other CO_2 lines. In the present context, recall that one 1000 MW coal-fired

Box 4.1 Specimen CO_2 quality specifications

The Product delivered by Seller or Seller's representative to Buyer at the Canyon Reef Carriers Delivery Meter shall meet the following specifications, which herein are collectively called 'Quality Specifications':

(a) **Carbon Dioxide**. Product shall contain at least ninety-five mole percent (95%) of Carbon Dioxide as measured at the SACROC delivery meter.
(b) **Water.** Product shall contain no free water, and shall not contain more than 0.48 9 m^{-3} in the vapour phase.
(c) **Hydrogen Sulphide.** Product shall not contain more than fifteen hundred (1500) parts per million, by weight, of hydrogen sulphide.
(d) **Total Sulphur.** Product shall not contain more than fourteen hundred and fifty (1450) parts per million, by weight, of total sulphur.
(e) **Temperature.** Product shall not exceed a temperature of 48.9 ºC.
(f) **Nitrogen.** Product shall not contain more than four mole percent (4%) of nitrogen.
(g) **Hydrocarbons.** Product shall not contain more than five mole percent (5%) of hydrocarbons and the dew point of Product (with respect to such hydrocarbons) shall not exceed –28.9 ºC.
(h) **Oxygen.** Product shall not contain more than ten (10) parts per million, by weight, of oxygen.
(i) **Glycol.** Product shall not contain more than 4 x 10^{-5} L m^{-3} of glycol and at no time shall such glycol be present in a liquid state at the pressure and temperature conditions of the pipeline.

Table 4.1 Existing long-distance CO_2 pipelines (Gale and Davison, 2002) and CO_2 pipelines in North America (Courtesy of Oil and Gas Journal).

Pipeline	Location	Operator	Capacity ($MtCO_2\ yr^{-1}$)	Length (km)	Year finished	Origin of CO_2
Cortez	USA	Kinder Morgan	19.3	808	1984	McElmoDome
Sheep Mountain	USA	BP Amoco	9.5	660	-	Sheep Mountain
Bravo	USA	BP Amoco	7.3	350	1984	Bravo Dome
Canyon Reef Carriers	USA	Kinder Morgan	5.2	225	1972	Gasification plants
Val Verde	USA	Petrosource	2.5	130	1998	Val Verde Gas Plants
Bati Raman	Turkey	Turkish Petroleum	1.1	90	1983	Dodan Field
Weyburn	USA & Canada	North Dakota Gasification Co.	5	328	2000	Gasification Plant
Total			49.9	2591		

power station produces about 7 Mt CO_2 yr^{-1}, and so one Cortez pipeline could handle the emissions of three of those stations.

The Cortez Pipeline passes through two built-up areas, Placitas, New Mexico (30 km north of Albuquerque, New Mexico) and Edgewood/Moriarty, New Mexico (40 km east of Albuquerque). The line is buried at least 1 m deep and is marked within its right of way. Near houses and built-up areas it is marked more frequently to ensure the residents are aware of the pipeline locations. The entire pipeline is patrolled by air every two weeks, and in built-up areas is frequently patrolled by employees in company vehicles. The public education programme includes the mailing of a brochure describing CO_2, signs of a leak and where to report a suspected leak, together with information about the operator and the "one-call" centre.

4.2.2.4 Sheep Mountain Pipeline

BP Oil constructed this 610 mm (24-inch) 772 km line capable of carrying 9.2 $MtCO_2$ yr^{-1} from another naturally occurring source in southeast Colorado. It connects to the Bravo Dome line and into the other major carriers at Denver City and now is operated by Kinder Morgan.

Figure 4.1 CO_2 pipelines in North America. (Courtesy of Oil and Gas Journal).

4.2.2.5 Weyburn Pipeline

This 330 km, (305-356 mm diameter) system carries more than 5000 tonne day^{-1} (1.8 Mt yr^{-1}) of CO_2 from the Great Plains Synfuels Plant near Beulah, North Dakota to the Weyburn EOR project in Saskatchewan. The composition of the gas carried by the pipeline is typically CO_2 96%, H_2S 0.9%, CH_4 0.7%, C2+ hydrocarbons 2.3%, CO 0.1%, N_2 less than 300 ppm, O_2 less than 50 ppm and H_2O less than 20 ppm (UK Department of Trade and Industry, 2002). The delivery pressure at Weyburn is 15.2 MPa. There are no intermediate compressor stations. The amount allocated to build the pipeline was 110 US $ million (0.33 x 10^6 US$ km^{-1}) in 1997.

4.2.3 Design

The physical, environmental and social factors that determine the design of a pipeline are summarized in a design basis, which then forms the input for the conceptual design. This includes a system definition for the preliminary route and design aspects for cost-estimating and concept-definition purposes. It is also necessary to consider the process data defining the physical characteristics of product mixture transported, the optimal sizing and pressures for the pipeline, and the mechanical design, such as operating, valves, pumps, compressors, seals, etc. The topography of the pipeline right-of-way must be examined. Topography may include mountains, deserts, river and stream crossings, and for offshore pipelines, the differing challenges of very deep or shallow water, and uneven seabed. It is also important to include geotechnical considerations. For example, is this pipeline to be constructed on thin soil overlaying granite? The local environmental data need to be included, as well as the annual variation in temperature during operation and during construction, potentially unstable slopes, frost heave and seismic activity. Also included are water depth, sea currents, permafrost, ice gouging in Arctic seas, biological growth, aquifers, and other environmental considerations such as protected habitats. The next set of challenges is how the pipeline will accommodate existing and future infrastructure – road, rail, pipeline crossings, military/governmental restrictions and the possible impact of other activities – as well as shipping lanes, rural or urban settings, fishing restrictions, and conflicting uses such as dredging. Finally, this integrated study will serve as the basis for a safety review.

Conceptual design

The conceptual design includes the following components:

- Mechanical design: follows standard procedures, described in detail in (Palmer et al., 2004).
- Stability design: standard methods and software are used to perform stability calculations, offshore (Veritec, 1988) or onshore, though the offshore methods have been questioned. New guidelines for stability will be published in 2005 by Det Norske Veritas and will be designated DNV-RP-F109 On-Bottom Stability
- Protection against corrosion: a well-understood subject of which the application to CO_2 pipelines is described below.
- Trenching and backfilling: onshore lines are usually buried to depth of 1 m. Offshore lines are almost always buried in shallow water. In deeper water pipelines narrower than 400 mm are trenched and sometimes buried to protect them against damage by fishing gear.
- CO_2 pipelines may be more subject to longitudinal running fracture than hydrocarbon gas pipelines. Fracture arresters are installed at intervals of about 500 m.

West (1974) describes the design of the SACROC CO_2 pipeline (Section 4.2.2.1 above). The transportation options examined were:

(i) a low-pressure CO_2 gas pipeline operating at a maximum pressure of 4.8 MPa;
(ii) a high-pressure CO_2 gas pipeline operating at a minimum pressure of 9.6 MPa, so that the gas would remain in a dense phase state at all temperatures;
(iii) a refrigerated liquid CO_2 pipeline;
(iv) road tank trucks;
(v) rail tankers, possibly in combination with road tank trucks.

The tank truck and rail options cost more than twice as much as a pipeline. The refrigerated pipeline was rejected because of cost and technical difficulties with liquefaction. The dense phase (Option ii) was 20% cheaper than a low-pressure CO_2 gas pipeline (Option i). The intermediate 4.8 to 9.6 MPa pressure range was avoided so that two-phase flow would not occur. An added advantage of dense-phase transport was that high delivery pressures were required for CO_2 injection.

The final design conforms to the ANSI B31.8 code for gas pipelines and to the DOT regulations applicable at the time. The main 290 km section is 406.4 mm (16 inch) outside diameter and 9.53 mm wall thickness made from grade X65 pipe (specified minimum yield stress of 448 MPa). A shorter 60 km section is 323.85 mm (12.75 inch) outside diameter, 8.74 mm wall thickness, grade X65. Tests showed that dry CO_2 would not corrode the pipeline steel; 304L corrosion-resistant alloy was used for short sections upstream of the glycol dehydrator. The line is buried to a minimum of 0.9 m, and any point on the line is within 16 km of a block valve.

There are six compressor stations, totalling 60 MW, including a station at the SACROC delivery point. The compressor stations are not equally spaced, and the longest distance between two stations is about 160 km. This is consistent with general practice, but some long pipelines have 400 km or more between compressor stations.

Significant nitrogen and oxygen components in CO_2 would shift the boundary of the two-phase region towards higher pressures, and would require a higher operating pressure to avoid two-phase flow.

4.2.4 Construction of land pipelines

Construction planning can begin either before or after rights of way are secured, but a decision to construct will not come before a legal right to construct a pipeline is secured and all governmental regulations met. Onshore and underwater CO_2 pipelines are constructed in the same way as hydrocarbon pipelines, and for both there is an established and well-understood base of engineering experience. Subsection 4.2.5 describes underwater construction.

The construction phases of a land pipeline are outlined below. Some of the operations can take place concurrently.

Environmental and social factors may influence the season of the year in which construction takes place. The land is cleared and the trench excavated. The longest lead items come first: urban areas, river and road crossings. Pipe is received into the pipe yard and welded into double joints (24 m long); transported to staging areas for placement along the pipe route, welded, tested, coated and wrapped, and then lowered into the trench. A hydrostatic test is carried out, and the line is dried. The trench is then backfilled, and the land and the vegetation restored.

4.2.5 Underwater pipelines

Most underwater pipelines are constructed by the lay-barge method, in which 12 or 24 m lengths of pipe are brought to a dynamically positioned or anchored barge, and welded one by one to the end of the pipeline. The barge moves slowly forward, and the pipeline leaves the barge over the stern, and passes first over a support structure ('stinger') and then down through the water in a suspended span, until it reaches the seabed. Some lines up to 450 mm diameter are constructed by the reel method, in which the pipeline is welded together onshore, wound onto a reel on a ship, and then unwound from the reel into its final position. Some short lines and lines for shore crossings in shallow water are constructed by various tow and pull methods, in which the line is welded together onshore and then pulled into its final location.

If the design requires that the pipeline be trenched, that is usually done after it has been laid on the seabed, by a jetting sled, a plough or a mechanical cutting device that is pulled along the line. On the other hand, in shore crossings and in very shallow water the trench is often excavated before the pipeline is laid, and that is done by dredgers, backhoes or draglines in soft sediments, or in rock by blasting followed by clamshell excavators. Many shore crossings are drilled horizontally from the shore; this procedure eliminates many uncertainties associated with the surf zone, and reduces the environmental impact of construction.

Underwater connections are made by various kinds of mechanical connection systems, by hyperbaric welding (in air under the local hydrostatic pressure) or by lifting the pipe ends above the surface, welding them together and lowering the connected line to the bottom.

These technologies are established and understood (Palmer and King, 2004). Underwater pipelines up to 1422 mm in diameter have been constructed in many different environments, and pipelines have been laid in depths up to 2200 m. Figure 4.2 plots the diameters and maximum depths of major deepwater pipelines constructed up to 2004. The difficulty of construction is roughly proportional to the depth multiplied by the diameter, and the maximum value of that product has multiplied fourfold since 1980. Still larger and deeper pipelines are technically feasible with today's technology.

4.2.6 Operations

Operational aspects of pipelines are divided into three areas: daily operations, maintenance, and health, safety and environment. Operations of a CO_2 pipeline in the USA, for instance, must follow federal operations guidelines (49 CFR 195). Overall operational considerations include training, inspections, safety integration, signs and pipeline markers, public education, damage prevention programmes, communication, facility security and leak detection. Pipelines outside the USA generally have similar regulatory operational requirements.

Personnel form a central part of operations and must be qualified. Personnel are required to be continuously trained and updated on safety procedures, including safety procedures that apply to contractors working on or near the pipeline, as well as to the public.

Operations include daily maintenance, scheduled planning and policies for inspecting, maintaining and repairing all equipment on the line and the pipeline itself, as well as supporting the line and pipeline. This equipment and support includes valves, compressors, pumps, tanks, rights of way, public signs and line markers as well as periodic pipeline flyovers.

Long-distance pipelines are instrumented at intervals so that the flow can be monitored. The monitoring points, compressor stations and block valves are tied back to a central operations centre. Computers control much of the operation, and manual intervention is necessary only in unusual upsets or emergency conditions. The system has inbuilt redundancies to prevent loss of operational capability if a component fails.

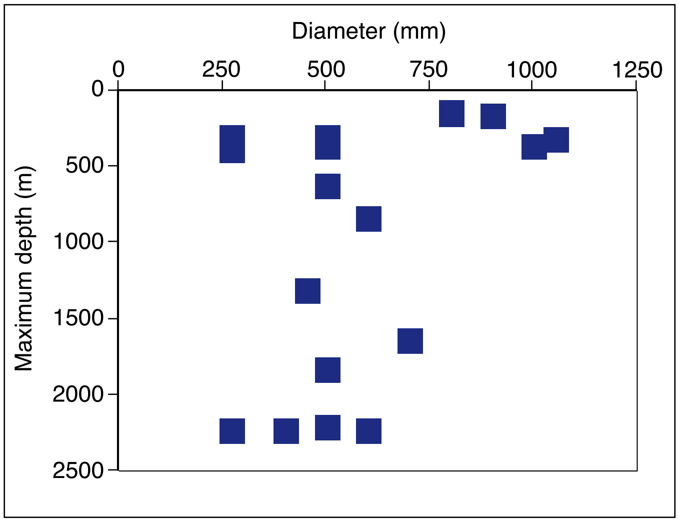

Figure 4.2 Pipelines in deep water.

Pipelines are cleaned and inspected by 'pigs', piston-like devices driven along the line by the gas pressure. Pigs have reached a high level of sophistication, and can measure internal corrosion, mechanical deformation, external corrosion, the precise position of the line, and the development of spans in underwater lines. Further functionality will develop as pig technology evolves, and there is no reason why pigs used for hydrocarbon pipelines should not be used for carbon dioxide.

Pipelines are also monitored externally. Land pipelines are inspected from the air, at intervals agreed between the operator and the regulatory authorities. Inspection from the air detects unauthorized excavation or construction before damage occurs. Currently, underwater pipelines are monitored by remotely operated vehicles, small unmanned submersibles that move along the line and make video records, and in the future, by autonomous underwater vehicles that do not need to be connected to a mother ship by a cable. Some pipelines have independent leak detection systems that find leaks acoustically or by measuring chemical releases, or by picking up pressure changes or small changes in mass balance. This technology is available and routine.

4.3 Ships for CO_2 transportation

4.3.1 Marine transportation system

Carbon dioxide is continuously captured at the plant on land, but the cycle of ship transport is discrete, and so a marine transportation system includes temporary storage on land and a loading facility. The capacity, service speed, number of ships and shipping schedule will be planned, taking into consideration, the capture rate of CO_2, transport distance, and social and technical restrictions. This issue is, of course, not specific to the case of CO_2 transport; CO_2 transportation by ship has a number of similarities to liquefied petroleum gas (LPG) transportation by ship.

What happens at the delivery point depends on the CO_2 storage system. If the delivery point is onshore, the CO_2 is unloaded from the ships into temporary storage tanks. If the delivery point is offshore – as in the ocean storage option – ships might unload to a platform, to a floating storage facility (similar to a floating production and storage facility routinely applied to offshore petroleum production), to a single-buoy mooring or directly to a storage system.

4.3.2 Existing experience

The use of ships for transporting CO_2 across the sea is today in an embryonic stage. Worldwide there are only four small ships used for this purpose. These ships transport liquefied food-grade CO_2 from large point sources of concentrated carbon dioxide such as ammonia plants in northern Europe to coastal distribution terminals in the consuming regions. From these distribution terminals CO_2 is transported to the customers either by tanker trucks or in pressurized cylinders. Design work is ongoing in Norway and Japan for larger CO_2 ships and their associated liquefaction and intermediate storage facilities.

4.3.3 Design

For the design of hull and tank structure of liquid gas transport ships, such as LPG carriers and LNG carriers, the International Maritime Organization adopted the International Gas Carrier Code in order to prevent the significant secondary damage from accidental damage to ships. CO_2 tankers are designed and constructed under this code.

There are three types of tank structure for liquid gas transport ships: pressure type, low temperature type and semi-refrigerated type. The pressure type is designed to prevent the cargo gas from boiling under ambient air conditions. On the other hand, the low temperature type is designed to operate at a sufficiently low temperature to keep cargo gas as a liquid under the atmospheric pressure. Most small gas carriers are pressure type, and large LPG and LNG carriers are of the low temperature type. The low temperature type is suitable for mass transport because the tank size restriction is not severe. The semi-refrigerated type, including the existing CO_2 carriers, is designed taking into consideration the combined conditions of temperature and pressure necessary for cargo gas to be kept as a liquid. Some tankers such as semi-refrigerated LPG carriers are designed for applicability to the range of cargo conditions between normal temperature/high pressure and low temperature/atmospheric pressure.

Annex I to this report includes the CO_2 phase diagram. At atmospheric pressure, CO_2 is in gas or solid phase, depending on the temperature. Lowering the temperature at atmospheric pressure cannot by itself cause CO_2 to liquefy, but only to make so-called 'dry ice' or solid CO_2. Liquid CO_2 can only exist at a combination of low temperature and pressures well above atmospheric pressure. Hence, a CO_2 cargo tank should be of the pressure-type or semi-refrigerated. The semi-refrigerated type is preferred by ship designers, and the design point of the cargo tank would be around –54 ºC per 6 bar to –50ºC per 7 bar, which is near the point of CO_2. In a standard design, semi-refrigerated type LPG carriers operate at a design point of –50°C and 7 bar, when transporting a volume of 22,000 m^3.

Carbon dioxide could leak into the atmosphere during transportation. The total loss to the atmosphere from ships is between 3 and 4% per 1000 km, counting both boil-off and exhaust from the ship's engines; both components could be reduced by capture and liquefaction, and recapture onshore would reduce the loss to 1 to 2% per 1000 km.

4.3.4 Construction

Carbon dioxide tankers are constructed using the same technology as existing liquefied gas carriers. The latest LNG carriers reach more than 200,000 m^3 capacity. (Such a vessel could carry 230 kt of liquid CO_2.) The same type of yards that today build LPG and LNG ships can carry out the construction of a CO_2 tanker. The actual building time will be from one to two years, depending on considerations such as the ship's size.

4.3.5 Operation

4.3.5.1 Loading

Liquid CO_2 is charged from the temporary storage tank to the cargo tank with pumps adapted for high pressure and low temperature CO_2 service. The cargo tanks are first filled and pressurized with gaseous CO_2 to prevent contamination by humid air and the formation of dry ice.

4.3.5.2 Transport to the site

Heat transfer from the environment through the wall of the cargo tank will boil CO_2 and raise the pressure in the tank. It is not dangerous to discharge the CO_2 boil-off gas together with the exhaust gas from the ship's engines, but doing so does, of course, release CO_2 to the air. The objective of zero CO_2 emissions during the process of capture and storage can be achieved by using a refrigeration unit to capture and liquefy boil-off and exhaust CO_2.

4.3.5.3 Unloading

Liquid CO_2 is unloaded at the destination site. The volume occupied by liquid CO_2 in the cargo tanks is replaced with dry gaseous CO_2, so that humid air does not contaminate the tanks. This CO_2 could be recycled and reliquefied when the tank is refilled.

4.3.5.4 Return to port in ballast, and dry-docking

The CO_2 tanker will return to the port for the next voyage. When the CO_2 tanker is in dock for repair or regular inspection, gas CO_2 in cargo tank should be purged with air for safe working. For the first loading after docking, cargo tanks should be fully dried, purged and filled with CO_2 gas.

Ships of similar construction with a combination of cooling and pressure are currently operated for carrying other industrial gases.

4.4 Risk, safety and monitoring

4.4.1 Introduction

There are calculable and perceivable risks for any transportation option. We are not considering perceivable risks because this is beyond the scope of the document. Risks in special cases such as military conflicts and terrorist actions have now been investigated. At least two conferences on pipeline safety and security have taken place, and additional conferences and workshops are planned. However, it is unlikely that these will lead to peer-reviewed journal articles because of the sensitivity of the issue.

Pipelines and marine transportation systems have an established and good safety record. Comparison of CO_2 systems with these existing systems for long-distance pipeline transportation of gas and oil or with marine transportation of oil, yidds that risks should be comparable in terms of failure and accident rates.For the existing transport system these incidents seem to be perceived by the broad community as acceptable in spite of occasional serious pollution incidents such as the *Exxon Valdes* and *Torrey Canyon* disasters (van Bernem and Lubbe, 1997). Because the *consequences* of CO_2 pipeline accidents potentially are of significant concern, stricter regulations for CO_2 pipelines than those for natural gas pipelines currently are in force in the USA.

4.4.2 Land pipelines

Land pipelines are built to defined standards and are subject to regulatory approval. This sometimes includes independent design reviews. Their routes are frequently the subject of public inquiries. The process of securing regulatory approval generally includes approval of a safety plan, of detailed monitoring and inspection procedures and of emergency response plans. In densely populated areas the process of planning, licensing and building new pipelines may be difficult and time-consuming. In some places it may be possible to convert existing hydrocarbon pipelines into CO_2 pipelines.

Pipelines in operation are monitored internally by pigs (internal pipeline inspection devices) and externally by corrosion monitoring and leak detection systems. Monitoring is also done by patrols on foot and by aircraft.

The incidence of failure is relatively small. Guijt (2004) and the European Gas Pipeline Incident Data Group (2002) show that the incidence of failure has markedly decreased. Guijt quotes an incident rate of almost 0.0010 km^{-1} $year^{-1}$ in 1972 falling to below 0.0002 km^{-1} $year^{-1}$ in 2002. Most of the incidents refer to very small pipelines, less than 100 mm in diameter, principally applied to gas distribution systems. The failure incidence for 500 mm and larger pipelines is very much lower, below 0.00005 km^{-1} $year^{-1}$. These figures include all unintentional releases outside the limits of facilities (such as compressor stations) originating from pipelines whose design pressures are greater than 1.5 MPa. They cover many kinds of incidents, not all of them serious, and there is substantial variation between pipelines, reflecting factors such as system age and inspection frequency.

The corresponding incident figures for western European oil pipelines have been published by CONCAWE (2002). In 1997-2001 the incident frequency was 0.0003 km^{-1} yr^{-1}. The corresponding figure for US onshore gas pipelines was 0.00011 km^{-1} yr^{-1} for the 1986-2002 period, defining an incident as an event that released gas and caused death, inpatient hospitalization or property loss of US$ 50,000: this difference in reporting threshold is thought to account for the difference between European and US statistics (Guijt, 2004).

Lelieveld et al. (2005) examined leakage in 2400 km of the Russian natural gas pipeline system, including compressor stations, valves and machine halls, and concluded that '...overall, the leakage from Russian natural gas transport systems is about 1.4% (with a range of 1.0-2.5%), which is comparable with the amount lost from pipelines in the United States (1.5±0.5%)'. Those numbers refer to total leakage, not to leakage per kilometre.

Gale and Davison (2002) quote incident statistics for CO_2

pipelines in the USA. In the 1990-2002 period there were 10 incidents, with property damage totalling US$ 469,000, and no injuries nor fatalities. The incident rate was 0.00032 km^{-1} yr^{-1}. However, unlike oil and gas, CO_2 does not form flammable or explosive mixtures with air. Existing CO_2 pipelines are mainly in areas of low population density, which would also tend to result in lower average impacts. The reasons for the incidents at CO_2 pipelines were relief valve failure (4 failures), weld/gasket/valve packing failure (3), corrosion (2) and outside force (1). In contrast, the principal cause of incidents for natural gas pipelines is outside force, such as damage by excavator buckets. Penetration by excavators can lead to loss of pipeline fluid and sometimes to fractures that propagate great distances. Preventative measures such as increasing the depth of cover and use of concrete barriers above a pipeline and warning tape can greatly reduce the risk. For example, increasing cover from 1 m to 2 m reduces the damage frequency by a factor of 10 in rural areas and by 3.5 in suburban areas (Guijt, 2004).

Carbon dioxide leaking from a pipeline forms a potential physiological hazard for humans and animals. The consequences of CO_2 incidents can be modelled and assessed on a site-specific basis using standard industrial methods, taking into account local topography, meteorological conditions, population density and other local conditions. A study by Vendrig et al. (2003) has modelled the risks of CO_2 pipelines and booster stations. A property of CO_2 that needs to be considered when selecting a pipeline route is the fact that CO_2 is denser than air and can therefore accumulate to potentially dangerous concentrations in low lying areas. Any leak transfers CO_2 to the atmosphere.

If substantial quantities of impurities, particularly H_2S, are included in the CO_2, this could affect the potential impacts of a pipeline leak or rupture. The exposure threshold at which H_2S is immediately dangerous to life or health, according to the National Institute for Occupational Safety and Health, is 100 ppm, compared to 40,000 ppm for CO_2.

If CO_2 is transported for significant distances in densely populated regions, the number of people potentially exposed to risks from CO_2 transportation facilities may be greater than the number exposed to potential risks from CO_2 capture and storage facilities. Public concerns about CO_2 transportation may form a significant barrier to large-scale use of CCS. At present most electricity generation or other fuel conversion plants are built close to energy consumers or sources of fuel supply. New plants with CO_2 capture could be built close to CO_2 storage sites, to minimize CO_2 transportation. However, this may necessitate greater transportation of fuels or electricity, which have their own environmental impacts, potential risks and public concerns. A gathering system would be needed if CO_2 were brought from distributed sources to a trunk pipeline, and for some storage options a distribution system would also be needed: these systems would need to be planned and executed with the same regard for risk outlined here.

4.4.3 Marine pipelines

Marine pipelines are subject to a similar regulatory regime. The incidence of failure in service is again low. Dragging ships' anchors causes some failures, but that only occurs in shallow water (less than 50 m). Very rarely do ships sink on to pipelines, or do objects fall on to them. Pipelines of 400 mm diameter and larger have been found to be safe from damage caused by fishing gear, but smaller pipelines are trenched to protect them. Damage to underwater pipelines was examined in detail at a conference reported on in Morris and Breaux (1995). Palmer and King (2004) examine case studies of marine pipeline failures, and the technologies of trenching and monitoring. Most failures result from human error. Ecological impacts from a CO_2 pipeline accident have yet to be assessed.

Marine pipelines are monitored internally by inspection devices called 'pigs' (as described earlier in Section 4.2.5), and externally by regular visual inspection from remotely operated vehicles. Some have independent leak detection systems.

4.4.4 Ships

Ship systems can fail in various ways: through collision, foundering, stranding and fire. Perrow's book on accidents (1984) includes many thought-provoking case studies. Many of the ships that he refers to were old, badly maintained and crewed by inadequately trained people. However, it is incorrect to think that marine accidents happen only to poorly regulated 'flag-of-convenience' ships. Gottschalch and Stadler (1990) share Perrow's opinion that many marine accidents can be attributed to system failures and human factors, whereas accidents arising as a consequence of purely technical factors are relatively uncommon.

Ship casualties are well summarized by Lloyds Maritime Information Service. Over 22.5 years between 1978 and 2000, there were 41,086 incidents of varying degrees of severity identified, of which 2,129 were classified as 'serious' (See Table 4.2).

Tankers can be seen to have higher standards than ships in general. Stranding is the source of most of the tanker incidents that have led to public concern. It can be controlled by careful navigation along prescribed routes, and by rigorous standards of operation. LNG tankers are potentially dangerous, but are carefully designed and appear to be operated to very high standards. There have been no accidental losses of cargo from LNG ships. The LNG tanker *El Paso Paul Kaiser* ran aground at 17 knots in 1979, and incurred substantial hull damage, but the LNG tanks were not penetrated and no cargo was lost. There is extensive literature on marine transport of liquefied gas, with a strong emphasis on safety, for example, in Ffooks (1993).

Carbon dioxide tankers and terminals are clearly much less at risk from fire, but there is an asphyxiation risk if collision should rupture a tank. This risk can be minimized by making certain that the high standards of construction and operation currently applied to LPG are also applied to carbon dioxide.

An accident to a liquid CO_2 tanker might release liquefied gas onto the surface of the sea. However, consideration of such an event is a knowledge gap that requires further study. CO_2 releases are anticipated not to have the long-term environmental

Table 4.2 Statistics of serious incidents, depending on the ship type.

Ship type	Number of ships 2000	Serious incidents 1978-2000	Frequency (incidents/ship year)
LPG tankers	982	20	0.00091
LNG tankers	121	1	0.00037
Oil tankers	9678	314	0.00144
Cargo/bulk carriers	21407	1203	0.00250

impacts of crude oil spills. CO_2 would behave differently from LNG, because liquid CO_2 in a tanker is not as cold as LNG but much denser. Its interactions with the sea would be complex: hydrates and ice might form, and temperature differences would induce strong currents. Some of the gas would dissolve in the sea, but some would be released to the atmosphere. If there were little wind and a temperature inversion, clouds of CO_2 gas might lead to asphyxiation and might stop the ship's engines.

The risk can be minimized by careful planning of routes, and by high standards of training and management.

4.5 Legal issues, codes and standards

Transportation of CO_2 by ships and sub-sea pipelines, and across national boundaries, is governed by various international legal conventions. Many jurisdictions/states have environmental impact assessment and strategic environmental assessment legislation that will come into consideration in pipeline building. If a pipeline is constructed across another country's territory (e.g. landlocked states), or if the pipeline is laid in certain zones of the sea, other countries may have the right to participate in the environmental assessment decision-making process or challenge another state's project.

4.5.1 International conventions

Various international conventions could have implications for storage of CO_2, the most significant being the UN Law of the Sea Convention, the London Convention, the Convention on Environmental Impact Assessment in a Transboundary Context (Espoo Convention) and OSPAR (see Chapter 5). The Espoo convention covers environmental assessment, a procedure that seeks to ensure the acquisition of adequate and early information on likely environmental consequences of development projects or activities, and on measures to mitigate harm. Pipelines are subject to environmental assessment. The most significant aspect of the Convention is that it lays down the general obligation of states to notify and consult each other if a project under consideration is likely to have a significant environmental impact across boundaries. In some cases the acceptability of CO_2 storage under these conventions could depend on the method of transportation to the storage site. Conventions that are primarily concerned with discharge and placement rather than transport are discussed in detail in the chapters on ocean and geological storage.

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal came into force in 1992 (UNEP, 2000). The Basel Convention was conceived partly on the basis that enhanced control of transboundary movement of wastes will act as an incentive for their environmentally sound management and for the reduction of the volume of movement. However, there is no indication that CO_2 will be defined as a hazardous waste under the convention except in relation to the presence of impurities such as heavy metals and some organic compounds that may be entrained during the capture of CO_2. Adoption of schemes where emissions of SO_2 and NO_x would be included with the CO_2 may require such a review. Accordingly, the Basel Convention does not appear to directly impose any restriction on the transportation of CO_2 (IEA GHG, 2003a).

In addition to the provisions of the Basel Convention, any transport of CO_2 would have to comply with international transport regulations. There are numerous specific agreements, some of which are conventions and others protocols of other conventions that apply depending on the mode of transport. There are also a variety of regional agreements dealing with transport of goods. International transport codes and agreements adhere to the UN Recommendations on the Transport of Dangerous Goods: Model Regulations published by the United Nations (2001). CO_2 in gaseous and refrigerated liquid forms is classified as a non-flammable, non-toxic gas; while solid CO_2 (dry ice) is classified under the heading of miscellaneous dangerous substances and articles. Any transportation of CO_2 adhering to the Recommendations on the Transport of Dangerous Goods: Model Regulations can be expected to meet all relevant agreements and conventions covering transportation by whatever means. Nothing in these recommendations would imply that transportation of CO_2 would be prevented by international transport agreements and conventions (IEA GHG, 2003a).

4.5.2 National codes and standards

The transport of CO_2 by pipeline has been practiced for over 25 years. Internationally adopted standards such as ASME B31.4, Liquid transportation systems for hydrocarbons, liquid petroleum gas, anhydrous ammonia and alcohols' and the widely-applied Norwegian standard (DNV, 2000) specifically mention CO_2. There is considerable experience in the application and use of these standards. Existing standards and codes vary between different countries but gradual unification of these documents is being advanced by such international bodies as ISO and CEN as part of their function. A full review of relevant standards categorized by issues is presented in IEA GHG, 2003b.

Public concern could highlight the issue of leakage of CO_2 from transportation systems, either by rupture or minor leaks, as discussed in Section 4.4. It is possible that standards may be changed in future to address specific public concerns. Odorants are often added to domestic low-pressure gas distribution systems, but not to gas in long-distance pipelines; they could, in principle, be added to CO_2 in pipelines. Mercaptans, naturally present in the Weyburn pipeline system, are the most effective odorants but are not generally suitable for this application because they are degraded by O_2, even at very low concentrations (Katz, 1959). Disulphides, thioethers and ring compounds containing sulphur are alternatives. The value and impact of odorization could be established by a quantitative risk assessment.

4.6 Costs

4.6.1 Costs of pipeline transport

The costs of pipelines can be categorized into three items

- Construction costs
  - Material/equipment costs (pipe, pipe coating, cathodic protection, telecommunication equipment; possible booster stations)
  - Installation costs (labour)
- Operation and maintenance costs
  - Monitoring costs
  - Maintenance costs
  - (Possible) energy costs
- Other costs (design, project management, regulatory filing fees, insurances costs, right-of-way costs, contingencies allowances)

The pipeline material costs depend on the length of the pipeline, the diameter, the amount of CO_2 to be transported and the quality of the carbon dioxide. Corrosion issues are examined in Section 4.2.2 For costs it is assumed that CO_2 is delivered from the capture system at 10 MPa.

Figure 4.3 shows capital investment costs for pipelines. Investments are higher when compressor station(s) are required to compensate for pressure loss along the pipeline, or for longer pipelines or for hilly terrain. Compressor stations may be avoided by increasing the pipeline diameter and reducing the flow velocity. Reported transport velocity varies from 1 to 5 m s^{-1}. The actual design will be optimized with regard to pipeline diameter, pressure loss (required compressor stations and power) and pipeline wall thickness.

Costs depend on the terrain. Onshore pipeline costs may increase by 50 to 100% or more when the pipeline route is congested and heavily populated. Costs also increase in mountains, in nature reserve areas, in areas with obstacles such as rivers and freeways, and in heavily urbanized areas because of accessibility to construction and additional required safety measures. Offshore pipelines generally operate at higher pressures and lower temperatures than onshore pipelines, and are often, but not always, 40 to 70% more expensive.

It is cheaper to collect CO_2 from several sources into a single pipeline than to transport smaller amounts separately. Early and smaller projects will face relatively high transport costs, and therefore be sensitive to transport distance, whereas an evolution towards higher capacities (large and wide-spread application) may result in a decrease in transport costs. Implementation of a 'backbone' transport structure may facilitate access to large remote storage reservoirs, but infrastructure of this kind will require large initial upfront investment decisions. Further study is required to determine the possible advantages of such pipeline system.

Figure 4.4 presents onshore and offshore transport costs versus pipeline diameter; where costs are based on investment cost information from various sources. Figure 4.5 gives a cost window for specific transport as function of the flow. Steel is a cost component for both pipelines and ships, and steel prices doubled in the two years up to 2005: this may be temporary.

4.6.2 Costs of marine transportation systems

Costs of a marine transport system comprise many cost elements. Besides investments for ships, investments are required for loading and unloading facilities, intermediate storage and liquefaction units. Further costs are for operation (e.g. labour, ship fuel costs, electricity costs, harbour fees), and maintenance. An optimal use of installations and ships in the transport cycle is crucial. Extra facilities (e.g. an expanded storage requirement) have to be created to be able to anticipate on possible disruptions in the transport system.

The cost of marine transport systems is not known in detail at present, since no system has been implemented on a scale required for CCS projects (i.e. in the range of several million tonnes of carbon dioxide handling per year). Designs have been submitted for tender, so a reasonable amount of knowledge is available. Nevertheless, cost estimates vary widely, because CO_2 shipping chains of this size have never been built and economies of scale may be anticipated to have a major impact on the costs.

A ship designed for carrying CO_2 from harbour to harbour may cost about 30-50% more than a similar size semi-refrigerated LPG ship (Statoil, 2004). However, since the density of liquid CO_2 is about 1100 kg m^{-3}, CO_2 ships will carry more mass than an equivalent LNG or LPG ship, where the cargo density is about 500 kg m^{-3}. The estimated cost of ships of 20 to 30 kt capacity is between 50 and 70 M$ (Statoil, 2004). Another source (IEA GHG, 2004) estimates ship construction costs at US$ 34 million for 10 kt-sized ship, US$ 60 million with a capacity of 30 kt, or US$ 85 million with a capacity of 50 kt. A time charter rate of about 25,000 US$ day^{-1} covering capital charges, manning and maintenance is not unreasonable for a ship in the 20 kt carrying capacity range.

The cost for a liquefaction facility is estimated by Statoil (2004) at US$ 35 to US$ 50 million for a capacity of 1 Mt per year. The present largest liquefaction unit is 0.35 Mt yr^{-1}.

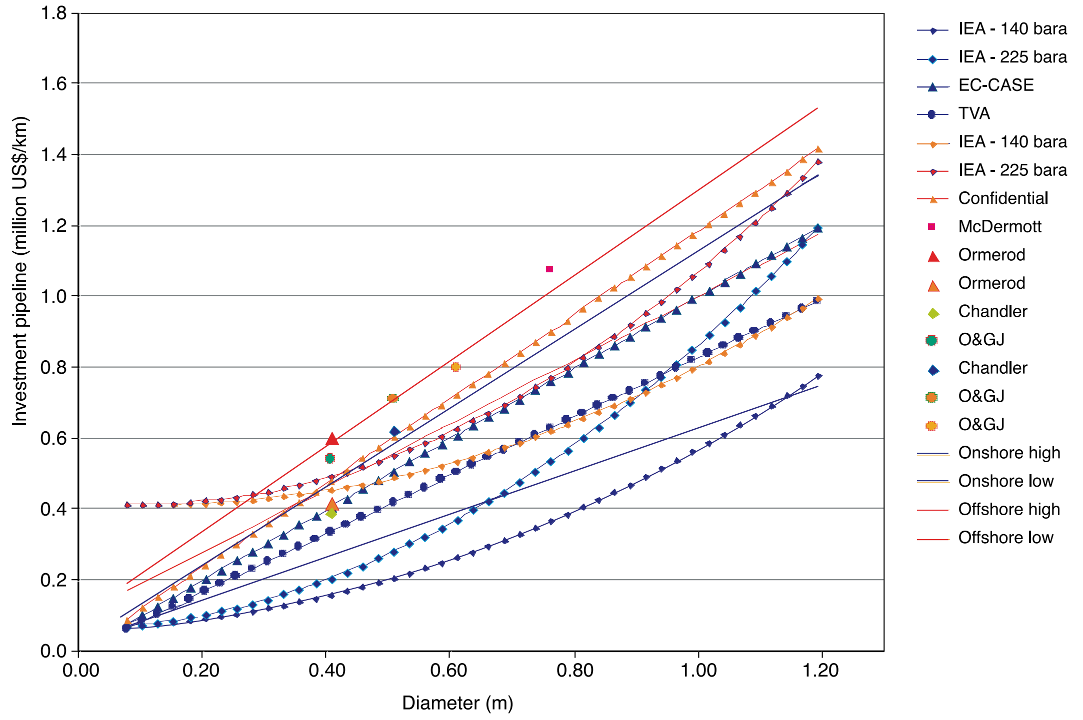

Figure 4.3 Total investment costs for pipelines from various information sources for offshore and onshore pipelines. Costs exclude possible booster stations (IEA GHG, 2002; Hendriks et al., 2005; Bock, 2003; Sarv, 2000; 2001a; 2001b; Ormerod, 1994; Chandler, 2000; O&GJ, 2000).

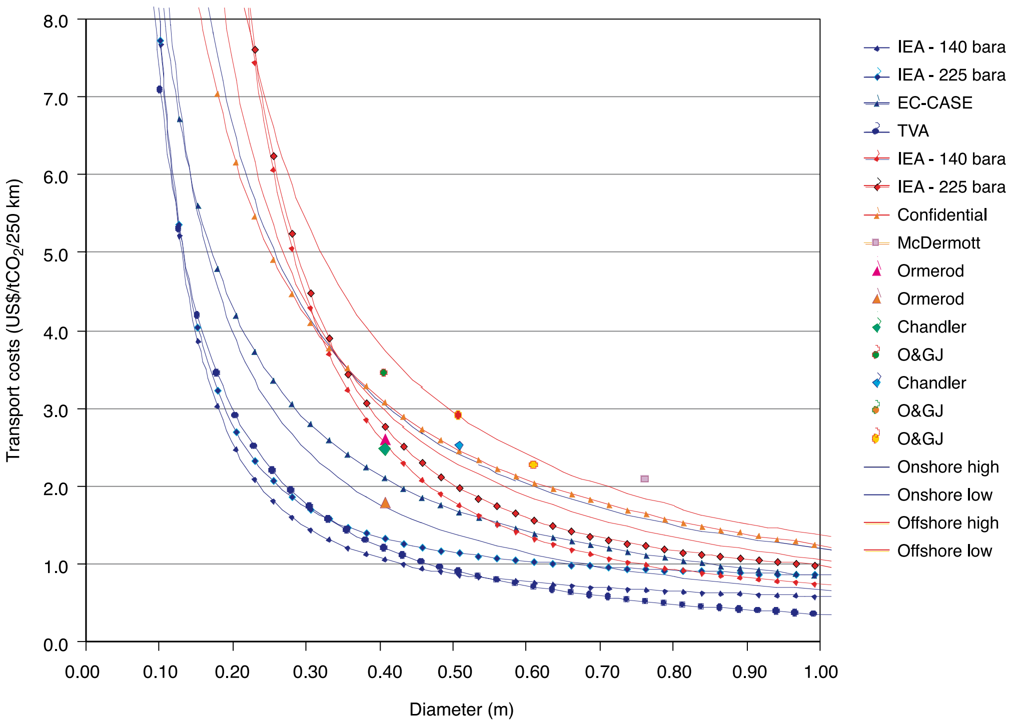

Figure 4.4 Transport costs derived from various information sources for offshore and onshore pipelines. Costs exclude possible booster stations, applying a capital charge rate of 15% and a load factor of 100% (IEA GHG, 2002; Hendriks et al., 2005; Bock, 2003; Sarv, 2000; 2001a; 2001b; Ormerod, 1994; Chandler, 2000; O&GJ, 2000)

IEA GHG (2004) estimates a considerable lower investment for a liquefaction facility, namely US$ 80 million for 6.2 Mt yr^{-1}. Investment costs are reduced to US$ 30 million when carbon dioxide at 100 bar is delivered to the plant. This pressure level is assumed to be delivered from the capture unit. Cost estimates are influenced by local conditions; for example, the absence of sufficient cooling water may call for a more expensive ammonia driven cooling cycle. The difference in numbers also reflects the uncertainty accompanied by scaling up of such facilities

A detailed study (Statoil, 2004) considered a marine transportation system for 5.5 Mt yr^{-1}. The base case had 20 kt tankers with a speed of 35 km h^{-1}, sailing 7600 km on each trip; 17 tankers were required. The annual cost was estimated at US$ 188 million, excluding linquefaction and US$ 300 million, including liquefaction, decreasing to US$ 232 million if compression is allowed (to avoid double counting). The corresponding specific transport costs are 34, 55, and 42 US$ t^{-1}. The study also considered sensitivity to distance: for the case excluding liquefaction, the specific costs were 20 US$ t^{-1} for 500 km, 22 US$ t^{-1} for 1500 km, and 28 US$ t^{-1} for 4500 km.

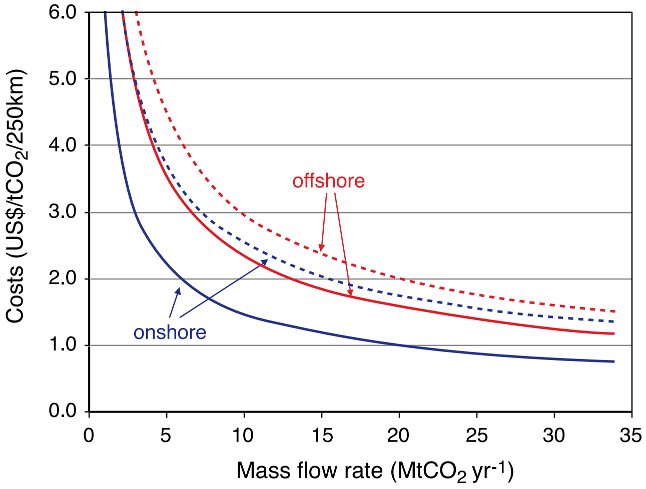

Figure 4.5 Transport costs for onshore and offshore pipelines per 250 km. High (broken lines) and low range (continuous lines) are indicated.

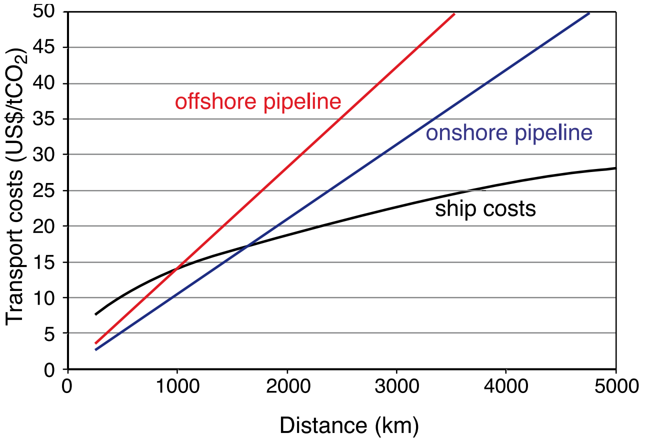

Figure 4.6 Costs, plotted as transportation cost in US$/$tCO_2$ against distance, for onshore and offshore pipelines, and ship transport. The costs include intermediate storage facilities, harbour fees, fuel costs and loading/unloading activities. Costs also include additional costs for liquefaction compared to compression. There is a capital charge factor of 11% for all transport options.

A study on a comparable ship transportation system carried out for the IEA shows lower costs. For a distance of 7600 km using 30 kt ships, the costs are estimated at 35 US$ t^{-1}. These costs are reduced to 30 US$ $tonne^{-1}$ for 50 kt ships. The IEA study also showed a stronger cost dependency on distance than the Statoil (2004) study.

It should be noted that marine transport induces more associated CO_2 transport emissions than pipelines due to additional energy use for liquefaction and fuel use in ships. IEA GHG (2004) estimated 2.5% extra CO_2 emissions for a transport distance of 200 km and about 18% for 12,000 km. The extra CO_2 emissions for each 1000 km pipelines come to about 1 to 2%.

Ship transport becomes cost-competitive with pipeline transport over larger distances. Figure 4.6 shows an estimate of the costs for transporting 6 Mt yr^{-1} by offshore pipeline and by ship. The break-even distance, i.e. the distance for which the costs per transport mode are the same, is about 1000 km for this example. Transport of larger quantities will shift the break-even distance towards larger distances. However, the cross-over point beyond which ship transportation becomes cheaper than pipeline transportation is not simply a matter of distance alone. It involves many other factors, including loading terminals, pipeline shore crossings, water depth, seabed stability, fuel cost, construction costs, different operating costs in different locations, security, and interaction between land and marine transportation routes.

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5

Underground geological storage

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Contents

EXECUTIVE SUMMARY

Underground accumulation of carbon dioxide (CO_2) is a widespread geological phenomenon, with natural trapping of CO_2 in underground reservoirs. Information and experience gained from the injection and/or storage of CO_2 from a large number of existing enhanced oil recovery (EOR) and acid gas projects, as well as from the Sleipner, Weyburn and In Salah projects, indicate that it is feasible to store CO_2 in geological formations as a CO_2 mitigation option. Industrial analogues, including underground natural gas storage projects around the world and acid gas injection projects, provide additional indications that CO_2 can be safely injected and stored at well-characterized and properly managed sites. While there are differences between natural accumulations and engineered storage, injecting CO_2 into deep geological formations at carefully selected sites can store it underground for long periods of time: it is considered likely that 99% or more of the injected CO_2 will be retained for 1000 years. Depleted oil and gas reservoirs, possibly coal formations and particularly saline formations (deep underground porous reservoir rocks saturated with brackish water or brine), can be used for storage of CO_2. At depths below about 800–1000 m, supercritical CO_2 has a liquid-like density that provides the potential for efficient utilization of underground storage space in the pores of sedimentary rocks. Carbon dioxide can remain trapped underground by virtue of a number of mechanisms, such as: trapping below an impermeable, confining layer (caprock); retention as an immobile phase trapped in the pore spaces of the storage formation; dissolution in the *in situ* formation fluids; and/or adsorption onto organic matter in coal and shale. Additionally, it may be trapped by reacting with the minerals in the storage formation and caprock to produce carbonate minerals. Models are available to predict what happens when CO_2 is injected underground. Also, by avoiding deteriorated wells or open fractures or faults, injected CO_2 will be retained for very long periods of time. Moreover, CO_2 becomes less mobile over time as a result of multiple trapping mechanisms, further lowering the prospect of leakage.

Injection of CO_2 in deep geological formations uses technologies that have been developed for and applied by, the oil and gas industry. Well-drilling technology, injection technology, computer simulation of storage reservoir dynamics and monitoring methods can potentially be adapted from existing applications to meet the needs of geological storage. Beyond conventional oil and gas technology, other successful underground injection practices – including natural gas storage, acid gas disposal and deep injection of liquid wastes – as well as the industry's extensive experience with subsurface disposal of oil-field brines, can provide useful information about designing programmes for long-term storage of CO_2. Geological storage of CO_2 is in practice today beneath the North Sea, where nearly 1 $MtCO_2$ has been successfully injected annually at Sleipner since 1996 and in Algeria at the In-Salah gas field. Carbon dioxide is also injected underground to recover oil. About 30 Mt of non-anthropogenic CO_2 are injected annually, mostly in west Texas, to recover oil from over 50 individual projects, some of which started in the early 1970s. The Weyburn Project in Canada, where currently 1–2 $MtCO_2$ are injected annually, combines EOR with a comprehensive monitoring and modelling programme to evaluate CO_2 storage. Several more storage projects are under development at this time.

In areas with suitable hydrocarbon accumulations, CO_2-EOR may be implemented because of the added economic benefit of incremental oil production, which may offset some of the costs of CO_2 capture, transport and injection. Storage of CO_2 in coal beds, in conjunction with enhanced coal bed methane (ECBM) production, is potentially attractive because of the prospect of enhanced production of methane, the cleanest of the fossil fuels. This technology, however, is not well developed and a better understanding of injection and storage processes in coals is needed. Carbon dioxide storage in depleted oil and gas reservoirs is very promising in some areas, because these structures are well known and significant infrastructures are already in place. Nevertheless, relatively few hydrocarbon reservoirs are currently depleted or near depletion and CO_2 storage will have to be staged to fit the time of reservoir availability. Deep saline formations are believed to have by far the largest capacity for CO_2 storage and are much more widespread than other options.

While there are uncertainties, the global capacity to store CO_2 deep underground is large. Depleted oil and gas reservoirs are estimated to have a storage capacity of 675–900 $GtCO_2$. Deep saline formations are very likely to have a storage capacity of at least 1000 $GtCO_2$ and some studies suggest it may be an order of magnitude greater than this, but quantification of the upper range is difficult until additional studies are undertaken. Capacity of unminable coal formations is uncertain, with estimates ranging from as little as 3 $GtCO_2$ up to 200 $GtCO_2$. Potential storage sites are likely to be broadly distributed in many of the world's sedimentary basins, located in the same region as many of the world's emission sources and are likely to be adequate to store a significant proportion of those emissions well into the future.

The cost of geological storage of CO_2 is highly site-specific, depending on factors such as the depth of the storage formation, the number of wells needed for injection and whether the project is onshore or offshore – but costs for storage, including monitoring, appear to lie in the range of 0.6–8.3 US\$/tCO_2 stored. This cost is small compared to present-day costs of CO_2 capture from flue gases, as indicated in Chapter 3. EOR could lead to negative storage costs of 10–16 US\$/tCO_2 for oil prices of 15–20 US\$ per barrel and more for higher oil prices.

Potential risks to humans and ecosystems from geological storage may arise from leaking injection wells, abandoned wells, leakage across faults and ineffective confining layers. Leakage of CO_2 could potentially degrade the quality of groundwater, damage some hydrocarbon or mineral resources, and have lethal effects on plants and sub-soil animals. Release of CO_2 back into the atmosphere could also create local health and safety concerns. Avoiding or mitigating these impacts will require careful site selection, effective regulatory oversight, an appropriate monitoring programme that provides

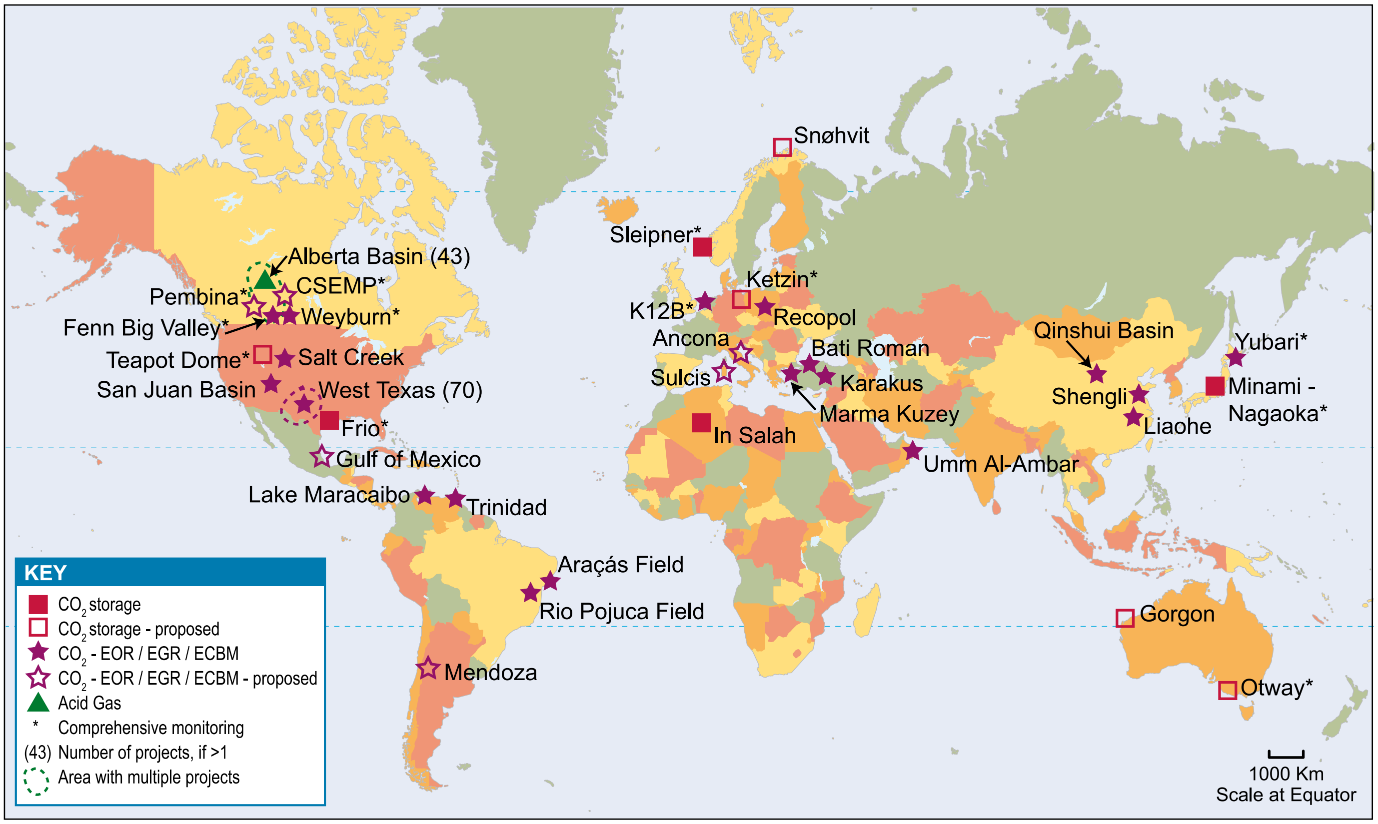

Figure 5.1 Location of sites where activities relevant to CO_2 storage are planned or under way.

early warning that the storage site is not functioning as anticipated and implementation of remediation methods to stop or control CO_2 releases. Methods to accomplish these are being developed and tested.

There are few, if any, national regulations specifically dealing with CO_2 storage, but regulations dealing with oil and gas, groundwater and the underground injection of fluids can in many cases be readily adapted and/or adopted. However, there are no regulations relating specifically to long-term responsibility for storage. A number of international laws that predate any consideration of CO_2 storage are relevant to offshore geological storage; consideration of whether these laws do or do not permit offshore geological storage is under way.

There are gaps in our knowledge, such as regional storage-capacity estimates for many parts of the world. Similarly, better estimation of leakage rates, improved cost data, better intervention and remediation options, more pilot and demonstration projects and clarity on the issue of long-term stewardship all require consideration. Despite the fact that more work is needed to improve technologies and decrease uncertainty, there appear to be no insurmountable technical barriers to an increased uptake of geological storage as an effective mitigation option.

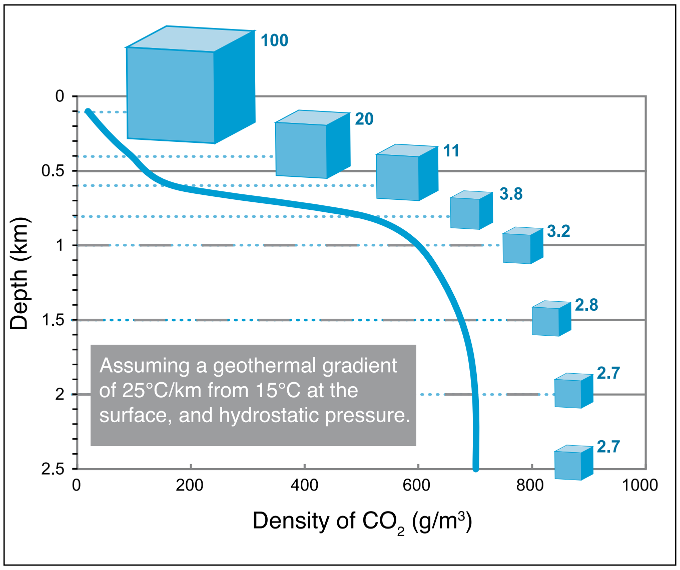

Figure 5.2 Variation of CO_2 density with depth, assuming hydrostatic pressure and a geothermal gradient of 25°C km^{-1} from 15°C at the surface (based on the density data of Angus *et al.*, 1973). Carbon dioxide density increases rapidly at approximately 800 m depth, when the CO_2 reaches a supercritical state. Cubes represent the relative volume occupied by the CO_2 and down to 800 m, this volume can be seen to dramatically decrease with depth. At depths below 1.5 km, the density and specific volume become nearly constant.

5.1 Introduction

5.1.1 *What is geological storage?*

Capture and geological storage of CO_2 provide a way to avoid emitting CO_2 into the atmosphere, by capturing CO_2 from major stationary sources (Chapter 3), transporting it usually by pipeline (Chapter 4) and injecting it into suitable deep rock formations. This chapter explores the nature of geological storage and considers its potential as a mitigation option.

The subsurface is the Earth's largest carbon reservoir, where the vast majority of the world's carbon is held in coals, oil, gas organic-rich shales and carbonate rocks. Geological storage of CO_2 has been a natural process in the Earth's upper crust for hundreds of millions of years. Carbon dioxide derived from biological activity, igneous activity and chemical reactions between rocks and fluids accumulates in the natural subsurface environment as carbonate minerals, in solution or in a gaseous or supercritical form, either as a gas mixture or as pure CO_2. The engineered injection of CO_2 into subsurface geological formations was first undertaken in Texas, USA, in the early 1970s, as part of enhanced oil recovery (EOR) projects and has been ongoing there and at many other locations ever since.

Geological storage of anthropogenic CO_2 as a greenhouse gas mitigation option was first proposed in the 1970s, but little research was done until the early 1990s, when the idea gained credibility through the work of individuals and research groups (Marchetti, 1977; Baes *et al.*, 1980; Kaarstad, 1992; Koide *et al.*, 1992; van der Meer, 1992; Gunter *et al.*, 1993; Holloway and Savage, 1993; Bachu *et al.*, 1994; Korbol and Kaddour, 1994). The subsurface disposal of acid gas (a by-product of petroleum production with a CO_2 content of up to 98%) in the Alberta Basin of Canada and in the United States provides additional useful experience. In 1996, the world's first large-scale storage project was initiated by Statoil and its partners at the Sleipner Gas Field in the North Sea.

By the late 1990s, a number of publicly and privately funded research programmes were under way in the United States, Canada, Japan, Europe and Australia. Throughout this time, though less publicly, a number of oil companies became increasingly interested in geological storage as a mitigation option, particularly for gas fields with a high natural CO_2 content such as Natuna in Indonesia, In Salah in Algeria and Gorgon in Australia. More recently, coal mining companies and electricity-generation companies have started to investigate geological storage as a mitigation option of relevance to their industry.

In a little over a decade, geological storage of CO_2 has

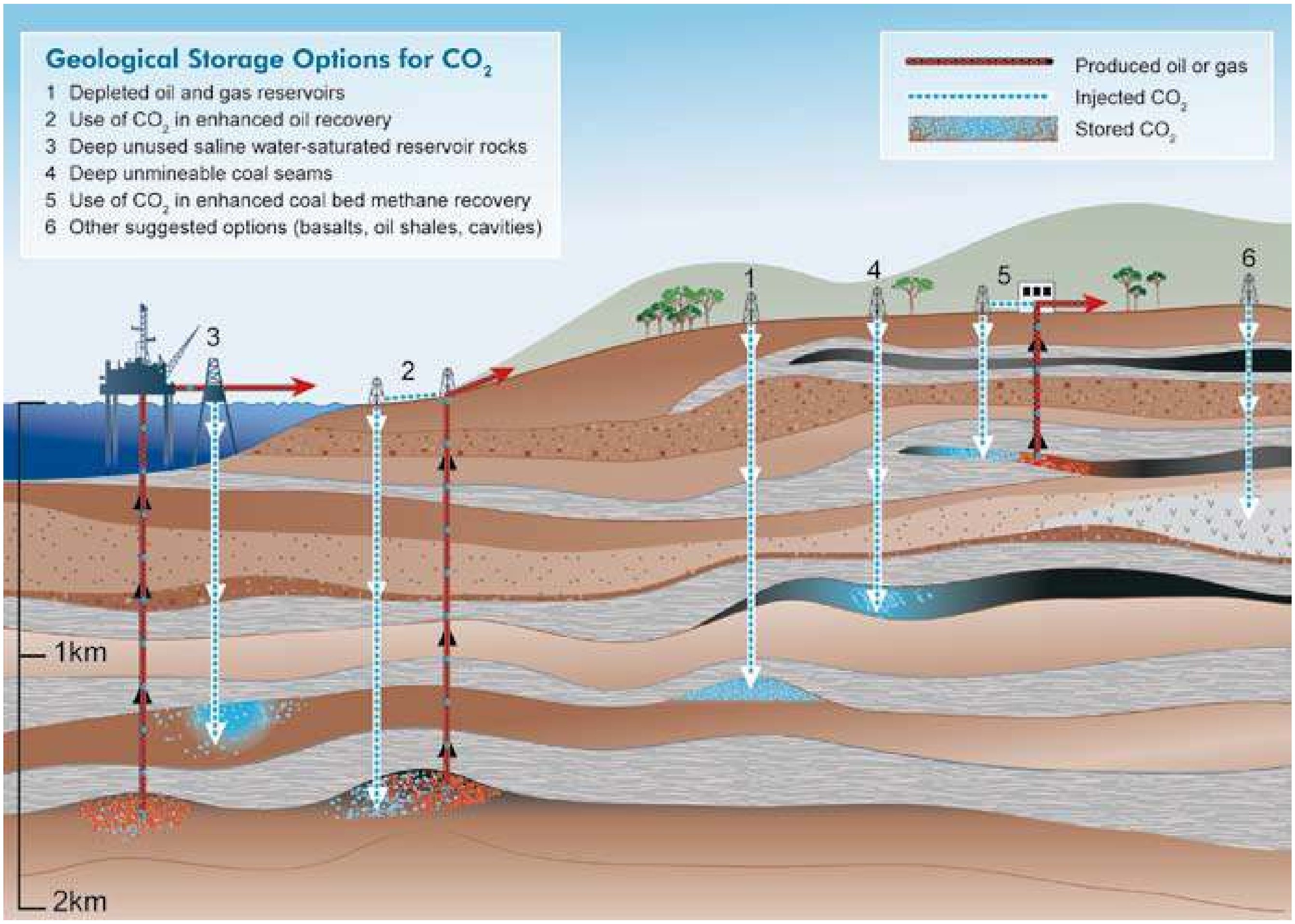

Figure 5.3 Options for storing CO_2 in deep underground geological formations (after Cook, 1999).

grown from a concept of limited interest to one that is quite widely regarded as a potentially important mitigation option (Figure 5.1). There are several reasons for this. First, as research has progressed and as demonstration and commercial projects have been successfully undertaken, the level of confidence in the technology has increased. Second, there is consensus that a broad portfolio of mitigation options is needed. Third, geological storage (in conjunction with CO_2 capture) could help to make deep cuts to atmospheric CO_2 emissions. However, if that potential is to be realized, the technique must be safe, environmentally sustainable, cost-effective and capable of being broadly applied. This chapter explores these issues.

To geologically store CO_2, it must first be compressed, usually to a dense fluid state known as 'supercritical' (see Glossary). Depending on the rate that temperature increases with depth (the geothermal gradient), the density of CO_2 will increase with depth, until at about 800 m or greater, the injected CO_2 will be in a dense supercritical state (Figure 5.2).

Geological storage of CO_2 can be undertaken in a variety of geological settings in sedimentary basins. Within these basins, oil fields, depleted gas fields, deep coal seams and saline formations are all possible storage formations (Figure 5.3).

Subsurface geological storage is possible both onshore and offshore, with offshore sites accessed through pipelines from the shore or from offshore platforms. The continental shelf and some adjacent deep-marine sedimentary basins are potential offshore storage sites, but the majority of sediments of the abyssal deep ocean floor are too thin and impermeable to be suitable for geological storage (Cook and Carleton, 2000). In addition to storage in sedimentary formations, some consideration has been given to storage in caverns, basalt and organic-rich shales (Section 5.3.5).

Fluids have been injected on a massive scale into the deep subsurface for many years to dispose of unwanted chemicals, pollutants or by-products of petroleum production, to enhance the production of oil and gas or to recharge depleted formations (Wilson *et al.*, 2003). The principles involved in such activities are well established and in most countries there are regulations governing these activities. Natural gas has also been injected and stored in the subsurface on a large scale in many parts of the world for many years. Injection of CO_2 to date has been done at a relatively small scale, but if it were to be used to significantly decrease emissions from existing stationary sources, then the injection rates would have to be at a scale similar to other injection operations under way at present.

But what is the world's geological storage capacity and does it occur where we need it? These questions were first raised in Chapter 2, but Section 5.3.8 of this chapter considers geographical matching of CO_2 sources to geological storage sites in detail. Not all sedimentary basins are suitable for CO_2 storage; some are too shallow and others are dominated by rocks with low permeability or poor confining characteristics. Basins suitable for CO_2 storage have characteristics such as thick accumulations of sediments, permeable rock formations saturated with saline water (saline formations), extensive covers of low porosity rocks (acting as seals) and structural simplicity. While many basins show such features, many others do not.

Is there likely to be sufficient storage capacity to meet the world's needs in the years ahead? To consider this issue, it is useful to draw parallels with the terms 'resources' and 'reserves' used for mineral deposits (McKelvey, 1972). Deposits of minerals or fossil fuels are often cited with very large resource figures, but the 'proven' reserve is only some fraction of the resource. The resource figures are based on the selling price of the commodity, the cost of exploiting the commodity, the availability of appropriate technologies, proof that the commodity exists and whether the environmental or social impact of exploiting the commodity is acceptable to the community. Similarly, to turn technical geological storage capacity into economical storage capacity, the storage project must be economically viable, technically feasible, safe, environmentally and socially sustainable and acceptable to the community. Given these constraints, it is inevitable that the storage capacity that will actually be used will be significantly less than the technical potential. Section 5.3 explores this issue. It is likely that usable storage capacity will exist in many areas where people live and where CO_2 is generated from large stationary sources. This geographical congruence of storage-need and storage-capacity should not come as a surprise, because much of the world's population is concentrated in regions underlain by sedimentary basins (Gunter *et al.*, 2004).

It is also important to know how securely and for how long stored CO_2 will be retained – for decades, centuries, millennia or for geological time? To assure public safety, storage sites must be designed and operated to minimize the possibility of leakage. Consequently, potential leakage pathways must be identified and procedures must be established, to set appropriate design and operational standards as well as monitoring, measurement and verification requirements. Sections 5.4, 5.6 and 5.7 consider these issues.

In this chapter, we primarily consider storage of pure or nearly pure, CO_2. It has been suggested that it may be economically favourable to co-store CO_2 along with H_2S, SO_2 or NO_2. Since only a few scientific studies have evaluated the impacts of these added constituents on storage performance or risks, they are not addressed comprehensively here. Moreover, the limited information gained from practical experience with acid gas injection in Canada is insufficient to assess the impacts of the added components on storage security.

5.1.2 Existing and planned CO_2 projects

A number of pilot and commercial CO_2 storage projects are under way or proposed (Figure 5.1). To date, most actual or planned commercial projects are associated with major gas production facilities that have gas streams containing CO_2 in the range of 10–15% by volume, such as Sleipner in the North Sea, Snohvit in the Barents Sea, In Salah in Algeria and Gorgon in Australia (Figure 5.1), as well as the acid gas injection projects in Canada and the United States. At the Sleipner Project, operated by Statoil, more than 7 $MtCO_2$ has been injected into a deep sub-sea saline formation since 1996 (Box 5.1). Existing and planned

Table 5.1 A selection of current and planned geological storage projects.

Project	Country	Scale of Project	Lead organizations	Injection start date	Approximate average daily injection rate	Total storage	Storage type	Geological storage formation	Age of formation	Lithology	Monitoring
Sleipner	Norway	Commercial	Statoil, IEA	1996	3000 t day^{-1}	20 Mt planned	Aquifer	Utsira Formation	Tertiary	Sandstone	4D seismic plus gravity
Weyburn	Canada	Commercial	EnCana, IEA	May 2000	3-5000 t day^{-1}	20 Mt planned	CO_2-EOR	Midale Formation	Mississippian	Carbonate	Comprehensive
Minami-Nagoaka	Japan	Demo	Research Institute of Innovative Technology for the Earth	2002	Max 40 t day^{-1}	10,000 t planned	Aquifer (Sth. Nagoaka Gas Field)	Haizume Formation	Pleistocene	Sandstone	Crosswell seismic + well monitoring
Yubari	Japan	Demo	Japanese Ministry of Economy, Trade and Industry	2004	10 t day^{-1}	200 t Planned	CO_2-ECBM	Yubari Formation (Ishikari Coal Basin)	Tertiary	Coal	Comprehensive
In Salah	Algeria	Commercial	Sonatrach, BP, Statoil	2004	3-4000 t day^{-1}	17 Mt planned	Depleted hydrocarbon reservoirs	Krechba Formation	Carboniferous	Sandstone	Planned comprehensive
Frio	USA	Pilot	Bureau of Economic Geology of the University of Texas	4-13 Oct. 2004	Approx. 177 t day^{-1} for 9 days	1600t	Saline formation	Frio Formation	Tertiary	Brine-bearing sandstone-shale	Comprehensive
K12B	Netherlands	Demo	Gaz de France	2004	100-1000 t day^{-1} (2006+)	Approx 8 Mt	EGR	Rotleigendes	Permian	Sandstone	Comprehensive
Fenn Big Valley	Canada	Pilot	Alberta Research Council	1998	50 t day^{-1}	200 t	CO_2-ECBM	Mannville Group	Cretaceous	Coal	P, T, flow
Recopol	Poland	Pilot	TNO-NITG (Netherlands)	2003	1 t day^{-1}	10 t	CO_2-ECBM	Silesian Basin	Carboniferous	Coal	
Qinshui Basin	China	Pilot	Alberta Research Council	2003	30 t day^{-1}	150 t	CO_2-ECBM	Shanxi Formation	Carboniferous-Permian	Coal	P, T, flow
Salt Creek	USA	Commercial	Anadarko	2004	5-6000 t day^{-1}	27 Mt	CO_2-EOR	Frontier	Cretaceous	Sandstone	Under development
Planned Projects (2005 onwards)											
Snøhvit	Norway	Decided Commercial	Statoil	2006	2000 t day^{-1}		Saline formation	Tubaen Formation	Lower Jurassic	Sandstone	Under development
Gorgon	Australia	Planned Commercial	Chevron	Planned 2009	Approx. 10,000 t day^{-1}		Saline formation	Dupuy Formation	Late Jurassic	Massive sandstone with shale seal	Under development
Ketzin	Germany	Demo	GFZ Potsdam	2006	100 t day^{-1}	60 kt	Saline formation	Stuttgart Formation	Triassic	Sandstone	Comprehensive
Otway	Australia	Pilot	CO2CRC	Planned late 2005	160 t day^{-1} for 2 years	0.1 Mt	Saline fm and depleted gas field	Waarre Formation	Cretaceous	Sandstone	Comprehensive
Teapot Dome	USA	Proposed Demo	RMOTC	Proposed 2006	170 t day^{-1} for 3 months	10 kt	Saline fm and CO_2-EOR	Tensleep and Red Peak Fm	Permian	Sandstone	Comprehensive
CSEMP	Canada	Pilot	Suncor Energy	2005	50 t day^{-1}	10 kt	CO_2-ECBM	Ardley Fm	Tertiary	Coal	Comprehensive
Pembina	Canada	Pilot	Penn West	2005	50 t day^{-1}	50 kt	CO_2-EOR	Cardium Fm	Cretaceous	Sandstone	Comprehensive

storage projects are also listed in Table 5.1.

At the In Salah Gas Field in Algeria, Sonatrack, BP and Statoil inject CO_2 stripped from natural gas into the gas reservoir outside the boundaries of the gas field (Box 5.2). Statoil is planning another project in the Barents Sea, where CO_2 from the Snohvit field will be stripped from the gas and injected into a geological formation below the gas field. Chevron is proposing to produce gas from the Gorgon field off Western Australia, containing approximately 14% CO_2. The CO_2 will be injected into the Dupuy Formation at Barrow Island (Oen, 2003). In The Netherlands, CO_2 is being injected at pilot scale into the almost depleted K12-B offshore gas field (van der Meer *et al*., 2005).

Forty-four CO_2-rich acid gas injection projects are currently operating in Western Canada, ongoing since the early 1990s (Bachu and Haug, 2005). Although they are mostly small scale, they provide important examples of effectively managing injection of CO_2 and hazardous gases such as H_2S (Section 5.2.4.2).

Box 5.1 The Sleipner Project, North Sea.

The Sleipner Project, operated by Statoil in the North Sea about 250 km off the coast of Norway, is the first commercial-scale project dedicated to geological CO_2 storage in a saline formation. The CO_2 (about 9%) from Sleipner West Gas Field is separated, then injected into a large, deep, saline formation 800 m below the seabed of the North Sea. The Saline Aquifer CO_2 Storage (SACS) project was established to monitor and research the storage of CO_2. From 1995, the IEA Greenhouse Gas R&D Programme has worked with Statoil to arrange the monitoring and research activities. Approximately 1 $MtCO_2$ is removed from the produced natural gas and injected underground annually in the field. The CO_2 injection operation started in October 1996 and, by early 2005, more than 7 $MtCO_2$ had been injected at a rate of approximately 2700 t day^{-1}. Over the lifetime of the project, a total of 20 $MtCO_2$ is expected to be stored. A simplified diagram of the Sleipner scheme is given in Figure 5.4.

The saline formation into which the CO_2 is injected is a brine-saturated unconsolidated sandstone about 800–1000 m below the sea floor. The formation also contains secondary thin shale layers, which influence the internal movement of injected CO_2. The saline formation has a very large storage capacity, on the order of 1–10 $GtCO_2$. The top of the formation is fairly flat on a regional scale, although it contains numerous small, low-amplitude closures. The overlying primary seal is an extensive, thick, shale layer.

This project is being carried out in three phases. Phase-0 involved baseline data gathering and evaluation, which was completed in November 1998. Phase-1 involved establishment of project status after three years of CO_2 injection. Five main project areas involve descriptions of reservoir geology, reservoir simulation, geochemistry, assessment of need and cost for monitoring wells and geophysical modelling. Phase-2, involving data interpretation and model verification, began in April 2000.

The fate and transport of the CO_2 plume in the storage formation has been monitored successfully by seismic time-lapse surveys (Figure 5.16). The surveys also show that the caprock is an effective seal that prevents CO_2 migration out of the storage formation. Today, the footprint of the plume at Sleipner extends over an area of approximately 5 km^2. Reservoir studies and simulations covering hundreds to thousands of years have shown that CO_2 will eventually dissolve in the pore water, which will become heavier and sink, thus minimizing the potential for long-term leakage (Lindeberg and Bergmo, 2003).

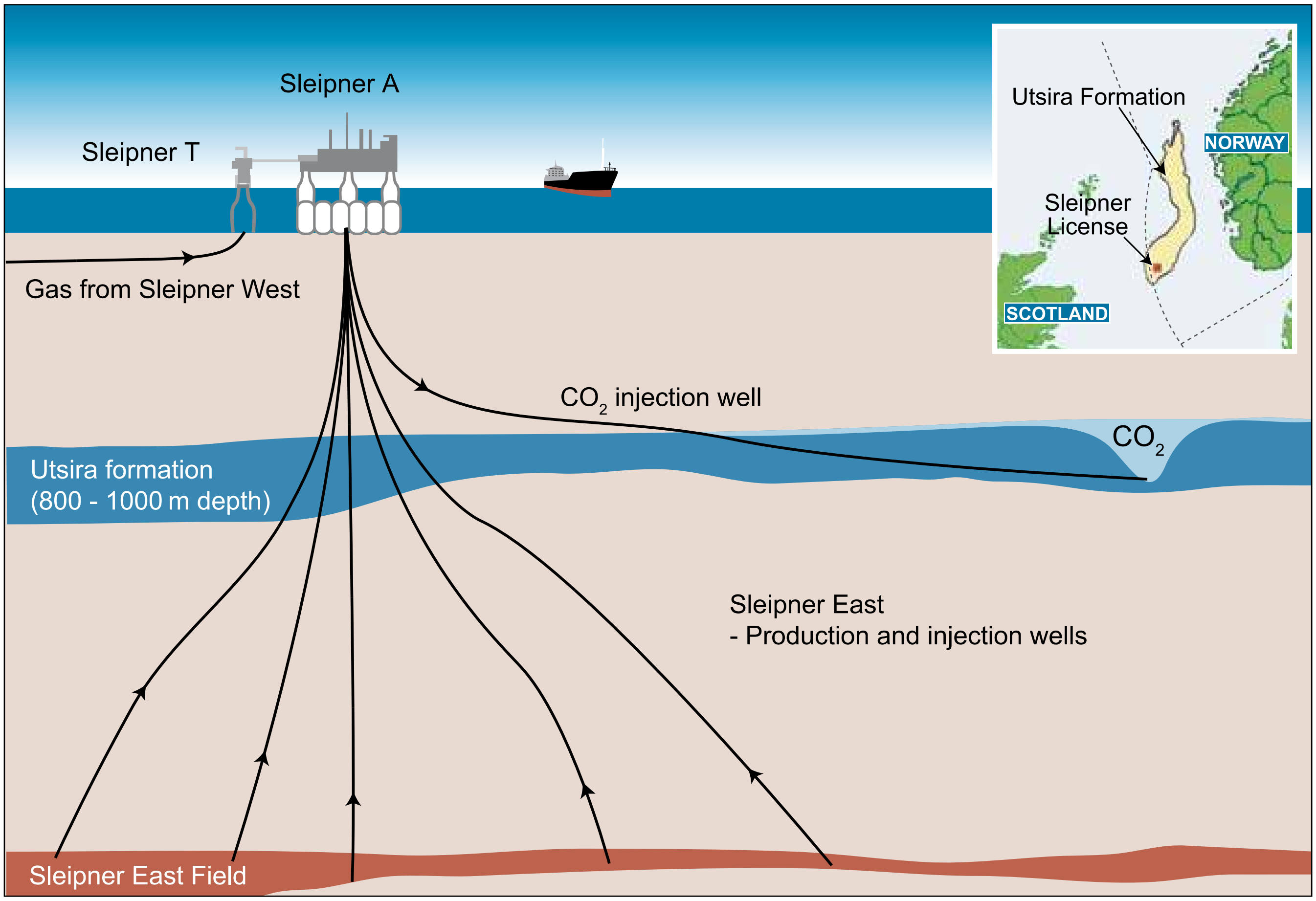

Figure 5.4 Simplified diagram of the Sleipner CO_2 Storage Project. Inset: location and extent of the Utsira formation.

Box 5.2 The In Salah, Algeria, CO_2 Storage Project.

The In Salah Gas Project, a joint venture among Sonatrach, BP and Statoil located in the central Saharan region of Algeria, is the world's first large-scale CO_2 storage project in a gas reservoir (Riddiford *et al*., 2003). The Krechba Field at In Salah produces natural gas containing up to 10% CO_2 from several geological reservoirs and delivers it to markets in Europe, after processing and stripping the CO_2 to meet commercial specifications. The project involves re-injecting the CO_2 into a sandstone reservoir at a depth of 1800 m and storing up to 1.2 $MtCO_2$ yr^{-1}. Carbon dioxide injection started in April 2004 and, over the life of the project, it is estimated that 17 $MtCO_2$ will be geologically stored. The project consists of four production and three injection wells (Figure 5.5). Long-reach (up to 1.5 km) horizontal wells are used to inject CO_2 into the 5-mD permeability reservoir.

The Krechba Field is a relatively simple anticline. Carbon dioxide injection takes place down-dip from the gas/water contact in the gas-bearing reservoir. The injected CO_2 is expected to eventually migrate into the area of the current gas field after depletion of the gas zone. The field has been mapped with three-dimensional seismic and well data from the field. Deep faults have been mapped, but at shallower levels, the structure is unfaulted. The storage target in the reservoir interval therefore carries minimal structural uncertainty or risk. The top seal is a thick succession of mudstones up to 950 m thick.

A preliminary risk assessment of CO_2 storage integrity has been carried out and baseline data acquired. Processes that could result in CO_2 migration from the injection interval have been quantified and a monitoring programme is planned involving a range of technologies, including noble gas tracers, pressure surveys, tomography, gravity baseline studies, microbiological studies, four-dimensional seismic and geomechanical monitoring.

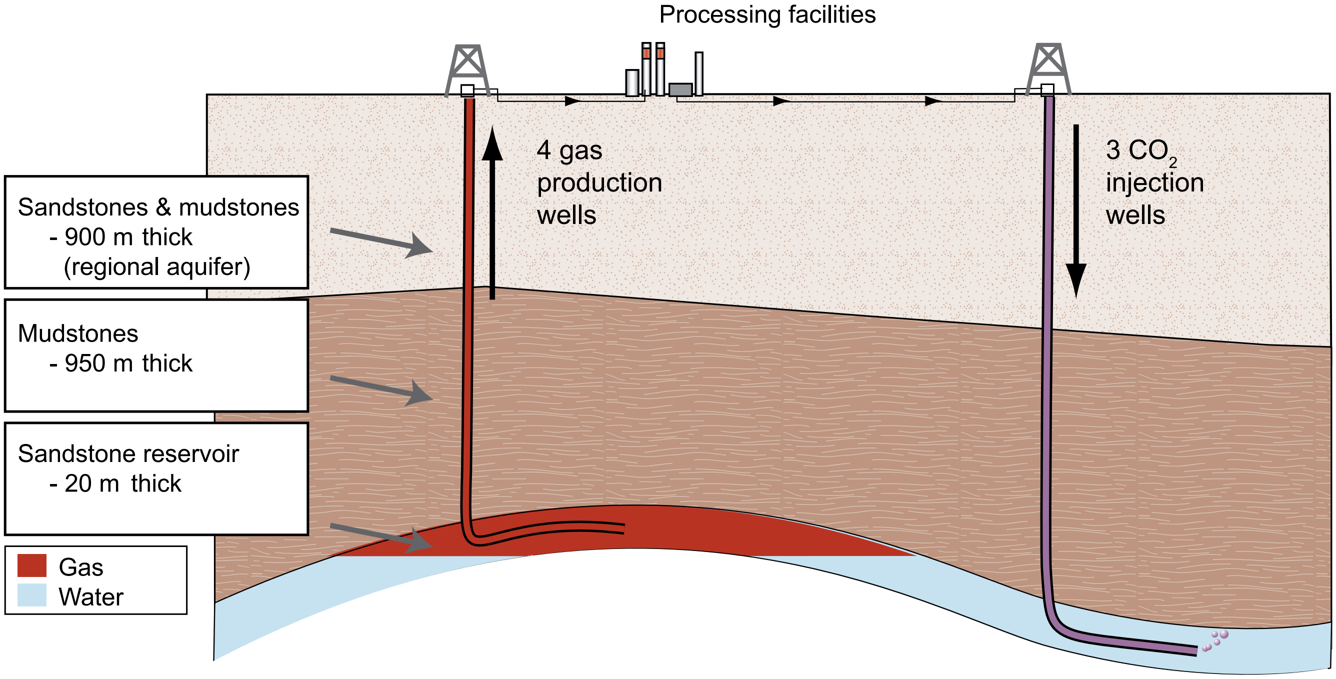

Figure 5.5 Schematic of the In Salah Gas Project, Algeria. One $MtCO_2$ will be stored annually in the gas reservoir. Long-reach horizontal wells with slotted intervals of up to 1.5 km are used to inject CO_2 into the water-filled parts of the gas reservoir.

Opportunities for enhanced oil recovery (EOR) have increased interest in CO_2 storage (Stevens *et al*., 2001b; Moberg *et al*., 2003; Moritis, 2003; Riddiford *et al*., 2003; Torp and Gale, 2003). Although not designed for CO_2 storage, CO_2-EOR projects can demonstrate associated storage of CO_2, although lack of comprehensive monitoring of EOR projects (other than at the International Energy Agency Greenhouse Gas (IEA-GHG) Weyburn Project in Canada) makes it difficult to quantify storage. In the United States, approximately 73 CO_2-EOR operations inject up to 30 $MtCO_2$ yr^{-1}, most of which comes from natural CO_2 accumulations – although approximately 3 $MtCO_2$ is from anthropogenic sources, such as gas processing and fertiliser plants (Stevens *et al*., 2001b). The SACROC project in Texas was the first large-scale commercial CO_2-EOR project in the world. It used anthropogenic CO_2 during the period 1972 to 1995. The Rangely Weber project (Box 5.6) injects anthropogenic CO_2 from a gas-processing plant in Wyoming.

In Canada, a CO_2-EOR project has been established by EnCana at the Weyburn Oil Field in southern Saskatchewan (Box 5.3). The project is expected to inject 23 $MtCO_2$ and extend the life of the oil field by 25 years (Moberg *et al*.,

Box 5.3 The Weyburn CO_2-EOR Project.

The Weyburn CO_2-enhanced oil recovery (CO_2-EOR) project is located in the Williston Basin, a geological structure extending from south-central Canada into north-central United States. The project aims to permanently store almost all of the injected CO_2 by eliminating the CO_2 that would normally be released during the end of the field life.

The source of the CO_2 for the Weyburn CO_2-EOR Project is the Dakota Gasification Company facility, located approximately 325 km south of Weyburn, in Beulah, North Dakota, USA. At the plant, coal is gasified to make synthetic gas (methane), with a relatively pure stream of CO_2 as a by-product. This CO_2 stream is dehydrated, compressed and piped to Weyburn in southeastern Saskatchewan, Canada, for use in the field. The Weyburn CO_2-EOR Project is designed to take CO_2 from the pipeline for about 15 years, with delivered volumes dropping from 5000 to about 3000 t day^{-1} over the life of the project.

The Weyburn field covers an area of 180 km^2, with original oil in place on the order of 222 million m^3 (1396 million barrels). Over the life of the CO_2-EOR project (20–25 years), it is expected that some 20 $MtCO_2$ will be stored in the field, under current economic conditions and oil recovery technology. The oil field layout and operation is relatively conventional for oil field operations. The field has been designed with a combination of vertical and horizontal wells to optimize the sweep efficiency of the CO_2. In all cases, production and injection strings are used within the wells to protect the integrity of the casing of the well.

The oil reservoir is a fractured carbonate, 20–27 m thick. The primary upper seal for the reservoir is an anhydrite zone. At the northern limit of the reservoir, the carbonate thins against a regional unconformity. The basal seal is also anhydrite, but is less consistent across the area of the reservoir. A thick, flat-lying shale above the unconformity forms a good regional barrier to leakage from the reservoir. In addition, several high-permeability formations containing saline groundwater would form good conduits for lateral migration of any CO_2 that might reach these zones, with rapid dissolution of the CO_2 in the formation fluids.

Since CO_2 injection began in late 2000, the EOR project has performed largely as predicted. Currently, some 1600 m^3 (10,063 barrels) day^{-1} of incremental oil is being produced from the field. All produced CO_2 is captured and recompressed for reinjection into the production zone. Currently, some 1000 tCO_2 day^{-1} is reinjected; this will increase as the project matures. Monitoring is extensive, with high-resolution seismic surveys and surface monitoring to determine any potential leakage. Surface monitoring includes sampling and analysis of potable groundwater, as well as soil gas sampling and analysis (Moberg *et al*., 2003). To date, there has been no indication of CO_2 leakage to the surface and near-surface environment (White, 2005; Strutt *et al*., 2003).

2003; Law, 2005). The fate of the injected CO_2 is being closely monitored through the IEA GHG Weyburn Project (Wilson and Monea, 2005). Carbon dioxide-EOR is under consideration for the North Sea, although there is as yet little, if any, operational experience for offshore CO_2-EOR. Carbon dioxide-EOR projects are also currently under way in a number of countries including Trinidad, Turkey and Brazil (Moritis, 2002). Saudi Aramco, the world's largest producer and exporter of crude oil, is evaluating the technical feasibility of CO_2-EOR in some of its Saudi Arabian reservoirs.

In addition to these commercial storage or EOR projects, a number of pilot storage projects are under way or planned. The Frio Brine Project in Texas, USA, involved injection and storage of 1900 tCO_2 in a highly permeable formation with a regionally extensive shale seal (Hovorka *et al*., 2005). Pilot projects are proposed for Ketzin, west of Berlin, Germany, for the Otway Basin of southeast Australia and for Teapot Dome, Wyoming, USA (Figure 5.1). The American FutureGen project, proposed for late this decade, will be a geological storage project linked to coal-fired electricity generation. A small-scale CO_2 injection and monitoring project is being carried out by RITE at Nagoaka in northwest Honshu, Japan. Small-scale injection projects to test CO_2 storage in coal have been carried out in Europe (RECOPOL) and Japan (Yamaguchi *et al*., 2005). A CO_2-enhanced coal bed methane (ECBM) recovery demonstration project has been undertaken in the northern San Juan Basin of New Mexico, USA (Reeves, 2003a) (Box 5.7). Further CO_2-ECBM projects are under consideration for China, Canada, Italy and Poland (Gale, 2003). In all, some 59 opportunities for CO_2-ECBM have been identified worldwide, the majority in China (van Bergen *et al*., 2003a).

These projects (Figure 5.1; Table 5.1) demonstrate that subsurface injection of CO_2 is not for the distant future, but is being implemented now for environmental and/or commercial reasons.

5.1.3 Key questions

In the previous section, the point is made that deep injection of CO_2 is under way in a number of places (Figure 5.1). However, if CO_2 storage is to be undertaken on the scale necessary to make deep cuts to atmospheric CO_2 emissions, there must be hundreds, and perhaps even thousands, of large-scale geological storage projects under way worldwide. The extent to which this is or might be, feasible depends on the answers to the key questions outlined below and addressed subsequently in this chapter:

- How is CO_2 stored underground? What happens to the CO_2 when it is injected? What are the physico-chemical and chemical processes involved? What are the geological

controls? (Sections 5.2 and 5.3)
- How long can CO_2 remain stored underground? (Section 5.2)
- How much and where can CO_2 be stored in the subsurface, locally, regionally, globally? Is it a modest niche opportunity or is the total storage capacity sufficient to contain a large proportion of the CO_2 currently emitted to the atmosphere? (Section 5.3)
- Are there significant opportunities for CO_2-enhanced oil and gas recovery? (Section 5.3)
- How is a suitable storage site identified and what are its geological characteristics? (see Section 5.4)
- What technologies are currently available for geological storage of CO_2? (Section 5.5)
- Can we monitor CO_2 once it is geologically stored? (Section 5.6)
- Will a storage site leak and what would be the likely consequences? (Sections 5.6 and 5.7)
- Can a CO_2 storage site be remediated if something does go wrong? (Sections 5.6 and 5.7)
- Can a geological storage site be operated safely and if so, how? (Section 5.7)
- Are there legal and regulatory issues for geological storage and is there a legal/regulatory framework that enables it to be undertaken? (Section 5.8)
- What is the likely cost of geological storage of CO_2? (Section 5.9)
- After reviewing our current state of knowledge, are there things that we still need to know? What are these gaps in knowledge? (Section 5.10).

The remainder of this chapter seeks to address these questions.

5.2 Storage mechanisms and storage security

Geological formations in the subsurface are composed of transported and deposited rock grains organic material and minerals that form after the rocks are deposited. The pore space between grains or minerals is occupied by fluid (mostly water, with proportionally minute occurrences of oil and gas). Open fractures and cavities are also filled with fluid. Injection of CO_2 into the pore space and fractures of a permeable formation can displace the *in situ* fluid or the CO_2 may dissolve in or mix with the fluid or react with the mineral grains or there may be some combination of these processes. This section examines these processes and their influence on geological storage of CO_2.

5.2.1 CO_2 flow and transport processes

Injection of fluids into deep geological formations is achieved by pumping fluids down into a well (see Section 5.5). The part of the well in the storage zone is either perforated or covered with a permeable screen to enable the CO_2 to enter the formation. The perforated or screened interval is usually on the order of 10–100 m thick, depending on the permeability and thickness of the formation. Injection raises the pressure near the well, allowing CO_2 to enter the pore spaces initially occupied by the *in situ* formation fluids. The amount and spatial distribution of pressure buildup in the formation will depend on the rate of injection, the permeability and thickness of the injection formation, the presence or absence of permeability barriers within it and the geometry of the regional underground water (hydrogeological) system.

Once injected into the formation, the primary flow and transport mechanisms that control the spread of CO_2 include:
- Fluid flow (migration) in response to pressure gradients created by the injection process;
- Fluid flow in response to natural hydraulic gradients;
- Buoyancy caused by the density differences between CO_2 and the formation fluids;
- Diffusion;
- Dispersion and fingering caused by formation heterogeneities and mobility contrast between CO_2 and formation fluid;
- Dissolution into the formation fluid;
- Mineralization;
- Pore space (relative permeability) trapping;
- Adsorption of CO_2 onto organic material.

The rate of fluid flow depends on the number and properties of the fluid phases present in the formation. When two or more fluids mix in any proportion, they are referred to as miscible fluids. If they do not mix, they are referred to as immiscible. The presence of several different phases may decrease the permeability and slow the rate of migration. If CO_2 is injected into a gas reservoir, a single miscible fluid phase consisting of natural gas and CO_2 is formed locally. When CO_2 is injected into a deep saline formation in a liquid or liquid-like supercritical dense phase, it is immiscible in water. Carbon dioxide injected into an oil reservoir may be miscible or immiscible, depending on the oil composition and the pressure and temperature of the system (Section 5.3.2). When CO_2 is injected into coal beds, in addition to some of the processes listed above, adsorption and desorption of gases (particularly methane) previously adsorbed on the coal take place, as well as swelling or shrinkage of the coal itself (Section 5.3.4).

Because supercritical CO_2 is much less viscous than water and oil (by an order of magnitude or more), migration is controlled by the contrast in mobility of CO_2 and the *in situ* formation fluids (Celia *et al*., 2005; Nordbotten *et al*., 2005a). Because of the comparatively high mobility of CO_2, only some of the oil or water will be displaced, leading to an average saturation of CO_2 in the range of 30–60%. Viscous fingering can cause CO_2 to bypass much of the pore space, depending on the heterogeneity and anisotropy of rock permeability (van der Meer, 1995; Ennis-King and Paterson, 2001; Flett *et al*., 2005). In natural gas reservoirs, CO_2 is more viscous than natural gas, so the ‘front’ will be stable and viscous fingering limited.

The magnitude of the buoyancy forces that drive vertical flow depends on the type of fluid in the formation. In saline formations, the comparatively large density difference (30–50%) between CO_2 and formation water creates strong buoyancy forces that drive CO_2 upwards. In oil reservoirs, the density difference and buoyancy forces are not as large, particularly if the oil and CO_2 are miscible (Kovscek, 2002). In gas reservoirs, the opposite effect will occur, with CO_2 migrating downwards under buoyancy forces, because CO_2 is denser than natural gas (Oldenburg *et al*., 2001).

In saline formations and oil reservoirs, the buoyant plume of injected CO_2 migrates upwards, but not evenly. This is because a lower permeability layer acts as a barrier and causes the CO_2 to migrate laterally, filling any stratigraphic or structural trap it encounters. The shape of the CO_2 plume rising through the rock matrix (Figure 5.6) is strongly affected by formation heterogeneity, such as low-permeability shale lenses (Flett *et al*., 2005). Low-permeability layers within the storage formation therefore have the effect of slowing the upward migration of CO_2, which would otherwise cause CO_2 to bypass deeper parts of the storage formation (Doughty *et al*., 2001).

As CO_2 migrates through the formation, some of it will dissolve into the formation water. In systems with slowly flowing water, reservoir-scale numerical simulations show that, over tens of years, a significant amount, up to 30% of the injected CO_2, will dissolve in formation water (Doughty *et al*., 2001). Basin-scale simulations suggest that over centuries, the entire CO_2 plume dissolves in formation water (McPherson and Cole, 2000; Ennis-King *et al*., 2003). If the injected CO_2 is contained in a closed structure (no flow of formation water), it will take much longer for CO_2 to completely dissolve because of reduced contact with unsaturated formation water. Once CO_2 is dissolved in the formation fluid, it migrates along with the regional groundwater flow. For deep sedimentary basins characterized by low permeability and high salinity, groundwater flow velocities are very low, typically on the order of millimetres to centimetres per year (Bachu *et al*., 1994). Thus, migration rates of dissolved CO_2 are substantially lower than for separate-phase CO_2.

Water saturated with CO_2 is slightly denser (approximately 1%) than the original formation water, depending on salinity (Enick and Klara, 1990; Bachu and Adams, 2003). With high vertical permeability, this may lead to free convection, replacing the CO_2-saturated water from the plume vicinity with unsaturated water, producing faster rates of CO_2 dissolution (Lindeberg and Wessel-Berg, 1997; Ennis-King and Paterson, 2003). Figure 5.7 illustrates the formation of convection cells and dissolution of CO_2 over several thousand years. The solubility of CO_2 in brine decreases with increasing pressure, decreasing temperature and increasing salinity (Annex 1). Calculations indicate that, depending on the salinity and depth, 20–60 $kgCO_2$ can dissolve in 1 m^3 of formation fluid (Holt *et al*., 1995; Koide *et al*., 1995). With the use of a homogeneous model rather than a heterogeneous one, the time required for complete CO_2 dissolution may be underestimated.

As CO_2 migrates through a formation, some of it is retained in the pore space by capillary forces (Figure 5.6), commonly referred to as 'residual CO_2 trapping', which may immobilize significant amounts of CO_2 (Obdam *et al*., 2003; Kumar *et al*., 2005). Figure 5.8 illustrates that when the degree of trapping is high and CO_2 is injected at the bottom of a thick formation, all of the CO_2 may be trapped by this mechanism, even before it reaches the caprock at the top of the formation. While this effect is formation-specific, Holtz (2002) has demonstrated that residual CO_2 saturations may be as high as 15–25% for many typical storage formations. Over time, much of the trapped CO_2 dissolves in the formation water (Ennis-King and

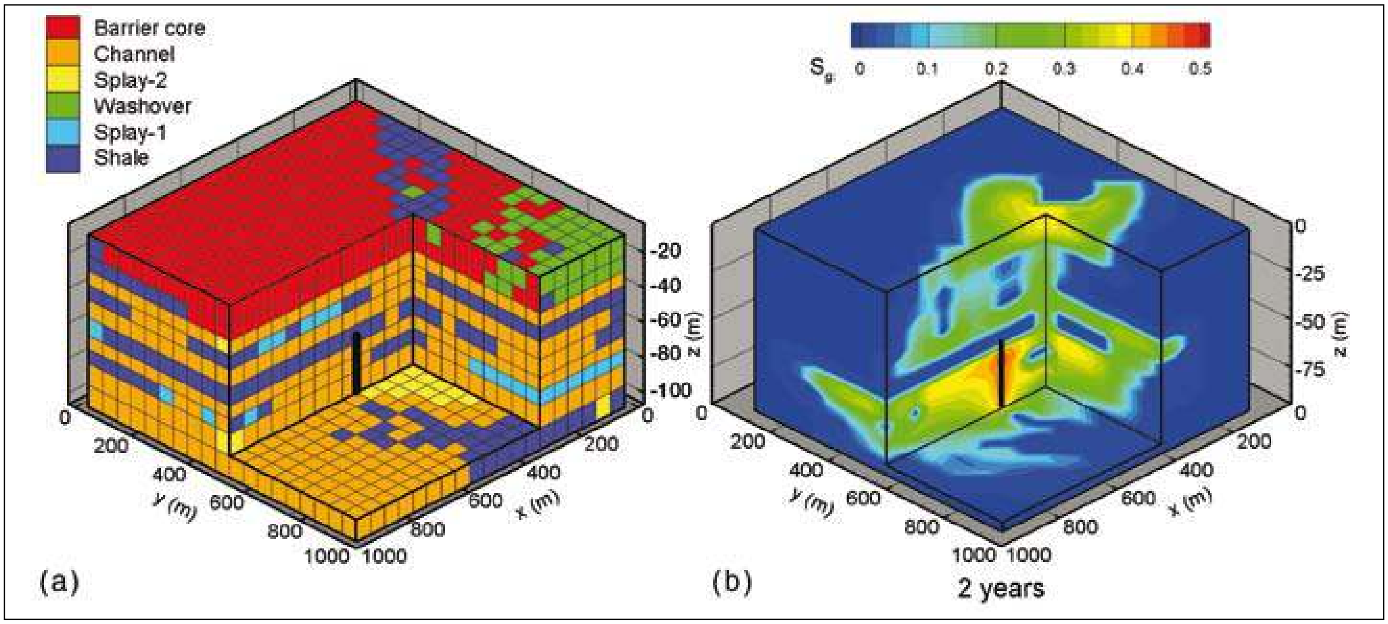

Figure 5.6 Simulated distribution of CO_2 injected into a heterogeneous formation with low-permeability layers that block upward migration of CO_2. (a) Illustration of a heterogeneous formation facies grid model. The location of the injection well is indicated by the vertical line in the lower portion of the grid. (b) The CO_2 distribution after two years of injection. Note that the simulated distribution of CO_2 is strongly influenced by the low-permeability layers that block and delay upward movement of CO_2 (after Doughty and Pruess, 2004).

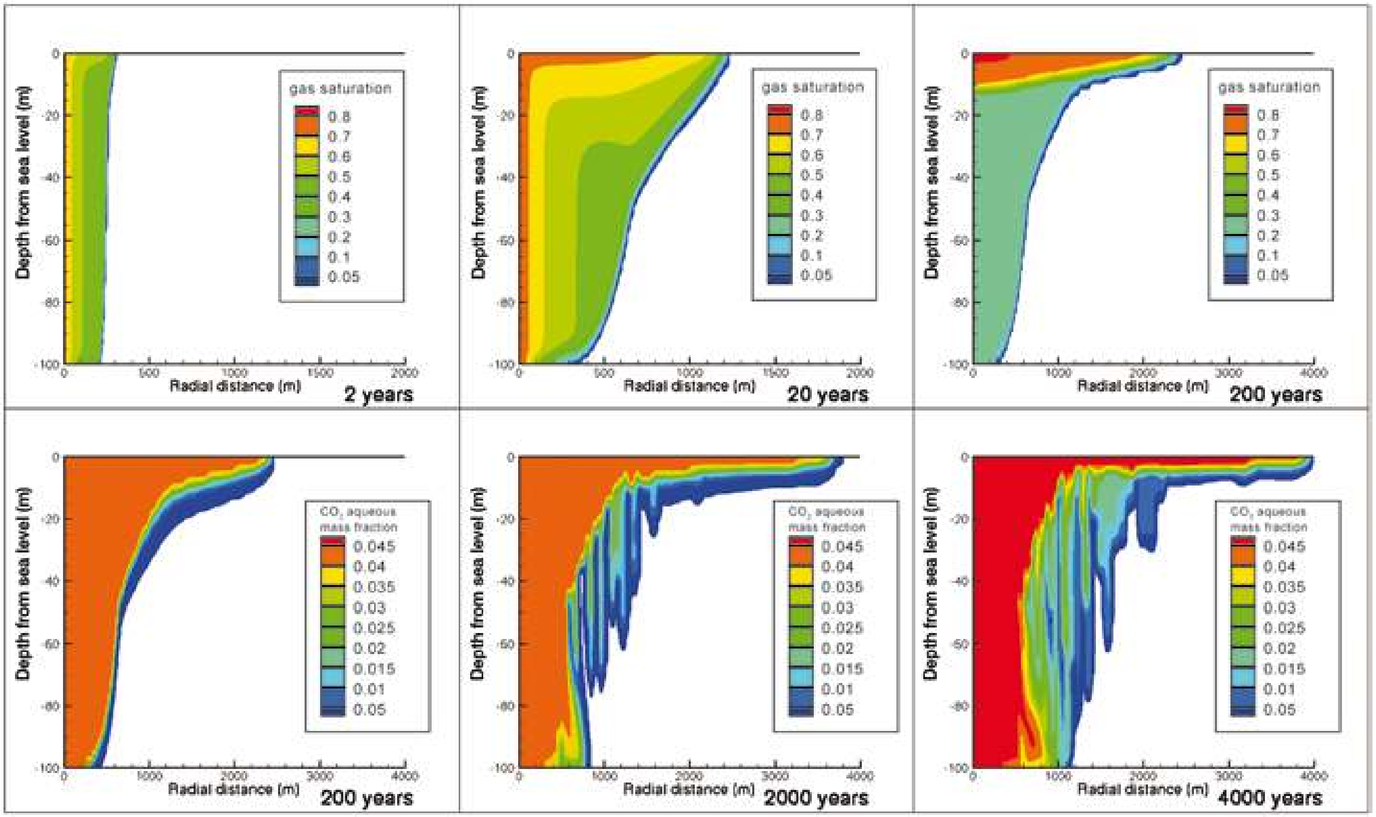

Figure 5.7 Radial simulations of CO_2 injection into a homogeneous formation 100 m thick, at a depth of 1 km, where the pressure is 10 MPa and the temperature is 40°C. The injection rate is 1 $MtCO_2$ yr^{-1} for 20 years, the horizontal permeability is 10^{-13} m^2 (approximately 100 mD) and the vertical permeability is one-tenth of that. The residual CO_2 saturation is 20%. The first three parts of the figure at 2, 20 and 200 years, show the gas saturation in the porous medium; the second three parts of the figure at 200, 2000 and 4000 years, show the mass fraction of dissolved CO_2 in the aqueous phase (after Ennis-King and Paterson, 2003).

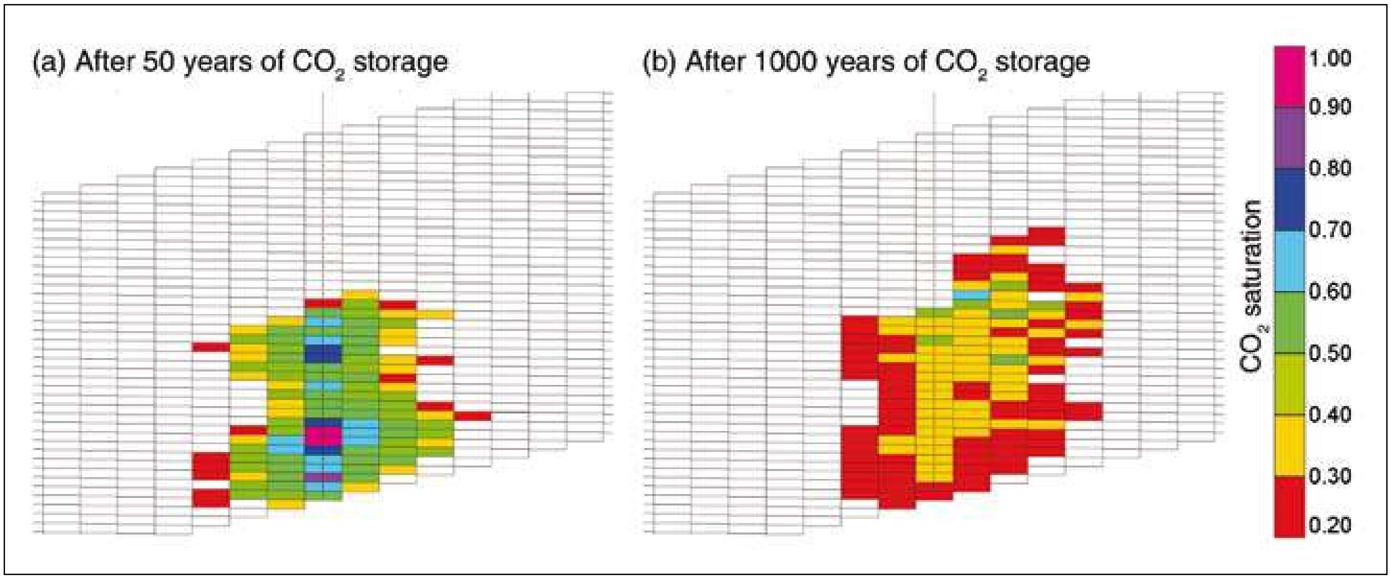

Figure 5.8 Simulation of 50 years of injection of CO_2 into the base of a saline formation. Capillary forces trap CO_2 in the pore spaces of sedimentary rocks. (a) After the 50-year injection period, most CO_2 is still mobile, driven upwards by buoyancy forces. (b) After 1000 years, buoyancy-driven flow has expanded the volume affected by CO_2 and much is trapped as residual CO_2 saturation or dissolved in brine (not shown). Little CO_2 is mobile and all CO_2 is contained within the aquifer (after Kumar et al., 2005).

Paterson, 2003), although appropriate reservoir engineering can accelerate or modify solubility trapping (Keith *et al*., 2005).

5.2.2 CO_2 storage mechanisms in geological formations

The effectiveness of geological storage depends on a combination of physical and geochemical trapping mechanisms (Figure 5.9). The most effective storage sites are those where CO_2 is immobile because it is trapped permanently under a thick, low-permeability seal or is converted to solid minerals or is adsorbed on the surfaces of coal micropores or through a combination of physical and chemical trapping mechanisms.

5.2.2.1 Physical trapping: stratigraphic and structural

Initially, physical trapping of CO_2 below low-permeability seals (caprocks), such as very-low-permeability shale or salt beds, is the principal means to store CO_2 in geological formations (Figure 5.3). In some high latitude areas, shallow gas hydrates may conceivably act as a seal. Sedimentary basins have such closed, physically bound traps or structures, which are occupied mainly by saline water, oil and gas. Structural traps include those formed by folded or fractured rocks. Faults can act as permeability barriers in some circumstances and as preferential pathways for fluid flow in other circumstances (Salvi *et al*., 2000). Stratigraphic traps are formed by changes in rock type caused by variation in the setting where the rocks were deposited. Both of these types of traps are suitable for CO_2 storage, although, as discussed in Section 5.5, care must be taken not to exceed the allowable overpressure to avoid fracturing the caprock or re-activating faults (Streit *et al*., 2005).

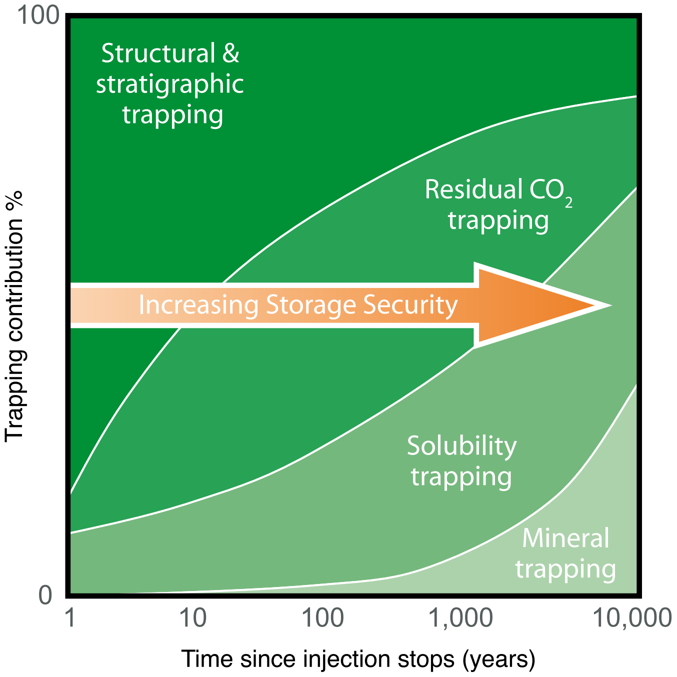

Figure 5.9 Storage security depends on a combination of physical and geochemical trapping. Over time, the physical process of residual CO_2 trapping and geochemical processes of solubility trapping and mineral trapping increase.

5.2.2.2 Physical trapping: hydrodynamic

Hydrodynamic trapping can occur in saline formations that do not have a closed trap, but where fluids migrate very slowly over long distances. When CO_2 is injected into a formation, it displaces saline formation water and then migrates buoyantly upwards, because it is less dense than the water. When it reaches the top of the formation, it continues to migrate as a separate phase until it is trapped as residual CO_2 saturation or in local structural or stratigraphic traps within the sealing formation. In the longer term, significant quantities of CO_2 dissolve in the formation water and then migrate with the groundwater. Where the distance from the deep injection site to the end of the overlying impermeable formation is hundreds of kilometres, the time scale for fluid to reach the surface from the deep basin can be millions of years (Bachu *et al*., 1994).

5.2.2.3 Geochemical trapping

Carbon dioxide in the subsurface can undergo a sequence of geochemical interactions with the rock and formation water that will further increase storage capacity and effectiveness. First, when CO_2 dissolves in formation water, a process commonly called solubility trapping occurs. The primary benefit of solubility trapping is that once CO_2 is dissolved, it no longer exists as a separate phase, thereby eliminating the buoyant forces that drive it upwards. Next, it will form ionic species as the rock dissolves, accompanied by a rise in the pH. Finally, some fraction may be converted to stable carbonate minerals (mineral trapping), the most permanent form of geological storage (Gunter *et al*., 1993). Mineral trapping is believed to be comparatively slow, potentially taking a thousand years or longer. Nevertheless, the permanence of mineral storage, combined with the potentially large storage capacity present in some geological settings, makes this a desirable feature of long-term storage.

Dissolution of CO_2 in formation waters can be represented by the chemical reaction:

$$CO_2\,(g) + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+$$

The CO_2 solubility in formation water decreases as temperature and salinity increase. Dissolution is rapid when formation water and CO_2 share the same pore space, but once the formation fluid is saturated with CO_2, the rate slows and is controlled by diffusion and convection rates.

CO_2 dissolved in water produces a weak acid, which reacts with the sodium and potassium basic silicate or calcium, magnesium and iron carbonate or silicate minerals in the reservoir or formation to form bicarbonate ions by chemical reactions approximating to:

$$3\text{ K-feldspar} + 2H_2O + 2CO_2 \leftrightarrow \text{Muscovite} + 6\text{ Quartz} + 2K^+ + 2HCO_3^-$$

Reaction of the dissolved CO_2 with minerals can be rapid (days) in the case of some carbonate minerals, but slow (hundreds to thousands of years) in the case of silicate minerals.

Formation of carbonate minerals occurs from continued reaction of the bicarbonate ions with calcium, magnesium and iron from silicate minerals such as clays, micas, chlorites and feldspars present in the rock matrix (Gunter *et al*., 1993, 1997).

Perkins *et al*. (2005) estimate that over 5000 years, all the CO_2 injected into the Weyburn Oil Field will dissolve or be converted to carbonate minerals within the storage formation. Equally importantly, they show that the caprock and overlying rock formations have an even greater capacity for mineralization. This is significant for leakage risk assessment (Section 5.7) because once CO_2 is dissolved, it is unavailable for leakage as a discrete phase. Modelling by Holtz (2002) suggests more than 60% of CO_2 is trapped by residual CO_2 trapping by the end of the injection phase (100% after 1000 years), although laboratory experiments (Section 5.2.1) suggest somewhat lower percentages. When CO_2 is trapped at residual saturation, it is effectively immobile. However, should there be leakage through the caprock, then saturated brine may degas as it is depressurized, although, as illustrated in Figure 5.7 the tendency of saturated brine is to sink rather than to rise. Reaction of the CO_2 with formation water and rocks may result in reaction products that affect the porosity of the rock and the

Box 5.4 Storage security mechanisms and changes over time.

When the CO_2 is injected, it forms a bubble around the injection well, displacing the mobile water and oil both laterally and vertically within the injection horizon. The interactions between the water and CO_2 phase allow geochemical trapping mechanisms to take effect. Over time, CO_2 that is not immobilized by residual CO_2 trapping can react with *in situ* fluid to form carbonic acid (i.e., H_2CO_3 called solubility trapping – dominates from tens to hundreds of years). Dissolved CO_2 can eventually react with reservoir minerals if an appropriate mineralogy is encountered to form carbon-bearing ionic species (i.e., HCO_3^- and CO_3^{2-} called ionic trapping – dominates from hundreds to thousands of years). Further breakdown of these minerals could precipitate new carbonate minerals that would fix injected CO_2 in its most secure state (i.e., mineral trapping – dominates over thousands to millions of years).

Four injection scenarios are shown in Figure 5.10. Scenarios A, B and C show injection into hydrodynamic traps, essentially systems open to lateral flow of fluids and gas within the injection horizon. Scenario D represents injection into a physically restricted flow regime, similar to those of many producing and depleted oil and gas reservoirs.

In Scenario A, the injected CO_2 is never physically contained laterally. The CO_2 plume migrates within the injection horizon and is ultimately consumed via all types of geochemical trapping mechanisms, including carbonate mineralization. Mineral and ionic trapping dominate. The proportions of CO_2 stored in each geochemical trap will depend strongly on the *in situ* mineralogy, pore space structure and water composition.

In Scenario B, the migration of the CO_2 plume is similar to that of Scenario A, but the mineralogy and water chemistry are such that reaction of CO_2 with minerals is minor and solubility trapping and hydrodynamic trapping dominate.

In Scenario C, the CO_2 is injected into a zone initially similar to Scenario B. However, during lateral migration the CO_2 plume migrates into a zone of physical heterogeneity in the injection horizon. This zone may be characterized by variable porosity and permeability caused by a facies change. The facies change is accompanied by a more reactive mineralogy that causes an abrupt change in path. In the final state, ionic and mineral trapping predominate.

Scenario D illustrates CO_2 injection into a well-constrained flow zone but, similar to Scenario B, it does not have *in-situ* fluid chemistry and mineralogy suitable for ionic or mineral trapping. The bulk of the injected CO_2 is trapped geochemically via solubility trapping and physically via stratigraphic or structural trapping.

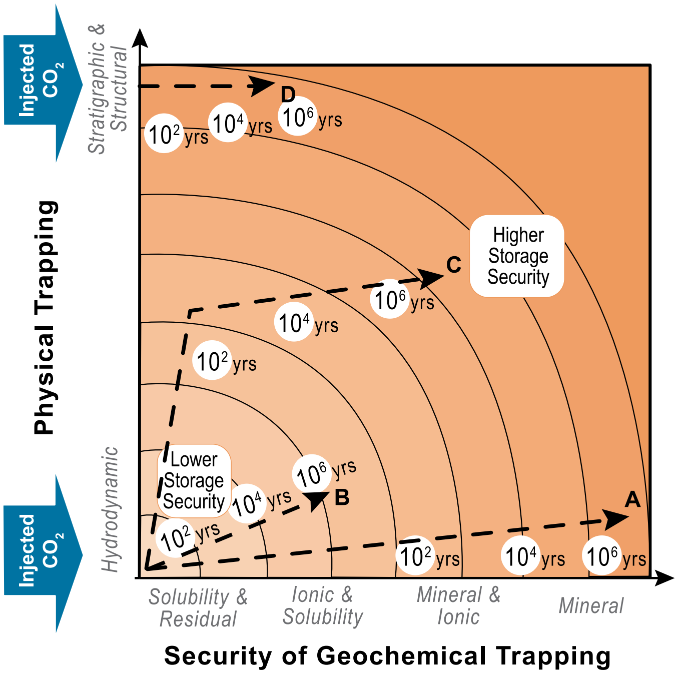

Figure 5.10 Storage expressed as a combination of physical and geochemical trapping. The level of security is proportional to distance from the origin. Dashed lines are examples of million-year pathways, discussed in Box 5.4.

flow of solution through the pores. This possibility has not, however, been observed experimentally and its possible effects cannot be quantified.

Yet another type of fixation occurs when CO_2 is preferentially adsorbed onto coal or organic-rich shales (Section 5.3.4). This has been observed in batch and column experiments in the laboratory, as well as in field experiments at the Fenn Big Valley, Canada and the San Juan Basin, USA (Box 5.7). A rather different form of fixation can occur when CO_2 hydrate is formed in the deep ocean seafloor and onshore in permafrost regions (Koide *et al*., 1997).

5.2.3 Natural geological accumulations of CO_2

Natural sources of CO_2 occur, as gaseous accumulations of CO_2, CO_2 mixed with natural gas and CO_2 dissolved in formation water (Figure 5.11). These natural accumulations have been studied in the United States, Australia and Europe (Pearce *et al*., 1996; Allis *et al*., 2001; Stevens *et al*., 2003; Watson *et al*., 2004) as analogues for storage of CO_2, as well as for leakage from engineered storage sites. Production of CO_2 for EOR and other uses provides operational experience relevant to CO_2 capture and storage. There are, of course, differences between natural accumulations of CO_2 and engineered CO_2 storage sites: natural accumulations of CO_2 collect over very long periods of time and at random sites, some of which might be naturally 'leaky'. At engineered sites, CO_2 injection rates will be rapid and the sites will necessarily be penetrated by injection wells (Celia and Bachu, 2003; Johnson *et al*., 2005). Therefore, care must be taken to keep injection pressures low enough to avoid damaging the caprock (Section 5.5) and to make sure that the wells are properly sealed (Section 5.5).

Natural accumulations of relatively pure CO_2 are found all over the world in a range of geological settings, particularly in sedimentary basins, intra-plate volcanic regions (Figure 5.11) and in faulted areas or in quiescent volcanic structures. Natural accumulations occur in a number of different types of sedimentary rocks, principally limestones, dolomites and sandstones and with a variety of seals (mudstone, shale, salt and anhydrite) and a range of trap types, reservoir depths and CO_2-bearing phases.

Carbon dioxide fields in the Colorado Plateau and Rocky Mountains, USA, are comparable to conventional natural gas reservoirs (Allis *et al*., 2001). Studies of three of these fields (McElmo Dome, St. Johns Field and Jackson Dome) have shown that each contains 1600 $MtCO_2$, with measurable leakage (Stevens *et al*., 2001a). Two hundred Mt trapped in the Pisgah Anticline, northeast of the Jackson Dome, is thought to have been generated more than 65 million years ago (Studlick *et al*., 1990), with no evidence of leakage, providing additional

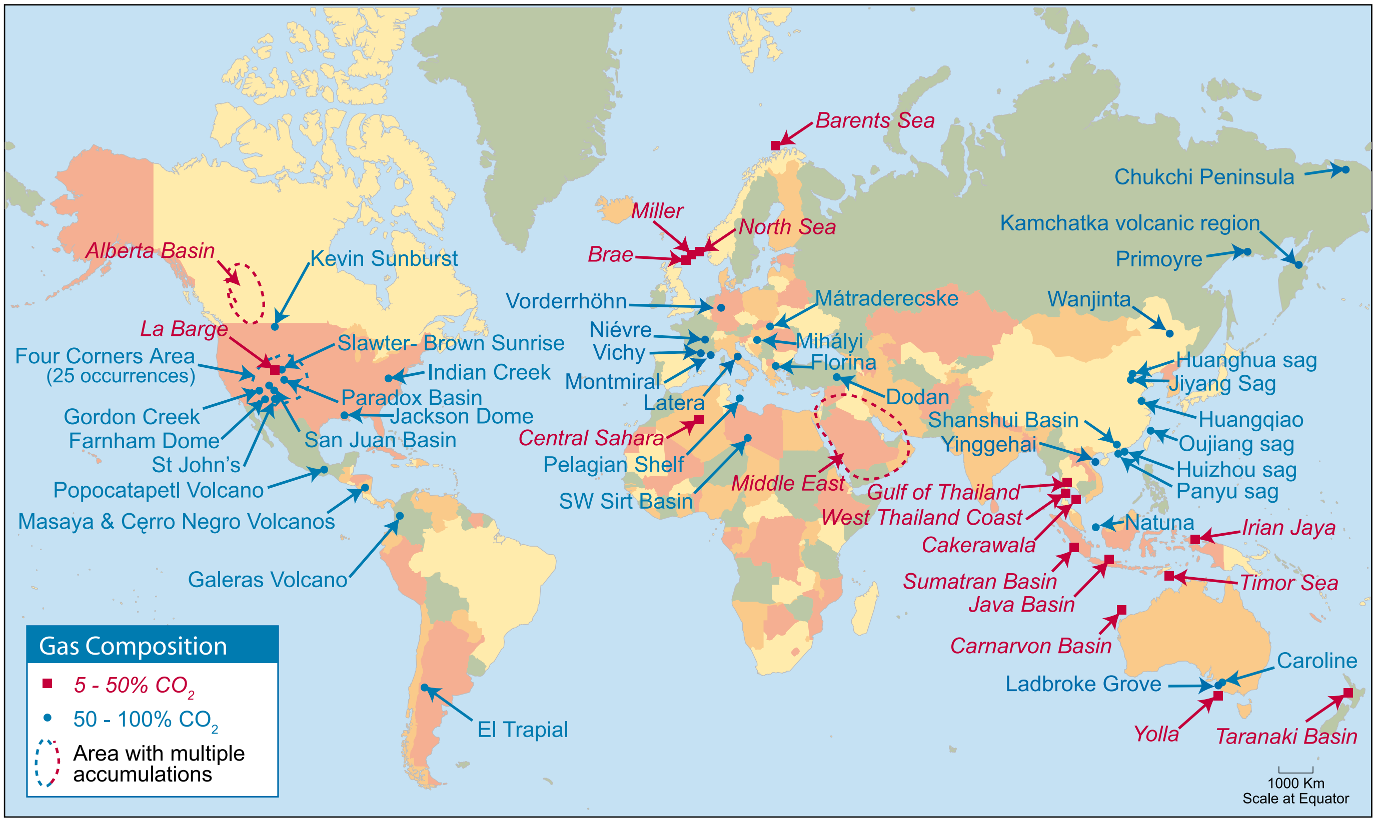

Figure 5.11 Examples of natural accumulations of CO_2 around the world. Regions containing many occurrences are enclosed by a dashed line. Natural accumulations can be useful as analogues for certain aspects of storage and for assessing the environmental impacts of leakage. Data quality is variable and the apparent absence of accumulations in South America, southern Africa and central and northern Asia is probably more a reflection of lack of data than a lack of CO_2 accumulations.

evidence of long-term trapping of CO_2. Extensive studies have been undertaken on small-scale CO_2 accumulations in the Otway Basin in Australia (Watson *et al*., 2004) and in France, Germany, Hungary and Greece (Pearce *et al*., 2003).

Conversely, some systems, typically spas and volcanic systems, are leaky and not useful analogues for geological storage. The Kileaua Volcano emits on average 4 $MtCO_2$ yr^{-1}. More than 1200 tCO_2 day^{-1} (438,000 tCO_2 yr^{-1}) leaked into the Mammoth Mountain area, California, between 1990 and 1995, with flux variations linked to seismicity (USGS, 2001b). Average flux densities of 80–160 tCO_2 m^{-2} yr^{-1} are observed near Matraderecske, Hungary, but along faults, the flux density can reach approximately 6600 t m^{-2} yr^{-1} (Pearce *et al*., 2003). These high seepage rates result from release of CO_2 from faulted volcanic systems, whereas a normal baseline CO_2 flux is of the order of 10–100 gCO_2 m^{-2} day^{-1} under temperate climate conditions (Pizzino *et al*., 2002). Seepage of CO_2 into Lake Nyos (Cameroon) resulted in CO_2 saturation of water deep in the lake, which in 1987 produced a very large-scale and (for more than 1700 persons) ultimately fatal release of CO_2 when the lake overturned (Kling *et al*., 1987). The overturn of Lake Nyos (a deep, stratified tropical lake) and release of CO_2 are not representative of the seepage through wells or fractures that may occur from underground geological storage sites. Engineered CO_2 storage sites will be chosen to minimize the prospect of leakage. Natural storage and events such as Lake Nyos are not representative of geological storage for predicting seepage from engineered sites, but can be useful for studying the health, safety and environmental effects of CO_2 leakage (Section 5.7.4).

Carbon dioxide is found in some oil and gas fields as a separate gas phase or dissolved in oil. This type of storage is relatively common in Southeast Asia, China and Australia, less common in other oil and gas provinces such as in Algeria, Russia, the Paradox Basin (USA) and the Alberta Basin (western Canada). In the North Sea and Barents Sea, a few fields have up to 10% CO_2, including Sleipner and Snohvit (Figure 5.11). The La Barge natural gas field in Wyoming, USA, has 3300 Mt of gas reserves, with an average of 65% CO_2 by volume. In the Appennine region of Italy, many deep wells (1–3 km depth) have trapped gas containing 90% or more CO_2 by volume. Major CO_2 accumulations around the South China Sea include the world's largest known CO_2 accumulation, the Natuna D Alpha field in Indonesia, with more than 9100 $MtCO_2$ (720 Mt natural gas). Concentrations of CO_2 can be highly variable between different fields in a basin and between different reservoir zones within the same field, reflecting complex generation, migration and mixing processes. In Australia's Otway Basin, the timing of CO_2 input and trapping ranges from 5000 years to a million years (Watson *et al*., 2004).

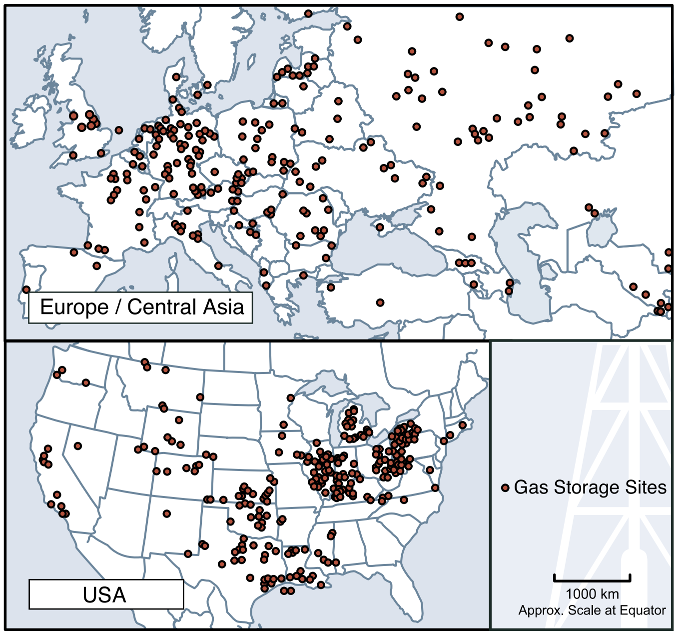

Figure 5.12 Location of some natural gas storage projects.

5.2.4 *Industrial analogues for CO_2 storage*

5.2.4.1 Natural gas storage

Underground natural gas storage projects that offer experience relevant to CO_2 storage (Lippmann and Benson, 2003; Perry, 2005) have operated successfully for almost 100 years and in many parts of the world (Figure 5.12). These projects provide for peak loads and balance seasonal fluctuations in gas supply and demand. The Berlin Natural Gas Storage Project is an example of this (Box 5.5). The majority of gas storage projects are in depleted oil and gas reservoirs and saline formations, although caverns in salt have also been used extensively. A number of factors are critical to the success of these projects, including a suitable and adequately characterized site (permeability, thickness and extent of storage reservoir, tightness of caprock, geological structure, lithology, etc.). Injection wells must be properly designed, installed, monitored and maintained and abandoned wells in and near the project must be located and plugged. Finally, taking into account a range of solubility, density and trapping conditions, overpressuring the storage reservoir (injecting gas at a pressure that is well in excess of the in situ formation pressure) must be avoided.

While underground natural gas storage is safe and effective, some projects have leaked, mostly caused by poorly completed or improperly plugged and abandoned wells and by leaky faults (Gurevich *et al*., 1993; Lippmann and Benson, 2003; Perry, 2005). Abandoned oil and gas fields are easier to assess as natural gas storage sites than are saline formations, because the geological structure and caprock are usually well characterized from existing wells. At most natural gas storage sites, monitoring requirements focus on ensuring that the injection well is not leaking (by the use of pressure measurements and through *in situ* downhole measurements of temperature, pressure, noise/sonic, casing conditions, etc.). Observation wells are sometimes used to verify that gas has not leaked into shallower strata.

Box 5.5 The Berlin Natural Gas Storage Facility.

The Berlin Natural Gas Storage Facility is located in central Berlin, Germany, in an area that combines high population density with nature and water conservation reservations. This facility, with a capacity of 1085 million m^3, was originally designed to be a reserve natural gas storage unit for limited seasonal quantity equalization. A storage production rate of 450,000 $m^3 h^{-1}$ can be achieved with the existing storage wells and surface facilities. Although the geological and engineering aspects and scale of the facility make it a useful analogue for a small CO_2 storage project, this project is more complex because the input and output for natural gas is highly variable, depending on consumer demand. The risk profiles are also different, considering the highly flammable and explosive nature of natural gas and conversely the reactive nature of CO_2.

The facility lies to the east of the North German Basin, which is part of a complex of basin structures extending from The Netherlands to Poland. The sandstone storage horizons are at approximately 800 m below sea level. The gas storage layers are covered with layers of claystone, anhydrite and halite, approximately 200 m thick. This site has complicated tectonics and heterogeneous reservoir lithologies.

Twelve wells drilled at three sites are available for natural gas storage operation. The varying storage sand types also require different methods of completion of the wells. The wells also have major differences in their production behaviour. The wellheads of the storage wells and of the water disposal wells are housed in 5 m deep cellars covered with concrete plates, with special steel covers over the wellheads to allow for wireline logging. Because of the urban location, a total of 16 deviated storage wells and water disposal wells were concentrated at four sites. Facilities containing substances that could endanger water are set up within fluid-tight concrete enclosures and/or have their own watertight concrete enclosures.

5.2.4.2 Acid gas injection

Acid gas injection operations represent a commercial analogue for some aspects of geological CO_2 storage. Acid gas is a mixture of H_2S and CO_2, with minor amounts of hydrocarbon gases that can result from petroleum production or processing. In Western Canada, operators are increasingly turning to acid gas disposal by injection into deep geological formations. Although the purpose of the acid gas injection operations is to dispose of H_2S, significant quantities of CO_2 are injected at the same time because it is uneconomic to separate the two gases.

Currently, regulatory agencies in Western Canada approve the maximum H_2S fraction, maximum wellhead injection pressure and rate and maximum injection volume. Acid gas is currently injected into 51 different formations at 44 different locations across the Alberta Basin in the provinces of Alberta and British Columbia (Figure 5.13). Carbon dioxide often represents the largest component of the injected acid gas stream, in many cases, 14–98% of the total volume. A total of 2.5 $MtCO_2$ and 2 MtH_2S had been injected in Western Canada by the end of 2003, at rates of 840–500,720 m^3 day^{-1} per site, with an aggregate injection rate in 2003 of 0.45 $MtCO_2$ yr^{-1} and 0.55 MtH_2S yr^{-1}, with no detectable leakage.

Acid gas injection in Western Canada occurs over a wide range of formation and reservoir types, acid gas compositions and operating conditions. Injection takes place in deep saline formations at 27 sites, into depleted oil and/or gas reservoirs at 19 sites and into the underlying water leg of depleted oil and gas reservoirs at 4 sites. Carbonates form the reservoir at 29 sites and quartz-rich sandstones dominate at the remaining 21 (Figure 5.13). In most cases, shale constitutes the overlying confining unit (caprock), with the remainder of the injection zones being confined by tight limestones, evaporites and anhydrites.

Since the first acid-gas injection operation in 1990, 51 different injection sites have been approved, of which 44 are currently active. One operation was not implemented, three were rescinded after a period of operation (either because injection volumes reached the approved limit or because the gas plant producing the acid gas was decommissioned) and three sites were suspended by the regulatory agency because of reservoir overpressuring.

5.2.4.3 Liquid waste injection

In many parts of the world, large volumes of liquid waste are injected into the deep subsurface every day. For example, for the past 60 years, approximately 9 billion gallons (34.1 million m^3) of hazardous waste is injected into saline formations in the United States from about 500 wells each year. In addition, more than 750 billion gallons (2843 million m^3) of oil field brines are injected from 150,000 wells each year. This combined annual US injectate volume of about 3000 million m^3, when converted to volume equivalent, corresponds to the volume of approximately 2 $GtCO_2$ at a depth of 1 km. Therefore, the experience gained from existing deep-fluid-injection projects is relevant in terms of the style of operation and is of a similar magnitude to that which may be required for geological storage of CO_2.

5.2.5 Security and duration of CO_2 storage in geological formations

Evidence from oil and gas fields indicates that hydrocarbons and other gases and fluids including CO_2 can remain trapped for millions of years (Magoon and Dow, 1994; Bradshaw *et al.*, 2005). Carbon dioxide has a tendency to remain in the subsurface (relative to hydrocarbons) via its many physico-chemical immobilization mechanisms. World-class petroleum provinces have storage times for oil and gas of 5–100 million years, others for 350 million years, while some minor petroleum

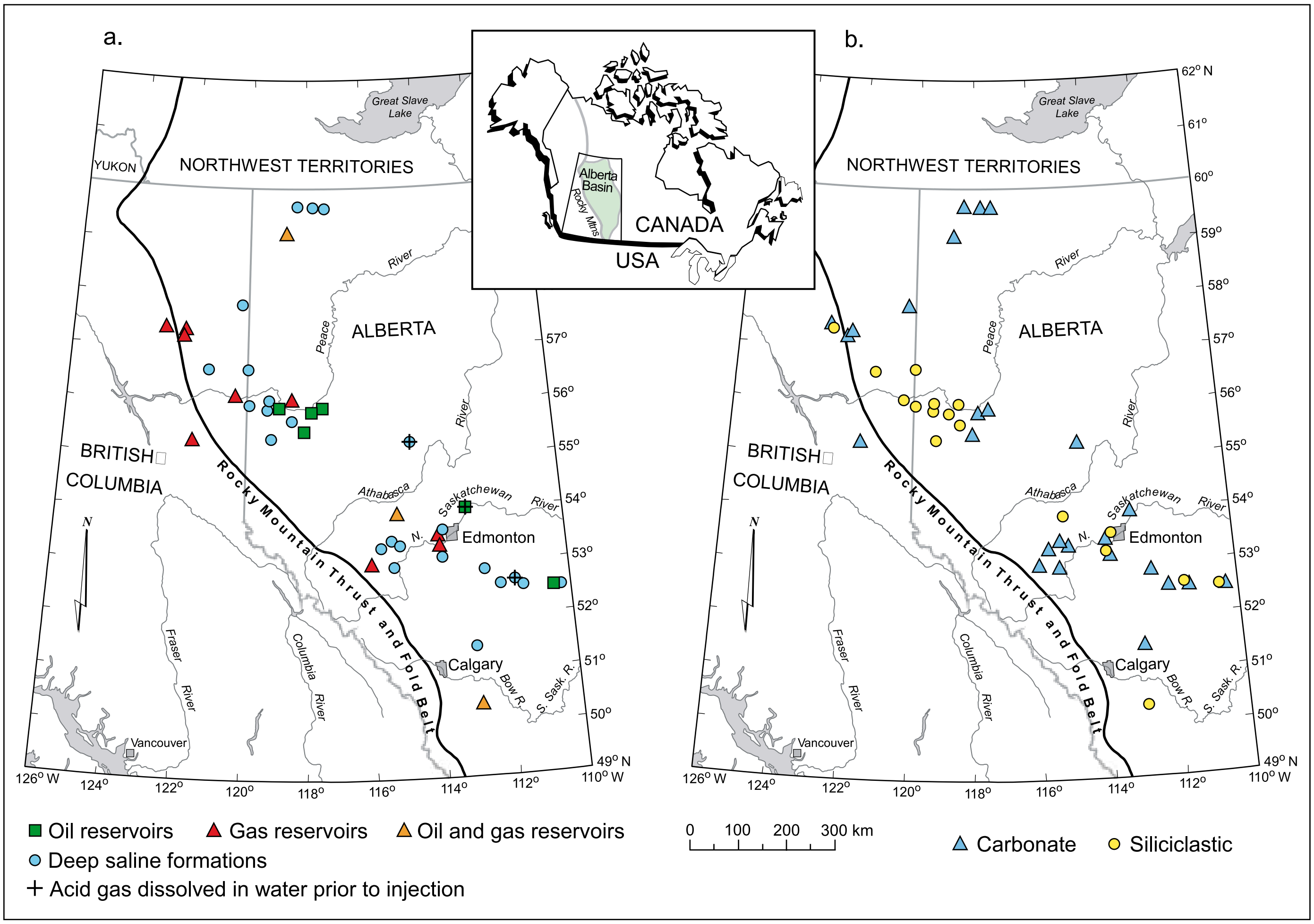

Figure 5.13 Locations of acid gas injection sites in the Alberta Basin, Canada: (a) classified by injection unit; (b) the same locations classified by rock type (from Bachu and Haug, 2005).

accumulations have been stored for up to 1400 million years. However, some natural traps do leak, which reinforces the need for careful site selection (Section 5.3), characterization (Section 5.4) and injection practices (Section 5.5).

5.3 Storage formations, capacity and geographical distribution

In this section, the following issues are addressed: In what types of geological formations can CO_2 be stored? Are such formations widespread? How much CO_2 can be geologically stored?

5.3.1 General site-selection criteria

There are many sedimentary regions in the world (Figures 2.4–2.6 and Figure 5.14) variously suited for CO_2 storage. In general, geological storage sites should have (1) adequate capacity and injectivity, (2) a satisfactory sealing caprock or confining unit and (3) a sufficiently stable geological environment to avoid compromising the integrity of the storage site. Criteria for assessing basin suitability (Bachu, 2000, 2003; Bradshaw *et al.*, 2002) include: basin characteristics (tectonic activity, sediment type, geothermal and hydrodynamic regimes); basin resources (hydrocarbons, coal, salt), industry maturity and infrastructure; and societal issues such as level of development, economy, environmental concerns, public education and attitudes.

The suitability of sedimentary basins for CO_2 storage depends in part on their location on the continental plate. Basins formed in mid-continent locations or near the edge of stable continental plates, are excellent targets for long-term CO_2 storage because of their stability and structure. Such basins are found within most continents and around the Atlantic, Arctic and Indian Oceans. The storage potential of basins found behind mountains formed by plate collision is likely to be good and these include the Rocky Mountain, Appalachian and Andean basins in the Americas, European basins immediately north of the Alps and Carpathians and west of the Urals and those located south of the Zagros and Himalayas in Asia. Basins located in tectonically active areas, such as those around the Pacific Ocean or the northern Mediterranean, may be less suitable for CO_2 storage and sites in these regions must be selected carefully because of the potential for CO_2 leakage (Chiodini *et al.*, 2001; Granieri *et al.*, 2003). Basins located on the edges of plates

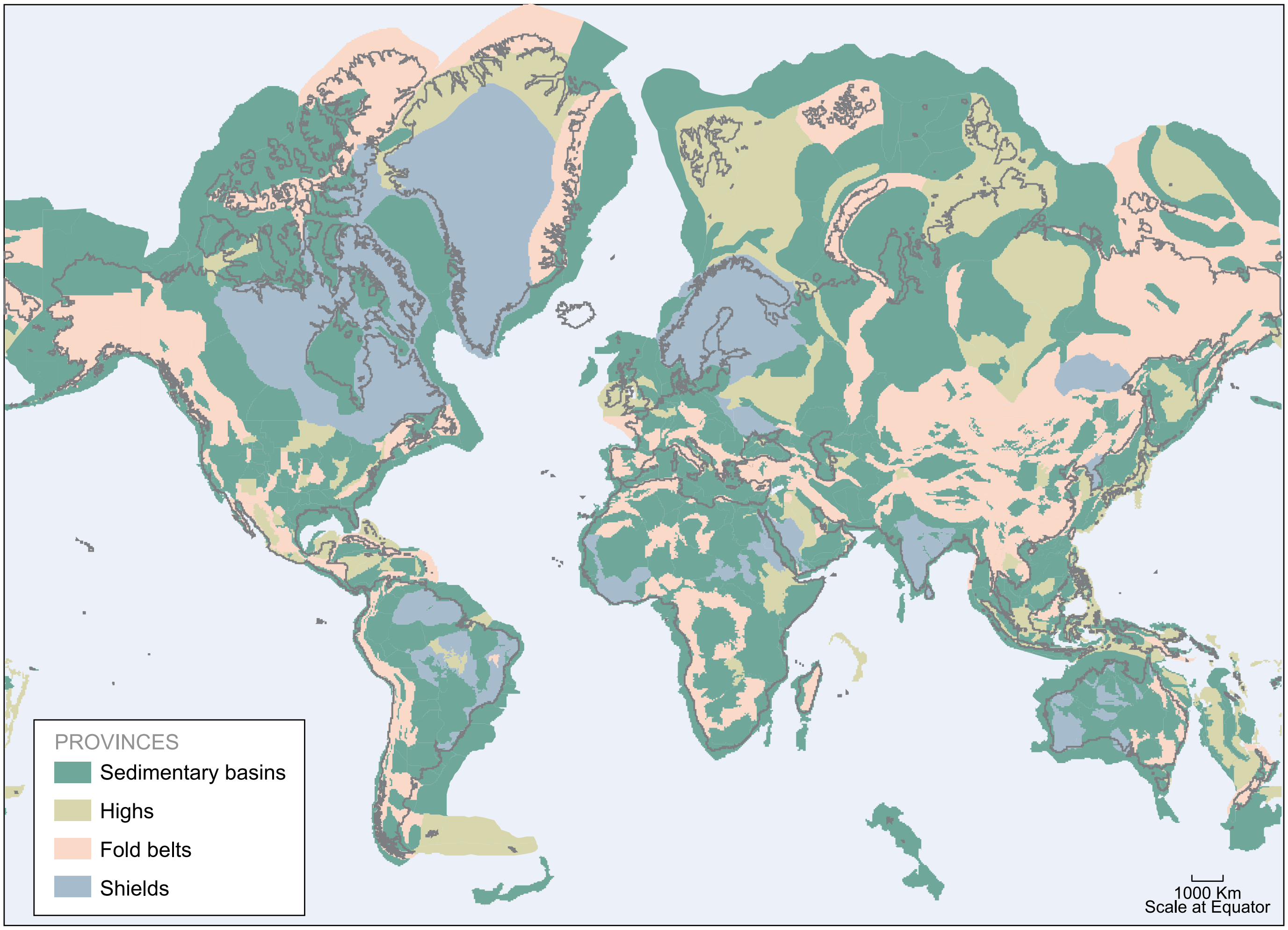

Figure 5.14 Distribution of sedimentary basins around the world (after Bradshaw and Dance, 2005; and USGS, 2001a). In general, sedimentary basins are likely to be the most prospective areas for storage sites. However, storage sites may also be found in some areas of fold belts and in some of the highs. Shield areas constitute regions with low prospectivity for storage. The Mercator projection used here is to provide comparison with Figures 5.1, 5.11 and 5.27. The apparent dimensions of the sedimentary basins, particularly in the northern hemisphere, should not be taken as an indication of their likely storage capacity.

where subduction is occurring or between active mountain ranges, are likely to be strongly folded and faulted and provide less certainty for storage. However, basins must be assessed on an individual basis. For example, the Los Angeles Basin and Sacramento Valley in California, where significant hydrocarbon accumulations have been found, have demonstrated good local storage capacity. Poor CO_2 storage potential is likely to be exhibited by basins that (1) are thin (≤1000 m), (2) have poor reservoir and seal relationships, (3) are highly faulted and fractured, (4) are within fold belts, (5) have strongly discordant sequences, (6) have undergone significant diagenesis or (7) have overpressured reservoirs.

The efficiency of CO_2 storage in geological media, defined as the amount of CO_2 stored per unit volume (Brennan and Burruss, 2003), increases with increasing CO_2 density. Storage safety also increases with increasing density, because buoyancy, which drives upward migration, is stronger for a lighter fluid. Density increases significantly with depth while CO_2 is in gaseous phase, increases only slightly or levels off after passing from the gaseous phase into the dense phase and may even decrease with a further increase in depth, depending on the temperature gradient (Ennis-King and Paterson, 2001; Bachu, 2003). 'Cold' sedimentary basins, characterized by low temperature gradients, are more favourable for CO_2 storage (Bachu, 2003) because CO_2 attains higher density at shallower depths (700–1000 m) than in 'warm' sedimentary basins, characterized by high temperature gradients where dense-fluid conditions are reached at greater depths (1000–1500 m). The depth of the storage formation (leading to increased drilling and compression costs for deeper formations) may also influence the selection of storage sites.

Adequate porosity and thickness (for storage capacity) and permeability (for injectivity) are critical; porosity usually decreases with depth because of compaction and cementation, which reduces storage capacity and efficiency. The storage formation should be capped by extensive confining units (such as shale, salt or anhydrite beds) to ensure that CO_2 does not escape into overlying, shallower rock units and ultimately to the surface. Extensively faulted and fractured sedimentary basins or parts thereof, particularly in seismically active areas, require careful characterization to be good candidates for CO_2 storage, unless the faults and fractures are sealed and CO_2 injection will not open them (Holloway, 1997; Zarlenga *et al*., 2004).

The pressure and flow regimes of formation waters in a sedimentary basin are important factors in selecting sites for CO_2 storage (Bachu *et al*., 1994). Injection of CO_2 into formations overpressured by compaction and/or hydrocarbon generation may raise technological and safety issues that make them unsuitable. Underpressured formations in basins located mid-continent, near the edge of stable continental plates or behind mountains formed by plate collision may be well suited for CO_2 storage. Storage of CO_2 in deep saline formations with fluids having long residence times (millions of years) is conducive to hydrodynamic and mineral trapping (Section 5.2).

The possible presence of fossil fuels and the exploration and production maturity of a basin are additional considerations for selection of storage sites (Bachu, 2000). Basins with little exploration for hydrocarbons may be uncertain targets for CO_2 storage because of limited availability of geological information or potential for contamination of as-yet-undiscovered hydrocarbon resources. Mature sedimentary basins may be prime targets for CO_2 storage because: (1) they have well-known characteristics; (2) hydrocarbon pools and/or coal beds have been discovered and produced; (3) some petroleum reservoirs might be already depleted, nearing depletion or abandoned as uneconomic; (4) the infrastructure needed for CO_2 transport and injection may already be in place. The presence of wells penetrating the subsurface in mature sedimentary basins can create potential CO_2 leakage pathways that may compromise the security of a storage site (Celia and Bachu, 2003). Nevertheless, at Weyburn, despite the presence of many hundreds of existing wells, after four years of CO_2 injection there has been no measurable leakage (Strutt *et al*., 2003).

5.3.2 *Oil and gas fields*

5.3.2.1 *Abandoned oil and gas fields*

Depleted oil and gas reservoirs are prime candidates for CO_2 storage for several reasons. First, the oil and gas that originally accumulated in traps (structural and stratigraphic) did not escape (in some cases for many millions of years), demonstrating their integrity and safety. Second, the geological structure and physical properties of most oil and gas fields have been extensively studied and characterized. Third, computer models have been developed in the oil and gas industry to predict the movement, displacement behaviour and trapping of hydrocarbons. Finally, some of the infrastructure and wells already in place may be used for handling CO_2 storage operations. Depleted fields will not be adversely affected by CO_2 (having already contained hydrocarbons) and if hydrocarbon fields are still in production, a CO_2 storage scheme can be optimized to enhance oil (or gas) production. However, plugging of abandoned wells in many mature fields began many decades ago when wells were simply filled with a mud-laden fluid. Subsequently, cement plugs were required to be strategically placed within the wellbore, but not with any consideration that they may one day be relied upon to contain a reactive and potentially buoyant fluid such as CO_2. Therefore, the condition of wells penetrating the caprock must be assessed (Winter and Bergman, 1993). In many cases, even locating the wells may be difficult and caprock integrity may need to be confirmed by pressure and tracer monitoring.

The capacity of a reservoir will be limited by the need to avoid exceeding pressures that damage the caprock (Section 5.5.3). Reservoirs should have limited sensitivity to reductions in permeability caused by plugging of the near-injector region and by reservoir stress fluctuations (Kovscek, 2002; Bossie-Codreanu *et al*., 2003). Storage in reservoirs at depths less than approximately 800 m may be technically and economically feasible, but the low storage capacity of shallow reservoirs, where CO_2 may be in the gas phase, could be problematic.

5.3.2.2 *Enhanced oil recovery*

Enhanced oil recovery (EOR) through CO_2 flooding (by injection) offers potential economic gain from incremental oil production. Of the original oil in place, 5–40% is usually recovered by conventional primary production (Holt *et al*., 1995). An additional 10–20% of oil in place is produced by secondary recovery that uses water flooding (Bondor, 1992). Various miscible agents, among them CO_2, have been used for enhanced (tertiary) oil recovery or EOR, with an incremental oil recovery of 7–23% (average 13.2%) of the original oil in place (Martin and Taber, 1992; Moritis, 2003). Descriptions of CO_2-EOR projects are provided in Box 5.3 and Box 5.6, and an illustration is given in Figure 5.15.

Many CO_2 injection schemes have been suggested, including continuous CO_2 injection or alternate water and CO_2 gas injection (Klins and Farouq Ali, 1982; Klins, 1984). Oil displacement by CO_2 injection relies on the phase behaviour of CO_2 and crude oil mixtures that are strongly dependent on reservoir temperature, pressure and crude oil composition. These mechanisms range from oil swelling and viscosity reduction for injection of immiscible fluids (at low pressures) to completely miscible displacement in high-pressure applications. In these applications, more than 50% and up to 67% of the injected CO_2 returns with the produced oil (Bondor, 1992) and is usually separated and re-injected into the reservoir to minimize operating costs. The remainder is trapped in the oil reservoir by various means, such as irreducible saturation and dissolution in reservoir oil that it is not produced and in pore space that is not connected to the flow path for the producing wells.

For enhanced CO_2 storage in EOR operations, oil reservoirs may need to meet additional criteria (Klins, 1984; Taber *et al*., 1997; Kovscek, 2002; Shaw and Bachu, 2002). Generally, reservoir depth must be more than 600 m. Injection of immiscible fluids must often suffice for heavy- to-medium-gravity oils (oil gravity 12–25 API). The more desirable miscible flooding is applicable to light, low-viscosity oils (oil gravity 25–48 API). For miscible floods, the reservoir pressure must be higher than the minimum miscibility pressure (10–15 MPa) needed for achieving miscibility between reservoir oil and CO_2, depending on oil composition and gravity, reservoir temperature and CO_2 purity (Metcalfe, 1982). To achieve effective removal of the

Box 5.6 The Rangely, Colorado, CO_2-EOR Project.

The Rangely CO_2-EOR Project is located in Colorado, USA and is operated by Chevron. The CO_2 is purchased from the Exxon-Mobil LaBarge natural gas processing facility in Wyoming and transported 283 km via pipeline to the Rangely field. Additional spurs carry CO_2 over 400 km from LaBarge to Lost Soldier and Wertz fields in central Wyoming, currently ending at the Salt Creek field in eastern Wyoming.

The sandstone reservoir of the Rangely field has been CO_2 flooded, by the water alternating gas (WAG) process, since 1986. Primary and secondary recovery, carried out between 1944 and 1986, recovered 1.9 US billion barrels (302 million m^3) of oil (21% of the original oil in place). With use of CO_2 floods, ultimate tertiary recovery of a further 129 million barrels (21 million m^3) of oil (6.8% of original oil in place) is expected. Average daily CO_2 injection in 2003 was equivalent to 2.97 $MtCO_2$ yr^{-1}, with production of 13,913 barrels oil per day. Of the total 2.97 Mt injected, recycled gas comprised around 2.29 Mt and purchased gas about 0.74 Mt. Cumulative CO_2 stored to date is estimated at 22.2 Mt. A simplified flow diagram for the Rangely field is given in Figure 5.15.

The Rangely field, covering an area of 78 km^2, is an asymmetric anticline. A major northeast-to-southwest fault in the eastern half of the field and other faults and fractures significantly influence fluid movement within the reservoir. The sandstone reservoirs have an average gross and effective thickness of 160 m and 40 m, respectively and are comprised of six persistent producing sandstone horizons (depths of 1675–1980 m) with average porosity of 12%. Permeability averages 10 mD (Hefner and Barrow, 1992).

By the end of 2003, there were 248 active injectors, of which 160 are used for CO_2 injection and 348 active producers. Produced gas is processed through two parallel single-column natural-gas-liquids recovery facilities and subsequently compressed to approximately 14.5 MPa. Compressed-produced gas (recycled gas) is combined with purchased CO_2 for reinjection mostly by the WAG process.

Carbon dioxide-EOR operation in the field maintains compliance with government regulations for production, injection, protection of potable water formations, surface use, flaring and venting. A number of protocols have been instituted to ensure containment of CO_2 – for example, pre-injection well-integrity verification, a radioactive tracer survey run on the first injection, injection-profile tracer surveys, mechanical integrity tests, soil gas surveys and round-the-clock field monitoring. Surface release from the storage reservoir is below the detection limit of 170 t yr^{-1} or an annual leakage rate of less than 0.00076% of the total stored CO_2 (Klusman, 2003). Methane leakage is estimated to be 400 t yr^{-1}, possibly due to increased CO_2 injection pressure above original reservoir pressure. The water chemistry portion of the study indicates that the injected CO_2 is dissolving in the water and may be responsible for dissolution of ferroan calcite and dolomite. There is currently no evidence of mineral precipitation that may result in mineral storage of CO_2.

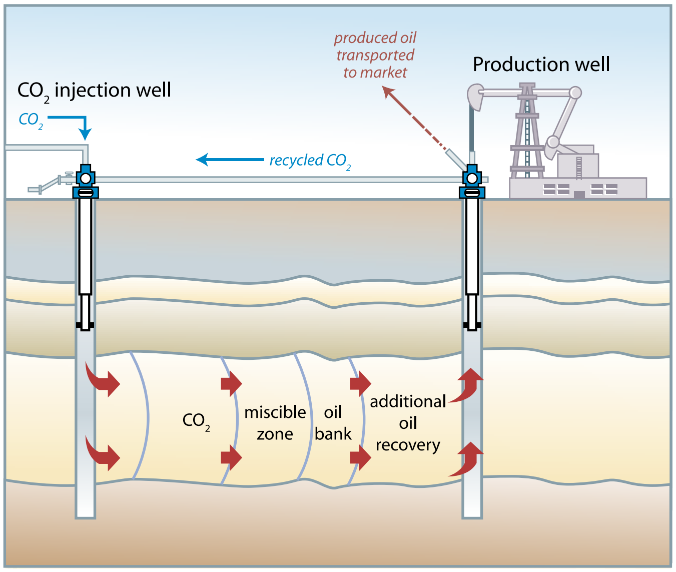

Figure 5.15 Injection of CO_2 for enhanced oil recovery (EOR) with some storage of retained CO_2 (after IEA Greenhouse Gas R&D Programme). The CO_2 that is produced with the oil is separated and re-injected back into the formation. Recycling of produced CO_2 decreases the amount of CO_2 that must be purchased and avoids emissions to the atmosphere.

oil, other preferred criteria for both types of flooding include relatively thin reservoirs (less than 20 m), high reservoir angle, homogenous formation and low vertical permeability. For horizontal reservoirs, the absence of natural water flow, major gas cap and major natural fractures are preferred. Reservoir thickness and permeability are not critical factors.

Reservoir heterogeneity also affects CO_2 storage efficiency. The density difference between the lighter CO_2 and the reservoir oil and water leads to movement of the CO_2 along the top of the reservoir, particularly if the reservoir is relatively homogeneous and has high permeability, negatively affecting the CO_2 storage and oil recovery. Consequently, reservoir heterogeneity may have a positive effect, slowing down the rise of CO_2 to the top of the reservoir and forcing it to spread laterally, giving more complete invasion of the formation and greater storage potential (Bondor, 1992; Kovscek, 2002; Flett *et al*., 2005).

5.3.2.3 Enhanced gas recovery

Although up to 95% of original gas in place can be produced, CO_2 could potentially be injected into depleted gas reservoirs to enhance gas recovery by repressurizing the reservoir (van der Burgt *et al*., 1992; Koide and Yamazaki, 2001; Oldenburg *et al*., 2001). Enhanced gas recovery has so far been implemented only at pilot scale (Gaz de France K12B project, Netherlands,

Table 5.1) and some authors have suggested that CO_2 injection might result in lower gas recovery factors, particularly for very heterogeneous fields (Clemens and Wit, 2002).

5.3.3 Saline formations

Saline formations are deep sedimentary rocks saturated with formation waters or brines containing high concentrations of dissolved salts. These formations are widespread and contain enormous quantities of water, but are unsuitable for agriculture or human consumption. Saline brines are used locally by the chemical industry and formation waters of varying salinity are used in health spas and for producing low-enthalpy geothermal energy. Because the use of geothermal energy is likely to increase, potential geothermal areas may not be suitable for CO_2 storage. It has been suggested that combined geological storage and geothermal energy may be feasible, but regions with good geothermal energy potential are generally less favourable for CO_2 geological storage because of the high degree of faulting and fracturing and the sharp increase of temperature with depth. In very arid regions, deep saline formations may be considered for future water desalinization.

The Sleipner Project in the North Sea is the best available example of a CO_2 storage project in a saline formation (Box 5.1). It was the first commercial-scale project dedicated to geological CO_2 storage. Approximately 1 $MtCO_2$ is removed annually from the produced natural gas and injected underground at Sleipner. The operation started in October 1996 and over the lifetime of the project a total of 20 $MtCO_2$ is expected to be stored. A simplified diagram of the Sleipner scheme is given in Figure 5.4.

The CO_2 is injected into poorly cemented sands about 800–1000 m below the sea floor. The sandstone contains secondary thin shale or clay layers, which influence the internal movement of injected CO_2. The overlying primary seal is an extensive thick shale or clay layer. The saline formation into which CO_2 is injected has a very large storage capacity.

The fate and transport of the Sleipner CO_2 plume has been successfully monitored (Figure 5.16) by seismic time-lapse surveys (Section 5.6). These surveys have helped improve the conceptual model for the fate and transport of stored CO_2. The vertical cross-section of the plume shown in Figure 5.16 indicates both the upward migration of CO_2 (due to buoyancy forces) and the role of lower permeability strata within the formation, diverting some of the CO_2 laterally, thus spreading out the plume over a larger area. The survey also shows that the caprock prevents migration out of the storage formation. The seismic data shown in Figure 5.16 illustrate the gradual growth of the plume. Today, the footprint of the plume at Sleipner extends over approximately 5 km^2. Reservoir studies and simulations (Section 5.4.2) have shown that the CO_2-saturated brine will eventually become denser and sink, eliminating the potential for long-term leakage (Lindeberg and Bergmo, 2003).

5.3.4 Coal seams

Coal contains fractures (cleats) that impart some permeability to the system. Between cleats, solid coal has a very large number of micropores into which gas molecules from the cleats can diffuse and be tightly adsorbed. Coal can physically adsorb many gases and may contain up to 25 normal m^3 (m^3 at 1 atm and 0°C) methane per tonne of coal at coal seam pressures. It has a higher affinity to adsorb gaseous CO_2 than methane (Figure 5.17). The volumetric ratio of adsorbable CO_2:CH_4 ranges from as low as one for mature coals such as anthracite, to ten or more for younger, immature coals such as lignite. Gaseous CO_2 injected through wells will flow through the cleat system of the coal, diffuse into the coal matrix and be adsorbed onto the coal micropore surfaces, freeing up gases with lower affinity to coal (i.e., methane).

The process of CO_2 trapping in coals for temperatures and pressures above the critical point is not well understood (Larsen, 2003). It seems that adsorption is gradually replaced by absorption and the CO_2 diffuses or 'dissolves' in coal. Carbon dioxide is a 'plasticizer' for coal, lowering the temperature required to cause the transition from a glassy, brittle structure to a rubbery, plastic structure (coal softening). In one case, the transition temperature was interpreted to drop from about 400ºC at 3 MPa to <30ºC at 5.5 MPa CO_2 pressure (Larsen, 2003). The transition temperature is dependent on the maturity of the coal, the maceral content, the ash content and the confining stress and is not easily extrapolated to the field. Coal plasticization or softening, may adversely affect the permeability that would allow CO_2 injection. Furthermore, coal swells as CO_2 is adsorbed and/or absorbed, which reduces permeability and injectivity by orders of magnitude or more (Shi and Durucan, 2005) and which may be counteracted by increasing the injection pressures (Clarkson and Bustin, 1997; Palmer and Mansoori, 1998; Krooss *et al.*, 2002; Larsen, 2003). Some studies suggest that the injected CO_2 may react with coal (Zhang *et al.*, 1993), further highlighting the difficulty in injecting CO_2 into low-permeability coal.

If CO_2 is injected into coal seams, it can displace methane, thereby enhancing CBM recovery. Carbon dioxide has been injected successfully at the Allison Project (Box 5.7) and in the Alberta Basin, Canada (Gunter *et al.*, 2005), at depths greater than that corresponding to the CO_2 critical point. Carbon dioxide-ECBM has the potential to increase the amount of produced methane to nearly 90% of the gas, compared to conventional recovery of only 50% by reservoir-pressure depletion alone (Stevens *et al.*, 1996).

Coal permeability is one of several determining factors in selection of a storage site. Coal permeability varies widely and generally decreases with increasing depth as a result of cleat closure with increasing effective stress. Most CBM-producing wells in the world are less than 1000 m deep.

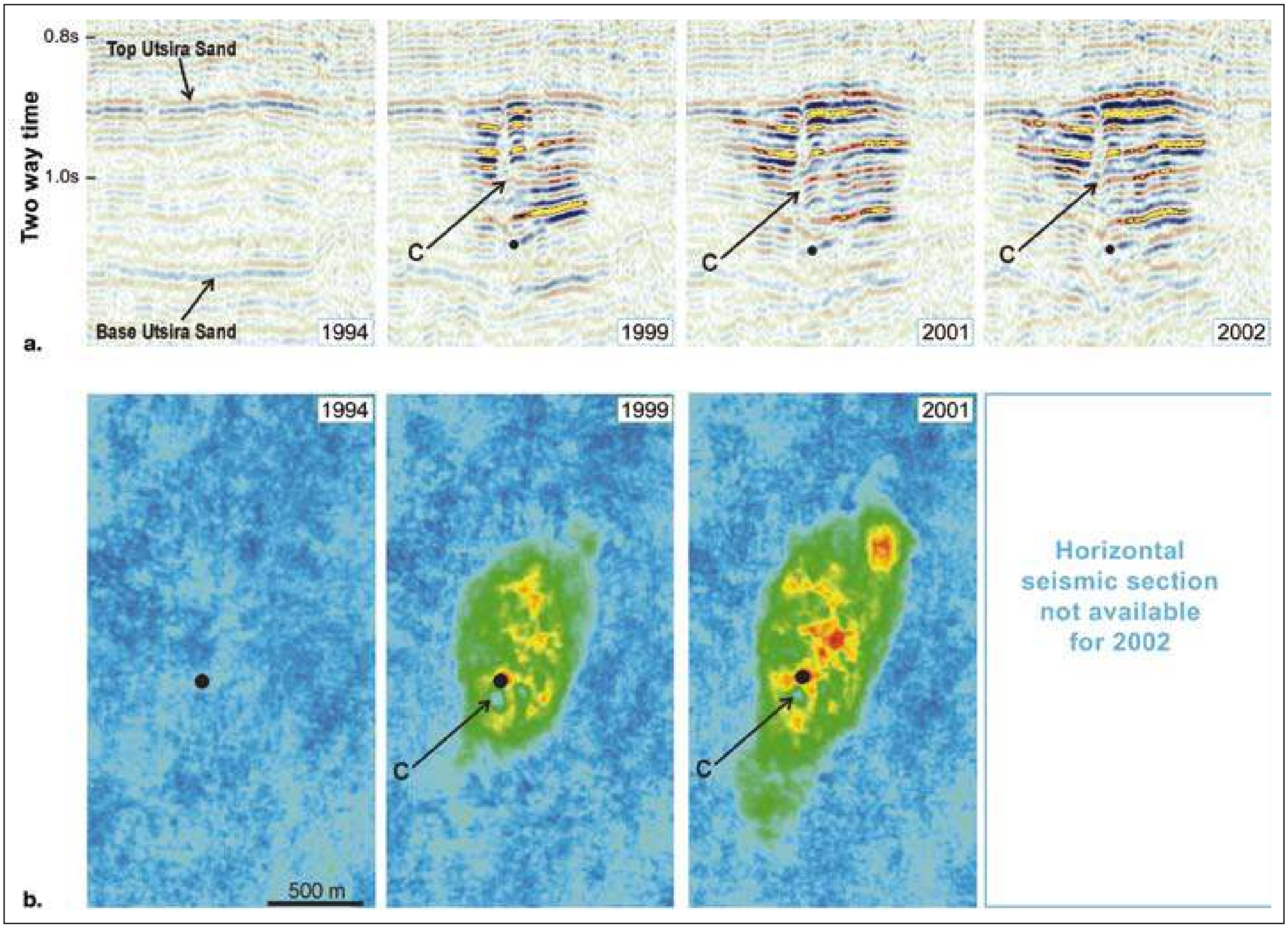

Figure 5.16 (a) Vertical seismic sections through the CO_2 plume in the Utsira Sand at the Sleipner gas field, North Sea, showing its development over time. Note the chimney of high CO_2 saturation (c) above the injection point (black dot) and the bright layers corresponding to high acoustic response due to CO_2 in a gas form being resident in sandstone beneath thin low-permeability horizons within the reservoir. (b) Horizontal seismic sections through the developing CO_2 plume at Sleipner showing its growth over time. The CO_2 plume-specific monitoring was completed in 2001; therefore data for 2002 was not available (courtesy of Andy Chadwick and the CO2STORE project).

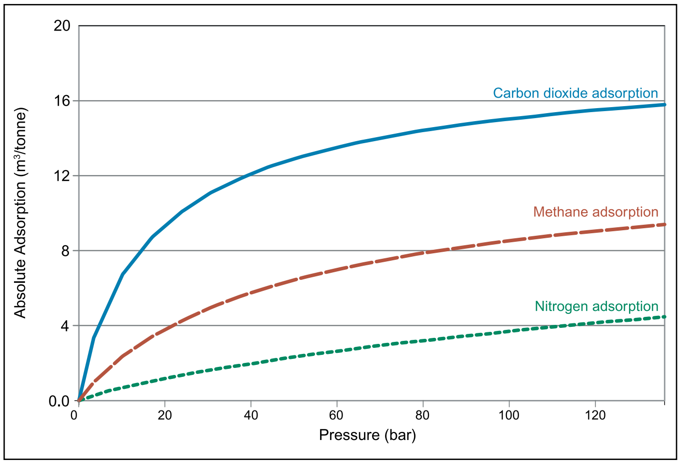

Figure 5.17 Pure gas absolute adsorption in standard cubic feet per tonne (SCF per tonne) on Tiffany Coals at 55°C (after Gasem et al., 2002).

Original screening criteria proposed in selecting favourable areas for CO_2 ECBM (IEA-GHG, 1998) include:

- Adequate permeability (minimum values have not yet been determined);
- Suitable coal geometry (a few, thick seams rather than multiple, thin seams);
- Simple structure (minimal faulting and folding);
- Homogeneous and confined coal seam(s) that are laterally continuous and vertically isolated;
- Adequate depth (down to 1500 m, greater depths have not yet been studied);
- Suitable gas saturation conditions (high gas saturation for ECBM);
- Ability to dewater the formation.

However, more recent studies have indicated that coal rank may play a more significant role than previously thought, owing to the dependence on coal rank of the relative adsorptive capacities

Box 5.7 The Allison Unit CO_2-ECBM Pilot.

The Allison Unit CO_2-ECBM Recovery Pilot Project, located in the northern New Mexico portion of the San Juan Basin, USA, is owned and operated by Burlington Resources. Production from the Allison field began in July 1989 and CO_2 injection operations for ECBM recovery commenced in April 1995. Carbon dioxide injection was suspended in August 2001 to evaluate the results of the pilot. Since this pilot was undertaken purely for the purposes of ECBM production, no CO_2 monitoring programme was implemented.

The CO_2 was sourced from the McElmo Dome in Colorado and delivered to the site through a (then) Shell (now Kinder-Morgan) CO_2 pipeline. The Allison Unit has a CBM resource of 242 million m^3 km^{-2}. A total of 181 million m^3 (6.4 Bcf) of natural CO_2 was injected into the reservoir over six years, of which 45 million m^3 (1.6 Bcf) is forecast to be ultimately produced back, resulting in a net storage volume of 277,000 tCO_2. The pilot consists of 16 methane production wells, 4 CO_2 injection wells and 1 pressure observation well. The injection operations were undertaken at constant surface injection pressures on the order of 10.4 MPa.

The wells were completed in the Fruitland coal, which is capped by shale. The reservoir has a thickness of 13 m, is located at a depth of 950 m and had an original reservoir pressure of 11.5 MPa. In a study conducted under the Coal-Seq Project performed for the US Department of Energy (www.coal-seq.com), a detailed reservoir characterization and modelling of the pilot was developed with the COMET2 reservoir simulator and future field performance was forecast under various operating conditions.

This study provides evidence of significant coal-permeability reduction with CO_2 injection. This permeability reduction resulted in a two-fold reduction in injectivity. This effect compromised incremental methane recovery and project economics. Finding ways to overcome and/or prevent this effect is therefore an important topic for future research. The injection of CO_2 at the Allison Unit has resulted in an increase in methane recovery from an estimated 77% of original gas in place to 95% of the original gas in place within the project area. The recovery of methane was in a proportion of approximately one volume of methane for every three volumes of CO_2 injected (Reeves *et al.*, 2004).

An economic analysis of the pilot indicated a net present value of negative US$ 627,000, assuming a discount rate of 12% and an initial capital expenditure of US$ 2.6 million, but not including the beneficial impact of any tax credits for production from non-conventional reservoirs. This was based on a gas price of 2.09 US$ GJ^{-1} (2.20 US$/MMbtu) (at the time) and a CO_2 price of 5.19 US$ t^{-1} (0.30 US$/Mcf). The results of the financial analysis will change, depending on the cost of oil and gas (the analysis indicated that the pilot would have yielded a positive net present value of US$2.6 million at today's gas prices) and the cost of CO_2. It was also estimated that if injectivity had been improved by a factor of four (but still using 2.09 US$ GJ^{-1} (2.20 US$/MMbtu)), the net present value would have increased to US$ 3.6 million. Increased injectivity and today's gas prices combined would have yielded a net present value for the pilot of US$ 15 million or a profit of 34 US$/$tCO_2$ retained in the reservoir (Reeves *et al.*, 2003).

of methane and CO_2 (Reeves *et al.*, 2004).

If the coal is never mined or depressurized, it is likely CO_2 will be stored for geological time, but, as with any geological storage option, disturbance of the formation could void any storage. The likely future fate of a coal seam is, therefore, a key determinant of its suitability for storage and in storage site selection and conflicts between mining and CO_2 storage are possible, particularly for shallow coals.

5.3.5 Other geological media

Other geological media and/or structures – including basalts, oil or gas shale, salt caverns and abandoned mines – may locally provide niche options for geological storage of CO_2.

5.3.5.1 Basalts

Flows and layered intrusions of basalt occur globally, with large volumes present around the world (McGrail *et al.*, 2003). Basalt commonly has low porosity, low permeability and low pore space continuity and any permeability is generally associated with fractures through which CO_2 will leak unless there is a suitable caprock. Nonetheless, basalt may have some potential for mineral trapping of CO_2, because injected CO_2 may react with silicates in the basalt to form carbonate minerals (McGrail *et al.*, 2003). More research is needed, but in general, basalts appear unlikely to be suitable for CO_2 storage.

5.3.5.2 Oil or gas rich shale

Deposits of oil or gas shale or organic-rich shale, occur in many parts of the world. The trapping mechanism for oil shale is similar to that for coal beds, namely CO_2 adsorption onto organic material. Carbon dioxide-enhanced shale-gas production (like ECBM) has the potential to reduce storage costs. The potential for storage of CO_2 in oil or gas shale is currently unknown, but the large volumes of shale suggest that storage capacity may be significant. If site-selection criteria, such as minimum depth, are developed and applied to these shales, then volumes could be limited, but the very low permeability of these shales is likely to preclude injection of large volumes of CO_2.

5.3.5.3 Salt caverns

Storage of CO_2 in salt caverns created by solution mining could use the technology developed for the storage of liquid natural gas and petroleum products in salt beds and domes in Western Canada and the Gulf of Mexico (Dusseault *et al*., 2004). A single salt cavern can reach more than 500,000 m^3. Storage of CO_2 in salt caverns differs from natural gas and compressed air storage because in the latter case, the caverns are cyclically pressurized and depressurized on a daily-to-annual time scale, whereas CO_2 storage must be effective on a centuries-to-millennia time scale. Owing to the creep properties of salt, a cavern filled with supercritical CO_2 will decrease in volume, until the pressure inside the cavern equalizes the external stress in the salt bed (Bachu and Dusseault, 2005). Although a single cavern 100 m in diameter may hold only about 0.5 Mt of high density CO_2, arrays of caverns could be built for large-scale storage. Cavern sealing is important in preventing leakage and collapse of cavern roofs, which could release large quantities of gas (Katzung *et al*., 1996). Advantages of CO_2 storage in salt caverns include high capacity per unit volume ($kgCO_2\ m^{-3}$), efficiency and injection flow rate. Disadvantages are the potential for CO_2 release in the case of system failure, the relatively small capacity of most individual caverns and the environmental problems of disposing of brine from a solution cavity. Salt caverns can also be used for temporary storage of CO_2 in collector and distributor systems between sources and sinks of CO_2.

5.3.5.4 Abandoned mines

The suitability of mines for CO_2 storage depends on the nature and sealing capacity of the rock in which mining occurs. Heavily fractured rock, typical of igneous and metamorphic terrains, would be difficult to seal. Mines in sedimentary rocks may offer some CO_2-storage opportunities (e.g., potash and salt mines or stratabound lead and zinc deposits). Abandoned coal mines offer the opportunity to store CO_2, with the added benefit of adsorption of CO_2 onto coal remaining in the mined-out area (Piessens and Dusar, 2004). However, the rocks above coal mines are strongly fractured, which increases the risk of gas leakage. In addition, long-term, safe, high-pressure, CO_2-resistant shaft seals have not been developed and any shaft failure could result in release of large quantities of CO_2. Nevertheless, in Colorado, USA, there is a natural gas storage facility in an abandoned coal mine.

5.3.6 Effects of impurities on storage capacity

The presence of impurities in the CO_2 gas stream affects the engineering processes of capture, transport and injection (Chapters 3 and 4), as well as the trapping mechanisms and capacity for CO_2 storage in geological media. Some contaminants in the CO_2 stream (e.g., SO_x, NO_x, H_2S) may require classification as hazardous, imposing different requirements for injection and disposal than if the stream were pure (Bergman *et al*., 1997). Gas impurities in the CO_2 stream affect the compressibility of the injected CO_2 (and hence the volume needed for storing a given amount) and reduce the capacity for storage in free phase, because of the storage space taken by these gases. Additionally, depending on the type of geological storage, the presence of impurities may have some other specific effects.

In EOR operations, impurities affect the oil recovery because they change the solubility of CO_2 in oil and the ability of CO_2 to vaporize oil components (Metcalfe, 1982). Methane and nitrogen decrease oil recovery, whereas hydrogen sulphide, propane and heavier hydrocarbons have the opposite effect (Alston *et al*., 1985; Sebastian *et al*., 1985). The presence of SO_x may improve oil recovery, whereas the presence of NO_x can retard miscibility and thus reduce oil recovery (Bryant and Lake, 2005) and O_2 can react exothermally with oil in the reservoir.

In the case of CO_2 storage in deep saline formations, the presence of gas impurities affects the rate and amount of CO_2 storage through dissolution and precipitation. Additionally, leaching of heavy metals from the minerals in the rock matrix by SO_2 or O_2 contaminants is possible. Experience to date with acid gas injection (Section 5.2.4.2) suggests that the effect of impurities is not significant, although Knauss *et al*. (2005) suggest that SO_x injection with CO_2 produces substantially different chemical, mobilization and mineral reactions. Clarity is needed about the range of gas compositions that industry might wish to store, other than pure CO_2 (Anheden *et al*., 2005), because although there might be environmental issues to address, there might be cost savings in co-storage of CO_2 and contaminants.

In the case of CO_2 storage in coal seams, impurities may also have a positive or negative effect, similar to EOR operations. If a stream of gas containing H_2S or SO_2 is injected into coal beds, these will likely be preferentially adsorbed because they have a higher affinity to coal than CO_2, thus reducing the storage capacity for CO_2 (Chikatamarla and Bustin, 2003). If oxygen is present, it will react irreversibly with the coal, reducing the sorption surface and, hence, the adsorption capacity. On the other hand, some impure CO_2 waste streams, such as coal-fired flue gas (i.e., primarily $N_2 + CO_2$), may be used for ECBM because the CO_2 is stripped out (retained) by the coal reservoir, because it has higher sorption selectivity than N_2 and CH_4.

5.3.7 Geographical distribution and storage capacity estimates

Identifying potential sites for CO_2 geological storage and estimating their capacity on a regional or local scale should conceptually be a simple task. The differences between the various mechanisms and means of trapping (Sections 5.2.2) suggest in principle the following methods:

- For volumetric trapping, capacity is the product of available volume (pore space or cavity) and CO_2 density at *in situ* pressure and temperature;
- For solubility trapping, capacity is the amount of CO_2 that can be dissolved in the formation fluid (oil in oil reservoirs, brackish water or brine in saline formations);
- For adsorption trapping, capacity is the product of coal volume and its capacity for adsorbing CO_2;

- For mineral trapping, capacity is calculated on the basis of available minerals for carbonate precipitation and the amount of CO_2 that will be used in these reactions.

The major impediments to applying these simple methods for estimating the capacity for CO_2 storage in geological media are the lack of data, their uncertainty, the resources needed to process data when available and the fact that frequently more than one trapping mechanism is active. This leads to two situations:

- Global capacity estimates have been calculated by simplifying assumptions and using very simplistic methods and hence are not reliable;
- Country- and region- or basin-specific estimates are more detailed and precise, but are still affected by the limitations imposed by availability of data and the methodology used. Country- or basin-specific capacity estimates are available only for North America, Western Europe, Australia and Japan.

The geographical distribution and capacity estimates are presented below and summarized in Table 5.2.

5.3.7.1 Storage in oil and gas reservoirs

This CO_2 storage option is restricted to hydrocarbon-producing basins, which represent numerically less than half of the sedimentary provinces in the world. It is generally assumed that oil and gas reservoirs can be used for CO_2 storage after their oil or gas reserves are depleted, although storage combined with enhanced oil or gas production can occur sooner. Short of a detailed, reservoir-by-reservoir analysis, the CO_2 storage capacity can and should be calculated from databases of reserves and production (e.g., Winter and Bergman, 1993; Stevens *et al*., 2001b; Bachu and Shaw, 2003, 2005; Beecy and Kuuskra, 2005).

In hydrocarbon reservoirs with little water encroachment, the injected CO_2 will generally occupy the pore volume previously occupied by oil and/or natural gas. However, not all the previously (hydrocarbon-saturated) pore space will be available for CO_2 because some residual water may be trapped in the pore space due to capillarity, viscous fingering and gravity effects (Stevens *et al*., 2001c). In open hydrocarbon reservoirs (where pressure is maintained by water influx), in addition to the capacity reduction caused by capillarity and other local effects, a significant fraction of the pore space will be invaded by water, decreasing the pore space available for CO_2 storage, if repressuring the reservoir is limited to preserve reservoir integrity. In Western Canada, this loss was estimated to be in the order of 30% for gas reservoirs and 50% for oil reservoirs if reservoir repressuring with CO_2 is limited to the initial reservoir pressure (Bachu *et al*., 2004). The capacity estimates presented here for oil and gas reservoirs have not included any 'discounting' that may be appropriate for water-drive reservoirs because detailed site-specific reservoir analysis is needed to assess the effects of water-drive on capacity on a case-by-case basis.

Many storage-capacity estimates for oil and gas fields do not distinguish capacity relating to oil and gas that has already been produced from capacity relating to remaining reserves yet to be produced and that will become available in future years. In some global assessments, estimates also attribute capacity to undiscovered oil and gas fields that might be discovered in future years. There is uncertainty about when oil and gas fields will be depleted and become available for CO_2 storage. The depletion of oil and gas fields is mostly affected by economic rather than technical considerations, particularly oil and gas prices. It is possible that production from near-depleted fields will be extended if future economic considerations allow more hydrocarbons to be recovered, thus delaying access to such fields for CO_2 storage. Currently few of the world's large oil and gas fields are depleted.

A variety of regional and global estimates of storage capacity in oil and gas fields have been made. Regional and national assessments use a 'bottom-up' approach that is based on field reserves data from each area's existing and discovered oil and gas fields. Although the methodologies used may differ, there is a higher level of confidence in these than the global estimates, for the reasons outlined previously. Currently, this type of assessment is available only for northwestern Europe, United States, Canada and Australia. In Europe, there have been three bottom-up attempts to estimate the CO_2 storage capacity of oil and gas reservoirs covering parts of Europe, but comprising most of Europe's storage capacity since they include the North Sea (Holloway, 1996; Wildenborg *et al*., 2005b). The methodology used in all three studies was based on the assumption that the total reservoir volume of hydrocarbons could be replaced by CO_2. The operators' estimate of 'ultimately recoverable reserves' (URR) was used for each field where available or was estimated. The underground volume occupied by the URR and the amount of CO_2 that could be stored in that space under reservoir conditions was then calculated. Undiscovered reserves were excluded. For Canada, the assumption was that

Table 5.2 Storage capacity for several geological storage options. The storage capacity includes storage options that are not economical.

Reservoir type	Lower estimate of storage capacity ($GtCO_2$)	Upper estimate of storage capacity ($GtCO_2$)
Oil and gas fields	675[a]	900[a]
Unminable coal seams (ECBM)	3-15	200
Deep saline formations	1000	Uncertain, but possibly 10^4

[a] These numbers would increase by 25% if "undiscovered" oil and gas fields were included in this assessment.

the produced reserves (not the original oil or gas in place) could be replaced by CO_2 (theoretical capacity) for all reservoirs in Western Canada, on the basis of *in situ* pressure, temperature and pore volume. Reduction coefficients were then applied to account for aquifer invasion and all other effects (effective capacity). This value was then reduced for depth (900–3500 m) and size (practical capacity) (Bachu and Shaw, 2005).

The storage potential of northwestern Europe is estimated at more than 40 $GtCO_2$ for gas reservoirs and 7 $GtCO_2$ for oil fields (Wildenborg *et al.*, 2005b). The European estimates are based on all reserves (no significant fields occur above 800 m). Carbon dioxide density was calculated from the depth, pressure and temperature of fields in most cases; where these were not available, a density of 700 kg m^{-3} was used. No assumption was made about the amount of oil recovered from the fields before CO_2 storage was initiated and tertiary recovery by EOR was not included. In Western Canada, the practical CO_2 storage potential in the Alberta and Williston basins in reservoirs with capacity more than 1 $MtCO_2$ each was estimated to be about 1 $GtCO_2$ in oil reservoirs and about 4 $GtCO_2$ in gas reservoirs. The capacity in all discovered oil and gas reservoirs is approximately 10 $GtCO_2$ (Bachu *et al.*, 2004; Bachu and Shaw, 2005). For Canada, the CO_2 density was calculated for each reservoir from the pressure and temperature. The oil and gas recovery was that provided in the reserves databases or was based on actual production. For reservoirs suitable for EOR, an analytical method was developed to estimate how much would be produced and how much CO_2 would be stored (Shaw and Bachu, 2002). In the United States, the total storage capacity in discovered oil and gas fields is estimated to be approximately 98 $GtCO_2$ (Winter and Bergman, 1993; Bergman *et al.*, 1997). Data on production to date and known reserves and resources indicate that Australia has up to 15 $GtCO_2$ storage capacity in gas reservoirs and 0.7 $GtCO_2$ in oil reservoirs. The Australian estimates used field data to recalculate the CO_2 that could occupy the producible volume at field conditions. The total storage capacity in discovered fields for these regions with bottom-up assessments is 170 $GtCO_2$.

Although not yet assessed, it is almost certain that significant storage potential exists in all other oil and gas provinces around the world, such as the Middle East, Russia, Asia, Africa and Latin America.

Global capacity for CO_2-EOR opportunities is estimated to have a geological storage capacity of 61–123 $GtCO_2$, although as practised today, CO_2-EOR is not engineered to maximize CO_2 storage. In fact, it is optimized to maximize revenues from oil production, which in many cases requires minimizing the amount of CO_2 retained in the reservoir. In the future, if storing CO_2 has an economic value, co-optimizing CO_2 storage and EOR may increase capacity estimates. In European capacity studies, it was considered likely that EOR would be attempted at all oil fields where CO_2 storage took place, because it would generate additional revenue. The calculation in Wildenborg *et al.* (2005b) allows for different recovery factors based on API (American Petroleum Institute) gravity of oil. For Canada, all 10,000 oil reservoirs in Western Canada were screened for suitability for EOR on the basis of a set of criteria developed from EOR literature. Those oil reservoirs that passed were considered further in storage calculations (Shaw and Bachu, 2002).

Global estimates of storage capacity in oil reservoirs vary from 126 to 400 $GtCO_2$ (Freund, 2001). These assessments, made on a top-down basis, include potential in undiscovered reservoirs. Comparable global capacity for CO_2 storage in gas reservoirs is estimated at 800 $GtCO_2$ (Freund, 2001). The combined estimate of total ultimate storage capacity in discovered oil and gas fields is therefore very likely 675–900 $GtCO_2$. If undiscovered oil and gas fields are included, this figure would increase to 900–1200 $GtCO_2$, but the confidence level would decrease.[1]

In comparison, more detailed regional estimates made for northwestern Europe, United States, Australia and Canada indicate a total of about 170 $GtCO_2$ storage capacity in their existing oil and gas fields, with the discovered oil and gas reserves of these countries accounting for 18.9% of the world total (USGS, 2001a). Global storage estimates that are based on proportionality suggest that discovered worldwide oil and gas reservoirs have a capacity of 900 $GtCO_2$, which is comparable to the global estimates by Freund (2001) of 800 $GtCO_2$ for gas (Stevens *et al.*, 2000) and 123 $GtCO_2$ for oil and is assessed as a reliable value, although water invasion was not always taken into account.

5.3.7.2 Storage in deep saline formations

Saline formations occur in sedimentary basins throughout the world, both onshore and on the continental shelves (Chapter 2 and Section 5.3.3) and are not limited to hydrocarbon provinces or coal basins. However, estimating the CO_2 storage capacity of deep saline formations is presently a challenge for the following reasons:

- There are multiple mechanisms for storage, including physical trapping beneath low permeability caprock, dissolution and mineralization;
- These mechanisms operate both simultaneously and on different time scales, such that the time frame of CO_2 storage affects the capacity estimate; volumetric storage is important initially, but later CO_2 dissolves and reacts with minerals;
- Relations and interactions between these various mechanisms are very complex, evolve with time and are highly dependent on local conditions;
- There is no single, consistent, broadly available methodology for estimating CO_2 storage capacity (various studies have used different methods that do not allow comparison).
- Only limited seismic and well data are normally available (unlike data on oil and gas reservoirs).

To understand the difficulties in assessing CO_2 storage capacity in deep saline formations, we need to understand the interplay

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[1] Estimates of the undiscovered oil and gas are based on the USGS assessment that 30% more oil and gas will be discovered, compared to the resources known today.

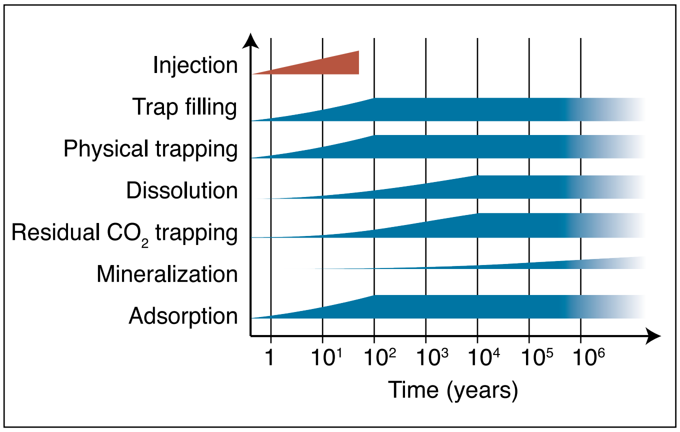


Figure 5.18 Schematic showing the time evolution of various CO_2 storage mechanisms operating in deep saline formations, during and after injection. Assessing storage capacity is complicated by the different time and spatial scales over which these processes occur.

of the various trapping mechanisms during the evolution of a CO_2 plume (Section 5.2 and Figure 5.18). In addition, the storage capacity of deep saline formations can be determined only on a case-by-case basis.

To date, most of the estimates of CO_2 storage capacity in deep saline formations focus on physical trapping and/or dissolution. These estimates make the simplifying assumption that no geochemical reactions take place concurrent with CO_2 injection, flow and dissolution. Some recent work suggests that it can take several thousand years for geochemical reactions to have a significant impact (Xu *et al.*, 2003). The CO_2 storage capacity from mineral trapping can be comparable to the capacity in solution per unit volume of sedimentary rock when formation porosity is taken into account (Bachu and Adams, 2003; Perkins *et al.*, 2005), although the rates and time frames of these two processes are different.

More than 14 global assessments of capacity have been made by using these types of approaches (IEA-GHG, 2004). The range of estimates from these studies is large (200–56,000 $GtCO_2$), reflecting both the different assumptions used to make these estimates and the uncertainty in the parameters. Most of the estimates are in the range of several hundred Gtonnes of CO_2. Volumetric capacity estimates that are based on local, reservoir-scale numerical simulations of CO_2 injection suggest occupancy of the pore space by CO_2 on the order of a few percent as a result of gravity segregation and viscous fingering (van der Meer, 1992, 1995; Krom *et al.*, 1993; Ispen and Jacobsen, 1996). Koide *et al.* (1992) used the areal method of projecting natural resources reserves and assumed that 1% of the total area of the world's sedimentary basins can be used for CO_2 storage. Other studies considered that 2–6% of formation area can be used for CO_2 storage. However, Bradshaw and Dance (2005) have shown there is no correlation between geographic area of a sedimentary basin and its capacity for either hydrocarbons (oil and gas reserves) or CO_2 storage.

The storage capacity of Europe has been estimated as 30–577 $GtCO_2$ (Holloway, 1996; Bøe *et al.*, 2002; Wildenborg *et al.*, 2005b). The main uncertainties for Europe are estimates of the amount trapped (estimated to be 3%) and storage efficiency, estimated as 2–6% (2% for closed aquifer with permeability barriers; 6% for open aquifer with almost infinite extent), 4% if open/closed status is not known. The volume in traps is assumed to be proportional to the total pore volume, which may not necessarily be correct. Early estimates of the total US storage capacity in deep saline formations suggested a total of up to 500 $GtCO_2$ (Bergman and Winter, 1995). A more recent estimate of the capacity of a single deep formation in the United States, the Mount Simon Sandstone, is 160–800 $GtCO_2$ (Gupta *et al.*, 1999), suggesting that the total US storage capacity may be higher than earlier estimates. Assuming that CO_2 will dissolve to saturation in all deep formations, Bachu and Adams (2003) estimated the storage capacity of the Alberta basin in Western Canada to be approximately 4000 $GtCO_2$, which is a theoretical maximum assuming that all the pore water in the Alberta Basin could become saturated with CO_2, which is not likely. An Australian storage capacity estimate of 740 $GtCO_2$ was determined by a cumulative risked-capacity approach for 65 potentially viable sites from 48 basins (Bradshaw *et al.*, 2003). The total capacity in Japan has been estimated as 1.5–80 $GtCO_2$, mostly in offshore formations (Tanaka *et al.*, 1995).

Within these wide ranges, the lower figure is generally the estimated storage capacity of volumetric traps within the deep saline formations, where free-phase CO_2 would accumulate. The larger figure is based on additional storage mechanisms, mainly dissolution but also mineral trapping. The various methods and data used in these capacity estimates demonstrate a high degree of uncertainty in estimating regional or global storage capacity in deep saline formations. In the examples from Europe and Japan, the maximum estimate is 15 to 50 times larger than the low estimate. Similarly, global estimates of storage capacity show a wide range, 100–200,000 $GtCO_2$, reflecting different methodologies, levels of uncertainties and considerations of effective trapping mechanisms.

The assessment of this report is that it is very likely that global storage capacity in deep saline formations is at least 1000 $GtCO_2$. Confidence in this assessment comes from the fact that oil and gas fields 'discovered' have a global storage capacity of approximately 675–900 $GtCO_2$ and that they occupy only a small fraction of the pore volume in sedimentary basins, the rest being occupied by brackish water and brine. Moreover, oil and gas reservoirs occur only in about half of the world's sedimentary basins. Additionally, regional estimates suggest that significant storage capacity is available. Significantly more storage capacity is likely to be available in deep saline formations. The literature is not adequate to support a robust estimate of the maximum geological storage capacity. Some studies suggest that it might be little more than 1000 $GtCO_2$, while others indicate that the upper figure could be an order of magnitude higher. More detailed regional and local capacity assessments are required to resolve this issue.

5.3.7.3 Storage in coal

No commercial CO_2-ECBM operations exist and a comprehensive realistic assessment of the potential for CO_2

storage in coal formations has not yet been made. Normally, commercial CBM reservoirs are shallower than 1500 m, whereas coal mining in Europe and elsewhere has reached depths of 1000 m. Because CO_2 should not be stored in coals that could be potentially mined, there is a relatively narrow depth window for CO_2 storage.

Assuming that bituminous coals can adsorb twice as much CO_2 as methane, a preliminary analysis of the theoretical CO_2 storage potential for ECBM recovery projects suggests that approximately 60–200 $GtCO_2$ could be stored worldwide in bituminous coal seams (IEA-GHG, 1998). More recent estimates for North America range from 60 to 90 $GtCO_2$ (Reeves, 2003b; Dooley *et al*., 2005), by including sub-bituminous coals and lignites. Technical and economic considerations suggest a practical storage potential of approximately 7 $GtCO_2$ for bituminous coals (Gale and Freund, 2001; Gale, 2004). Assuming that CO_2 would not be stored in coal seams without recovering the CBM, a storage capacity of 3–15 $GtCO_2$ is calculated, for a US annual production of CBM in 2003 of approximately 0.04 trillion m^3 and projected global production levels of 0.20 trillion m^3 in the future. This calculation assumes that 0.1 $GtCO_2$ can be stored for every Tcf of produced CBM (3.53 $GtCO_2$ for every trillion m^3) and compares well to Gale (2004).

5.3.8 *Matching of CO_2 sources and geological storage sites*

Matching of CO_2 sources with geological storage sites requires detailed assessment of source quality and quantity, transport and economic and environmental factors. If the storage site is far from CO_2 sources or is associated with a high level of technical uncertainty, then its storage potential may never be realized.

5.3.8.1 Regional studies

Matching sources of CO_2 to potential storage sites, taking into account projections for future socio-economic development, will be particularly important for some of the rapidly developing economies. Assessment of sources and storage sites, together with numerical simulations, emissions mapping and identification of transport routes, has been undertaken for a number of regions in Europe (Holloway, 1996; Larsen *et al*., 2005). In Japan, studies have modelled and optimized the linkages between 20 onshore emission regions and 20 offshore storage regions, including both ocean storage and geological storage (Akimoto *et al*., 2003). Preliminary studies have also begun in India (Garg *et al*., 2005) and Argentina (Amadeo *et al*., 2005). For the United States, a study that used a Geographic Information System (GIS) and a broad-based economic analysis (Dooley *et al*., 2005) shows that about two-thirds of power stations are adjacent to potential geological storage locations, but a number would require transportation of hundreds of kilometres.

Studies of Canadian sedimentary basins that include descriptions of the type of data and flow diagrams of the assessment process have been carried out by Bachu (2003). Results for the Western Canada Sedimentary Basin show that, while the total capacity of oil and gas reservoirs in the basin is several Gtonnes of CO_2, the capacity of underlying deep saline formations is two to three orders of magnitude higher. Most major CO_2 emitters have potential storage sites relatively close by, with the notable exception of the oil sands plants in northeastern Alberta (current CO_2 emissions of about 20 $MtCO_2\ yr^{-1}$).

In Australia, a portfolio approach was undertaken for the continent to identify a range of geological storage sites (Rigg *et al*., 2001; Bradshaw *et al*., 2002). The initial assessment screened 300 sedimentary basins down to 48 basins and 65 areas. Methodology was developed for ranking storage sites (technical and economic risks) and proximity of large CO_2 emission sites. Region-wide solutions were sought, incorporating an economic model to assess full project economics over 20 to 30 years, including costs of transport, storage, monitoring and Monte Carlo analysis. The study produced three storage estimates:

- Total capacity of 740 $GtCO_2$, equivalent to 1600 years of current emissions, but with no economic barriers considered;
- 'Realistic' capacity of 100–115 $MtCO_2\ yr^{-1}$ or 50% of annual stationary emissions, determined by matching sources with the closest viable storage sites and assuming economic incentives for storage;
- 'Cost curve' capacity of 20–180 $MtCO_2\ yr^{-1}$, with increasing storage capacity depending on future CO_2 values.

5.3.8.2 Methodology and assessment criteria

Although some commonality exists in the various approaches for capacity assessment, each study is influenced by the available data and resources, the aims of the respective study and whether local or whole-region solutions are being sought. The next level of analysis covers regional aspects and detail at the prospect or project level, including screening and selection of potential CO_2 storage sites on the basis of technical, environmental, safety and economic criteria. Finally, integration and analysis of various scenarios can lead to identification of potential storage sites that should then become targets of detailed engineering and economic studies.

The following factors should be considered when selecting CO_2 storage sites and matching them with CO_2 sources (Winter and Bergman, 1993; Bergman *et al*., 1997; Kovscek, 2002): volume, purity and rate of the CO_2 stream; suitability of the storage sites, including the seal; proximity of the source and storage sites; infrastructure for the capture and delivery of CO_2; existence of a large number of storage sites to allow diversification; known or undiscovered energy, mineral or groundwater resources that might be compromised; existing wells and infrastructure; viability and safety of the storage site; injection strategies and, in the case of EOR and ECBM, production strategies, which together affect the number of wells and their spacing; terrain and right of way; location of population centres; local expertise; and overall costs and economics.

Although technical suitability criteria are initial indicators for identifying potential CO_2 storage sites, once the best candidates have been selected, further considerations will be controlled by economic, safety and environmental aspects. These criteria must be assessed for the anticipated lifetime of the operation, to ascertain whether storage capacity can match supply volume and whether injection rates can match the supply rate. Other issues might include whether CO_2 sources and storage sites are matched on a one-to-one basis or whether a collection and distribution system is implemented, to form an integrated industrial system. Such deliberations affect cost outcomes, as will the supply rates, through economies of scale. Early opportunities for source-storage matching could involve sites where an economic benefit might accrue through the enhanced production of oil or gas (Holtz *et al.*, 2001; van Bergen *et al.*, 2003b).

Assigning technical risks is important for matching of CO_2 sources and storage sites, for five risk factors: storage capacity, injectivity, containment, site and natural resources (Bradshaw *et al.*, 2002, 2003). These screening criteria introduce reality checks to large storage-capacity estimates and indicate which regions to concentrate upon in future detailed studies. The use of 'cost curve' capacity introduces another level of sophistication that helps in identifying how sensitive any storage capacity estimate is to the cost of CO_2. Combining the technical criteria into an economic assessment reveals that costs are quite project-specific.

5.4 Characterization and performance prediction for identified sites

Key goals for geological CO_2 storage site characterization are to assess how much CO_2 can be stored at a potential storage site and to demonstrate that the site is capable of meeting required storage performance criteria (Figure 5.19). Site characterization requires the collection of the wide variety of geological data that are needed to achieve these goals. Much of the data will necessarily be site-specific. Most data will be integrated into geological models that will be used to simulate and predict the performance of the site. These and related issues are considered below.

5.4.1 Characterization of identified sites

Storage site requirements depend greatly upon the trapping mechanism and the geological medium in which storage is proposed (e.g., deep saline formation, depleted oil or gas field or coal seam). Data availability and quality vary greatly between each of these options (Table 5.3). In many cases, oil and gas fields will be better characterized than deep saline formations because a relevant data set was collected during hydrocarbon exploration and production. However, this may not always be the case. There are many examples of deep saline formations whose character and performance for CO_2 storage can be predicted reliably over a large area (Chadwick *et al.*, 2003; Bradshaw *et al.*, 2003).

5.4.1.1 Data types

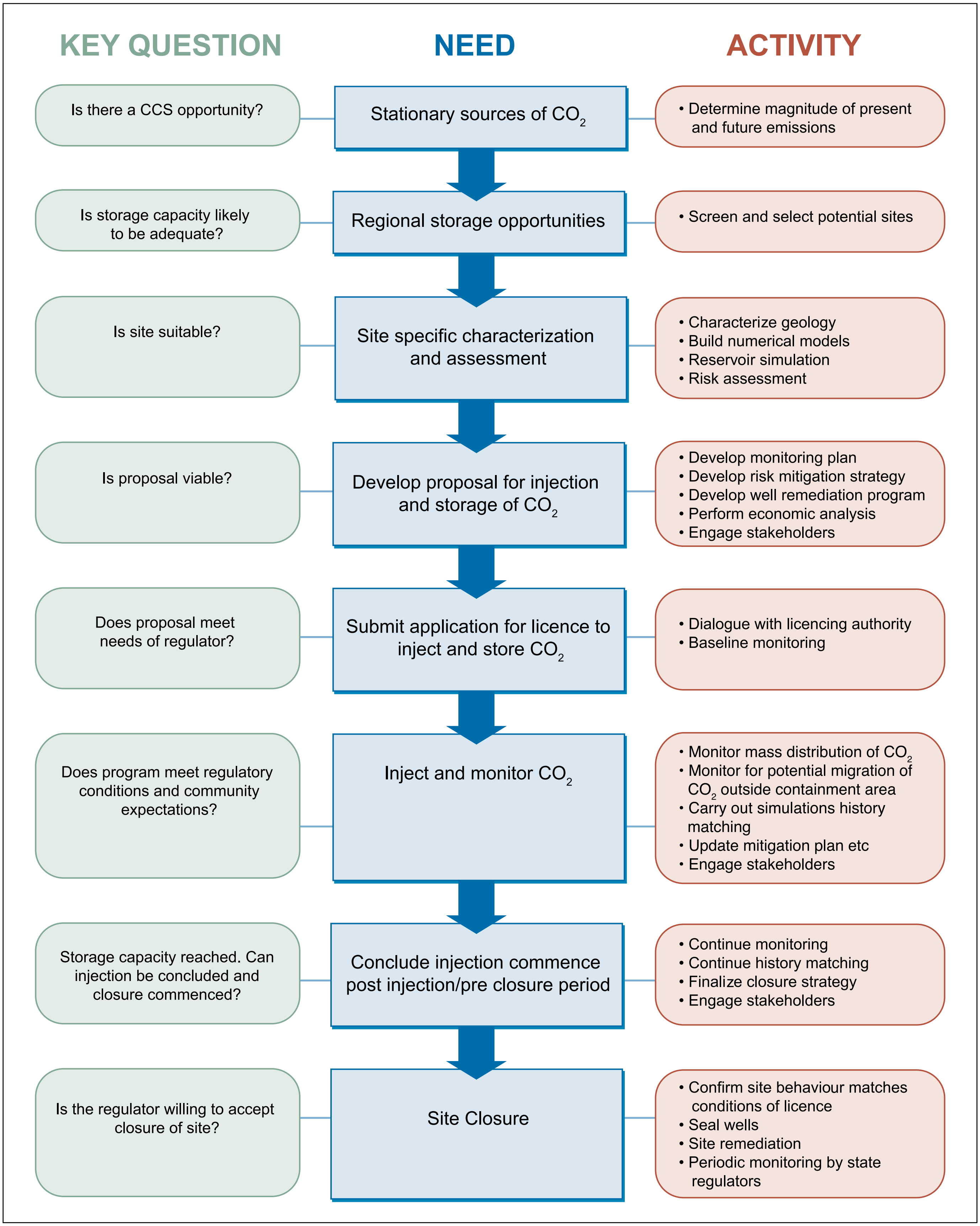
The storage site and its surroundings need to be characterized in terms of geology, hydrogeology, geochemistry and geomechanics (structural geology and deformation in response to stress changes). The greatest emphasis will be placed on the reservoir and its sealing horizons. However, the strata above the storage formation and caprock also need to be assessed because if CO_2 leaked it would migrate through them (Haidl *et al.*, 2005). Documentation of the characteristics of any particular storage site will rely on data that have been obtained directly from the reservoir, such as core and fluids produced from wells at or near the proposed storage site, pressure transient tests conducted to test seal efficiency and indirect remote sensing measurements such as seismic reflection data and regional hydrodynamic pressure gradients. Integration of all of the different types of data is needed to develop a reliable model that can be used to assess whether a site is suitable for CO_2 storage.

During the site-selection process that may follow an initial screening, detailed reservoir simulation (Section 5.4.2 will be necessary to meaningfully assess a potential storage site. A range of geophysical, geological, hydrogeological and geomechanical information is required to perform the modelling associated with a reservoir simulation. This information must be built into a three-dimensional geological model, populated with known and extrapolated data at an appropriate scale. Examples of the basic types of data and products that may be useful are listed in Table 5.3.

Financial constraints may limit the types of data that can be collected as part of the site characterization and selection process. Today, no standard methodology prescribes how a site must be characterized. Instead, selections about site characterization data will be made on a site-specific basis, choosing those data sets that will be most valuable in the particular geological setting. However, some data sets are likely to be selected for every case. Geological site description from wellbores and outcrops are needed to characterize the storage formation and seal properties. Seismic surveys are needed to define the subsurface geological structure and identify faults or fractures that could create leakage pathways. Formation pressure measurements are needed to map the rate and direction of groundwater flow. Water quality samples are needed to demonstrate the isolation between deep and shallow groundwater.

5.4.1.2 Assessment of stratigraphic factors affecting site integrity

Caprocks or seals are the permeability barriers (mostly vertical but sometimes lateral) that prevent or impede migration of CO_2 from the injection site. The integrity of a seal depends on spatial distribution and physical properties. Ideally, a sealing rock unit should be regional in nature and uniform in lithology, especially at its base. Where there are lateral changes in the basal units of a seal rock, the chance of migration out of the primary reservoir into higher intervals increases. However, if the seal rock is uniform, regionally extensive and thick, then the main issues will be the physical rock strength, any natural or anthropomorphic penetrations (faults, fractures and wells) and



KEY QUESTION	NEED	ACTIVITY
Is there a CCS opportunity?	Stationary sources of CO_2	• Determine magnitude of present and future emissions
Is storage capacity likely to be adequate?	Regional storage opportunities	• Screen and select potential sites
Is site suitable?	Site specific characterization and assessment	• Characterize geology • Build numerical models • Reservoir simulation • Risk assessment
Is proposal viable?	Develop proposal for injection and storage of CO_2	• Develop monitoring plan • Develop risk mitigation strategy • Develop well remediation program • Perform economic analysis • Engage stakeholders
Does proposal meet needs of regulator?	Submit application for licence to inject and store CO_2	• Dialogue with licencing authority • Baseline monitoring
Does program meet regulatory conditions and community expectations?	Inject and monitor CO_2	• Monitor mass distribution of CO_2 • Monitor for potential migration of CO_2 outside containment area • Carry out simulations history matching • Update mitigation plan etc • Engage stakeholders
Storage capacity reached. Can injection be concluded and closure commenced?	Conclude injection commence post injection/pre closure period	• Continue monitoring • Continue history matching • Finalize closure strategy • Engage stakeholders
Is the regulator willing to accept closure of site?	Site Closure	• Confirm site behaviour matches conditions of licence • Seal wells • Site remediation • Periodic monitoring by state regulators

Figure 5.19 Life cycle of a CO_2 storage project showing the importance of integrating site characterization with a range of regulatory, monitoring, economic, risking and engineering issues.

Table 5.3 Types of data that are used to characterize and select geological CO_2 storage sites.

- Seismic profiles across the area of interest, preferably three-dimensional or closely spaced two-dimensional surveys;
- Structure contour maps of reservoirs, seals and aquifers;
- Detailed maps of the structural boundaries of the trap where the CO_2 will accumulate, especially highlighting potential spill points;
- Maps of the predicted pathway along which the CO_2 will migrate from the point of injection;
- Documentation and maps of faults and fault;
- Facies maps showing any lateral facies changes in the reservoirs or seals;
- Core and drill cuttings samples from the reservoir and seal intervals;
- Well logs, preferably a consistent suite, including geological, geophysical and engineering logs;
- Fluid analyses and tests from downhole sampling and production testing;
- Oil and gas production data (if a hydrocarbon field);
- Pressure transient tests for measuring reservoir and seal permeability;
- Petrophysical measurements, including porosity, permeability, mineralogy (petrography), seal capacity, pressure, temperature, salinity and laboratory rock strength testing;
- Pressure, temperature, water salinity;
- In situ stress analysis to determine potential for fault reactivation and fault slip tendency and thus identify the maximum sustainable pore fluid pressure during injection in regard to the reservoir, seal and faults;
- Hydrodynamic analysis to identify the magnitude and direction of water flow, hydraulic interconnectivity of formations and pressure decrease associated with hydrocarbon production;
- Seismological data, geomorphological data and tectonic investigations to indicate neotectonic activity.

potential CO_2-water-rock reactions that could weaken the seal rock or increase its porosity and permeability.

Methods have been described for making field-scale measurements of the permeability of caprocks for formation gas storage projects, based on theoretical developments in the 1950s and 1960s (Hantush and Jacobs, 1955; Hantush, 1960). These use water-pumping tests to measure the rate of leakage across the caprock (Witherspoon *et al.*, 1968). A related type of test, called a pressure 'leak-off' test, can be used to measure caprock permeability and *in situ* stress. The capacity of a seal rock to hold back fluids can also be estimated from core samples by mercury injection capillary pressure (MICP) analysis, a method widely used in the oil and gas industry (Vavra *et al.*, 1992). MICP analysis measures the pressures required to move mercury through the pore network system of a seal rock. The resulting data can be used to derive the height of a column of reservoir rock saturated by a particular fluid (e.g., CO_2) that the sealing strata would be capable of holding back (Gibson-Poole *et al.*, 2002).

5.4.1.3 Geomechanical factors affecting site integrity

When CO_2 is injected into a porous and permeable reservoir rock, it will be forced into pores at a pressure higher than that in the surrounding formation. This pressure could lead to deformation of the reservoir rock or the seal rock, resulting in the opening of fractures or failure along a fault plane. Geomechanical modelling of the subsurface is necessary in any storage site assessment and should focus on the maximum formation pressures that can be sustained in a storage site. As an example, at Weyburn, where the initial reservoir pressure is 14.2 MPa, the maximum injection pressure (90% of fracture pressure) is in the range of 25–27 MPa and fracture pressure is in the range of 29–31 MPa. Coupled geomechanical-geochemical modelling may also be needed to document fracture sealing by precipitation of carbonates in fractures or pores. Modelling these will require knowledge of pore fluid composition, mineralogy, *in situ* stresses, pore fluid pressures and pre-existing fault orientations and their frictional properties (Streit and Hillis, 2003; Johnson *et al.*, 2005). These estimates can be made from conventional well and seismic data and leak-off tests, but the results can be enhanced by access to physical measurements of rock strength. Application of this methodology at a regional scale is documented by Gibson-Poole *et al.* (2002).

The efficacy of an oil or gas field seal rock can be characterized by examining its capillary entry pressure and the potential hydrocarbon column height that it can sustain (see above). However, Jimenez and Chalaturnyk (2003) suggest that the geomechanical processes, during depletion and subsequent CO_2 injection, may affect the hydraulic integrity of the seal rock in hydrocarbon fields. Movement along faults can be produced in a hydrocarbon field by induced changes in the pre-production stress regime. This can happen when fluid pressures are substantially depleted during hydrocarbon production (Streit and Hillis, 2003). Determining whether the induced stress changes result in compaction or pore collapse is critical in assessment of a depleted field. If pore collapse occurs, then it might not be possible to return a pressure-depleted field to its original pore pressure without the risk of induced failure. By having a reduced maximum pore fluid pressure, the total volume of CO_2 that can be stored in a depleted field could be substantially less than otherwise estimated.

5.4.1.4 Geochemical factors affecting site integrity

The mixing of CO_2 and water in the pore system of the reservoir rock will create dissolved CO_2, carbonic acid and bicarbonate ions. The acidification of the pore water reduces the amount of CO_2 that can be dissolved. As a consequence, rocks that buffer the pore water *p*H to higher values (reducing the acidity) facilitate the storage of CO_2 as a dissolved phase (Section 5.2). The CO_2-rich water may react with minerals in the reservoir rock or caprock matrix or with the primary pore fluid. Importantly, it may also react with borehole cements and steels (see discussion below). Such reactions may cause either mineral dissolution and potential breakdown of the rock (or cement) matrix or mineral precipitation and plugging of the pore system (and thus, reduction in permeability).

A carbonate mineral formation effectively traps stored CO_2 as an immobile solid phase (Section 5.2). If the mineralogical composition of the rock matrix is strongly dominated by quartz, geochemical reactions will be dominated by simple dissolution into the brine and CO_2-water-rock reactions can be neglected. In this case, complex geochemical simulations of rock-water interactions will not be needed. However, for more complex mineralogies, sophisticated simulations, based on laboratory experimental data that use reservoir and caprock samples and native pore fluids, may be necessary to fully assess the potential effects of such reactions in more complex systems (Bachu *et al.*, 1994; Czernichowski-Lauriol *et al.*, 1996; Rochelle *et al.*, 1999, 2004; Gunter *et al.*, 2000). Studies of rock samples recovered from natural systems rich in CO_2 can provide indications of what reactions might occur in the very long term (Pearce *et al.*, 1996). Reactions in boreholes are considered by Crolet (1983), Rochelle *et al.* (2004) and Schremp and Roberson (1975). Natural CO_2 reservoirs also allow sampling of solid and fluid reactants and reaction products, thus allowing formulation of geochemical models that can be verified with numerical simulations, further facilitating quantitative predictions of water-CO_2-rock reactions (May, 1998).

5.4.1.5 Anthropogenic factors affecting storage integrity

As discussed at greater length in Section 5.7.2, anthropogenic factors such as active or abandoned wells, mine shafts and subsurface production can impact storage security. Abandoned wells that penetrate the storage formation can be of particular concern because they may provide short circuits for CO_2 to leak from the storage formation to the surface (Celia and Bachu, 2003; Gasda *et al.*, 2004). Therefore, locating and assessing the condition of abandoned and active wells is an important component of site characterization. It is possible to locate abandoned wells with airborne magnetometer surveys. In most cases, abandoned wells will have metal casings, but this may not be the case for wells drilled long ago or those never completed for oil or gas production. Countries with oil and gas production will have at least some records of the more recently drilled wells, depth of wells and other information stored in a geographic database. The consistency and quality of record keeping of drilled wells (oil and gas, mining exploration and water) varies considerably, from excellent for recent wells to nonexistent, particularly for older wells (Stenhouse *et al.*, 2004).

5.4.2 Performance prediction and optimization modelling

Computer simulation also has a key role in the design and operation of field projects for underground injection of CO_2. Predictions of the storage capacity of the site or the expected incremental recovery in enhanced recovery projects, are vital to an initial assessment of economic feasibility. In a similar vein, simulation can be used in tandem with economic assessments to optimize the location, number, design and depth of injection wells. For enhanced recovery projects, the timing of CO_2 injection relative to production is vital to the success of the operation and the effect of various strategies can be assessed by simulation. Simulations of the long-term distribution of CO_2 in the subsurface (e.g., migration rate and direction and rate of dissolution in the formation water) are important for the design of cost-effective monitoring programmes, since the results will influence the location of monitoring wells and the frequency of repeat measurements, such as for seismic, soil gas or water chemistry. During injection and monitoring operations, simulation models can be adjusted to match field observations and then used to assess the impact of possible operational changes, such as drilling new wells or altering injection rates, often with the goal of further improving recovery (in the context of hydrocarbon extraction) or of avoiding migration of CO_2 past a likely spill-point.

Section 5.2 described the important physical, chemical and geomechanical processes that must be considered when evaluating a storage project. Numerical simulators currently in use in the oil, gas and geothermal energy industries provide important subsets of the required capabilities. They have served as convenient starting points for recent and ongoing development efforts specifically targeted at modelling the geological storage of CO_2. Many simulation codes have been used and adapted for this purpose (White, 1995; Nitao, 1996; White and Oostrom, 1997; Pruess *et al.*, 1999; Lichtner, 2001; Steefel, 2001; Xu *et al.*, 2003).

Simulation codes are available for multiphase flow processes, chemical reactions and geomechanical changes, but most codes account for only a subset of these processes. Capabilities for a comprehensive treatment of different processes are limited at present. This is especially true for the coupling of multiphase fluid flow, geochemical reactions and (particularly) geomechanics, which are very important for the integrity of potential geological storage sites (Rutqvist and Tsang, 2002). Demonstrating that they can model the important physical and chemical processes accurately and reliably is necessary for establishing credibility as practical engineering tools. Recently, an analytical model developed for predicting the evolution of a plume of CO_2 injected into a deep saline formation, as well as potential CO_2 leakage rates through abandoned wells, has shown good matching with results obtained from the industry numerical simulator ECLIPSE (Celia *et al.*, 2005; Nordbotten *et al.*, 2005b).

A code intercomparison study involving ten research groups from six countries was conducted recently to evaluate the capabilities and accuracy of numerical simulators for geological storage of greenhouse gases (Pruess *et al.*, 2004). The test problems addressed CO_2 storage in saline formations and oil and gas reservoirs. The results of the intercomparison were encouraging in that substantial agreement was found between results obtained with different simulators. However, there were also areas with only fair agreement, as well as some significant discrepancies. Most discrepancies could be traced to differences in fluid property descriptions, such as fluid densities and viscosities and mutual solubility of CO_2 and water. The study concluded that 'although code development work undoubtedly must continue . . . codes are available now that can model the complex phenomena accompanying geological storage of CO_2 in a robust manner and with quantitatively similar results' (Pruess *et al*., 2004).

Another, similar intercomparison study was conducted for simulation of storage of CO_2 in coal beds, considering both pure CO_2 injection and injection of flue gases (Law *et al*., 2003). Again, there was good agreement between the simulation results from different codes. Code intercomparisons are useful for checking mathematical methods and numerical approximations and to provide insight into relevant phenomena by using the different descriptions of the physics (or chemistry) implemented. However, establishing the realism and accuracy of physical and chemical process models is a more demanding task, one that requires carefully controlled and monitored field and laboratory experiments. Only after simulation models have been shown to be capable of adequately representing real-world observations can they be relied upon for engineering design and analysis. Methods for calibrating models to complex engineered subsurface systems are available, but validating them requires field testing that is time consuming and expensive.

The principal difficulty is that the complex geological models on which the simulation models are based are subject to considerable uncertainties, resulting both from uncertainties in data interpretation and, in some cases, sparse data sets. Measurements taken at wells provide information on rock and fluid properties at that location, but statistical techniques must be used to estimate properties away from the wells. When simulating a field in which injection or production is already occurring, a standard approach in the oil and gas industry is to adjust some parameters of the geological model to match selected field observations. This does not prove that the model is correct, but it does provide additional constraints on the model parameters. In the case of saline formation storage, history matching is generally not feasible for constraining uncertainties, due to a lack of underground data for comparison. Systematic parameter variation routines and statistical functions should be included in future coupled simulators to allow uncertainty estimates for numerical reservoir simulation results.

Field tests of CO_2 injection are under way or planned in several countries and these tests provide opportunities to validate simulation models. For example, in Statoil's Sleipner project, simulation results have been matched to information on the distribution of CO_2 in the subsurface, based on the interpretation of repeat three-dimensional seismic surveys (Lindeberg *et al*., 2001; van der Meer *et al*., 2001; see also Section 5.4.3. At the Weyburn project in Canada, repeat seismic surveys and water chemistry sampling provide information on CO_2 distribution that can likewise be used to adjust the simulation models (Moberg *et al*., 2003; White *et al*., 2004).

Predictions of the long-term distribution of injected CO_2, including the effects of geochemical reactions, cannot be directly validated on a field scale because these reactions may take hundreds to thousands of years. However, the simulation of important mechanisms, such as the convective mixing of dissolved CO_2, can be tested by comparison to laboratory analogues (Ennis-King and Paterson, 2003). Another possible route is to match simulations to the geochemical changes that have occurred in appropriate natural underground accumulations of CO_2, such as the precipitation of carbonate minerals, since these provide evidence for the slow processes that affect the long-term distribution of CO_2 (Johnson *et al*., 2005). It is also important to have reliable and accurate data regarding the thermophysical properties of CO_2 and mixtures of CO_2 with methane, water and potential contaminants such as H_2S and SO_2. Similarly, it is important to have data on relative permeability and capillary pressure under drainage and imbibition conditions. Code comparison studies show that the largest discrepancies between different simulators can be traced to uncertainties in these parameters (Pruess *et al*., 2004). For sites where few, if any, CO_2-water-rock interactions occur, reactive chemical transport modelling may not be needed and simpler simulations that consider only CO_2-water reactions will suffice.

5.4.3 *Examples of storage site characterization and performance prediction*

Following are examples and lessons learned from two case studies of characterization of a CO_2 storage site: one of an actual operating CO_2 storage site (Sleipner Gas Field in the North Sea) and the other of a potential or theoretical site (Petrel Sub-basin offshore northwest Australia). A common theme throughout these studies is the integration and multidisciplinary approach required to adequately document and monitor any injection site. There are lessons to be learned from these studies, because they have identified issues that in hindsight should be examined prior to any CO_2 injection.

5.4.3.1 Sleipner

Studies of the Sleipner CO_2 Injection Project (Box 5.1) highlighted the advantages of detailed knowledge of the reservoir stratigraphy (Chadwick *et al*., 2003). After the initial CO_2 injection, small layers of low-permeability sediments within the saline formation interval and sandy lenses near the base of the seal were clearly seen to be exercising an important control on the distribution of CO_2 within the reservoir rock (Figure 5.16a,b). Time-lapse three-dimensional seismic imaging of the developing CO_2 plume also identified the need for precision depth mapping of the bottom of the caprock interval. At Sleipner, the top of the reservoir is almost flat at a regional scale. Hence, any subtle variance in the actual versus predicted depth could substantially affect migration patterns and rate. Identification and mapping of a sand lens above what was initially interpreted as the top of the reservoir resulted in a significant change to the predicted migration direction of the CO_2 (Figure 5.16a,b). These results show the benefit of repeated three-dimensional seismic monitoring and integration of monitoring results into modelling during the injection phase of the project. Refinement of the storage-site characterization continues after injection has started.

5.4.3.2 Petrel Sub-basin

A theoretical case study of the Petrel Sub-basin offshore northwest Australia examined the basin-wide storage potential of a combined hydrodynamic and solution trapping mechanism and identified how sensitive a reservoir simulation will be to the collected data and models built during the characterization of a storage site (Gibson-Poole *et al*., 2002; Ennis-King *et al*., 2003). As at Sleipner, the Petrel study identified that vertical permeability and shale beds within the reservoir interval of the geological model strongly influenced the vertical CO_2 migration rate. In the reservoir simulation, use of coarser grids overestimated the dissolution rate of CO_2 during the injection period, but underestimated it during the long-term migration period. Lower values of residual CO_2 saturation led to faster dissolution during the long-term migration period and the rate of complete dissolution depended on the vertical permeability. Migration distance depended on the rate of dissolution and residual CO_2 trapping. The conclusion of the characterization and performance prediction studies is that the Petrel Sub-basin has a regionally extensive reservoir-seal pair suitable for hydrodynamic trapping (Section 5.2). While the characterization was performed on the basis of only a few wells with limited data, analogue studies helped define the characteristics of the formation. Although this is not the ideal situation, performing a reservoir simulation by using geological analogues may often be the only option. However, understanding which elements will be the most sensitive in the simulation will help geoscientists to understand where to prioritize their efforts in data collection and interpretation.

5.5 Injection well technology and field operations

So far in this chapter, we have considered only the nature of the storage site. But once a suitable site is identified, do we have the technology available to inject large quantities of CO_2 (1–10 $MtCO_2$ yr^{-1}) into the subsurface and to operate the site effectively and safely? This section examines the issue of technology availability.

5.5.1 Injection well technologies

As pointed out earlier in this chapter, many of the technologies required for large-scale geological storage of CO_2 already exist. Drilling and completion technology for injection wells in the oil and gas industry has evolved to a highly sophisticated state, such that it is now possible to drill and complete vertical and extended reach wells (including horizontal wells) in deep formations, wells with multiple completions and wells able to handle corrosive fluids. On the basis of extensive oil industry experience, the technologies for drilling, injection, stimulations and completions for CO_2 injection wells exist and are being practised with some adaptations in current CO_2 storage projects. In a CO_2 injection well, the principal well design considerations include pressure, corrosion-resistant materials and production and injection rates.

The design of a CO_2 injection well is very similar to that of a gas injection well in an oil field or natural gas storage project. Most downhole components need to be upgraded for higher pressure ratings and corrosion resistance. The technology for handling CO_2 has already been developed for EOR operations and for the disposal of acid gas (Section 5.2.4.) Horizontal and extended reach wells can be good options for improving the rate of CO_2 injection from individual wells. The Weyburn field in Canada (Box 5.3) is an example in which the use of horizontal injection wells is improving oil recovery and increasing CO_2 storage. The horizontal injectors reduce the number of injection wells required for field development. A horizontal injection well has the added advantage that it can create injection profiles that reduce the adverse effects of injected-gas preferential flow through high-permeability zones.

The number of wells required for a storage project will depend on a number of factors, including total injection rate, permeability and thickness of the formation, maximum injection pressures and availability of land-surface area for the injection wells. In general, fewer wells will be needed for high-permeability sediments in thick storage formations and for those projects with horizontal wells for injection. For example, the Sleipner Project, which injects CO_2 into a high-permeability, 200-m-thick formation uses only one well to inject 1 $MtCO_2$ yr^{-1} (Korbol and Kaddour, 1994). In contrast, at the In Salah Project in Algeria, CO_2 is injected into a 20-m-thick formation with much lower permeability (Riddiford *et al*., 2003). Here, three long-reach horizontal wells with slotted intervals over 1 km are used to inject 1 $MtCO_2$ yr^{-1} (Figure 5.5). Cost will depend, to some degree, on the number and completion techniques for these wells. Therefore, careful design and optimization of the number and slotted intervals is important for cost-effective storage projects.

An injection well and a wellhead are depicted in Figure 5.20. Injection wells commonly are equipped with two valves for well control, one for regular use and one reserved for safety shutoff. In acid gas injection wells, a downhole safety valve is incorporated in the tubing, so that if equipment fails at the surface, the well is automatically shut down to prevent back flow. Jarrell *et al*. (2002) recommend an automatic shutoff valve on all CO_2 wells to ensure that no release occurs and to prevent CO_2 from inadvertently flowing back into the injection system. A typical downhole configuration for an injection well includes a double-grip packer, an on-off tool and a downhole shutoff valve. Annular pressure monitors help detect leaks in packers and tubing, which is important for taking rapid corrective action. To prevent dangerous high-pressure buildup on surface equipment and avoid CO_2 releases into the atmosphere, CO_2 injection must be stopped as soon as leaks occur. Rupture disks and safety valves can be used to relieve built-up pressure. Adequate plans need to be in place for dealing with excess CO_2 if the injection well needs to be shut in. Options include having

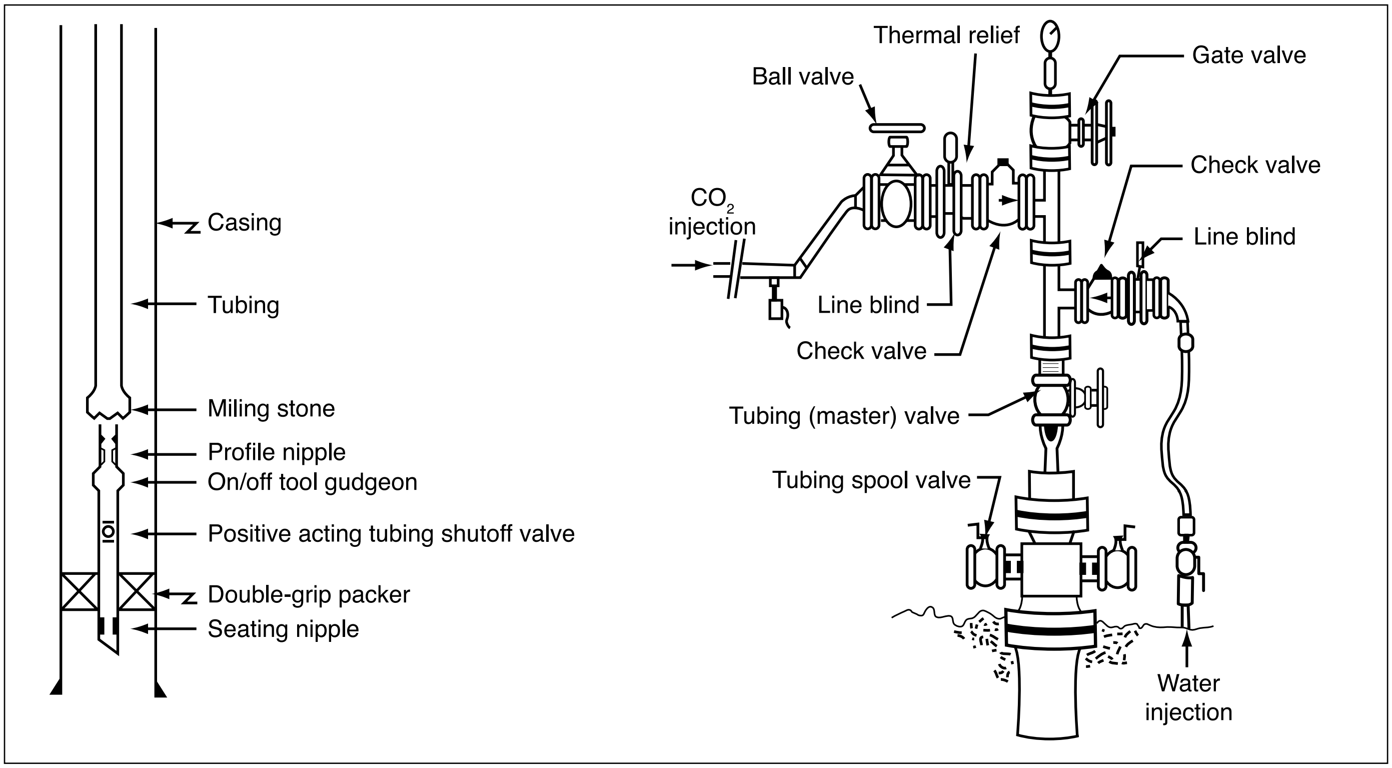


Figure 5.20 Typical CO_2 injection well and wellhead configuration.

a backup injection well or methods to safely vent CO_2 to the atmosphere.

Proper maintenance of CO_2 injection wells is necessary to avoid leakage and well failures. Several practical procedures can be used to reduce probabilities of CO_2 blow-out (uncontrolled flow) and mitigate the adverse effects if one should occur. These include periodic wellbore integrity surveys on drilled injection wells, improved blow-out prevention (BOP) maintenance, installation of additional BOP on suspect wells, improved crew awareness, contingency planning and emergency response training (Skinner, 2003).

For CO_2 injection through existing and old wells, key factors include the mechanical condition of the well and quality of the cement and well maintenance. A leaking wellbore annulus can be a pathway for CO_2 migration. Detailed logging programmes for checking wellbore integrity can be conducted by the operator to protect formations and prevent reservoir cross-flow. A well used for injection (Figure 5.20) must be equipped with a packer to isolate pressure to the injection interval. All materials used in injection wells should be designed to anticipate peak volume, pressure and temperature. In the case of wet gas (containing free water), use of corrosion-resistant material is essential.

5.5.2 *Well abandonment procedures*

Abandonment procedures for oil, gas and injection wells are designed to protect drinking water aquifers from contamination. If a well remains open after it is no longer in use, brines, hydrocarbons or CO_2 could migrate up the well and into shallow drinking water aquifers. To avoid this, many countries have developed regulations for well 'abandonment' or 'closure' (for example, United States Code of Federal Regulations 40 Part 144 and Alberta Energy and Utilities Board, 2003). These procedures usually require placing cement or mechanical plugs in all or part of the well. Extra care is usually taken to seal the well adjacent to drinking water aquifers. Examples of well abandonment procedures for cased and uncased wells are shown in Figure 5.21. Tests are often required to locate the depth of the plugs and test their mechanical strength under pressure.

It is expected that abandonment procedures for CO_2 wells could broadly follow the abandonment methodology used for oil and gas wells and acid-gas disposal wells. However, special care has to be taken to use sealing plugs and cement that are resistant to degradation from CO_2. Carbon dioxide-resistant cements have been developed for oil field and geothermal applications. It has been suggested that removing the casing and the liner penetrating the caprock could avoid corrosion of the steel that may later create channels for leakage. The production casing can be removed by pulling or drilling (milling) it out. After removing the casing, a cement plug can be put into the open borehole, as illustrated in Figure 5.21.

The cement plug will act as the main barrier to future CO_2 migration. A major issue is related to the sealing quality of the cement plug and the bonding quality with the penetrated caprock. Microchannels created near the wellbore during drilling or milling operations should be sealed with cement. Fluid could also be flushed into the storage reservoir to displace the CO_2 and help to improve the cementing quality and bonding to the sealing caprock. Casing protective materials and alternative casing materials, such as composites, should also be evaluated

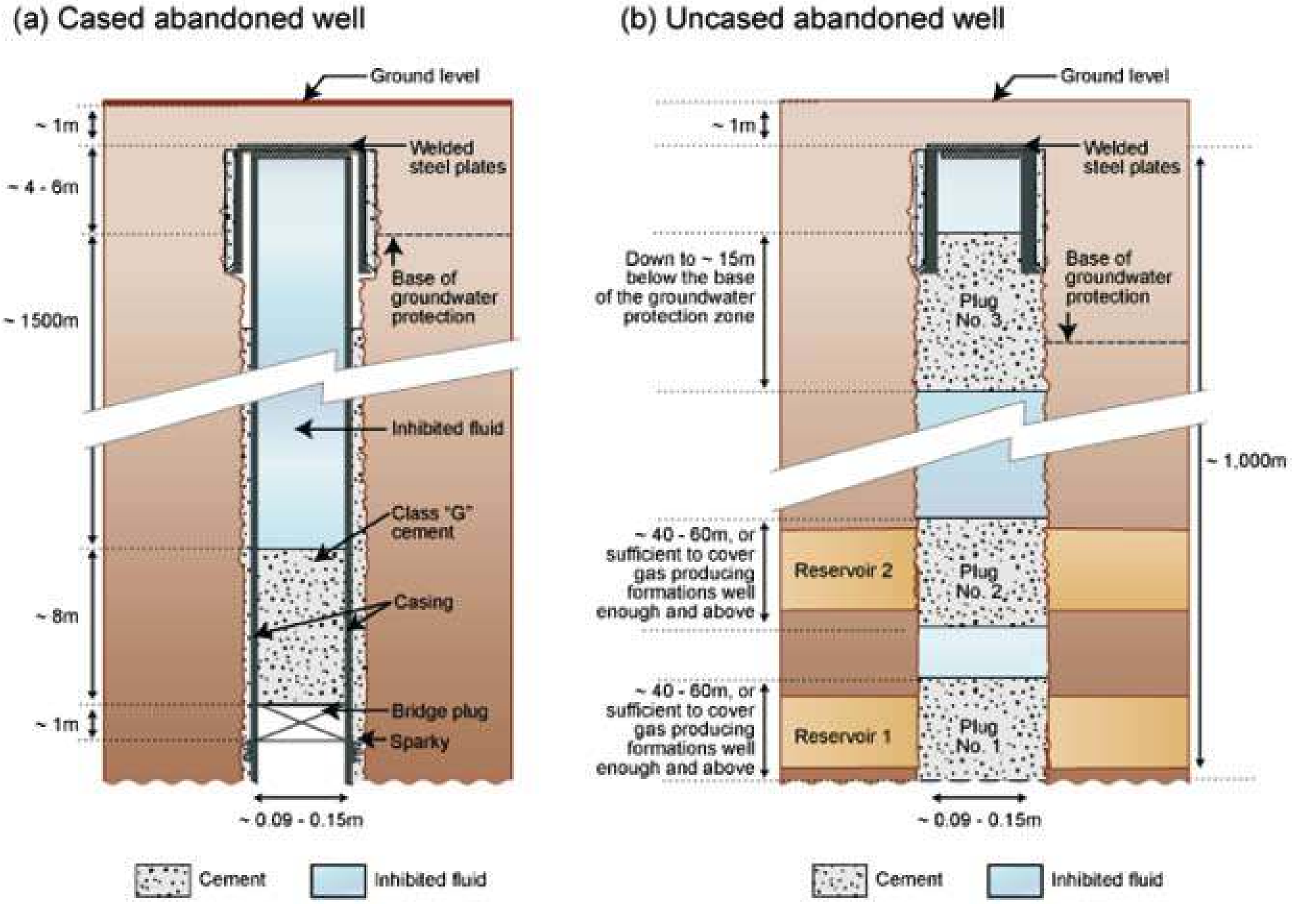


Figure 5.21 Examples of how cased and uncased wells are abandoned today. Special requirements may be developed for abandoning CO_2 storage wells, including use of corrosion-resistant cement plugs and removing all or part of the casing in the injection interval and caprock.

for possible and alternative abandonment procedures. Sealing performance of abandoned wells may need to be monitored for some time after storage operations are completed.

5.5.3 Injection well pressure and reservoir constraints

Injectivity characterizes the ease with which fluid can be injected into a geological formation and is defined as the injection rate divided by the pressure difference between the injection point inside the well and the formation. Although CO_2 injectivity should be significantly greater than brine injectivity (because CO_2 has a much lower viscosity than brine), this is not always the case. Grigg (2005) analyzed the performance of CO_2 floods in west Texas and concluded that, in more than half of the projects, injectivity was lower than expected or decreased over time. Christman and Gorell (1990) showed that unexpected CO_2-injectivity behaviour in EOR operations is caused primarily by differences in flow geometry and fluid properties of the oil. Injectivity changes can also be related to insufficiently known relative permeability effects.

To introduce CO_2 into the storage formation, the downhole injection pressure must be higher than the reservoir fluid pressure. On the other hand, increasing formation pressure may induce fractures in the formation. Regulatory agencies normally limit the maximum downhole pressure to avoid fracturing the injection formation. Measurements of *in-situ* formation stresses and pore fluid pressure are needed for establishing safe injection pressures. Depletion of fluid pressure during production can affect the state of stress in the reservoir. Analysis of some depleted reservoirs indicated that horizontal rock stress decreased by 50–80% of the pore pressure decrease, which increased the possibility of fracturing the reservoir (Streit and Hillis, 2003).

Safe injection pressures can vary widely, depending on the state of stress and tectonic history of a basin. Regulatory agencies have determined safe injection pressures from experience in specific oil and gas provinces. Van der Meer (1996) has derived a relationship for the maximum safe injection pressure. This relationship indicated that for a depth down to 1000 m, the maximum injection pressure is estimated to be 1.35 times the hydrostatic pressure – and this increased to 2.4 for depths of 1–5 km. The maximum pressure gradient allowed for natural gas stored in an aquifer in Germany is 16.8 kPa m^{-1} (Sedlacek, 1999). This value exceeds the natural pressure gradients of formation waters in northeastern Germany, which are on the order of 10.5–13.1 kPa m^{-1}. In Denmark or Great Britain, the maximum pressure gradients for aquifer storage of natural gas do not exceed hydrostatic gradients. In the United States,

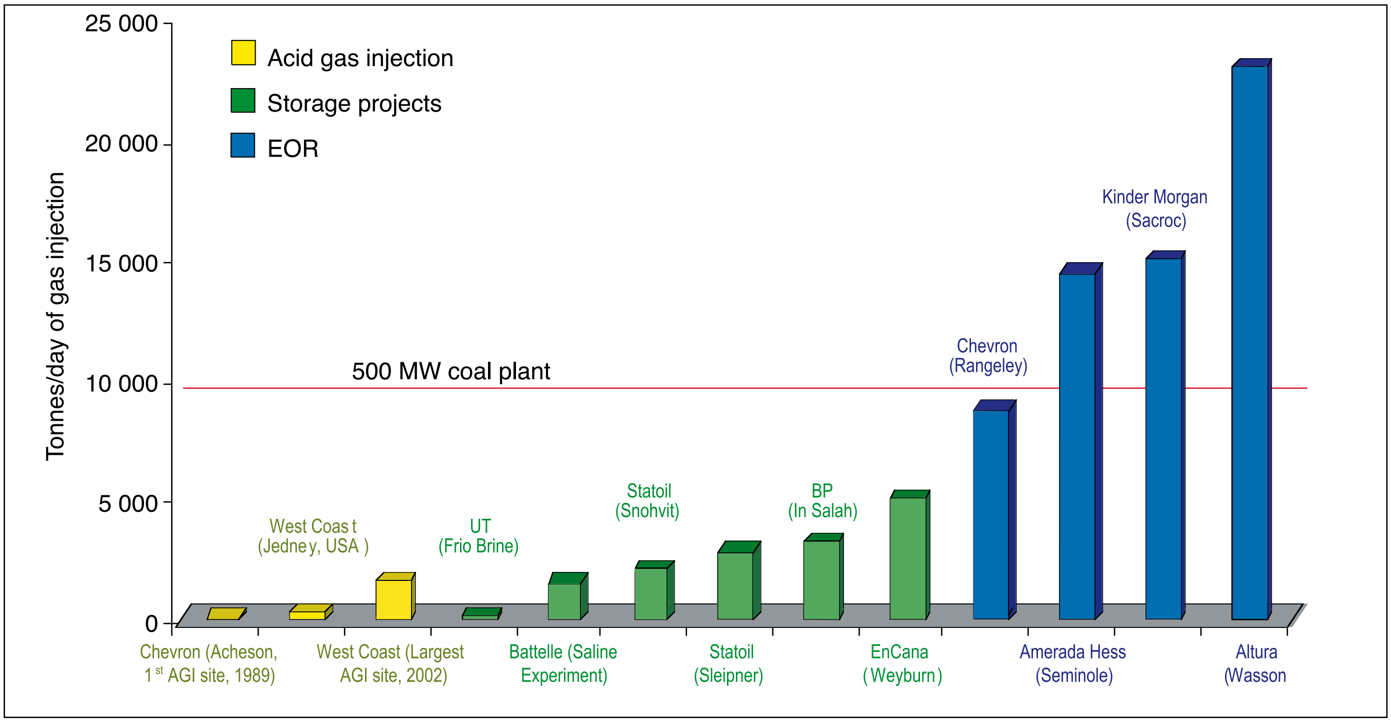


Figure 5.22 Comparison of the magnitude of CO_2 injection activities illustrating that the storage operations from a typical 500-MW coal plant will be the same order of magnitude as existing CO_2 injection operations (after Heinrich *et al.*, 2003).

for industrial waste-water injection wells, injection pressure must not exceed fracture initiation or propagation pressures in the injection formation (USEPA, 1994). For oil and gas field injection wells, injection pressures must not exceed those that would initiate or propagate fractures in the confining units. In the United States, each state has been delegated authority to establish maximum injection pressures. Until the 1990s, many states set state-wide standards for maximum injection pressures; values ranged from 13 to18 kPa m^{-1}. More recently, regulations have changed to require site-specific tests to establish maximum injection pressure gradients. Practical experience in the USEPA's Underground Injection Control Program has shown that fracture pressures range from 11 to 21 kPa m^{-1}.

5.5.4 Field operations and surface facilities

Injection rates for selected current CO_2 storage projects in EOR and acid gas injection are compared in Figure 5.22. As indicated, the amount of CO_2 injected from a 500-MW coal-fired power plant would fall within the range of existing experience of CO_2 injection operations for EOR. These examples therefore offer a great deal of insight as to how a geological storage regime might evolve, operate and be managed safely and effectively.

CO_2-EOR operations fall into one of three groups (Jarrell *et al.*, 2002):

- Reservoir management – what to inject, how fast to inject, how much to inject, how to manage water-alternating-gas (WAG), how to maximize sweep efficiency and so on;
- Well management – producing method and remedial work, including selection of workovers, chemical treatment and CO_2 breakthrough;
- Facility management – reinjection plant, separation, metering, corrosion control and facility organization.

Typically, CO_2 is transported from its source to an EOR site through a pipeline and is then injected into the reservoir through an injection well, usually after compression. Before entering the compressor, a suction scrubber will remove any residual liquids present in the CO_2 stream. In EOR operations, CO_2 produced from the production well along with oil and water is separated and then injected back through the injection well.

The field application of CO_2-ECBM technology is broadly similar to that of EOR operations. Carbon dioxide is transported to the CBM field and injected in the coal seam through dedicated injection wells. At the production well, coal-seam gas and formation water is lifted to the surface by electric pumps.

According to Jarrell *et al.* (2002), surface facilities for CO_2-EOR projects include:

- Production systems-fluid separation, gas gathering, production satellite, liquid gathering, central battery, field compression and emergency shutdown systems;
- Injection systems-gas repressurization, water injection and CO_2 distribution systems;
- Gas processing systems-gas processing plant, H_2S removal systems and sulphur recovery and disposal systems.

Jarrell *et al.* (2002) point out that CO_2 facilities are similar to those used in conventional facilities such as for waterfloods. Differences result from the effects of multiphase flow, selection of different materials and the higher pressure that must be handled. The CO_2 field operation setup for the Weyburn Field is shown in Figure 5.23.

It is common to use existing facilities for new CO_2 projects to reduce capital costs, although physical restrictions are always present. Starting a CO_2 flood in an old oil field can affect almost every process and facility (Jarrell *et al*., 2002); for example, (1) the presence of CO_2 makes the produced water much more corrosive; (2) makeup water from new sources may interact with formation water to create new problems with scale or corrosion; (3) a CO_2 flood may cause paraffins and asphaltenes to precipitate out of the oil, which can cause plugging and emulsion problems; and (4) the potentially dramatic increase in production caused by the flood could cause more formation fines to be entrained in the oil, potentially causing plugging, erosion and processing problems.

5.6 Monitoring and verification technology

What actually happens to CO_2 in the subsurface and how do we know what is happening? In other words, can we monitor CO_2 once it is injected? What techniques are available for monitoring whether CO_2 is leaking out of the storage formation and how sensitive are they? Can we verify that CO_2 is safely and effectively stored underground? How long is monitoring needed? These questions are addressed in this section of the report.

5.6.1 Purposes for monitoring

Monitoring is needed for a wide variety of purposes. Specifically, monitoring can be used to:

- Ensure and document effective injection well controls, specifically for monitoring the condition of the injection well and measuring injection rates, wellhead and formation pressures. Petroleum industry experience suggests that leakage from the injection well itself, resulting from improper completion or deterioration of the casing, packers or cement, is one of the most significant potential failure modes for injection projects (Apps, 2005; Perry, 2005);
- Verify the quantity of injected CO_2 that has been stored by various mechanisms;
- Optimize the efficiency of the storage project, including utilization of the storage volume, injection pressures and drilling of new injection wells;
- Demonstrate with appropriate monitoring techniques that CO_2 remains contained in the intended storage formation(s). This is currently the principal method for assuring that the CO_2 remains stored and that performance predictions can be verified;
- Detect leakage and provide an early warning of any seepage or leakage that might require mitigating action.

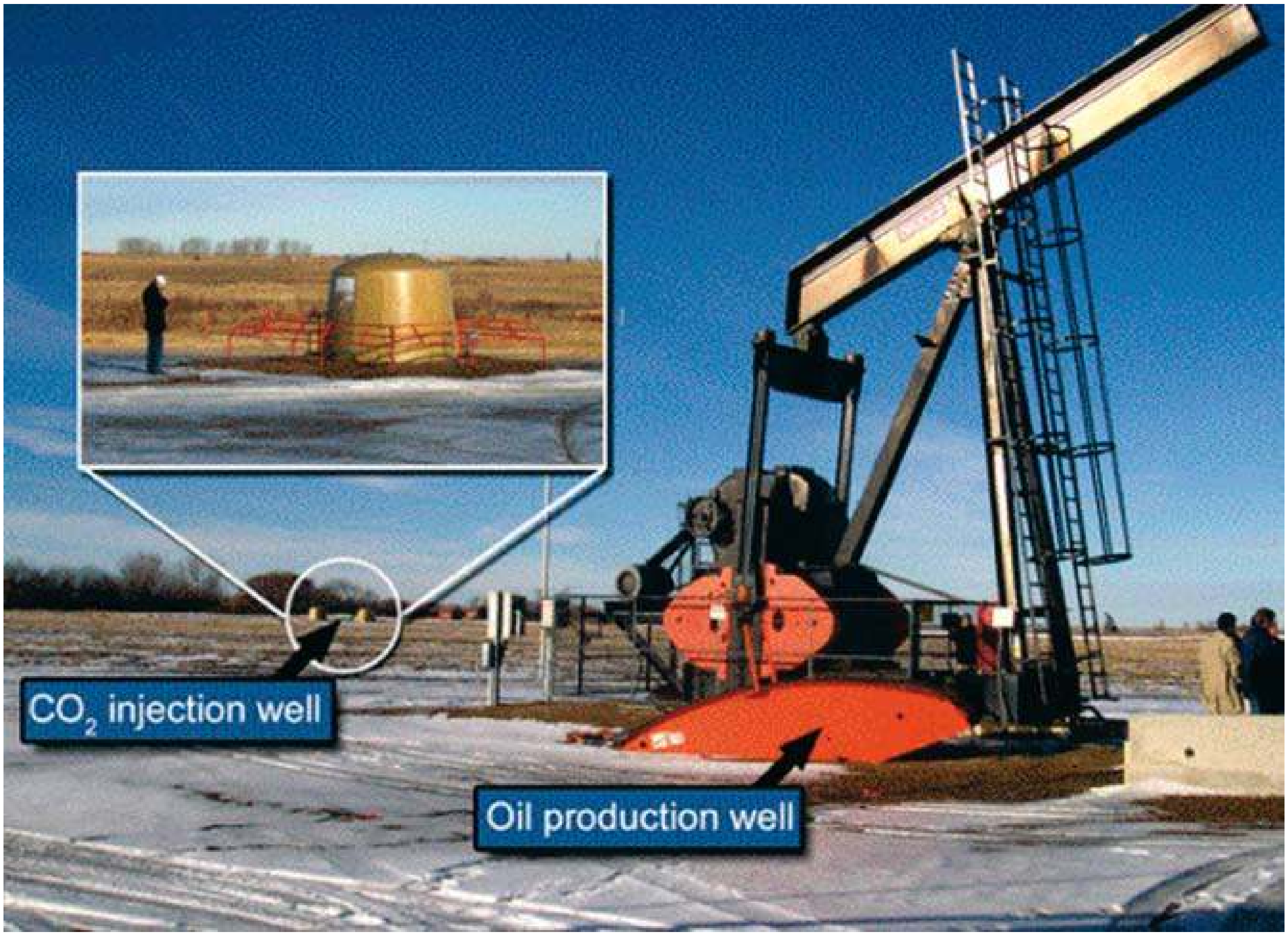


Figure 5.23 Typical CO_2 field operation setup: Weyburn surface facilities.

In addition to essential elements of a monitoring strategy, other parameters can be used to optimize storage projects, deal with unintended leakage and address regulatory, legal and social issues. Other important purposes for monitoring include assessing the integrity of plugged or abandoned wells, calibrating and confirming performance assessment models (including 'history matching'), establishing baseline parameters for the storage site to ensure that CO_2-induced changes are recognized (Wilson and Monea, 2005), detecting microseismicity associated with a storage project, measuring surface fluxes of CO_2 and designing and monitoring remediation activities (Benson *et al.*, 2004).

Before monitoring of subsurface storage can take place effectively, a baseline survey must be taken. This survey provides the point of comparison for subsequent surveys. This is particularly true of seismic and other remote-sensing technologies, where the identification of saturation of fluids with CO_2 is based on comparative analysis. Baseline monitoring is also a prerequisite for geochemical monitoring, where anomalies are identified relative to background concentrations. Additionally, establishing a baseline of CO_2 fluxes resulting from ecosystem cycling of CO_2, both on diurnal and annual cycles, are useful for distinguishing natural fluxes from potential storage-related releases.

Much of the monitoring technology described below was developed for application in the oil and gas industry. Most of these techniques can be applied to monitoring storage projects in all types of geological formations, although much remains to be learned about monitoring coal formations. Monitoring experience from natural gas storage in saline aquifers can also provide a useful industrial analogue.

5.6.2 Technologies for monitoring injection rates and pressures

Measurements of CO_2 injection rates are a common oil field practice and instruments for this purpose are available commercially. Measurements are made by gauges either at the injection wellhead or near distribution manifolds. Typical systems use orifice meters or other devices that relate the pressure drop across the device to the flow rate. The accuracy of the measurements depends on a number of factors that have been described in general by Morrow *et al.* (2003) and specifically for CO_2 by Wright and Majek (1998). For CO_2, accurate estimation of the density is most important for improving measurement accuracy. Small changes in temperature, pressure and composition can have large effects on density. Wright and Majek (1998) developed an oil field CO_2 flow rate system by combining pressure, temperature and differential pressure measurements with gas chromatography. The improved system had an accuracy of 0.6%, compared to 8% for the conventional system. Standards for measurement accuracy vary and are usually established by governments or industrial associations. For example, in the United States, current auditing practices for CO_2-EOR accept flow meter precision of ±4%.

Measurements of injection pressure at the surface and in the formation are also routine. Pressure gauges are installed on most injection wells through orifices in the surface piping near the wellhead. Downhole pressure measurements are routine, but are used for injection well testing or under special circumstances in which surface measurements do not provide reliable information about the downhole pressure. A wide variety of pressure sensors are available and suitable for monitoring pressures at the wellhead or in the formation. Continuous data are available and typically transmitted to a central control room. Surface pressure gauges are often connected to shut-off valves that will stop or curtail injection if the pressure exceeds a predetermined safe threshold or if there is a drop in pressure as a result of a leak. In effect, surface pressures can be used to ensure that downhole pressures do not exceed the threshold of reservoir fracture pressure. A relatively recent innovation, fibre-optic pressure and temperature sensors, is commercially available. Fibre-optic cables are lowered into the wells, connected to sensors and provide real-time formation pressure and temperature measurements. These new systems are expected to provide more reliable measurements and well control.

The current state of the technology is more than adequate to meet the needs for monitoring injection rates, wellhead and formation pressures. Combined with temperature measurements, the collected data will provide information on the state of the CO_2 (supercritical, liquid or gas) and accurate measurement of the amount of CO_2 injected for inventories, reporting and verification, as well as input to modelling. In the case of the Weyburn project, for example, the gas stream is also analyzed to determine the impurities in the CO_2, thus allowing computation of the volume of CO_2 injected.

5.6.3 Technologies for monitoring subsurface distribution of CO_2

A number of techniques can be used to monitor the distribution and migration of CO_2 in the subsurface. Table 5.4 summarizes these techniques and how they can be applied to CO_2 storage projects. The applicability and sensitivity of these techniques are somewhat site-specific. Detailed descriptions, including limitations and resolution, are provided in Sections 5.6.3.1 and 5.6.3.2.

5.6.3.1 Direct techniques for monitoring CO_2 migration

Direct techniques for monitoring are limited in availability at present. During CO_2 injection for EOR, the injected CO_2 spreads through the reservoir in a heterogeneous manner, because of permeability variations in the reservoir (Moberg *et al.*, 2003). In the case of CO_2-EOR, once the CO_2 reaches a production well, its produced volume can be readily determined. In the case of Weyburn, the carbon in the injected CO_2 has a different isotopic composition from the carbon in the reservoir (Emberley *et al.*, 2002), so the distribution of the CO_2 can be determined on a gross basis by evaluating the arrival of the introduced CO_2 at different production wells. With multiple injection wells in any producing area, the arrival of CO_2 can give only a general indication of distribution in the reservoir.

Table 5.4 Summary of direct and indirect techniques that can be used to monitor CO_2 storage projects.

Measurement technique	Measurement parameters	Example applications
Introduced and natural tracers	Travel time Partitioning of CO_2 into brine or oil Identification sources of CO_2	Tracing movement of CO_2 in the storage formation Quantifying solubility trapping Tracing leakage
Water composition	CO_2, HCO_3^-, CO_3^{2-} Major ions Trace elements Salinity	Quantifying solubility and mineral trapping Quantifying CO_2-water-rock interactions Detecting leakage into shallow groundwater aquifers
Subsurface pressure	Formation pressure Annulus pressure Groundwater aquifer pressure	Control of formation pressure below fracture gradient Wellbore and injection tubing condition Leakage out of the storage formation
Well logs	Brine salinity Sonic velocity CO_2 saturation	Tracking CO_2 movement in and above storage formation Tracking migration of brine into shallow aquifers Calibrating seismic velocities for 3D seismic surveys
Time-lapse 3D seismic imaging	P and S wave velocity Reflection horizons Seismic amplitude attenuation	Tracking CO_2 movement in and above storage formation
Vertical seismic profiling and crosswell seismic imaging	P and S wave velocity Reflection horizons Seismic amplitude attenuation	Detecting detailed distribution of CO_2 in the storage formation Detection leakage through faults and fractures
Passive seismic monitoring	Location, magnitude and source characteristics of seismic events	Development of microfractures in formation or caprock CO_2 migration pathways
Electrical and electromagnetic techniques	Formation conductivity Electromagnetic induction	Tracking movement of CO_2 in and above the storage formation Detecting migration of brine into shallow aquifers
Time-lapse gravity measurements	Density changes caused by fluid displacement	Detect CO_2 movement in or above storage formation CO_2 mass balance in the subsurface
Land surface deformation	Tilt Vertical and horizontal displacement using interferometry and GPS	Detect geomechanical effects on storage formation and caprock Locate CO_2 migration pathways
Visible and infrared imaging from satellite or planes	Hyperspectral imaging of land surface	Detect vegetative stress
CO_2 land surface flux monitoring using flux chambers or eddycovariance	CO_2 fluxes between the land surface and atmosphere	Detect, locate and quantify CO_2 releases
Soil gas sampling	Soil gas composition Isotopic analysis of CO_2	Detect elevated levels of CO_2 Identify source of elevated soil gas CO_2 Evaluate ecosystem impacts

A more accurate approach is to use tracers (gases or gas isotopes not present in the reservoir system) injected into specific wells. The timing of the arrival of the tracers at production or monitoring wells will indicate the path the CO_2 is taking through the reservoir. Monitoring wells may also be used to passively record the movement of CO_2 past the well, although it should be noted that the use of such invasive techniques potentially creates new pathways for leakage to the surface. The movement of tracers or isotopically distinct carbon (in the CO_2) to production or monitoring wells provides some indication of the lateral distribution of the CO_2 in a storage reservoir. In thick formations, multiple sampling along vertical monitoring or production wells would provide some indication of the vertical distribution of the CO_2 in the formation. With many wells and frequently in horizontal wells, the lack of casing (open hole completion) precludes direct measurement of the location of CO_2 influx along the length of the well, although it may be possible to run surveys to identify the location of major influx.

Direct measurement of migration beyond the storage site can be achieved in a number of ways, depending on where the migration takes the CO_2. Comparison between baseline surveys of water quality and/or isotopic composition can be used to identify new CO_2 arrival at a specific location from natural CO_2 pre-existing at that site. Geochemical techniques can also be used to understand more about the CO_2 and its movement through the reservoir (Czernichowski-Lauriol *et al*., 1996; Gunter *et al*., 2000; Wilson and Monea, 2005). The chemical changes that occur in the reservoir fluids indicate the increase in acidity and the chemical effects of this change, in particular the bicarbonate ion levels in the fluids. At the surface, direct measurement can be undertaken by sampling for CO_2 or tracers in soil gas and near surface water-bearing horizons (from existing water wells or new observation wells). Surface CO_2 fluxes may be directly measurable by techniques such as infrared spectroscopy (Miles *et al*., 2005; Pickles, 2005; Shuler and Tang, 2005).

5.6.3.2 Indirect techniques for monitoring CO_2 migration

Indirect techniques for measuring CO_2 distribution in the subsurface include a variety of seismic and non-seismic geophysical and geochemical techniques (Benson *et al*., 2004; Arts and Winthaegen, 2005; Hoversten and Gasperikova, 2005). Seismic techniques basically measure the velocity and energy absorption of waves, generated artificially or naturally, through rocks. The transmission is modified by the nature of the rock and its contained fluids. In general, energy waves are generated artificially by explosions or ground vibration. Wave generators and sensors may be on the surface (conventional seismic) or modified with the sensors in wells within the subsurface and the source on the surface (vertical seismic profiling). It is also possible to place both sensors and sources in the subsurface to transmit the wave pulses horizontally through the reservoir (inter-well or cross-well tomography). By taking a series of surveys over time, it is possible to trace the distribution of the CO_2 in the reservoir, assuming the free-phase CO_2 volume at the site is sufficiently high to identify from the processed data. A baseline survey with no CO_2 present provides the basis against which comparisons can be made. It would appear that relatively low volumes of free-phase CO_2 (approximately 5% or more) may be identified by these seismic techniques; at present, attempts are being made to quantify the amount of CO_2 in the pore space of the rocks and the distribution within the reservoir (Hoversten *et al*., 2003). A number of techniques have been actively tested at Weyburn (Section 5.6.3.3), including time-lapse surface three-dimensional seismic (both 3- and 9-component), at one-year intervals (baseline and baseline plus one and two years), vertical seismic profiling and cross-well (horizontal and vertical) tomography between pairs of wells.

For deep accumulations of CO_2 in the subsurface, where CO_2 density approaches the density of fluids in the storage formation, the sensitivity of surface seismic profiles would suggest that resolution on the order of 2500–10,000 t of free-phase CO_2 can be identified (Myer *et al*., 2003; White *et al*., 2004; Arts *et al*., 2005). At Weyburn, areas with low injection rates (<2% hydrocarbon pore volume) demonstrate little or no visible seismic response. In areas with high injection rates (3–13% hydrocarbon pore volume), significant seismic anomalies are observed. Work at Sleipner shows that the CO_2 plume comprises several distinct layers of CO_2, each up to about 10 m thick. These are mostly beneath the strict limit of seismic resolution, but amplitude studies suggest that layer thicknesses as low as 1 m can be mapped (Arts *et al*., 2005; Chadwick *et al*., 2005). Seismic resolution will decrease with depth and certain other rock-related properties, so the above discussion of resolution will not apply uniformly in all storage scenarios. One possible way of increasing the accuracy of surveys over time is to create a permanent array of sensors or even sensors and energy sources (US Patent 6813566), to eliminate the problems associated with surveying locations for sensors and energy sources.

For CO_2 that has migrated even shallower in the subsurface, its gas-like properties will vastly increase the detection limit; hence, even smaller threshold levels of resolution are expected. To date, no quantitative studies have been performed to establish precise detection levels. However, the high compressibility of CO_2 gas, combined with its low density, indicate that much lower levels of detection should be possible.

The use of passive seismic (microseismic) techniques also has potential value. Passive seismic monitoring detects microseismic events induced in the reservoir by dynamic responses to the modification of pore pressures or the reactivation or creation of small fractures. These discrete microearthquakes, with magnitudes on the order of -4 to 0 on the Richter scale (Wilson and Monea, 2005), are picked up by static arrays of sensors, often cemented into abandoned wells. These microseismic events are extremely small, but monitoring the microseismic events may allow the tracking of pressure changes and, possibly, the movement of gas in the reservoir or saline formation.

Non-seismic geophysical techniques include the use of electrical and electromagnetic and self-potential techniques (Benson *et al*., 2004; Hoversten and Gasperikova, 2005). In addition, gravity techniques (ground or air-based) can be used to determine the migration of the CO_2 plume in the subsurface. Finally, tiltmeters or remote methods (geospatial surveys from aircraft or satellites) for measuring ground distortion may be used in some environments to assess subsurface movement of the plume. Tiltmeters and other techniques are most applicable in areas where natural variations in the surface, such as frost heave or wetting-drying cycles, do not mask the changes that occur from pressure changes. Gravity measurements will respond to changes in the subsurface brought on by density changes caused by the displacement of one fluid by another of different density (e.g., CO_2 replacing water). Gravity is used with numerical modelling to infer those changes in density that best fit the observed data. The estimations of Benson *et al.* (2004) suggest that gravity will not have the same level of resolution as seismic, with minimum levels of CO_2 needed for detection on the order of several hundred thousand tonnes (an order of magnitude greater than seismic). This may be adequate for plume movement, but not for the early definition of possible leaks. A seabed gravity survey was acquired at Sleipner in 2002 and a repeat survey is planned for 2005. Results from these surveys have not yet been published.

Electrical and electromagnetic techniques measure the conducting of the subsurface. Conductivity changes created by a change in the fluid, particularly the displacement of high conductivity saline waters with low-conductive CO_2, can be detected by electrical or electromagnetic surveys. In addition to traditional electrical or electromagnetic techniques, the self-potential the natural electrical potential of the Earth can be measured to determine plume migration. The injection of CO_2 will enhance fluid flow in the rock. This flow can produce an electrical potential that is measured against a reference electrode. This technique is low cost, but is also of low resolution. It can, however, be a useful tool for measuring the plume movement. According to Hoversten and Gasperikova (2005), this technique will require more work to determine its resolution and overall effectiveness.

5.6.3.3 Monitoring case study: IEA-GHG Weyburn Monitoring and Storage Project

At Weyburn (Box 5.3), a monitoring programme was added to a commercial EOR project to develop and evaluate methods for tracking CO_2. Baseline data was collected prior to CO_2 injection (beginning in late 2000). These data included fluid samples (water and oil) and seismic surveys. Two levels of seismic surveys were undertaken, with an extensive three-dimensional (3D), 3-component survey over the original injection area and a detailed 3D, 9-component survey over a limited portion of the injection area. In addition, vertical seismic profiling and cross-well seismic tomography (between two vertical or horizontal wells) was undertaken. Passive seismic (microseismic) monitoring has recently been installed at the site. Other monitoring includes surface gas surveys (Strutt *et al.*, 2003) and potable water monitoring (the Weyburn field underlies an area with limited surface water availability, so groundwater provides the major potable water supply). Injected volumes (CO_2 and water) were also monitored. Any leaks from surface facilities are carefully monitored. Additionally, several wells were converted to observation wells to allow access to the reservoir. Subsequently, one well was abandoned, but seismic monitors were cemented into place in the well for passive seismic monitoring to be undertaken.

Since injection began, reservoir fluids have been regularly collected and analyzed. Analysis includes chemical and isotopic analyses of reservoir water samples, as well as maintaining an understanding of miscibility relationships between the oil and the injected CO_2. Several seismic surveys have been conducted (one year and two years after injection of CO_2 was initiated) with the processed data clearly showing the movement of CO_2 in the reservoir. Annual surface analysis of soil gas is also continuing (Strutt *et al.*, 2003), as is analysis of near-surface water. The analyses are being synthesized to gain a comprehensive knowledge of CO_2 migration in the reservoir, to understand

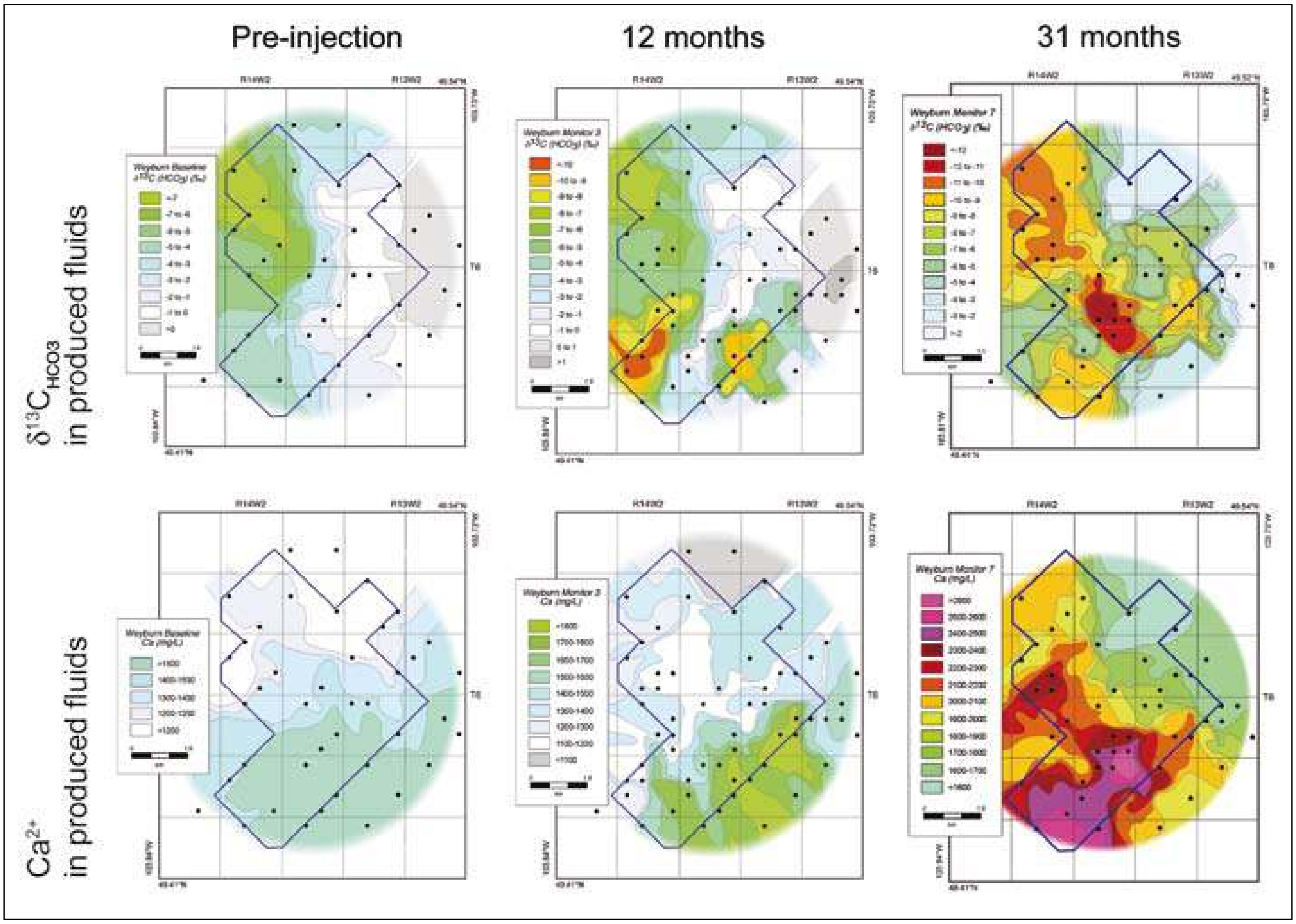


Figure 5.24 The produced water chemistry before CO_2 injection and the produced water chemistry after 12 months and 31 months of injection at Weyburn has been contoured from fluid samples taken at various production wells. The black dots show the location of the sample wells: (a) $\delta^{13}C_{HCO3}$ in the produced water, showing the effect of supercritical CO_2 dissolution and mineral reaction. (b) Calcium concentrations in the produced water, showing the result of mineral dissolution (after Perkins et al., 2005).

geochemical interactions with the reservoir rock and to clearly identify the integrity of the reservoir as a container for long-term storage. Additionally, there is a programme to evaluate the potential role of existing active and abandoned wells in leakage. This includes an analysis of the age of the wells, the use of existing information on cement type and bonding effectiveness and work to better understand the effect of historical and changing fluid chemistry on the cement and steel casing of the well.

The Weyburn summary report (Wilson and Monea, 2005) describes the overall results of the research project, in particular the effectiveness of the seismic monitoring for determining the spread of CO_2 and of the geochemical analysis for determining when CO_2 was about to reach the production wells. Geochemical data also help explain the processes under way in the reservoir itself and the time required to establish a new chemical equilibrium. Figure 5.24 illustrates the change in the chemical composition of the formation water, which forms the basis for assessing the extent to which solubility and mineral trapping will contribute to long-term storage security (Perkins *et al.*, 2005). The initial change in $\delta^{13}C_{HCO3}$ is the result of the supercritical CO_2 dissolving into the water. This change is then muted by the short-term dissolution of reservoir carbonate minerals, as indicated by the increase of calcium concentration, shown in Figure 5.24. In particular, the geochemistry confirms the storage of CO_2 in water in the bicarbonate phase and also CO_2 in the oil phase.

5.6.4 Technologies for monitoring injection well integrity

A number of standard technologies are available for monitoring the integrity of active injection wells. Cement bond logs are used to assess the bond and the continuity of the cement around well casing. Periodic cement bond logs can help detect deterioration in the cemented portion of the well and may also indicate any chemical interaction of the acidized formation fluids with the cement. The initial use of cement bond logs as part of the well-integrity testing can indicate problems with bonding and even the absence of cement.

Prior to converting a well to other uses, such as CO_2 injection, the well usually undergoes testing to ensure its integrity under pressure. These tests are relatively straightforward, with the well being sealed top and bottom (or in the zone to be tested), pressured up and its ability to hold pressure measured. In general, particularly on land, the well will be abandoned if it fails the test and a new well will be drilled, as opposed to attempting any remediation on the defective well.

Injection takes place through a pipe that is lowered into the well and packed off above the perforations or open-hole portion of the well to ensure that the injectant reaches the appropriate level. The pressure in the annulus, the space between the casing and the injection pipe, can be monitored to ensure the integrity of the packer, casing and the injection pipe. Changes in pressure or gas composition in the annulus will alert the operator to problems.

As noted above, the injection pressure is carefully monitored to ensure that there are no problems. A rapid increase in pressure could indicate problems with the well, although industry interpretations suggest that it is more likely to be loss of injectivity in the reservoir.

Temperature logs and ‘noise’ logs are also often run on a routine basis to detect well failures in natural gas storage projects. Rapid changes in temperature along the length of the wellbore are diagnostic of casing leaks. Similarly, ‘noise’ associated with leaks in the injection tubing can be used to locate small leaks (Lippmann and Benson, 2003).

5.6.5 Technologies for monitoring local environmental effects

5.6.5.1 Groundwater

If CO_2 leaks from the deep geological storage formation and migrates upwards into overlying shallow groundwater aquifers, methods are available to detect and assess changes in groundwater quality. Of course, it is preferable to identify leakage shortly after it leaks and long before the CO_2 enters the groundwater aquifer, so that measures can be taken to intervene and prevent further migration (see Section 5.7.6). Seismic monitoring methods and potentially others (described in Section 5.6.3.2), can be used to identify leaks before the CO_2 reaches the groundwater zone.

Nevertheless, if CO_2 does migrate into a groundwater aquifer, potential impacts can be assessed by collecting groundwater samples and analyzing them for major ions (e.g., Na, K, Ca, Mg, Mn, Cl, Si, HCO_3^- and SO_4^{2-}), *p*H, alkalinity, stable isotopes (e.g., ^{13}C, ^{14}C, ^{18}O, ^{2}H) and gases, including hydrocarbon gases, CO_2 and its associated isotopes (Gunter *et al.*, 1998). Additionally, if shallow groundwater contamination occurs, samples could be analyzed for trace elements such as arsenic and lead, which are mobilized by acidic water (Section 5.5). Methods such as atomic absorption and inductively coupled plasma mass spectroscopy self-potential can be used to accurately measure water quality. Less sensitive field tests or other analytical methods are also available (Clesceri *et al.*, 1998). Standard analytical methods are available to monitor all of these parameters, including the possibility of continuous real-time monitoring for some of the geochemical parameters.

Natural tracers (isotopes of C, O, H and noble gases associated with the injected CO_2) and introduced tracers (noble gases, SF_6 and perfluorocarbons) also may provide insight into the impacts of storage projects on groundwater (Emberley *et al.*, 2002; Nimz and Hudson, 2005). (SF_6 and perfluorocarbons are greenhouse gases with extremely high global warming potentials and therefore caution is warranted in the use of these gases, to avoid their release to the atmosphere.) Natural tracers such as C and O isotopes may be able to link changes in groundwater quality directly to the stored CO_2 by ‘fingerprinting’ the CO_2, thus distinguishing storage-induced changes from changes in groundwater quality caused by other factors. Introduced tracers such as perfluorocarbons that can be detected at very low concentrations (1 part per trillion) may also be useful for determining whether CO_2 has leaked and is responsible for changes in groundwater quality. Synthetic tracers could be added periodically to determine movement in the reservoir or leakage paths, while natural tracers are present in the reservoir or introduced gases.

5.6.5.2 Air quality and atmospheric fluxes

Continuous sensors for monitoring CO_2 in air are used in a variety of applications, including HVAC (heating, ventilation and air conditioning) systems, greenhouses, combustion emissions measurement and environments in which CO_2 is a significant hazard (such as breweries). Such devices rely on infrared detection principles and are referred to as infrared gas analyzers. These gas analyzers are small and portable and commonly used in occupational settings. Most use non-dispersive infrared or Fourier Transform infrared detectors. Both methods use light attenuation by CO_2 at a specific wavelength, usually 4.26 microns. For extra assurance and validation of real-time monitoring data, US regulatory bodies, such as NIOSH, OSHA and the EPA, use periodic concentration measurement by gas chromatography. Mass spectrometry is the most accurate method for measuring CO_2 concentration, but it is also the least portable. Electrochemical solid state CO_2 detectors exist, but they are not cost effective at this time (e.g., Tamura *et al*., 2001).

Common field applications in environmental science include the measurement of CO_2 concentrations in soil air, flux from soils and ecosystem-scale carbon dynamics. Diffuse soil flux measurements are made by simple infrared analyzers (Oskarsson *et al*., 1999). The USGS measures CO_2 flux on Mammoth Mountain, in California (Sorey *et al*., 1996; USGS, 2001b). Biogeochemists studying ecosystem-scale carbon cycling use data from CO_2 detectors on 2 to 5 m tall towers with wind and temperature data to reconstruct average CO_2 flux over large areas.

Miles *et al*. (2005) concluded that eddy covariance is promising for the monitoring of CO_2 storage projects, both for hazardous leaks and for leaks that would damage the economic viability of geological storage. For a storage project of 100 Mt, Miles *et al*. (2005) estimate that, for leakage rates of 0.01% yr^{-1}, fluxes will range from 1 to 10^4 times the magnitude of typical ecological fluxes (depending on the size of the area over which CO_2 is leaking). Note that a leakage rate of 0.01% yr^{-1} is equivalent to a fraction retained of 90% over 1000 years. This should easily be detectable if background ecological fluxes are measured in advance to determine diurnal and annual cycles. However, with the technology currently available to us, quantifying leakage rates for tracking returns to the atmosphere is likely to be more of a challenge than identifying leaks in the storage reservoir.

Satellite-based remote sensing of CO_2 releases to the atmosphere may also be possible, but this method remains challenging because of the long path length through the atmosphere over which CO_2 is measured and the inherent variability of atmospheric CO_2. Infrared detectors measure average CO_2 concentration over a given path length, so a diffuse or low-level leak viewed through the atmosphere by satellite would be undetectable. As an example, even large CO_2 seeps, such as that at Mammoth Mountain, are difficult to identify today (Martini and Silver, 2002; Pickles, 2005). Aeroplane-based measurement using this same principle may be possible. Carbon dioxide has been measured either directly in the plume by a separate infrared detector or calculated from SO_2 measurements and direct ground sampling of the SO_2:CO_2 ratio for a given volcano or event (Hobbs *et al*., 1991; USGS, 2001b). Remote-sensing techniques currently under investigation for CO_2 detection are LIDAR (light detection and range-finding), a scanning airborne laser and DIAL (differential absorption LIDAR), which looks at reflections from multiple lasers at different frequencies (Hobbs *et al*., 1991; Menzies *et al*., 2001).

In summary, monitoring of CO_2 for occupational safety is well established. On the other hand, while some promising technologies are under development for environmental monitoring and leak detection, measurement and monitoring approaches on the temporal and space scales relevant to geological storage need improvement to be truly effective.

5.6.5.3 Ecosystems

The health of terrestrial and subsurface ecosystems can be determined directly by measuring the productivity and biodiversity of flora and fauna and in some cases (such as at Mammoth Mountain in California) indirectly by using remote-sensing techniques such as hyperspectral imaging (Martini and Silver, 2002; Onstott, 2005; Pickles, 2005). In many areas with natural CO_2 seeps, even those with very low CO_2 fluxes, the seeps are generally quite conspicuous features. They are easily recognized in populated areas, both in agriculture and natural vegetation, by reduced plant growth and the presence of precipitants of minerals leached from rocks by acidic water. Therefore, any conspicuous site could be quickly and easily checked for excess CO_2 concentrations without any large remote-sensing ecosystem studies or surveys. However, in desert environments where vegetation is sparse, direct observation may not be possible. In addition to direct ecosystem observations, analyses of soil gas composition and soil mineralogy can be used to indicate the presence of CO_2 and its impact on soil properties. Detection of elevated concentrations of CO_2 or evidence of excessive soil weathering would indicate the potential for ecosystem impacts.

For aquatic ecosystems, water quality and in particular low *p*H, would provide a diagnostic for potential impacts. Direct measurements of ecosystem productivity and biodiversity can also be obtained by using standard techniques developed for lakes and marine ecosystems. See Chapter 6 for additional discussion about the impact of elevated CO_2 concentrations on marine environments.

5.6.6 Monitoring network design

There are currently no standard protocols or established network designs for monitoring leakage of CO_2. Monitoring network design will depend on the objectives and requirements of the monitoring programme, which will be determined by regulatory requirements and perceived risks posed by the site (Chalaturnyk and Gunter, 2005). For example, current monitoring for EOR is designed to assess the sweep efficiency of the solvent flood and to deal with health and safety issues. In this regard, the monitoring designed for the Weyburn Project uses seismic surveys to determine the lateral migration of CO_2 over time. This is compared with the simulations undertaken to design the operational practices of the CO_2 flood. For health and safety, the programme is designed to test groundwater for contamination and to monitor for gas buildup in working areas of the field to ensure worker safety. The surface procedure also uses pressure monitoring to ensure that the fracture pressure of the formation is not exceeded (Chalaturnyk and Gunter, 2005).

The Weyburn Project is designed to assess the integrity of an oil reservoir for long-term storage of CO_2 (Wilson and Monea, 2005). In this regard, the demonstrated ability of seismic surveys to measure migration of CO_2 within the formation is important, but in the long term it may be more important to detect CO_2 that has leaked out of the storage reservoir. In this case, the monitoring programme should be designed to achieve the resolution and sensitivity needed to detect CO_2 that has leaked out of the reservoir and is migrating vertically. The use of geochemical monitoring will determine the rate of dissolution of the CO_2 into fluids and the capacity of the minerals within the reservoir to react with the CO_2 and permanently store it. For identification of potential CO_2 leaks, monitoring includes soil gas and groundwater surveys. The soil gas surveys use a grid pattern superimposed on the field to evaluate any change in gas chemistry. Because grid patterns may miss narrow, linear anomalies, the study also looks at the pattern of linear anomalies on the surface that may reflect deeper fault and fracture systems, which could become natural migration pathways.

Current projects, in particular Sleipner and Weyburn, are testing a variety of techniques to determine those that are most effective and least costly. In Western Canada, acid-gas injection wells use pressure monitoring and set maximum wellhead injection pressures to ensure that reservoir fracture pressures are not exceeded. No subsurface monitoring is currently required for these projects. Chalaturnyk and Gunter (2005) suggest that an effectively designed monitoring programme should allow decisions to be made in the future that are based on ongoing interpretation of the data. The data from the programme should also provide the information necessary to decrease uncertainties over time or increase monitoring demand if things develop unexpectedly. The corollary to this is that unexpected changes may result in the requirement of increased monitoring until new uncertainties are resolved.

5.6.7 Long-term stewardship monitoring

The purpose of long-term monitoring is to identify movement of CO_2 that may lead to releases that could impact long-term storage security and safety, as well as trigger the need for remedial action. Long-term monitoring can be accomplished with the same suite of monitoring technologies used during the injection phase. However, at the present time, there are no established protocols for the kind of monitoring that will be required, by whom, for how long and with what purpose. Geological storage of CO_2 may persist over many millions of years. The long duration of storage raises some questions about long-term monitoring – an issue that is also addressed in Section 5.8.

Several studies have attempted to address these issues. Keith and Wilson (2002) have proposed that governments assume responsibility for monitoring after the active phase of the storage project is over, as long as all regulatory requirements have been met during operation. This study did not, however, specify long-term requirements for monitoring. Though perhaps somewhat impractical in terms of implementation, White *et al.* (2003) suggested that monitoring might be required for thousands of years. An alternative point of view is presented by Chow *et al.* (2003) and Benson *et al.* (2004), who suggest that once it has been demonstrated that the plume of CO_2 is no longer moving, further monitoring should not be required. The rationale for this point of view is that long-term monitoring provides little value if the plume is no longer migrating or the cessation of migration can be accurately predicted and verified by a combination of modelling and short- to mid-term monitoring.

If and when long-term monitoring is required, cost-effective, easily deployed methods for monitoring will be preferred. Methods that do not require wells that penetrate the plume will be desirable, because they will not increase the risk of leakage up the monitoring well itself. Technologies are available today, such as 3D seismic imaging, that can provide satisfactory images of CO_2 plume location. While seismic surveys are perceived to be costly, a recent study by Benson *et al.* (2004) suggests that this may be a misconception and indicates that monitoring costs on a discounted basis (10% discount rate) are likely to be no higher than 0.10 US\$/tCO_2 stored. However, seismic imaging has its limitations, as is evidenced by continued drilling of non-productive hydrocarbon wells, but confidence in its ability to meet most, but not all, of the needs of monitoring CO_2 storage projects is growing. Less expensive and more passive alternatives that could be deployed remotely, such as satellite-based systems, may be desirable, but are not currently able to track underground migration. However, if CO_2 has seeped to the surface, associated vegetative stress can be detected readily in some ecosystems (Martini and Silver, 2002).

Until long-term monitoring requirements are established (Stenhouse *et al.*, 2005), it is not possible to evaluate which technology or combination of technologies for monitoring will be needed or desired. However, today's technology could be deployed to continue monitoring the location of the CO_2 plume over very long time periods with sufficient accuracy to assess the risk of the plume intersecting potential pathways, natural or human, out of the storage site into overlying zones. If CO_2 escapes from the primary storage reservoir with no prospect of remedial action to prevent leakage, technologies are available to monitor the consequent environmental impact on groundwater, soils, ecosystems and the atmosphere.

5.6.8 Verification of CO_2 injection and storage inventory

Verification as a topic is often combined with monitoring such as in the Storage, Monitoring and Verification (SMV) project of the Carbon Capture Project (CCP) or the Monitoring, Mitigation and Verification (MMV) subsection of the DOE-NETL Carbon Sequestration Technology Roadmap and Program Plan (NETL, 2004). In view of this frequently-used combination of terms, there is some overlap in usage between the terms 'verification' and 'monitoring'. For this report, 'verification' is defined as the set of activities used for assessing the amount of CO_2 that is stored underground and for assessing how much, if any, is leaking back into the atmosphere.

No standard protocols have been developed specifically for verification of geological storage. However, experience at the Weyburn and Sleipner projects has demonstrated the utility of various techniques for most if not all aspects of verification (Wilson and Monea, 2005; Sleipner Best Practice Manual, 2004). At the very least, verification will require measurement of the quantity of CO_2 stored. Demonstrating that it remains within the storage site, from both a lateral and vertical migration perspective, is likely to require some combination of models and monitoring. Requirements may be site-specific, depending on the regulatory environment, requirements for economic instruments and the degree of risk of leakage. The oversight for verification may be handled by regulators, either directly or by independent third parties contracted by regulators under national law.

5.7 Risk management, risk assessment and remediation

What are the risks of storing CO_2 in deep geological formations? Can a geological storage site be operated safely? What are the safety concerns and environmental impact if a storage site leaks? Can a CO_2 storage site be fixed if something does go wrong? These questions are addressed in this section of the report.

5.7.1 Framework for assessing environmental risks

The environmental impacts arising from geological storage fall into two broad categories: local environmental effects and global effects arising from the release of stored CO_2 to the atmosphere. Global effects of CO_2 storage may be viewed as the uncertainty in the effectiveness of CO_2 storage. Estimates of the likelihood of release to the atmosphere are discussed below (Section 5.7.3), while the policy implications of potential release from storage are discussed elsewhere (Chapters 1, 8 and 9).

Local health, safety and environmental hazards arise from three distinct causes:

- Direct effects of elevated gas-phase CO_2 concentrations in the shallow subsurface and near-surface environment;
- Effects of dissolved CO_2 on groundwater chemistry;
- Effects that arise from the displacement of fluids by the injected CO_2.

In this section, assessment of possible local and regional environmental hazards is organized by the kind of hazard (e.g., human health and ecosystem hazards are treated separately) and by the underlying physical mechanism (e.g., seismic hazards). For example, the discussion of hazards to groundwater quality includes effects that arise directly from the effect of dissolved CO_2 in groundwater, as well as indirect effects resulting from contamination by displaced brines.

Risks are proportional to the magnitude of the potential hazards and the probability that these hazards will occur. For hazards that arise from locally elevated CO_2 concentrations – in the near-surface atmosphere, soil gas or in aqueous solution – the risks depend on the probability of leakage from the deep storage site to the surface. Thus, most of the hazards described in Section 5.7.4 should be weighted by the probability of release described in Section 5.7.3. Regarding those risks associated with routine operation of the facility and well maintenance, such risks are expected to be comparable to CO_2-EOR operations.

There are two important exceptions to the rule that risk is proportional to the probability of release. First, local impacts will be strongly dependent on the spatial and temporal distribution of fluxes and the resulting CO_2 concentrations. Episodic and localized seepage will likely tend to have more significant impacts per unit of CO_2 released than will seepage that is continuous and or spatially dispersed. Global impacts arising from release of CO_2 to the atmosphere depend only on the average quantity released over time scales of decades to centuries. Second, the hazards arising from displacement, such as the risk of induced seismicity, are roughly independent of the probability of release.

Although we have limited experience with injection of CO_2 for the explicit purpose of avoiding atmospheric emissions, a wealth of closely related industrial experience and scientific knowledge exists that can serve as a basis for appropriate risk management. In addition to the discussion in this section, relevant industrial experience has been described in Sections 5.1 to 5.6.

5.7.2 Processes and pathways for release of CO_2 from geological storage sites

Carbon dioxide that exists as a separate phase (supercritical, liquid or gas) may escape from formations used for geological storage through the following pathways (Figure 5.25):

- Through the pore system in low-permeability caprocks such as shales, if the capillary entry pressure at which CO_2 may enter the caprock is exceeded;
- Through openings in the caprock or fractures and faults;

- Through anthropomorphic pathways, such as poorly completed and/or abandoned pre-existing wells.

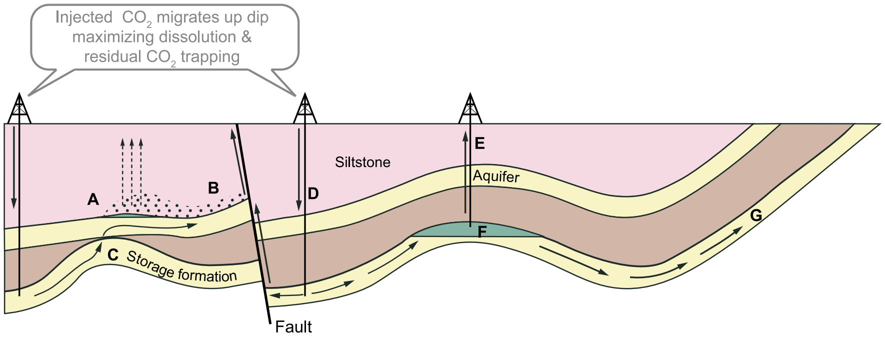
For onshore storage sites, CO_2 that has leaked may reach the water table and migrate into the overlying vadose zone. This occurrence would likely include CO_2 contact with drinking-water aquifers. Depending on the mineral composition of the rock matrix within the groundwater aquifer or vadose zone, the reaction of CO_2 with the rock matrix could release contaminants. The US Environmental Protection Agency (USEPA) has witnessed problems with projects designed to replenish groundwater with rainfall wherein mineralized (fixed) contaminants were inadvertently mobilized in concentrations sufficient to cause undesirable contamination.

The vadose zone is only partly saturated with water; the rest of the pore space is filled with soil gas (air). Because it is heavier than air, CO_2 will displace ambient soil gas, leading to concentrations that locally may potentially approach 100% in parts of the vadose zone, even for small leakage fluxes. The dissipating effects of seepage into the surface layer are controlled mostly by pressure-driven flow and diffusion (Oldenburg and Unger, 2003). These occur predominantly in most shallow parts of the vadose zone, leaving the deeper part of the vadose zone potentially subject to accumulation of leaking CO_2. The processes of CO_2 migration in the vadose zone can be modelled, subject to limitations in the characterization of actual complex vadose zone and CO_2 leakage scenarios.

For storage sites that are offshore, CO_2 that has leaked may reach the ocean bottom sediments and then, if lighter than the surrounding water, migrate up through the water column until it reaches the atmosphere. Depending upon the leakage rate, it may either remain as a separate phase or completely dissolve into the water column. When CO_2 dissolves, biological impacts to ocean bottom and marine organisms will be of concern. For those sites where separate-phase CO_2 reaches the ocean surface, hazards to offshore platform workers may be of concern for very large and sudden release rates.

Once through the vadose zone, escaping CO_2 reaches the surface layer of the atmosphere and the surface environment, where humans and other animals can be exposed to it. Carbon dioxide dispersion and mixing result from surface winds and associated turbulence and eddies. As a result, CO_2 concentrations diminish rapidly with elevation, meaning that ground-dwelling animals are more likely to be affected by exposure than are humans (Oldenburg and Unger, 2004). Calm conditions and local topography capable of containing the dense gas will tend to prevent mixing. But such conditions are the exception and in general, the surface layer can be counted on to strongly dilute seeping CO_2. Nevertheless, potential concerns related to buildup of CO_2 concentrations on calm days must be carefully considered in any risk assessment of a CO_2 storage site. Additionally, high subsurface CO_2 concentrations may accumulate in basements, subsurface vaults and other subsurface infrastructures where humans may be exposed to risk.

Carbon dioxide injected into coal seams can escape only if it is in free phase (i.e., not adsorbed onto the coal) via the following pathways (Wo and Liang 2005; Wo *et al.* 2005): flow into surrounding strata during injection when high pressures are used to inject CO_2 into low-permeability coal, either where the cleat system reaches the top of the seam or via hydrofractures induced to improve the contact between the cleat system and CBM production wells; through faults or other natural pathways intersecting the coal seam; via poorly abandoned coal or CBM exploration wells; and through anthropomorphic pathways such



Potential Escape Mechanisms	Remedial Measures
A. CO_2 gas pressure exceeds capillary pressure & passes through siltstone	***A.*** *Extract & purify ground-water*
B. Free CO_2 leaks from A into upper aquifer up fault	***B.*** *Extract & purify ground-water*
C. CO_2 escapes through 'gap' in cap rock into higher aquifer	***C.*** *Remove CO_2 & reinject elsewhere*
D. Injected CO_2 migrates up dip, increases reservoir pressure & permeability of fault	***D.*** *Lower injection rates or pressures*
E. CO_2 escapes via poorly plugged old abandoned well	***E.*** *Re-plug well with cement*
F. Natural flow dissolves CO_2 at CO_2 / water interface & transports it out of closure	***F.*** *Intercept & reinject CO_2*
G. Dissolved CO_2 escapes to atmosphere or ocean	***G.*** *Intercept & reinject CO_2*

Figure 5.25 Some potential escape routes for CO_2 injected into saline formations.

as coal mines or mining-induced subsidence cracks.

In general, however, CO_2 retained by sorption onto coal will remain confined to the seam even without caprocks, unless the pressure in the coal seam is reduced (e.g., by mining). Changes in pressure and/or temperature lead to changes in the maximum gas content. If the pressure drops markedly, any excess CO_2 may desorb from the coal and flow freely through cleats.

Injection wells and abandoned wells have been identified as one of the most probable leakage pathways for CO_2 storage projects (Gasda *et al.*, 2004; Benson, 2005). When a well is drilled, a continuous, open conduit is created between the land surface and the deep subsurface. If, at the time of drilling, the operator decides that the target formation does not look sufficiently productive, then the well is abandoned as a 'dry hole', in accordance with proper regulatory guidelines. Current guidelines typically require filling sections of the hole with cement (Section 5.5 and Figure 5.21).

Drilling and completion of a well involve not only creation of a hole in the Earth, but also the introduction of engineered materials into the subsurface, such as well cements and well casing. The overall effect of well drilling is replacement of small but potentially significant cylindrical volumes of rock, including low-permeability caprock, with anthropomorphic materials that have properties different from those of the original materials. A number of possible leakage pathways can occur along abandoned wells, as illustrated in Figure 5.26 (Gasda *et al.*, 2004). These include leakage between the cement and the outside of the casing (Figure 5.26a), between the cement and the inside of the metal casing (Figure 5.26b), within the cement plug itself (Figure 5.26c), through deterioration (corrosion) of the metal casing (Figure 5.26d), deterioration of the cement in the annulus (Figure 5.26e) and leakage in the annular region between the formation and the cement (Figure 5.26f). The potential for long-term degradation of cement and metal casing in the presence of CO_2 is a topic of extensive investigations at this time (e.g., Scherer *et al.*, 2005).

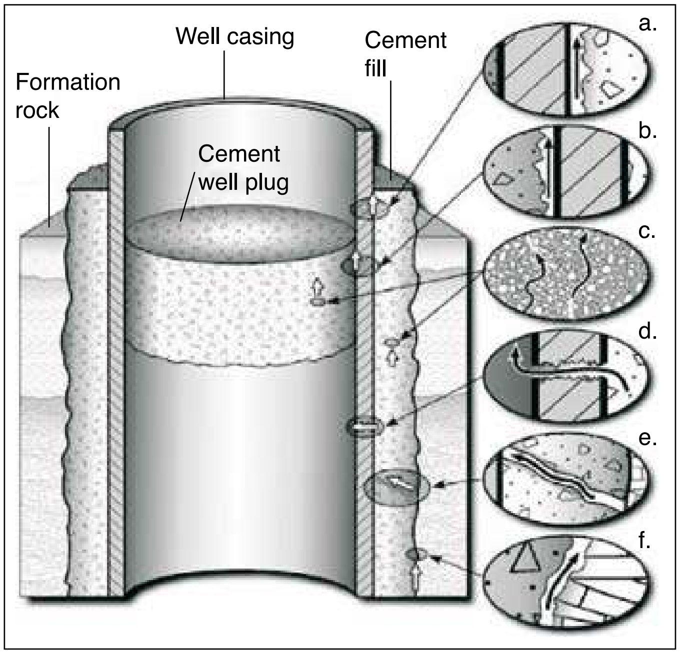


Figure 5.26 Possible leakage pathways in an abandoned well: (a) and (b) between casing and cement wall and plug, respectively; (c) through cement plugs; (d) through casing; (e) through cement wall; and (f) between the cement wall and rock (after Gasda *et al.*, 2004).

The risk of leakage through abandoned wells is proportional to the number of wells intersected by the CO_2 plume, their depth and the abandonment method used. For mature sedimentary basins, the number of wells in proximity to a possible injection well can be large, on the order of many hundreds. For example, in the Alberta Basin in western Canada, more than 350,000 wells have been drilled. Currently, drilling continues at the rate of approximately 20,000 wells per year. The wells are distributed spatially in clusters, with densities that average around four wells per km^2 (Gasda *et al.*, 2004). Worldwide well densities are provided in Figure 5.27 and illustrate that many areas have much lower well density. Nevertheless, the data provided in Figure 5.27 illustrate an important point made in Section 5.3 – namely that storage security in mature oil and gas provinces may be compromised if a large number of wells penetrate the caprocks. Steps need to be taken to address this potential risk.

5.7.3 *Probability of release from geological storage sites*

Storage sites will presumably be designed to confine all injected CO_2 for geological time scales. Nevertheless, experience with engineered systems suggest a small fraction of operational storage sites may release CO_2 to the atmosphere. No existing studies systematically estimate the probability and magnitude of release across a sample of credible geological storage systems. In the absence of such studies, this section synthesizes the lines of evidence that enable rough quantitative estimates of achievable fractions retained in storage. Five kinds of evidence are relevant to assessing storage effectiveness:

- Data from natural systems, including trapped accumulations of natural gas and CO_2, as well as oil;
- Data from engineered systems, including natural gas storage, gas re-injection for pressure support, CO_2 or miscible hydrocarbon EOR, disposal of acid gases and disposal of other fluids;
- Fundamental physical, chemical and mechanical processes regarding the fate and transport of CO_2 in the subsurface;
- Results from numerical models of CO_2 transport;
- Results from current geological storage projects.

5.7.3.1 *Natural systems*

Natural systems allow inferences about the quality and quantity of geological formations that could be used to store CO_2. The widespread presence of oil, gas and CO_2 trapped in formations for many millions of years implies that within sedimentary basins, impermeable formations (caprocks) of sufficient quality to confine CO_2 for geological time periods are present. For example, the about 200 $MtCO_2$ trapped in the Pisgah Anticline, northeast of the Jackson Dome (Mississippi), is thought to have been generated in Late Cretaceous times, more than 65 million years ago (Studlick *et al*., 1990). Retention times longer than 10 million years are found in many of the world's petroleum basins (Bradshaw *et al*., 2005). Therefore evidence from natural systems demonstrates that reservoir seals exist that are able to confine CO_2 for millions of years and longer.

5.7.3.2 Engineered systems

Evidence from natural gas storage systems enables performance assessments of engineered barriers (wells and associated management and remediation) and of the performance of natural systems that have been altered by pressure cycling (Lippmann and Benson, 2003; Perry, 2005). Approximately 470 natural gas storage facilities are currently operating in the United States with a total storage capacity exceeding 160 Mt natural gas (Figure 5.12). There have been nine documented incidents of significant leakage: five were related to wellbore integrity, each of which was resolved by reworking the wells; three arose from leaks in caprocks, two of which were remediated and one of which led to project abandonment. The final incident involved early project abandonment owing to poor site selection (Perry, 2005). There are no estimates of the total volumes of gas lost resulting from leakage across all the projects. In one recent serious example of leakage, involving wellbore failure at a facility in Kansas, the total mass released was about 3000 t (Lee, 2001), equal to less than 0.002% of the total gas in storage in the United States and Canada. The capacity-weighted median age of the approximately 470 facilities exceeds 25 years. Given that the Kansas failure was among the worst in the cumulative operating history of gas storage facilities, the average annual release rates, expressed as a fraction of stored gas released per year, are likely below 10^{-5}. While such estimates of the expected (or statistical average) release rates are a useful measure of storage effectiveness, they should not be interpreted as implying that release will be a continuous process.

The performance of natural gas storage systems may be regarded as a lower bound on that of CO_2 storage. One reason for this is that natural gas systems are designed for (and subject to) rapid pressure cycling that increases the probability of caprock leakage. On the other hand, CO_2 will dissolve in pore waters (if present), thereby reducing the risk of leakage. Perhaps the only respect in which gas storage systems present lower risks is that CH_4 is less corrosive than CO_2 to metallic components, such as well casings. Risks are higher in the case of leakage from natural gas storage sites because of the flammable nature of the gas.

5.7.3.3 Fundamental physical, chemical and mechanical processes regarding fate and transport of CO_2 in the subsurface

As described in Section 5.2, scientific understanding of CO_2 storage and in particular performance of storage systems, rests on a large body of knowledge in hydrogeology, petroleum geology, reservoir engineering and related geosciences. Current evaluation has identified a number of processes that alone or in combination can result in very long-term storage. Specifically, the combination of structural and stratigraphic trapping of separate-phase CO_2 below low-permeability caprocks, residual CO_2 trapping, solubility trapping and mineral trapping can create secure storage over geological time scales.

5.7.3.4 Numerical simulations of long-term storage performance

Simulations of CO_2 confinement in large-scale storage projects suggest that, neglecting abandoned wells, the movement of

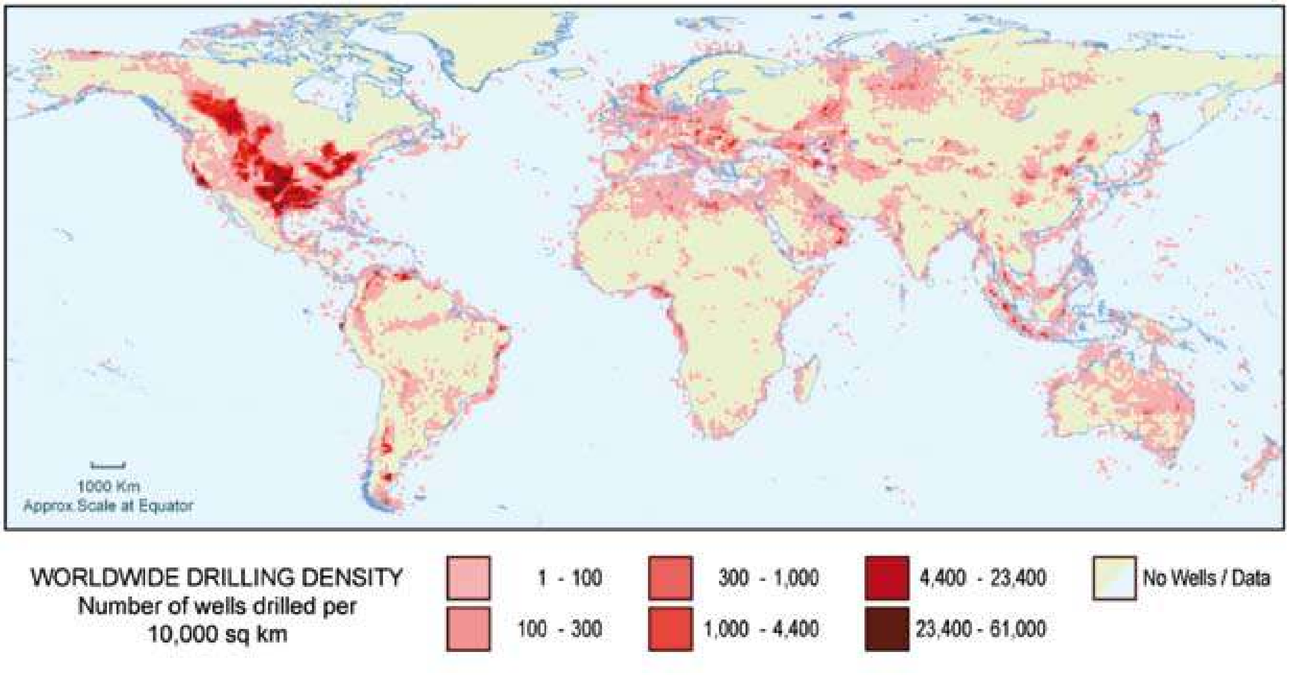


Figure 5.27 World oil and gas well distribution and density (courtesy of IHS Energy).

CO_2 through the subsurface will be slow. For example, Cawley *et al*. (2005) studied the effect of uncertainties in parameters such as the flow velocity in the aquifer and capillary entry pressure into caprock in their examination of CO_2 storage in the Forties Oilfield in the North Sea. Over the 1000 year time scale examined in their study, Cawley *et al*. (2005) found that less than 0.2% of the stored CO_2 enters into the overlying layers and even in the worse case, the maximum vertical distance moved by any of the CO_2 was less than halfway to the seabed. Similarly, Lindeberg and Bergmo (2003) studied the Sleipner field and found that CO_2 would not begin to migrate into the North Sea for 100,000 years and that even after a million years, the annual rate of release would be about 10^{-6} of the stored CO_2 per year.

Simulations designed to explore the possible release of stored CO_2 to the biosphere by multiple routes, including abandoned wells and other disturbances, have recently become available as a component of more general risk assessment activities (Section 5.7.5). Two studies of the Weyburn site, for example, assessed the probability of release to the biosphere. Walton *et al*. (2005) used a fully probabilistic model, with a simplified representation of CO_2 transport, to compute a probability distribution for the cumulative fraction released to the biosphere. Walton *et al*. found that after 5000 years, the probability was equal that the cumulative amount released would be larger or smaller than 0.1% (the median release fraction) and found a 95% probability that <1% of the total amount stored would be released. Using a deterministic model of CO_2 transport in the subsurface, Zhou *et al*. (2005) found no release to the biosphere in 5000 years. While using a probabilistic model of transport through abandoned wells, they found a statistical mean release of 0.001% and a maximum release of 0.14% (expressed as the cumulative fraction of stored CO_2 released over 5000 years).

In saline formations or oil and gas reservoirs with significant brine content, much of the CO_2 will eventually dissolve in the brine (Figure 5.7), be trapped as a residual immobile phase (Figure 5.8) or be immobilized by geochemical reactions. The time scale for dissolution is typically short compared to the time for CO_2 to migrate out of the storage formation by other processes (Ennis-King and Paterson, 2003; Lindeberg and Bergmo, 2003; Walton *et al*., 2005). It is expected that many storage projects could be selected and operated so that a very large fraction of the injected CO_2 will dissolve. Once dissolved, CO_2 can eventually be transported out of the injection site by basin-scale circulation or upward migration, but the time scales (millions of years) of such transport are typically sufficiently long that they can (arguably) be ignored in assessing the risk of leakage.

As described in Section 5.1, several CO_2 storage projects are now in operation and being carefully monitored. While no leakage of stored CO_2 out of the storage formations has been observed in any of the current projects, time is too short and overall monitoring too limited, to enable direct empirical conclusions about the long-term performance of geological storage. Rather than providing a direct test of performance, the current projects improve the quality of long-duration performance predictions by testing and sharpening understanding of CO_2 transport and trapping mechanisms.

5.7.3.5 *Assessing the ability of operational geological storage projects to retain CO_2 for long time periods*

Assessment of the fraction retained for geological storage projects is highly site-specific, depending on (1) the storage system design, including the geological characteristics of the selected storage site; (2) the injection system and related reservoir engineering; and (3) the methods of abandonment, including the performance of well-sealing technologies. If the above information is available, it is possible to estimate the fraction retained by using the models described in Section 5.4.2 and risk assessment methods described in Section 5.7.5. Therefore, it is also possible, in principle, to estimate the expected performance of an ensemble of storage projects that adhere to design guidelines such as site selection, seal integrity, injection depth and well closure technologies. Table 5.5 summarizes disparate lines of evidence on the integrity of CO_2 storage systems.

For large-scale operational CO_2 storage projects, assuming that sites are well selected, designed, operated and appropriately monitored, the balance of available evidence suggests the following:

- It is very likely the fraction of stored CO_2 retained is more than 99% over the first 100 years.
- It is likely the fraction of stored CO_2 retained is more than 99% over the first 1000 years.

5.7.4 *Possible local and regional environmental hazards*

5.7.4.1 *Potential hazards to human health and safety*

Risks to human health and safety arise (almost) exclusively from elevated CO_2 concentrations in ambient air, either in confined outdoor environments, in caves or in buildings. Physiological and toxicological responses to elevated CO_2 concentrations are relatively well understood (AI.3.3). At concentrations above about 2%, CO_2 has a strong effect on respiratory physiology and at concentrations above 7–10%, it can cause unconsciousness and death. Exposure studies have not revealed any adverse health effect of chronic exposure to concentrations below 1%.

The principal challenge in estimating the risks posed by CO_2 that might seep from storage sites lies in estimating the spatial and temporal distribution of CO_2 fluxes reaching the shallow subsurface and in predicting ambient CO_2 concentration resulting from a given CO_2 flux. Concentrations in surface air will be strongly influenced by surface topography and atmospheric conditions. Because CO_2 is 50% denser than air, it tends to migrate downwards, flowing along the ground and collecting in shallow depressions, potentially creating much higher concentrations in confined spaces than in open terrain.

Seepage of CO_2 is not uncommon in regions influenced by volcanism. Naturally occurring releases of CO_2 provide a basis for understanding the transport of CO_2 from the vadose zone to the atmosphere, as well as providing empirical data that link CO_2 fluxes into the shallow subsurface with CO_2 concentrations

Table 5.5 Summary of evidence for CO_2 retention and release rates.

Kind of evidence	Average annual fraction released	Representative references
CO_2 in natural formations	The lifetime of CO_2 in natural formations (>10 million yr in some cases) suggests an average release fraction $<10^{-7}$ yr^{-1} for CO_2 trapped in sedimentary basins. In highly fractured volcanic systems, rate of release can be many orders of magnitude faster.	Stevens *et al.*, 2001a; Baines and Worden, 2001
Oil and gas	The presence of buoyant fluids trapped for geological timescales demonstrates the widespread presence of geological systems (seals and caprock) that are capable of confining gasses with release rates $<10^{-7}$ yr^{-1}.	Bradshaw *et al.*, 2005
Natural gas storage	The cumulative experience of natural gas storage systems exceeds 10,000 facility-years and demonstrates that operational engineered storage systems can contain methane with release rates of 10^{-4} to 10^{-6} yr^{-1}.	Lippmann and Benson, 2003; Perry, 2005
Enhanced oil recovery (EOR)	More than 100 $MtCO_2$ has been injected for EOR. Data from the few sites where surface fluxes have been measured suggest that fractional release rates are near zero.	Moritis, 2002; Klusman, 2003
Models of flow through the undisturbed subsurface	Numerical models show that release of CO_2 by subsurface flow through undisturbed geological media (excluding wells) may be near zero at appropriately selected storage sites and is very likely $<10^{-6}$ in the few studies that attempted probabilistic estimates.	Walton *et al.*, 2005; Zhou *et al.*, 2005; Lindeberg and Bergmo, 2003; Cawley *et al.*, 2005
Models of flow through wells	Evidence from a small number of risk assessment studies suggests that average release of CO_2 can be 10^{-5} to 10^{-7} yr^{-1} even in existing oil fields with many abandoned wells, such as Weyburn. Simulations with idealized systems with 'open' wells show that release rates can exceed 10^{-2}, though in practice such wells would presumably be closed as soon as CO_2 was detected.	Walton *et al.*, 2005; Zhou et al., 2005; Nordbotten *et al.*, 2005b
Current CO_2 storage projects	Data from current CO_2 storage projects demonstrate that monitoring techniques are able to detect movement of CO_2 in the storage reservoirs. Although no release to the surface has been detected, little can be concluded given the short history and few sites.	Wilson and Monea, 2005; Arts *et al.*, 2005; Chadwick, *et al.*, 2005

in the ambient air – and the consequent health and safety risks. Such seeps do not, however, provide a useful basis for estimating the spatial and temporal distribution of CO_2 fluxes leaking from a deep storage site, because (in general) the seeps occur in highly fractured volcanic zones, unlike the interiors of stable sedimentary basins, the likely locations for CO_2 storage (Section 5.3).

Natural seeps are widely distributed in tectonically active regions of the world (Morner and Etiope, 2002). In central Italy, for example, CO_2 is emitted from vents, surface degassing and diffuse emission from CO_2-rich groundwater. Fluxes from vents range from less than 100 to more than 430 tCO_2 day^{-1}, which have shown to be lethal to animal and plants. At Poggio dell'Ulivo, for example, a flux of 200 tCO_2 day^{-1} is emitted from diffuse soil degassing. At least ten people have died from CO_2 releases in the region of Lazio over the last 20 years.

Natural and engineered analogues show that it is possible, though improbable, that slow releases from CO_2 storage reservoirs will pose a threat to humans. Sudden, catastrophic releases of natural accumulations of CO_2 have occurred, associated with volcanism or subsurface mining activities. Thus, they are of limited relevance to understanding risks arising from CO_2 stored in sedimentary basins. However, mining or drilling in areas with CO_2 storage sites may pose a long-term risk after site abandonment if institutional knowledge and precautions are not in place to avoid accidentally penetrating a storage formation.

5.7.4.2 Hazards to groundwater from CO_2 leakage and brine displacement

Increases in dissolved CO_2 concentration that might occur as CO_2 migrates from a storage reservoir to the surface will alter groundwater chemistry, potentially affecting shallow groundwater used for potable water and industrial and agricultural needs. Dissolved CO_2 forms carbonic acid, altering the pH of the solution and potentially causing indirect effects, including mobilization of (toxic) metals, sulphate or chloride; and possibly giving the water an odd odour, colour or taste. In the worst case, contamination might reach dangerous levels, excluding the use of groundwater for drinking or irrigation.

Wang and Jaffé (2004) used a chemical transport model to investigate the effect of releasing CO_2 from a point source at 100 m depth into a shallow water formation that contained a high concentration of mineralized lead (galena). They found that in weakly buffered formations, the escaping CO_2 could mobilize sufficient dissolved lead to pose a health hazard over a radius of a few hundred metres from the CO_2 source. This analysis represents an extreme upper bound to the risk of metal leaching, since few natural formations have mineral composition so susceptible to the effects of CO_2-mediated leaching and one of the expressed requirements of a storage site is to avoid compromising other potential resources, such as mineral deposits.

The injection of CO_2 or any other fluid deep underground necessarily causes changes in pore-fluid pressures and in the geomechanical stress fields that reach far beyond the volume occupied by the injected fluid. Brines displaced from deep formations by injected CO_2 can potentially migrate or leak through fractures or defective wells to shallow aquifers and contaminate shallower drinking water formations by increasing their salinity. In the worst case, infiltration of saline water into groundwater or into the shallow subsurface could impact wildlife habitat, restrict or eliminate agricultural use of land and pollute surface waters.

As is the case for induced seismicity, the experience with injection of different fluids provides an empirical basis for assessing the likelihood that groundwater contamination will occur by brine displacement. As discussed in Section 5.5 and shown in Figure 5.22, the current site-specific injection rates of fluids into the deep subsurface are roughly comparable to the rates at which CO_2 would be injected if geological storage were adopted for storage of CO_2 from large-scale power plants. Contamination of groundwater by brines displaced from injection wells is rare and it is therefore expected that contamination arising from large-scale CO_2 storage activities would also be rare. Density differences between CO_2 and other fluids with which we have extensive experience do not compromise this conclusion, because brine displacement is driven primarily by the pressure/hydraulic head differential of the injected CO_2, not by buoyancy forces.

5.7.4.3 Hazards to terrestrial and marine ecosystems

Stored CO_2 and any accompanying substances, may affect the flora and fauna with which it comes into contact. Impacts might be expected on microbes in the deep subsurface and on plants and animals in shallower soils and at the surface. The remainder of this discussion focuses only on the hazards where exposures to CO_2 do occur. As discussed in Section 5.7.3, the probability of leakage is low. Nevertheless, it is important to understand the hazards should exposures occur.

In the last three decades, microbes dubbed 'extremophiles', living in environments where life was previously considered impossible, have been identified in many underground habitats. These microorganisms have limited nutrient supply and exhibit very low metabolic rates (D'Hondt *et al*., 2002). Recent studies have described populations in deep saline formations (Haveman and Pedersen, 2001), oil and gas reservoirs (Orphan *et al*., 2000) and sediments up to 850 m below the sea floor (Parkes *et al*., 2000). The mass of subsurface microbes may well exceed the mass of biota on the Earth's surface (Whitman *et al*., 2001). The working assumption may be that unless there are conditions preventing it, microbes can be found everywhere at the depths being considered for CO_2 storage and consequently CO_2 storage sites may generally contain microbes that could be affected by injected CO_2.

The effect of CO_2 on subsurface microbial populations is not well studied. A low-*p*H, high-CO_2 environment may favour some species and harm others. In strongly reducing environments, the injection of CO_2 may stimulate microbial communities that would reduce the CO_2 to CH_4; while in other reservoirs, CO_2 injection could cause a short-term stimulation of Fe(III)-reducing communities (Onstott, 2005). From an operational perspective, creation of biofilms may reduce the effective permeability of the formation.

Should CO_2 leak from the storage formation and find its way to the surface, it will enter a much more biologically active area. While elevated CO_2 concentrations in ambient air can accelerate plant growth, such fertilization will generally be overwhelmed by the detrimental effects of elevated CO_2 in soils, because CO_2 fluxes large enough to significantly increase concentrations in the free air will typically be associated with much higher CO_2 concentrations in soils. The effects of elevated CO_2 concentrations would be mediated by several factors: the type and density of vegetation; the exposure to other environmental stresses; the prevailing environmental conditions like wind speed and rainfall; the presence of low-lying areas; and the density of nearby animal populations.

The main characteristic of long-term elevated CO_2 zones at the surface is the lack of vegetation. New CO_2 releases into vegetated areas cause noticeable die-off. In those areas where significant impacts to vegetation have occurred, CO_2 makes up about 20–95% of the soil gas, whereas normal soil gas usually contains about 0.2–4% CO_2. Carbon dioxide concentrations above 5% may be dangerous for vegetation and as concentration approach 20%, CO_2 becomes phytotoxic. Carbon dioxide can cause death of plants through 'root anoxia', together with low oxygen concentration (Leone *et al*., 1977; Flower *et al*., 1981).

One example of plant die-off occurred at Mammoth Mountain, California, USA, where a resurgence of volcanic activity resulted in high CO_2 fluxes. In 1989, a series of small earthquakes occurred near Mammoth Mountain. A year later, 4 ha of pine trees were discovered to be losing their needles and by 1997, the area of dead and dying trees had expanded to 40 ha (Farrar *et al*., 1999). Soil CO_2 levels above 10–20% inhibit root development and decrease water and nutrient uptake; soil oil-gas testing at Mammoth Mountain in 1994 discovered soil gas readings of up to 95% CO_2 by volume. Total CO_2 flux in the affected areas averaged about 530 t day^{-1} in 1996. Measurements in 2001 showed soil CO_2 levels of 15–90%, with flux rates at the largest affected area (Horseshoe Lake) averaging 90–100 tCO_2 day^{-1} (Gerlach *et al*., 1999; Rogie *et al*., 2001). A study of the impact of elevated CO_2 on soils found there was a lower pH and higher moisture content in summer. Wells in the high CO_2 area showed higher levels of silicon, aluminum, magnesium and iron, consistent with enhanced weathering of the soils. Tree-ring data show that CO_2 releases have occurred prior to 1990 (Cook *et al*., 2001). Data from airborne remote sensing are now being used to map tree health and measure anomalous CO_2 levels, which may help determine how CO_2 affects forest ecosystems (Martini and Silver, 2002).

There is no evidence of any terrestrial impact from current CO_2 storage projects. Likewise, there is no evidence from EOR projects that indicate impacts to vegetation such as those described above. However, no systematic studies have occurred to look for terrestrial impacts from current EOR projects.

Natural CO_2 seepage in volcanic regions, therefore, provides examples of possible impacts from leaky CO_2 storage, although (as mentioned in Section 5.2.3) seeps in volcanic provinces provide a poor analogue to seepage that would occur from CO_2 storage sites in sedimentary basins. As described above, CO_2 seepage can pose substantial hazards. In the Alban Hills, south of Rome (Italy), for example, 29 cows and 8 sheep were asphyxiated in several separate incidents between September 1999 and October 2001 (Carapezza *et al*., 2003). The measured CO_2 flux was about 60 t day^{-1} of 98% CO_2 and up to 2% H_2S, creating hazardous levels of each gas in localized areas, particularly in low-wind conditions. The high CO_2 and H_2S fluxes resulted from a combination of magmatic activity and faulting.

Human activities have caused detrimental releases of CO_2 from the deep subsurface. In the late 1990s, vegetation died off above an approximately 3-km deep geothermal field being exploited for a 62 MW power plant, in Dixie Valley, Nevada, USA (Bergfeld *et al*., 2001). A maximum flux of 570 gCO_2 m^{-2} day^{-1} was measured, as compared to a background level of 7 gCO_2 m^{-2} day^{-1}. By 1999, CO_2 flow in the measured area ceased and vegetation began to return.

The relevance of these natural analogues to leakage from CO_2 storage varies. For examples presented here, the fluxes and therefore the risks, are much higher than might be expected from a CO_2 storage facility: the annual flow of CO_2 at the Mammoth Mountain site is roughly equal to a release rate on the order of 0.2% yr^{-1} from a storage site containing 100 $MtCO_2$. This corresponds to a fraction retained of 13.5% over 1000 years and, thus, is not representative of a typical storage site.

Seepage from offshore geological storage sites may pose a hazard to benthic environments and organisms as the CO_2 moves from deep geological structures through benthic sediments to the ocean. While leaking CO_2 might be hazardous to the benthic environment, the seabed and overlying seawater can also provide a barrier, reducing the escape of seeping CO_2 to the atmosphere. These hazards are distinctly different from the environmental effects of the dissolved CO_2 on aquatic life in the water column, which are discussed in Chapter 6. No studies specifically address the environmental effects of seepage from sub-seabed geological storage sites.

5.7.4.4 *Induced seismicity*

Underground injection of CO_2 or other fluids into porous rock at pressures substantially higher than formation pressures can induce fracturing and movement along faults (see Section 5.5.4 and Healy *et al*., 1968; Gibbs *et al*., 1973; Raleigh *et al*., 1976; Sminchak *et al*., 2002; Streit *et al*., 2005; Wo *et al*., 2005). Induced fracturing and fault activation may pose two kinds of risks. First, brittle failure and associated microseismicity induced by overpressuring can create or enhance fracture permeability, thus providing pathways for unwanted CO_2 migration (Streit and Hillis, 2003). Second, fault activation can, in principle, induce earthquakes large enough to cause damage (e.g., Healy *et al*., 1968).

Fluid injection into boreholes can induce microseismic activity, as for example at the Rangely Oil Field in Colorado, USA (Gibbs *et al*., 1973; Raleigh *et al*., 1976), in test sites such as the drillholes of the German continental deep drilling programme (Shapiro *et al*., 1997; Zoback and Harjes, 1997) or the Cold Lake Oil Field, Alberta, Canada (Talebi *et al*., 1998). Deep-well injection of waste fluids may induce earthquakes with moderate local magnitudes (M_L), as suggested for the 1967 Denver earthquakes (M_L of 5.3; Healy *et al*., 1968; Wyss and Molnar, 1972) and the 1986–1987 Ohio earthquakes (M_L of 4.9; Ahmad and Smith, 1988) in the United States. Seismicity induced by fluid injection is usually assumed to result from increased pore-fluid pressure in the hypocentral region of the seismic event (e.g., Healy *et al*., 1968; Talebi *et al*., 1998).

Readily applicable methods exist to assess and control induced fracturing or fault activation (see Section 5.5.3). Several geomechanical methods have been identified for assessing the stability of faults and estimating maximum sustainable pore-fluid pressures for CO_2 storage (Streit and Hillis, 2003). Such methods, which require the determination of *in situ* stresses, fault geometries and relevant rock strengths, are based on brittle failure criteria and have been applied to several study sites for potential CO_2 storage (Rigg *et al*., 2001; Gibson-Poole *et al*., 2002).

The monitoring of microseismic events, especially in the vicinity of injection wells, can indicate whether pore fluid pressures have locally exceeded the strength of faults, fractures or intact rock. Acoustic transducers that record microseismic events in monitoring wells of CO_2 storage sites can be used to provide real-time control to keep injection pressures below the levels that induce seismicity. Together with the modelling techniques mentioned above, monitoring can reduce the chance of damage to top seals and fault seals (at CO_2 storage sites) caused by injection-related pore-pressure increases.

Fault activation is primarily dependent on the extent and magnitude of the pore-fluid-pressure perturbations. It is therefore determined more by the quantity and rate than by the kind of fluid injected. Estimates of the risk of inducing significant earthquakes may therefore be based on the diverse and extensive experience with deep-well injection of various aqueous and gaseous streams for disposal and storage. Perhaps the most pertinent experience is the injection of CO_2 for EOR; about 30 $MtCO_2$ yr^{-1} is now injected for EOR worldwide and the cumulative total injected exceeds 0.5 $GtCO_2$, yet there have been no significant seismic effects attributed to CO_2-EOR. In addition to CO_2, injected fluids include brines associated with oil and gas production (>2 Gt yr^{-1}); Floridan aquifer wastewater (>0.5 Gt yr^{-1}); hazardous wastes (>30 Mt yr^{-1}); and natural gas (>100 Mt yr^{-1}) (Wilson *et al*., 2003).

While few of these cases may precisely mirror the conditions under which CO_2 would be injected for storage (the peak pressures in CO_2-EOR may, for example, be lower than would be used in formation storage), these quantities compare to or exceed, plausible flows of CO_2 into storage. For example, in some cases such as the Rangely Oil Field, USA, current reservoir pressures even exceed the original formation pressure (Raleigh *et al*., 1976). Thus, they provide a substantial body of empirical data upon which to assess the likelihood of induced seismicity resulting from fluid injection. The fact that only a few individual seismic events associated with deep-well injection have been recorded suggests that the risks are low. Perhaps more importantly, these experiences demonstrate that the regulatory limits imposed on injection pressures are sufficient to avoid significant injection-induced seismicity. Designing CO_2 storage projects to operate within these parameters should be possible. Nevertheless, because formation pressures in CO_2 storage formations may exceed those found in CO_2-EOR projects, more experience with industrial-scale CO_2 storage projects will be needed to fully assess risks of microseismicity.

5.7.4.5 Implications of gas impurity

Under some circumstances, H_2S, SO_2, NO_2 and other trace gases may be stored along with CO_2 (Bryant and Lake, 2005; Knauss *et al.*, 2005) and this may affect the level of risk. For example, H_2S is considerably more toxic than CO_2 and well blow-outs containing H_2S may present higher risks than well blow-outs from storage sites that contain only CO_2. Similarly, dissolution of SO_2 in groundwater creates a far stronger acid than does dissolution of CO_2; hence, the mobilization of metals in groundwater and soils may be higher, leading to greater risk of exposure to hazardous levels of trace metals. While there has not been a systematic and comprehensive assessment of how these additional constituents would affect the risks associated with CO_2 storage, it is worth noting that at Weyburn, one of the most carefully monitored CO_2 injection projects and one for which a considerable effort has been devoted to risk assessment, the injected gas contains approximately 2% H_2S (Wilson and Monea, 2005). To date, most risk assessment studies have assumed that only CO_2 is stored; therefore, insufficient information is available to assess the risks associated with gas impurities at the present time.

5.7.5 Risk assessment methodology

Risk assessment aims to identify and quantify potential risks caused by the subsurface injection of CO_2, where risk denotes a combination (often the product) of the probability of an event happening and the consequences of the event. Risk assessment should be an integral element of risk-management activities, spanning site selection, site characterization, storage system design, monitoring and, if necessary, remediation.

The operation of a CO_2 storage facility will necessarily involve risks arising from the operation of surface facilities such as pipelines, compressors and wellheads. The assessment of such risks is routine practice in the oil and gas industry and available assessment methods like hazard and operability and quantitative risk assessment are directly applicable. Assessment of such risks can be made with considerable confidence, because estimates of failure probabilities and the consequences of failure can be based directly on experience. Techniques used for assessment of operational risks will not, in general, be readily applicable to assessment of risks arising from long-term storage of CO_2 underground. However, they are applicable to the operating phase of a storage project. The remainder of this subsection addresses the long-term risks.

Risk assessment methodologies are diverse; new methodologies arise in response to new classes of problems. Because analysis of the risks posed by geological storage of CO_2 is a new field, no well-established methodology for assessing such risks exists. Methods dealing with the long-term risks posed by the transport of materials through the subsurface have been developed in the area of hazardous and nuclear waste management (Hodgkinson and Sumerling, 1990; North, 1999). These techniques provide a useful basis for assessing the risks of CO_2 storage. Their applicability may be limited, however, because the focus of these techniques has been on assessing the low-volume disposal of hazardous materials, whereas the geological storage of CO_2 is high-volume disposal of a material that involves comparatively mild hazards.

Several substantial efforts are under way to assess the risks posed by particular storage sites (Gale, 2003). These risk assessment activities cover a wide range of reservoirs, use a diversity of methods and consider a very wide class of risks. The description of a representative selection of these risk assessment efforts is summarized in Table 5.6.

The development of a comprehensive catalogue of the risks and of the mechanisms that underlie them, provides a good foundation for systematic risk assessment. Many of the ongoing risk assessment efforts are now cooperating to identify, classify and screen all factors that may influence the safety of storage facilities, by using the features, events and processes (FEP) methodology. In this context, *features* includes a list of parameters, such as storage reservoir permeability, caprock thickness and number of injection wells. *Events* includes processes such as seismic events, well blow-outs and penetration of the storage site by new wells. *Processes* refers to the physical and chemical processes, such as multiphase flow, chemical reactions and geomechanical stress changes that influence storage capacity and security. FEP databases tie information on individual FEPs to relevant literature and allow classification with respect to likelihood, spatial scale, time scale and so on. However, there are alternative approaches.

Most risk assessments involve the use of scenarios that describe possible future states of the storage facility and events that result in leakage of CO_2 or other risks. Each scenario may be considered as an assemblage of selected FEPs. Some risk assessments define a reference scenario that represents the most probable evolution of the system. Variant scenarios are then constructed with alternative FEPs. Various methods are used to structure and rationalize the process of scenario definition in an attempt to reduce the role of subjective judgements in determining the outcomes.

Scenarios are the starting points for selecting and developing mathematical-physical models (Section 5.4.2). Such performance assessment models may include representations of all relevant components including the stored CO_2, the reservoir, the seal, the overburden, the soil and the atmosphere. Many of the fluid-transport models used for risk assessment are derived from (or identical to) well-established models used in the oil and gas or groundwater management industries (Section 5.4.2). The detail or resolution of various components may vary greatly. Some

Table 5.6 Representative selection of risk assessment models and efforts.

Project title	Description and status
Weyburn/ECOMatters	New model, CQUESTRA, developed to enable probabilistic risk assessment. A simple box model is used with explicit representation of transport between boxes caused by failure of wells.
Weyburn/Monitor Scientific	Scenario-based modelling that uses an industry standard reservoir simulation tool (Eclipse3000) based on a realistic model of known reservoir conditions. Initial treatment of wells involves assigning a uniform permeability.
NGCAS/ECL technology	Probabilistic risk assessment using fault tree and FEP (features, events and processes) database. Initial study focused on the Forties oil and gas field located offshore in the North Sea. Concluded that flow through caprock transport by advection in formation waters not important, work on assessing leakage due to well failures ongoing.
SAMARCADS (safety aspects of CO_2 storage)	Methods and tools for HSE risk assessment applied to two storage systems an onshore gas storage facility and an offshore formation.
RITE	Scenario-based analysis of leakage risks in a large offshore formation. Will assess scenarios involving rapid release through faults activated by seismic events.
Battelle	Probabilistic risk assessment of an onshore formation storage site that is intended to represent the Mountaineer site.
GEODISC	Completed a quantitative risk assessment for four sites in Australia: the Petrel Sub-basin; the Dongra depleted oil and gas field; the offshore Gippsland Basin; and, offshore Barrow Island. Also produced a risk assessment report that addressed the socio-political needs of stakeholders.
UK-DTI	Probabilistic risk assessment of failures in surface facilities that uses models and operational data. Assessment of risk of release from geological storage that uses an expert-based Delphi process.

models are designed to allow explicit treatment of uncertainty in input parameters (Saripalli *et al*., 2003; Stenhouse *et al*., 2005; Wildenborg *et al*., 2005a).

Our understanding of abandoned-well behaviour over long time scales is at present relatively poor. Several groups are now collecting data on the performance of well construction materials in high-CO_2 environments and building wellbore simulation models that will couple geomechanics, geochemistry and fluid transport (Scherer *et al*., 2005; Wilson and Monea, 2005). The combination of better models and new data should enable the integration of physically based predictive models of wellbore performance into larger performance-assessment models, enabling more systematic assessment of leakage from wells.

The parameter values (e.g., permeability of a caprock) and the structure of the performance assessment models (e.g., the processes included or excluded) will both be, in general, uncertain. Risk analysis may or may not treat this uncertainty explicitly. When risks are assessed deterministically, fixed parameter values are chosen to represent the (often unknown) probability distributions. Often the parameter values are selected 'conservatively'; that is, they are selected so that risks are overestimated, although in practice such selections are problematic because the relationship between the parameter value and the risk may itself be uncertain.

Wherever possible, it is preferable to treat uncertainty explicitly. In probabilistic risk assessments, explicit probability distributions are used for some (or all) parameters. Methods such as Monte Carlo analysis are then used to produce probability distributions for various risks. The required probability distributions may be derived directly from data or may involve formal quantification of expert judgements (Morgan and Henrion, 1999). In some cases, probabilistic risk assessment may require that the models be simplified because of limitations on available computing resources.

Studies of natural and engineered analogues provide a strong basis for understanding and quantifying the health, safety and environmental risks that arise from CO_2 that seeps from the shallow subsurface to the atmosphere. Natural analogues are of less utility in assessing the likelihood of various processes that transport CO_2 from the storage reservoir to the near-surface environment. This is because the geological character of such analogues (e.g., CO_2 transport and seepage in highly fractured zones shaped by volcanism) will typically be very different from sites chosen for geological storage. Engineered analogues such as natural gas storage and CO_2-EOR can provide a basis for deriving quantitative probabilistic models of well performance.

Results from actual risk and assessment for CO_2 storage are provided in 5.7.3.

5.7.6 *Risk management*

Risk management entails the application of a structured process to identify and quantify the risks associated with a given process, to evaluate these, taking into account stakeholder input and context, to modify the process to remove excess risks and to identify and implement appropriate monitoring and intervention strategies to manage the remaining risks.

For geological storage, effective risk mitigation consists of four interrelated activities:

- Careful site selection, including performance and risk

assessment (Section 5.4) and socio-economic and environmental factors;
- Monitoring to provide assurance that the storage project is performing as expected and to provide early warning in the event that it begins to leak (Section 5.6);
- Effective regulatory oversight (Section 5.8);
- Implementation of remediation measures to eliminate or limit the causes and impacts of leakage (Section 5.7.7).

Risk management strategies must use the inputs from the risk assessment process to enable quantitative estimates of the degree of risk mitigation that can be achieved by various measures and to establish an appropriate level of monitoring, with intervention options available if necessary. Experience from natural gas storage projects and disposal of liquid wastes has demonstrated the effectiveness of this approach to risk mitigation (Wilson *et al.*, 2003; Apps, 2005; Perry, 2005).

5.7.7 Remediation of leaking storage projects

Geological storage projects will be selected and operated to avoid leakage. However, in rare cases, leakage may occur and remediation measures will be needed, either to stop the leak or to prevent human or ecosystem impact. Moreover, the availability of remediation options may provide an additional level of assurance to the public that geological storage can be safe and effective. While little effort has focused on remediation options thus far, Benson and Hepple (2005) surveyed the practices used to remediate natural gas storage projects, groundwater and soil contamination, as well as disposal of liquid waste in deep geological formations. On the basis of these surveys, remediation options were identified for most of the leakage scenarios that have been identified, namely:
- Leaks within the storage reservoir;
- Leakage out of the storage formation up faults and fractures;
- Shallow groundwater;
- Vadose zone and soil;
- Surface fluxes;
- CO_2 in indoor air, especially basements;
- Surface water.

Identifying options for remediating leakage of CO_2 from active or abandoned wells is particularly important, because they are known vulnerabilities (Gasda *et al.*, 2004; Perry, 2005). Stopping blow-outs or leaks from injection or abandoned wells can be accomplished with standard techniques, such as injecting a heavy mud into the well casing. If the wellhead is not accessible, a nearby well can be drilled to intercept the casing below the ground surface and then pump mud down into the interception well. After control of the well is re-established, the well can be repaired or abandoned. Leaking injection wells can be repaired by replacing the injection tubing and packers. If the annular space behind the casing is leaking, the casing can be perforated to allow injection (squeezing) of cement behind the casing until the leak is stopped. If the well cannot be repaired, it can be abandoned by following the procedure outlined in Section 5.5.2.

Table 5.7 provides an overview of the remediation options available for the leakage scenarios listed above. Some methods are well established, while others are more speculative. Additional detailed studies are needed to further assess the feasibility of applying these to geological storage projects – studies that are based on realistic scenarios, simulations and field studies.

5.8 Legal issues and public acceptance

What legal and regulatory issues might be involved in CO_2 storage? How do they differ from one country to the next and from onshore to offshore? What international treaties exist that have bearing on geological storage? How does and how will the public view geological storage? These subjects are addressed in this section, which is primarily concerned with geological storage, both onshore and offshore.

5.8.1 International law

This section considers the legal position of geological CO_2 storage under international law. Primary sources, namely the relevant treaties, provide the basis for any assessment of the legal position. While States, either individually or jointly, apply their own interpretations to treaty provisions, any determination of the 'correct' interpretation will fall to the International Court of Justice or an arbitral tribunal in accordance with the dispute settlement mechanism under that treaty.

5.8.1.1 Sources and nature of international obligations

According to general principles of customary international law, States can exercise their sovereignty in their territories and therefore could engage in activities such as the storage of CO_2 (both geological and ocean) in those areas under their jurisdiction. However, if such storage causes transboundary impacts, States have the responsibility to ensure that activities within their jurisdiction or control do not cause damage to the environment of other States or of areas beyond the limits of national jurisdiction.

More specifically, there exist a number of global and regional environmental treaties, notably those on climate change and the law of the sea and marine environment, which, as presently drafted, could be interpreted as relevant to the permissibility of CO_2 storage, particularly offshore geological storage (Table 5.8).

Before making any assessment of the compatibility of CO_2 storage with the international legal obligations under these treaties, the general nature of such obligations should be recalled – namely that:
- Obligations under a treaty fall only on the Parties to that treaty;
- States take such obligations seriously and so will look to the provisions of such treaties before reaching policy decisions;

Table 5.7. Remediation options for geological CO_2 storage projects (after Benson and Hepple, 2005).

Scenario	Remediation options
Leakage up faults, fractures and spill points	• Lower injection pressure by injecting at a lower rate or through more wells (Buschbach and Bond, 1974); • Lower reservoir pressure by removing water or other fluids from the storage structure; • Intersect the leakage with extraction wells in the vicinity of the leak; • Create a hydraulic barrier by increasing the reservoir pressure upstream of the leak; • Lower the reservoir pressure by creating a pathway to access new compartments in the storage reservoir; • Stop injection to stabilize the project; • Stop injection, produce the CO_2 from the storage reservoir and reinject it back into a more suitable storage structure.
Leakage through active or abandoned wells	• Repair leaking injection wells with standard well recompletion techniques such as replacing the injection tubing and packers; • Repair leaking injection wells by squeezing cement behind the well casing to plug leaks behind the casing; • Plug and abandon injection wells that cannot be repaired by the methods listed above; • Stop blow-outs from injection or abandoned wells with standard techniques to 'kill' a well such as injecting a heavy mud into the well casing. After control of the well is re-established, the recompletion or abandonment practices described above can be used. If the wellhead is not accessible, a nearby well can be drilled to intercept the casing below the ground surface and 'kill' the well by pumping mud down the interception well (DOGGR, 1974).
Accumulation of CO_2 in the vadose zone and soil gas	• Accumulations of gaseous CO_2 in groundwater can be removed or at least made immobile, by drilling wells that intersect the accumulations and extracting the CO_2. The extracted CO_2 could be vented to the atmosphere or reinjected back into a suitable storage site; • Residual CO_2 that is trapped as an immobile gas phase can be removed by dissolving it in water and extracting it as a dissolved phase through groundwater extraction well; • CO_2 that has dissolved in the shallow groundwater could be removed, if needed, by pumping to the surface and aerating it to remove the CO_2. The groundwater could then either be used directly or reinjected back into the groundwate; • If metals or other trace contaminants have been mobilized by acidification of the groundwater, 'pump-and-treat' methods can be used to remove them. Alternatively, hydraulic barriers can be created to immobilize and contain the contaminants by appropriately placed injection and extraction wells. In addition to these active methods of remediation, passive methods that rely on natural biogeochemical processes may also be used.
Leakage into the vadose zone and accumulation in soil gas (Looney and Falta, 2000)	• CO_2 can be extracted from the vadose zone and soil gas by standard vapor extraction techniques from horizontal or vertical wells; • Fluxes from the vadose zone to the ground surface could be decreased or stopped by caps or gas vapour barriers. Pumping below the cap or vapour barrier could be used to deplete the accumulation of CO_2 in the vadose zone; • Since CO_2 is a dense gas, it could be collected in subsurface trenches. Accumulated gas could be pumped from the trenches and released to the atmosphere or reinjected back underground; • Passive remediation techniques that rely only on diffusion and 'barometric pumping' could be used to slowly deplete one-time releases of CO_2 into the vadose zone. This method will not be effective for managing ongoing releases because it is relatively slow; • Acidification of the soils from contact with CO_2 could be remediated by irrigation and drainage. Alternatively, agricultural supplements such as lime could be used to neutralize the soil;
Large releases of CO_2 to the atmosphere	• For releases inside a building or confined space, large fans could be used to rapidly dilute CO_2 to safe levels; • For large releases spread out over a large area, dilution from natural atmospheric mixing (wind) will be the only practical method for diluting the CO_2; • For ongoing leakage in established areas, risks of exposure to high concentrations of CO_2 in confined spaces (e.g. cellar around a wellhead) or during periods of very low wind, fans could be used to keep the rate of air circulation high enough to ensure adequate dilution.
Accumulation of CO_2 in indoor environments with chronic low-level leakage	• Slow releases into structures can be eliminated by using techniques that have been developed for controlling release of radon and volatile organic compounds into buildings. The two primary methods for managing indoor releases are basement/substructure venting or pressurization. Both would have the effect of diluting the CO_2 before it enters the indoor environment (Gadgil *et al.*, 1994; Fischer *et al.*, 1996).
Accumulation in surface water	• Shallow surface water bodies that have significant turnover (shallow lakes) or turbulence (streams) will quickly release dissolved CO_2 back into the atmosphere; • For deep, stably stratified lakes, active systems for venting gas accumulations have been developed and applied at Lake Nyos and Monoun in Cameroon (http://perso.wanadoo.fr/mhalb/nyos/).

Table 5.8 Main international treaties for consideration in the context of geological CO_2 storage (full titles are given in the Glossary).

Treaty	Adoption (Signature)	Entry into Force	Number of Parties/Ratifications
UNFCCC	1992	1994	189
Kyoto Protocol (KP)	1997	2005	132[a]
UNCLOS	1982	1994	145
London Convention (LC)	1972	1975	80
London Protocol (LP)	1996	No	20[a] (26)
OSPAR	1992	1998	15
Basel Convention	1989	1992	162

[a] Several other countries have also announced that their ratification is under way.

- Most environmental treaties contain underlying concepts, such as sustainable development, precautionary approach or principles, that should be taken into account when applying their provisions;
- In terms of supremacy of different treaties, later treaties will supersede earlier ones, but this will depend on *lex specialis,* that is, provisions on a specific subject will supersede general ones (relevant to the relationship between the United Nations Framework Convention on Climate Change (UNFCCC) and its Kyoto Protocol (KP) and the marine treaties);
- Amendment of treaties, if needed to permit CO_2 storage, requires further negotiations, a minimum level of support for their adoption and subsequent entry into force and will amend earlier treaties only for those Parties that have ratified the amendments.

5.8.1.2 *Key issues in the application of the marine treaties to CO_2 storage*

When interpreting the treaties for the purposes of determining the permissibility of CO_2 storage, particularly offshore geological storage, it is important to bear in mind that the treaties were not drafted to facilitate geological storage but to prohibit marine dumping. Issues to bear in mind include the following:

- Whether storage constitutes 'dumping', that is, it does not if the placement of the CO_2 is 'other than for the purposes of the mere disposal thereof' in accordance with the United Nations Convention on the Law of the Sea (UNCLOS), the London Convention (LC), the London Protocol (LP) and the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR). Alternative scenarios include experiments and storage for the purposes of enhanced oil recovery;
- Whether CO_2 storage can benefit from treaty exemptions concerning wastes arising from the normal operations of offshore installations (LC/LP) or as discharges or emissions from them (OSPAR);
- Is storage in the seabed expressly covered in the treaties or is it limited to the water column (UNCLOS, LC/LP, OSPAR)?
- Is CO_2 (or the substance captured if containing impurities) an 'industrial waste' (LC), 'hazardous waste' (Basel Convention) or does the process of its storage constitute 'pollution' (UNCLOS) or is it none of these?
- Does the method of the CO_2 reaching the disposal site involve pipelines, vessels or offshore structures (LC/LP, OSPAR)?

5.8.1.3 *Literature on geological storage under international law*

While it is necessary to look at and interpret the treaty provisions themselves to determine the permissibility of CO_2 storage, secondary sources contain States' or authors' individual interpretations of the treaties.

In their analysis, Purdy and Macrory (2004) conclude that since stored CO_2 does not enter the atmosphere, it will not be classed as an 'emission' for the purposes of the UNFCCC/KP, but as an 'emission reduction'. Emission reductions by CO_2 storage are permitted under the UNFCCC/KP, which allows projects that reduce greenhouse gases at the source. However, the authors consider a potential problem in UNFCCC/KP providing for transparent verification of emission reductions and there could be concerns over permanence, leakage and security.

In terms of marine treaties and in relation to OSPAR, which applies to the North East Atlantic, a report from the OSPAR Group of Jurists and Linguists contains the State Parties' interpretation of OSPAR on the issue of geological (and ocean) offshore storage (OSPAR Commission, 2004). It concludes that, as there is the possibility of pollution or of other adverse environmental effects, the precautionary principle must be applied. More specifically, the report interprets OSPAR as allowing CO_2 placement in the North East Atlantic (including seabed and subsoil) through a *pipeline from land*, provided it does not involve subsequent activities through a vessel or an offshore installation (e.g., an oil or gas platform). The report states, however, that placement from a vessel is prohibited, unless for the purpose of experimentation (which would then require being carried out in accordance with other relevant provisions of OSPAR). In the case of placement in the OSPAR maritime area from an *offshore installation*, this depends upon whether the CO_2 to be stored results from offshore or land-based activities. In the case of offshore-derived CO_2, experimental placement will again be subject to the Convention's provisions, while placement for EOR, climate change mitigation or indeed mere disposal will be strictly subject to authorization or regulation. As regards onshore-derived CO_2, placement only for experimental or EOR purposes will be allowed, subject to the same caveats as for offshore-derived CO_2. The report concludes that, since the applicable OSPAR regime is determined by the method and purpose of placement and not by the effect of placement on the marine environment, the results may well be that placements with different impacts on the environment (for example, placement in the water column and placement in underground strata) may not be distinguished, while different methods of placement having the same impact may be treated differently. A similar analytical exercise concerning the LC/LP has been initiated by Parties to that Convention.

There is uncertainty regarding the extent to which CO_2 storage falls under the jurisdiction of the marine treaties. Some authors argue they will probably not allow such storage or that the LC (globally) and OSPAR (in the North East Atlantic) could significantly restrict geological offshore storage (Lenstra and van Engelenburg, 2002; Bewers, 2003). Specifically regarding the issues raised above, the following propositions have been suggested:

- The long-term storage of CO_2 amounts to 'dumping' under the conventions (Purdy and Macrory, 2004); if CO_2 were to be injected for an industrial purpose, that is, EOR, it would not be considered dumping of waste and would be allowed under the LC (Wall *et al.*, 2005);
- CO_2 captured from an oil or natural gas extraction operation and stored offshore in a geological formation would not be considered 'dumping' under the LC (Wall *et al.*, 2005);
- There remain some ambiguities in the provisions of some conventions, especially in relation to the option of geological storage under the seabed (Ducroux and Bewers, 2005). UNCLOS provides the international legal basis for a range of future uses for the seafloor that could potentially include geological storage of CO_2 (Cook and Carleton, 2000);
- Under the LC, CO_2 might fall under the 'industrial waste' category in the list of wastes prohibited for disposal, while under the LP and OSPAR, it would probably not fall under the categories approved for dumping and should therefore be considered as waste and this is prohibited (Purdy and Macrory, 2004).

If CO_2 is transported *by ship* and then disposed of, either directly from the ship or from an offshore installation, this will be prohibited under the LC/LP (Wall *et al.*, 2005) and OSPAR (Purdy and Macrory, 2004). If CO_2 is transported *by pipeline* to an offshore installation and then disposed of, that would be prohibited under the LC/LP, but not necessarily under OSPAR, where prohibition against dumping applies only to installations carrying out activities concerning hydrocarbons (Purdy and Macrory, 2004). The option of storing CO_2 transported through a pipeline from land appears to remain open under most conventions (Ducroux and Bewers, 2005); the LC/LP apply only to activities that involve ships or platforms and contain no further controls governing pipeline discharges from land-based sources. Any such discharges would probably be excluded from control by the LC because it would not involve 'disposal at sea' (Wall *et al.*, 2005). Under OSPAR, however, States have general environmental obligations with respect to land-based sources (Purdy and Macrory, 2004) (and discharges from pipelines from land will be regulated, although not prohibited).

5.8.2 National regulations and standards

States can regulate subsurface injection and storage of CO_2 within their jurisdiction in accordance with their national rules and regulations. Such rules and regulations could be provided by the mining laws, resource conservation laws, laws on drinking water, waste disposal, oil and gas production, treatment of high-pressurized gases and others. An analysis of existing regulations in North America, Europe, Japan and Australia highlights the lack of regulations that are specifically relevant for CO_2 storage and the lack of clarity relating to post-injection responsibilities (IEA-GHG, 2003; IOGCC, 2005).

Presently, CO_2 is injected into the subsurface for EOR and for disposal of acid gas (Section 5.2.4). Most of these recovery or disposal activities inject relatively small quantities of CO_2 into reasonably well-characterized formations. Generally, the longevity of CO_2 storage underground and the extent of long-term monitoring of the injected fluids are not specified in the regulation of these activities, which are generally regulated under the larger umbrella of upstream oil and gas production and waste disposal regulations that do not specify storage time and need for post-operational monitoring.

In Canada, the practice of deep-well injection of fluids in the subsurface, including disposal of liquid wastes, is legal and regulated. As a result of provincial jurisdiction over energy and mineral resources, there are no generally applicable national laws that specifically regulate deep-well injection of fluids. Onshore CO_2 geological storage would fall under provincial laws and regulations, while storage offshore and in federally administered territories would fall under federal laws and regulations. In the western provinces that are major oil and gas producers, substantive regulations specifically manage the use of injection wells. In Alberta, for example, there are detailed procedural regulations regarding well construction, operation and abandonment, within which specific standards are delineated for five classes of injection wells (Alberta Energy and Utilities Board, 1994). In Saskatchewan, *The Oil and Gas Conservation Regulations 1985* (with Amendments through 2000) prescribe standards for disposal of oil field brine and other wastes. In addition, capture, transport and operational injection of fluids, including acid gas and CO_2, are by and large covered under existing regulations, but no regulations are in place for monitoring the fate of the injected fluids in the subsurface and/or for the post-abandonment stage of an injection operation.

In the United States, the Safe Drinking Water Act regulates most underground injection activities. The USEPA Underground Injection and Control (UIC) Program, created in 1980 to provide minimum standards, helps harmonize regulatory requirements for underground injection activities. The explicit goal of the UIC programme is to protect current and potential sources of public drinking water. The Safe Drinking Water Act expressly prohibits underground injection that 'endangers' an underground source of drinking water. Endangerment is defined with reference to national primary drinking water regulations and adverse human health effects. For certain types or 'classes' of wells, regulations by the USEPA prohibit injection that causes the movement of any contaminant into an underground source of drinking water.

Wells injecting hazardous wastes require the additional development of a no-migration petition to be submitted to the regulators. These petitions place the onus of proof on the project proponent that injected fluid will not migrate from the disposal site for 10,000 years or more. The fluids can exhibit buoyancy effects, as disposed fluids can be less dense than the connate fluids of the receiving formation. Operators are required to use models to demonstrate they can satisfy the 'no-migration' requirement over 10,000 years. Wilson *et al.* (2003) suggests that this process of proving containment could provide a model for long-term storage of CO_2. While detailed requirements exist for siting, constructing and monitoring injection well operation, there are no federal requirements for monitoring or verification of the actual movement of fluids within the injection zone, nor are there general requirements for monitoring in overlying zones to detect leakage. However, there are requirements for ambient monitoring in deep hazardous and industrial waste wells, with the degree of rigour varying from state to state.

Vine (2004) provides an extensive overview of environmental regulations that might affect geological CO_2 storage projects in California. Given that a developer may need to acquire up to 15 permits from federal, state and local authorities, Vine stresses the need for research to quantitatively assess the impacts of regulations on project development.

In Australia, permitting responsibility for onshore oil and gas activities reside with the State Governments, while offshore activities are primarily the responsibility of the Federal Government. A comprehensive assessment of the Australian regulatory regime is under way, but so far only South Australia has adopted legislation regulating the underground injection of gases such as CO_2 for EOR and for storage. Stringent environmental impact assessments are required for all activities that could compromise the quality of surface water or groundwater.

The 25 member states of the European Union (EU) have to ensure that geological storage of CO_2 is in conformity with relevant EU Directives. A number of directives could have an influence on CO_2 geological storage in the EU, notably those on waste (75/442/EEC), landfill (1999/31/EC), water (2000/60/EC), environmental impact assessment (85/337/EEC) and strategic environmental assessment (2001/42/EC). These directives were designed in a situation where CO_2 capture and storage was not taken into account and is not specifically mentioned.

There is one comprehensive Dutch study detailing legal and regulatory aspects of CO_2 underground injection and storage (CRUST Legal Task Force, 2001), including ownership of the stored CO_2, duty of care, liability and claim settlement. It has as its basis the legal situation established by the Dutch Mining Act of 2003 that covers 'substances' stored underground and unites previously divided regulation of onshore and offshore activities. Storage is defined as 'placing or keeping substances at depth of more than 100 m below the surface of the earth'. Legal interpretation indicates that CO_2 intended for storage would have to be treated as waste, because it was collected with the explicit purpose of disposal.

Regulating CO_2 storage presents a variety of challenges: the scale of the activity, the need to monitor and verify containment and any leakage of a buoyant fluid and the long storage time – all of which require specific regulatory considerations. Additionally, injecting large quantities of CO_2 into saline formations that have not been extensively characterized or may be close to populated areas creates potential risks that will need to be considered. Eventually, linkages between a CO_2 storage programme and a larger national and international CO_2 accounting regime will need to be credibly established.

5.8.3 *Subsurface property rights*

Storage of CO_2 in the subsurface raises several questions: Could rights to pore space be transferred to another party? Who owns CO_2 stored in pore space? How can storage of CO_2 in the pore space be managed so as to assure minimal damage to other property rights (e.g., mineral resources, water rights) sharing the same space? Rights to use subsurface pore space could be granted, separating them from ownership of the surface property. This, for example, appears to apply to most European countries and Canada, whereas in the United States, while there are currently no specific property-rights issues that could govern CO_2 storage, the rights to the subsurface can be severed from the land.

Scale is also an important issue. Simulations have shown that the areal extent of a plume of CO_2 injected from a 1 GW coal-fired power plant over 30 years into a 100-m-thick zone will be approximately 100 km^2 (Rutqvist and Tsang, 2002) and may grow after injection ceases. The approach to dealing with this issue will vary, depending on the legal framework for ownership of subsurface pore space. In Europe, for example, pore space is owned by the State and, therefore, utilization is addressed in the licensing process. In the United States, on the other hand, the determination of subsurface property rights on non-federal lands will vary according to state jurisdiction. In most jurisdictions, the surface owner is entitled to exclusive possession of the space formerly occupied by the subsurface minerals when the minerals are exhausted, that is, the 'pore space'. In other jurisdictions, however, no such precedent exists (Wilson, 2004). Some guidance for answering these questions can be found in the property rights arrangements associated with natural gas storage (McKinnon, 1998).

5.8.4 *Long-term liability*

It is important that liabilities that may apply to a storage project are clear to its proponent, including those liabilities that are applicable after the conclusion of the project. While a White

Paper by the European Commission outlines the general approach to environmental liability (EU, 2000), literature specifically addressing liability regimes for CO_2 storage is sparse. De Figueiredo *et al.* (2005) propose a framework to examine the implications of different types of liability on the viability of geological CO_2 storage and stress that the way in which liability is addressed may have a significant impact on costs and on public perception of CO_2 geological storage.

A number of novel issues arise with CO_2 geological storage. In addition to long-term *in-situ* risk liability, which may become a public liability after project decommissioning, global risks associated with leakage of CO_2 to the atmosphere may need to be considered. Current injection practices do not require any long-term monitoring or verification regime. The cost of monitoring and verification regimes and risk of leakage will be important in managing liability.

There are also considerations about the longevity of institutions and transferability of institutional knowledge. If long-term liability for CO_2 geological storage is transformed into a public liability, can ongoing monitoring and verification be assured and who will pay for these actions? How will information on storage locations be tracked and disseminated to other parties interested in using the subsurface? What are the time frames for storage? Is it realistic (or necessary) to put monitoring or information systems in place for hundreds of years?

Any discussion of long-term CO_2 geological storage also involves intergenerational liability and thus justification of such activities involves an ethical dimension. Some aspects of storage security, such as leakage up abandoned wells, may be realized only over a long time frame, thus posing a risk to future generations. Assumptions on cost, discounting and the rate of technological progress can all lead to dramatically different interpretations of liability and its importance and need to be closely examined.

5.8.5 Public perception and acceptance

There is insufficient public knowledge of climate change issues and of the various mitigation options, their potential impact and their practicality. The study of public perceptions and perceived acceptability of CO_2 capture and storage is at an early stage with few studies (Gough *et al.*, 2002; Palmgren *et al.*, 2004; Shackley *et al.*, 2004; Curry *et al.*, 2005; Itaoka *et al.*, 2005). Research on perceptions of CO_2 capture and storage is challenging because of (1) the relatively technical and 'remote' nature of the issue, with few immediate points of connection in the lay public's frame of reference to many key concepts; and (2) the early stage of the technology, with few examples and experiences in the public domain to draw upon as illustrations.

5.8.5.1 Survey research

Curry *et al.* (2005) surveyed more than 1200 people representing a general population sample of the United States. They found that less than 4% of the respondents were familiar with the terms *carbon dioxide capture and storage* or *carbon storage*. Moreover, there was no evidence that those who expressed familiarity were any more likely to correctly identify that the problem being addressed was global warming rather than water pollution or toxic waste. The authors also showed that there was a lack of knowledge of other power generation technologies (e.g., nuclear power, renewables) in terms of their environmental impacts and costs. Eurobarometer (2003) made similar findings across the European Union. The preference of the sample for different methods to address global warming (do nothing, expand nuclear power, continue to use fossil fuels with CO_2 capture and storage, expand renewables, etc.) was quite sensitive to information provided on relative costs and environmental characteristics.

Itaoka *et al.* (2005) conducted a survey of approximately a thousand people in Japan. They found much higher claimed levels of awareness of CO_2 capture and storage (31%) and general support for this mitigation strategy as part of a broader national climate change policy, but generally negative views on specific implementation of CO_2 capture and storage. Ocean storage was viewed most negatively, while offshore geological storage was perceived as the least negative. Part of the sample was provided with more information about CO_2 capture and storage, but this did not appear to make a large difference in the response. Factor analysis was conducted and revealed that four factors were important in influencing public opinion, namely perceptions of the environmental impacts and risks (e.g., leakage), responsibility for reducing CO_2 emissions, the effectiveness of CO_2 capture and storage as a mitigation option and the extent to which it permits the continued use of fossil fuels.

Shackley *et al.* (2004) conducted 212 face-to-face interviews at a UK airport regarding offshore geological storage. They found the sample was in general moderately supportive of the concept of CO_2 capture and storage as a contribution to a 60% reduction in CO_2 emissions in the UK by 2050 (the government's policy target). Provision of basic information on the technology increased the support that was given to it, though just under half of the sample were still undecided or expressed negative views. When compared with other mitigation options, support for CO_2 capture and storage increased slightly, though other options (such as renewable energy and energy efficiency) were strongly preferred. On the other hand, CO_2 capture and storage was much preferred to nuclear power or higher energy bills (no information on price or the environmental impact of other options was provided). When asked, unprompted, if they could think of any negative effects of CO_2 capture and storage, half of the respondents' mentioned leakage, while others mentioned associated potential impacts upon ecosystems and human health. Others viewed CO_2 capture and storage negatively on the grounds it was avoiding the real problem, was short-termist or indicated a reluctance to change.

Huijts (2003) polled 112 individuals living in an area above a gas field in The Netherlands that had experienced two small earthquakes (in 1994 and 2001). She found the sample was mildly positive about CO_2 capture and storage in general terms, but neutral to negative about storage in the immediate neighbourhood. The respondents also thought that the risks and drawbacks were somewhat larger than the benefits to the environment and society. The respondents considered that the personal benefits of CO_2 capture and storage were 'small' or 'reasonably small'. On the basis of her findings, Huijts (2003) observed the storage location could make a large difference to its acceptability; onshore storage below residential areas would probably not be viewed positively, although it has to be borne in mind that the study area had experienced recent earthquakes. Huijts also notes that many respondents (25%) tended to choose a neutral answer to questions about CO_2 capture and storage, suggesting they did not yet have a well-formed opinion.

Palmgren *et al.* (2004) conducted 18 face-to-face interviews in the Pittsburgh, Pennsylvania, USA, area, followed by a closed-form survey administered to a sample of 126 individuals. The study found that provision of more information led the survey respondents to adopt a more negative view towards CO_2 capture and storage. The study also found that, when asked in terms of willingness to pay, the respondents were less favourable towards CO_2 capture and storage as a mitigation option than they were to all the other options provided (which were rated, in descending order, as follows: solar, hydro, wind, natural gas, energy efficiency, nuclear, biomass, geological storage and ocean storage). Ocean storage was viewed more negatively than geological storage, especially after information was provided.

5.8.5.2 *Focus-group research*

Focus-group research on CO_2 capture and storage was conducted in the UK in 2001 and 2003 (Gough *et al.*, 2002; Shackley *et al.*, 2004). Initial reactions tended to be sceptical; only within the context of the broader discussion of climate change and the need for large cuts in CO_2 emissions, did opinions become more receptive. Typically, participants in these groups were clear that other approaches such as energy efficiency, demand-reduction measures and renewable energy should be pursued as a priority and that CO_2 geological storage should be developed alongside and not as a straight alternative to, these other options. There was general support for use of CO_2 capture and storage as a 'bridging measure' while other zero or low carbon energy technologies are developed or as an emergency stop-gap option if such technologies are not developed in time. There was a moderate level of scepticism among participants towards both government and industry and what may motivate their promotion of CO_2 storage, but there was also some distrust of messages promoted by environmental groups. Levels of trust in key institutions and the role of the media were perceived to have a major influence on how CO_2 capture and storage would be received by the public, a point also made by Huijts (2003).

5.8.5.3 *Implications of the research*

The existing research described above has applied different methodologies, research designs and terminology, making direct comparisons impossible. Inconsistencies in results have arisen concerning the effect of providing more detailed information to respondents and the evaluation of CO_2 capture and storage in general terms and in comparison with other low-carbon mitigation options. Explanations for these differences might include the extent of concern expressed regarding future climate change. Representative samples in the USA and EU (Curry *et al.*, 2005) and most of the smaller samples (Shackley *et al.*, 2004; Itaoka *et al.*, 2005) find moderate to high levels of concern over climate change, whereas respondents in the Palmgren *et al.* (2004) study rated climate change as the least of their environmental concerns. A further explanation of the difference in perceptions might be the extent to which perceptions of onshore and offshore geological storage have been distinguished in the research.

From this limited research, it appears that at least three conditions may have to be met before CO_2 capture and storage is considered by the public as a credible technology, alongside other better known options: (1) anthropogenic global climate change has to be regarded as a relatively serious problem; (2) there must be acceptance of the need for large reductions in CO_2 emissions to reduce the threat of global climate change; (3) the public has to accept this technology as a non-harmful and effective option that will contribute to the resolution of (1) and (2). As noted above, many existing surveys have indicated fairly widespread concern over the problem of global climate change and a prevailing feeling that the negative impact outweighs any positive effects (e.g., Kempton *et al.*, 1995; Poortinga and Pidgeon, 2003). On the other hand, some survey and focus-group research suggests that widespread acceptance of the above factors amongst the public – in particular the need for large reduction in CO_2 emissions – is sporadic and variable within and between national populations. Lack of knowledge and uncertainty regarding the economic and environmental characteristics of other principal mitigation options have also been identified as an impediment to evaluating the CO_2 capture and storage option (Curry *et al.*, 2005).

Acceptance of the three conditions does not imply support for CO_2 capture and storage. The technology may still be rejected by some as too 'end of pipe', treating the symptoms not the cause, delaying the point at which the decision to move away from the use of fossil fuels is taken, diverting attention from the development of renewable energy options and holding potential long-term risks that are too difficult to assess with certainty. Conversely, there may be little realization of the practical difficulties in meeting existing and future energy needs from renewables. Acceptance of CO_2 capture and storage, where it occurs, is frequently 'reluctant' rather than 'enthusiastic' and in some cases reflects the perception that CO_2 capture and storage might be required because of failure to reduce CO_2 emissions in other ways. Furthermore, several of the studies above indicate that an 'in principle' acceptance of the technology can be very different from acceptance of storage at a specific site.

5.8.5.4 *Underground storage of other fluids*

Given minimal experience with storage of CO_2, efforts have been made to find analogues that have similar regulatory (and hence public acceptance) characteristics (Reiner and Herzog, 2004). Proposals for underground natural gas storage schemes have generated public opposition in some localities, despite similar facilities operating close by without apparent concern (Gough *et al.*, 2002). Concern regarding the effects of underground natural gas storage upon local property prices and difficult-to-assess risks appear in one case to have been taken up and possibly amplified by the local media. Public opposition to onshore underground storage is likely to be heightened by accidents such as the two deaths from explosions in 2001 in Hutchinson, Kansas (USA), when compressed natural gas escaped from salt cavern storage facilities (Lee, 2001). However, throughout the world today, many hundreds of natural gas storage sites are evidently acceptable to local communities. There has also been a study of the Underground Injection Control programme in the United States, because of the perceived similarity of the governing regulatory regime (Wilson *et al.*, 2003).

5.9 Costs of geological storage

How much will geological storage cost? What are the major factors driving storage costs? Can costs be offset by enhanced oil and gas production? These questions are covered in this section. It starts with a review of the cost elements and factors that affect storage costs and then presents estimated costs for different storage options. The system boundary for the storage costs used here is the delivery point between the transport system and the storage site facilities. It is generally expected that CO_2 will be delivered as a dense fluid (liquid or supercritical) under pressure at this boundary. The costs of capture, compression and transport to the site are excluded from the storage costs presented here. The figures presented are levelized costs, which incorporate economic assumptions such as the project lifetime, discount rates and inflation (see Section 3.7.2). They incorporate both capital and operating costs.

5.9.1 Cost elements for geological storage

The major capital costs for CO_2 geological storage are drilling wells, infrastructure and project management. For some storage sites, there may be in-field pipelines to distribute and deliver CO_2 from centralized facilities to wells within the site. Where required, these are included in storage cost estimates. For enhanced oil, gas and coal bed methane options, additional facilities may be required to handle produced oil and gas. Reuse of infrastructure and wells may reduce costs at some sites. At some sites, there may be additional costs for remediation work for well abandonment that are not included in existing estimates. Operating costs include manpower, maintenance and fuel. The costs for licensing, geological, geophysical and engineering feasibility studies required for site selection, reservoir characterization and evaluation before storage starts are included in the cost estimates. Bock *et al.* (2003) estimate these as US$ 1.685 million for saline formation and depleted oil and gas field storage case studies in the United States. Characterization costs will vary widely from site to site, depending on the extent of pre-existing data, geological complexity of the storage formations and caprock and risks of leakage. In addition, to some degree, economies of scale may lower the cost per tonne of larger projects; this possibility has not been considered in these estimates.

Monitoring of storage will add further costs and is usually reported separately from the storage cost estimates in the literature. These costs will be sensitive to the regulatory requirements and duration of monitoring. Over the long term, there may be additional costs for remediation and for liabilities.

The cost of CO_2 geological storage is site-specific, which leads to a high degree of variability. Cost depends on the type of storage option (e.g., oil or gas reservoir, saline formation), location, depth and characteristics of the storage reservoir formation and the benefits and prices of any saleable products. Onshore storage costs depend on the location, terrain and other geographic factors. The unit costs are usually higher offshore, reflecting the need for platforms or sub-sea facilities and higher operating costs, as shown in separate studies for Europe (Hendriks *et al.*, 2002) and Australia (Allinson *et al.*, 2003). The equipment and technologies required for storage are already widely used in the energy industries, so that costs can be estimated with confidence.

5.9.2 Cost estimates

There are comprehensive assessments of storage costs for the United States, Australia and Europe (Hendriks *et al.*, 2002; Allinson *et al.*, 2003; Bock *et al.*, 2003). These are based on representative geological characteristics for the regions. In some cases, the original cost estimates include compression and pipeline costs and corrections have been made to derive storage costs (Table 5.9). These estimates include capital, operating and site characterization costs, but exclude monitoring costs, remediation and any additional costs required to address long-term liabilities.

The storage option type, depth and geological characteristics affect the number, spacing and cost of wells, as well as the facilities cost. Well and compression costs both increase with depth. Well costs depend on the specific technology, the location, the scale of the operation and local regulations. The cost of wells is a major component; however, the cost of individual wells ranges from about US$ 200,000 for some onshore sites (Bock *et al.,* 2003) to US$ 25 million for offshore horizontal wells (Table 5.10; Kaarstad, 2002). Increasing storage costs with depth have been demonstrated (Hendriks *et al.*, 2002). The geological characteristics of the injection formation are another major cost driver, that is, the reservoir thickness, permeability and effective radius that affect the amount and rate of CO_2 injection and therefore the number of wells needed. It is more costly to inject and store other gases (NO_x, SO_x, H_2S) with CO_2 because of their corrosive and hazardous nature, although the capture cost may be reduced (Allinson *et al.*, 2003).

Table 5.9 Compilation of CO_2 storage cost estimates for different options.

Option type	On or offshore	Location	US$/tCO$_2$ stored			Comments	Nature of Midpoint value
			Low	Mid	High		
Saline formation	Onshore	Australia	0.2	0.5	5.1	Statistics for 20 sites[a]	Median
Saline formation	Onshore	Europe	1.9	2.8	6.2	Representative range[b]	Most likely value
Saline formation	Onshore	USA	0.4	0.5	4.5	Low/base/high cases for USA[c]	Base case for average parameters
Saline formation	Offshore	Australia	0.5	3.4	30.2	Statistics for 34 sites[a]	Median
Saline formation	Offshore	N. Sea	4.7	7.7	12.0	Representative range[b]	Most likely value
Depleted oil field	Onshore	USA	0.5	1.3	4.0	Low/base/high cases for USA[c]	Base case for average parameters
Depleted gas field	Onshore	USA	0.5	2.4	12.2	Low/base/high cases for USA[c]	Base case for average parameters
Disused oil or gas field	Onshore	Europe	1.2	1.7	3.8	Representative range[b]	Most likely value
Disused oil or gas field	Offshore	N. Sea	3.8	6.0	8.1	Low/base/high cases for USA[c]	Most likely value

Note: The ranges and low, most likely (mid), high values reported in different studies were calculated in different ways. The estimates exclude monitoring costs.

a. Figures from Allinson *et al*., (2003) are statistics for multiple cases from different sites in Australia. Low is the minimum value, most likely is median, high is maximum value of all the cases. The main determinants of storage costs are rate of injection and reservoir characteristics such as permeability, thickness, reservoir depth rather than reservoir type (such as saline aquifer, depleted field, etc.). The reservoir type could be high or low cost depending on these characteristics. The figures are adjusted to exclude compression and transport costs.

b. Figures from Hendriks *et al*., (2002) are described as a representative range of values for storage options 1000-3000 m depth. The full range of costs is acknowledged to be larger than shown. The figures are converted from Euros to US$.

c. Bock *et al*., (2003) define a base case, low- and high-cost cases from analysis of typical reservoirs for US sites. Each case has different depth, reservoir, cost and oil/gas price parameters. The figures are adjusted to exclude compression and transport costs.

Table 5.10 Investment costs for industry CO_2 storage projects.

Project	Sleipner	Snøhvit
Country	Norway	Norway
Start	1996	2006
Storage type	Aquifer	Aquifer
Annual CO_2 injection rate ($MtCO_2$ yr^{-1})	1	0.7
Onshore/Offshore	Offshore	Offshore
Number of wells	1	1
Pipeline length (km)	0	160
Capital Investment Costs (US$ million)		
Capture and Transport	79	143
Compression and dehydration	79	70
Pipeline	none	73
Storage	15	48
Drilling and well completion	15	25
Facilities	[a]	12
Other	[a]	11
Total capital investment costs (US$ million)	94	191
Operating Costs (US$ million)		
Fuel and CO_2 tax	7	
References	Torp and Brown, 2005	Kaarstad, 2002

[a] No further breakdown figures are available. Subset of a larger system of capital and operating costs for several processes, mostly natural gas and condensate processing.

5.9.3 Cost estimates for CO_2 geological storage

This section reviews storage costs for options without benefits from enhanced oil or gas production. It describes the detailed cost estimates for different storage options.

5.9.3.1 Saline formations

The comprehensive review by Allinson *et al.*, (2003), covering storage costs for more than 50 sites around Australia, illustrates the variability that might occur across a range of sites at the national or regional scale. Onshore costs for 20 sites have a median cost of 0.5 US\$/tCO_2 stored, with a range of 0.2–5.1 US\$/tCO_2 stored. The 37 offshore sites have a median value of 3.4 US\$/tCO_2 stored and a range of 0.5–30.2 US\$/tCO_2 stored. This work includes sensitivity studies that use Monte Carlo analyses of estimated costs to changes in input parameters. The main determinants of storage costs are reservoir and injection characteristics such as permeability, thickness and reservoir depth, that affect injection rate and well costs rather than option type (such as saline formation or depleted field).

Bock *et al.* (2003) have made detailed cost estimates on a series of cases for storage in onshore saline formations in the United States. Their assumptions on geological characteristics are based on a statistical review of more than 20 different formations. These formations represent wide ranges in depth (700–1800 m), thickness, permeability, injection rate and well numbers. The base-case estimate for average characteristics has a storage cost of 0.5 US\$/tCO_2 stored. High- and low-cost cases representing a range of formations and input parameters are 0.4–4.5 US\$/tCO_2 stored. This illustrates the variability resulting from input parameters.

Onshore storage costs for saline formations in Europe for depths of 1000–3000 m are 1.9–6.2 US\$/tCO_2, with a most likely value of 2.8 US\$/tCO_2 stored (Hendriks *et al.*, 2002). This study also presents estimated costs for offshore storage over the same depth range. These estimates cover reuse of existing oil and gas platforms (Hendriks *et al.*, 2002). The range is 4.7–12.0 US\$/tCO_2 stored, showing that offshore costs are higher than onshore costs.

5.9.3.2 Disused oil and gas reservoirs

It has been shown that storage costs in disused oil and gas fields in North America and Europe are comparable to those for saline formations (Hendriks *et al.*, 2002; Bock *et al.*, 2003). Bock *et al.* (2003) present costs for representative oil and gas reservoirs in the Permian Basin (west Texas, USA). For disused gas fields, the base-case estimate has a storage cost of 2.4 US\$/tCO_2 stored, with low and high cost cases of 0.5 and 12.2 US\$/tCO_2 stored. For depleted oil fields, the base-case cost estimate is 1.3 US\$/tCO_2 stored, with low- and highcost cases of 0.5 and 4.0 US\$/tCO_2 stored. Some reduction in these costs may be possible by reusing existing wells in these fields, but remediation of abandoned wells would increase the costs if required.

In Europe, storage costs for onshore disused oil and gas fields at depths of 1000–3000 m are 1.2–3.8 US\$/tCO_2 stored. The most likely value is 1.7 US\$/tCO_2 stored. Offshore oil and gas fields at the same depths have storage costs of 3.8–8.1 US\$/tCO_2 stored (most likely value is 6.0 US\$/tCO_2 stored). The costs depend on the depth of the reservoir and reuse of platforms. Disused fields may benefit from reduced exploration and monitoring costs.

5.9.3.3 Representative storage costs

The different studies for saline formations and disused oil and gas fields show a very wide range of costs, 0.2–30.0 US\$/tCO_2 stored, because of the site-specific nature of the costs. This reflects the wide range of geological parameters that occur in any region or country. In effect, there will be multiple sites in any geographic area with a cost curve, providing increasing storage capacity with increasing cost.

The extensive Australian data set indicates that storage costs are less than 5.1 US\$/tCO_2 stored for all the onshore sites and more than half the offshore sites. Studies for USA and Europe also show that storage costs are generally less than 8 US\$/tCO_2, except for high-cost cases for offshore sites in Europe and depleted gas fields in the United States. A recent study suggests that 90% of European storage capacity could be used for costs less that 2 US\$/tCO_2 (Wildenborg *et al.*, 2005b).

Assessment of these cost estimates indicates that there is significant potential for storage at costs in the range of 0.5–8 US\$/tCO_2 stored, estimates that are based on the median, base case or most likely values presented for the different studies (Table 5.9). These exclude monitoring costs, well remediation and longer term costs.

5.9.3.4 Investment costs for storage projects

Some information is available on the capital and operating costs of industry capture and storage projects (Table 5.10). At Sleipner, the incremental capital cost for the storage component comprising a horizontal well to inject 1 MtCO_2 yr^{-1} was US\$ 15 million (Torp and Brown, 2005). Note that at Sleipner, CO_2 had to be removed from the natural gas to ready it for sale on the open market. The decision to store the captured CO_2 was at least in part driven by a 40 US\$/tCO_2 tax on offshore CO_2 emissions. Details of the energy penalty and levelized costs are not available. At the planned Snohvit project, the estimated capital costs for storage are US\$ 48 million for injection of 0.7 MtCO_2 yr^{-1} (Kaarstad, 2002). This data set is limited and additional data on the actual costs of industry projects is needed.

5.9.4 Cost estimates for storage with enhanced oil and gas recovery

The costs of CO_2 geological storage may be offset by additional revenues for production of oil or gas, where CO_2 injection and storage is combined with enhanced oil or gas recovery or ECBM. At present, in commercial EOR and ECBM projects that use CO_2 injection, the CO_2 is purchased for the project and is a significant proportion of operating costs. The economic benefits from enhanced production make EOR and ECBM potential early options for CO_2 geological storage.

5.9.4.1 Enhanced oil recovery

The costs of onshore CO_2-flooding EOR projects in North America are well documented (Klins, 1984; Jarrell *et al.*, 2002). Carbon dioxide EOR projects are business ventures to increase oil recovery. Although CO_2 is injected and stored, this is not the primary driver and EOR projects are not optimized for CO_2 storage.

The commercial basis of conventional CO_2-EOR operations is that the revenues from incremental oil compensate for the additional costs incurred (including purchase of CO_2) and provide a return on the investment. The costs differ from project to project. The capital investment components are compressors, separation equipment and H_2S removal, well drilling and well conversions and completions. New wells are not required for some projects. Operating costs are the CO_2 purchase price, fuel costs and field operating costs.

In Texas, the cost of CO_2 purchase was 55–75% of the total cost for a number of EOR fields (averaging 68% of total costs) and is a major investment uncertainty for EOR. Tax and fiscal incentives, government regulations and oil and gas prices are the other main investment uncertainties (e.g., Jarrell *et al.*, 2002).

The CO_2 price is usually indexed to oil prices, with an indicative price of 11.7 US\$/tCO_2 (0.62 US\$/Mscf) at a West Texas Intermediate oil price of 18 US\$ per barrel, 16.3 US\$/tCO_2 at 25 US\$ per barrel of oil and 32.7 US\$/tCO_2 at 50 US\$ per barrel of oil (Jarrell *et al.*, 2002). The CO_2 purchase price indicates the scale of benefit for EOR to offset CO_2 storage costs.

5.9.4.2 Cost of CO_2 storage with enhanced oil recovery

Recent studies have estimated the cost of CO_2 storage in EOR sites (Bock *et al.*, 2003; Hendriks *et al.*, 2002). Estimates of CO_2 storage costs for onshore EOR options in North America have been made by Bock *et al.* (2003). Estimates for a 2-MtCO_2 yr^{-1} storage scenario are based on assumptions and parameters from existing EOR operations and industry cost data. These include estimates of the effectiveness of CO_2-EOR, in terms of CO_2 injected for each additional barrel of oil. The methodology for these estimates of storage costs is to calculate the break-even CO_2 price (0.3 tCO_2).

Experience from field operations across North America provides information about how much of the injected CO_2 remains in the oil reservoir during EOR. An average of 170 standard m^3 CO_2 of new CO_2 is required for each barrel of enhanced oil production, with a range of 85 (0.15 tCO_2) to 227 (0.4 tCO_2) standard m^3 (Bock *et al.*, 2003). Typically, produced CO_2 is separated from the oil and reinjected back underground, which reduces the cost of CO_2 purchases.

The base case for a representative reservoir at a depth of 1219 m, based on average EOR parameters in the United States with an oil price of 15 US\$ per barrel, has a net storage cost of –14.8 US\$/tCO_2 stored. Negative costs indicate the amount of cost reduction that a particular storage option offers to the overall capture and storage system. Low- and high-cost cases representing a range of CO_2 effectiveness, depth, transport distance and oil price are –92.0 and +66.7 US\$/tCO_2 stored. The low-cost case assumes favourable assumptions for all parameters (effectiveness, reservoir depth, productivity) and a 20 US\$ per barrel oil price. Higher oil prices, such as the 50 US\$ per barrel prices of 2005, will considerably change the economics of CO_2-EOR projects. No published studies are available for these higher oil prices.

Other estimates for onshore EOR storage costs all show potential at negative net costs. These include a range of –10.5 to +10.5 US\$/tCO_2 stored for European sites (Hendriks *et al.*, 2002). These studies show that use of CO_2 enhanced oil recovery for CO_2 storage can be a lower cost option than saline formations and disused oil and gas fields.

At present, there are no commercial offshore EOR operations and limited information is available on CO_2 storage costs for EOR options in offshore settings. Indicative storage cost estimates for offshore EOR are presented by Hendriks *et al.* (2002). Their range is –10.5 to +21.0 US\$/tCO_2 stored. For the North Sea Forties Field, it has been shown that CO_2-flooding EOR is technically attractive and could increase oil recovery, although at present it is not economically attractive as a stand-alone EOR project (Espie *et al.*, 2003). Impediments are the large capital requirement for adapting facilities, wells and flowlines, as well as tax costs and CO_2 supply. It is noted that the economics will change with additional value for storage of CO_2.

The potential benefit of EOR can be deduced from the CO_2 purchase price and the net storage costs for CO_2-EOR storage case studies. The indicative value of the potential benefit from enhanced oil production to CO_2 storage is usually in the range of 0–16 US\$/tCO_2. In some cases, there is no benefit from EOR. The maximum estimate of the benefit ranges up to \$92 per tonne of CO_2 for a single case study involving favourable parameters. In general, higher benefits will occur at high-oil-price scenarios similar to those that have occurred since 2003 and for highly favourable sites, as shown above. At 50 US\$ per barrel of oil, the range may increase up to 30 US\$/tCO_2.

5.9.4.3 Cost of CO_2 storage with enhanced gas recovery

CO_2-enhanced gas recovery is a less mature technology than EOR and it is not in commercial use. Issues are the cost of CO_2 and infrastructure, concerns about excessive mixing and the high primary recovery rates of many gas reservoirs. Cost estimates show that CO_2-EGR (enhanced gas recovery) can provide a benefit of 4–16 US\$/tCO_2, depending on the price of gas and the effectiveness of recovery (Oldenburg *et al.*, 2002).

5.9.4.4 Cost of CO_2 storage with enhanced coal bed methane

The injection of CO_2 for ECBM production is an immature technology not yet in commercial use. In CO_2-ECBM, the revenues from the produced gas could offset the investment costs and provide a source of income for investors. Cost data are based on other types of CBM operations that are in use.

There is significant uncertainty in the effectiveness of CO_2 storage in coal beds in conjunction with ECBM, because there is no commercial experience. The suggested metric for CO_2 retention is 1.5–10 m^3 of CO_2 per m^3 of produced methane. The revenue benefit of the enhanced production will depend on gas prices.

Well costs are a major factor in ECBM because many wells are required. In one recent study for an ECBM project (Schreurs, 2002), the cost per production well was given as approximately US$750,000 per well, plus 1500 US$ m^{-1} of in-seam drilling. The cost of each injection well was approximately US$430,000.

The IEA-GHG (1998) developed a global cost curve for CO_2-ECBM, with storage costs ranging from –20 to +150 US$/t$CO_2$. It concluded that only the most favourable sites, representing less than 10% of global capacity, could have negative costs. Estimates of onshore CO_2-ECBM storage costs in the United States have been made by using the approach described for EOR (Bock *et al.*, 2003). They estimate the effectiveness of ECBM in terms of CO_2 injected for incremental gas produced, ranging from 1.5 to 10 units (base case value of 2) of CO_2 per unit of enhanced methane. Other key inputs are the gas well production rate, the ratio of producers to injectors, well depth and the number of wells. The base case, storing 2.1 MtCO_2 per year for a representative reservoir at 610 m depth in a newly built facility, requires 270 wells. The assumed gas price is US$1.90 per GJ (US$2.00 per Mbtu). It has a net storage cost of –8.1 US$/t$CO_2$ stored. Low- and high-cost cases representing a range of parameters are –26.4 and +11.1 US$/t$CO_2$ stored. The range of these estimates is comparable to other estimates – for example, those for Canada (Wong *et al.*, 2001) and Europe (Hendriks *et al.*, 2002), 0 to +31.5 US$/t$CO_2$. Enhanced CBM has not been considered in detail for offshore situations and cost estimates are not available.

Only one industrial-scale CO_2-ECBM demonstration project has taken place to date, the Allison project in the United States and it is no longer injecting CO_2 (Box 5.7). One analysis of the Allison project, which has extremely favourable geological characteristics, suggests the economics of ECBM in the United States are dubious under current fiscal conditions and gas prices (IEA-GHG, 2004). The economic analyses suggest this would be commercial, with high gas prices about 4 US$ per GJ) and a credit of 12–18 US$/t$CO_2$. Alternatively, Reeves (2005) used detailed modelling and economic analysis to show a break-even gas price of US$2.44 per GJ (US$2.57 per Mbtu), including costs of 5.19 US$/t$CO_2$ for CO_2 purchased at the field.

5.9.5 Cost of monitoring

While there has been extensive discussion of possible monitoring strategies in the literature and technologies that may be applicable, there is limited information on monitoring costs. These will depend on the monitoring strategy and technologies used and how these are adapted for the duration of storage projects. Some of the technologies likely to be used are already in widespread use in the oil and gas and CBM industries. The costs of individual technologies in current use are well constrained.

Repeated use of seismic surveys was found to be an effective monitoring technology at Sleipner. Its applicability will vary between options and sites. Seismic survey costs are highly variable, according to the technology used, location and terrain and complexity. Seismic monitoring costs have been reviewed for an onshore storage project for a 1000 MW power plant with a 30-year life (Myer *et al.*, 2003). Assuming repeat surveys at five-year intervals during the injection period, monitoring costs are estimated as 0.03 US$/t$CO_2$, suggesting that seismic monitoring may represent only a small fraction of overall storage costs. No discounting was used to develop this estimate.

Benson *et al.* (2005) have estimated life-cycle monitoring costs for two scenarios: (1) storage in an oil field with EOR and (2) storage in a saline formation. For these scenarios, no explicit leakage was considered. If leakage were to occur, the 'enhanced' monitoring programme should be sufficient to detect and locate the leakage and may be sufficient to quantify leakage rates as well. For each scenario, cost estimates were developed for the 'basic' and 'enhanced' monitoring package. The basic monitoring package included periodic seismic surveys, microseismicity, wellhead pressure and injection-rate monitoring. The enhanced package included all of the elements of the 'basic' package and added periodic well logging, surface CO_2 flux monitoring and other advanced technologies. For the basic monitoring package, costs for both scenarios are 0.05 US$/t$CO_2$, based on a discount rate of 10% (0.16–0.19 US$/t$CO_2$ undiscounted). The cost for the enhanced monitoring package is 0.069–0.085 US$/t$CO_2$ (0.27–0.30 US$/t$CO_2$ undiscounted). The assumed duration of monitoring includes the 30-year period of injection, as well as further monitoring after site closure of 20 years for EOR sites and 50 years for saline formations. Increasing the duration of monitoring to 1000 years increased the discounted cost by 10%. These calculations are made assuming a discount rate of 10% for the first 30 years and a discount rate of 1% thereafter.

5.9.6 Cost of remediation of leaky storage projects

No estimates have been made regarding the costs of remediation for leaking storage projects. Remediation methods listed in Table 5.7 have been used in other applications and, therefore, could be extrapolated to CO_2 storage sites. However, this has not been done yet.

5.9.7 Cost reduction

There is little literature on cost-reduction potential for CO_2 geological storage. Economies of scale are likely to be important (Allinson *et al.*, 2003). It is also anticipated that further cost reduction will be achieved with application of learning from early storage projects, optimization of new projects and application of advanced technologies, such as horizontal and multilateral wells, which are now widely used in the oil and gas industry.

5.10 Knowledge gaps

Knowledge regarding CO_2 geological storage is founded on basic knowledge in the earth sciences, on the experience of the oil and gas industry (extending over the last hundred years or more) and on a large number of commercial activities involving the injection and geological storage of CO_2 conducted over the past 10–30 years. Nevertheless, CO_2 storage is a new technology and many questions remain. Here, we summarize what we know now and what gaps remain.

1. Current storage capacity estimates are imperfect:
    - There is need for more development and agreement on assessment methodologies.
    - There are many gaps in capacity estimates at the global, regional and local levels.
    - The knowledge base for geological storage is for the most part based on Australian, Japanese, North American and west European data.
    - There is a need to obtain much more information on storage capacity in other areas, particularly in areas likely to experience the greatest growth in energy use, such as China, Southeast Asia, India, Russia/Former Soviet Union, Eastern Europe, the Middle East and parts of South America and southern Africa.

2. Overall, storage science is understood, but there is need for greater knowledge of particular mechanisms, including:
    - The kinetics of geochemical trapping and the long-term impact of CO_2 on reservoir fluids and rocks.
    - The fundamental processes of CO_2 adsorption and CH_4 desorption on coal during storage operations.

3. Available information indicates that geological storage operations can be conducted without presenting any greater risks for health and the local environment than similar operations in the oil and gas industry, when carried out at high-quality and well-characterized sites. However, confidence would be further enhanced by increased knowledge and assessment ability, particularly regarding:
    - Risks of leakage from abandoned wells caused by material and cement degradation.
    - The temporal variability and spatial distribution of leaks that might arise from inadequate storage sites.
    - Microbial impacts in the deep subsurface.
    - Environmental impact of CO_2 on the marine seafloor.
    - Methods to conduct end-to-end quantitative assessment of risks to human health and the local environment.

4. There is strong evidence that storage of CO_2 in geological storage sites will be long term; however, it would be beneficial to have:
    - Quantification of potential leakage rates from more storage sites.
    - Reliable coupled hydrogeological-geochemical-geo–mechanical simulation models to predict long-term storage performance accurately.
    - Reliable probabilistic methods for predicting leakage rates from storage sites.
    - Further knowledge of the history of natural accumulations of CO_2.
    - Effective and demonstrated protocols for achieving desirable storage duration and local safety.

5. Monitoring technology is available for determining the behaviour of CO_2 at the surface or in the subsurface; however, there is scope for improvement in the following areas:
    - Quantification and resolution of location and forms of CO_2 in the subsurface, by geophysical techniques.
    - Detection and monitoring of subaquatic CO_2 seepage.
    - Remote-sensing and cost-effective surface methods for temporally variable leak detection and quantification, especially for dispersed leaks.
    - Fracture detection and characterization of leakage potential.
    - Development of appropriate long-term monitoring approaches and strategies.

6. Mitigation and remediation options and technologies are available, but there is no track record of remediation for leaked CO_2. While this could be seen as positive, some stakeholders suggest it might be valuable to have an engineered (and controlled) leakage event that could be used as a learning experience.

7. The potential cost of geological storage is known reasonably well, but:
    - There are only a few experience-based cost data from non-EOR CO_2 storage projects.
    - There is little knowledge of regulatory compliance costs.
    - There is inadequate information on monitoring strategies and requirements, which affect costs.

8. The regulatory and responsibility or liability framework for CO_2 storage is yet to be established or unclear. The following issues need to be considered:
    - The role of pilot and demonstration projects in developing regulations.
    - Approaches for verification of CO_2 storage for accounting purposes.
    - Approaches to regulatory oversight for selecting, operating and monitoring CO_2 storage sites, both in the short and long term.
    - Clarity on the need for and approaches to long-term stewardship.
    - Requirements for decommissioning a storage project.

Additional information on all of these topics would improve technologies and decrease uncertainties, but there appear to be no insurmountable technical barriers to an increased uptake of geological storage as a mitigation option.

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6

Ocean storage

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Contents

EXECUTIVE SUMMARY

Captured CO_2 could be deliberately injected into the ocean at great depth, where most of it would remain isolated from the atmosphere for centuries. CO_2 can be transported via pipeline or ship for release in the ocean or on the sea floor. There have been small-scale field experiments and 25 years of theoretical, laboratory, and modelling studies of intentional ocean storage of CO_2, but ocean storage has not yet been deployed or thoroughly tested.

The increase in atmospheric CO_2 concentrations due to anthropogenic emissions has resulted in the oceans taking up CO_2 at a rate of about 7 $GtCO_2yr^{-1}$ (2 $GtCyr^{-1}$). Over the past 200 years the oceans have taken up 500 $GtCO_2$ from the atmosphere out of 1300 $GtCO_2$ total anthropogenic emissions. Anthropogenic CO_2 resides primarily in the upper ocean and has thus far resulted in a decrease of *p*H of about 0.1 at the ocean surface with virtually no change in *p*H deep in the oceans. Models predict that the oceans will take up most CO_2 released to the atmosphere over several centuries as CO_2 is dissolved at the ocean surface and mixed with deep ocean waters.

The Earth's oceans cover over 70% of the Earth's surface with an average depth of about 3,800 metres; hence, there is no practical physical limit to the amount of anthropogenic CO_2 that could be placed in the ocean. However, the amount that is stored in the ocean on the millennial time scale depends on oceanic equilibration with the atmosphere. Over millennia, CO_2 injected into the oceans at great depth will approach approximately the same equilibrium as if it were released to the atmosphere. Sustained atmospheric CO_2 concentrations in the range of 350 to 1000 ppmv imply that 2,300 ± 260 to 10,700 ± 1,000 Gt of anthropogenic CO_2 will eventually reside in the ocean.

Analyses of ocean observations and models agree that injected CO_2 will be isolated from the atmosphere for several hundreds of years and that the fraction retained tends to be larger with deeper injection. Additional concepts to prolong CO_2 retention include forming solid CO_2 hydrates and liquid CO_2 lakes on the sea floor, and increasing CO_2 solubility by, for example, dissolving mineral carbonates. Over centuries, ocean mixing results in loss of isolation of injected CO_2 and exchange with the atmosphere. This would be gradual from large regions of the ocean. There are no known mechanisms for sudden or catastrophic release of injected CO_2.

Injection up to a few $GtCO_2$ would produce a measurable change in ocean chemistry in the region of injection, whereas injection of hundreds of $GtCO_2$ would eventually produce measurable change over the entire ocean volume.

Experiments show that added CO_2 can harm marine organisms. Effects of elevated CO_2 levels have mostly been studied on time scales up to several months in individual organisms that live near the ocean surface. Observed phenomena include reduced rates of calcification, reproduction, growth, circulatory oxygen supply and mobility as well as increased mortality over time. In some organisms these effects are seen in response to small additions of CO_2. Immediate mortality is expected close to injection points or CO_2 lakes. Chronic effects may set in with small degrees of long-term CO_2 accumulation, such as might result far from an injection site, however, long-term chronic effects have not been studied in deep-sea organisms.

CO_2 effects on marine organisms will have ecosystem consequences; however, no controlled ecosystem experiments have been performed in the deep ocean. Thus, only a preliminary assessment of potential ecosystem effects can be given. It is expected that ecosystem consequences will increase with increasing CO_2 concentration, but no environmental thresholds have been identified. It is also presently unclear, how species and ecosystems would adapt to sustained, elevated CO_2 levels.

Chemical and biological monitoring of an injection project, including observations of the spatial and temporal evolution of the resulting CO_2 plume, would help evaluate the amount of materials released, the retention of CO_2, and some of the potential environmental effects.

For water column and sea floor release, capture and compression/liquefaction are thought to be the dominant cost factors. Transport (i.e., piping, and shipping) costs are expected to be the next largest cost component and scale with proximity to the deep ocean. The costs of monitoring, injection nozzles etc. are expected to be small in comparison.

Dissolving mineral carbonates, if found practical, could cause stored carbon to be retained in the ocean for 10,000 years, minimize changes in ocean *p*H and CO_2 partial pressure, and may avoid the need for prior separation of CO_2. Large amounts of limestone and materials handling would be required for this approach.

Several different global and regional treaties on the law of the sea and marine environment could be relevant to intentional release of CO_2 into the ocean but the legal status of intentional carbon storage in the ocean has not yet been adjudicated.

It is not known whether the public will accept the deliberate storage of CO_2 in the ocean as part of a climate change mitigation strategy. Deep ocean storage could help reduce the impact of CO_2 emissions on surface ocean biology but at the expense of effects on deep-ocean biology.

6.1 Introduction and background

6.1.1 Intentional storage of CO_2 in the ocean

This report assesses what is known about intentional storage of carbon dioxide in the ocean by inorganic strategies that could be applied at industrial scale. Various technologies have been envisioned to enable and increase ocean CO_2 storage (Figure 6.1). One class of options involves storing a relatively pure stream of carbon dioxide that has been captured and compressed. This CO_2 can be placed on a ship, injected directly into the ocean, or deposited on the sea floor. CO_2 loaded on ships could either be dispersed from a towed pipe or transported to fixed platforms feeding a CO_2 lake on the sea floor. Such CO_2 lakes must be

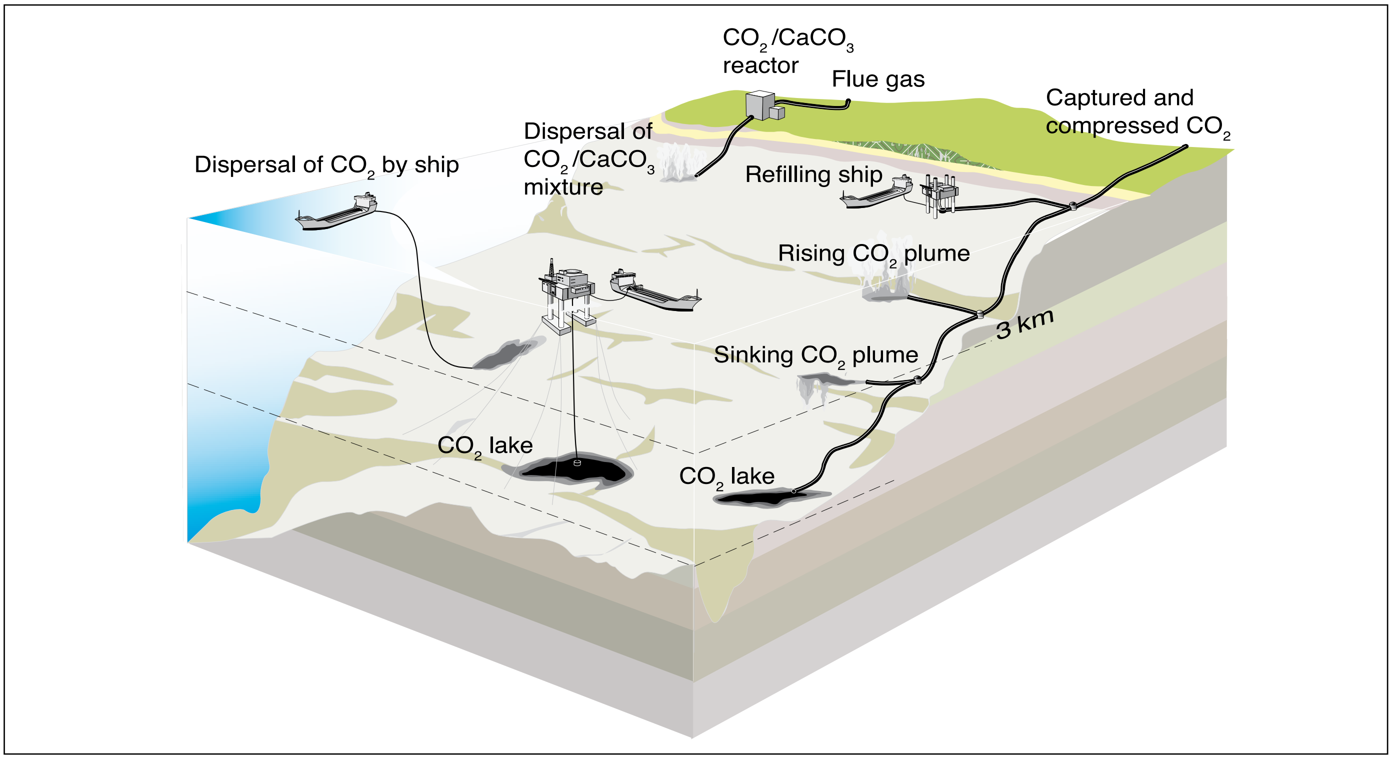

Figure 6.1 Illustration of some of the ocean storage strategies described in this chapter (Artwork courtesy Sean Goddard, University of Exeter.)

deeper than 3 km where CO_2 is denser than sea water. Any of these approaches could in principle be used in conjunction with neutralization with carbonate minerals.

Research, development and analysis of ocean CO_2 storage concepts has progressed to consider key questions and issues that could affect the prospects of ocean storage as a response option to climate change (Section 6.2). Accumulated understanding of the ocean carbon cycle is being used to estimate how long CO_2 released into the oceans will remain isolated from the atmosphere. Such estimates are used to assess the effectiveness of ocean storage concepts (Section 6.3).

Numerical models of the ocean indicate that placing CO_2 in the deep ocean would isolate most of the CO_2 from the atmosphere for several centuries, but over longer times the ocean and atmosphere would equilibrate. Relative to atmospheric release, direct injection of CO_2 into the ocean could reduce maximum amounts and rates of atmospheric CO_2 increase over the next several centuries. Direct injection of CO_2 in the ocean would not reduce atmospheric CO_2 content on the millennial time scale (Table 6.1; Figures 6.2 and 6.3; Hoffert *et al.*, 1979; Kheshgi *et al.*, 1994).

Table 6.1 Amount of additional CO_2 residing in the ocean after atmosphere-ocean equilibration for different atmospheric stabilization concentrations. The uncertainty range represents the influence of climate sensitivity to a CO_2 doubling in the range of 1.5 ºC to 4.5 ºC (Kheshgi et al., 2005; Kheshgi 2004a). This table considers the possibility of increased carbon storage in the terrestrial biosphere. Such an increase, if permanent, would allow a corresponding increase in total cumulative emissions. This table does not consider natural or engineered dissolution of carbonate minerals, which would increase ocean storage of anthropogenic carbon. The amount already in the oceans exceeds 500 $GtCO_2$ (= 440 $GtCO_2$ for 1994 (Sabine et al., 2004) plus CO_2 absorption since that time). The long-term amount of CO_2 stored in the deep ocean is independent of whether the CO_2 is initially released to the atmosphere or the deep ocean.

Atmospheric CO_2 stabilization concentration (ppmv)	Total cumulative ocean + atmosphere CO_2 release ($GtCO_2$)	Amount of anthropogenic CO_2 stored in the ocean in equilibrium ($GtCO_2$)
350	2880 ± 260	2290 ± 260
450	5890 ± 480	4530 ± 480
550	8350 ± 640	6210 ± 640
650	10,460 ± 750	7540 ± 750
750	12,330 ± 840	8630 ± 840
1000	16,380 ± 1000	10,730 ± 1000

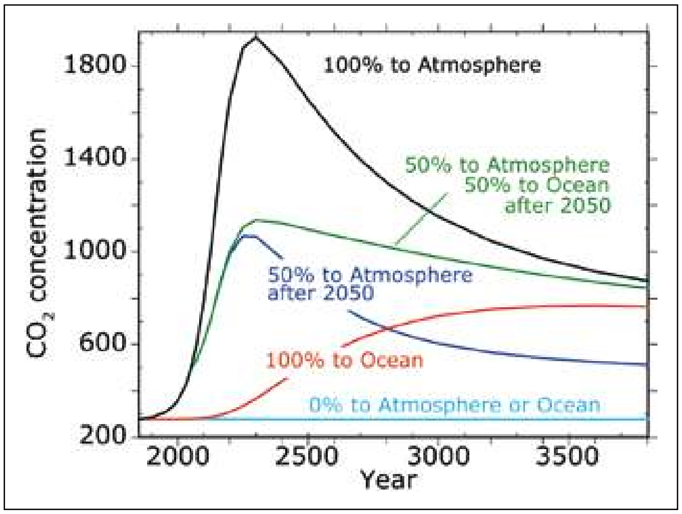

Figure 6.2 Simulated atmospheric CO_2 resulting from CO_2 release to the atmosphere or injection into the ocean at 3,000 m depth (Kheshgi and Archer, 2004). Emissions follow a logistic trajectory with cumulative emissions of 18,000 $GtCO_2$. Illustrative cases include 100% of emissions released to the atmosphere leading to a peak in concentration, 100% of emissions injected into the ocean, and no emissions (i.e., other mitigation approaches are used). Additional cases include atmospheric emission to year 2050, followed by either 50% to atmosphere and 50% to ocean after 2050 or 50% to atmosphere and 50% by other mitigation approaches after 2050. Ocean injection results in lower peak concentrations than atmospheric release but higher than if other mitigation approaches are used (e.g., renewables or permanent storage).

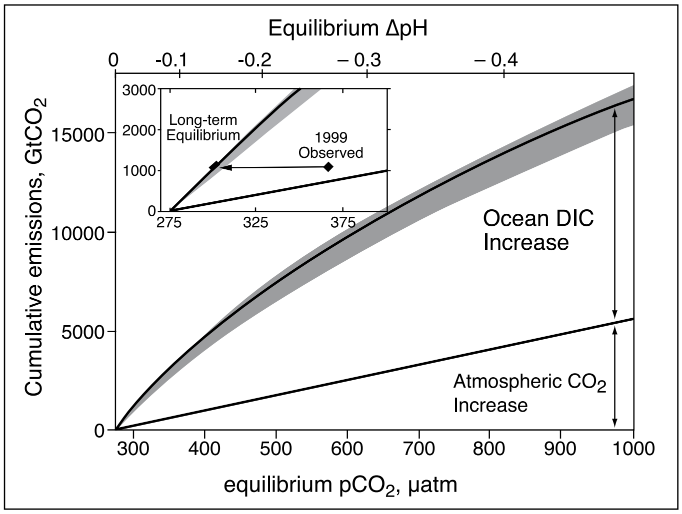

Figure 6.3 Equilibrium partitioning of CO_2 between the ocean and atmosphere. On the time scale of millennia, complete mixing of the oceans leads to a partitioning of cumulative CO_2 emissions between the oceans and atmosphere with the bulk of emissions eventually residing in the oceans as dissolved inorganic carbon. The ocean partition depends nonlinearly on CO_2 concentration according to carbonate chemical equilibrium (Box 6.1) and has limited sensitivity to changes in surface water temperature (shown by the grey area for a range of climate sensitivity of 1.5 to 4.5°C for CO_2 doubling) (adapted from Kheshgi et al., 2005; Kheshgi, 2004a). Δ*p*H evaluated from pCO_2 of 275 ppm. This calculation is relevant on the time scale of several centuries, and does not consider changes in ocean alkalinity that increase ocean CO_2 uptake over several millennia (Archer et al., 1997).

There has been limited experience with handling CO_2 in the deep sea that could form a basis for the development of ocean CO_2 storage technologies. Before they could be deployed, such technologies would require further development and field testing. Associated with the limited level of development, estimates of the costs of ocean CO_2 storage technologies are at a primitive state, however, the costs of the actual dispersal technologies are expected to be low in comparison to the costs of CO_2 capture and transport to the deep sea (but still non-negligible; Section 6.9). Proximity to the deep sea is a factor, as the deep oceans are remote to many sources of CO_2 (Section 6.4). Ocean storage would require CO_2 transport by ship or deep-sea pipelines. Pipelines and drilling platforms, especially in oil and gas applications, are reaching ever-greater depths, yet not on the scale or to the depth relevant for ocean CO_2 storage (Chapter 4). No insurmountable technical barrier to storage of CO_2 in the oceans is apparent.

Putting CO_2 directly into the deep ocean means that the chemical environment of the deep ocean would be altered immediately, and in concepts where release is from a point, change in ocean chemistry would be greater proximate to the release location. Given only rudimentary understanding of deep-sea ecosystems, only a limited and preliminary assessment of potential ecosystem effects can be given (Section 6.7).

Technologies exist to monitor deep-sea activities (Section 6.6). Practices for monitoring and verification of ocean storage would depend on which, as of yet undeveloped, ocean storage technology would potentially be deployed, and on environmental impacts to be avoided.

More carbon dioxide could be stored in the ocean with less of an effect on atmospheric CO_2 and fewer adverse effects on the marine environment if the alkalinity of the ocean could be increased, perhaps by dissolving carbonate minerals in sea water. Proposals based on this concept are discussed primarily in Section 6.2.

For ocean storage of CO_2, issues remain regarding environmental consequences, public acceptance, implications of existing laws, safeguards and practices that would need to be developed, and gaps in our understanding of ocean CO_2 storage (Sections 6.7, 6.8, and 6.10).

6.1.2 Relevant background in physical and chemical oceanography

The oceans, atmosphere, and plants and soils are the primary components of the global carbon cycle and actively exchange carbon (Prentice *et al.*, 2001). The oceans cover 71% of the Earth's surface with an average depth of 3,800 m and contain roughly 50 times the quantity of carbon currently contained in the atmosphere and roughly 20 times the quantity of carbon currently contained in plants and soils. The ocean contains so much CO_2 because of its large volume and because CO_2 dissolves in sea water to form various ionic species (Box 6.1).

The increase in atmospheric CO_2 over the past few centuries has been driving CO_2 from the atmosphere into the oceans. The oceans serve as an important sink of CO_2 emitted to the atmosphere taking up on average about 7 $GtCO_2$ yr^{-1} (2 GtC yr^{-1}) over the 20 years from 1980 to 2000 with ocean uptake over the past 200 years estimated to be > 500 $GtCO_2$ (135 GtC) (Prentice *et al.*, 2001; Sabine *et al.*, 2004). On average, the anthropogenic CO_2 signal is detectable to about 1000 m depth; its near absence in the deep ocean is due to the slow exchange between ocean surface and deep –sea waters.

Ocean uptake of anthropogenic CO_2 has led to a perturbation of the chemical environment primarily in ocean surface waters. Increasing ocean CO_2 concentration leads to decreasing carbonate ion concentration and increasing hydrogen ion activity (Box 6.1). The increase in atmospheric CO_2 from about 280 ppm in 1800 to 380 ppm in 2004 has caused an average decrease across the surface of the oceans of about 0.1 *p*H units ($\Delta p\text{H} \approx -0.1$) from an initial average surface ocean *p*H of about 8.2. Further increase in atmospheric CO_2 will result in a further change in the chemistry of ocean surface waters that will eventually reach the deep ocean (Figure 6.4). The anthropogenic perturbation of ocean chemistry is greatest in the upper ocean where biological activity is high.

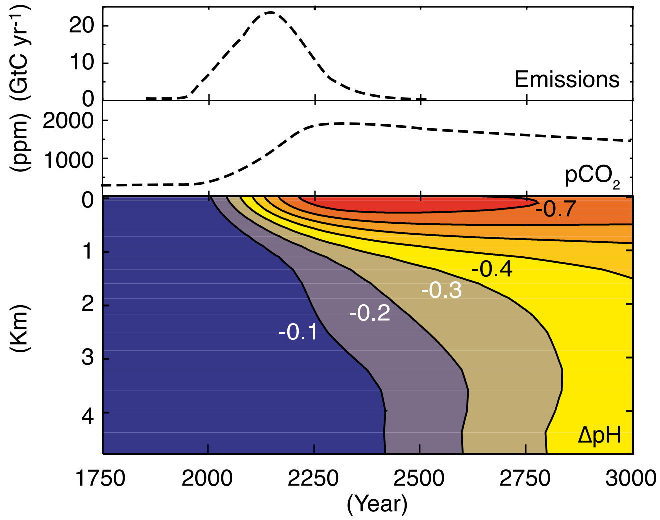

Figure 6.4 Simulated ocean *p*H changes from CO_2 release to the atmosphere. Modelled atmospheric CO_2 change and horizontally averaged ΔpH driven by a CO_2 emissions scenario: historic atmospheric CO_2 up to 2000, IS92a from 2000 to 2100, and logistic curve extending beyond 2100 with 18,000 $GtCO_2$ (Moomaw et al., 2001) cumulative emissions from 2000 onward (comparable to estimates of fossil-fuel resources – predominantly coal; Caldeira and Wickett, 2003). Since year 1800, the *p*H of the surface of the oceans has decreased about 0.1 *p*H units (from an initial average surface ocean *p*H of about 8.2) and CO_3^{2-} has decreased about 40 μmol kg^{-1}. There are a number of *p*H scales used by ocean chemists and biologists to characterize the hydrogen ion content of sea water, but ΔpH computed on different scales varies little from scale to scale (Brewer et al., 1995).

Most carbon dioxide released to either the atmosphere or the ocean will eventually reside in the ocean, as ocean chemistry equilibrates with the atmosphere. Thus, stabilization of atmospheric CO_2 concentration at levels above the natural level of 280 ppm implies long-term addition of carbon dioxide to the ocean. In equilibrium, the fraction of an increment of CO_2 released that will reside in the ocean depends on the atmospheric CO_2 concentration (Table 6.1; Figure 6.3; Kheshgi *et al.*, 2005; Kheshgi, 2004a).

The capacity of the oceans to absorb CO_2 in equilibrium with the atmosphere is a function of the chemistry of sea water. The rate at which this capacity can be brought into play is a function of the rate of ocean mixing. Over time scales of decades to centuries, exchange of dissolved inorganic carbon between ocean surface waters and the deep ocean is the primary barrier limiting the rate of ocean uptake of increased atmospheric CO_2. Over many centuries (Kheshgi, 2004a), changes in dissolved inorganic carbon will mix throughout the ocean volume with the oceans containing most of the cumulative CO_2 emissions to the atmosphere/ocean system (Table 6.1; Figure 6.3). Over longer times (millennia), dissolution of $CaCO_3$ causes an even greater fraction of released CO_2 (85–92%) to reside in the ocean (Archer *et al.*, 1997).

Both biological and physical processes lead to the observed distribution of *p*H and its variability in the world ocean (Figure 6.6). As they transit from the Atlantic to Pacific Basins, deep ocean waters accumulate about 10% more dissolved inorganic carbon dioxide, primarily from the oxidation of sinking organic matter (Figure 6.7).

6.2 Approaches to release of CO_2 into the ocean

6.2.1 Approaches to releasing CO_2 that has been captured, compressed, and transported into the ocean

6.2.1.1 Basic approach

The basic concept of intentional CO_2 storage in the ocean is to take a stream of CO_2 that has been captured and compressed (Chapter 3), and transport it (Chapter 4) to the deep ocean for release at or above the sea floor. (Other ocean storage approaches are discussed in Sections 6.2.2 and 6.2.3.) Once released, the CO_2 would dissolve into the surrounding sea water, disperse and become part of the ocean carbon cycle.

Marchetti (1977) first proposed injecting liquefied CO_2 into the waters flowing over the Mediterranean sill into the mid-depth North Atlantic, where the CO_2 would be isolated from the atmosphere for centuries. This concept relies on the slow exchange of deep ocean waters with the surface to isolate CO_2 from the atmosphere. The effectiveness of ocean storage will depend on how long CO_2 remains isolated from the atmosphere. Over the centuries and millennia, CO_2 released to the deep ocean will mix throughout the oceans and affect atmospheric CO_2 concentration. The object is to transfer the CO_2 to deep waters because the degree of isolation from the atmosphere generally increases with depth in the ocean. Proposed methods

Box 6.1. Chemical properties of CO_2

The oceans absorb large quantities of CO_2 from the atmosphere principally because CO_2 is a weakly acidic gas, and the minerals dissolved in sea water have created a mildly alkaline ocean. The exchange of atmospheric CO_2 with ocean surface waters is determined by the chemical equilibrium between CO_2 and carbonic acid H_2CO_3 in sea water, the partial pressure of CO_2 (pCO_2) in the atmosphere and the rate of air/sea exchange. Carbonic acid dissociates into bicarbonate ion HCO_3^-, carbonate ion CO_3^{2-}, and hydronium ion H^+ by the reactions (see Annex AI.3):

$$CO_2\ (g) + H_2O \leftrightarrow H_2CO_3\ (aq) \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+ \qquad (1)$$

Total dissolved inorganic carbon (DIC) is the sum of carbon contained in H_2CO_3, HCO_3^-, and CO_3^{2-}. The atmospheric concentration of CO_2 in equilibrium with surface water can be calculated from well-known chemical equilibria that depend on ocean total dissolved inorganic carbon, alkalinity, temperature and salinity (Zeebe and Wolf-Gladrow, 2001). The partial pressure of CO_2 in the ocean mixed layer equilibrates with the atmosphere on a time scale of about one year.

The ocean is a highly buffered system, that is the concentration of the chemical species whose equilibrium controls *p*H is significantly higher than the concentrations of H^+ or OH^-. The *p*H of sea water is the base–10 log of activity of H^+. Total Alkalinity (TAlk) is the excess of alkaline components, and is defined as the amount of strong acid required to bring sea water to the 'equivalence point' at which the HCO_3– and H_2CO_3 contributions are equal (Dickson, 1981).

The principal effect of adding CO_2 to sea water is to form bicarbonate ion, for example,

$$CO_2 + H_2O + CO_3^{2-} \rightarrow 2HCO_3^-. \qquad (2)$$

In addition, some CO_2 undergoes simple reaction with water, for example,

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-. \qquad (3)$$

In either case, Total Alkalinity does not change. The combined reactions lower both ocean *p*H, and carbonate ion concentration. For current ocean composition, CO_2 that is added to sea water is partitioned primarily into HCO_3^- with the net reaction resulting in the generation of H^+ and thus decreasing *p*H and making sea water more acidic; adding CO_2 thereby decreases the concentration of CO_3^{2-}.

Total Alkalinity is increased when, for example, alkaline minerals such as $CaCO_3$ are dissolved in sea water through the reaction,

$$CaCO_3\ (s) \leftrightarrow Ca^{2+} + CO_3^{2-} \qquad (4)$$

which releases 2 mole-equivalents of Total Alkalinity and 1 mol of Dissolved Inorganic Carbon for each mole of $CaCO_3$ dissolved. Increasing TAlk more than DIC leads to a decrease in the partial pressure of CO_2 as seen in Figure 6.5. Because most Dissolved Inorganic Carbon is in the form of HCO_3^-, the main effect of dissolving $CaCO_3$ in surface waters is (see Kheshgi, 1995)

$$CaCO_3\ (s) + CO_2\ (g) + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \qquad (5)$$

thereby shifting CO_2 from the atmosphere to the oceans in equilibrium, neutralizing the effect of CO_2 on *p*H.

Ocean surface waters are super-saturated with respect to CaCO3, allowing the growth of corals and other organisms that produce shells or skeletons of carbonate minerals. In contrast, the deepest ocean waters have lower *p*H and lower CO_3^{2-} concentrations, and are thus undersaturated with respect to $CaCO_3$. Marine organisms produce calcium carbonate particles in the surface ocean that settle and dissolve in undersaturated regions of the deep oceans.

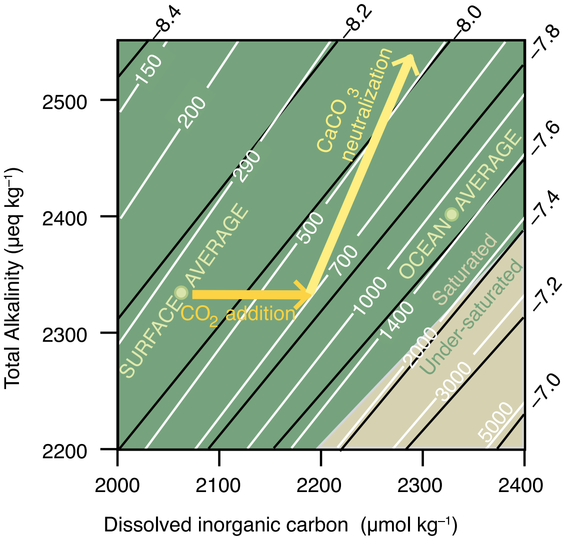

Figure 6.5 Composition diagram for ocean surface waters at 15°C (adapted from Baes, 1982). The white lines denote compositions with the same value of pCO_2 (in ppm); the black lines denote compositions with the same *p*H. The tan shaded region is undersaturated and the green shaded region is supersaturated with respect to calcite at atmospheric pressure (calcite solubility increases with depth). Surface water and average ocean compositions are also indicated. Adding CO_2 increases Dissolved Inorganic Carbon (DIC) without changing Total Alkalinity (TAlk); dissolving $CaCO_3$ increases both DIC and TAlk, with 2 moles of TAlk added for each mole of DIC added.

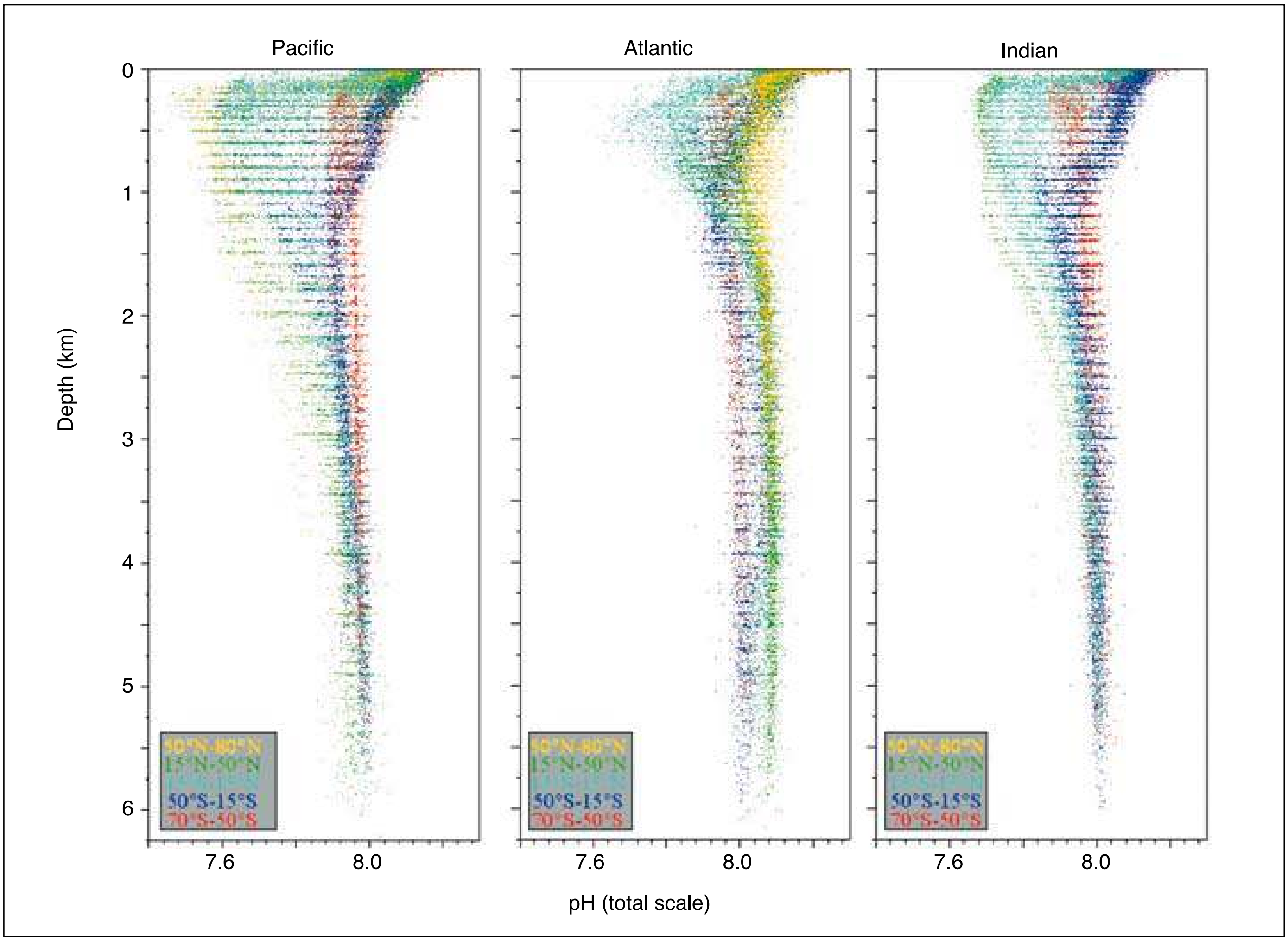

Figure 6.6 Observed variation in open ocean *p*H for the 1990s (shown on the total hydrogen scale; data from Key et al., 2004). In this figure the oceans are separated into separate panels. The three panels are on the same scale and coloured by latitude band to illustrate the large north-south changes in the *p*H of intermediate waters. Pre-industrial surface values would have been about 0.1 *p*H units greater than in the 1990s.

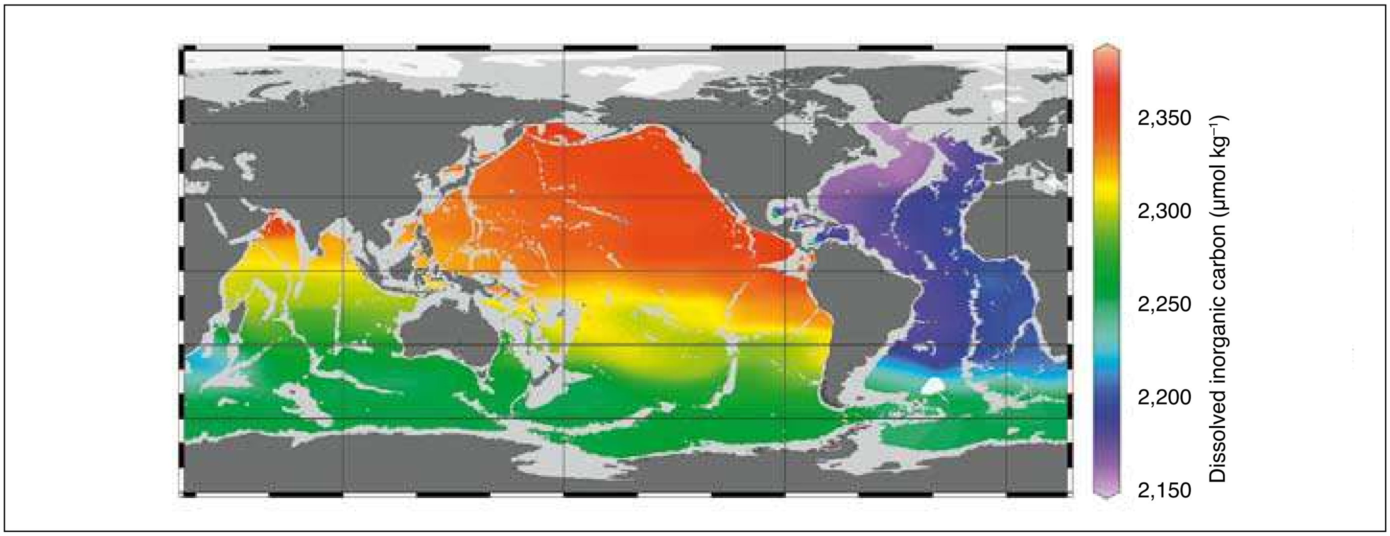

Figure 6.7 Natural variation in total dissolved inorganic carbon concentration at 3000 m depth (data from Key et al., 2004). Ocean carbon concentrations increase roughly 10% as deep ocean waters transit from the North Atlantic to the North Pacific due to the oxidation of organic carbon in the deep ocean.

would inject the CO_2 below the thermocline[1] for more effective storage.

Depending on the details of the release and local sea floor topography, the CO_2 stream could be engineered to dissolve in the ocean or sink to form a lake on the sea floor. CO_2, dissolved in sea water at high concentrations can form a dense plume or sinking current along an inclined sea floor. If release is at a great enough depth, CO_2 liquid will sink and could accumulate on the sea floor as a pool containing a mixture of liquid and hydrate. In the short-term, fixed or towed pipes appear to be the most viable methods for oceanic CO_2 release, relying on technology that is already largely commercially available.

6.2.1.2 *Status of development*

To date, injection of CO_2 into sea water has only been investigated in the laboratory, in small-scale *in-situ* experiments, and in models. Larger-scale *in-situ* experiments have not yet been carried out.

An international consortium involving engineers, oceanographers and ecologists from 15 institutions in the United States, Norway, Japan and Canada proposed an *in-situ* experiment to help evaluate the feasibility of ocean carbon storage as a means of mitigating atmospheric increases. This was to be a collaborative study of the physical, chemical, and biological changes associated with direct injection of CO_2 into the ocean (Adams *et al*., 2002). The proposed CO_2 Ocean Sequestration Field Experiment was to inject less than 60 tonnes of pure liquid carbon dioxide (CO_2) into the deep ocean near Keahole Point on the Kona coast of the Island of Hawaii. This would have been the largest intentional CO_2 release into the ocean water column. The test was to have taken place in water about 800 m deep, over a period of about two weeks during the summer of 2001. Total project cost was to have been roughly US$ 5 million. A small steel pipeline, about 4 cm in diameter, was to have been deployed from a ship down to the injection depth, with a short section of pipeline resting on the sea floor to facilitate data collection. The liquid CO_2 was to have been dispersed through a nozzle, with CO_2 droplets briefly ascending from the injection point while dissolving into the sea water. However, the project met with opposition from environmental organizations and was never able to acquire all of the necessary permits within the prescribed budget and schedule (de Figueiredo, 2002).

Following this experience, the group developed a plan to release 5.4 tonnes of liquefied CO_2 at a depth of 800 metres off the coast of Norway, and monitor its dispersion in the Norwegian Sea. The Norwegian Pollution Control Authority granted a permit for the experiment. The Conservative Party environment minister in Norway's coalition government, Børge Brende, decided to review the Norwegian Pollution Control Authorities' initial decision. After the public hearing procedure and subsequent decision by the Authority to confirm their initial permit, Brende said, 'The possible future use of the sea as storage for CO_2 is controversial. … Such a deposit could be in defiance of international marine laws and the ministry therefore had to reject the application.' The Norwegian Environment ministry subsequently announced that the project would not go ahead (Giles, 2002).

Several smaller scale scientific experiments (less than 100 litres of CO_2) have however been executed (Brewer *et al*., 1999, Brewer *et al*., 2005) and the necessary permits have also been issued for experiments within a marine sanctuary.

6.2.1.3 *Basic behaviour of CO_2 released in different forms*

The near-field behaviour of CO_2 released into the ocean depends on the physical properties of CO_2 (Box 6.2) and the method for CO_2 release. Dissolved CO_2 increases the density of sea water (e.g., Bradshaw, 1973; Song, *et al*., 2005) and this affects transport and mixing. The near field may be defined as that region in which it is important to take effects of CO_2-induced density changes on the fluid dynamics of the ocean into consideration. The size of this region depends on the scale and design of CO_2 release (Section 6.2.1.4).

CO_2 plume dynamics depend on the way in which CO_2 is released into the ocean water column. CO_2 can be initially in the form of a gas, liquid, solid or solid hydrate. All of these forms of CO_2 would dissolve in sea water, given enough time (Box 6.1). The dissolution rate of CO_2 in sea water is quite variable and depends on the form (gas, liquid, solid, or hydrate), the depth and temperature of disposal, and the local water velocities. Higher flow rates increase the dissolution rate.

Gas. CO_2 could potentially be released as a gas above roughly 500 m depth (Figure 6.8). Below this depth, pressures are too great for CO_2 to exist as a gas. The gas bubbles would be less dense than the surrounding sea water so tend to rise towards the surface, dissolving at a radial speed of about 0.1 cm hr^{-1} (0.26 to 1.1 μmol cm^{-2} s^{-1}; Teng *et al*., 1996). In waters colder than about 9°C, a CO_2 hydrate film could form on the bubble wall. CO_2 diffusers could produce gaseous CO_2 bubbles that are small enough to dissolve completely before reaching the surface.

Liquid. Below roughly 500 m depth, CO_2 can exist in the ocean as a liquid. Above roughly 2500 m depth CO_2 is less dense than sea water, so liquid CO_2 released shallower than 2500 m would tend to rise towards the surface. Because most ocean water in this depth range is colder than 9°C, CO_2 hydrate would tend to form on the droplet wall. Under these conditions, the radius of the droplet would diminish at a speed of about 0.5 cm hr^{-1} (= 3 μmol cm^{-2} s^{-1}; Brewer *et al*., 2002). Under these conditions a 0.9 cm diameter droplet would rise about 400 m in an hour before dissolving completely; 90% of its mass would be lost in the first 200 m (Brewer *et al*., 2002). Thus, CO_2 diffusers could be designed to produce droplets that will dissolve within roughly 100 m of the depth of release. If the droplet reached approximately 500 m depth, it would become a gas bubble.

CO_2 is more compressible than sea water; below roughly

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[1] The thermocline is the layer of the ocean between about 100 and 1000 m depth that is stably stratified by large temperature and density gradients, thus inhibiting vertical mixing. Vertical mixing rates in the thermocline can be about 1000 times less than those in the deep sea. This zone of slow mixing would act as a barrier to slow degassing of CO_2 released in the deep ocean to the atmosphere.

Box 6.2 Physical properties of CO_2.

The properties of CO_2 in sea water affect its fate upon release to the deep-sea environment. The conditions under which CO_2 can exist in a gas, liquid, solid hydrate, or aqueous phase in sea water are given in Figure 6.8 (see Annex I).

At typical pressures and temperatures that exist in the ocean, pure CO_2 would be a gas above approximately 500 m and a liquid below that depth. Between about 500 and 2700 m depth, liquid CO_2 is lighter than sea water. Deeper than 3000 m, CO_2 is denser than sea water. The buoyancy of CO_2 released into the ocean determines whether released CO_2 rises or falls in the ocean column (Figure 6.9). In the gas phase, CO_2 is lighter than sea water and rises. In the liquid phase CO_2 is a highly compressible fluid compared to sea water. A fully formed crystalline CO_2 hydrate is denser than sea water and will form a sinking mass (Aya *et al*., 2003); hydrate formation can thus aid ocean CO_2 storage by more rapid transport to depth, and by slowing dissolution. It may also create a nuisance by impeding flow in pipelines or at injectors.

The formation of a solid CO_2 hydrate (Sloan, 1998) is a dynamic process (Figure 6.10; Brewer *et al*., 1998, 1999, 2000) and the nature of hydrate nucleation in such systems is imperfectly understood. Exposed to an excess of sea water, CO_2 will eventually dissolve forming an aqueous phase with density higher than surrounding sea water. Release of dense or buoyant CO_2 – in a gas, liquid, hydrate or aqueous phase – would entrain surrounding sea water and form plumes that sink, or rise, until dispersed.

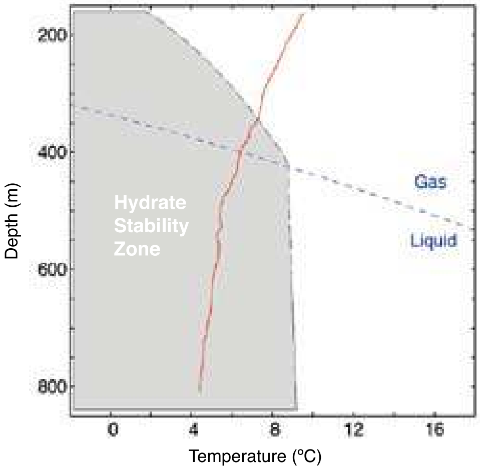

Figure 6.8 CO_2 sea water phase diagram. CO_2 is stable in the liquid phase when temperature and pressure (increasing with ocean depth) fall in the region below the blue curve; a gas phase is stable under conditions above the blue dashed line. In contact with sea water and at temperature and pressure in the shaded region, CO_2 reacts with sea water to from a solid ice-like hydrate $CO_2 \cdot 6H_2O$. CO_2 will dissolve in sea water that is not saturated with CO_2. The red line shows how temperature varies with depth at a site off the coast of California; liquid and hydrated CO_2 can exist below about 400 m (Brewer et al., 2004).

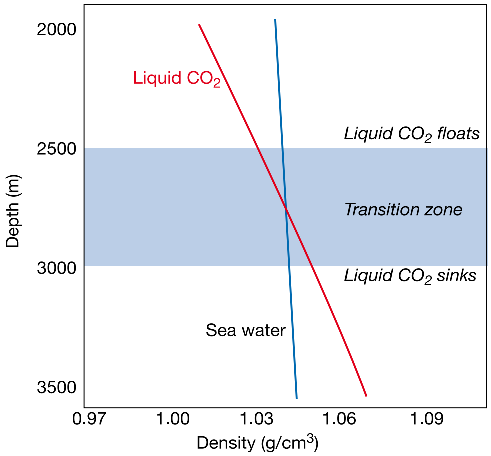

Figure 6.9 Shallower than 2500 m, liquid CO_2 is less dense than sea water, and thus tends to float upward. Deeper than 3000 m, liquid CO_2 is denser than sea water, and thus tends to sink downwards. Between these two depths, the behaviour can vary with location (depending mostly on temperature) and CO_2 can be neutrally buoyant (neither rises nor falls). Conditions shown for the northwest Atlantic Ocean.

Figure 6.10 Liquid CO_2 released at 3600 metres initially forms a liquid CO_2 pool on the sea floor in a small deep ocean experiment (upper picture). In time, released liquid CO_2 reacts with sea water to form a solid CO_2 hydrate in a similar pool (lower picture).

3000 m, liquid CO_2 is denser than the surrounding sea water and sinks. CO_2 nozzles could be engineered to produce large droplets that would sink to the sea floor or small droplets that would dissolve in the sea water before contacting the sea floor. Natural ocean mixing and droplet motion are expected to prevent concentrations of dissolved CO_2 from approaching saturation, except near liquid CO_2 that has been intentionally placed in topographic depressions on the sea floor.

Solid. Solid CO_2 is denser than sea water and thus would tend to sink. Solid CO_2 surfaces would dissolve in sea water at a speed of about 0.2 cm hr^{-1} (inferred from Aya *et al.*, 1997). Thus small quantities of solid CO_2 would dissolve completely before reaching the sea floor; large masses could potentially reach the sea floor before complete dissolution.

Hydrate. CO_2 hydrate is a form of CO_2 in which a cage of water molecules surrounds each molecule of CO_2. It can form in average ocean waters below about 400 m depth. A fully formed crystalline CO_2 hydrate is denser than sea water and will sink (Aya *et al.*, 2003). The surface of this mass would dissolve at a speed similar to that of solid CO_2, about 0.2 cm hr^{-1} (0.47 to 0.60 μm s^{-1}; Rehder *et al.*, 2004; Teng *et al.*, 1999), and thus droplets could be produced that either dissolve completely in the sea water or sink to the sea floor. Pure CO_2 hydrate is a hard crystalline solid and will not flow through a pipe; however a paste-like composite of hydrate and sea water may be extruded (Tsouris *et al.*, 2004), and this will have a dissolution rate intermediate between those of CO_2 droplets and a pure CO_2 hydrate.

6.2.1.4 Behaviour of injected CO_2 in the near field: CO_2-rich plumes

As it leaves the near field, CO_2 enriched water will reside at a depth determined by its density. The oceans are generally stably stratified with density increasing with depth. Parcels of water tend to move upward or downward until they reach water of the same density, then there are no buoyancy forces to induce further motion.

The dynamics of CO_2-rich plumes determine both the depth at which the CO_2 leaves the near-field environment and the amount of initial dilution (and consequently the amount of *p*H change). When CO_2 is released in any form into seawater, the CO_2 can move upward or downward depending on whether the CO_2 is less or more dense than the surrounding seawater. Drag forces transfer momentum from the CO_2 droplets to the surrounding water column producing motion in the adjacent water, initially in the direction of droplet motion. Simultaneously, the CO_2 dissolves into the surrounding water, making the surrounding water denser and more likely to sink. As the CO_2-enriched water moves, it mixes with surrounding water that is less enriched in CO_2, leading to additional dilution and diminishing the density contrast between the CO_2-enriched water and the surrounding water.

CO_2 releases could be engineered to produce CO_2 plumes with different characteristics (Chen *et al.*, 2003; Sato and Sato, 2002; Alendal and Drange, 2001; Crounse *et al.*, 2001; Drange *et al.*, 2001; Figure 6.11). Modelling studies indicate that releases of small droplets at slow rates produce smaller plumes than release of large droplets at rapid rates. Where CO_2 is denser than seawater, larger droplet sizes would allow the CO_2 to sink more deeply. CO_2 injected at intermediate depths could increase the density of CO_2-enriched sea water sufficiently to generate a sinking plume that would carry the CO_2 into the deep ocean (Liro *et al.*, 1992; Haugan and Drange, 1992). Apparent coriolis forces would operate on such a plume, turning it towards the right in the Northern Hemisphere and towards the left in the Southern Hemisphere (Alendal *et al.,* 1994). The channelling effects of submarine canyons or other topographic features could help steer dense plumes to greater depth with minimal dilution (Adams *et al.*, 1995).

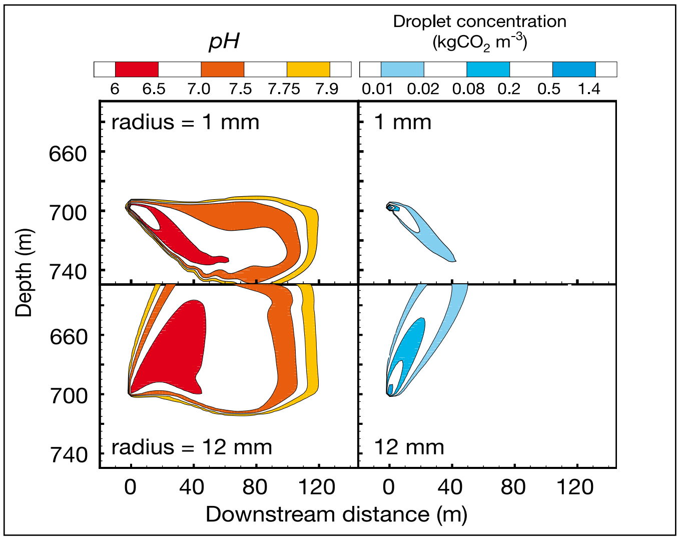

Figure 6.11 Simulated CO_2 enriched sea water plumes (left panels; indicated by pH) and CO_2 droplet plumes (right panels; indicated by kgCO_2 m^{-3}) created by injecting 1 cm and 12 cm liquid CO_2 droplets (top and bottom panels, respectively) into the ocean from fixed nozzles (elapsed time is 30 min; injection rate is 1.0 kgCO_2 s^{-1}; ocean current speed is 5 cm s^{-1}; Alendal and Drange, 2001). By varying droplet size, the plume can be made to sink (top panels) or rise (bottom panels).

6.2.1.5 Behaviour of injected CO_2 in the far field

The far field is defined as the region in which the concentration of added CO_2 is low enough such that the resulting density increase does not significantly affect transport, and thus CO_2 may be considered a passive tracer in the ocean. Typically, this would apply within a few kilometres of an injection point in midwater, but if CO_2 is released at the sea floor and guided along topography, concentration may remain high and influence transport for several tens of kilometres. CO_2 is transported by ocean currents and undergoes further mixing and dilution with other water masses (Alendal and Drange, 2001). Most of this mixing and transport occurs along surfaces of nearly constant density, because buoyancy forces inhibit vertical mixing in a stratified fluid. Over time, a release of CO_2 becomes increasingly diluted but affects ever greater volumes of water.

The concept of ocean injection from a moving ship towing a trailing pipe was developed in order to minimize the local

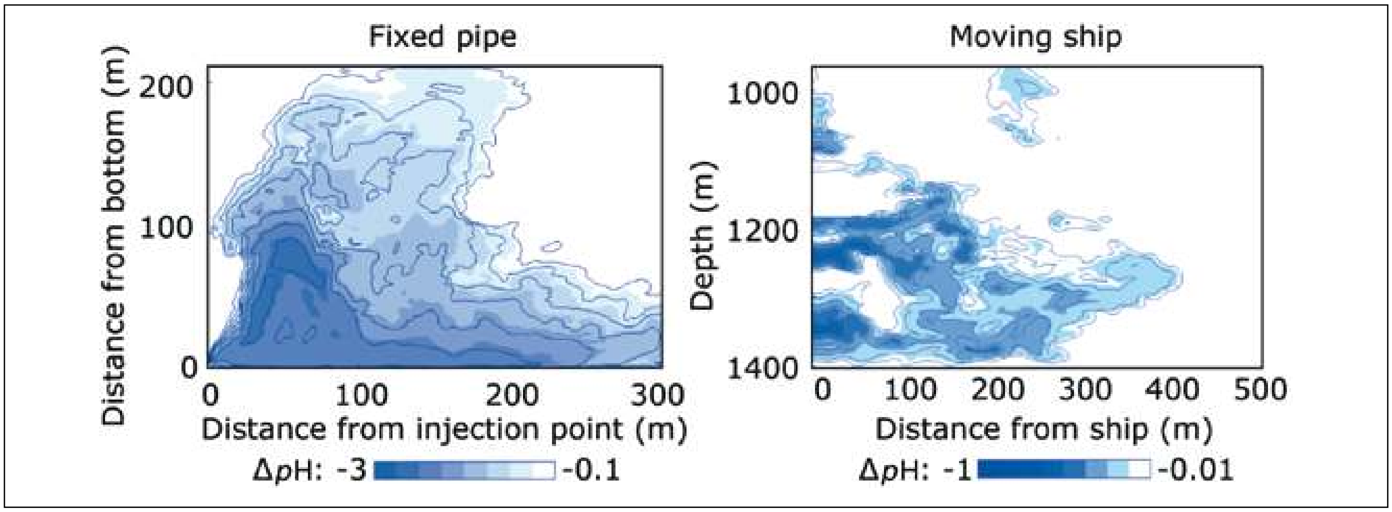

Figure 6.12 Simulated plumes (Chen *et al*., 2005) created by injecting liquid CO_2 into the ocean from a fixed pipe (left panel) and a moving ship (right panel) at a rate of 100 kg s^{-1} (roughly equal to the CO_2 from a 500 MWe coal-fired power plant). Left panel: injection at 875 m depth (12 m from the sea floor) with an ocean current speed of 2.3 cm s^{-1}. Right panel: injection at 1340 m depth from a ship moving at a speed of 3 m s^{-1}. Note difference in *p*H scales; maximum *p*H perturbations are smaller in the moving ship simulation.

environmental impacts by accelerating the dissolution and dispersion of injected liquid CO_2 (Ozaki, 1997; Minamiura *et al*., 2004). A moving ship could be used to produce a sea water plume with relatively dilute initial CO_2 concentrations (Figures 6.12 and 6.13). In the upper ocean where $CO_2$is less dense than seawater, nozzles engineered to produce mm-scale droplets would generate CO_2 plumes that would rise less than 100 m.

Ocean general circulation models have been used to predict changes in ocean chemistry resulting from the dispersion of injected CO_2 for hypothetical examples of ocean storage (e.g., Orr, 2004). Wickett *et al*. (2003) estimated that injection into the deep ocean at a rate of 0.37 $GtCO_2$ yr^{-1} (= 0.1 GtC yr^{-1}) for 100 years would produce a Δ*p*H < –0.3 over a volume of sea water equivalent to 0.01% or less of total ocean volume (Figure 6.14). In this example, for each $GtCO_2$ released to the deep ocean, less than about 0.0001%, 0.001% and 0.01% of

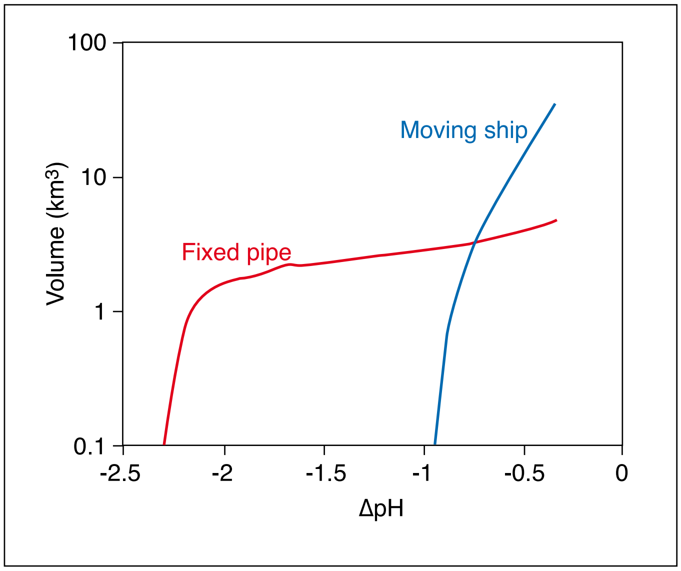

Figure 6.13 Volume of water with a Δ*p*H less than the value shown on the horizontal axis for the simulations shown in Figure 6.12 corresponding to CO_2 releases from a 500 MW_e power plant. The fixed pipe simulation produces a region with Δ*p*H < –1, however, the moving ship disperses the CO_2 more widely, largely avoiding *p*H changes of this magnitude.

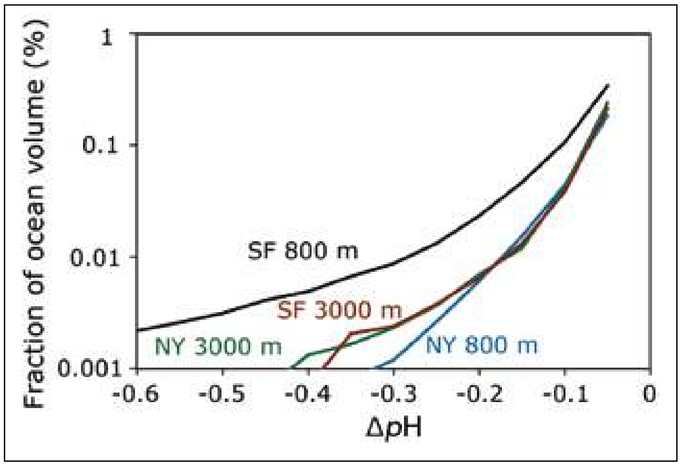

Figure 6.14 Estimated volume of *p*H perturbations at basin scale (Wickett *et al*., 2003). Simulated fraction of global ocean volume with a Δ*p*H less than the amount shown on the horizontal axis, after 100 years of simulated injection at a rate of 0.37 $GtCO_2$ yr^{-1} (= 0.1 GtC yr^{-1}) at each of four different points (two different depths near New York City and San Francisco). Model results indicate, for example, that injecting CO_2 at this rate at a single location for 100 years could be expected to produce a volume of sea water with a Δ*p*H < –0.3 units in 0.01% or less of total ocean volume (0.01% of the ocean is roughly 10^5 km^3). As with other simulations of direct CO_2 injection in the ocean, results for the upper ocean (e.g., 800 m) tend to be more site-specific than are results for the deep ocean (e.g., 3000 m).

the ocean volume has Δ*p*H of less than –0.3, –0.2, and –0.1 *p*H units respectively. Caldeira and Wickett (2005) predicted volumes of water undergoing a range of *p*H changes for several atmospheric emission and carbon stabilization pathways, including pathways in which direct injection of CO_2 into the deep ocean was assumed to provide either 10% or 100% of the total atmospheric CO_2 mitigation effort needed to stabilize atmospheric CO_2 according to the WRE550 pathway. This assumed a CO_2 production scenario in which all known fossil-fuel resources were ultimately combusted. Simulations in which ocean injection provided 10% of the total mitigation effort, resulted in significant changes in ocean *p*H in year 2100 over roughly 1% of the ocean volume (Figure 6.15). By year 2300, injection rates have slowed but previously injected carbon has spread through much of the ocean resulting in an additional 0.1 *p*H unit reduction in ocean *p*H over most of the ocean volume compared to WRE550.

6.2.1.6 Behaviour of CO_2 lakes on the sea floor

Long-term storage of carbon dioxide might be more effective if CO_2 were stored on the sea floor in liquid or hydrate form below 3000 metres, where CO_2 is denser than sea water (Box 6.2; Ohsumi, 1995; Shindo *et al.*, 1995). Liquid carbon dioxide could be introduced at depth to form a lake of CO_2 on the sea floor (Ohsumi, 1993). Alternatively, CO_2 hydrate could be created in an apparatus designed to produce a hydrate pile or pool on the sea floor (Saji *et al.*, 1992). To date, the concept of CO_2 lakes on the sea floor has been investigated only in the laboratory, in small-scale (tens of litres) *in-situ* experiments and in numerical models. Larger-scale *in-situ* experiments have not yet been carried out.

Liquid or hydrate deposition of CO_2 on the sea floor could increase isolation, however in the absence of a physical barrier the CO_2 would dissolve into the overlying water (Mori and Mochizuki, 1998; Haugan and Alendal, 2005). In this aspect, most sea floor deposition proposals can be viewed as a means of 'time-delayed release' of CO_2 into the ocean. Thus, many issues relevant to sea floor options, especially the far-field behaviour, are discussed in sections relating to CO_2 release into the water column (e.g., Section 6.2.1.5).

CO_2 released onto the sea floor deeper than 3 km is denser than surrounding sea water and is expected to fill topographic depressions, accumulating as a lake of CO_2 over which a thin hydrate layer would form. This hydrate layer would retard dissolution, but it would not insulate the lake from the overlying water. The hydrate would dissolve into the overlying water (or sink to the bottom of the CO_2 lake), but the hydrate layer would be continuously renewed through the formation of new crystals (Mori, 1998). Laboratory experiments (Aya *et al.*, 1995) and small deep ocean experiments (Brewer *et al.*, 1999) show that deep-sea storage of CO_2 would lead to CO_2 hydrate formation (and subsequent dissolution).

Predictions of the fate of large-scale CO_2 lakes rely on numerical simulations because no large-scale field experiments have yet been performed. For a CO_2 lake with an initial depth of 50 m, the time of complete dissolution varies from 30 to 400 years depending on the local ocean and sea floor environment. The time to dissolve a CO_2 lake depends on its depth, complex

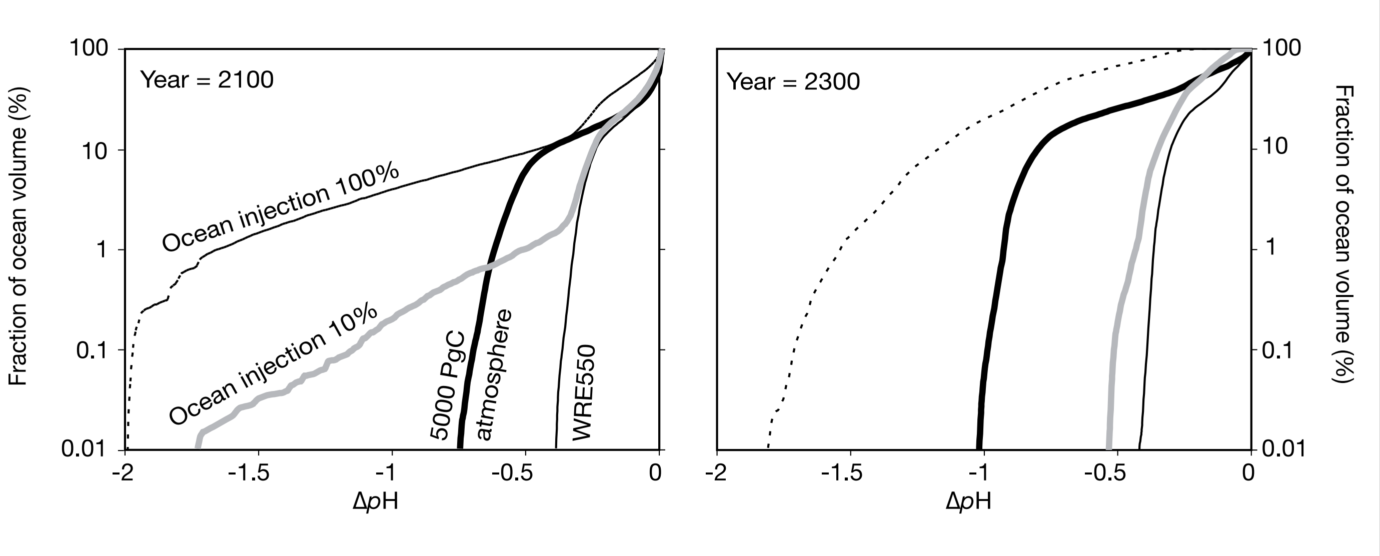

Figure 6.15 Estimated volume of *p*H perturbations at global scale for hypothetical examples in which injection of CO_2 into the ocean interior provides 100% or 10% of the mitigation effort needed to move from a logistic emissions curve cumulatively releasing 18,000 $GtCO_2$ (=5000 GtC) to emissions consistent with atmospheric CO_2 stabilization at 550 ppm according to the WRE550 pathway (Wigley *et al.*, 1996). The curves show the simulated fraction of ocean volume with a *p*H reduction greater than the amount shown on the horizontal axis. For the 10% case, in year 2100, injection rates are high and about1% of the ocean volume has significant pH reductions; in year 2300, injection rates are low, but previously injected CO_2 has decreased ocean pH by about 0.1 unit below the value produced by a WRE550 atmospheric CO_2 pathway in the absence of CO_2 release directly to the ocean (Caldeira and Wickett, 2005).

dynamics of the ocean bottom boundary layer and its turbulence characteristics, mechanism of CO_2 hydrate dissolution, and properties of CO_2 in solution (Haugan and Alendal, 2005). The lifetime of a CO_2 lake would be longest in relatively confined environments, such as might be found in some trenches or depressions with restricted flow (Ohgaki and Akano, 1992). Strong flows have been observed in trenches (Nakashiki, 1997). Nevertheless, simulation of CO_2 storage in a deep trench (Kobayashi, 2003) indicates that the bottom topography can weaken vertical momentum and mass transfer, slowing the CO_2 dissolution rate. In a quiescent environment, transport would be dominated by diffusion. Double-diffusion in the presence of strong stratification may produce long lake lifetimes. In contrast, the flow of sea water across the lake surface would increase mass transfer and dissolution. For example, CO_2 lake lifetimes of >10,000 yr for a 50 m thick lake can be estimated from the dissolution rate of 0.44 cm yr^{-1} for a quiescent, purely diffusive system (Ohsumi, 1997). Fer and Haugan (2003) found that a mean horizontal velocity of 0.05 m s^{-1} would cause the CO_2 lake to dissolve >25 times more rapidly (12 cm yr^{-1}). Furthermore, they found that an ocean bottom storm with a horizontal velocity of 0.20 m s^{-1} could increase the dissolution rate to 170 cm yr^{-1}.

6.2.2 CO_2 storage by dissolution of carbonate minerals

Over thousands of years, increased sea water acidity resulting from CO_2 addition will be largely neutralized by the slow natural dissolution of carbonate minerals in sea-floor sediments and on land. This neutralization allows the ocean to absorb more CO_2 from the atmosphere with less of a change in ocean *p*H, carbonate ion concentration, and pCO_2 (Archer *et al*., 1997, 1998). Various approaches have been proposed to accelerate carbonate neutralization, and thereby store CO_2 in the oceans by promoting the dissolution of carbonate minerals[2]. These approaches (e.g., Kheshgi, 1995; Rau and Caldeira, 1999) do not entail initial separate CO_2 capture and transport steps. However, no tests of these approaches have yet been performed at sea, so inferences about enhanced ocean CO_2 storage, and effects on ocean *p*H are based on laboratory experiments (Morse and Mackenzie, 1990; Morse and Arvidson, 2002), calculations (Kheshgi, 1995), and models (Caldeira and Rau, 2000).

Carbonate neutralization approaches attempt to promote reaction (5) (in Box 6.1) in which limestone reacts with carbon dioxide and water to form calcium and bicarbonate ions in solution. Accounting for speciation of dissolved inorganic carbon in sea water (Kheshgi, 1995), for each mole of $CaCO_3$ dissolved there would be 0.8 mole of additional CO_2 stored in sea water in equilibrium with fixed CO_2 partial pressure (i.e., about 2.8 tonnes of limestone per tonne CO_2). Adding alkalinity to the ocean would increase ocean carbon storage, both in the near term and on millennial time scales (Kheshgi, 1995). The duration of increased ocean carbon storage would be limited by eventual $CaCO_3$ sedimentation, or reduced $CaCO_3$ sediment dissolution, which is modelled to occur through natural processes on the time scale of about 6,000 years (Archer *et al*., 1997, 1998).

Carbonate minerals have been proposed as the primary source of alkalinity for neutralization of CO_2 acidity (Kheshgi 1995; Rau and Caldeira, 1999). There have been many experiments and observations related to the kinetics of carbonate mineral dissolution and precipitation, both in fresh water and in sea water (Morse and Mackenzie, 1990; Morse and Arvidson, 2002). Carbonate minerals and other alkaline compounds that dissolve readily in surface sea water (such as Na_2CO_3), however, have not been found in sufficient quantities to store carbon in the ocean on scales comparable to fossil CO_2 emissions (Kheshgi, 1995). Carbonate minerals that are abundant do not dissolve in surface ocean waters. Surface ocean waters are typically oversaturated with respect to carbonate minerals (Broecker and Peng, 1982; Emerson and Archer, 1990; Archer, 1996), but carbonate minerals typically do not precipitate in sea water due to kinetic inhibitions (Morse and Mackenzie, 1990).

To circumvent the problem of oversaturated surface waters, Kheshgi (1995) considered promoting reaction (5) by calcining limestone to form CaO, which is readily soluble. If the energy for the calcining step was provided by a CO_2-emission-free source, and the CO_2 released from $CaCO_3$ were captured and stored (e.g., in a geologic formation), then this process would store 1.8 mole CO_2 per mole CaO introduced into the ocean. If the CO_2 from the calcining step were not stored, then a net 0.8 mole CO_2 would be stored per mole CaO. However, if coal without CO_2 capture were used to provide the energy for calcination, and the CO_2 produced in calcining was not captured, only 0.4 mole CO_2 would be stored net per mole lime (CaO) to the ocean, assuming existing high-efficiency kilns (Kheshgi, 1995). This approach would increase the ocean sink of CO_2, and does not need to be connected to a concentrated CO_2 source or require transport to the deep sea. Such a process would, however, need to avoid rapid re-precipitation of $CaCO_3$, a critical issue yet to be addressed.

Rau and Caldeira (1999) proposed extraction of CO_2 from flue gas via reaction with crushed limestone and seawater. Exhaust gases from coal-fired power plants typically have 15,000 ppmv of CO_2 – over 400 times that of ambient air. A carbonic acid solution formed by contacting sea water with flue gases would accelerate the dissolution of calcite, aragonite, dolomite, limestone, and other carbonate-containing minerals, especially if minerals were crushed to increase reactive surface area. The solution of, for example, Ca^{2+} and dissolved inorganic carbon (primarily in the form of HCO_3^-) in sea water could then be released back into the ocean, where it would be diluted by additional seawater. Caldeira and Rau (2000) estimate that dilution of one part effluent from a carbonate neutralization reactor with 100 parts ambient sea water would result, after equilibration with the atmosphere, in a 10% increase in the

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[2] This approach is fundamentally different than the carbonate mineralization approach assessed in Chapter 7. In that approach CO_2 is stored by reacting it with non-carbonate minerals to form carbonate minerals. In this approach, carbonate minerals are dissolved in the ocean, thereby increasing ocean alkalinity and increasing ocean storage of CO_2. This approach could also make use of non-carbonate minerals, if their dissolution would increase ocean alkalinity.

calcite saturation state, which they contend would not induce precipitation. This approach does not rely on deep-sea release, avoiding the need for energy to separate, transport and inject CO_2 into the deep ocean. The wastewater generated by this carbonate-neutralization approach has been conjectured to be relatively benign (Rau and Caldeira, 1999). For example, the addition of calcium bicarbonate, the primary constituent of the effluent, has been observed to promote coral growth (Marubini and Thake, 1999). This approach will not remove all the CO_2 from a gas stream, because excess CO_2 is required to produce a solution that is corrosive to carbonate minerals. If greater CO_2 removal were required, this approach could be combined with other techniques of CO_2 capture and storage.

Process wastewater could be engineered to contain different ratios of added carbon and calcium, and different ratios of flue gas CO_2 to dissolved limestone (Caldeira and Wickett, 2005). Processes involving greater amounts of limestone dissolution per mole CO_2 added lead to a greater CO_2 fraction being retained. The effluent from a carbonate-dissolution reactor could have the same pH, $p\mathrm{CO}_2$, or $[CO_3^{2-}]$ as ambient seawater, although processing costs may be reduced by allowing effluent composition to vary from these values (Caldeira and Rau, 2000). Elevation in Ca^{2+} and bicarbonate content from this approach is anticipated to be small relative to the already existing concentrations in sea water (Caldeira and Rau, 2000), but effects of the new physicochemical equilibria on physiological performance are unknown. Neutralization of carbon acidity by dissolution of carbonate minerals could reduce impacts on marine ecosystems associated with pH and CO_3^{2-} decline (Section 6.7).

Carbonate neutralization approaches require large amounts of carbonate minerals. Sedimentary carbonates are abundant with estimates of 5×10^{17} tonnes (Berner *et al*., 1983), roughly 10,000 times greater than the mass of fossil-fuel carbon. Nevertheless, up to about 1.5 mole of carbonate mineral must be dissolved for each mole of anthropogenic CO_2 permanently stored in the ocean (Caldeira and Rau, 2000); therefore, the mass of $CaCO_3$ used would be up to 3.5 times the mass of CO_2 stored. Worldwide, 3 Gt $CaCO_3$ is mined annually (Kheshgi, 1995). Thus, large-scale deployment of carbonate neutralization approaches would require greatly expanded mining and transport of limestone and attendant environmental impacts. In addition, impurities in dissolved carbonate minerals may cause deleterious effects and have yet to be studied.

6.2.3 Other ocean storage approaches

Solid hydrate. Water reacts with concentrated CO_2 to form a solid hydrate ($CO_2 \cdot 6H_2O$) under typical ocean conditions at quite modest depths (Løken and Austvik, 1993; Holdren and Baldwin, 2001). Rehder *et al*. (2004) showed that the hydrate dissolves rapidly into the relatively dilute ocean waters. The density of pure CO_2 hydrate is greater than seawater, and this has led to efforts to create a sinking plume of released CO_2 in the ocean water column. Pure CO_2 hydrate is a hard crystalline solid and thus will not flow through a pipe, and so some form of CO_2 slurry is required for flow assurance (Tsouris *et al.,* 2004).

Water-$CaCO_3$-CO_2 *emulsion*. Mineral carbonate could be used to physically emulsify and entrain CO_2 injected in sea water (Swett *et al*. 2005); a 1:1 CO_2:$CaCO_3$ emulsion of CO_2 in water could be stabilized by pulverized limestone ($CaCO_3$). The emulsion plume would have a bulk density of 40% greater than that of seawater. Because the emulsion plume is heavier than seawater, the $CaCO_3$coated CO_2 slurries may sink all the way to the ocean floor. It has been suggested that the emulsion plume would have a pH that is at least 2 units higher than would a plume of liquid CO_2. Carbonate minerals could be mined on land, and then crushed, or fine-grained lime mud could be extracted from the sea floor. These fine-grain carbonate particles could be suspended in sea water upstream from the CO_2-rich plume emanating from the direct CO_2 injection site. The suspended carbonate minerals could then be transported with the ambient sea water into the plume, where the minerals could dissolve, increasing ocean CO_2 storage effectiveness and diminishing the pH impacts of direct injection.

Emplacement in carbonate sediments. Murray *et al*. (1997) have suggested emplacement of CO_2 into carbonate sediments on the sea floor. Insofar as this CO_2 remained isolated from the ocean, this could be categorized as a form of geological storage (Chapter 5).

Dry ice torpedoes. CO_2 could be released from a ship as dry ice at the ocean surface (Steinberg,1985). One costly method is to produce solid CO_2 blocks (Murray *et al.,* 1996). With a density of 1.5 t m^{-3}, these blocks would sink rapidly to the sea floor and could potentially penetrate into the sea floor sediment.

Direct flue-gas injection. Another proposal is to take a power plant flue gas, and pump it directly into the deep ocean without any separation of CO_2 from the flue gas, however costs of compression are likely to render this approach infeasible.

6.3 Capacity and fractions retained

6.3.1 Capacity

The physical capacity for storage of CO_2 in the ocean is large relative to fossil-fuel resources. The degree to which this capacity will be utilized may be based on factors such as cost, equilibrium $p\mathrm{CO}_2$, and environmental consequences.

Storage capacity for CO_2 in the ocean can be defined relative to an atmospheric CO_2 stabilization concentration. For example, roughly 2,300 to 10,700 GtCO_2 (above the natural pre-industrial background) would be added to the ocean in equilibrium with atmospheric CO_2 stabilization concentrations, ranging from 350 ppmv to 1000 ppmv, regardless of whether the CO_2 is initially released to the ocean or the atmosphere (Table 6.1, Figure 6.3; Kheshgi *et al.,* 2005; Sorai and Ohsumi, 2005). The capacity of the ocean for CO_2 storage could be increased with the addition of alkalinity to the ocean (e.g., dissolved limestone).

6.3.2 Measures of fraction retained

Effectiveness of ocean CO_2 storage has been reported in a variety of ways. These different ways of reporting result in very different numerical values (Box 6.3).

Over several centuries, CO_2 released to the deep ocean would be transported to the ocean surface and interact with the atmosphere. The CO_2-enriched water would then exchange CO_2 with the atmosphere as it approaches chemical equilibrium. In this chemical equilibrium, most of the injected CO_2 remains in the ocean even though it is no longer isolated from the atmosphere (Table 6.1; Figure 6.3). CO_2 that has interacted with the atmosphere is considered to be part of the natural carbon cycle, much in the way that CO_2 released directly to the atmosphere is considered to be part of the natural carbon cycle. Such CO_2 cannot be considered to be isolated from the atmosphere in a way that can be attributable to an ocean storage project.

Loss of isolation of injected CO_2 does not mean loss of all of the injected CO_2 to the atmosphere. In chemical equilibrium with an atmosphere containing 280 ppm CO_2, about 85% of any carbon injected would remain the ocean. If atmospheric CO_2 partial pressures were to approach 1000 ppm, about 66% of the injected CO_2 would remain in the ocean after equilibration with the atmosphere (Table 6.1). Thus, roughly 1/5 to 1/3 of the CO_2 injected into the ocean will eventually reside in the atmosphere, with this airborne fraction depending on the long-term atmosphere-ocean CO_2 equilibrium (Kheshgi, 1995, 2004b). The airborne fraction is the appropriate measure to quantify the effect of ocean storage on atmospheric composition.

6.3.3 *Estimation of fraction retained from ocean observations*

Observations of radiocarbon, CFCs, and other tracers indicate the degree of isolation of the deep sea from the atmosphere (Prentice *et al*., 2001). Radiocarbon is absorbed by the oceans from the atmosphere and is transported to the deep-sea, undergoing radioactive decay as it ages. Radiocarbon age (Figure 6.16) is not a perfect indicator of time since a water parcel last contacted the atmosphere because of incomplete equilibration with the atmosphere (Orr, 2004). Taking this partial equilibration into account, the age of North Pacific deep water is estimated to be in the range of 700 to 1000 years. Other basins, such as the North Atlantic, have characteristic overturning times of 300 years or more. This data suggests that, generally, carbon injected in the deep ocean would equilibrate with the atmosphere over a time scale of 300 to 1000 years.

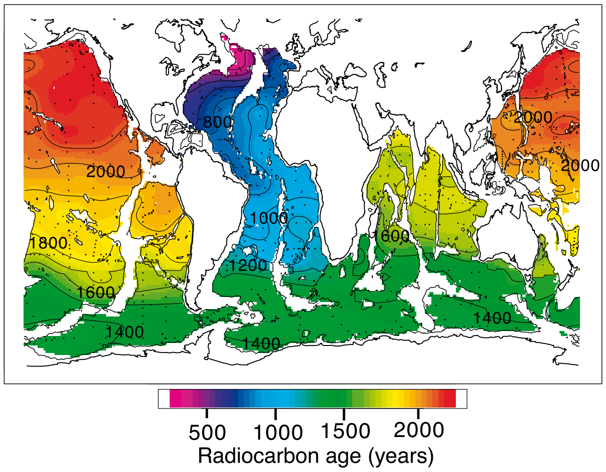

Figure 6.16 Map of radiocarbon (^{14}C) age at 3500 m (Matsumoto and Key, 2004).

6.3.4 *Estimation of fraction retained from model results*

Ocean models have been used to predict the isolation of injected CO_2 from the atmosphere. Many models are calibrated using ocean radiocarbon data, so model-based estimates of retention of injected CO_2 are not completely independent of the estimates based more directly on observations (Section 6.3.3).

A wide number of studies have used three-dimensional ocean general circulation models to study retention of CO_2 injected into the ocean water column (Bacastow and Stegen, 1991; Bacastow et al., 1997; Nakashiki and Ohsumi, 1997; Dewey *et al.,* 1997, 1999; Archer *et al.,* 1998; Xu *et al.,* 1999; Orr, 2004; Hill *et al.,* 2004). These modelling studies generally confirm inferences based on simpler models and considerations of ocean chemistry and radiocarbon decay rates. In ocean general circulation simulations performed by seven modelling groups (Orr, 2004), CO_2 was injected for 100 years at each of seven different locations and at three different depths. Model results indicate that deeper injections will be isolated from the atmosphere for longer durations. Figure 6.17 shows the effect of injection depth on retained fraction for the mean of seven ocean sites (Orr, 2004). Ranges of model results indicate some uncertainty in forecasts of isolation of CO_2 released to the deep ocean, although for all models the time extent of CO_2 isolation is longer for deeper CO_2 release, and isolation is nearly complete for 100 years following CO_2 release at 3000 m depth (Figure 6.18 and 6.19). However, present-day models disagree as to the degassing time scale for particular locations (Figure 6.19). There seems to be no simple and robust correlation of CO_2 retention other than depth of injection (Caldeira *et al*., 2002), however, there is some indication that the mean fraction retained for stored carbon is greater in the Pacific Ocean than the Atlantic Ocean, but not all models agree on this. Model results indicate that for injection at 1500 m depth, the time scale of the partial CO_2 degassing is sensitive to the location of the injection, but at 3000 m, results are relatively insensitive to injection location. Model results have been found to be sensitive to differences in numerical schemes and model parameterizations (Mignone *et al*., 2004).

6.4 Site selection

6.4.1 *Background*

There are no published papers specifically on site selection for intentional ocean storage of CO_2; hence, we can discuss only general factors that might be considered when selecting sites for

Box 6.3 Measures of the fraction of CO_2 retained in storage

Different measures have been used to describe how effective intentional storage of carbon dioxide in the ocean is to mitigate climate change (Mueller *et al.*, 2004). Here, we illustrate several of these measures using schematic model results reported by Herzog *et al.* (2003) for injection of CO_2 at three different depths (Figure 6.17).

Fraction retained (see Chapter 1) is the fraction of the cumulative amount of injected CO_2 that is retained in the storage reservoir over a specified period of time, and thereby does not have the opportunity to affect atmospheric CO_2 concentration (Mignone *et al.*, 2004). The retained fraction approaches zero (Figure 6.17) over long times, indicating that nearly all injected CO_2 will interact with the atmosphere (although a small amount would interact first with carbonate sediments).

Airborne Fraction is the fraction of released CO_2 that adds to atmospheric CO_2 content (Kheshgi and Archer, 2004). For atmospheric release, airborne fraction is initially one and decays to roughly 0.2 (depending on atmospheric CO_2 concentration) as the added CO_2 is mixed throughout the ocean, and decays further to about 0.08 as CO_2 reacts with sediments (Archer *et al.*, 1997). For deep-sea release, airborne fraction is initially zero and then approaches that of atmospheric release. Note that the asymptotic airborne fraction depends on the concentration of CO_2 of surface waters (Figure 6.3).

Fraction retained is used throughout this report to indicate how long the CO_2 is stored. In addition the following measures can be used to compare the effectiveness of ocean carbon storage with other options, for example:

- The **Net Present Value** (NPV) approach (Herzog et al., 2003) considers temporary storage to be equivalent to delayed emission of CO_2 to the atmosphere. The value of delaying CO_2 emissions depends on the future costs of CO_2 emission and economic discount rates. There is economic value to temporary storage (i.e., delayed emission) if the cost of CO_2 emissions increases at a rate that is less than the discount rate (Herzog et al., 2003).
- The **Global-Warming Potential** (GWP) is a measure defined by the IPCC to compare the climatic effect of different greenhouse-gas emissions. It is computed by accumulating the radiative climate forcing of a greenhouse-gas emission over a specified time horizon. This measure has been applied to compare the radiative forcing from oceanic and atmospheric releases of carbon dioxide (Kheshgi et al., 1994, Ramaswamy et al., 2001). Haugan and Joos (2004) propose a modification to the GWP approach that compares the climate effects of the airborne fraction of a CO_2 release to the ocean with those from a release to the atmosphere. Table 6.2 compares these measures for results from a schematic model at three depths.

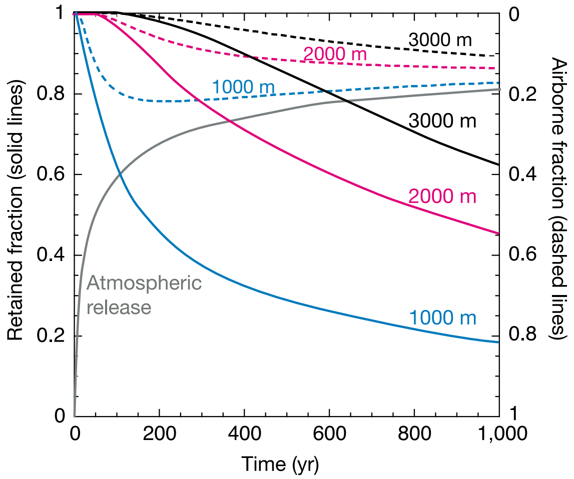

Figure 6.17 Fraction of carbon in the ocean from injection at three different depths and the atmosphere illustrated with results from a schematic model (Herzog et al., 2003). Calculations assume a background 280 ppm of CO_2 in the atmosphere.

Table 6.2 Evaluation of measures described in the text illustrated using schematic model results shown in Figure 6.17. For the Net Present Value measure, the percentage represents the discount rate minus the rate of increase in the cost of CO_2 emission. (If these are equal, the Net Present Value of temporary carbon storage is zero) Two significant digits shown for illustration exceed the accuracy of model results.

Measure		**Atmospheric release**	**Injection depth**		
			1000 m	**2000 m**	**3000 m**
Effective Retained Fraction	at 20 years	0	0.96	1.00	1.00
	at 100 years	0	0.63	0.97	1.00
	at 500 years	0	0.28	0.65	0.85
Airborne Fraction	at 20 years	0.61	0.03	6×10^{-6}	7×10^{-10}
	at 100 years	0.40	0.19	0.02	9×10^{-4}
	at 500 years	0.24	0.20	0.12	0.06
Net Present Value (constant emissions cost)	5% per year	0	0.95	1.00	1.00
	1% per year	0	0.72	0.95	0.99
	0.2% per year	0	0.41	0.72	0.85
Global Warming Potential	20 year horizon	1	0.01	1×10^{-6}	6×10^{-10}
	100 year horizon	1	0.21	0.01	4×10^{-4}
	500 year horizon	1	0.56	0.20	0.06

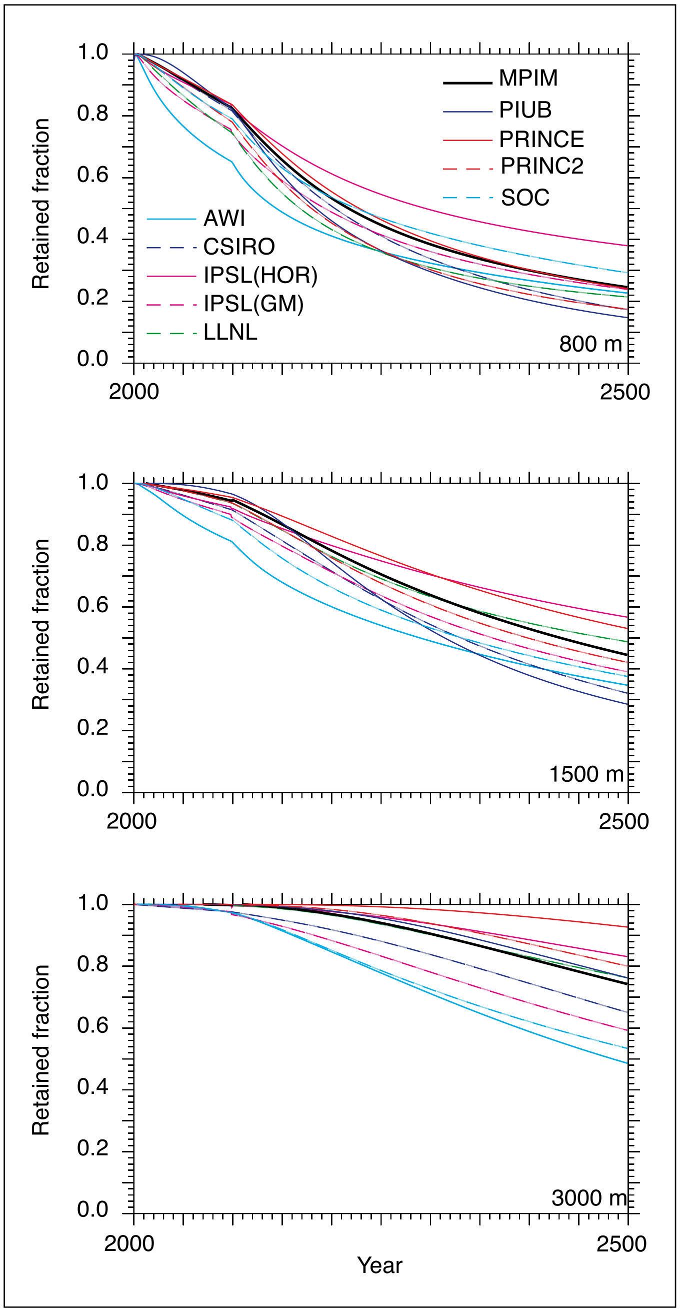

Figure 6.18 Results are shown for seven ocean general circulation models at three different depths averaged over seven injection locations (Orr, 2004). The percentage efficiency shown is the retained fraction for an injection at a constant rate from 2000 to 2100. Models agree that deeper injection isolates CO_2 from the atmosphere longer than shallower injection. For release at 3000 m, most of the added carbon was still isolated from the atmosphere at the end of the 500 year simulations.

ocean storage. Among these considerations are environmental consequences, costs, safety, and international issues (including cross border transport). Because environmental consequences, costs, and social and political issues are addressed in other parts of this report, here we briefly consider site selection factors that enhance the fraction retained or reduce the costs.

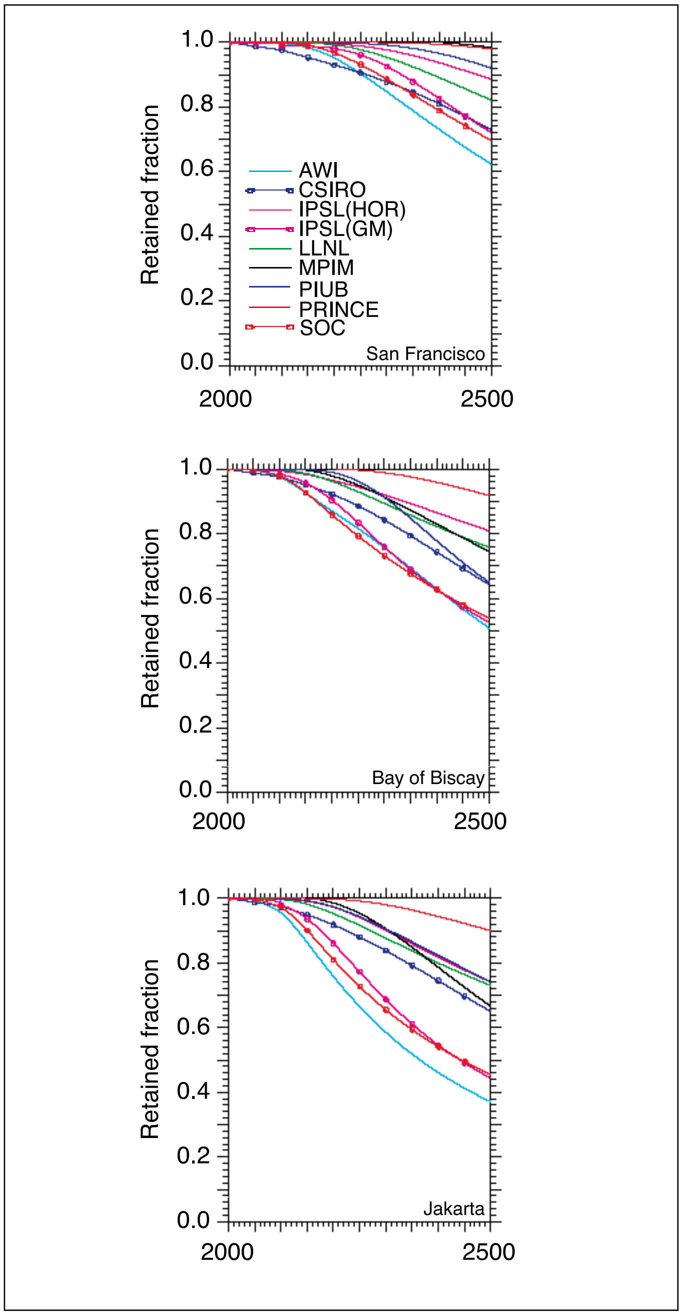

Figure 6.19 Comparison of storage results for three injection locations (at 3000 m depth) in ten ocean model simulations (Orr, 2004). Models differ on predictions of CO_2 fraction retained for release in different oceans.

6.4.2 Water column release

Large point sources of CO_2 located near deep water would generally be the most cost effective settings in which to carry out direct CO_2 injection (Figure 6.21; Section 6.9). While models indicate that site-specific differences exist, they do not yet agree on the ranking of potential sites for effectiveness of direct injection CO_2 operations (Orr, 2004).

6.4.3 CO_2 lakes on the sea floor

CO_2 lakes must be on the sea floor at a depth below 3000 m (Figures 6.20 and 6.21), because the liquid CO_2 must be denser than surrounding sea water (Box 6.2).

These ocean general circulation model calculations did not consider interactions with $CaCO_3$ sediments or marine biota. Increased CO_2 concentrations in the ocean promote dissolution of $CaCO_3$ sediments, which would tend to increase predicted CO_2 retention. This has been modelled for the deep sea with results of greater retention for release in the Atlantic because of high $CaCO_3$ inventory in Atlantic sediments (Archer et al., 1998).

Preliminary numerical simulations of ocean CO_2 injection predict increased oceanic retention of injected CO_2 with concurrent global warming due to weaker overturning and a more stratified ocean (Jain and Cao, 2005). Some evidence indicates recent increases in stratification in all major ocean basins (e.g., Joos, 2003; McPhaden and Zhang, 2002; Palmer et al., 2004; Stramma et al., 2004).

6.4.4 Limestone neutralization

The amounts of sea water and limestone required to neutralize the acidity of added CO_2 indicate that limestone neutralization would be most suitable for CO_2 point sources located near both the ocean and large deposits of limestone (Rau and Caldeira, 1999).

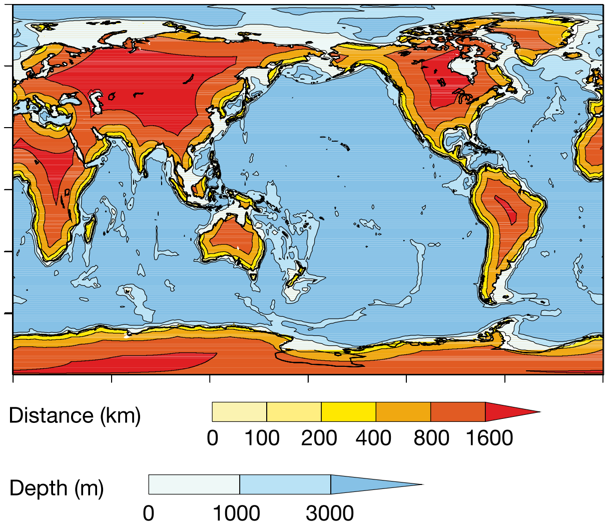

Figure 6.20 Locations of ocean water at least 1 km and 3 km deep. Distance over land to water that is at least 3 km deep (Caldeira and Wickett, 2005). In general, land areas with the lightest colours would be the most-cost effective land-based settings for a CO_2-injection operation. However, each potential site would need to be evaluated prior to deployment.

6.5 Injection technology and operations

6.5.1 Background

The development of ocean storage technology is generally at a conceptual stage; thus, we will only discuss general principles. There has been limited engineering analysis and experimental studies of these conceptual technologies for ocean storage (Nihous, 1997), and no field-testing. No operational experience exists. Various technology concepts have been proposed to improve isolation from the atmosphere or diminish environmental consequences of CO_2 injected into the ocean. Further research and development would be needed to make technologies available, but no major technical barriers are apparent.

6.5.2 Water column release

Dispersal of liquid CO_2 at a depth of 1000 m or deeper is technologically feasible. Since liquid CO_2 may be relatively easily transported to appropriate depths, the preferred release mode is thought at this time to be as a liquid or dense gas phase (achieved by compression beyond its critical point, 72.8 bar at 31°C). The pipes that would carry this CO_2 to the deep ocean would be similar to the pipes that have been used commercially on land to transport CO_2 for use in CO_2 enhanced oil recovery projects (Ozaki *et al*., 1997). Models (Liro *et al*., 1992, Drange and Haugan, 1992) predict that, with a properly designed diffuser, nearly all the CO_2 would dissolve in the ocean within a 100 m of the injection depth. Then, this CO_2-rich water would be diluted as it disperses, primarily horizontally along surfaces of constant density.

Water column injection schemes typically envision minimizing local changes to ocean chemistry by producing a

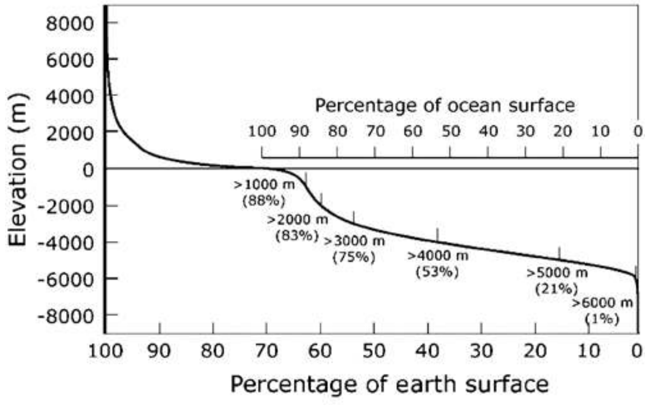

Figure 6.21 Relationship between depth and sea floor area. Flow in ocean bottom boundary layers would need to be taken into account when selecting a site for a CO_2 lake. Bottom friction and turbulence can enhance the dissolution rate and vertical transport of dissolved CO_2 and lead to a short lifetime for the lake (Section 6.2.1.6). It has been suggested that CO_2 lakes would be preferentially sited in relatively restricted depressions or in trenches on sea floor (Ohsumi, 1995).

relatively dilute initial injection through a series of diffusers or by other means. Dilution would reduce exposure of organisms to very low *p*H (very high CO_2) environments (Section 6.7).

One set of options for releasing CO_2 to the ocean involves transporting liquid CO_2 from shore to the deep ocean in a pipeline. This would not present any major new problems in design, 'according to petroleum engineers and naval architects speaking at one of the IEA Greenhouse Gas R&D Programme ocean storage workshops' (Ormerod *et al.*, 2002). The oil industry has been making great advances in undersea offshore technology, with projects routinely working at depths greater than 1000 m. The oil and the gas industry already places pipes on the bottom of the sea in depths down to 1600 m, and design studies have shown 3000 m to be technically feasible (Ormerod *et al.*, 2002). The 1 m diameter pipe would have the capacity to transport 70,000 tCO_2 day^{-1}, enough for CO_2 captured from 3 GW_e of a coal-fired electric power plant (Ormerod *et al.*, 2002). Liro *et al.* (1992) proposed injecting liquid CO_2 at a depth of about 1000 m from a manifold lying near the ocean bottom to form a rising droplet plume. Nihous *et al.* (2002) proposed injecting liquid CO_2 at a depth of below 3000 m from a manifold lying near the ocean bottom and forming a sinking droplet plume. Engineering work would need to be done to assure that, below 500 m depth, hydrates do not form inside the discharged pipe and nozzles, as this could block pipe or nozzle flow.

CO_2 could be transported by tanker for release from a stationary platform (Ozaki *et al.*, 1995) or through a towed pipe (Ozaki *et al.*, 2001). In either case, the design of CO_2 tankers would be nearly identical to those that are now used to transport liquid petroleum gas (LPG). Cooling would be used, in order to reduce pressure requirements, with design conditions of –55 degrees C and 6 bar pressure (Ormerod *et al.*, 2002). Producing a dispersed initial concentration would diminish the magnitude of the maximum *p*H excursion. This would probably involve designing for the size of the initial liquid CO_2 droplet and the turbulent mixing behind the towed pipe (Tsushima *et al.*, 2002). Diffusers could be designed so that CO_2 droplets would dissolve completely before they reach the liquid-gas phase boundary.

CO_2 hydrate is about 15% denser than sea water, so it tends to sink, dissolving into sea water over a broad depth horizon (Wannamaker and Adams, 2002). Kajishima *et al.* (1997) and Saito *et al.* (2001) investigated a proposal to create a dense CO_2-seawater mixture at a depth of between 500 and 1000 m to form a current sinking along the sloping ocean bottom. Another proposal (Tsouris *et al.*, 2004; West *et al.*, 2003) envisions releasing a sinking CO_2-hydrate/seawater slurry at between 1000 and 1500 m depth. This sinking plume would dissolve as it sinks, potentially distributing the CO_2 over kilometres of vertical distance, and achieving some fraction of the CO_2 retained in deep storage despite the initial release into intermediate waters. The production of a hydrate/seawater slurry has been experimentally demonstrated at sea (Tsouris *et al.*, 2004). Tsouris *et al.* (2004) have carried out a field experiment at 1000 m ocean depth in which rapid mixing of sea water with CO_2 in a capillary nozzle to a neutrally buoyant composite paste takes place. This would enhance ocean retention time compared to that from creation of a buoyant plume. Aya *et al.* (2004) have shown that a rapidly sinking plume of CO_2 can be formed by release of a slurry combining cold liquid and solid CO_2 with a hydrate skin. This would effectively transfer ship released CO_2 at shallow ocean depth to the deep ocean without the cost of a long pipe. In all of these schemes the fate of the CO_2 is to be dissolved into the ocean, with increased depth of dissolution, and thus increased retention.

6.5.3 *Production of a CO_2 lake*

Nakashiki (1997) investigated several different kinds of discharge pipes that could be used from a liquid CO_2 tanker to create a CO_2 lake on the sea floor. They concluded that a 'floating discharge pipe' might be the best option because it is simpler than the alternatives and less likely to be damaged by wind and waves in storm conditions.

Aya *et al.* (2003) proposed creating a slurry of liquid CO_2 mixed with dry ice and releasing into the ocean at around 200 to 500 m depth. The dry ice is denser that the surrounding sea water and would cause the slurry to sink. An *in situ* experiment carried out off the coast of California found that a CO_2 slurry and dry ice mass with initial diameter about 8.0 cm sank approximately 50 metres within two minutes before the dry ice melted (Aya *et al.*, 2003). The initial size of CO_2 slurry and dry ice is a critical factor making it possible to sink more than 3000 m to the sea floor. To meet performance criteria, the dry ice content would be controlled with a system consisting of a main power engine, a compressor, a condenser, and some pipe systems.

6.6 Monitoring and verification

6.6.1 *Background*

Monitoring (Figure 6.22) would be done for at least two different purposes: (1) to gain specific information relating to a particular CO_2 storage operation and (2) to gain general scientific understanding. A monitoring program should attempt to quantify the mass and distribution of CO_2 from each point source and could record related biological and geochemical parameters. These same issues may relate to monitoring of potential leakages from subsea geologic storage, or for verification that such leakage does not occur. Monitoring protocols for submarine sewage disposal for example are already well established, and experience may be drawn from that.

6.6.2 *Monitoring amounts and distributions of materials released*

6.6.2.1 Monitoring the near field

It appears that there is no serious impediment to verifying plant compliance with likely performance standards for flow through a pipe. Once CO_2 is discharged from the pipe then the specific monitoring protocols will depend upon whether the plume is buoyant or sinking. Fixed location injections present fewer verification difficulties than moving ship options.

For ocean injection from large point sources on land, verifying compliance involves above ground inspection of facilities for verification of flow and the CO_2 purity being consistent with environmental regulations (e.g., trace metal concentrations, etc.). For a power plant, flue gases could be monitored for flow rate and CO_2 partial pressure, thus allowing a full power plant carbon audit.

There are a variety of strategies for monitoring release of CO_2 into the ocean from fixed locations. Brewer *et al.* (2005) observed a plume of CO_2-rich sea water emanating from a small-scale experimental release at 4 km depth with an array of *p*H and conductivity sensors. Measurements of ocean *p*H and current profiles at sufficiently high temporal resolution could be used to evaluate the rate of CO_2 release, local CO_2 accumulation and net transport away from the site (Sundfjord *et al.*, 2001). Undersea video cameras can monitor the point of release to observe CO_2 flow. The very large sound velocity contrast between liquid CO_2 (about 300 m s^{-1}) and sea water (about 1,500 m s^{-1}) offers the potential for very efficient monitoring of the liquid CO_2 phase using acoustic techniques (e.g., sonar).

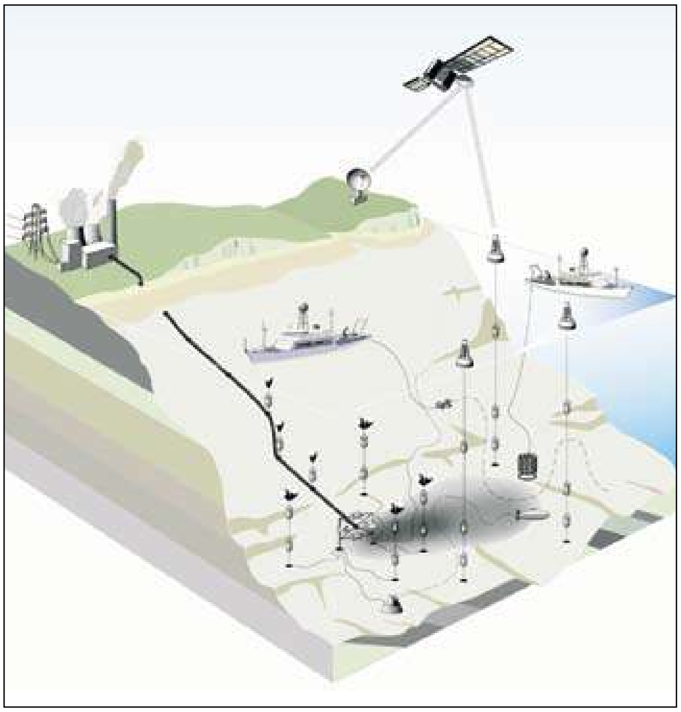

Figure 6.22 Schematic of possible approaches for monitoring the injection of CO_2 into the deep ocean via a pipeline. The grey region represents a plume of high CO_2/low *p*H water extending from the end of the pipeline. Two sets of chemical, biological and current sensors and two underwater cameras are shown at the end of the pipeline. An array of moored sensors to monitor the direction and magnitude of the resulting plume can be seen around the pipe and are also located along the pipeline to monitor for possible leaks. A shore-based facility provides power to the sensors and for obtaining real-time data and an autonomous underwater vehicle maps the near-field distribution of the plume. A towed undulating pumping system monitors at distances of more than a few kilometres from the injection site. The towed system could provide much greater measurement accuracy and precision, but would also be able to provide measurements over large areas in a relatively short period of time. Moored systems are used to monitor the plume between mapping cruises. These moorings have surface buoys and make daily transmissions back to the monitoring facility via satellite. The very far-field distributions are monitored with hydrographic section cruises conducted every 2–5 years using standard discrete sampling approaches. These approaches provide the accuracy and precision required to detect the small CO_2 signals that add to background variations.

The placement of CO_2 directly in a lake on the sea floor can be verified, and the quantity and loss rate determined by a combination of acoustic, *p*H, and velocity measurements, and by direct inspection with underwater vehicles. Undersea vehicles, tethered or autonomous, could play a prominent role in monitoring and verification. Autonomous vehicles have been developed that can be programmed to efficiently follow a variety of complex trajectories over large areas (Simonetti, 1998), but accurate *p*H sensing in a rapidly changing pressure and temperature field has yet to be demonstrated. Deep-sea *p*H monitoring from tethered vehicles has been shown to be very precise (Brewer *et al.*, 2004), and these vehicles can routinely collect precisely located samples for later analysis.

6.6.2.2 *Monitoring the far field*

It will be possible to monitor the far field distributions of injected CO_2 using a combination of shipboard measurements and modelling approaches. The ability to identify *p*H plumes in the ocean has been well demonstrated (Figure 6.23). Current analytical techniques for measuring total CO_2 in the ocean are accurate to about ±0.05% (Johnson *et al.*, 1998). Thus, measurable changes could be seen with the addition of approximately 90 tonnes of CO_2 per km^3. In other words,

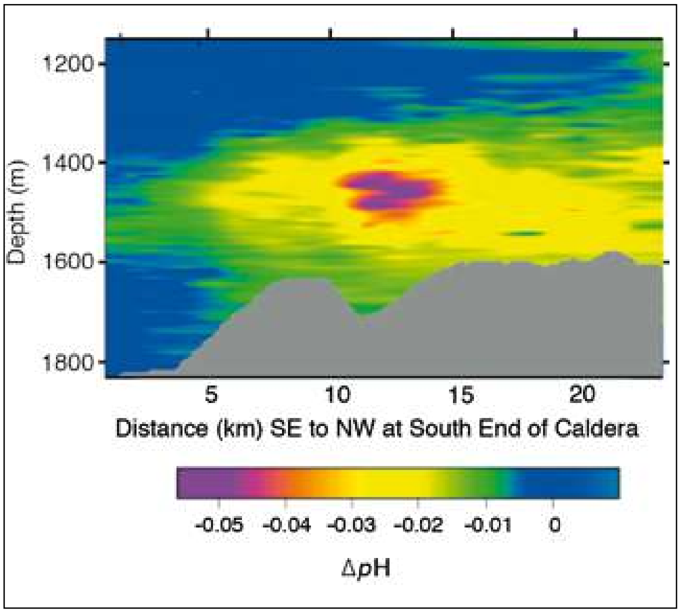

Figure 6.23 Measurements showing the ability to measure chemical effects of a natural CO_2 plume. Profiles for *p*H were taken in June 1999 near the Axial Volcano at 46ºN 130ºW, in the ocean near Portland, Oregon, United States.

1 $GtCO_2$ could be detected even if it were dispersed over 10^7 km^3 (i.e., 5000 km x 2000 km x 1 km), if the dissolved inorganic carbon concentrations in the region were mapped out with high-density surveys before the injection began.

Variability in the upper ocean mixed layer would make it difficult to directly monitor small changes in CO_2 in waters shallower than the annual maximum mixed-layer depth. Seasonal mixing from the surface can extend as deep as 800 m in some places, but is less than 200 m in most regions of the ocean. Below the seasonal mixed layer, however, periodic ship-based surveys (every 2 to 5 years) could quantify the expansion of the injection plume.

We do not have a direct means of measuring the evasion of carbon stored in the ocean to the atmosphere. In most cases of practical interest the flux of stored CO_2 from the ocean to atmosphere will be small relative to natural variability and the accuracy of our measurements. Operationally, it would be impossible to differentiate between carbon that has and has not interacted with the atmosphere. The use of prognostic models in evaluating the long-term fate of the injected CO_2 is critical for properly attributing the net storage from a particular site.

Given the natural background variability in ocean carbon concentrations, it would be extremely difficult, if not impossible, to measure CO_2 injected very far from the injection source. The attribution of a signal to a particular point source would become increasingly difficult if injection plumes from different locations began to overlap and mix. In some parts of the ocean it would be difficult to assign the rise in CO_2 to intentional ocean storage as opposed to CO_2 from atmospheric absorption.

6.6.3 Approaches and technologies for monitoring environmental effects

Techniques now being used for field experiments could be used to monitor some near field consequences of direct CO_2 injection (Section 6.7). For example, researchers (Barry *et al.*, 2004, 2005; Carman *et al.*, 2004; Thistle *et al.*, 2005) have been developing experimental means for observing the consequences of elevated CO_2 on organisms in the deep ocean. However, such experiments and studies typically look for evidence of acute toxicity in a narrow range of species (Sato, 2004; Caulfield *et al.,* 1997; Adams *et al.*, 1997; Tamburri *et al.*, 2000). Sub-lethal effects have been studied by Kurihara *et al.* (2004). Process studies, surveys of biogeochemical tracers, and ocean bottom studies could be used to evaluate changes in ecosystem structure and dynamics both before and after an injection.

It is less clear how best to monitor the health of broad reaches of the ocean interior (Sections 6.7.3 and 6.7.4). Ongoing long-term surveys of biogeochemical tracers and deep-sea biota could help to detect long-term changes in deep-sea ecology.

6.7 Environmental impacts, risks, and risk management

6.7.1 Introduction to biological impacts and risk

Overall, there is limited knowledge of deep-sea population and community structure and of deep-sea ecological interactions (Box 6.4). Thus the sensitivities of deep ocean ecosystems to intentional carbon storage and the effects on possibly unidentified goods and services that they may provide remain largely unknown.

Most ocean storage proposals seek to minimize the volume of water with high CO_2 concentrations either by diluting the CO_2 in a large volume of water or by isolating the CO_2 in a small volume (e.g., in CO_2 lakes). Nevertheless, if deployed widely, CO_2 injection strategies ultimately will produce large volumes of water with somewhat elevated CO_2 concentrations (Figure 6.15). Because large amounts of relatively pure CO_2 have never been introduced to the deep ocean in a controlled experiment, conclusions about environmental risk must be based primarily on laboratory and small-scale *in-situ* experiments and extrapolation from these experiments using conceptual and mathematical models. Natural analogues (Box 6.5) can be relevant, but differ significantly from proposed ocean engineering projects.

Compared to the surface, most of the deep sea is stable and varies little in its physiochemical factors over time (Box 6.4). The process of evolutionary selection has probably eliminated individuals apt to endure environmental perturbation. As a result, deep-sea organisms may be more sensitive to environmental disturbance than their shallow water cousins (Shirayama, 1997).

Ocean storage would occur deep in the ocean where there is virtually no light and photosynthesizing organisms are lacking, thus the following discussion primarily addresses CO_2 effects on heterotrophic organisms, mostly animals. The diverse fauna that lives in the waters and sediments of the deep ocean can be affected by ocean CO_2 storage, leading to change in ecosystem composition and functioning. Thus, the effects of CO_2 need to be identified at the level of both the individual (physiological) and the ecosystem.

As described in Section 6.2, introduction of CO_2 into the ocean either directly into sea water or as a lake on the sea floor would result in changes in dissolved CO_2 near to and down current from a discharge point. Dissolving CO_2 in sea water (Box 6.1; Table 6.3) increases the partial pressure of CO_2 (pCO_2, expressed as a ppm fraction of atmospheric pressure, equivalent to μatm), causes decreased pH (more acidic) and decreased CO_3^{2-} concentrations (less saturated). This can lead to dissolution of $CaCO_3$ in sediments or in shells of organisms. Bicarbonate (HCO_3^-) is then produced from carbonate (CO_3^{2-}).

The spatial extent of the waters with increased CO_2 content and decreased pH will depend on the amount of CO_2 released and the technology and approach used to introduce that CO_2 into the ocean. Table 6.3 shows the amount of sea water needed to dilute each tonne of CO_2 to a specified ΔpH reduction. Further dilution would reduce the fraction of ocean at one $\boldsymbol{\Delta p}$H

Box 6.4 Relevant background in biological oceanography.

Photosynthesis produces organic matter in the ocean almost exclusively in the upper 200 m where there is both light and nutrients (e.g., PO_4, NO_3, NH_4^+, Fe). Photosynthesis forms the base of a marine food chain that recycles much of the carbon and nutrients in the upper ocean. Some of this organic matter ultimately sinks to the deep ocean as particles and some of it is mixed into the deep ocean as dissolved organic matter. The flux of organic matter from the surface ocean provides most of the energy and nutrients to support the heterotrophic ecosystems of the deep ocean (Gage and Tyler, 1991). With the exception of the oxygen minimum zone and near volcanic CO_2 vents, most organisms living in the deep ocean live in low and more or less constant CO_2 levels.

At low latitudes, oxygen consumption and CO_2 release can produce a zone at around 1000 m depth characterized by low O_2 and high CO_2 concentrations, known as the 'oxygen minimum zone'. Bacteria are the primary consumers of organic matter in the deep ocean. They obtain energy predominately by consuming dissolved oxygen in reactions that oxidize organic carbon into CO_2. In the oxygen minimum layer, sea water *p*H may be less than 7.7, roughly 0.5 *p*H units lower than average *p*H of natural surface waters (Figure 6.6).

At some locations near the sea floor, especially near submarine volcanic CO_2 sources, CO_2 concentrations can fluctuate greatly. Near deep-sea hydrothermal vents CO_2 partial pressures (pCO_2, expressed as a ppm fraction of atmospheric pressure, equivalent to μatm) of up to 80,000 ppm have been observed. These are more than 100 times the typical value for deep-sea water. Typically, these vents are associated with fauna that have adapted to these conditions over evolutionary time. For example, tube worms can make use of high CO_2 levels for chemosynthetic CO_2 fixation in association with symbiotic bacteria (Childress *et al.*, 1993). High CO_2 levels (up to a pCO_2 of 16,000 ppm; Knoll *et al.*, 1996) have been observed in ocean bottom waters and marine sediments where there are high rates organic matter oxidation and low rates of mixing with the overlying seawater. Under these conditions, high CO_2 concentrations are often accompanied by low O_2 concentrations. Near the surface at night, respiratory fluxes in some relatively confined rock pools of the intertidal zone can produce high CO_2 levels. These patterns suggest that in some environments, organisms have evolved to tolerate relatively wide *p*H oscillations and/or low *p*H values.

Deep-sea ecosystems generally depend on sinking particles of organic carbon made by photosynthesis near the ocean surface settling down through the water. Most species living in the deep sea display very low metabolic rates (Childress, 1995), especially in oxygen minimum layers (Seibel *et al.*, 1997). Organisms living in the deep seawaters have adapted to the energy-limited environment by conserving energy stores and minimizing energy turnover. As a result of energy limitations and cold temperatures found in the deep sea, biological activities tend to be extremely low. For example, respiration rates of rat-tail fish are roughly 0.1% that of their shallow-water relatives. Community respiration declines exponentially with depth along the California margin, however, rapid turnover of large quantities of organic matter has been observed on the ocean floor (Mahaut *et al.*, 1995; Smith and Demopoulos, 2003). Thus, biological activity of some animals living on the deep sea floor can be as great as is found in relatives living on the sea floor in shallow waters.

Deep-sea ecosystems may take a long time to recover from disturbances that reduce population size. Organisms have adapted to the energy-limited environment of the deep sea by limiting investment in reproduction, thus most deep-sea species produce few offspring. Deep-sea species tend to invest heavily in each of their eggs, making them large and rich in yolk to provide the offspring with the resources they will need for survival. Due to their low metabolic rates, deep-sea species tend to grow slowly and have much longer lifespans than their upper-ocean cousins. For example, on the deep-sea floor, a bivalve less than 1 cm across can be more than 100 years old (Gage, 1991). This means that populations of deep-sea species will be more greatly affected by the loss of individual larvae than would upper ocean species. Upon disturbance, recolonization and community recovery in the deep ocean follows similar patterns to those in shallow waters, but on much longer time scales (several years compared to weeks or months in shallow waters, Smith and Demopoulos, 2003).

The numbers of organisms living on the sea floor per unit area decreases exponentially with depth, probably associated with the diminishing flux of food with depth. On the sea floor of the deepest ocean and of the upper ocean, the fauna can be dominated by a few species. Between 2000 and 3000 m depth ecosystems tend to have high species diversity with a low number of individuals, meaning that each species has a low population size (Snelgrove and Smith, 2002). The fauna living in the water column appear to be less diverse than that on the sea floor, probably due to the relative uniformity of vast volumes of water in the deep ocean.

Box 6.5 Natural analogues and Earth history.

There are several examples of natural systems with strong CO_2 sources in the ocean, and fluid pools toxic to marine life that may be examined to better understand possible physical and biological effects of active CO_2 injection.

Most natural environments that are heavily enriched in CO_2 (or toxic substances) host life forms that have adapted to these special conditions on evolutionary time scales. During Earth history much of the oceans may have hosted life forms specialized on elevated pCO_2, which are now extinct. This limits the use of natural analogues or Earth history to predict and generalize effects of CO_2 injection on most extant marine life.

- *Venting of carbon dioxide-rich fluids:* Hydrothermal vents, often associated with mid-ocean-ridge systems, often release CO_2 rich fluids into the ocean and can be used to study CO_2 behaviour and effects. For example, Sakai *et al.* (1990) observed buoyant hydrate forming fluids containing 86–91% CO_2 (with H_2S, and methane etc. making up the residual) released from the sea floor at 1335–1550 m depth from a hydrothermal vent field. These fluids would be similar to a heavily contaminated industrial CO_2 source. These fluids arise from the reaction of sea water with acid and intermediate volcanic rocks at high temperature; they are released into sea water of 3.8°C. A buoyant hydrate-coated mass forms at the sea floor, which then floats upwards dissolving into the ocean water. Sea floor venting of aqueous fluids, rich in CO_2 and low in *p*H (3.5–4.4), is also to be found in some hydrothermal systems (Massoth *et al.,* 1989; Karl, 1995).

  Near volcanic vents, deep-sea ecosystems can be sustained by a geochemical input of chemical energy and CO_2. While there has been extensive investigation of these sites, and the plumes emanating from them, this has not yet been in the context of analogues for industrial CO_2 storage effects. Such an investigation would show how a fauna has evolved to adapt to a high-CO_2 environment; it would not show how biota adapted to normal ocean water would respond to increased CO_2 concentrations.*
- *Deep saline brine pools:* The ocean floor is known to have a large number of highly saline brine pools that are anoxic and toxic to marine life. The salty brines freely dissolve, but mixing into the overlying ocean waters is impeded by the stable stratification imparted by the high density of the dissolving brines. The Red Sea contains many such brine pools (Degens and Ross, 1969; Anschutz *et al.,* 1999), some up to 60 km^2 in area, filled with high-temperature hyper-saline, anoxic, brine. Animals cannot survive in these conditions, and the heat and salt that are transported across the brine-seawater interface form a plume into the surrounding bottom water. Hydrothermal sources resupply brine at the bottom of the brine pool (Anschutz and Blanc, 1996). The Gulf of Mexico contains numerous brine pools. The largest known is the Orca Basin, where a 90 km^2 brine pool in 2250 m water depth is fed by drainage from exposed salt deposits. The salt is toxic to life, but biogeochemical cycles operate at the interface with the overlying ocean (van Cappellen *et al.,* 1998). The Mediterranean also contains numerous large hypersaline basins (MEDRIFF Consortium, 1995).

  Taken together these naturally occurring brine pools provide examples of vast volumes of soluble, dense, fluids, hostile to marine life, on the sea floor. The number, volume, and extent of these pools exceed those for scenarios for CO_2 lake formation yet considered. There has been little study of the impact of the plumes emanating from these sources. These could be examined to yield information that may be relevant to environmental impacts of a lake of CO_2 on the ocean floor.
- *Changes over geological time:* In certain times in Earth's geological past the oceans may have contained more dissolved inorganic carbon and/or have had a lower *p*H.

  There is evidence of large-scale changes in calcifying organism distributions in the oceans in the geological record that may be related in changes in carbonate mineral saturation states in the surface ocean. For example, Barker and Elderfield (2002) demonstrated that glacial-interglacial changes in the shell weights of several species of planktonic foraminifera are negatively correlated with atmospheric CO_2 concentrations, suggesting a causal relationship.

  Cambrian CO_2 levels (i.e., about 500 million years ago) were as high as 5000 ppm and mean values decreased progressively thereafter (see. Dudley, 1998; Berner, 2002). Two to three times higher than extant ocean calcium levels ensured that calcification of, for example, coral reefs was enabled in paleo-oceans despite high CO_2 levels (Arp *et al.*, 2001). High performance animal life appeared in the sea only after atmospheric CO_2 began to diminish. The success of these creatures may have depended on the reduction of atmospheric CO_2 levels (reviewed by Pörtner *et al.*, 2004, 2005).

  CO_2 is also thought to have been a potential key factor in the late Permian/Triassic mass extinction, which affected corals, articulate brachiopods, bryozoans, and echinoderms to a larger extent than molluscs, arthropods and chordates (Knoll *et al.*, 1996; Berner, 2002; Bambach *et al.*, 2002). Pörtner *et al.* (2004) hypothesized that this may be due to the corrosive effect of CO_2 on heavily calcified skeletons. CO_2 excursions would have occurred in the context of large climate oscillations. Effects of temperature oscillations, hypoxia events and CO_2 excursions probably contributed to extinctions (Pörtner *et al.*, 2005, see section 6.7.3).

Table 6.3 Relationships between Δ*p*H, changes in pCO_2, and dissolved inorganic carbon concentration calculated for mean deep-sea conditions. Also shown are volumes of water needed to dilute 1 tCO_2 to the specified Δ*p*H, and the amount of CO_2 that, if uniformly distributed throughout the ocean, would produce this Δ*p*H.

pH change Δ*p*H	Increase in CO_2 partial pressure ΔpCO_2 (ppm)	Increase in dissolved inorganic carbon ΔDIC (μmol kg^{-1})	Seawater volume to dilute 1 tCO_2 to Δ*p*H (m^3)	$GtCO_2$ to produce Δ*p*H in entire ocean volume
0	0	0	-	-
-0.1	150	30	656,000	2000
-0.2	340	70	340,000	3800
-0.3	580	100	232,000	5600
-0.5	1260	160	141,000	9200
-1	5250	400	54,800	24,000
-2	57,800	3,260	6800	190,000
-3	586,000	31,900	700	1,850,000

while increasing the volume of water experiencing a lesser Δ*p*H. Further examples indicating the spatial extent of ocean chemistry change from added CO_2 are represented in Figures 6.11, 6.12, 6.13, 6.14, and 6.15.

On evolutionary time scales most extant animal life has adapted to, on average, low ambient CO_2 levels. Accordingly, extant animal life may rely on these low pCO_2 values and it is unclear to what extent species would be able to adapt to permanently elevated CO_2 levels. Exposure to high CO_2 levels and extremely acidic water can cause acute mortality, but more limited shifts in CO_2, *p*H, and carbonate levels can be tolerated at least temporarily. Studies of shallow water organisms have identified a variety of physiological mechanisms by which changes in the chemical environment can affect fauna. These mechanisms should also apply to organisms living in the deep ocean. However, knowing physiological mechanisms alone does not enable full assessment of impacts at ecosystem levels. Long-term effects, for intervals greater than the duration of the reproduction cycle or the lifespan of an individual, may be overlooked, yet may still drastically change an ecosystem.

Species living in the open ocean are exposed to low and relatively constant CO_2 levels, and thus may be sensitive to CO_2 exposure. In contrast, species dwelling in marine sediments, especially in the intertidal zone, are regularly exposed to CO_2 fluctuations and thus may be better adapted to high and variable CO_2 concentrations. Physiological mechanisms associated with CO_2 adaptation have been studied mostly in these organisms. They respond to elevated CO_2 concentrations by transiently diminishing energy turnover. However, such responses are likely become detrimental during long-term exposure, as reduced metabolism involves a reduction in physical activity, growth, and reproduction. Overall, marine invertebrates appear more sensitive than fish (Pörtner *et al*., 2005).

CO_2 effects have been studied primarily in fish and invertebrates from shallow waters, although some of these cover wide depth ranges down to below 2000 m or are adapted to cold temperatures (e.g., Langenbuch and Pörtner, 2003, 2004). Some *in situ* biological experiments used CO_2 in the deep ocean (See Box 6.6).

6.7.2 Physiological effects of CO_2

6.7.2.1 Effects of CO_2 on cold-blooded water breathing animals

Hypercapnia is the condition attained when an organism (or part thereof) is surrounded by high concentrations of CO_2. Under these conditions, CO_2 enters the organisms by diffusion across body and especially respiratory surfaces and equilibrates with all body compartments. This internal accumulation of CO_2 will be responsible for most of the effects observed in animals (reviewed by Pörtner and Reipschläger, 1996, Seibel and Walsh, 2001, Ishimatsu *et al*., 2004, 2005; Pörtner *et al*., 2004, 2005). Respiratory distress, narcosis, and mortality are the most obvious short-term effects at high CO_2 concentrations, but lower concentrations may have important effects on longer time scales. The CO_2 level to which an organism has acclimated may affect its acute critical CO_2 thresholds, however, the capacity to acclimate has not been investigated to date.

6.7.2.2 Effects of CO_2 versus pH

Typically, tolerance limits to CO_2 have been characterized by changes in ocean *p*H or pCO_2 (see Shirayama, 1995; Auerbach *et al*., 1997). However, changes in molecular CO_2, carbonate, and bicarbonate concentrations in ambient water and body fluids may each have specific effects on marine organisms (Pörtner and Reipschläger, 1996). In water breathers like fish or invertebrates CO_2 entry causes immediate disturbances in acid-base status, which need to be compensated for by ion exchange mechanisms. The acute effect of CO_2 accumulation is more severe than that of the reduction in *p*H or carbonate-ion concentrations. For example, fish larvae are more sensitive to low *p*H and high CO_2 than low *p*H and low CO_2 (achieved by addition of HCl with pCO_2 levels kept low by aeration; Ishimatsu *et al*., 2004).

CO_2 added to sea water will change the hydrogen ion concentration (*p*H). This change in hydrogen ion concentration may affect marine life through mechanisms that do not directly involve CO_2. Studies of effects of lowered *p*H (without concomitant CO_2 accumulation) on aquatic organisms have a

Box 6.6 *In-situ* observations of the response of deep-sea biota to added CO_2.

In-situ experiments concerning the sensitivity of deep and shallow-living marine biota to elevated carbon dioxide levels have been limited in scope. Significant CO_2 effects have been observed in experiments, consistent with the mechanisms of CO_2 action reported in Section 6.7.2. Some animals avoid CO_2 plumes, others do not.

Studies evaluating the behaviour and survival of deep-sea animals exposed to liquid CO_2 or to CO_2-rich sea water have been performed on the continental slope and rise off California. Experiments in which about 20–70 kg of liquid CO_2 were released in small corrals on the sea floor at 3600 m depth were used to measure the response of animals that came in contact with liquid CO_2, and to the dissolution plume emanating from CO_2 pools (Barry *et al*., 2004). Larger bottom-living animals collected from the sea floor were held in cages and placed at distances of 1–50 m from CO_2 pools. In addition, organisms living in the sediment were collected at a range of distances from CO_2 pools, both before CO_2 release and 1–3 months later.

The response of animals to direct contact with liquid CO_2 varied among species. Sea cucumbers (holothurians like Scotoplanes sp.) and brittle stars (ophiuroids, unidentified species) died immediately after contact with liquid CO_2 (Barry *et al*., 2005). A few individuals (<5 individuals) of deep-sea fish (grenadiers, *Coryphaenoides armatus*) that approached CO_2 pools and made contact with the fluid turned immediately and swam out of view. Other deep-sea experiments (Tamburri *et al*. 2000) evaluating the behavioural response of animals to a saturated CO_2 / sea water solution have shown that some scavenger species (deep-sea hagfish) will not avoid acidic, CO_2-rich seawater if chemical cues from decaying bait are also present. In fact, hagfish would maintain contact with the CO_2-rich / bait-scented plume long enough to be apparently ‘narcotized’ by the CO_2.

Survival rates of abyssal animals exposed to CO_2 dissolution plumes in these experiments varied with the range of *p*H perturbation and the distance from the CO_2 source. Abyssal animals held in cages or inhabiting sediments that were near (<1 m) CO_2 pools, and which were exposed episodically to large *p*H reduction (1–1.5 *p*H units) experienced high rates of mortality (>80%). Animals affected included small (meio-)fauna (flagellates, amoebae, nematodes; Barry *et al*., 2004) and larger (macro and mega-)fauna (Ampeliscid amphipod species, invertebrates like holothurians, echinoids, and fish like macrourids). Other fish like eelpout (zoarcids), however, all survived month-long exposure to episodic *p*H shifts of about –1.0 *p*H units. Animals held further (3–10 m) from CO_2 pools were exposed to mild episodic *p*H reductions (about 0.1 – 0.2 *p*H units) exhibited mortality rates were (about 20–50%) higher than at control sites (Barry *et al*., 2005).

It is unknown whether mortality was caused primarily by short-term exposure to large *p*H / CO_2 shifts or by chronic, milder *p*H perturbations. Tidal variation in current direction resulted in a highly variable exposure to *p*H perturbations with the most intense exposure to dissolution plumes when the current was flowing directly towards the study animals. During other tidal periods there was often no *p*H reduction, increasing the difficulty of interpreting these experiments.

Three controlled *in-situ* experiments were carried out at 2000 m in the Kumano Trough using a specially designed chamber (Figure 6.24; Ishida *et al*. 2005) to address the impact of 5,000 and 20,000 ppm rises in pCO_2 (with resulting *p*Hs of 6.8 and 6.3) on the abundance and diversity of bacteria and of small animals (nano- and meiobenthos). Significant impacts of elevated pCO_2 on meiobenthic organisms could not be found except for one case where the abundance of foraminifera decreased significantly within 3 days at 20,000 ppm. The abundance of nanobenthos decreased significantly in most cases, whereas the abundance of bacteria increased at 20,000 ppm (Figure 6.25).

In-situ studies of short-term effects of elevated CO_2 concentrations on deep-sea megafauna have been conducted using CO_2 released naturally from the Loihi Seamount (Hawaii) at depths of 1200 to 1300 m (Vetter and Smith, 2005). A submersible was used to manipulate baited traps and bait parcels in Loihi’s CO_2 plume to explore the effects of elevated CO_2 on typical deep-sea scavengers. Vent-specialist shrimp were attracted to the bait and proved to be pre-adapted to the high CO_2 levels found close to volcanic vents. Free swimming, amphipods, synaphobranchid eels, and hexanchid sharks avoided open bait parcels placed in the CO_2 plumes

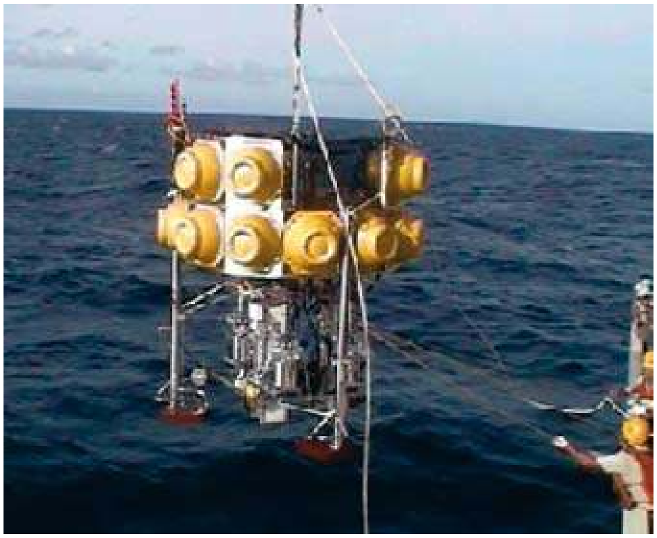

Figure 6.24 Experimental chamber going to the sea floor (Ishida *et al*. 2004). The bottom part houses a chamber that penetrates into the sediment. The top part houses electronics, pumps, valves, and water bags, that are used to control the CO_2 concentration inside the chamber, and to sample sea water in the chamber at designated times. At the time of recovery, the bottom of the chamber is closed, weights are released, and the system returns to the surface of the ocean using buoyancy provided by the glass bulbs (yellow structures around the top).

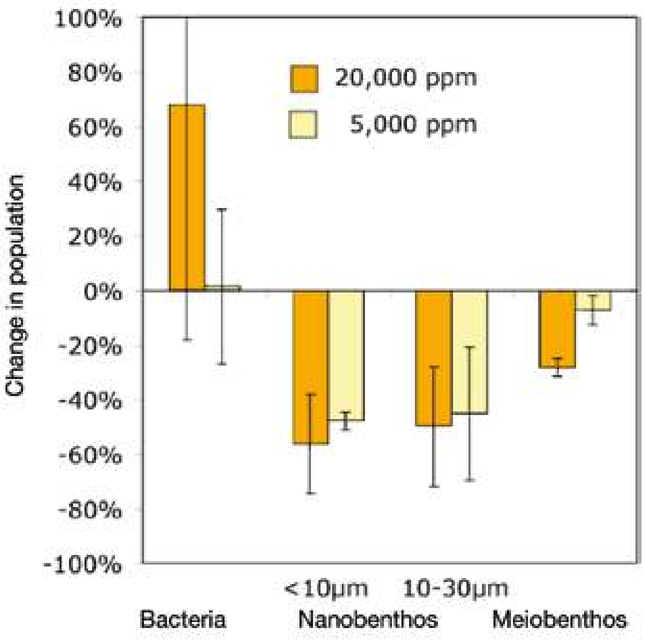

Figure 6.25 Preliminary investigations into the change of bacteria, nanobenthos and meiobenthos abundance after exposure to 20,000 and 5,000 ppm CO_2 for 77 to 375 hr during three experiments carried out at 2,000 m depth in Nankai Trough, north-western Pacific. Error bars represent one standard deviation (Ishida et al. 2005).

long history, with an emphasis on freshwater organisms (Wolff *et al*., 1988). Observed consequences of lowered water *p*H (at constant pCO_2) include changes in production/productivity patterns in algal and heterotrophic bacterial species, changes in biological calcification/ decalcification processes, and acute and sub-acute metabolic impacts on zooplankton species, ocean bottom species, and fish. Furthermore, changes in the *p*H of marine environments affect: (1) the carbonate system, (2) nitrification (Huesemann *et al*., 2002) and speciation of nutrients such as phosphate, silicate and ammonia (Zeebe and Wolf-Gladrow, 2001), and (3) speciation and uptake of essential and toxic trace elements. Observations and chemical calculations show that low *p*H conditions generally decrease the association of metals with particles and increase the proportion of biologically available free metals (Sadiq, 1992; Salomons and Forstner, 1984). Aquatic invertebrates take up both essential and non-essential metals, but final body concentrations of metals vary widely across invertebrates. In the case of many trace metals, enhanced bioavailability is likely to have toxicological implications, since free forms of metals are of the greatest toxicological significance (Rainbow, 2002).

6.7.2.3 Acute CO_2 sensitivity: oxygen transport in squid and fish

CO_2 accumulation and uptake can cause anaesthesia in many animal groups. This has been observed in deep-sea animals close to hydrothermal vents or experimental CO_2 pools. A narcotic effect of high, non-determined CO_2 levels was observed in deep-sea hagfish after CO_2 exposure *in situ* (Tamburri *et al*., 2000). Prior to anaesthesia high CO_2 levels can exert rapid effects on oxygen transport processes and thereby contribute to acute CO_2 effects including early mortality.

Among invertebrates, this type of CO_2 sensitivity may be highest in highly complex, high performance organisms like squid (reviewed by Pörtner *et al*., 2004). Blue-blooded squid do not possess red blood cells (erythrocytes) to protect their extracellular blood pigment (haemocyanin) from excessive *p*H fluctuations. Acute CO_2 exposure causes acidification of the blood, will hamper oxygen uptake and binding at the gills and reduce the amount of oxygen carried in the blood, limiting performance, and at high concentrations could cause death. Less oxygen is bound to haemocyanin in squid than is bound to haemoglobin in bony fish (teleosts). Jet-propulsion swimming of squid demands a lot of oxygen. Oxygen supply is supported by enhanced oxygen binding with rising blood *p*H (and reduced binding of oxygen with falling *p*H – a large Bohr effect[3]). Maximizing of oxygen transport in squid thus occurs by means of extracellular *p*H oscillations between arterial and venous blood. Therefore, finely controlled extracellular pH changes are important for oxygen transport. At high CO_2 concentrations, animals can asphyxiate because the blood cannot transport enough oxygen to support metabolic functions. In the most active open ocean squid (*Illex illecebrosus*), model calculations predict acute lethal effects with a rise in pCO_2 by 6500 ppm and a 0.25 unit drop in blood *p*H. However, acute CO_2 sensitivity varies between squid species. The less active coastal squid (*Loligo pealei*) is less sensitive to added CO_2.

In comparison to squid and other invertebrates, fish (teleosts) appear to be less sensitive to added CO_2, probably due to their lower metabolic rate, presence of red blood cells (erythrocytes containing haemoglobin) to carry oxygen, existence of a venous oxygen reserve, tighter epithelia, and more efficient acid-base regulation. Thus, adult teleosts (bony fish) exhibit a larger degree of independence from ambient CO_2. A number of tested shallow-water fish have shown relatively high tolerance to added CO_2, with short-term lethal limits of adult fish at a pCO_2 of about 50,000 to 70,000 ppm. European eels (*Anguilla anguilla*) displayed exceptional tolerance of acute hypercapnia up to 104,000 ppm (for review see Ishimatsu *et al*., 2004, Pörtner *et al*., 2004). The cause of death in fish involves a depression of cardiac functions followed by a collapse of oxygen delivery to tissues (Ishimatsu *et al*., 2004). With mean lethal CO_2 levels of 13,000 to 28,000 ppm, juveniles are more sensitive to acute CO_2 stress than adults. In all of these cases, the immediate cause of death appears to be entry of CO_2 into the organism (and not primarily some other *p*H-mediated effect).

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[3] The Bohr Effect is an adaptation in animals to release oxygen in the oxygen starved tissues in capillaries where respiratory carbon dioxide lowers blood pH. When blood *p*H decreases, the ability of the blood pigment to bind to oxygen decreases. This process helps the release of oxygen in the oxygen-poor environment of the tissues. Modified after ISCID Encyclopedia of Science and Philosophy. 2004. International Society for Complexity, Information, and Design. 12 October 2004 <http://www.iscid.org/encyclopedia/Bohr_Effect>.

Fish may be able to avoid contact to high CO_2 exposure because they possess highly sensitive CO_2 receptors that could be involved in behavioural responses to elevated CO_2 levels (Yamashita *et al*., 1989). However, not all animals avoid low pH and high concentrations of CO_2; they may actively swim into CO_2-rich regions that carry the odour of potential food (e.g., bait; Tamburri *et al*., 2000, Box 6.6).

Direct effects of dissolved CO_2 on diving marine air breathers (mammals, turtles) can likely be excluded since they possess higher pCO_2 values in their body fluids than water breathers and gas exchange is minimized during diving. They may nonetheless be indirectly affected through potential CO_2 effects on the food chain (see 6.7.5).

6.7.2.4 Deep compared with shallow acute CO_2 sensitivity

Deep-sea organisms may be less sensitive to high CO_2 levels than their cousins in surface waters, but this is controversial. Fish (and cephalopods) lead a sluggish mode of life with reduced oxygen demand at depths below 300 to 400 m. Metabolic activity of pelagic animals, including fish and cephalopods, generally decreases with depth (Childress, 1995; Seibel *et al*., 1997). However, Seibel and Walsh (2001) postulated that deep-sea animals would experience serious problems in oxygen supply under conditions of increased CO_2 concentrations. They refer to midwater organisms that may not be representative of deep-sea fauna; as residents of so-called ‘oxygen minimum layers’ they have special adaptations for efficient extraction of oxygen from low-oxygen waters (Sanders and Childress, 1990; Childress and Seibel, 1998).

6.7.2.5 Long-term CO_2 sensitivity

Long-term impacts of elevated CO_2 concentrations are more pronounced on early developmental than on adult stages of marine invertebrates and fish. Long-term depression of physiological rates may, over time scales of several months, contribute to enhanced mortality rates in a population (Shirayama and Thornton, 2002, Langenbuch and Pörtner, 2004). Prediction of future changes in ecosystem dynamics, structure and functioning therefore requires data on sub-lethal effects over the entire life history of organisms.

The mechanisms limiting performance and long-term survival under moderately elevated CO_2 levels are even less clear than those causing acute mortality. However, they appear more important since they may generate impacts in larger ocean volumes during widespread distribution of CO_2 at moderate levels on long time scales. In animals relying on calcareous exoskeletons, physical damage may occur under permanent CO_2 exposure through reduced calcification and even dissolution of the skeleton, however, effects of CO_2 on calcification processes in the deep ocean have not been studied to date. Numerous studies have demonstrated the sensitivity of calcifying organisms living in surface waters to elevated CO_2 levels on longer time scales (Gattuso *et al.* 1999, Reynaud *et al*., 2003, Feeley *et al*., 2004 and refs. therein). At least a dozen laboratory and field studies of corals and coralline algae have suggested reductions in calcification rates by 15–85% with a doubling of CO_2 (to 560 ppmv) from pre-industrial levels. Shirayama and Thornton (2002) demonstrated that increases in dissolved CO_2 levels to 560 ppm cause a reduction in growth rate and survival of shelled animals like echinoderms and gastropods. These findings indicate that previous atmospheric CO_2 accumulation may already be affecting the growth of calcifying organisms, with the potential for large-scale changes in surface-ocean ecosystem structure. Due to atmospheric CO_2 accumulation, global calcification rates could decrease by 50% over the next century (Zondervan *et al*., 2001), and there could be significant shifts in global biogeochemical cycles. Despite the potential importance of biogeochemical feedback induced by global change, our understanding of these processes is still in its infancy even in surface waters (Riebesell, 2004). Much less can be said about potential ecosystem shifts in the deep sea (Omori *et al*., 1998).

Long-term effects of CO_2 elevations identified in individual animal species affects processes in addition to calcification (reviewed by Ishimatsu *et al*., 2004, Pörtner and Reipschläger, 1996, Pörtner *et al*., 2004, 2005). In these cases, CO_2 entry into the organism as well as decreased water *p*H values are likely to have been the cause. Major effects occur through a disturbance in acid-base regulation of several body compartments. Falling *p*H values result and these affect many metabolic functions, since enzymes and ion transporters are only active over a narrow *p*H range. *p*H decreases from CO_2 accumulation are counteracted over time by an accumulation of bicarbonate anions in the affected body compartments (Heisler, 1986; Wheatly and Henry, 1992, Pörtner *et al*., 1998; Ishimatsu *et al*. 2004), but compensation is not always complete. Acid-base relevant ion transfer may disturb osmoregulation due to the required uptake of appropriate counter ions, which leads to an additional NaCl load of up to 10% in marine fish in high CO_2 environments (Evans, 1984; Ishimatsu *et al*., 2004). Long-term disturbances in ion equilibria could be involved in mortality of fish over long time scales despite more or less complete compensation of acidification.

Elevated CO_2 levels may cause a depression of aerobic energy metabolism, due to incomplete compensation of the acidosis, as observed in several invertebrate examples (reviewed by Pörtner *et al.* 2004, 2005). In one model organism, the peanut worm *Sipunculus nudus*, high CO_2 levels caused metabolic depression of up to 35% at 20,000 ppm pCO_2. A central nervous mechanism also contributed, indicated by the accumulation of adenosine in the nervous tissue under 10,000 ppm pCO_2. Adenosine caused metabolic depression linked to reduced ventilatory activity even more so when high CO_2 was combined with oxygen deficiency (anoxia; Lutz and Nilsson, 1997). Studies addressing the specific role of adenosine or other neurotransmitters at lower CO_2 levels or in marine fish during hypercapnia are not yet available.

The depression of metabolism observed under high CO_2 concentrations in marine invertebrates also includes inhibition of protein synthesis – a process that is fundamental to growth and reproduction. A CO_2 induced reduction of water *p*H to 7.3 caused a 55% reduction in growth of Mediterranean mussels (Michaelidis *et al.* 2005; for review see Pörtner *et al.* 2004, 2005). Fish may also grow slowly in high CO_2 waters. Reduced growth was observed in juvenile white sturgeon (Crocker and Cech, 1996). In this case, the stimulation of ventilation and the associated increase in oxygen consumption indicated a shift in energy budget towards maintenance metabolism, which occurred at the expense of growth. This effect was associated with reductions in foraging activity. A harmful influence of CO_2 on reproductive performance was found in two species of marine copepods (*Acartia steuri, Acartia erythrea*) and sea urchins (*Hemicentrotus purcherrimus, Echinometra mathaei*). While survival rates of adult copepods were not affected during 8 days at $p\mathrm{CO}_2$ up to 10,000 ppm, egg production and hatching rates of eggs were significantly reduced concomitant to an increased mortality of young-stage larvae seen at water *p*H 7.0 (Kurihara *et al*., 2004). In both sea urchin species tested, fertilization rates decreased with $p\mathrm{CO}_2$ rising above1000 ppm (below water *p*H 7.6; Kurihara *et al*., 2004). Hatching and survival of fish larvae also declined with water $p\mathrm{CO}_2$ and exposure time in all examined species (Ishimatsu *et al*., 2004).

6.7.3 From physiological mechanisms to ecosystems

CO_2 effects propagate from molecules via cells and tissues to whole animals and ecosystems (Figure 6.26; Table 6.4). Organisms are affected by chemistry changes that modulate crucial physiological functions. The success of a species can depend on effects on the most sensitive stages of its life cycle (e.g., egg, larvae, adult). Effects on molecules, cells, and tissues thus integrate into whole animal effects (Pörtner *et al*., 2004), affecting growth, behaviour, reproduction, and development of eggs and larvae. These processes then determine the ecological success (fitness) of a species, which can also depend on complex interaction among species. Differential effects of chemistry changes on the various species thus affect the entire ecosystem. Studies of CO_2 susceptibility and affected mechanisms in individual species (Figure 6.26) support development of a cause and effect understanding for an entire ecosystem's response to changes in ocean chemistry, but need to be complemented by field studies of ecosystem consequences.

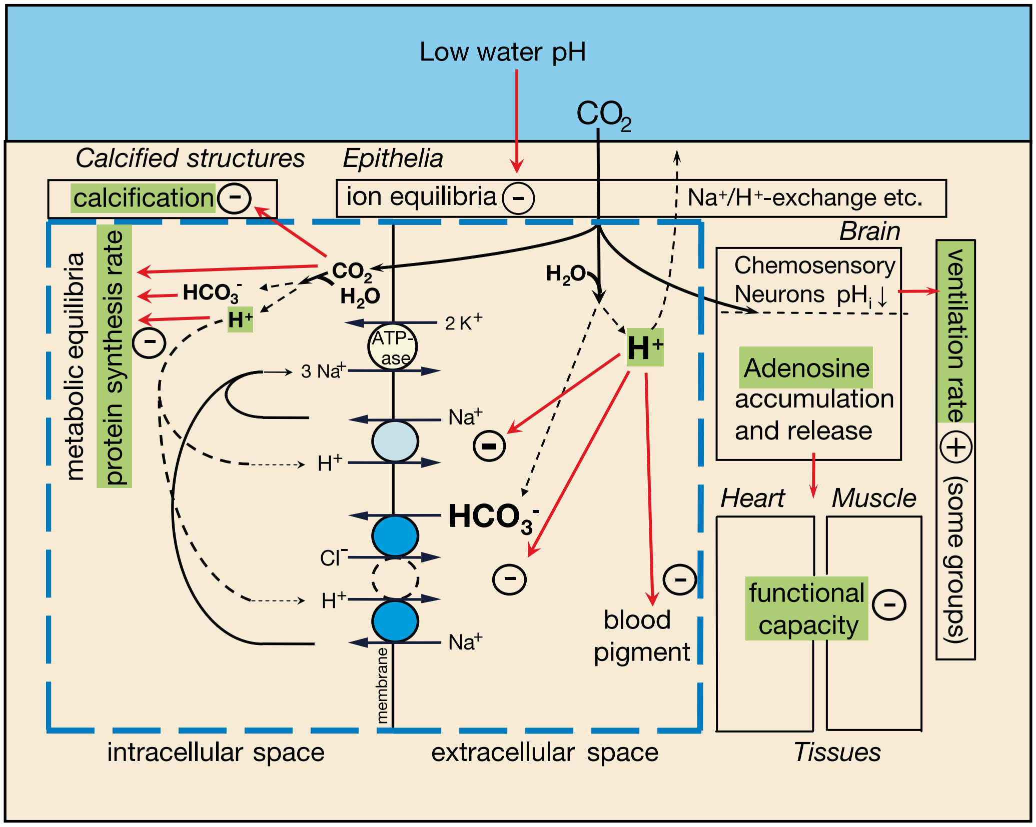

Figure 6.26 Effects of added CO_2 at the scale of molecule to organism and associated changes in proton (H^+), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) levels in a generalized and simplified marine invertebrate or fish. The blue region on top refers to open water; the tan region represents the organism. Generalized cellular processes are depicted on the left and occur in various tissues like brain, heart or muscle; depression of these processes has consequences (depicted on the right and top). Under CO_2 stress, whole animal functions, like growth, behaviours or reproduction are depressed (adopted from Pörtner et al., 2005, – or + denotes a depression or stimulation of the respective function). Black arrows reflect diffusive movement of CO_2 between compartments. Red arrows reflect effective factors, CO_2, H^+, HCO_3^- that modulate functions. Shaded areas indicate processes relevant for growth and energy budget.

Table 6.4 Physiological and ecological processes affected by CO_2 (note that listed effects on phytoplankton are not relevant in the deep sea, but may become operative during large-scale mixing of CO_2). Based on reviews by Heisler, 1986, Wheatly and Henry, 1992, Claiborne et al., 2002, Langdon et al., 2003 Shirayama, 2002, Kurihara et al., 2004, Ishimatsu et al., 2004, 2005, Pörtner et al. 2004, 2005, Riebesell, 2004, Feeley et al., 2004 and references therein.

Affected processes	**Organisms tested**
Calcification	• Corals • Calcareous benthos and plankton
Acid-base regulation	• Fish • Sipunculids • Crustaceans
Mortality	• Scallops • Fish • Copepods • Echinoderms/gastropods • Sipunculids
N-metabolism	• Sipunculids
Protein biosynthesis	• Fish • Sipunculids • Crustaceans
Ion homeostasis	• Fish, crustaceans • Sipunculids
Growth	• Crustaceans • Scallops • Mussels • Fish • Echinoderms/gastropods
Reproductive performance	• Echinoderms • Fish • Copepods
Cardio-respiratory functions	• Fish
Photosynthesis	• Phytoplankton
Growth and calcification	
Ecosystem structure	
Feedback on biogeochemical cycles (elemental stoichiometry C:N:P, DOC exudation)	

Tolerance thresholds likely vary between species and phyla, but still await quantification for most organisms. Due to differential sensitivities among and within organisms, a continuum of impacts on ecosystems is more likely than the existence of a well-defined threshold beyond which CO_2 cannot be tolerated. Many species may be able to tolerate transient CO_2 fluctuations, but may not be able to settle and thrive in areas where CO_2 levels remain permanently elevated. At concentrations that do not cause acute mortality, limited tolerance may include reduced capacities of higher functions, that is added CO_2 could reduce the capacity of growth and reproduction, or hamper resistance to infection (Burnett, 1997). It could also reduce the capacity to attack or escape predation, which would have consequences for the organism's food supply and thus overall fitness with consequences for the rest of the ecosystem.

Complex organisms like animals proved to be more sensitive to changing environmental conditions like temperature extremes than are simpler, especially unicellular, organisms (Pörtner, 2002). It is not known whether animals are also more sensitive to extremes in CO_2. CO_2 affects many physiological mechanisms that are also affected by temperature and hypoxia (Figure 6.26). Challenges presented by added CO_2 could lower long-term resistance to temperature extremes and thus narrow zoogeographical distribution ranges of affected species (Reynaud *et al.*, 2003, Pörtner *et al.*, 2005).

At the ecosystem level, few studies carried out in surface oceans report that species may benefit under elevated CO_2 levels. Riebesell (2004) summarized observations in surface ocean mesocosms under glacial (190 ppm) and increased CO_2 concentrations (790 ppm). High CO_2 concentrations caused higher net community production of phytoplankton. Diatoms dominated under glacial and elevated CO_2 conditions, whereas *Emiliania huxleyi* dominated under present CO_2 conditions. This example illustrates how species that are less sensitive to added CO_2 could become dominant in a high CO_2 environment, in this case due to stimulation of photosynthesis in resource limited phytoplankton species (Riebesell 2004). These conclusions have limited applicability to the deep sea, where animals and bacteria dominate. In animals, most processes are expected to be depressed by high CO_2 and low *p*H levels (Table 6.4).

6.7.4 Biological consequences for water column release scenarios

Overall, extrapolation from knowledge mostly available for surface oceans indicates that acute CO_2 effects (e.g., narcosis, mortality) will only occur in areas where pCO_2 plumes reach significantly above 5000 ppm of atmospheric pressure (in the most sensitive squid) or above 13,000 or 40,000 ppm for juvenile or adult fish, respectively. Such effects are thus expected at CO_2 increases with $\Delta pH < -1.0$ for squid. According to the example presented in Figure 6.12, a towed pipe could avoid *p*H changes of this magnitude, however a fixed pipe without design optimization would produce a volume of several km^3 with this *p*H change for an injection rate of 100 kg s^{-1}. Depending on the scale of injection such immediate effects may thus be chosen to be confined to a small region of the ocean (Figures 6.13 and 6.14).

Available knowledge of CO_2 effects and underlying mechanisms indicate that effects on marine fauna and their ecosystems will likely set in during long-term exposure to pCO_2 of more than 400 to 500 ppm or associated moderate *p*H changes (by about 0.1–0.3 units), primarily in marine invertebrates (Pörtner *et al.* 2005) and, possibly, unicellular organisms. For injection at a rate of 0.37 $GtCO_2$ yr^{-1} for 100 years (Figure 6.14), such critical *p*H shifts would occur in less than 1% of the total ocean volume by the end of this period. However, baseline *p*H shifts by 0.2 to 0.4 *p*H-units expected from the WRE550 stabilization scenario already reach that magnitude of change. Additional long-term repeated large-scale global injection of 10% of the CO_2 originating from 18,000 $GtCO_2$ fossil fuel would cause an extension of these *p*H shifts from the surface ocean to significantly larger (deeper) fractions of the ocean by 2100 to 2300 (Figure 6.15). Finally, large-scale ocean disposal of all of the CO_2 would lead to *p*H decreases of more than 0.3 and associated long-term effects in most of the ocean. Expected effects will include a reduction in the productivity of calcifying organisms leading to higher ratios of non-calcifiers over calcifiers (Pörtner *et al.*, 2005).

Reduced capacities for growth, productivity, behaviours, and reduced lifespan imply a reduction in population densities and productivities of some species, if not reduced biodiversity. Food chain length and composition may be reduced associated with reduced food availability for high trophic levels. This may diminish resources for local or global fisheries. The suggested scenarios of functional depression also include a CO_2 induced reduction in tolerance to thermal extremes, which may go hand in hand with reduced distribution ranges as well as enhanced geographical distribution shifts. All of these expectations result from extrapolations of current physiological and ecological knowledge and require verification in experimental field studies. The capacity of ecosystems to compensate or adjust to such CO_2 induced shifts is also unknown. Continued research efforts could identify critical mechanisms and address the potential for adaptation on evolutionary time scales.

6.7.5 Biological consequences associated with CO_2 lakes

Strategies that release liquid CO_2 close to the sea floor will be affecting two ecosystems: the ecosystem living on the sea floor, and deep-sea ecosystem living in the overlying water. Storage as a topographically confined 'CO_2 lake' would limit immediate large-scale effects of CO_2 addition, but result in the mortality of most organisms under the lake that are not able to flee and of organisms that wander into the lake. CO_2 will dissolve from the lake into the bottom water, and this will disperse around the lake, with effects similar to direct release of CO_2 into the overlying water. According to the scenarios depicted in Figures 6.11 and 6.12 for CO_2 releases near the sea floor, *p*H reductions expected in the near field are well within the scope of those expected to exert significant effect on marine biota, depending on the length of exposure**.**

6.7.6 Contaminants in CO_2 streams

The injection of large quantities of CO_2 into the deep ocean will itself be the topic of environmental concern, so the matter of possible small quantities of contaminants in the injected material is of additional but secondary concern. In general there are already stringent limits on contaminants in CO_2 streams due to human population concerns, and technical pipeline considerations. The setting of any additional limits for ocean disposal cannot be addressed with any certainty at this time.

There are prohibitions in general against ocean disposal; historical concerns have generally focused on heavy metals, petroleum products, and toxic industrial chemicals and their breakdown products.

A common contaminant in CO_2 streams is H_2S. There are very large sources of H_2S naturally occurring in the ocean: many marine sediments are anoxic and contain large quantities of sulphides; some large ocean basins (the Black Sea, the Cariaco Trench etc.) are anoxic and sulphidic. As a result ocean ecosystems that have adapted to deal with sulphide and sulphur-oxidizing bacteria are common throughout the worlds oceans. Nonetheless the presence of H_2S in the disposal stream would result in a lowering of local dissolved oxygen levels, and have an impact on respiration and performance of higher marine organisms.

6.7.7 Risk management

There is no peer-reviewed literature directly addressing risk management for intentional ocean carbon storage; however, there have been risk management studies related to other uses of the ocean. Oceanic CO_2 release carries no expectation of risk of catastrophic atmospheric degassing such as occurred at Lake Nyos (Box 6.7). Risks associated with transporting CO_2 to depth are discussed in Chapter 4 (Transport).

It may be possible to recover liquid CO_2 from a lake on the ocean floor. The potential reversibility of the production of CO_2 lakes might be considered a factor that diminishes risk associated with this option.

6.7.8 Social aspects; public and stakeholder perception

The study of public perceptions and perceived acceptability of intentional CO_2 storage in the ocean is at an early stage and comprises only a handful of studies (Curry *et al.*, 2005; Gough *et al.*, 2002; Itaoka *et al.*, 2004; Palmgren *et al.*, 2004). Issues crosscutting public perception of both geological and ocean storage are discussed in Section 5.8.5.

All studies addressing ocean storage published to date have shown that the public is largely uninformed about ocean carbon storage and thus holds no well-developed opinion. There is very little awareness among the public regarding intentional or unintentional ocean carbon storage. For example, Curry *et al.* (2005) found that the public was largely unaware of the role of the oceans in absorbing anthropogenic carbon dioxide released to the atmosphere. In the few relevant studies conducted thus far, the public has expressed more reservations regarding ocean carbon CO_2 storage than for geological CO_2 storage.

Education can affect the acceptance of ocean storage options. In a study conducted in Tokyo and Sapporo, Japan (Iatoka *et al*, 2004), when members of the public, after receiving some basic information, were asked to rate ocean and geologic storage options on a 1 to 5 scale (1 = no, 5 = yes) the mean rating for dilution-type ocean storage was 2.24, lake-type ocean storage was rated at 2.47, onshore geological storage was rated at 2.57, and offshore geological storage was rated at

Box 6.7 Lake Nyos and deep-sea carbon dioxide storage.

About 2 million tonnes of CO_2 gas produced by volcanic activity were released in one night in 1986 by Lake Nyos, Cameroon, causing the death of at least 1700 people (Kling *et al.*, 1994). Could CO_2 released in the deep sea produce similar catastrophic release at the ocean surface?

Such a catastrophic degassing involves the conversion of dissolved CO_2 into the gas phase. In the gas phase, CO_2 is buoyant and rises rapidly, entraining the surrounding water into the rising plume. As the water rises, CO_2 bubbles form more readily. These processes can result in the rapid release of CO_2 that has accumulated in the lake over a prolonged period of magmatic activity.

Bubbles of CO_2 gas can only form in sea water shallower than about 500 m when the partial pressure of CO_2 in sea water exceeds the ambient total pressure. Most release schemes envision CO_2 release deeper than this. CO_2 released below 3000 m would tend to sink and then dissolve into the surrounding seawater. CO_2 droplets released more shallowly generally dissolve within a few 100 vertical metres of release.

The resulting waters are too dilute in CO_2 to produce partial CO_2 pressures exceeding total ambient pressure, thus CO_2 bubbles would not form. Nevertheless, if somehow large volumes of liquid CO_2 were suddenly transported above the liquid-gas phase boundary, there is a possibility of a self-accelerating regime of fluid motion that could lead to rapid degassing at the surface. The disaster at Lake Nyos was exacerbated because the volcanic crater confined the CO_2 released by the lake; the open ocean surface does not provide such topographic confinement. Thus, there is no known mechanism that could produce an unstable volume of water containing 2 $MtCO_2$ at depths shallower than 500 m, and thus no mechanism known by which ocean carbon storage could produce a disaster like that at Lake Nyos.

2.75. After receiving additional information from researchers, the mean rating for dilution-type and lake-type ocean storage increased to 2.42 and 2.72, respectively, while the mean ratings for onshore and offshore geologic storage increased to 2.65 and 2.82, respectively. In a similar conducted study in Pittsburgh, USA, Palmgren *et al.* (2004) found that when asked to rate ocean and geologic storage on a 1 to 7 scale (1 = completely oppose, 7 = completely favour) respondents' mean rating was about 3.2 for ocean storage and about 3.5 for geological storage. After receiving information selected by the researchers, the respondents changed their ratings to about 2.4 for ocean storage and 3.0 for geological storage. Thus, in the Itaoka *et al.* (2004) study the information provided by the researchers increased the acceptance of all options considered whereas in the Study of Palmgren *et al.* (2004) the information provided by the researchers decreased the acceptance of all options considered. The differences could be due to many causes, nevertheless, they suggest that the way information is provided by researchers could affect whether the added information increases or decreases the acceptability of ocean storage options.

Gough *et al.* (2002) reported results from discussions of carbon storage from two unrepresentative focus groups comprising a total of 19 people. These focus groups also preferred geological storage to ocean storage; this preference appeared to be based, 'not primarily upon concerns for the deep-sea ecological environment', but on 'the lack of a visible barrier to prevent CO_2 escaping' from the oceans. Gough *et al.* (2002) notes that 'significant opposition' developed around a proposed ocean CO_2 release experiment in the Pacific Ocean (see Section 6.2.1.2).

6.8 Legal issues

6.8.1 International law

Please refer to Sections 5.8.1.1 (*Sources and nature of international obligations*) and 5.8.1.2 (*Key issues in the application of the treaties to* CO_2 *storage*) for the general position of both geological and ocean storage of CO_2 under international law. It is necessary to look at and interpret the primary sources, the treaty provisions themselves, to determine the permissibility or otherwise of ocean storage. Some secondary sources, principally the 2004 OSPAR Jurists Linguists' paper containing the States Parties' interpretation of the Convention (considered in detail in Section 5.8.1.3) and conference papers prepared for the IEA workshop in 1996, contain their authors' individual interpretations of the treaties.

McCullagh (1996) considered the international legal control of ocean storage, and found that, whilst the UN Framework Convention on Climate Change (UNFCCC) encourages the use of the oceans as a reservoir for CO_2, the UN Convention on the Law of the Sea (UNCLOS) is ambiguous in its application to ocean storage. Whilst ocean storage will reduce CO_2 emissions and combat climate change, to constitute an active use of sinks and reservoirs as required by the UNFCCC, ocean storage would need to be the most cost-effective mitigation option. As for UNCLOS, it is unclear whether ocean storage will be allowable in all areas of the ocean, but provisions on protecting and preserving the marine environment will be applicable if CO_2 is deemed to be 'pollution' under the Convention (which will be so, as the large quantity of CO_2 introduced is likely to cause harm to living marine resources). In fulfilling their obligation to prevent, reduce and control pollution of the marine environment, states must act so as not to transfer damage or hazards from one area to another or transform one type of pollution into another, a requirement that could be relied upon by proponents and opponents alike.

Churchill (1996) also focuses on UNCLOS in his assessment of the international legal issues, and finds that the consent of the coastal state would be required if ocean storage occurred in that state's territorial sea (up to12 miles from the coast). In that state's Exclusive Economic Zone (up to 200 miles), the storage of CO_2 via a vessel or platform (assuming it constituted 'dumping' under the Convention) would again require the consent of that state. Its discretion is limited by its obligation to have due regard to the rights and duties of other states in the Exclusive Economic Zone under the Convention, by other treaty obligations (London and OSPAR) and the Convention's general duty on parties not to cause damage by pollution to other states' territories or areas beyond their national jurisdiction. He finds that it is uncertain whether the definition of 'dumping' would apply to use of a pipeline system from land for ocean storage, but, in any event, concludes that the discharge of CO_2 from a pipeline will, in many circumstances, constitute pollution and thus require the coastal state to prevent, reduce and control such pollution from land-based sources. But ocean storage by a pipeline from land into the Exclusive Economic Zone will not fall within the rights of a coastal or any other state and any conflict between them will be resolved on the basis of equity and in the light of all the relevant circumstances, taking into account the respective importance of the interests involved to the parties as well as to the international community as a whole. He finds that coastal states do have the power to regulate and control research in their Exclusive Economic Zones, although such consent is not normally withheld except in some cases.

As for the permissibility of discharge of CO_2 into the high seas (the area beyond the Exclusive Economic Zone open to all states), Churchill (1996) concludes that this will depend upon whether the activity is a freedom of the high sea and is thus not prohibited under international law, and finds that the other marine treaties will be relevant in this regard.

Finally, the London Convention is considered by Campbell (1996), who focuses particularly on the 'industrial waste' definition contained in Annex I list of prohibited substances, but does not provide an opinion upon whether CO_2 is covered by that definition 'waste materials generated by manufacturing or processing operations', or indeed the so-called reverse list exceptions to this prohibition, or to the general prohibition under the 1996 Protocol.

6.8.2 National laws

6.8.2.1 Introduction

CO_2 ocean storage, excluding injection from vessels, platforms or other human-made structures into the subseabed to which the Assessment made in Section 5.8 applies, is categorized into the following two types according to the source of injection of the CO_2 (land or sea) and its destination (sea): (1) injection from land (via pipe) into the seawater; (2) injection from vessels, platforms or other human-made structures into sea water (water column, ocean floor).

States are obliged to comply with the provisions of international law mentioned above in Section 6.8.1, in particular treaty law to which they are parties. States have to implement their international obligations regarding CO_2 ocean storage either by enacting relevant national laws or revising existing ones. There have been a few commentaries and papers on the assessment of the legal position of ocean storage at national level. However, the number of countries covered has been quite limited. Summaries of the assessment of the national legal issues having regard to each type of storage mentioned above to be considered when implementing either experimental or fully-fledged ocean storage of CO_2 are provided below.

With regard to the United States, insofar as CO_2 from a fossil-fuel power plant is considered industrial waste, it would be proscribed under the Ocean Dumping Ban Act of 1988. The Marine Protection, Research, and Sanctuaries Act of 1972 (codified as 33 U.S.C. 1401–1445, 16 U.S.C. 1431–1447f, 33 U.S.C. 2801–2805), including the amendments known as the Ocean Dumping Ban Act of 1988, has the aim of regulating intentional ocean disposal of materials, while authorizing related research. The Ocean Dumping Ban Act of 1988 placed a ban on ocean disposal of sewage sludge and industrial wastes after 31 December 1991.

The US Environmental Protection Agency (US EPA) specified protective criteria for marine waters, which held *p*H to a value between 6.5 and 8.5, with a limit on overall excursion of no more than 0.2 *p*H units outside the naturally occurring range (see: Train, 1979). Much of the early work on marine organisms reflected concerns about the dumping of industrial acid wastes (e.g., acid iron wastes from TiO_2 manufacture) into marine waters. For the most part, however, these studies failed to differentiate between true *p*H effects and the effects due to CO_2 liberated by the introduction of acid into the test systems.

6.8.2.2 Injection from land (via pipe) into seawater

States can regulate the activity of injection within their jurisdiction in accordance with their own national rules and regulations. Such rules and regulations would be provided by, if any, the laws relating to the treatment of high-pressure gases, labour health and safety, control of water pollution, dumping at sea, waste disposal, biological diversity, environmental impact assessment etc. It is, therefore, necessary to check whether planned activities of injection fall under the control of relevant existing rules and regulations.

6.8.2.3 Injection from vessels, platforms or other humanmade structures into sea water (water column, ocean floor)

It is necessary to check whether the ocean storage of CO_2 is interpreted as 'dumping' of 'industrial waste' by relevant national laws, such as those on dumping at sea or waste disposal, because this could determine the applicability of the London Convention and London Protocol (see Section 6.8.1). Even if ocean storage is not prohibited, it is also necessary to check whether planned activities will comply with the existing relevant classes of rules and regulations, if any, mentioned above.

Table 6.5 Ocean storage cost estimate for CO_2 transport and injection at 3000 m depth from a floating platform. Scenario assumes three pulverized coal fired power plants with a net generation capacity of 600 MWe each transported either 100 or 500 km by a CO_2 tanker ship of 80,000 m^3 capacity to a single floating discharge platform.

Ship transport distance	100 km	500 km
Onshore CO_2 Storage (US\$/tCO_2 shipped)	3.3	3.3
Ship transport to injection platform (US\$/tCO_2 shipped)	2.9	4.2
Injection platform, pipe and nozzle (US\$/tCO_2 shipped)	5.3	5.3
Ocean storage cost (US\$/tCO_2 shipped)	11.5	12.8
Ocean storage cost (US\$/tCO_2 net stored)	11.9	13.2

6.9. Costs

6.9.1 Introduction

Studies on the engineering cost of ocean CO_2 storage have been published for cases where CO_2 is transported from a power plant located at the shore by either ship to an offshore injection platform or injection ship (Section 6.9.2), or pipeline running on the sea floor to an injection nozzle (Section 6.9.3). Costs considered in this section include those specific to ocean storage described below and include the costs of handling of CO_2 and transport of CO_2 offshore, but not costs of onshore transport (Chapter 4).

6.9.2 Dispersion from ocean platform or moving ship

Costs have been estimated for ship transport of CO_2 to an injection platform, with CO_2 injection from a vertical pipe into mid- to deep ocean water, or a ship trailing an injection pipe (Akai *et al*., 2004; IEA-GHG, 1999; Ozaki, 1997; Akai *et al*., 1995; Ozaki *et al*., 1995). In these cases, the tanker ship transports liquid CO_2 at low temperature (–55 to –50ºC) and high pressure (0.6 to 0.7 MPa).

Table 6.5 shows storage costs for cases (Akai *et al*., 2004) of ocean storage using an injection platform. In these cases, CO_2 captured from three power plants is transported by a CO_2 tanker ship to a single floating discharge platform for injection at a depth of 3000 m. The cost of ocean storage is the sum of three major components: tank storage of CO_2 onshore awaiting shipping; shipping of CO_2; and the injection platform pipe and nozzle. The sum of these three components is 11.5 to 12.8 US\$/tCO_2 shipped 100 to 500 km. Assuming an emission equal to 3% of shipped CO_2 from boil-off and fuel consumption, the estimated cost is 11.9 to 13.2 US\$/tCO_2 net stored.

Liquid CO_2 could be delivered by a CO_2 transport ship to the injection area and then transferred to a CO_2 injection ship, which would tow a pipe injecting the CO_2 into the ocean at a depth of 2,000 to 2,500 m. Estimated cost of ocean storage (Table 6.6) is again the sum of three major components: tank storage of CO_2 onshore awaiting shipping; shipping of CO_2; and the injection ship, pipe and nozzle (Table 6.6; Akai *et al*., 2004). The sum of these three components is 13.8 to 15.2 US\$/tCO_2 shipped 100 to 500 km. Assuming an emission equal to 3% of shipped CO_2 from boil-off and fuel consumption, the estimated cost is 14.2 to 15.7 US\$/tCO_2 net stored.

6.9.3 Dispersion by pipeline extending from shore into shallow to deep water

Compared with the ship transport option (6.9.2), pipeline transport of CO_2 is estimated to cost less for transport over shorter distances (e.g., 100 km) and more for longer distances (e.g., 500 km), since the cost of ocean storage via pipeline scales with pipeline length.

The cost for transporting CO_2 from a power plant located at the shore through a pipeline running on the sea floor to an injection nozzle has been estimated by IEA-GHG (1994) and Akai *et al*. (2004). In the recent estimate of Akai *et al*. (2004), CO_2 captured from a pulverized coal fired power plant with a net generation capacity of 600 MW_e is transported either 100 or 500 km by a CO_2 pipeline for injection at a depth of 3000 m at a cost of 6.2 US\$/tCO_2 net stored (100 km case) to 31.1 US\$/tCO_2 net stored (500 km case).

There are no published cost estimates specific to the production of a CO_2 lake on the sea floor; however, it might be reasonable to assume that there is no significant difference between the cost of CO_2 lake production and the cost of water column injection given this dominance of pipeline costs.

Table 6.6 Ocean storage cost estimate for CO_2 transport and injection at 2000-2500 m depth from a moving ship.

Ship transport distance	100 km	500 km
Onshore CO_2 Storage (US\$/tCO_2 shipped)	2.2	2.2
Ship transport to injection ship(US\$/tCO_2 shipped)	3.9	5.3
Injection ship, pipe and nozzle (US\$/tCO_2 shipped)	7.7	7.7
Ocean storage cost (US\$/tCO_2 shipped)	13.8	15.2
Ocean storage cost (US\$/tCO_2 net stored)	14.2	15.7

6.9.4 Cost of carbonate neutralization approach

Large-scale deployment of carbonate neutralization would require a substantial infrastructure to mine, transport, crush, and dissolve these minerals, as well as substantial pumping of seawater, presenting advantages for coastal power plants near carbonate mineral sources.

There are many trade-offs to be analyzed in the design of an economically optimal carbonate-neutralization reactor along the lines of that described by Rau and Caldeira (1999). Factors to be considered in reactor design include water flow rate, gas flow rate, particle size, pressure, temperature, hydrodynamic conditions, purity of reactants, gas-water contact area, etc. Consideration of these factors has led to preliminary cost estimates for this concept, including capture, transport, and energy penalties, of 10 to 110 US$/t$CO_2$ net stored (Rau and Caldeira, 1999).

6.9.5 Cost of monitoring and verification

The cost of a monitoring and verification program could involve deploying and maintaining a large array of sensors in the ocean. Technology exists to conduct such monitoring, but a significant fraction of the instrument development and production is limited to research level activities. No estimate of costs for near-field monitoring for ocean storage have been published, but the costs of limited near-field monitoring would be small compared to the costs of ocean storage in cases of the scale considered in 6.9.2 and 6.9.3. Far field monitoring can benefit from international research programs that are developing global monitoring networks.

6.10 Gaps in knowledge

The science and technology of ocean carbon storage could move forward by addressing the following major gaps:

- *Biology and ecology:* Studies of the response of biological systems in the deep sea to added CO_2, including studies that are longer in duration and larger in scale than yet performed.

- Research facilities: Research facilities where ocean storage concepts (e.g., release of CO_2 from a fixed pipe or ship, or carbonate-neutralization approaches) can be applied and their effectiveness and impacts assessed in situ at small-scale on a continuing basis for the purposes of both scientific research and technology development.

- *Engineering:* Investigation and development of technology for working in the deep sea, and the development of pipes, nozzles, diffusers, etc., which can be deployed in the deep sea with assured flow and be operated and maintained cost-effectively.

- *Monitoring:* Development of techniques and sensors to detect CO_2 plumes and their biological and geochemical consequences.

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7

Mineral carbonation and industrial uses of carbon dioxide

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EXECUTIVE SUMMARY

This Chapter describes two rather different options for carbon dioxide (CO_2) storage: (i) the fixation of CO_2 in the form of inorganic carbonates, also known as 'mineral carbonation' or 'mineral sequestration', and (ii) the industrial utilization of CO_2 as a technical fluid or as feedstock for carbon containing chemicals.

In the case of mineral carbonation (see Section 7.2), captured CO_2 is reacted with metal-oxide bearing materials, thus forming the corresponding carbonates and a solid byproduct, silica for example. Natural silicate minerals can be used in artificial processes that mimic natural weathering phenomena, but also alkaline industrial wastes can be considered. The products of mineral carbonation are naturally occurring stable solids that would provide storage capacity on a geological time scale. Moreover, magnesium and calcium silicate deposits are sufficient to fix the CO_2 that could be produced from the combustion of all fossil fuels resources. To fix a tonne of CO_2 requires about 1.6 to 3.7 tonnes of rock. From a thermodynamic viewpoint, inorganic carbonates represent a lower energy state than CO_2; hence the carbonation reaction is exothermic and can theoretically yield energy. However, the kinetics of natural mineral carbonation is slow; hence all currently implemented processes require energy intensive preparation of the solid reactants to achieve affordable conversion rates and/or additives that must be regenerated and recycled using external energy sources. The resulting carbonated solids must be stored at an environmentally suitable location. The technology is still in the development stage and is not yet ready for implementation. The best case studied so far is the wet carbonation of the natural silicate olivine, which costs between 50 and 100 US$/t$CO_2$ stored and translates into a 30-50% energy penalty on the original power plant. When accounting for the 10-40% energy penalty in the capture plant as well, a full CCS system with mineral carbonation would need 60-180% more energy than a power plant with equivalent output without CCS.

The industrial use of CO_2 (see Section 7.3) as a gas or a liquid or as feedstock for the production of chemicals could contribute to keeping captured CO_2 out of the atmosphere by storing it in anthropogenic carbon products. Industrial uses provide a carbon sink, as long as the pool size keeps growing and the lifetime of the compounds produced is long. Neither prerequisite is fulfilled in practice, since the scale of CO_2 utilization is small compared to anthropogenic CO_2 emissions, and the lifetime of the chemicals produced is too short with respect to the scale of interest in CO_2 storage. Therefore, the contribution of industrial uses of captured CO_2 to the mitigation of climate change is expected to be small.

7.1 Introduction

This chapter deals with: (i) the fixation of CO_2 in the form of inorganic carbonates, also known as 'mineral carbonation' or 'mineral sequestration' that is discussed in Section 7.2, and (ii) the industrial uses of CO_2 as a technical fluid or as feedstock for carbon containing chemicals, which is the subject of Section 7.3.

7.2 Mineral carbonation

7.2.1 Definitions, system boundaries and motivation

Mineral carbonation is based on the reaction of CO_2 with metal oxide bearing materials to form insoluble carbonates, with calcium and magnesium being the most attractive metals. In nature such a reaction is called silicate weathering and takes place on a geological time scale. It involves naturally occurring silicates as the source of alkaline and alkaline-earth metals and consumes atmospheric CO_2. This chapter deals, however, with so-called mineral carbonation, where high concentration CO_2 from a capture step (see Chapter 3) is brought into contact with metal oxide bearing materials with the purpose of fixing the CO_2 as carbonates (Seifritz, 1990; Dunsmore, 1992; Lackner *et al.*, 1995). Suitable materials may be abundant silicate rocks, serpentine and olivine minerals for example, or on a smaller-scale alkaline industrial residues, such as slag from steel production or fly ash. In the case of silicate rocks, carbonation can be carried out either *ex-situ* in a chemical processing plant after mining and pretreating the silicates, or *in-situ*, by injecting CO_2 in silicate-rich geological formations or in alkaline aquifers. Industrial residues on the other hand can be carbonated in the same plant where they are produced. It is worth noting that products of *in-situ* mineral carbonation and geological storage may be similar for the fraction of the CO_2 injected for geological storage that reacts with the alkaline or alkaline-earth metals in the cap rock leading to 'mineral trapping' (see Chapter 5.2.2).

In terms of material and energy balances, mineral carbonation can be schematized as illustrated in Figure 7.1, which applies to a power plant with CO_2 capture and subsequent storage through mineral carbonation. With respect to the same scheme for a power plant with capture and either geological or ocean storage (see Figure 1.4) two differences can be observed. First, there is an additional material flux corresponding to the metal oxide bearing materials; this is present as input and also as output, in the form of carbonates, silica, non-reacted minerals and for some input minerals product water. Secondly, for the same usable energy output, the relative amounts of fossil fuels as input and of energy rejected as lower grade heat are different. *In-situ* carbonation is an operation similar to geological storage, while *ex-situ* carbonation involves processing steps requiring additional energy input that are difficult to compensate for with the energy released by the carbonation reaction. Given the similarities of *in-situ* carbonation with geological storage, this chapter will focus on *ex-situ* mineral carbonation. With present technology there is always a net demand for high grade energy to drive the mineral carbonation process that is needed for: (i) the preparation of the solid reactants, including mining, transport, grinding and activation when necessary; (ii) the processing, including the equivalent energy associated with the use, recycling and possible losses of additives and catalysts; (iii) the disposal of carbonates and byproducts. The relative importance of the three items differs depending on the source of the metal oxides, for example whether they are natural silicates or industrial wastes.

Despite this potential energy penalty, interest in mineral carbonation stems from two features that make it unique among the different storage approaches, namely the abundance of metal oxide bearing materials, particularly of natural silicates, and the permanence of storage of CO_2 in a stable solid form. However,

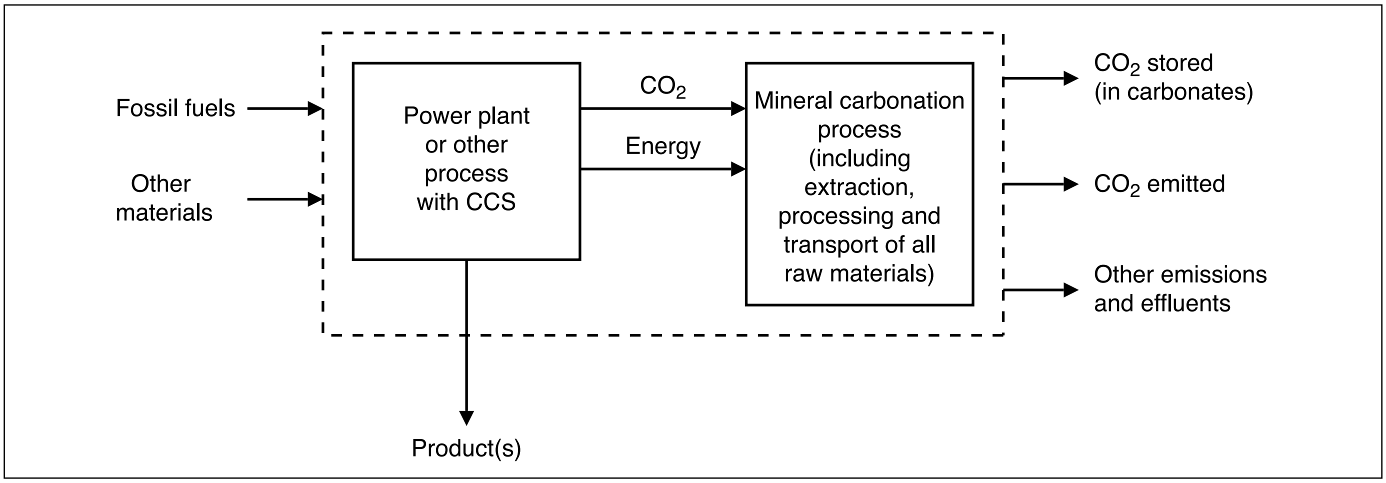

Figure 7.1 Material and energy balances through the system boundaries for a power plant with CO_2 capture and storage through mineral carbonation. The fossil fuel input provides energy both to the power plant that produces CO_2 and to the mineralization process (either directly or indirectly via the power plant). The 'other materials' input serves all processes within the system boundaries and includes the metal oxide bearing materials for mineralization. The 'other emissions' output is made up of the byproducts of the mineralization reaction - silica and possibly water - as well as of non-reacted input materials.

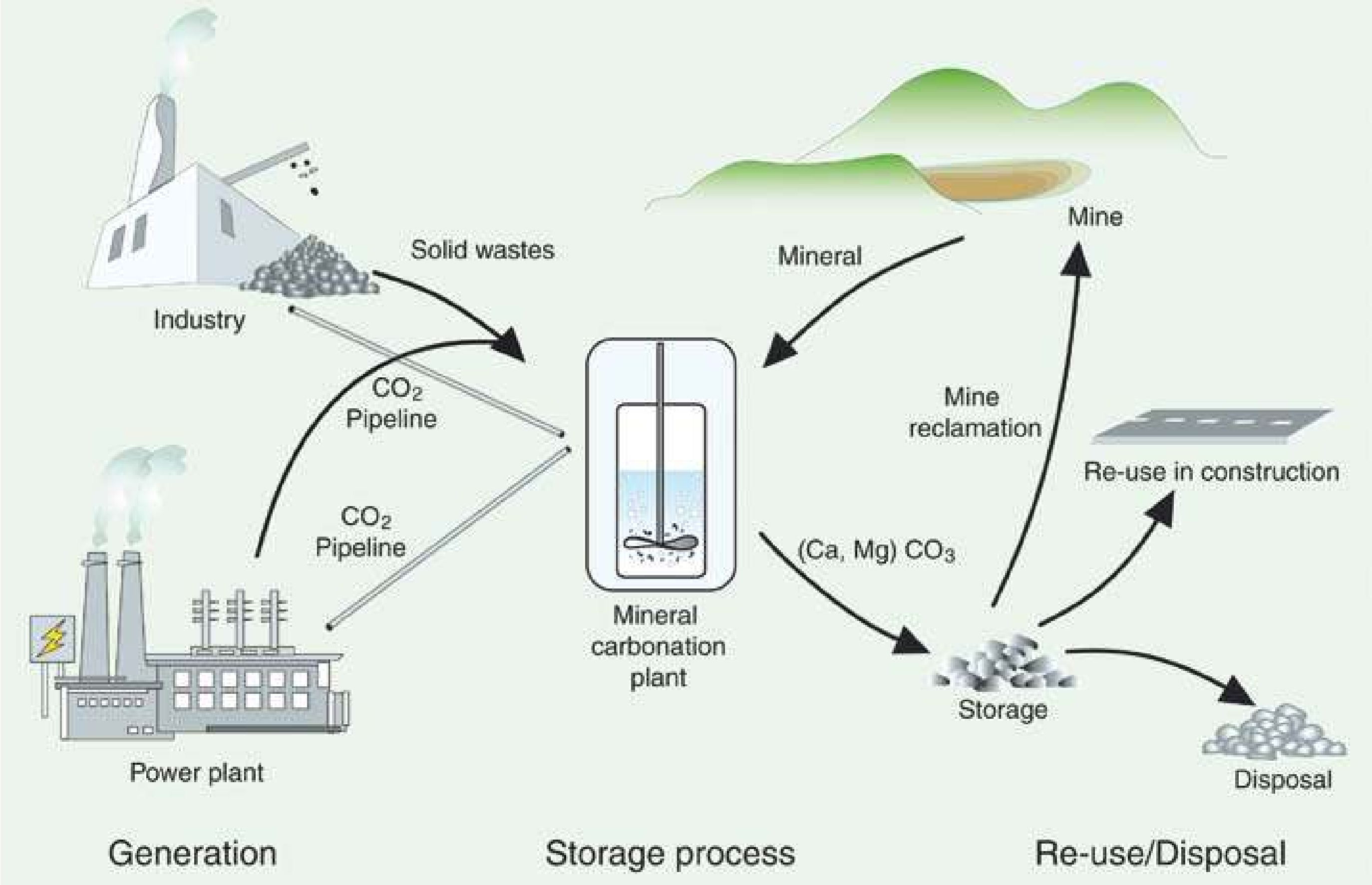

Figure 7.2 Material fluxes and process steps associated with the ex-situ mineral carbonation of silicate rocks or industrial residues (Courtesy Energy Research Centre of the Netherlands (ECN)).

mineral carbonation is today still an immature technology. Studies reported in the literature have not yet reached a level where a thorough assessment of the technology, potential, costs and impacts is possible.

7.2.2 *Chemistry of mineral carbonation*

When CO_2 reacts with metal oxides (indicated here as MO, where M is a divalent metal, e.g., calcium, magnesium, or iron) the corresponding carbonate is formed and heat is released according to the following chemical reaction:

$$MO + CO_2 \rightarrow MCO_3 + \text{heat} \qquad (1)$$

The amount of heat depends on the specific metal and on the material containing the metal oxide. In general this is a large fraction (up to 46% in the case of calcium oxide) of the heat released by the upstream combustion process forming CO_2 (393.8 kJ $mol^{-1}CO_2$ for combustion of elemental carbon). In the case of a few natural silicates the following exothermic chemical reactions take place (in all cases heat values are given per unit mol of CO_2 and standard conditions 25°C and 0.1 MPa, Robie *et al*. 1978):

Olivine:

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2 + 89 \text{ kJ mol}^{-1}CO_2 \qquad (2a)$$

Serpentine:

$$Mg_3Si_2O_5(OH)_4 + 3\ CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O + 64 \text{ kJ mol}^{-1}CO_2 \qquad (2b)$$

Wollastonite:

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 + 90 \text{ kJ mol}^{-1}CO_2 \qquad (2c)$$

Since the reaction releases heat, the formation of carbonates is thermodynamically favoured at low temperature, whereas at high temperature (above 900°C for calcium carbonate and above 300°C for magnesium carbonate, at a CO_2 partial pressure of one bar) the reverse reaction, that is calcination, is favoured. The representative member of the olivine family considered in the first reaction above is forsterite, which is iron-free. In nature most olivines contain some iron that can form iron oxides or siderite ($FeCO_3$).

Even at the low partial pressure of atmospheric CO_2 and at ambient temperature, carbonation of metal oxide bearing minerals occurs spontaneously, though on geological time scales (Robie *et al*., 1978; Lasaga and Berner, 1998). Limitations arise from the formation of silica or carbonate layers on the mineral surface during carbonation that tend to hinder further reaction and to limit conversion (Butt *et al.*, 1996) and from the rate of CO_2 uptake from the gas phase in the case of aqueous reactions. The challenge for mineral carbonation is to find ways to accelerate carbonation and to exploit the heat of reaction within the environmental constraints, for example with minimal energy and material losses.

7.2.3 Sources of metal oxides

Most processes under consideration for mineral carbonation focus on metal oxide bearing material that contains alkaline-earth metals (such as calcium and magnesium) as opposed to alkali metals (such as sodium and potassium) whose corresponding carbonates are very soluble in water. Oxides and hydroxides of calcium and magnesium would be the ideal source materials, but because of their reactivity they are also extremely rare in nature. Therefore, suitable metal oxide bearing minerals may be silicate rocks or alkaline industrial residues, the former being abundant but generally difficult to access and the latter scarcer but easily available.

Among silicate rocks, mafic and ultramafic rocks are rocks that contain high amounts of magnesium, calcium and iron and have a low content of sodium and potassium. Some of their main mineral constituents are olivines, serpentine, enstatite ($MgSiO_3$), talc ($Mg_3Si_4O_{10}(OH)_2$) and wollastonite. Although molar abundances of magnesium and calcium silicates in the Earth's crust are similar, rocks containing magnesium silicate exhibit a higher MgO concentration (up to 50% by weight, corresponding to a theoretical CO_2 storage capacity of 0.55 kg CO_2/kg rock), than rocks containing calcium silicates, for example basalts, that have CaO content of about 10% by weight only (with a theoretical CO_2 storage capacity of 0.08 kg CO_2/kg rock) (Goff and Lackner, 1998). Deposits of wollastonite, the most calcium-rich silicate, are much rarer than those of magnesium-rich silicates.

Serpentine and olivine are mainly found in ophiolite belts – geological zones where colliding continental plates lead to an uplifting of the earth's crust (Coleman 1977). For example, considering ultramafic deposits containing serpentine and olivine in the Eastern United States and in Puerto Rico, it was found that they have R_{CO2} values between 1.97 and 2.51, depending on purity and type (the R_{CO2} is the ratio of the mass of mineral needed to the mass of CO_2 fixed when assuming complete conversion of the mineral upon carbonation, that is the reciprocal of the theoretical CO_2 storage capacity introduced above). Peridotites and serpentinites exceed the total Mg requirement to neutralize the CO_2 from all worldwide coal resources estimated at 10,000 Gt (Lackner *et al.*, 1995). Specific ore deposits identified in two studies in the USA and Puerto Rico add to approximately 300GtCO_2 (Goff and Lackner, 1998; Goff *et al.*, 2000). This should be compared to CO_2 emissions of about 5.5 GtCO_2 in the United States and about 24 GtCO_2/yr^{-1} worldwide. No comprehensive mapping of the worldwide storage potential in ophiolite belts has been reported. However, their total surface exposure is estimated to be of the order of 1000 km by 100 km (Goff *et al.*, 2000). It is well known however that magnesium silicate reserves are present in all continents, but since they tend to follow present or ancient continental boundaries, they are not present in all countries. The feasibility of their use for *ex-situ* or *in-situ* mineral carbonation is yet to be established (Brownlow, 1979; Newall *et al.*, 2000).

On a smaller-scale, industrial wastes and mining tailings provide sources of alkalinity that are readily available and reactive. Even though their total amounts are too small to substantially reduce CO_2 emissions, they could help introduce the technology. Waste streams of calcium silicate materials that have been considered for mineral carbonation include pulverized fuel ash from coal fired power plants (with a calcium oxide content up to 65% by weight), bottom ash (about 20% by weight CaO) and fly ash (about 35% by weight CaO) from municipal solid waste incinerators, de-inking ash from paper recycling (about 35% by weight CaO), stainless steel slag (about 65% by weight CaO and MgO) and waste cement (Johnson, 2000; Fernández Bertos *et al.*, 2004; Iizuka *et al.*, 2004).

7.2.4 Processing

7.2.4.1 Mining and mine reclamation

Mining serpentine would not differ substantially from conventional mining of other minerals with similar properties, for example copper ores. Serpentine and olivine are both mined already, although rarely on the scale envisioned here (Goff and Lackner, 1998; Goff *et al.*, 2000). Like in other mining operations, disposal of tailings and mine reclamation are important issues to consider. Tailing disposal depends on the material characteristics – particle size and cohesion, moisture content and chemical stability against natural leaching processes – and these depend in turn on the specific process. It is likely that carbonation plants will be located near the metal oxide bearing material, either the factory producing the residues to be treated or the silicate mine, to avoid transport of solid materials (see Figure 7.2).

Economies of scale applying to today's mining technology suggest a minimum mining operation of 50,000 to 100,000 tonnes day^{-1} (Hartman, 1992), which translates into a minimum mineable volume of about 0.3 km^3 for a mine with a 30 year life. This is a rather small size for ophiolite ore bodies, which are often kilometres wide and hundreds of meters thick (Goff and Lackner, 1998; Goff *et al.*, 2000; Newall *et al.*, 2000). Since coal, in contrast to ophiolite bodies, occurs in thin seams and is buried under substantial overburden, it has been argued that a typical above ground coal mine must move more material (Lackner *et al.*, 1995) and disturb a far larger area (Ziock and Lackner, 2000) for the same amount of carbon atoms treated than the equivalent ophiolite mine, assuming maximum conversion of the mineral to carbonate (one carbon atom yields one CO_2 molecule upon combustion, which has to be fixed in one molecule of carbonate).

Serpentine can take many different forms, from decorative stones to chrysotile asbestos (O'Hanley, 1996). The possibility of encountering asbestos requires adequate precautions. With current best practice it would reportedly not be an obstacle

(Newall et al., 2000). Moreover, since the asbestos form of serpentine is the most reactive, reaction products are expected to be asbestos free (O'Connor et al., 2000). Mineral carbonation could therefore remediate large natural asbestos hazards that occur in certain areas, in California for example (Nichols, 2000).

7.2.4.2 *Mineral pretreatment*

Mineral pretreatment, excluding the chemical processing steps, involves crushing, grinding and milling, as well as some mechanical separation, for example magnetic extraction of magnetite (Fe_3O_4).

7.2.4.3 *CO_2 pre-processing*

Mineral carbonation requires little CO_2 pre-processing. If CO_2 is pipelined to the disposal site, the constraints on pipeline operations are likely to exceed pre-processing needs for mineral carbonation. The current state of research suggests that CO_2 should be used at a pressure similar to the pipeline pressure, thus requiring minimal or no compression (Lackner, 2002; O'Connor *et al.*, 2002). Purity demands in carbonation are minimal; acidic components of the flue gas could pass through the same process as they would also be neutralized by the base and could probably be disposed of in a similar manner. Most carbonation processes would preheat CO_2, typically to between 100°C and 150°C for aqueous processes, whereas in gas-solid reactions temperatures could reach 300°C to 500°C (Butt *et al.*, 1996).

7.2.4.4 *Carbonation reaction engineering*

The simplest approach to mineral carbonation would be the reaction of gaseous CO_2 with particulate metal oxide bearing material at suitable temperature and pressure levels. Unfortunately, such direct gas-solid reactions are too slow to be practical in the case of the materials mentioned in Section 7.2.3 (Newall *et al.*, 2000) and are only feasible at reasonable pressures for refined, rare materials like the oxides or hydroxides of calcium and magnesium (Butt and Lackner, 1997; Bearat *et al.,* 2002; Zevenhoven and Kavaliauskaite, 2004). As a result, mineral carbonation without refined materials cannot directly capture CO_2 from flue gases, but could possibly in the case of pressurized CO_2 rich gases from IGCC plants.

Since the direct fixation of carbon dioxide on solid unrefined material particles seems at present not feasible, the alternative requires the extraction of the metal from the solid. This can be accomplished by suspending the solid material in an aqueous solution and by letting it dissolve and release metal ions, for example calcium or magnesium ions. These ions come in contact with carbonic acid (H_2CO_3) that is formed in the same solution upon carbon dioxide dissolution. Conditions can be achieved where the carbonate and the byproducts – silica in the case of silicate carbonation for example – precipitate. This involves proper choice of the operating parameters of this single-step or multi-step process – particularly temperature, concentration of possible additives and CO_2 pressure (that controls the carbonic acid concentration in solution). At the end of the operation a suspension of fine particles of carbonate, byproducts and non-reacted solid materials remains. These have to be separated by filtration and drying from the solution from which residual metal ions and additives are to be quantitatively recovered.

This wet process scheme is currently in the research phase and has to overcome three major hurdles to become cost-effective and to be considered as a viable option for carbon storage: (i) acceleration of the overall rate of the process, which may be limited by the dissolution rate of the metal oxide bearing material; (ii) elimination of the interference between the concomitant metal oxide dissolution and carbonate precipitation; (iii) complete recovery of all the chemical species involved, if additives are used.

Mineral carbonation starting from natural silicates is a slow process that can be kinetically enhanced by raising the temperature, although thermodynamics are a limiting factor. In aqueous systems, this is typically kept below 200°C, since high temperature favours gaseous CO_2 over precipitated carbonates. It is believed that the metal oxide dissolution constitutes the rate-limiting step and most research efforts have been devoted to finding ways to speed up the metal extraction from the solid input materials. This could be achieved either by activating the mineral to make it more labile and reactive, or by enhancing the metal oxide extraction through the presence of additives or catalysts in solution. Activation can take different forms, namely heat-treatment at 650ºC for serpentine (Barnes *et al.*, 1950; Drägulescu *et al.*, 1972; O'Connor *et al.*, 2000) and ultra-fine (attrition) grinding for olivine and wollastonite (O'Connor *et al.*, 2002; Kim and Chung, 2002). The energy cost of activation has been estimated to be of 300 kWh t^{-1} of mineral and 70–150 kWh t^{-1} of mineral for thermal and mechanical activation, respectively (O'Connor *et al.*, 2005). Carbonation has been successfully performed after such pretreatment, but it is so expensive and energy-intensive that its feasibility is questionable (see Box 7.1 and O'Connor *et al.*, 2005). Dissolution catalysts that can be added to the aqueous solution include strong and weak acids (Pundsack, 1967; Lackner *et al.,* 1995; Fouda *et al.,* 1996; Park *et al.,* 2003; Maroto-Valer *et al.*, 2005), bases (Blencoe *et al.,* 2003) and chelating agents to extract SiO_2 or MgO groups from the mineral (Park *et al.,* 2003). All three approaches have been studied and at least partially experimentally tested, but in all cases catalyst recovery represents the key hurdle. It is worth noting that the carbonation of metal oxides from industrial wastes can be faster than that of natural silicates (Johnson, 2000; Fernández Bertos *et al.*, 2004; Huijgen *et al.*, 2004; Iizuka *et al.*, 2004; Stolaroff *et al.*, 2005).

Hydrochloric acid (HCl) dissolution of serpentine or olivine was proposed first (Houston, 1945; Barnes *et al.*, 1950; Wendt *et al.*, 1998a). The process requires a number of steps to precipitate magnesium hydroxide ($Mg(OH)_2$), which can then directly react with gaseous CO_2, and to recover HCl. Exothermic and endothermic steps alternate and heat recovery is not always possible, thus making the overall process very energy-intensive and not viable (Wendt *et al.*, 1998a; Newall *et al.*, 2000; Lackner, 2002). Likewise, strong alkaline solutions (with NaOH) will dissolve the silica from the magnesium

Box 7.1 Wet mineral carbonation process.

A comprehensive energy and economic evaluation of the single-step wet carbonation process has been reported (O'Connor et al., 2005). Though limited to the specific carbonation process illustrated in Figure 7.3, this study is based on about 600 experimental tests and looks not only at the fundamental and technical aspects of the process, but also at the matching of carbon dioxide sources and potential sinks that in this case are natural silicate deposits. In particular, seven large ultramafic ores in the USA have been considered (two olivines, four serpentines (three lizardites and one antigorite) and one wollastonite). Three are located on the west coast, three on the east coast and one in Texas. The selection of the seven ores has also been based on considerations of regional coal consumption and potential CO_2 availability.

The three different minerals exhibit different reactivity, measured as the extent of the carbonation reaction after one hour under specified operating conditions. A trade-off has been observed between the extent of reaction and mineral pretreatment, thus higher reactivity is obtained for more intense pretreatment, which represents an energy cost. Mechanical activation is effective for the olivine and the wollastonite and involves the use of both conventional rod and ball milling techniques with an energy consumption of up to about 100 kWh t^{-1} mineral (standard pretreatment) and ultra-fine grinding for up to more than 200 kWh t^{-1} mineral (activated process). Conversion is no more than 60% in the former case and up to above 80% in the latter. In the case of the serpentine, after milling (standard pretreatment), thermal activation at 630°C is effective for the antigorite (up to 92% conversion) but only partially for the lizardite (maximum conversion not larger than 40%) and requires an energy consumption of about 350 kWh t^{-1} mineral. Optimal operating conditions for this wet process are mineral dependent and correspond to 185°C and 15 MPa for the olivine, 155°C and 11.5 MPa for the heat treated serpentine, and 100°C and 4 MPa for the wollastonite. In the first two cases, the carbonation reaction takes place in the presence of 0.64 mol L^{-1} sodium bicarbonate and 1 mol L^{-1} sodium chloride.

Table 7.1 Mineral carbonation storage costs for CO_2.

Ore (type of pre-treatment)	Conversion after 1 hour (%)	Cost (US$/t ore)	Energy input[a] (kWh/tCO_2 stored)	Cost (US$/t$CO_2$ stored)
Olivine (standard)	61	19	310	55
Olivine (activated)	81	27	640	59
Lizardite (standard)	9	15	180	430
Lizardite (activated)	40	44	180+2120=2300	210
Antigorite (standard)	62	15	180	250
Antigorite (activated)	92	48	180+830=1010	78
Wollastonite (standard)	43	15	190	91
Wollastonite (activated)	82	19	430	64

[a] The study assumes a coal fired power plant with 35% efficiency, corresponding to one tonne of CO_2 released per 1000 kWh electricity. The equivalent heat value for the same coal input is then 2,850 kWh. The two items in the sum break the total energy input into electrical + thermal; in all other cases it is pure electrical energy.

Process costs have been calculated for these seven ores in the case of both standard mineral pretreatment and activated process. Costs include only storage, thus neither CO_2 capture nor CO_2 transport and are based on the assumption that CO_2 is received pure at 15 MPa at the plant. Investment costs are calculated accounting for the different reactor costs depending on the different operating conditions corresponding to the different mineral ores. Storage costs are calculated per tonne of silicate ore and per tonne of CO_2 stored and are complemented by the energy consumption per tonne of CO_2 stored in the above Table. The table highlights a trade-off between energy input associated with the pretreatment procedure and cost per unit carbon dioxide stored. Assuming that the cheapest technology is used for each mineral, costs range from 55 US$/t$CO_2$ stored for olivine (standard pretreatment), to 64 US$/t$CO_2$ stored for wollastonite (activated), to 78 US$/t$CO_2$ stored for antigorite (activated), to 210 US$/t$CO_2$ stored for lizardite (activated). Since the last case requires too large an energy input, the cost of the most realistic technologies falls into a range from 50 to 100 US$/t$CO_2$ stored.

silicate, thus allowing for further digestion of the remaining ($Mg(OH)_2$); however, also in this case the recovery of the NaOH catalyst seems to be very difficult (Blencoe *et al.,* 2003). To overcome the substantial energy penalty of water evaporation in the hydrochloric acid process, it was proposed to dissolve the silicate minerals in a magnesium chloride melt in order either to precipitate $Mg(OH)_2$ as before or to allow for direct carbonation in the melt (Wendt *et al.*, 1998a; 1998b; 1998c; 1998d). No experimental demonstration of this process has been provided, possibly also because of the corrosive conditions of the reaction; energy and material balances indicate that either version of the process will hardly be viable (Newall *et al.*, 2000; Haywood *et al.*, 2001).

Weaker acids that might reduce the energy requirements for recovery include acetic acid (Kakizawa *et al.*, 2001), oxalic acid (Park *et al.*, 2003), orthophosphoric acid (Park *et al.*, 2003) and ammonium bisulphate (Pundsack 1967). Among the possible chelating agents that keep either silicates or magnesium ions in solution by forming water-soluble complexes, is EDTA – ethylene-diamine-tetra-acetic acid (Carey *et al.*, 2003; Park *et al.*, 2003; Park and Fan, 2004). Citric acid is also effective because it combines its acidic properties with strong chelating properties (Carey *et al.*, 2003). All these additives have been proven to enhance the dissolution of silicate minerals, but only in the acetic acid case has a complete process scheme, including acid recovery, been described and evaluated (Kakizawa *et al.*, 2001). This is based on two steps, whereby the metal ions are extracted first using acetic acid and then the carbonate is

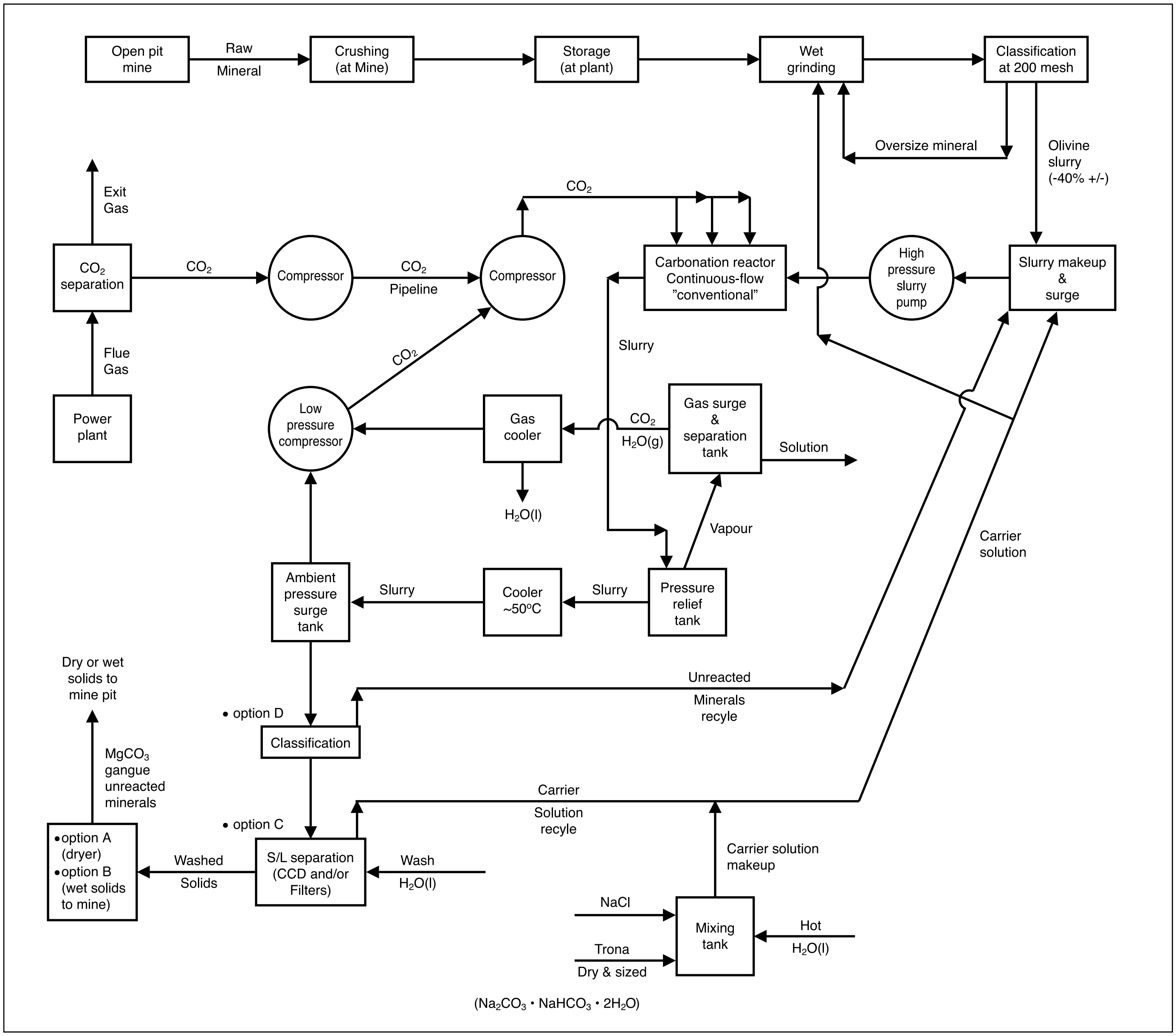

Figure 7.3 Process scheme of the single-step mineral carbonation of olivine in aqueous solution (Courtesy Albany Research Centre). 'Single-step' indicates that mineral dissolution and carbonate precipitation take place simultaneously in the same carbonation reactor, whereas more steps are of course needed for the whole process, including preparation of the reactants and separation of the products.

precipitated upon CO_2 addition. Acetic acid remains in solution as either calcium or magnesium acetate or free acid and can be recycled. The process has only been demonstrated for wollastonite. Experimental conversion levels of the wollastonite have not exceeded 20% (Kakizawa *et al.*, 2001).

7.2.4.5 A worked out example: single-step carbonation

Figure 7.3 illustrates the single step wet mineral carbonation process that can be applied to natural silicates as well as to industrial residues, for example steel slag (Huijgen *et al.*, 2004). The figure refers to the carbonation of olivine, whereby the mineral is ground first. Subsequently it is dissolved in an aqueous solution of sodium chloride (NaCl, 1 mol L^{-1}) and sodium bicarbonate ($NaHCO_3$, 0.64 mol L^{-1}) in contact with high pressure CO_2 and carbonated therein (O'Connor *et al.*, 2002; O'Connor *et al.*, 2005). The additives are easily recovered upon filtration of the solid particles, since the sodium and chloride ions do not participate in the reaction and remain in solution, whereas the bicarbonate ion is replenished by contacting the solution in the carbonation reactor with the CO_2 atmosphere. A maximum conversion of 81% in one hour was obtained with an olivine of 37 μm particle size, at a temperature of 185°C and a CO_2 partial pressure of 15 MPa. An important element of the process scheme in Figure 7.3 is the classification (sieving) that allows separating the carbonate and silica products from the olivine that has to be recycled. This is possible since non-reacted olivine minerals are coarse, whereas the carbonate and silica consist of finer particles (O'Connor *et al.*, 2002). An additional difficulty of single-step carbonation is when, upon extraction of the metal oxide from the solid particles, a silica layer forms or a carbonate layer precipitates on the particles themselves, thus hindering further dissolution. Experimental evidence indicates that this does not occur in the case of olivine (O'Connor *et al.*, 2002), whereas it does occur in the case of steel slag (Huijgen *et al.*, 2004).

Using the process scheme illustrated in Figure 7.3, it is possible to calculate the material balances by considering that the molecular mass of carbon dioxide is 44.0 g mol^{-1}, of magnesium carbonate is 84.3 g mol^{-1}, of silica is 60.1 g mol^{-1} and of olivine is 140.7 g mol^{-1}. For the sake of simplicity only two assumptions are made, namely the degree of conversion in the carbonation reactor – the fraction of olivine fed to the reactor that is converted to carbonate in a single pass – and the fraction of non-reacted mineral in the classifier that is not recycled, but ends up with the material for disposal. Based on the stoichiometry of the carbonation reaction, 1.6 tonnes of olivine would be needed to fix one tonne of CO_2, thus producing 2.6 tonnes of solid material for disposal. Assuming 90% carbonation conversion and 10% losses in the classifier, 1.62 tonnes of olivine would be needed and 2.62 tonnes of solids per tonne of CO_2 mineralized would be for disposal. Assuming only 50% conversion and 20% losses, for one tonne of CO_2 stored, 1.87 tonnes of olivine would be needed and 2.87 tonnes would be disposed of. In the latter case however the carbonation reactor would be twice as big as in the former case.

Olivine has the highest concentration of reactive magnesium oxide among the natural minerals (57% by weight). Other minerals in general contain a lower concentration. For pure serpentine the magnesium oxide concentration is about 44% and for typical ores about 50% of that of the pure mineral. Therefore, the mineral feedstock required to fix 1 tonne of CO_2 in carbonates is between 1.6 and 3.7 tonnes and the process yields between 2.6 and 4.7 tonnes of products to be handled. The carbonation process consumes energy and thus causes CO_2 emissions that reduce the net storage of CO_2 accordingly. For the olivine carbonation process, having the lowest unit cost among those described in Box 7.1, the energy requirement is 1.1 GJ/tCO_2. If this is provided by the same coal derived electricity it would cause CO_2 emissions equal to 30% of the fixed CO_2.

7.2.5 Product handling and disposal

Disposal options for mineral carbonates are determined by the mass of the resulting material (see Figure 7.2). It is not cost-effective to ship the bulk of these materials over long distances. As a result the obvious disposal location is at the mine site. As in any large-scale mining operation, the logistics of mining a site and reclaiming it after refilling it with the tailings is substantial, but it does not pose novel problems (Newall *et al.,* 2000). The amount of material to be disposed of is between 50 and 100% by volume more than that originally mined. These volumes are comparable to volumes commonly handled in mining operations and are subject to standard mine reclamation practice (Lackner *et al.*, 1997; Newall *et al.,* 2000).

The fine grinding of the mineral ore might allow for the extraction of valuable mineral constituents. Serpentine and olivine mines could provide iron ore that either would be removed as magnetite by magnetic separation or result from chemical precipitation during magnesium extraction, yielding concentrated iron oxide or hydroxide (Park and Fan, 2004). Peridotite rocks may contain chromite, elements like nickel and manganese and also elements in the platinum group, but how these can be recovered has still to be studied (Goff and Lackner, 1998). It has been suggested, that magnesium carbonate and silica may find uses as soil enhancers, roadfill or filler for mining operations. Eventually mineral carbonation would have to operate at scales that would saturate any product or byproduct market, but products and byproducts, when usable, could help make a demonstration of the process more viable (Lackner *et al.,* 1997; Goff and Lackner, 1998).

7.2.6 Environmental impact

The central environmental issue of mineral carbonation is the associated large-scale mining, ore preparation and waste-product disposal (Goff and Lackner, 1998). It can directly lead to land clearing and to the potential pollution of soil, water and air in surrounding areas. It may also indirectly result in habitat degradation. An environmental impact assessment would be required to identify and prevent or minimize air emissions, solid waste disposal, wastewater discharges, water use, as well as social disturbances. As for many other mining activities, the preventing and mitigating practices are relatively basic and well developed.

Land clearing: The amount of material required to store CO_2 involves extensive land clearing and the subsequent displacement of millions of tonnes of earth, rock and soil, increasing the potential for erosion, sedimentation and habitat loss in the area. Access roads would also lead to clearing of vegetation and soil. Standard practices recommended to minimize these impacts include storage of topsoil removed for use in future reclamation activities, use of existing tracks when constructing access roads and pipelines and use of drainage and sediment collection systems to catch runoff or divert surface water, minimizing erosion.

Air quality: Mining activities like blasting, drilling, earth moving and grading can generate dust and fine particulate matter that affect visibility and respiration and pollute local streams and vegetation. Dust prevention measures are widely applied at mining operations today, but if not properly controlled, dust can threaten human respiratory health. This is particularly important in serpentine mining because serpentine often contains chrysotile, a natural form of asbestos. Even though chrysotile is not as hazardous as amphibole asbestos (tremolite, actinolite) (Hume and Rimstidt, 1992), the presence of chrysotile requires covering of exposed veins and monitoring of air quality (Nichols, 2000). On the other hand, mineral carbonation products are asbestos free, as the reaction destroys chrysotile, which reacts faster than other serpentines, even if conversion of the starting material is not complete. This makes mineral carbonation a potentially effective method for the remediation of asbestos in serpentine tailing (O'Connor *et al.*, 2000). The resulting mineral carbonates are inert, but large volumes of powders would also have to be controlled, for example by cementing them together to avoid contamination of soil and vegetation, as well as habitat destruction.

Tailings: Tailings consist of finely ground particles, including ground-up ore and process byproducts. Tailings management systems should be designed and implemented from the earliest stages of the project. Usually tailings are stored in tailings impoundments designed to hold tailings behind earth-fill dams (Newall *et al.*, 2000). Other control measures depend on whether tailings are dry or wet, on particle size and chemical reactivity.

Leaching of metals: Although the low acidity of the resulting byproducts reduces the possibility of leaching, certainty about leaching can only be obtained by conducting tests. If necessary, a lining system would prevent ground water contamination. Leaching containment is also possible without lining where underlying rock has been shown to be impermeable.

Reclamation: To minimize water contamination, restore wildlife habitat and ecosystem health and improve the aesthetics of the landscape, a comprehensive reclamation programme has to be designed during the planning phase of the mining project and be implemented concurrently throughout operations. Concurrent incorporation of reclamation with the mining of the site reduces waste early, prevents clean-up costs and decreases potential liabilities. Land rehabilitation will involve the re-shaping of landform, because the volume of tailings will be larger than the mined rock. The main environmental concern regarding reclamation is major soil movements by erosion or landslides. This can be controlled by adequate vegetation cover and by covering the soil with protective mulch, by maintaining moisture in the soil, or by constructing windbreaks to protect the landform from exposure to high winds.

7.2.7 Life Cycle Assessment and costs

At the current stage of development, mineral carbonation consumes additional energy and produces additional CO_2 compared to other storage options. This is shown in Figure 7.1 and is why a Life Cycle Assessment of the specific process routes is particularly important. The potential of mineral carbonation depends on the trade-off between costs associated with the energy consuming steps (mining, pre-processing of the mineral ore, its subsequent disposal and mine reclamation) and benefits (the large potential capacity due to the vast availability of natural metal oxide bearing silicates and the permanence of CO_2 storage).

A life cycle analysis of the mining, size reduction process, waste disposal and site restoration calculated additional annual CO_2 emissions of 0.05 tCO_2/tCO_2 stored (Newall *et al.*, 2000). This included grinding of the rock to particle sizes less than 100 microns; a ratio of 2.6 tonnes of serpentine per tonne of CO_2 was assumed. The cost was assessed to be about 14 US\$/tCO_2 stored; the capital cost being about 20% of the total. All cost estimates were based on OECD Western labour costs and regulations. The conversion factor from electrical energy to CO_2 emissions was 0.83 tCO_2/MWh electricity. Costs were calculated on the basis of an electricity price of US\$ 0.05 kWh^{-1} electricity. Results from other studies were converted using these values (Newall *et al.*, 2000). Other estimates of these costs are between 6 and 10 US\$/tCO_2 stored, with 2% additional emissions (Lackner *et al.*, 1997).

As far as the scale of mining and disposal is concerned – about 1.6 to 3.7 tonnes of silicate and 2.6 to 4.7 tonnes of disposable materials per tonne of CO_2 fixed in carbonates, as reported in Section 7.2.4 – this is of course a major operation. When considering that one tonne of carbon dioxide corresponds to 0.27 tonnes of carbon only in theory, but in practice to about 2 tonnes of raw mineral due to the overburden, it follows that mineral carbonation to store the CO_2 produced by burning coal would require the installation of a mining industry of a scale comparable to the coal industry itself. Such large mining operations are significant, but placing them in the context of the operations needed for the use of fossil fuels and geological or ocean storage, the volumes are comparable.

The energy requirements and the costs of the carbonation reaction are very much process dependent and more difficult to estimate, due to scarcity of data. The most detailed study has been carried out for the process where the silicates are dissolved in a magnesium chloride melt (Newall *et al.*, 2000). An overall cost (including the operations mentioned in the previous paragraph) of 80 US$/t$CO_2$ stored was obtained, with 27.5% additional CO_2 emissions, thus leading to 110 US$/t$CO_2$ avoided. In the case of the two-step acetic acid process, an overall cost of 27 US$/t$CO_2$ avoided has been reported, but the assumptions are based on a rather limited set of experimental data (Kakizawa *et al*., 2001). A comprehensive energy and economic evaluation of the single step wet carbonation process illustrated in Figure 7.3 has been recently reported (O'Connor *et al*., 2005) and is discussed in detail in Box 7.1. This study calculates storage costs between 50 and 100 US$/t$CO_2$ stored, with between 30% and 50% of the energy produced needed as input to the mineral carbonation step, i.e. a corresponding reduction of power plant efficiency from 35% for instance to 25% and 18%, respectively. This implies that a full CCS system with mineral carbonation would need 60-180% more energy than a power plant with equivalent output without CCS, when the 10-40% energy penalty in the capture plant is accounted too. No similar economic evaluation is available for either dry mineral carbonation or carbonation using industrial residues. However, it is worth pointing out that the carbonation of toxic wastes may lead to stabilized materials with reduced leaching of heavy metals. Therefore these materials might be disposed of more easily or even used for applications such as in construction work (see Figure 7.2) (Venhuis and Reardon, 2001; Meima *et al*., 2002).

Once the carbon has been stored through mineral carbonation, there are virtually no emissions of CO_2 due to leakage. To the extent that weathering at the disposal site occurs and leaches out magnesium carbonate from the carbonation products, additional CO_2 would be bound in the transformation of solid magnesium carbonate to dissolved magnesium bicarbonate (Lackner, 2002). It can therefore be concluded that the fraction of carbon dioxide stored through mineral carbonation that is retained after 1000 years is virtually certain to be 100%. As a consequence, the need for monitoring the disposal sites will be limited in the case of mineral carbonation.

7.2.8 Future scope

7.2.8.1 Public acceptance

Public acceptance of mineral carbonation is contingent on the broader acceptance of CCS. Acceptance might be enhanced by the fact that this method of storage is highly verifiable and unquestionably permanent. On the downside, mineral carbonation involves large-scale mining and associated environmental concerns: terrain changes, dust pollution exacerbated by potential asbestos contamination and potential trace element mobilization. Generally, public acceptance will require a demonstration that everything possible is done to minimize secondary impacts on the environment.

7.2.8.2 Gap analysis

Mineral carbonation technology must reduce costs and reduce the energy requirements associated with mineral pretreatment by exploiting the exothermic nature of the reaction. Mineral carbonation will always be more expensive than most applications of geological storage, but in contrast has a virtually unlimited permanence and minimal monitoring requirements. Research towards reducing costs for the application of mineral carbonation to both natural silicates and industrial wastes, where the kinetics of the reaction is believed to be more favourable, is ongoing. Moreover, an evaluation is needed to determine the fraction of the natural reserves of silicates, which greatly exceed the needs, that can be effectively exploited for mineral carbonation. This will require thorough study, mapping the resources and matching sources and sinks, as in O'Connor *et al.* (2005). The actual size of the resource base will be significantly influenced by the legal and societal constraints at a specific location. Integrating power generation, mining, carbonation reaction, carbonates' disposal and the associated transport of materials and energy needs to be optimized in a site-specific manner. A final important gap in mineral carbonation is the lack of a demonstration plant.

7.3 Industrial uses of carbon dioxide and its emission reduction potential

7.3.1 Introduction

As an alternative to storing captured CO_2 in geological formations (see Chapter 5), in the oceans (see Chapter 6), or in mineral form as carbonates (see Section 7.2), this section of the report assesses the potential for reducing net CO_2 emissions to the atmosphere by using CO_2 either directly or as a feedstock in chemical processes that produce valuable carbon containing products. The utilization of CO_2 establishes an inventory of stored CO_2, the so-called carbon chemical pool, primarily in the form of carbon-containing fuels, chemicals and other products (Xiaoding and Moulijn, 1996). The production and use of these products involve a variety of different 'life cycles' (i.e., the chain of processes required to manufacture a product from raw materials, to use the product for its intended purpose and ultimately to dispose of it or to reuse it in some fashion). Depending on the product life-cycle, CO_2 is stored for varying periods of time and in varying amounts. As long as the recycled carbon remains in use, this carbon pool successfully stores carbon. Withdrawal from this pool, by decay or by disposal typically re-injects this carbon into the atmospheric pool.

CO_2 that has been captured using one of the options described in Chapter 3 could reduce net CO_2 emissions to the atmosphere if used in industrial processes as a source of carbon, only if the following criteria are met:

1. The use of captured CO_2 must not simply replace a source of CO_2 that would then be vented to the atmosphere. Replacement of CO_2 derived from a lime kiln or a fermentation process would not lead to a net reduction in CO_2 emissions, while on the other hand replacement of CO_2 derived from natural geological deposits, which would thus be left undisturbed, would lead to a net reduction of CO_2 emissions. This would apply to the majority of the CO_2 used for enhanced oil recovery in the USA (see Section 5.3.2)

that is currently provided from natural geological deposits (Audus et Oonk, 1997).

2. The compounds produced using captured CO_2 must have a long lifetime before the CO_2 is liberated by combustion or other degradation processes.
3. When considering the use of captured CO_2 in an industrial process, the overall system boundary must be carefully defined to include all materials, fossil fuels, energy flows, emissions and products in the full chain of processes used to produce a unit of product in order to correctly determine the overall (net) CO_2 avoided.

CO_2 reductions solely due to energy efficiency improvements are not within the scope of this report, which is focused on capture and storage rather than efficiency improvements. Similarly while environmental benefits like those obtained in replacing organic solvents with supercritical CO_2 may slightly increase the carbon chemical pool, these primary drivers are not discussed in this report. Similarly, this report specifically excludes all uses of captured CO_2 to replace other chemicals that are released into the atmosphere and that have high greenhouse-gas potential, fluorocarbons for example. This area is covered by the IPCC/TEAP Special Report on Safeguarding the Ozone Layer and the Global Climate System: issues related to Hydrofluorocarbons and Perfluorocarbons (IPCC/TEAP, 2005).

The third point is especially important in any effort to estimate the potential for net CO_2 reductions from the substitution of a CO_2-utilizing process for alternative routes to manufacturing a desired product. In particular, it is essential that the system boundary encompasses all 'upstream' processes in the overall life cycle and does not focus solely on the final production process of interest. The appropriate system boundary is shown schematically in Figure. 7.4 This is an extension of the system boundary diagrams shown earlier in Section 7.2 (Figure 7.1) and in Chapter 1 (Figure 1.4) in the context of a CO_2 capture and storage system. The inputs include all fossil fuels together with all other materials used within the system. The fossil fuel input provides energy to the power or industrial plant, including the CO_2 capture system, as well as the elemental carbon used as building blocks for the new chemical compound. Flows of CO_2, energy and materials pass from the primary fuel-consuming processes to the industrial process that utilizes the captured CO_2. This produces a desired product (containing carbon derived from captured CO_2) together with other products (such as useful energy from the power plant) and environmental emissions that may include CO_2 plus other gaseous, liquid or solid residuals.

Once the overall system has been defined and analyzed in this way, it can also be compared to an alternative system that does not involve the use of captured CO_2. Using basic mass and energy balances, the overall avoided CO_2 can then be assessed as the difference in net emissions associated with the production of a desired product. In general, the difference could be either positive or negative, thus meaning that utilization of CO_2 could result in either a decrease or increase in net CO_2 emissions, depending on the details of the processes being compared. Note that only fossil fuels as a primary energy source are considered in this framework. Renewable energy sources and nuclear power are specifically excluded, as their availability would have implications well beyond the analysis of CO_2 utilization options (see Chapter 8 for further discussion). Note too that other emissions from the process may include toxic or harmful materials, whose flows also could be either reduced or increased by the adoption of a CO_2-based process.

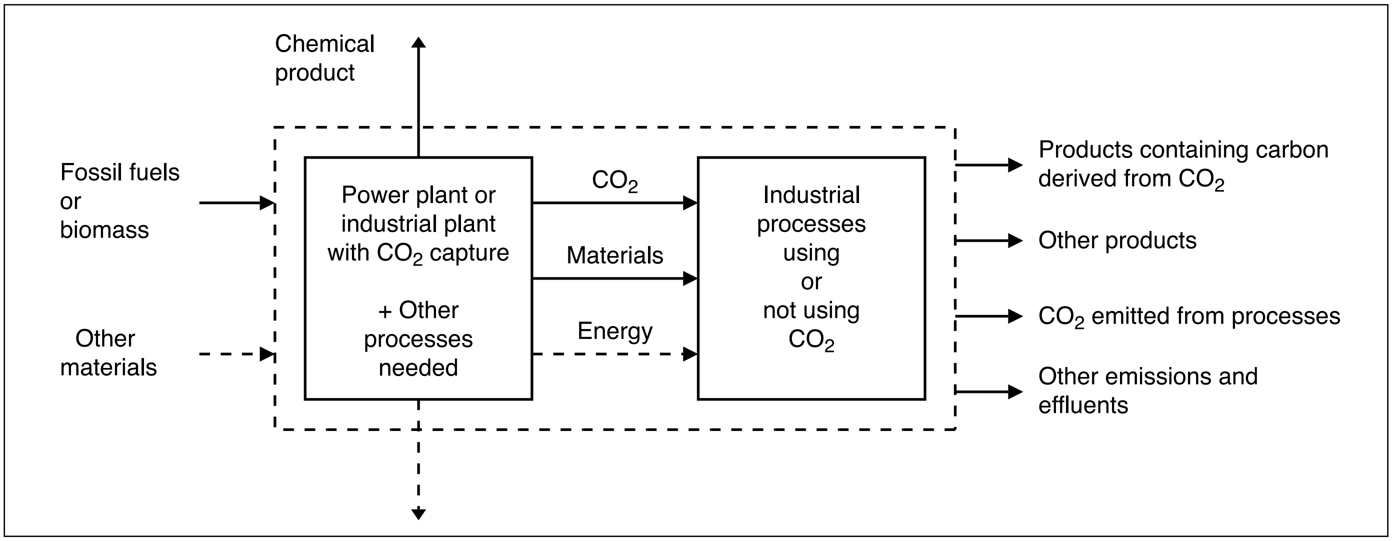

Figure 7.4 Material and energy balances through the system boundaries for a power plant or an industrial plant with CO_2 capture, followed by an industrial process using CO_2. The inputs include all fossil fuels together with all other materials used within the system. The fossil fuel input provides energy to the power or industrial plant, including the CO_2 capture system, as well as the elemental carbon used as building blocks for the new chemical compound. From the primary fuel-consuming processes, flows of CO_2, energy and materials pass to the industrial process, which utilizes the captured CO_2. This produces a desired product (containing carbon, derived from captured CO_2) together with other products (such as useful energy from the power plant) and environmental emissions that may include CO_2 plus other gaseous, liquid or solid residuals.

The application of this framework to the assessment of CO_2 utilization processes is discussed in more detail later in this chapter. First, however, we will examine current uses of CO_2 in industrial processes and their potential for long-term CO_2 storage.

7.3.2 Present industrial uses of carbon dioxide

Carbon dioxide is a valuable industrial gas with a large number of uses that include production of chemicals, for example urea, refrigeration systems, inert agent for food packaging, beverages, welding systems, fire extinguishers, water treatment processes, horticulture, precipitated calcium carbonate for the paper industry and many other smaller-scale applications. Large quantities of carbon dioxide are also used for enhanced oil recovery, particularly in the United States (see Section 5.3.2). Accordingly, there is extensive technical literature dealing with CO_2 uses in industry and active research groups are exploring new or improved CO_2 utilization processes.

Much of the carbon dioxide used commercially is recovered from synthetic fertilizer and hydrogen plants, using either a chemical or physical solvent scrubbing system (see Section 3.5.2). Other industrial sources of CO_2 include the fermentation of sugar (dextrose) used to produce ethyl alcohol:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \qquad (3)$$

Industrial CO_2 is also produced from limekilns, such as those used in the production of sodium carbonate and in the Kraft wood pulping process. This involves the heating (calcining) of a raw material such as limestone:

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (4)$$

In some parts of the world, such as the United States, Italy, Norway and Japan, some CO_2 is extracted from natural CO_2 wells. It is also recovered during the production and treatment of raw natural gas that often contains CO_2 as an impurity (see Chapter 2 for more details about CO_2 sources).

A large proportion of all CO_2 recovered is used at the point of production to make further chemicals of commercial importance, chiefly urea and methanol. The CO_2 recovered for other commercial uses is purified, liquefied, delivered and stored mostly as a liquid, typically at 20 bar and –18°C (Pierantozzi, 2003).

Table 7.2 shows the worldwide production and CO_2 usage rates for the major chemical or industrial applications currently using CO_2 (excluding enhanced oil recovery, which is dealt with in Chapter 5). The approximate lifetime of stored carbon before it is degraded to CO_2 that is emitted to the atmosphere is also shown. Such values mean that the fraction of the CO_2 used to produce the compounds in the different chemical classes or for the different applications, which is still stored after the period of time indicated in the last column of Table 7.2 drops to zero.

7.3.3 New processes for CO_2 abatement

7.3.3.1 Organic chemicals and polymers

A number of possible new process routes for the production of chemicals and polymers have been considered in which CO_2 is used as a substitute for other C_1 building blocks, such as carbon monoxide, methane and methanol. The use of CO_2, an inert gas whose carbon is in a highly oxidized state, requires development of efficient catalytic systems and, in general, the use of additional energy for CO_2 reduction. Chemicals that have been considered include polyurethanes and polycarbonates, where the motivation has primarily been to avoid the use of phosgene because of its extreme toxicity, rather than to find a sink for CO_2. The proposed processes can have a lower overall energy consumption than the current phosgene-based routes leading to further CO_2 emission reductions. Current world consumption of polycarbonates is about 2.7 Mt yr^{-1}. If all polycarbonate production was converted to CO_2-based processes the direct consumption of CO_2 would be about 0.6 $MtCO_2yr^{-1}$. Some CO_2

Table 7.2 Industrial applications of CO_2 (only products or applications at the Mtonne-scale): yearly market, amount of CO_2 used, its source, and product lifetime (Aresta and Tommasi, 1997; Hallman and Steinberg, 1999; Pelc et al., 2005). The figures in the table are associated with a large uncertainty.

Chemical product class or application	Yearly market (Mt yr^{-1})	Amount of CO_2 used per Mt product ($MtCO_2$)	Source of CO_2	Lifetime[b]
Urea	90	65	Industrial	Six months
Methanol (additive to CO)	24	<8	Industrial	Six months
Inorganic carbonates	8	3	Industrial, Natural[a]	Decades to centuries
Organic carbonates	2.6	0.2	Industrial, Natural[a]	Decades to centuries
Polyurethanes	10	<10	Industrial, Natural[a]	Decades to centuries
Technological	10	10	Industrial, Natural[a]	Days to years
Food	8	8	Industrial, Natural[a]	Months to years

[a] Natural sources include both geological wells and fermentation.

[b] The fraction of used CO_2 that is still stored after the indicated period of time drops to zero.

savings that are difficult to quantify from current published data are claimed for energy/materials changes in the process.

Similarly, if all world polyurethane production was converted, then direct CO_2 consumption would be about 2.7 $MtCO_2$/yr. However, little progress in commercial application of CO_2-based production has been reported. And as indicated earlier, these possible CO_2 applications directly affect only a very small fraction of the anthropogenic CO_2 emitted to the atmosphere. The net savings in CO_2 would be even smaller or could be negative, as the energy that was available in the hydrocarbon resource is missing in the CO_2 feedstock and unless compensated for by improved process efficiency it would have to be made up by additional energy supplies and their associated CO_2 emissions.

7.3.3.2 *Fuel production using carbon dioxide*

Liquid carbon-based fuels, gasoline and methanol for example, are attractive because of their high energy density and convenience of use, which is founded in part on a well-established infrastructure. Carbon dioxide could become the raw material for producing carbon-based fuels with the help of additional energy. Since energy is conserved, this cannot provide a net reduction in carbon dioxide emissions as long as the underlying energy source is fossil carbon. If a unit of energy from a primary resource produces a certain amount of CO_2, then producing a fuel from CO_2 will recycle CO_2 but release an equivalent amount of CO_2 to provide the necessary energy for the conversion. Since all these conversion processes involve energy losses, the total CO_2 generated during fuel synthesis tends to exceed the CO_2 converted, which once used up, is also emitted.

Production of liquid carbon-based fuels from CO_2 only reduces CO_2 emissions if the underlying energy infrastructure is not based on fossil energy. For example, one could still use gasoline or methanol rather than converting the transport sector to hydrogen, by using hydrogen and CO_2 as feedstocks for producing gasoline or methanol. The hydrogen would be produced from water, using hydropower, nuclear energy, solar energy or wind energy. As long as some power generation using fossil fuels remains, carbon dioxide for this conversion will be available (Eliasson, 1994). Alternatively, it might be possible to create a closed cycle with CO_2 being retrieved from the atmosphere by biological or chemical means. Such cycles would rely on the availability of cheap, clean and abundant non-fossil energy, as would the hydrogen economy, and as such they are beyond the scope of this report.

Methanol production is an example of the synthesis of liquid fuels from CO_2 and hydrogen. Today a mixture of CO, CO_2 and hydrogen is produced through reforming or partial oxidation or auto thermal reforming of fossil fuels, mainly natural gas. The methanol producing reactions, which are exothermic, take place over a copper/zinc/alumina catalyst at about 260°C (Inui, 1996; Arakawa, 1998; Ushikoshi *et al.*, 1998; Halmann and Steinberg, 1999):

$$CO + 2H_2 \rightarrow CH_3OH \quad (5)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad (6)$$

Alternatively one could exploit only reaction (6), by using captured CO_2 and hydrogen from water hydrolysis powered for instance by solar energy (Sano *et al.*, 1998).

7.3.3.3 *Capture of CO_2 in biomass*

Biomass production of fuels also falls into the category of generating fuels from CO_2. With the help of photosynthesis, solar energy can convert water and CO_2 into energetic organic compounds like starch. These in turn can be converted into industrial fuels like methane, methanol, hydrogen or bio-diesel (Larson, 1993). Biomass can be produced in natural or agricultural settings, or in industrial settings, where elevated concentrations of CO_2 from the off-gas of a power plant would feed micro-algae designed to convert CO_2 into useful chemicals (Benemann, 1997). Since biological processes collect their own CO_2, they actually perform CO_2 capture (Dyson, 1976). If the biomass is put to good use, they also recycle carbon by returning it to its energetic state. Biomass production eliminates the need for fossil fuels, because it creates a new generation of biomass-based carbonaceous fuels. As a replacement for fossil energy it is outside the scope of this report. As a CO_2 capture technology, biomass production is ultimately limited by the efficiency of converting light into chemically stored energy. Currently solar energy conversion efficiencies in agricultural biomass production are typically below 1% (300 GJ ha^{-1} yr^{-1} or 1 W m^{-2} (Larson, 1993)). Micro-algae production is operating at slightly higher rates of 1 to 2% derived by converting photon utilization efficiency into a ratio of chemical energy per unit of solar energy (Melis *et al.*, 1998; Richmond and Zou, 1999). Hence the solar energy collection required for micro-algae to capture a power plant's CO_2 output is about one hundred times larger than the power plant's electricity output. At an average of 200 W m^{-2} solar irradiation, a 100 MW power plant would require a solar collection area in the order of 50 km^2.

7.3.4 *Assessment of the mitigation potential of CO_2 utilization*

This final section aims at clarifying the following points: (i) to what extent the carbon chemical pool stores CO_2; (ii) how long CO_2 is stored in the carbon chemical pool; (iii) how large the contribution of the carbon chemical pool is to emission mitigation.

To consider the first point, the extent of CO_2 storage provided by the carbon chemical pool, it is worth referring again to Table 7.2. As reported there, total industrial CO_2 use is approximately 115 $MtCO_2$ yr^{1}. Production of urea is the largest consumer of CO_2, accounting for over 60% of that total. To put it in perspective, the total is only 0.5% of total anthropogenic CO_2 emissions – about 24 $GtCO_2$ yr^{1}. However, it is essential to realize that these figures represent only the yearly CO_2 flux in and out of the carbon chemical pool, and not the actual size of the pool, which is controlled by marketing and product distribution considerations and might be rather smaller than the total yearly CO_2 consumption. Moreover, the contribution to the storage of carbon – on a yearly basis for instance – does not correspond to the size of the pool, but to its size variation on a yearly basis, or in general on its rate of change that might be positive (increase of carbon storage and reduction of CO_2 emissions) or negative (decrease of carbon storage and increase of CO_2 emissions) depending on the evolution of the markets and of the distribution systems (see also Box 7.2 for a quantitative example). Data on the amount of carbon stored as inventory of these materials in the supply chain and on the rate of change of this amount is not available, but the figures in Table 7.2 and the analysis above indicate that the quantity of captured carbon that could be stored is very small compared with total anthropogenic carbon emissions. Thus, the use of captured CO_2 in industrial processes could have only a minute (if any) effect on reduction of net CO_2 emissions.

As to the second point, the duration of CO_2 storage in the carbon chemical pool and typical lifetime of the CO_2 consuming chemicals when in use before being degraded to CO_2 that is emitted to the atmosphere, are given in the last column of Table 7.2 Rather broad ranges are associated with classes of compounds consisting of a variety of different chemicals. The lifetime of the materials produced that could use captured CO_2 could vary from a few hours for a fuel such as methanol, to a few months for urea fertilizer, to decades for materials such as plastics and laminates, particularly those materials used in the construction industry. This indicates that even when there is a net storage of CO_2 as discussed in the previous paragraph, the duration of such storage is limited.

As to the last point, the extent of emission mitigation provided by the use of captured CO_2 to produce the compounds in the carbon chemical pool. Replacing carbon derived from a fossil fuel in a chemical process, for example a hydrocarbon, with captured CO_2 is sometimes possible, but does not affect the overall carbon budget, thus CO_2 does not replace the fossil fuel feedstock. The hydrocarbon has in fact two functions – it provides energy and it provides carbon as a building block. The CO_2 fails to provide energy, since it is at a lower energy level than the hydrocarbon (see Box 7.3). The energy of the hydrocarbon is often needed in the chemical process and, as in the production of most plastics, it is embodied in the end product. Alternatively, the energy of the hydrocarbon is available and likely to be utilized in other parts of the process, purification, pretreatment for example, or in other processes within the same plant. If this energy is missing, since CO_2 is used as carbon source, it has to be replaced somehow to close the energy balance of the plant. As long as the replacement energy is provided from fossil fuels, net CO_2 emissions will remain unchanged. It is worth noting that an economy with large non-fossil energy resources could consider CO_2 feedstocks to replace hydrocarbons in chemical synthesis. Such approaches are not covered here, since they are specific examples of converting to non-fossil energy and as such are driven by the merits of the new energy source rather than by the need for capture and storage of CO_2.

7.3.5 *Future scope*

The scale of the use of captured CO_2 in industrial processes is too small, the storage times too short and the energy balance too unfavourable for industrial uses of CO_2 to become significant as a means of mitigating climate change. There is a lack of data available to adequately assess the possible overall CO_2 inventory of processes that involve CO_2 substitution with associated energy balances and the effects of changes in other feedstocks

Box 7.2 Carbon chemical pool.

The carbon chemical pool is the ensemble of anthropogenic carbon containing organic chemicals. This box aims to provide criteria for measuring the quantitative impact on carbon mitigation of such a pool. If this impact were significant, using carbon from CO_2 could be an attractive storage option for captured CO_2.

Considering a specific chemical A, whose present worldwide production is 12 Mt yr^{-1}, whose worldwide inventory is 1 Mt – the monthly production – and whose lifetime before degradation to CO_2 and release to the atmosphere is less than one year. If next year production and inventory of A do not change, the contribution to CO_2 storage of this member of the chemical pool will be null. If production increased by a factor ten to 120 Mt yr^{-1}, whereas inventory were still 1 Mt, again the contribution of A to CO_2 storage would be null.

If on the contrary next year production increases and inventory also increases, for example to 3 Mt, to cope with increased market demand, the contribution of A to CO_2 storage over the year will be equivalent to the amount of CO_2 stoichiometrically needed to produce 2 Mt of A. However, if due to better distribution policies and despite increased production, the worldwide inventory of A decreased to 0.7 Mt, then A would yield a negative contribution to CO_2 storage, thus over the year the amount of CO_2 stoichiometrically needed to produce 0.3 Mt of A would be additionally emitted to the atmosphere.

Therefore, the impact on carbon dioxide mitigation of the carbon chemical pool does not depend on the amounts of carbon containing chemical products produced; there is CO_2 emission reduction in a certain time only if the pool has grown during that time. With increasing production, such impact can be positive or negative, as shown above. It is clear that since this would be a second or third order effect with respect to the overall production of carbon containing chemicals – itself much smaller in terms of fossil fuel consumption than fossil fuel combustion – this impact will be insignificant compared with the scale of the challenge that carbon dioxide capture and storage technologies have to confront.

Box 7.3. Energy gain or penalty in using CO_2 as a feedstock instead of carbon.

CO_2 can be used as a provider of carbon atoms for chemical synthesis, as an alternative to standard processes where the carbon atom source is fossil carbon, as coal or methane or other. This includes processes where the carbon atom in the CO_2 molecule is either reduced by providing energy, for example methanol synthesis, or does not change its oxidation state and does not need energy, synthesis of polycarbonates for example.

For the sake of simplicity let us consider a reaction from carbon to an organic final product A (containing n carbon atoms) that takes place in a chemical plant (standard process):

$$nC \rightarrow A \tag{7}$$

Let us also consider the alternative route whereby CO_2 captured from the power plant where carbon has been burnt is used in the chemical plant where the synthesis of A is carried out. In this case the sequence of reactions would be:

$$nC \rightarrow nCO_2 \rightarrow A \tag{8}$$

The overall energy change upon transformation of C into A, ΔH, is the same in both cases. The difference between the two cases is that in case (8) this overall energy change is split into two parts – $\Delta H=\Delta H_{com}+\Delta H_{syn}$ – one for combustion in the power plant and the other for the synthesis of A from CO_2 in the chemical plant (ΔH_{com} will be –400 which means 400 are made available by the combustion of carbon). If ΔH is negative, that means an overall exothermic reaction (1), then ΔH_{syn} will be either negative or even positive. If ΔH is positive, that means an overall endothermic reaction (7), then ΔH_{syn} will be even more positive. In both cases, exothermic or endothermic reaction, the chemical plant will lack 400 kJ/molC energy in case (2) with respect to case (1). This energy has already been exploited in the power plant and is no longer available in the chemical plant. It is worth noting that large-scale chemical plants (these are those of interest for the purpose of carbon dioxide emission mitigation) make the best possible use of their energy by applying so-called heat integration, for example by optimizing energy use through the whole plant and not just for individual processes. In case (1) chemical plants make good use of the 400 kJ/molC that are made available by the reaction (7) in excess of the second step of reaction (8).

Therefore, in terms of energy there is no benefit in choosing path (8) rather than path (7). In terms of efficiency of the whole chemical process there might be a potential improvement, but there might also be a potential disadvantage, since route (7) integrates the heat generation associated with the oxidation of carbon and the conversion to product A. These effects are of second order importance and have to be evaluated on a case-by-case basis. Nevertheless, the scale of the reduction in CO_2 emissions would be rather small, since it would be even smaller than the scale of the production of the chemicals that might be impacted by the technology change, that is by the change from path (7) to path (8) (Audus and Oonk, 1997).

and emissions. However, the analysis above demonstrates that, although the precise figures are difficult to estimate and even their sign is questionable, the contribution of these technologies to CO_2 storage is negligible. Research is continuing on the use of CO_2 in organic chemical polymer and plastics production, but the drivers are generally cost, elimination of hazardous chemical intermediates and the elimination of toxic wastes, rather than the storage of CO_2.

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