6

Ocean storage

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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

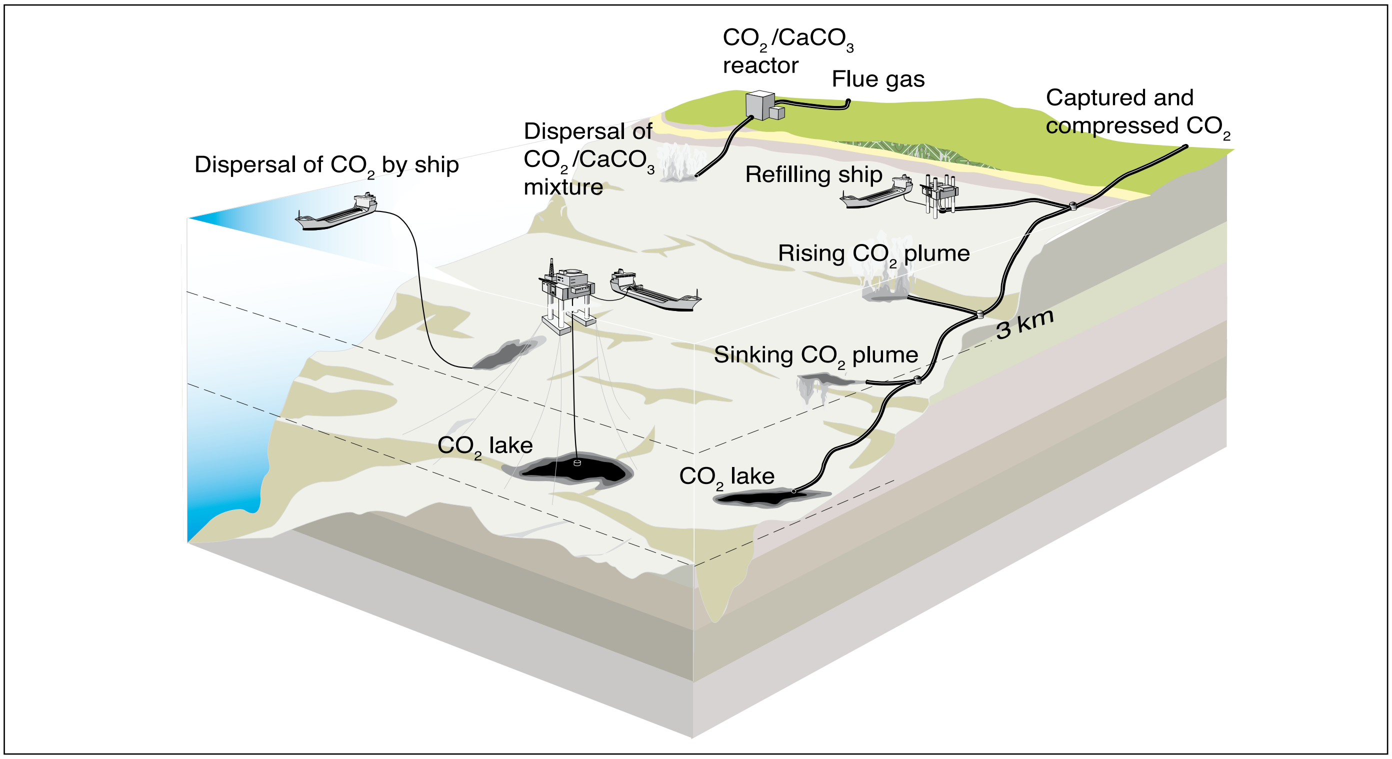

Figure 6.1 Illustration of some of the ocean storage strategies described in this chapter (Artwork courtesy Sean Goddard, University of Exeter.)

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

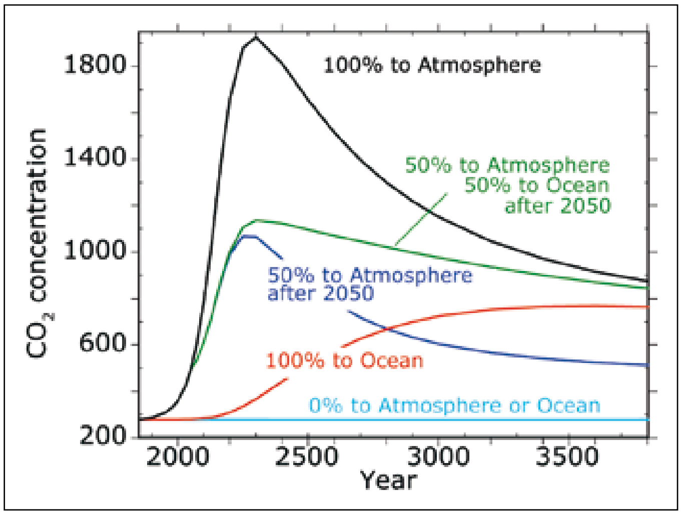

Figure 6.2 Simulated atmospheric CO_2 resulting from CO_2 release to the atmosphere or injection into the ocean at 3,000 m depth (Kheshgi and Archer, 2004). Emissions follow a logistic trajectory with cumulative emissions of 18,000 $GtCO_2$. Illustrative cases include 100% of emissions released to the 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).

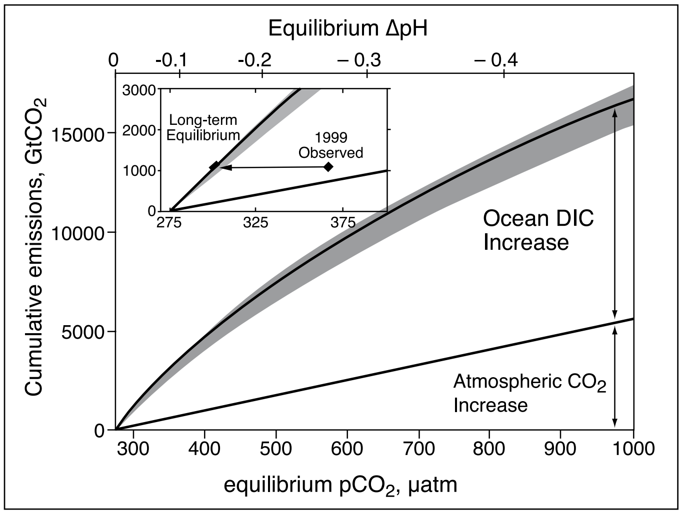

Figure 6.3 Equilibrium partitioning of CO_2 between the ocean and atmosphere. On the time scale of millennia, complete mixing of the oceans leads to a partitioning of cumulative CO_2 emissions between the oceans and atmosphere with the bulk of emissions eventually residing in the oceans as dissolved 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 (ΔpH ≈ –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.

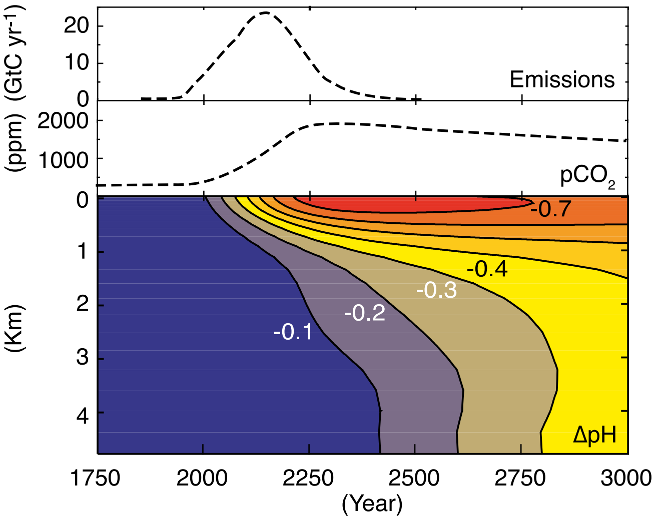

Figure 6.4 Simulated ocean *p*H changes from CO_2 release to the atmosphere. Modelled atmospheric CO_2 change and horizontally averaged ΔpH driven by a CO_2 emissions scenario: historic atmospheric CO_2 up to 2000, IS92a from 2000 to 2100, and logistic curve extending beyond 2100 with 18,000 $GtCO_2$ (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.

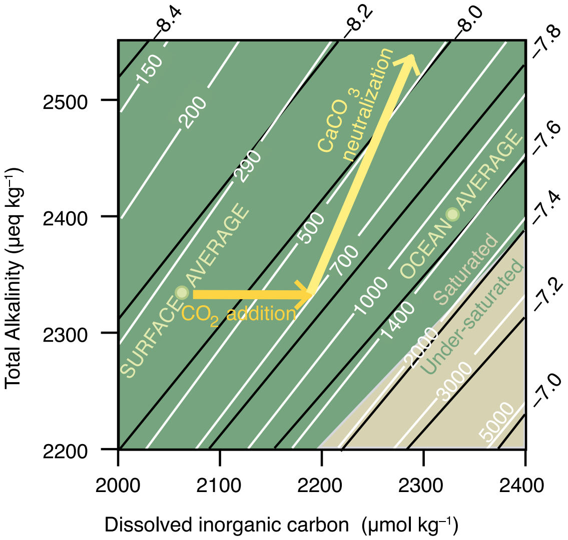

Figure 6.5 Composition diagram for ocean surface waters at 15°C (adapted from Baes, 1982). The white lines denote compositions with the same value of pCO_2 (in ppm); the black lines denote compositions with the same *p*H. The tan shaded region is undersaturated and the green shaded region is supersaturated 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.

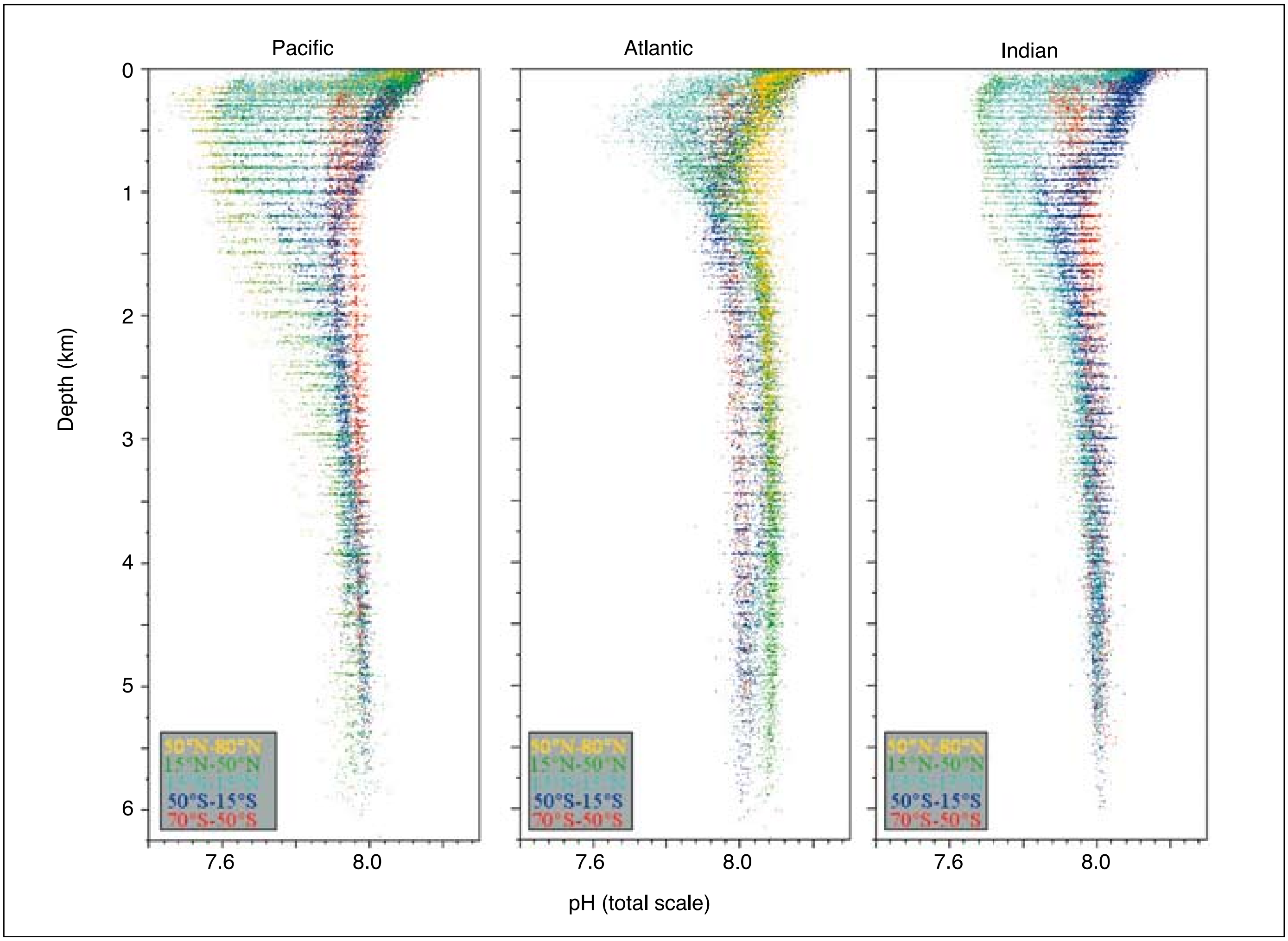

Figure 6.6 Observed variation in open ocean *p*H for the 1990s (shown on the total hydrogen scale; data from Key et al., 2004). In this figure the oceans are separated into separate panels. The three panels are on the same scale and coloured by latitude band to illustrate the large north-south changes 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.

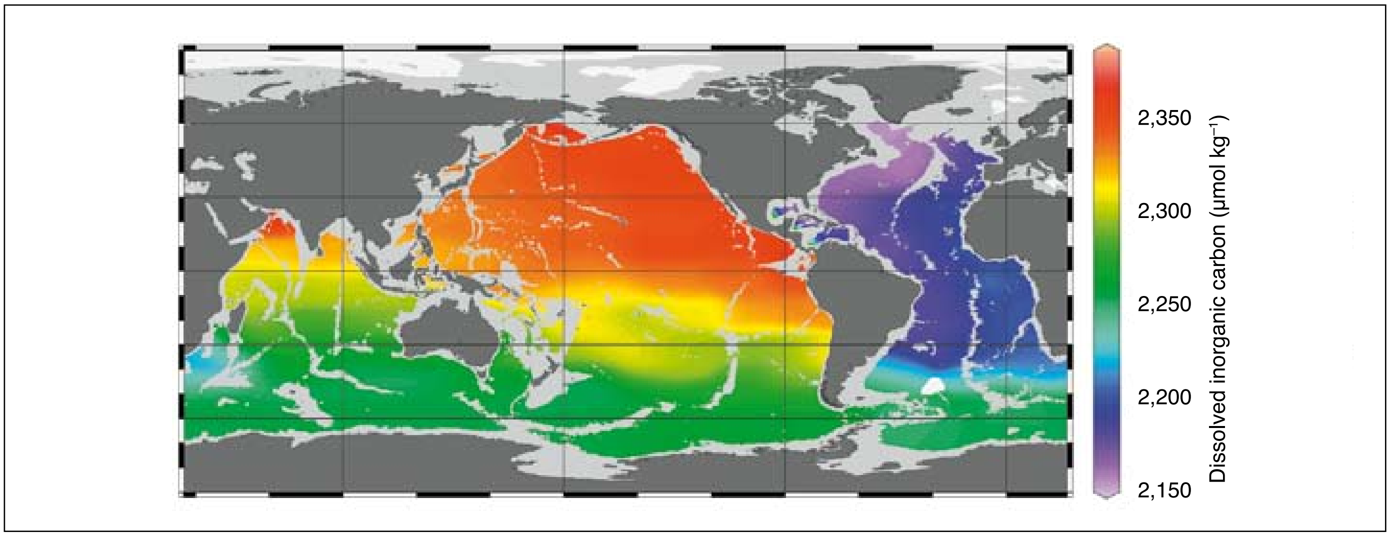

Figure 6.7 Natural variation in total dissolved inorganic carbon concentration at 3000 m depth (data from Key et al., 2004). Ocean carbon concentrations increase roughly 10% as deep ocean waters transit from the North Atlantic to the North Pacific due to the oxidation of organic carbon in the deep ocean.

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.

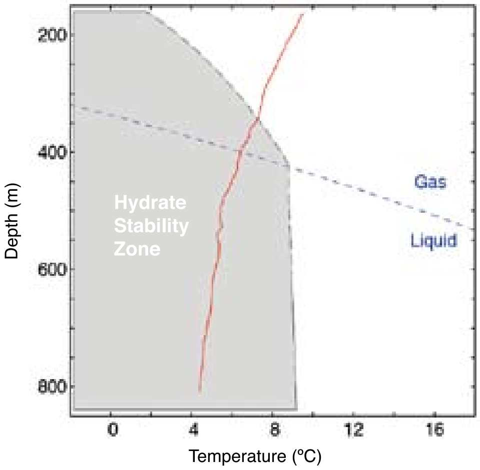

Figure 6.8 CO_2 sea water phase diagram. CO_2 is stable in the liquid phase when temperature and pressure (increasing with ocean depth) fall in the region below the blue curve; a gas phase is stable under conditions above the blue dashed line. In contact with sea water and at temperature and pressure 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).

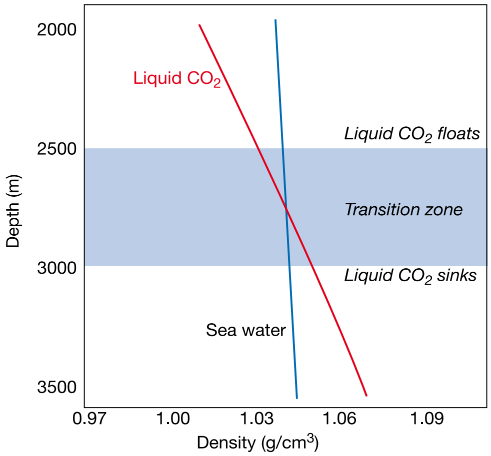

Figure 6.9 Shallower than 2500 m, liquid CO_2 is less dense than sea water, and thus tends to float upward. Deeper than 3000 m, liquid CO_2 is denser than sea water, and thus tends to sink downwards. Between these two depths, the behaviour can vary with location (depending mostly on temperature) and 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.

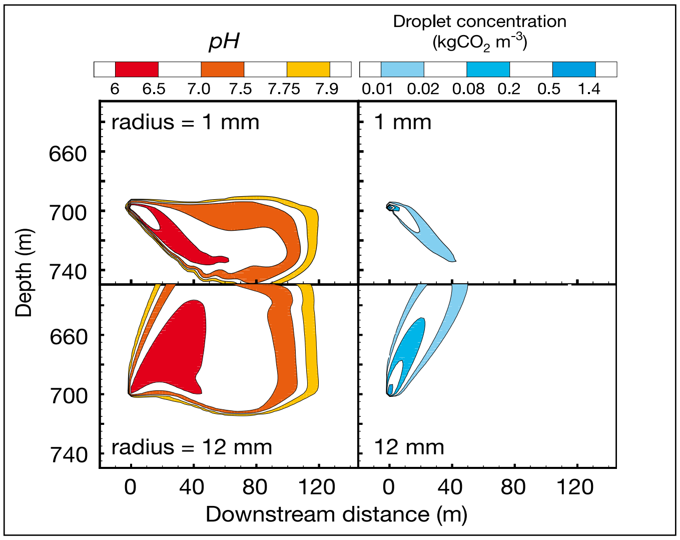

Figure 6.11 Simulated CO_2 enriched sea water plumes (left panels; indicated by pH) and CO_2 droplet plumes (right panels; indicated by $kgCO_2$ m^{-3}) created by injecting 1 cm and 12 cm liquid CO_2 droplets (top and bottom panels, respectively) into the ocean from fixed nozzles (elapsed time is 30 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).

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).

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

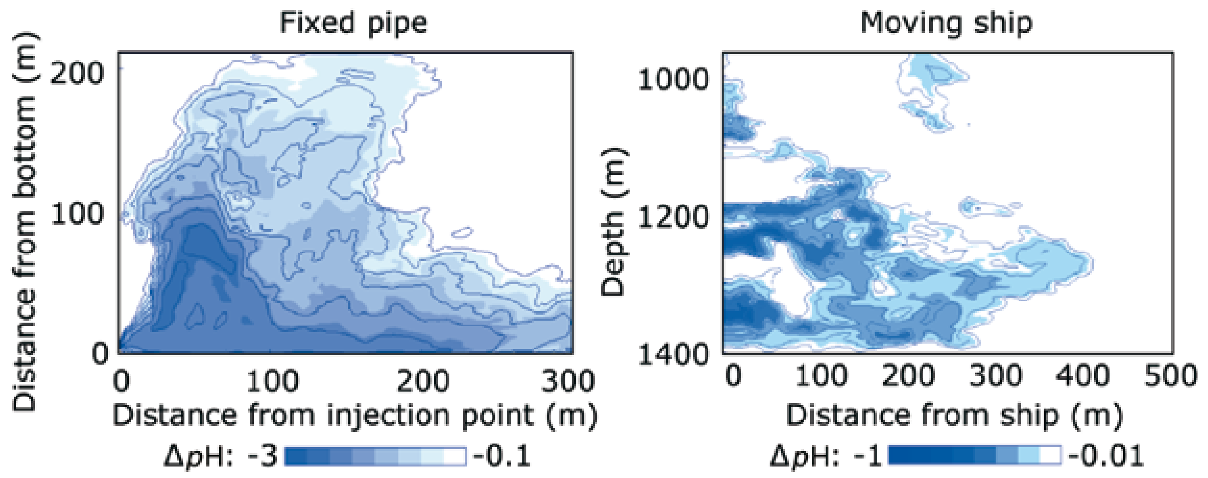

Figure 6.12 Simulated plumes (Chen *et al*., 2005) created by injecting liquid CO_2 into the ocean from a fixed pipe (left panel) and a moving ship (right panel) at a rate of 100 kg s^{-1} (roughly equal to the CO_2 from a 500 MWe coal-fired power plant). Left panel: injection at 875 m depth (12 m from 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

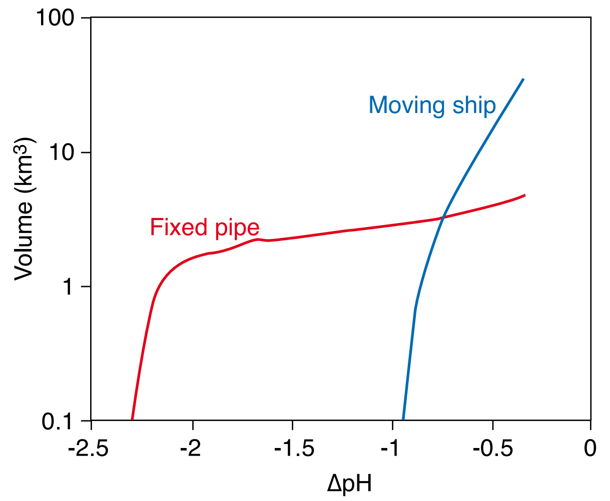

Figure 6.13 Volume of water with a Δ*p*H less than the value shown on the horizontal axis for the simulations shown in Figure 6.12 corresponding to CO_2 releases from a 500 MW_e power plant. The fixed pipe simulation produces a region with Δ*p*H < –1, however, the moving ship disperses the CO_2 more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

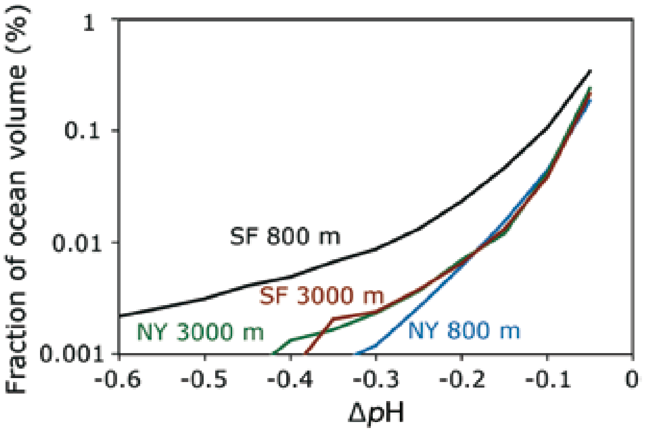

Figure 6.14 Estimated volume of *p*H perturbations at basin scale (Wickett *et al*., 2003). Simulated fraction of global ocean volume with a Δ*p*H less than the amount shown on the horizontal axis, after 100 years of simulated injection at a rate of 0.37 $GtCO_2$ yr^{-1} (= 0.1 GtC yr^{-1}) at each of 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

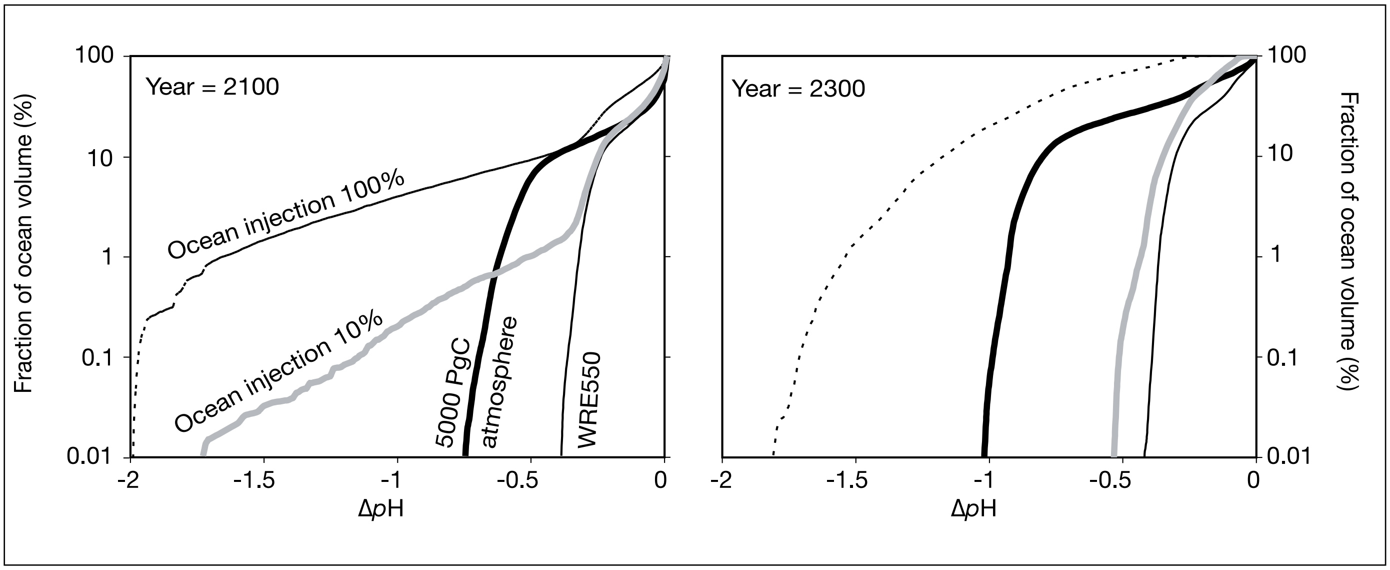

Figure 6.15 Estimated volume of *p*H perturbations at global scale for hypothetical examples in which injection of CO_2 into the ocean interior provides 100% or 10% of the mitigation effort needed to move from a logistic emissions curve cumulatively releasing 18,000 $GtCO_2$ (=5000 GtC) to emissions 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 *p*H, pCO_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 *p*H 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 *p*H 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 *p*H 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 pCO_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.

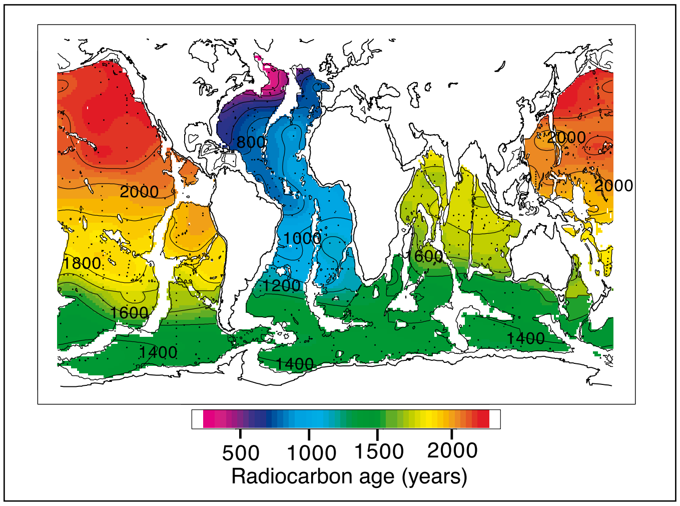

Figure 6.16 Map of radiocarbon (^{14}C) age at 3500 m (Matsumoto and Key, 2004).

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.

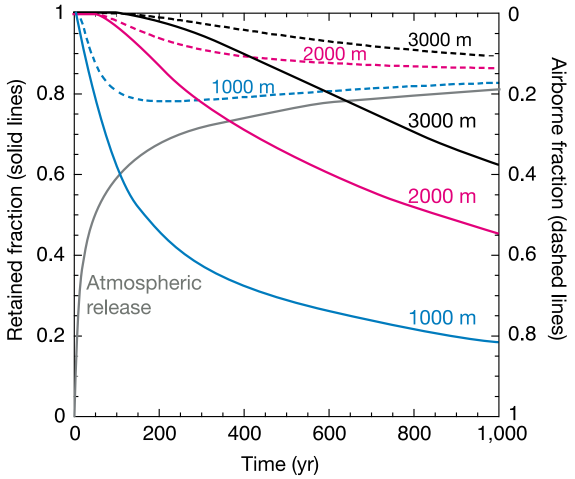

Figure 6.17 Fraction of carbon in the ocean from injection at three different depths and the atmosphere illustrated with results from a schematic model (Herzog et al., 2003). Calculations assume a background 280 ppm of CO_2 in the atmosphere.

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	at 20 years	0	0.96	1.00	1.00
Retained	at 100 years	0	0.63	0.97	1.00
Fraction	at 500 years	0	0.28	0.65	0.85
Airborne	at 20 years	0.61	0.03	6×10^{-6}	7×10^{-10}
Fraction	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	5% per year	0	0.95	1.00	1.00
Value (constant	1% per year	0	0.72	0.95	0.99
emissions cost)	0.2% per year	0	0.41	0.72	0.85
Global	20 year horizon	1	0.01	1×10^{-6}	6×10^{-10}
Warming	100 year horizon	1	0.21	0.01	4×10^{-4}
Potential	500 year horizon	1	0.56	0.20	0.06

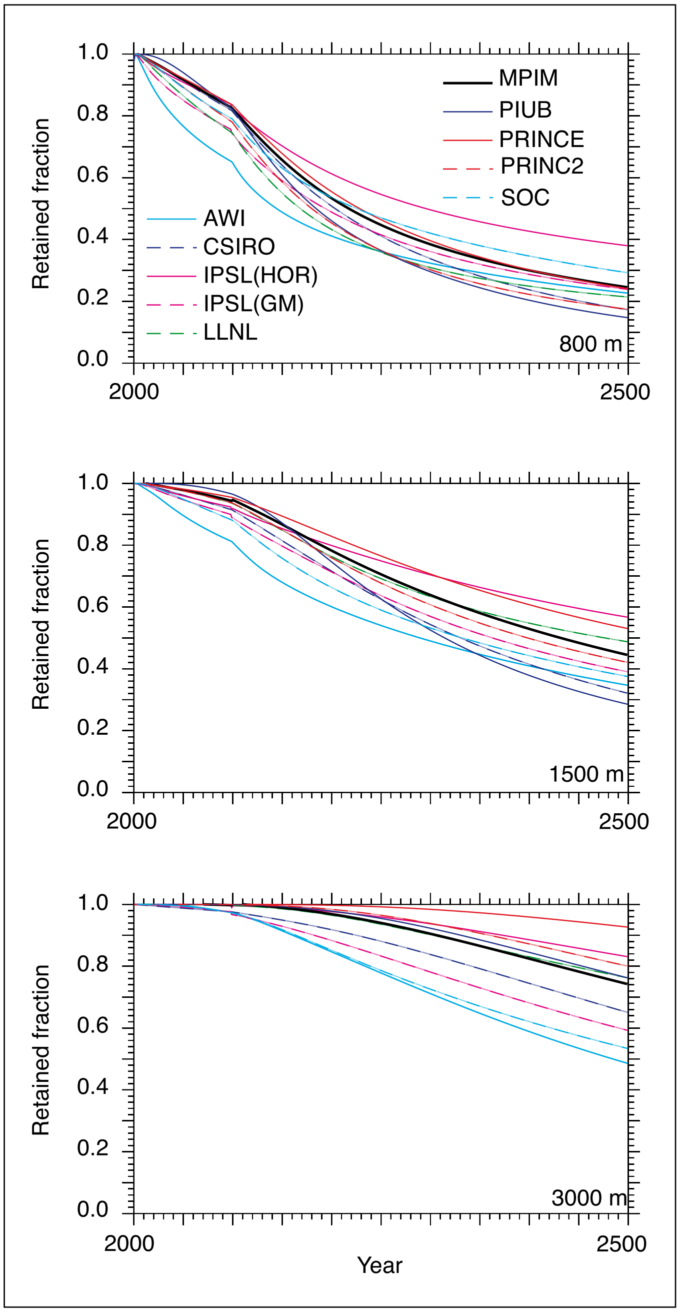

Figure 6.18 Results are shown for seven ocean general circulation models at three different depths averaged over seven injection locations (Orr, 2004). The percentage efficiency shown is the retained fraction for an injection at a constant rate from 2000 to 2100. Models agree that deeper injection isolates 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.

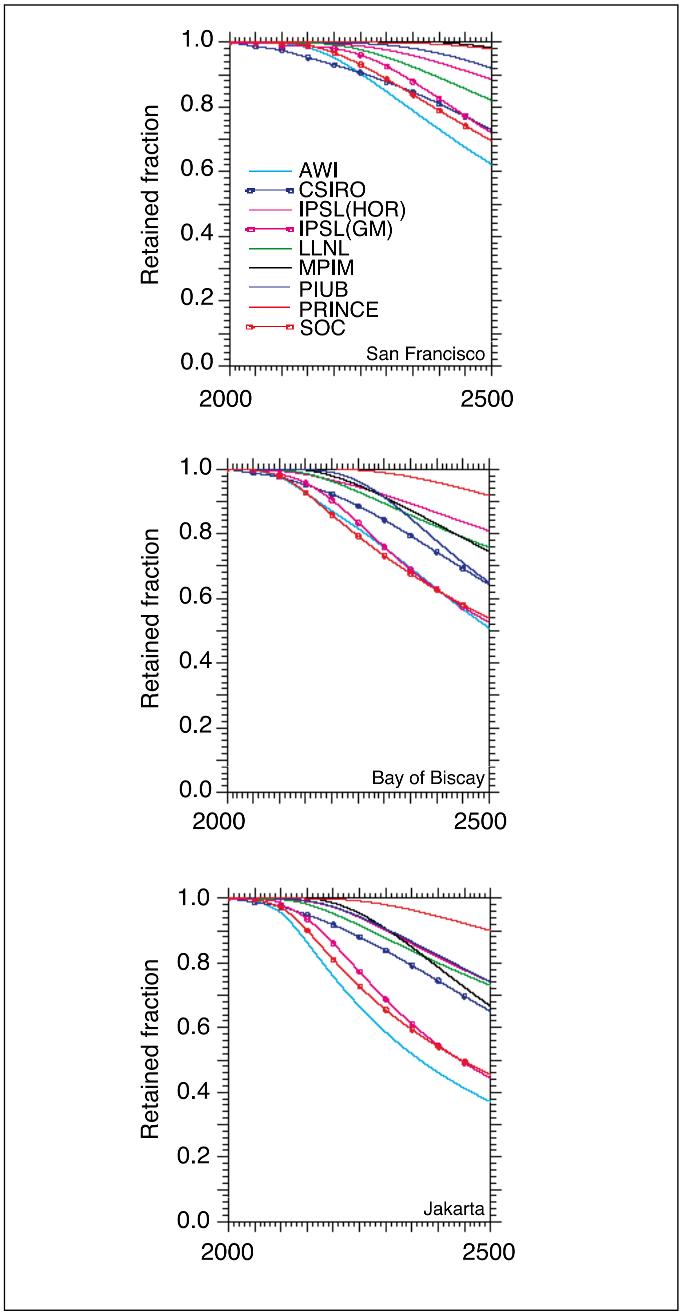

Figure 6.19 Comparison of storage results for three injection locations (at 3000 m depth) in ten ocean model simulations (Orr, 2004). Models differ on predictions of CO_2 fraction retained for release in different oceans.

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).

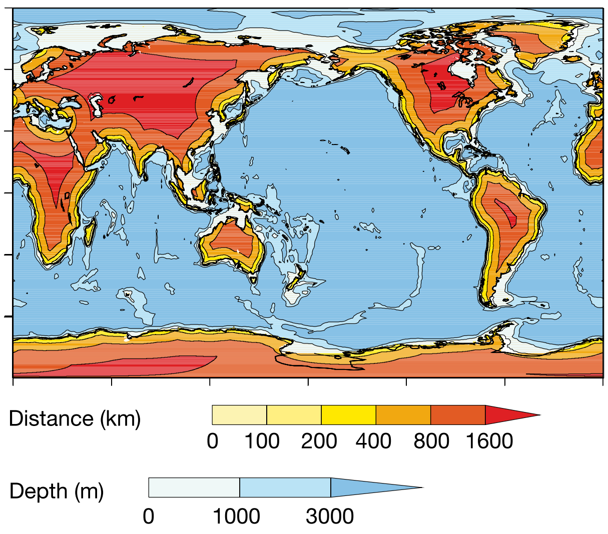

Figure 6.20 Locations of ocean water at least 1 km and 3 km deep. Distance over land to water that is at least 3 km deep (Caldeira and Wickett, 2005). In general, land areas with the lightest colours would be the most-cost effective land-based settings for a CO_2-injection operation. However, each potential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

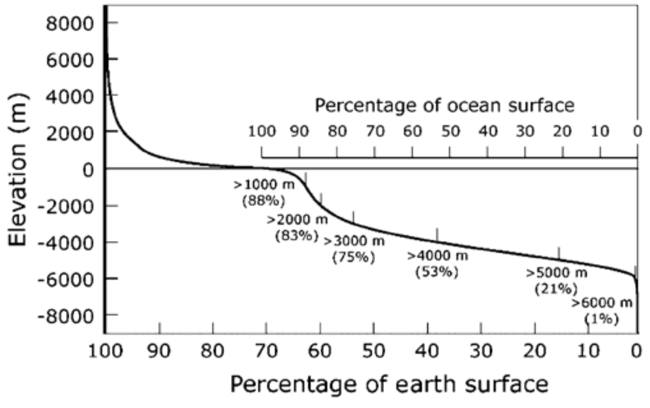

Figure 6.21 Relationship between depth and sea floor area. Flow in ocean bottom boundary layers would need to be taken into account when selecting a site for a CO_2 lake. Bottom friction and turbulence can enhance the dissolution rate and vertical transport of dissolved CO_2 and lead to a short lifetime 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).

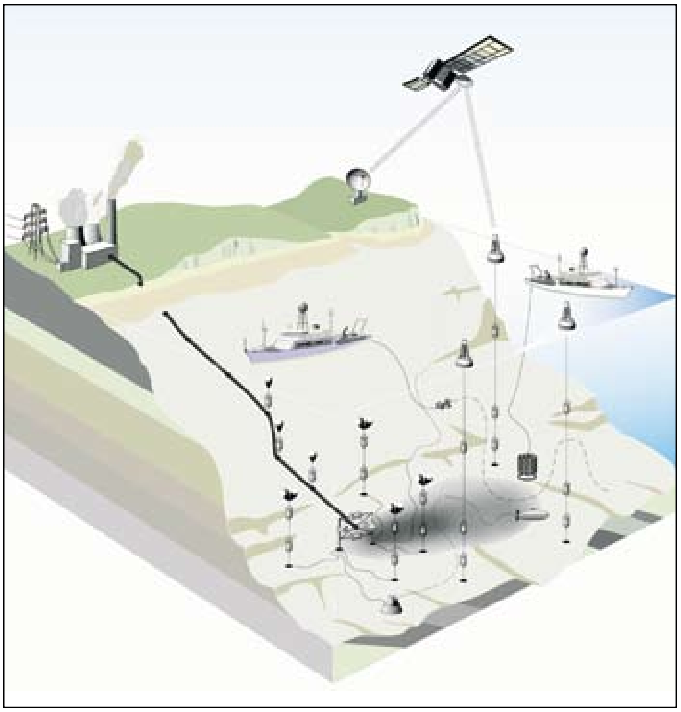

Figure 6.22 Schematic of possible approaches for monitoring the injection of CO_2 into the deep ocean via a pipeline. The grey region represents a plume of high CO_2/low *p*H water extending from the end of the pipeline. Two sets of chemical, biological and current sensors and two underwater cameras 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,

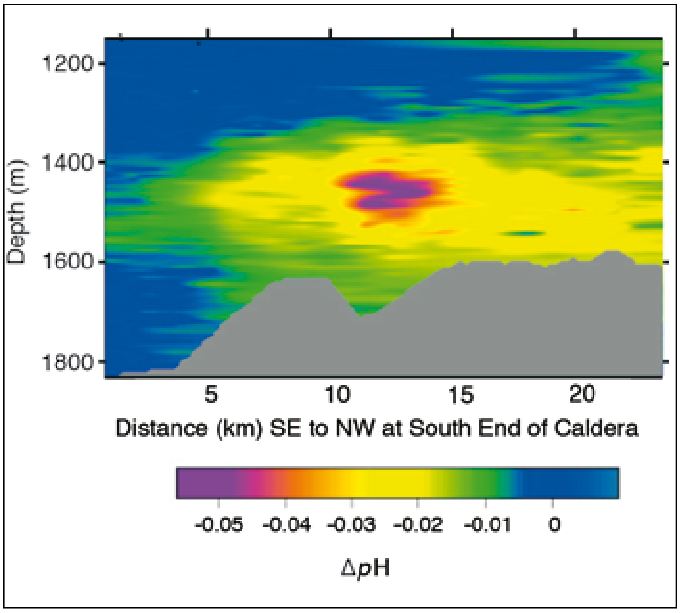

Figure 6.23 Measurements showing the ability to measure chemical effects of a natural CO_2 plume. Profiles for *p*H were taken in June 1999 near the Axial Volcano at 46ºN 130ºW, in the ocean near Portland, Oregon, United States.

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 ΔpH, 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 ΔpH, and the amount of CO$_2$ that, if uniformly distributed throughout the ocean, would produce this ΔpH.

pH change ΔpH	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 ΔpH (m^3)	GtCO$_2$ to produce ΔpH 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 ΔpH. 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$_2$, pH, 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 pH 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 pH or carbonate-ion concentrations. For example, fish larvae are more sensitive to low pH and high CO$_2$ than low pH 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 (pH). This change in hydrogen ion concentration may affect marine life through mechanisms that do not directly involve CO$_2$. Studies of effects of lowered pH (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

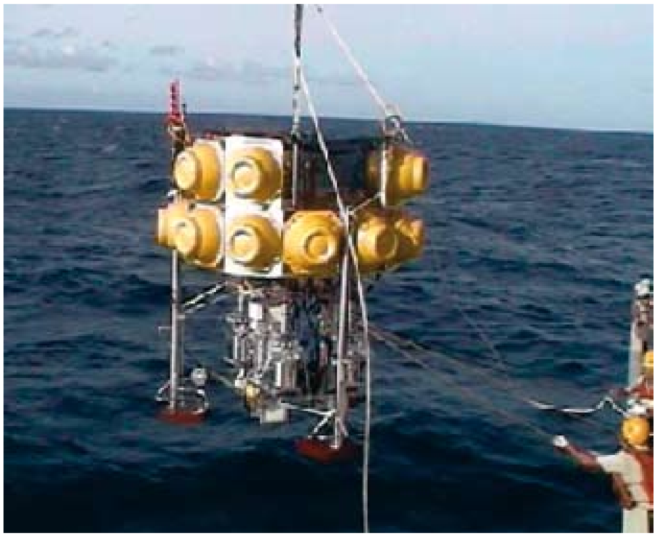

Figure 6.24 Experimental chamber going to the sea floor (Ishida *et al*. 2004). The bottom part houses a chamber that penetrates into the sediment. The top part houses electronics, pumps, valves, and water bags, that are used to control the CO_2 concentration inside the chamber, and to sample sea water 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).

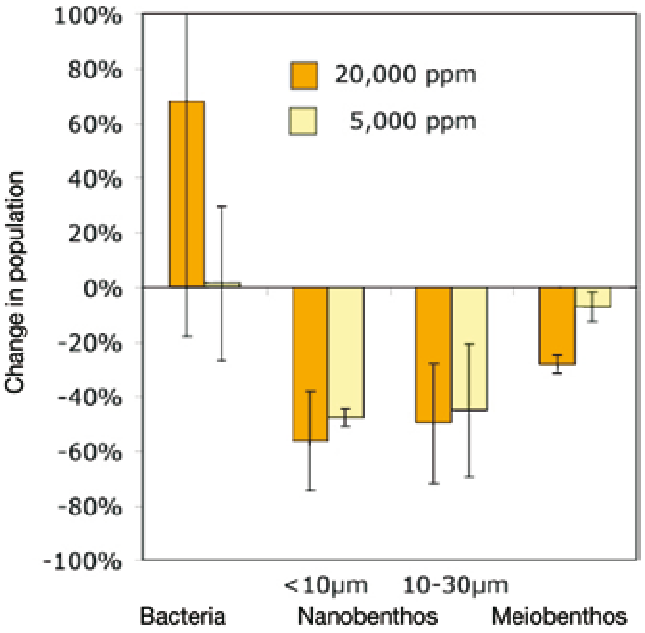

Figure 6.25 Preliminary investigations into the change of bacteria, nanobenthos and meiobenthos abundance after exposure to 20,000 and 5,000 ppm CO_2 for 77 to 375 hr during three experiments carried out at 2,000 m depth in Nankai Trough, north-western Pacific. Error bars represent one standard deviation (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.

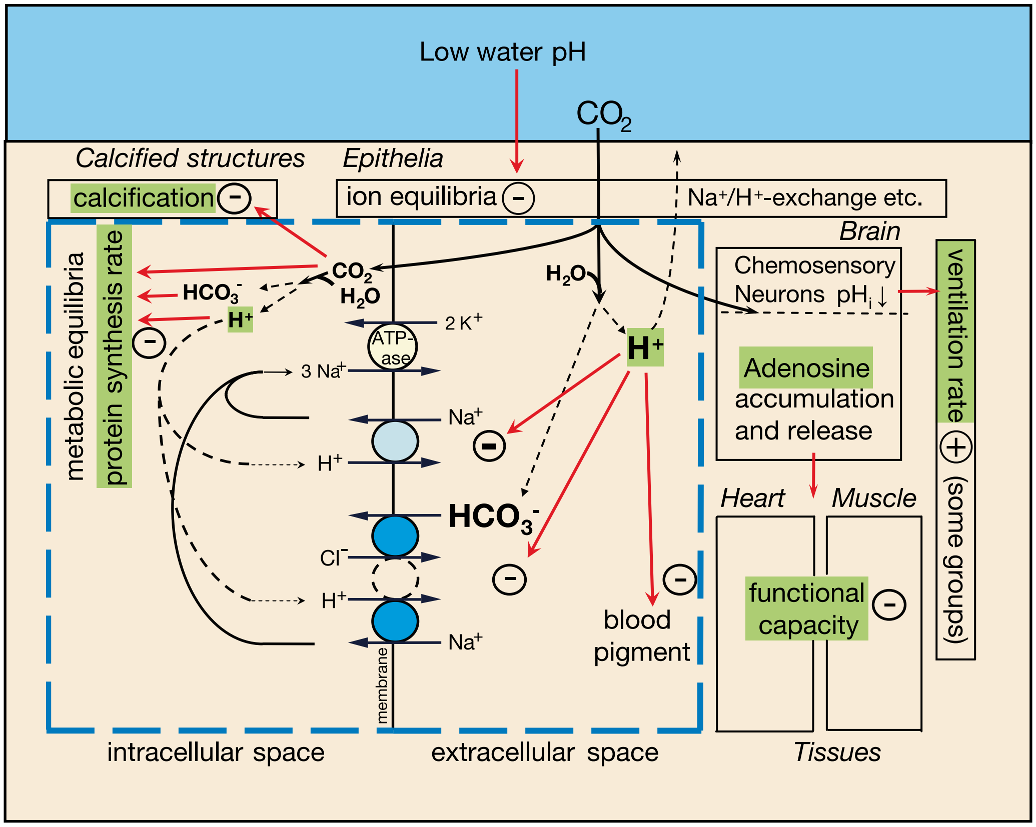

Figure 6.26 Effects of added CO_2 at the scale of molecule to organism and associated changes in proton (H^+), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) levels in a generalized and simplified marine invertebrate or fish. The blue region on top refers to open water; the tan region represents the 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 biogeo-chemical 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 $\Delta p\text{H} < -1.0$ 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$/t$CO_2$ shipped)	3.3	3.3
Ship transport to injection platform (US$/t$CO_2$ shipped)	2.9	4.2
Injection platform, pipe and nozzle (US$/t$CO_2$ shipped)	5.3	5.3
Ocean storage cost (US$/t$CO_2$ shipped)	11.5	12.8
Ocean storage cost (US$/t$CO_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$/t$CO_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$/t$CO_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$/t$CO_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$/t$CO_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$/t$CO_2$ net stored (100 km case) to 31.1 US$/t$CO_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$/t$CO_2$ shipped)	2.2	2.2
Ship transport to injection ship(US$/t$CO_2$ shipped)	3.9	5.3
Injection ship, pipe and nozzle (US$/t$CO_2$ shipped)	7.7	7.7
Ocean storage cost (US$/t$CO_2$ shipped)	13.8	15.2
Ocean storage cost (US$/t$CO_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\$/tCO_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,

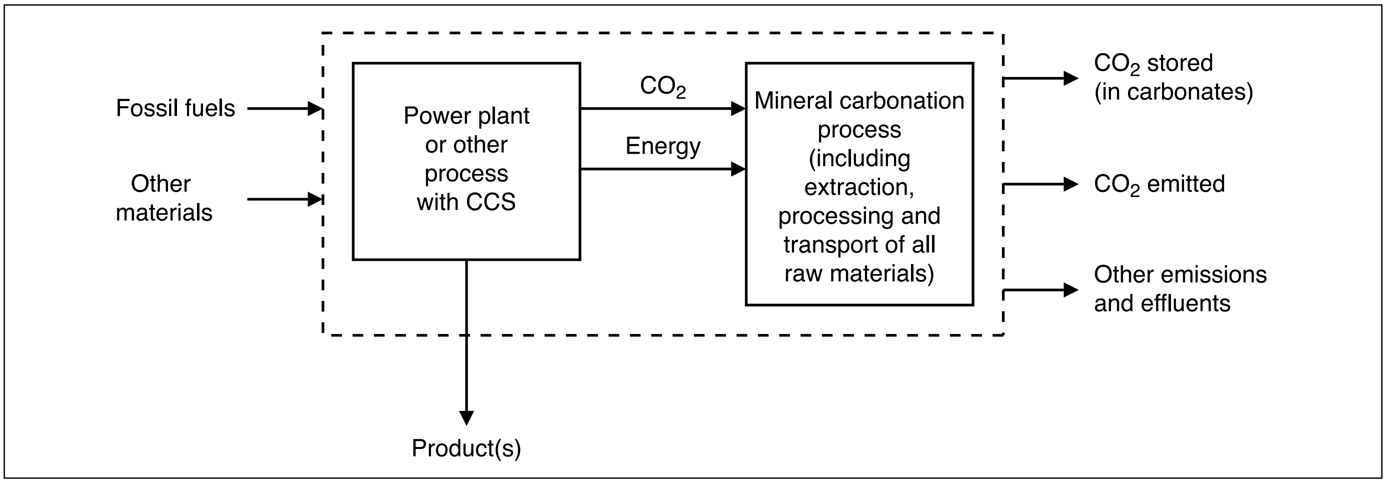

Figure 7.1 Material and energy balances through the system boundaries for a power plant with CO_2 capture and storage through mineral carbonation. The fossil fuel input provides energy both to the power plant that produces CO_2 and to the mineralization process (either directly or indirectly via the 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.

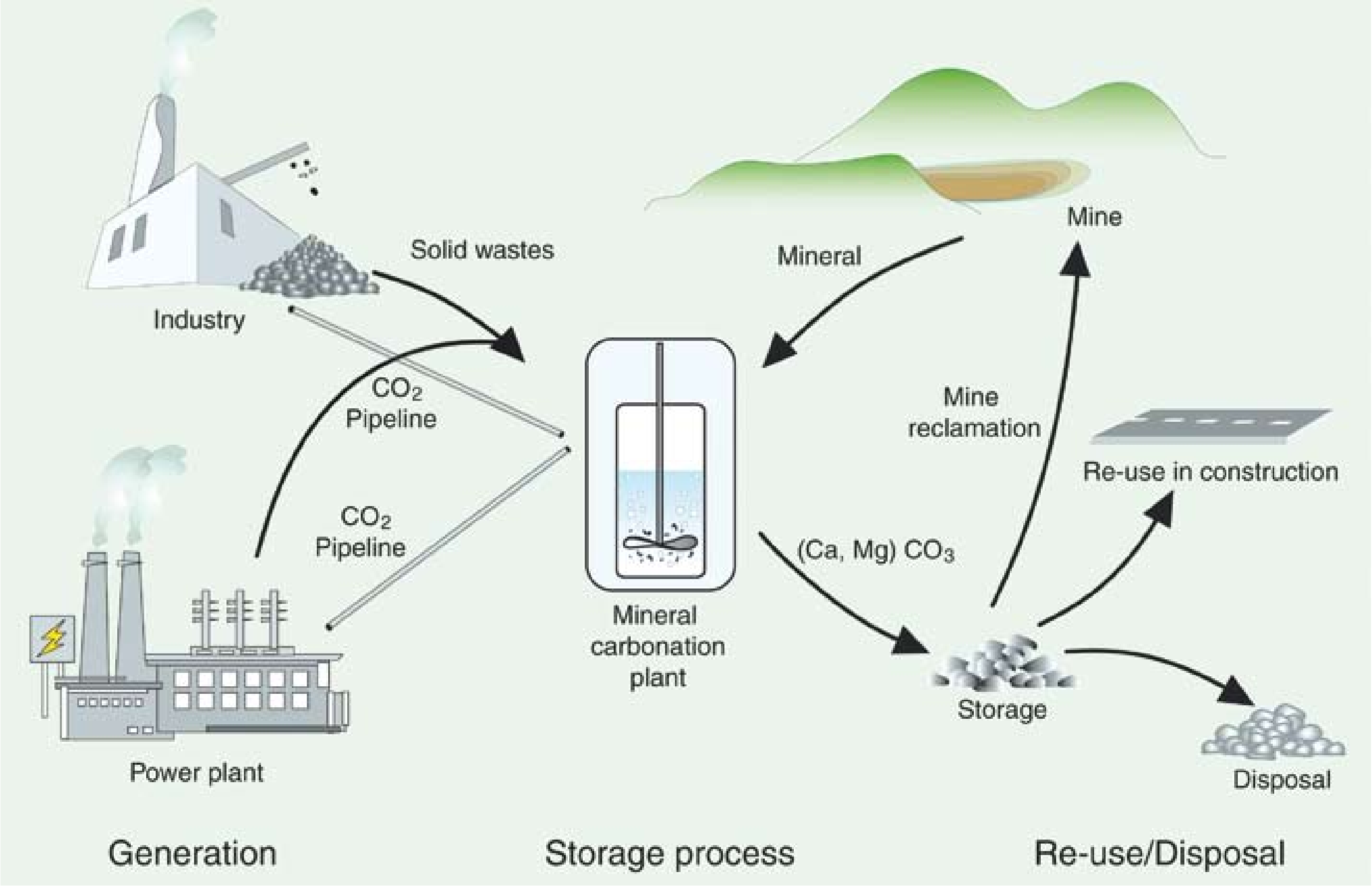

Figure 7.2 Material fluxes and process steps associated with the ex-situ mineral carbonation of silicate rocks or industrial residues (Courtesy Energy Research Centre of the Netherlands (ECN)).

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:

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2 + 89\ kJ\ mol^{-1}CO_2 \qquad (2a)$$

Serpentine:

$$Mg_3Si_2O_5(OH)_4 + 3\ CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O + 64\ kJ\ mol^{-1}CO_2 \qquad (2b)$$

Wollastonite:

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 + 90\ kJ\ mol^{-1}CO_2 \qquad (2c)$$

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

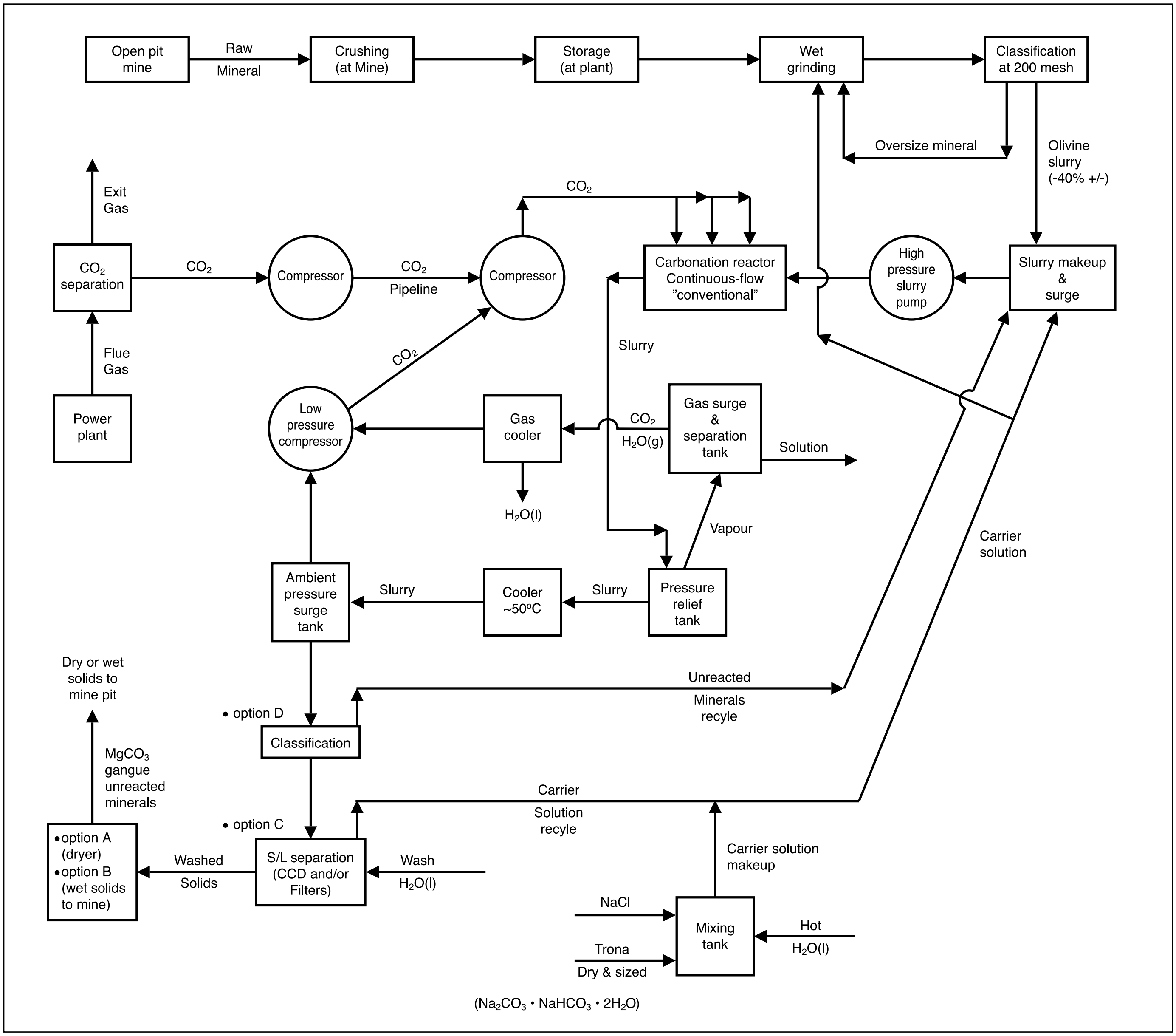

Figure 7.3 Process scheme of the single-step mineral carbonation of olivine in aqueous solution (Courtesy Albany Research Centre). 'Single-step' indicates that mineral dissolution and carbonate precipitation take place simultaneously in the same carbonation reactor, whereas more steps are of course needed 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\$/tCO_2 stored was obtained, with 27.5% additional CO_2 emissions, thus leading to 110 US\$/tCO_2 avoided. In the case of the two-step acetic acid process, an overall cost of 27 US\$/tCO_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\$/tCO_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.

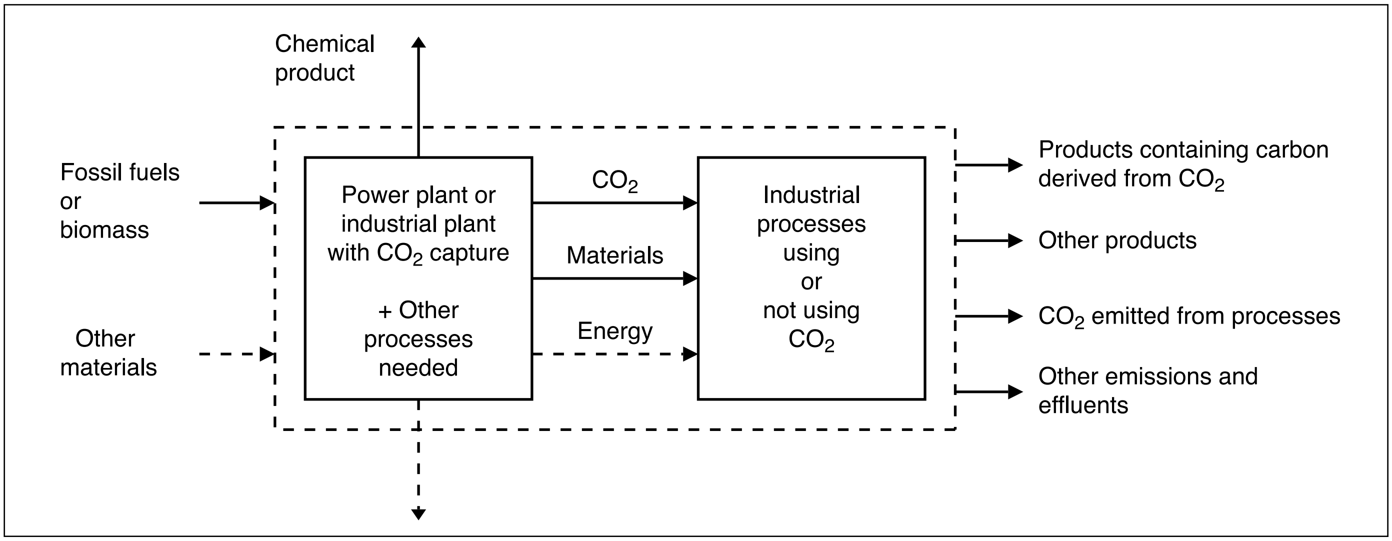

Figure 7.4 Material and energy balances through the system boundaries for a power plant or an industrial plant with CO_2 capture, followed by an industrial process using CO_2. The inputs include all fossil fuels together with all other materials used within the system. The fossil fuel input provides 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):

$$CO + 2H_2 \rightarrow CH_3OH \qquad (5)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad (6)$$

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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8

Cost and economic potential

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EXECUTIVE SUMMARY

The major components of a carbon dioxide capture and storage (CCS) system include capture (separation plus compression), transport, and storage (including measurement, monitoring and verification). In one form or another, these components are commercially available. However, there is relatively little commercial experience with configuring all of these components into fully integrated CCS systems at the kinds of scales which would likely characterize their future deployment. The literature reports a fairly wide range of costs for employing CCS systems with fossil-fired power production and various industrial processes. The range spanned by these cost estimates is driven primarily by site-specific considerations such as the technology characteristics of the power plant or industrial facility, the specific characteristics of the storage site, and the required transportation distance of carbon dioxide (CO_2). In addition, estimates of the future performance of components of the capture, transport, storage, measurement and monitoring systems are uncertain. The literature reflects a widely held belief that the cost of building and operating CO_2 capture systems will fall over time as a result of technological advances.

The cost of employing a full CCS system for electricity generation from a fossil-fired power plant is dominated by the cost of capture. The application of capture technology would add about 1.8 to 3.4 US\$ct kWh^{-1} to the cost of electricity from a pulverized coal power plant, 0.9 to 2.2 US\$ct kWh^{-1} to the cost for electricity from an integrated gasification combined cycle coal power plant, and 1.2 to 2.4 US\$ct kWh^{-1} from a natural-gas combined-cycle power plant. Transport and storage costs would add between –1 and 1 US\$ct kWh^{-1} to this range for coal plants, and about half as much for gas plants. The negative costs are associated with assumed offsetting revenues from CO_2 storage in enhanced oil recovery (EOR) or enhanced coal bed methane (ECBM) projects. Typical costs for transportation and geological storage from coal plants would range from 0.05–0.6 US\$ct kWh^{-1}. CCS technologies can also be applied to other industrial processes, such as hydrogen (H_2) production. In some of these non-power applications, the cost of capture is lower than for capture from fossil-fired power plants, but the concentrations and partial pressures of CO_2 in the flue gases from these sources vary widely, as do the costs. In addition to fossil-based energy conversion processes, CCS may be applied to biomass-fed energy systems to create useful energy (electricity or transportation fuels). The product cost of these systems is very sensitive to the potential price of the carbon permit and the associated credits obtained with systems resulting in negative emissions. These systems can be fuelled solely by biomass, or biomass can be co-fired in conventional coal-burning plants, in which case the quantity is normally limited to about 10–15% of the energy input.

Energy and economic models are used to study future scenarios for CCS deployment and costs. These models indicate that CCS systems are unlikely to be deployed on a large scale in the absence of an explicit policy that substantially limits greenhouse gas emissions to the atmosphere. The literature and current industrial experience indicate that, in the absence of measures to limit CO_2 emissions, there are only small, niche opportunities for the deployment of CCS technologies. These early opportunities for CCS deployment – that are likely to involve CO_2 captured from high-purity, low-cost sources and used for a value-added application such as EOR or ECBM production – could provide valuable early experience with CCS deployment, and create parts of the infrastructure and knowledge base needed for the future large-scale deployment of CCS systems.

With greenhouse gas emission limits imposed, many integrated assessment analyses indicate that CCS systems will be competitive with other large-scale mitigation options, such as nuclear power and renewable energy technologies. Most energy and economic modelling done to date suggests that the deployment of CCS systems starts to be significant when carbon prices begin to reach approximately 25–30 US\$/tCO_2 (90–110 US\$/tC). They foresee the large-scale deployment of CCS systems within a few decades from the start of any significant regime for mitigating global warming. The literature indicates that deployment of CCS systems will increase in line with the stringency of the modelled emission reduction regime. Least-cost CO_2 concentration stabilization scenarios, that also take into account the economic efficiency of the system, indicate that emissions mitigation becomes progressively more stringent over time. Most analyses indicate that, notwithstanding significant penetration of CCS systems by 2050, the majority of CCS deployment will occur in the second half of this century. They also indicate that early CCS deployment will be in the industrialized nations, with deployment eventually spreading worldwide. While different scenarios vary the quantitative mix of technologies needed to meet the modelled emissions constraint, the literature consensus is that CCS could be an important component of a broad portfolio of energy technologies and emission reduction approaches. In addition, CCS technologies are compatible with the deployment of other potentially important long-term greenhouse gas mitigation technologies such as H_2 production from biomass and fossil fuels.

Published estimates (for CO_2 stabilization scenarios between 450–750 ppmv) of the global cumulative amount of CO_2 that might be stored over the course of this century in the ocean and various geological formations span a wide range: from very small contributions to thousands of gigatonnes of CO_2. This wide range can largely be explained by the uncertainty of long-term, socio-economic, demographic and technological change, the main drivers of future CO_2 emissions. However, it is important to note that the majority of stabilization scenarios from 450–750 ppmv tend to cluster in the range of 220–2200 GtCO_2 (60–600 GtC). This demand for CO_2 storage appears to be within global estimates of total CO_2 storage capacity. The actual use of CCS is likely to be lower than the estimates for economic potential indicated by these energy and economic models, as there are other barriers to technology development not adequately accounted for in these modelling frameworks. Examples include concerns about environmental impact, the lack

of a clear legal framework and uncertainty about how quickly learning-by-doing will lower costs. This chapter concludes with a review of knowledge gaps that affect the reliability of these model results.

Given the potential for hundreds to thousands of gigatonnes of CO_2 to be stored in various geological formations and the ocean, questions have been raised about the implications of gradual leakage from these reservoirs. From an economic perspective, such leakage – if it were to occur – can be thought of as another potential source of future CO_2 emissions, with the cost of offsetting this leaked CO_2 being equal to the cost of emission offsets when the stored CO_2 leaks to the atmosphere. Within this purely economic framework, the few studies that have looked at this topic indicate that some CO_2 leakage can be accommodated while progressing towards the goal of stabilizing atmospheric concentrations of CO_2.

8.1 Introduction

In this chapter, we address two of the key questions about any CO_2 mitigation technology: 'How much will it cost?' and 'How do CCS technologies fit into a portfolio of greenhouse gas mitigation options?' There are no simple answers to these questions. Costs for CCS technologies depend on many factors: fuel prices, the cost of capital, and costs for meeting potential regulatory requirements like monitoring, to just name a few. Add to this the uncertainties associated with technology development, the resource base for storage potential, the regulatory environment, etc., and it becomes obvious why there are many answers to what appear to be simple questions.

This chapter starts (in Section 8.2) by looking at the costs of the system components, namely capture and compression, transport, and storage (including monitoring costs and by-product credits from operations such as EOR). The commercial operations associated with each of these components provide a basis for the assessment of current costs. Although it involves greater uncertainty, an assessment is also included of how these costs will change in the future. The chapter then reviews the findings from economic modelling (Section 8.3). These models take component costs at various levels of aggregation and then model how the costs change with time and how CCS technologies compete with other CO_2 mitigation options given a variety of economic and policy assumptions. The chapter concludes with an examination of the economic implications of different storage times (Section 8.4) and a summary of the known knowledge gaps (Section 8.5).

8.2 Component costs

This section presents cost summaries for the three key components of a CCS system, namely capture (including compression), transport, and storage. Sections 8.2.1–8.2.3 summarize the results from Chapters 3–7. Readers are referred to those chapters for more details of component costs. Results are presented here in the form most convenient for each section. Transport costs are given in US\$/tCO_2 per kilometre, while storage costs are stated in US\$/tCO_2 stored. Capture costs for different types of power plants are represented as an increase in the electricity generation cost (US\$ MWh^{-1}). A discussion of how one integrates the costs of capture, transport and storage for a particular system into a single value is presented in Section 8.2.4.

8.2.1 Capture and compression[1]

For most large sources of CO_2 (e.g., power plants), the cost of capturing CO_2 is the largest component of overall CCS costs. In this report, capture costs include the cost of compressing the CO_2 to a pressure suitable for pipeline transport (typically about 14 MPa). However, the cost of any additional booster compressors that may be needed is included in the cost of transport and/or storage.

The total cost of CO_2 capture includes the additional capital requirements, plus added operating and maintenance costs incurred for any particular application. For current technologies, a substantial portion of the overall cost is due to the energy requirements for capture and compression. As elaborated in Chapter 3, a large number of technical and economic factors related to the design and operation of both the CO_2 capture system, and the power plant or industrial process to which it is applied, influence the overall cost of capture. For this reason, the reported costs of CO_2 capture vary widely, even for similar applications.

Table 8.1 summarizes the CO_2 capture costs reported in Chapter 3 for baseload operations of new fossil fuel power plants (in the size range of 300–800 MW) employing current commercial technology. The most widely studied systems are new power plants based on coal combustion or gasification. For costs associated with retrofitting existing power plants, see Table 3.8. For a modern (high-efficiency) coal-burning power plant, CO_2 capture using an amine-based scrubber increases the cost of electricity generation (COE) by approximately 40 to 70 per cent while reducing CO_2 emissions per kilowatt-hour (kWh) by about 85%. The same CO_2 capture technology applied to a new natural gas combined cycle (NGCC) plant increases the COE by approximately 40 to 70 per cent. For a new coal-based plant employing an integrated gasification combined cycle (IGCC) system, a similar reduction in CO_2 using current technology (in this case, a water gas shift reactor followed by a physical absorption system) increases the COE by 20 to 55%. The lower incremental cost for IGCC systems is due in large part to the lower gas volumes and lower energy requirements for CO_2 capture relative to combustion-based systems. It should be noted that the absence of industrial experience with large-scale capture of CO_2 in the electricity sector means that these numbers are subject to uncertainties, as is explained in Section 3.7.

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[1] This section is based on material presented in Section 3.7. The reader is referred to that section for a more detailed analysis and literature references.

Table 8.1 Summary of new plant performance and CO_2 capture cost based on current technology.

Performance and Cost Measures	New NGCC Plant				New PC Plant				New IGCC Plant				New Hydrogen Plant				(Units for H_2 Plant)
	Range			Rep. Value	Range			Rep. Value	Range			Rep. Value	Range			Rep. Value	
	low		high		low		high		low		high		low		high		
Emission rate without capture (kg CO_2 MWh^{-1})	344	-	379	367	736	-	811	762	682	-	846	773	78	-	174	137	kg CO_2 GJ^{-1} (without capture)
Emission rate with capture (kg CO_2 MWh^{-1})	40	-	66	52	92	-	145	112	65	-	152	108	7	-	28	17	kg CO_2 GJ^{-1} (with capture)
Percent CO_2 reduction per kWh (%)	83	-	88	86	81	-	88	85	81	-	91	86	72	-	96	86	% reduction/unit of product
Plant efficiency with capture, LHV basis (%)	47	-	50	48	30	-	35	33	31	-	40	35	52	-	68	60	Capture plant efficiency (% LHV)
Capture energy requirement (% more input MWh^{-1})	11	-	22	16	24	-	40	31	14	-	25	19	4	-	22	8	% more energy input per GJ product
Total capital requirement without capture (US$ kW^{-1})	515	-	724	568	1161	-	1486	1286	1169	-	1565	1326	[No unique normalization for multi-product plants]				Capital requirement without capture
Total capital requirement with capture (US$ kW^{-1})	909	-	1261	998	1894	-	2578	2096	1414	-	2270	1825					Capital requirement with capture
Percent increase in capital cost with capture (%)	64	-	100	76	44	-	74	63	19	-	66	37	-2	-	54	18	% increase in capital cost
COE without capture (US$ MWh^{-1})	31	-	50	37	43	-	52	46	41	-	61	47	6.5	-	10.0	7.8	H_2 cost without capture (US$ GJ^{-1})
COE with capture only (US$ MWh^{-1})	43	-	72	54	62	-	86	73	54	-	79	62	7.5	-	13.3	9.1	H_2 cost with capture (US$ GJ^{-1})
Increase in COE with capture (US$ MWh^{-1})	12	-	24	17	18	-	34	27	9	-	22	16	0.3	-	3.3	1.3	Increase in H_2 cost (US$ GJ^{-1})
Percent increase in COE with capture (%)	37	-	69	46	42	-	66	57	20	-	55	33	5	-	33	15	% increase in H_2 cost
Cost of CO_2 captured (US$/t$CO_2$)	33	-	57	44	23	-	35	29	11	-	32	20	2	-	39	12	US$/t$CO_2$ captured
Cost of CO_2 avoided (US$/t$CO_2$)	37	-	74	53	29	-	51	41	13	-	37	23	2	-	56	15	US$/t$CO_2$ avoided
Capture cost confidence Level (see Table 3.7)	moderate				moderate				moderate				moderate to high				Confidence Level (see Table 3.7)

COE = Cost of electricity

Notes: [a] Ranges and representative values are based on data from Tables 3.7, 3.9, 3.10 and 3.11. All costs in this table are for capture only and do not include the costs of CO_2 transport and storage; see Chapter 8 for total CCS costs. [b] All PC and IGCC data are for bituminous coals only at costs of 1.0-1.5 US$ GJ^{-1} (LHV); all PC plants are supercritical units. [c] NGCC data based on natural gas prices of 2.8-4.4 US$ GJ^{-1} (LHV basis). [d] Costs are in constant US$ (approx. year 2002 basis). [e] Power plant sizes range from approximately 400-800 MW without capture and 300-700 MW with capture. [f] Capacity factors vary from 65-85% for coal plants and 50-95% for gas plants (average for each=80%). [g] Hydrogen plant feedstocks are natural gas (4.7-5.3 US$ GJ^{-1}) or coal (0.9-1.3 US$ GJ^{-1}); some plants in dataset produce electricity in addition to hydrogen. [h] Fixed charge factors vary from 11-16% for power plants and 13-20% for hydrogen plants. [i] All costs include CO_2 compression but not additional CO_2 transport and storage costs.

Studies indicate that, in most cases, IGCC plants are slightly higher in cost without capture and slightly lower in cost with capture than similarly sized PC plants fitted with a CCS system. On average, NGCC systems have a lower COE than both types of new coal-based plants with or without capture for baseload operation. However, the COE for each of these systems can vary markedly due to regional variations in fuel cost, plant utilization, and a host of other parameters. NGCC costs are especially sensitive to the price of natural gas, which has risen significantly in recent years. So comparisons of alternative power system costs require a particular context to be meaningful.

For existing, combustion-based, power plants, CO_2 capture can be accomplished by retrofitting an amine scrubber to the existing plant. However, a limited number of studies indicate that the post-combustion retrofit option is more cost-effective when accompanied by a major rebuild of the boiler and turbine to increase the efficiency and output of the existing plant by converting it to a supercritical unit. For some plants, similar benefits can be achieved by repowering with an IGCC system that includes CO_2 capture technology. The feasibility and cost of any of these options is highly dependent on site-specific circumstances, including the size, age and type of unit, and the availability of space for accommodating a CO_2 capture system. There has not yet been any systematic comparison of the feasibility and cost of alternative retrofit and repowering options for existing plants, as well as the potential for more cost-effective options employing advanced technology such as oxyfuel combustion.

Table 8.1 also illustrates the cost of CO_2 capture in the production of H_2, a commodity used extensively today for fuels and chemical production, but also widely viewed as a potential energy carrier for future energy systems. Here, the cost of CO_2 capture is mainly due to the cost of CO_2 compression, since separation of CO_2 is already carried out as part of the H_2 production process. Recent studies indicate that the cost of CO_2 capture for current processes adds approximately 5 to 30 per cent to the cost of the H_2 product.

In addition to fossil-based energy conversion processes, CO_2 could also be captured in power plants fuelled with biomass. At present, biomass plants are small in scale (<100 MW_e). Hence, the resulting costs of capturing CO_2 are relatively high compared to fossil alternatives. For example, the capturing of 0.19 $MtCO_2$ yr^{-1} in a 24 MW_e biomass IGCC plant is estimated to be about 82 US\$/tCO_2 (300 US\$/tC), corresponding to an increase of the electricity costs due to capture of about 80 US\$ MWh^{-1} (Audus and Freund, 2004). Similarly, CO_2 could be captured in biomass-fuelled H_2 plants. The cost is reported to be between 22 and 25 US\$/tCO_2 avoided (80–92 US\$/tC) in a plant producing 1 million Nm^3 d^{-1} of H_2 (Makihira *et al.*, 2003). This corresponds to an increase in the H_2 product costs of about 2.7 US\$ GJ^{-1} (i.e., 20% of the H_2 costs without CCS). The competitiveness of biomass CCS systems is very sensitive to the value of CO_2 emission reductions, and the associated credits obtained with systems resulting in negative emissions. Moreover, significantly larger biomass plants could benefit from economies of scale, bringing down costs of the CCS systems to broadly similar levels as those in coal plants. However, there is too little experience with large-scale biomass plants as yet, so that their feasibility has still not been proven and their costs are difficult to estimate.

CCS technologies can also be applied to other industrial processes. Since these other industrial processes produce off-gases that are very diverse in terms of pressure and CO_2 concentration, the costs range very widely. In some of these non-power applications where a relatively pure CO_2 stream is produced as a by-product of the process (e.g., natural gas processing, ammonia production), the cost of capture is significantly lower than capture from fossil-fuel-fired power plants. In other processes like cement or steel production, capture costs are similar to, or even higher than, capture from fossil-fuel-fired power plants.

New or improved technologies for CO_2 capture, combined with advanced power systems and industrial process designs, can significantly reduce the cost of CO_2 capture in the future. While there is considerable uncertainty about the magnitude and timing of future cost reductions, studies suggest that improvements to current commercial technologies could lower CO_2 capture costs by at least 20–30%, while new technologies currently under development may allow for more substantial cost reductions in the future. Previous experience indicates that the realization of cost reductions in the future requires sustained R&D in conjunction with the deployment and adoption of commercial technologies.

8.2.2 *Transport*[2]

The most common and usually the most economical method to transport large amounts of CO_2 is through pipelines. A cost-competitive transport option for longer distances at sea might be the use of large tankers.

The three major cost elements for pipelines are construction costs (e.g., material, labour, possible booster station), operation and maintenance costs (e.g., monitoring, maintenance, possible energy costs) and other costs (e.g., design, insurance, fees, right-of-way). Special land conditions, like heavily populated areas, protected areas such as national parks, or crossing major waterways, may have significant cost impacts. Offshore pipelines are about 40% to 70% more costly than onshore pipes of the same size. Pipeline construction is considered to be a mature technology and the literature does not foresee many cost reductions.

Figure 8.1 shows the transport costs for 'normal' terrain conditions. Note that economies of scale dramatically reduce the cost, but that transportation in mountainous or densely populated areas could increase cost.

Tankers could also be used for transport. Here, the main cost elements are the tankers themselves (or charter costs), loading and unloading facilities, intermediate storage facilities, harbour

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[2] This section is based on material presented in Section 4.6. The reader is referred to that section for a more detailed analysis and literature references.

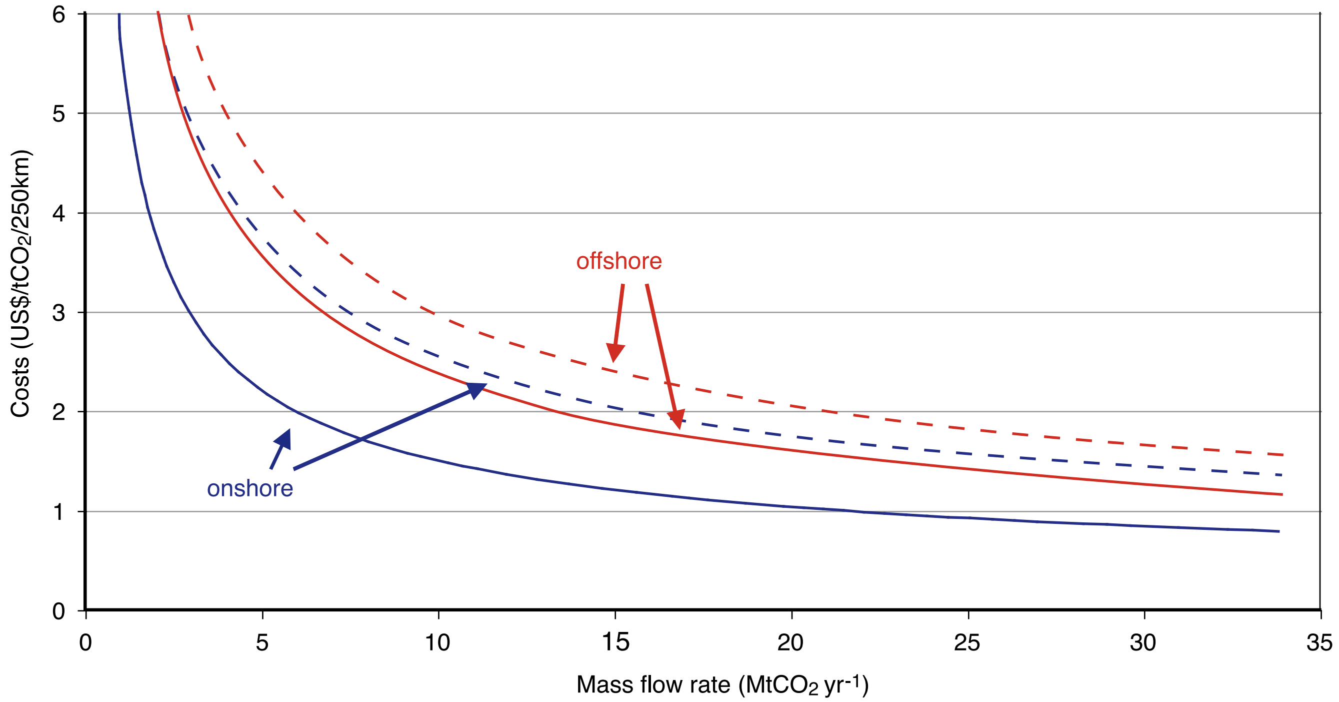

Figure 8.1 CO_2 transport costs range for onshore and offshore pipelines per 250 km, 'normal' terrain conditions. The figure shows low (solid lines) and high ranges (dotted lines). Data based on various sources (for details see Chapter 4).

fees, and bunker fuel. The construction costs for large special-purpose CO_2 tankers are not accurately known since none have been built to date. On the basis of preliminary designs, the costs of CO_2 tankers are estimated at US$ 34 million for ships of 10,000 tonnes, US$ 58 million for 30,000-tonne vessels, and US$ 82 million for ships with a capacity of 50,000 tonnes.

To transport 6 $MtCO_2$ per year a distance of 500 km by ship would cost about 10 US$/$tCO_2$ (37 US$/tC) or 5 US$/tCO_2/250km (18 US$/tC/250km). However, since the cost is relatively insensitive to distance, transporting the same 6 $MtCO_2$ a distance of 1250 km would cost about 15 US$/$tCO_2$ (55 US$/tC) or 3 US$/tCO_2/250km (11 US$/tC/250km). This is close to the cost of pipeline transport, illustrating the point that ship transport becomes cost-competitive with pipeline transport if CO_2 needs to be transported over larger distances. However, the break-even point beyond which ship transportation becomes cheaper than pipeline transportation is not simply a matter of distance; it involves many other aspects.

8.2.3 Storage

8.2.3.1 Geological storage[3]

Because the technologies and equipment used for geological storage are widely used in the oil and gas industries, the cost estimates can be made with confidence. However, there will be a significant range and variability of costs due to site-specific factors: onshore versus offshore, the reservoir depth and the geological characteristics of the storage formation (e.g., permeability, thickness, etc.). Representative estimates of the cost for storage in saline formations and disused oil and gas fields (see Table 8.2) are typically between 0.5–8.0 US$/$tCO_2$ stored (2–29 US$/tC), as explained in Section 5.9.3. The lowest storage costs will be associated with onshore, shallow, high permeability reservoirs and/or the reuse of wells and infrastructure in disused oil and gas fields.

The full range of cost estimates for individual options is very large. Cost information for storage monitoring is currently limited, but monitoring is estimated to add 0.1–0.3 US$ per tonne of CO_2 stored (0.4–1.1 US$/tC). These estimates do not include any well remediation or long-term liabilities. The costs of storage monitoring will depend on which technologies are used for how long, regulatory requirements and how long-term monitoring strategies evolve.

When storage is combined with EOR, enhanced gas recovery (EGR) or ECBM, the benefits of enhanced production can offset some of the capture and storage costs. Onshore EOR operations have paid in the range of 10–16 US$ per tonne of CO_2 (37–59 US$/tC). The economic benefit of enhanced production depends very much on oil and gas prices. It should be noted that most of the literature used as the basis for this report did not take into account the rise in oil and gas prices that started in 2003. For example, oil at 50 US$/barrel could justify a credit of 30 US$/$tCO_2$ (110 US$/tC). The economic benefits from enhanced production make EOR and ECBM potential early cost-effective options for geological storage.

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[3] This section is based on material presented in Section 5.9. The reader is referred to that section for a more detailed analysis and literature references.

Table 8.2 Estimates of CO_2 storage costs.

Option	**Representative Cost Range (US$/tonne CO_2 stored)**	**Representative Cost Range (US$/tonne C stored)**
Geological - Storage[a]	0.5-8.0	2-29
Geological - Monitoring	0.1-0.3	0.4-1.1
Ocean[b]		
Pipeline	6-31	22-114
Ship (Platform or Moving Ship Injection)	12-16	44-59
Mineral Carbonation[c]	50-100	180-370

[a] Does not include monitoring costs.

[b] Includes offshore transportation costs; range represents 100-500 km distance offshore and 3000 m depth.

[c] Unlike geological and ocean storage, mineral carbonation requires significant energy inputs equivalent to approximately 40% of the power plant output.

8.2.3.2 Ocean storage[4]

The cost of ocean storage is a function of the distance offshore and injection depth. Cost components include offshore transportation and injection of the CO_2. Various schemes for ocean storage have been considered. They include:

- tankers to transport low temperature (–55 to –50°C), high pressure (0.6–0.7 MPa) liquid CO_2 to a platform, from where it could be released through a vertical pipe to a depth of 3000 m;
- carrier ships to transport liquid CO_2, with injection through a towed pipe from a moving dispenser ship;
- undersea pipelines to transport CO_2 to an injection site.

Table 8.2 provides a summary of costs for transport distances of 100–500 km offshore and an injection depth of 3000 m.

Chapter 6 also discusses the option of carbonate neutralization, where flue-gas CO_2 is reacted with seawater and crushed limestone. The resulting mixture is then released into the upper ocean. The cost of this process has not been adequately addressed in the literature and therefore the possible cost of employing this process is not addressed here.

8.2.3.3 Storage via mineral carbonation[5]

Mineral carbonation is still in its R&D phase, so costs are uncertain. They include conventional mining and chemical processing. Mining costs include ore extraction, crushing and grinding, mine reclamation and the disposal of tailings and carbonates. These are conventional mining operations and several studies have produced cost estimates of 10 US$/t$CO_2$ (36 US$/tC) or less. Since these estimates are based on similar mature and efficient operations, this implies that there is a strong lower limit on the cost of mineral storage. Carbonation costs include chemical activation and carbonation. Translating today's laboratory implementations into industrial practice yields rough cost estimates of about 50–100 US$/t$CO_2$ stored (180–370 US$/tC). Costs and energy penalties (30–50% of the power plant output) are dominated by the activation of the ore necessary to accelerate the carbonation reaction. For mineral storage to become practical, additional research must reduce the cost of the carbonation step by a factor of three to four and eliminate a significant portion of the energy penalty by, for example, harnessing as much as possible the heat of carbonation.

8.2.4 Integrated systems

The component costs given in this section provide a basis for the calculation of integrated system costs. However, the cost of mitigating CO_2 emissions cannot be calculated simply by summing up the component costs for capture, transport and storage in units of 'US$/t$CO_2$'. This is because the amount of

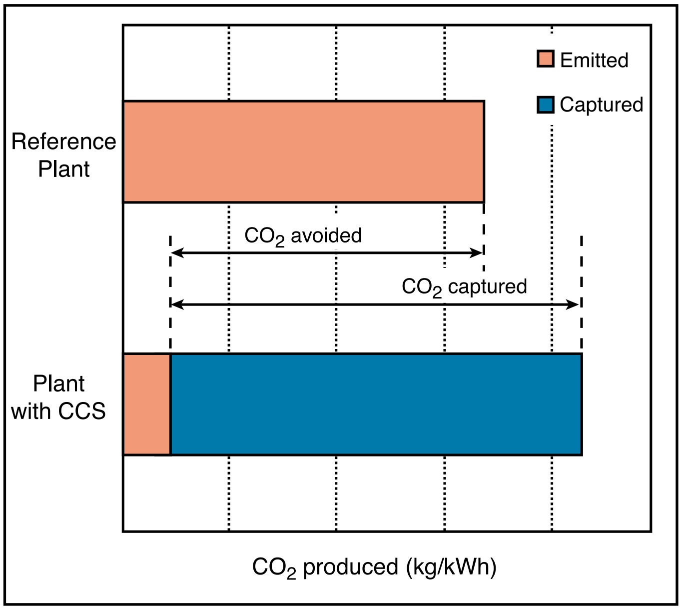

Figure 8.2 CO_2 capture and storage from power plants. The increased CO_2 production resulting from loss in overall efficiency of power plants due to the additional energy required for capture, transport and storage, and any leakage from transport result in a larger amount of 'CO_2 produced per unit of product'(lower bar) relative to the reference plant (upper bar) without capture

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[4] This section is based on material presented in Section 6.9. The reader is referred to that section for a more detailed analysis and literature references.

[5] This section is based on material presented in Section 7.2. The reader is referred to that section for a more detailed analysis and literature references.

Box 8.1 Defining avoided costs for a fossil fuel power plant

In general, the capture, transport, and storage of CO_2 require energy inputs. For a power plant, this means that amount of fuel input (and therefore CO_2 emissions) increases per unit of net power output. As a result, the amount of CO_2 produced per unit of product (e.g., a kWh of electricity) is greater for the power plant with CCS than the reference plant, as shown in Figure 8.2 To determine the CO_2 reductions one can attribute to CCS, one needs to compare CO_2 emissions of the plant with capture to those of the reference plant without capture. These are the avoided emissions. Unless the energy requirements for capture and storage are zero, the amount of CO_2 avoided is always less than the amount of CO_2 captured. The cost in US$/tonne avoided is therefore greater than the cost in US$/tonne captured.

CO_2 captured will be different from the amount of atmospheric CO_2 emissions 'avoided' during the production of a given amount of a useful product (e.g., a kilowatt-hour of electricity or a kilogram of H_2). So any cost expressed per tonne of CO_2 should be clearly defined in terms of its basis, e.g., either a *captured* basis or an *avoided* basis (see Box 8.1). Mitigation cost is best represented as avoided cost. Table 8.3 presents ranges for total avoided costs for CO_2 capture, transport, and storage from four types of sources.

The mitigation costs (US$/t$CO_2$ avoided) reported in Table 8.3 are context-specific and depend very much on what is chosen as a reference plant. In Table 8.3, the reference plant is a power plant of the same type as the power plant with CCS. The mitigation costs here therefore represent the incremental cost of capturing and storing CO_2 from a particular type of plant.

In some situations, it can be useful to calculate a cost of CO_2 avoided based on a reference plant that is different from the CCS plant (e.g., a PC or IGCC plant with CCS using an NGCC reference plant). In Table 8.4, the reference plant represents the least-cost plant that would 'normally' be built at a particular location in the absence of a carbon constraint. In many regions today, this would be either a PC plant or an NGCC plant.

A CO_2 mitigation cost also can be defined for a collection of plants, such as a national energy system, subject to a given level of CO_2 abatement. In this case the plant-level product costs presented in this section would be used as the basic inputs to energy-economic models that are widely used for policy analysis and for the quantification of overall mitigation strategies and costs for CO_2 abatement. Section 8.3 discusses the nature of these models and presents illustrative model results, including the cost of CCS, its economic potential, and its relationship to other mitigation options.

Table 8.3a Range of total costs for CO_2 capture, transport, and geological storage based on current technology for new power plants.

	Pulverized Coal Power Plant	**Natural Gas Combined Cycle Power Plant**	**Integrated Coal Gasification Combined Cycle Power Plant**
Cost of electricity without CCS (US$ MWh^{-1})	43-52	31-50	41-61
Power plant with capture			
Increased Fuel Requirement (%)	24-40	11-22	14-25
CO_2 captured (kg MWh^{-1})	820-970	360-410	670-940
CO_2 avoided (kg MWh^{-1})	620-700	300-320	590-730
% CO_2 avoided	81-88	83-88	81-91
Power plant with capture and geological storage[6]			
Cost of electricity (US$ MWh^{-1})	63-99	43-77	55-91
Electricity cost increase (US$ MWh^{-1})	19-47	12-29	10-32
% increase	43-91	37-85	21-78
Mitigation cost (US$/t$CO_2$ avoided)	30-71	38-91	14-53
Mitigation cost (US$/tC avoided)	110-260	140-330	51-200
Power plant with capture and enhanced oil recovery[7]			
Cost of electricity (US$ MWh^{-1})	49-81	37-70	40-75
Electricity cost increase (US$ MWh^{-1})	5-29	6-22	(-5)-19
% increase	12-57	19-63	(-10)-46
Mitigation cost (US$/t$CO_2$ avoided)	9-44	19-68	(-7)-31
Mitigation cost (US$/tC avoided)	31-160	71-250	(-25)-120

[6] Capture costs represent range from Tables 3.7, 3.9 and 3.10. Transport costs range from 0–5 US$/t$CO_2$. Geological storage cost (including monitoring) range from 0.6–8.3 US$/t$CO_2$.

[7] Capture costs represent range from Tables 3.7, 3.9 and 3.10. Transport costs range from 0–5 US$/t$CO_2$ stored. Costs for geological storage including EOR range from –10 to –16 US$/t$CO_2$ stored.

Table 8.3b Range of total costs for CO_2 capture, transport, and geological storage based on current technology for a new hydrogen production plant.

	Hydrogen Production Plant
Cost of H_2 without CCS (US\$ GJ^{-1})	6.5-10.0
Hydrogen plant with capture	
Increased fuel requirement (%)	4-22
CO_2 captured (kg GJ^{-1})	75-160
CO_2 avoided (kg GJ^{-1})	60-150
% CO_2 avoided	73-96
Hydrogen plant with capture and geological storage[8]	
Cost of H_2 (US\$ GJ^{-1})	7.6-14.4
H_2 cost increase (US\$ GJ^{-1})	0.4-4.4
% increase	6-54
Mitigation cost (US\$/tCO_2 avoided)	3-75
Mitigation cost (US\$ tC avoided)	10-280
Hydrogen plant with capture and enhanced oil recovery[9]	
Cost of H_2 (US\$ GJ^{-1})	5.2-12.9
H_2 cost increase (US\$ GJ^{-1})	(-2.0)-2.8
% increase	(-28)-28
Mitigation cost (US\$/tCO_2 avoided)	(-14)-49
Mitigation cost (US\$/tC avoided)	(-53)-180

8.3 CCS deployment scenarios

Energy-economic models seek the mathematical representation of key features of the energy system in order to represent the evolution of the system under alternative assumptions, such as population growth, economic development, technological change, and environmental sensitivity. These models have been employed increasingly to examine how CCS technologies would deploy in a greenhouse gas constrained environment. In this section we first provide a brief introduction to the types of energy and economic models and the main assumptions driving future greenhouse gas emissions and the corresponding measures to reduce them. We then turn to the principal focus of this section: an examination of the literature based on studies using these energy and economic models, with an emphasis on what they say about the potential use of CCS technologies.

8.3.1 Model approaches and baseline assumptions

The modelling of climate change abatement or mitigation scenarios is complex and a number of modelling techniques have been applied, including input-output models, macroeconomic (top-down) models, computable general equilibrium (CGE) models and energy-sector-based engineering models (bottom-up).

Table 8.4 Mitigation cost for different combinations of reference and CCS plants based on current technology and new power plants.

	NGCC Reference Plant		**PC Reference Plant**	
	US\$/tCO_2 avoided	**US\$/tC avoided**	**US\$/tCO_2 avoided**	**US\$/tC avoided**
Power plant with capture and geological storage				
NGCC	40-90	140-330	20-60	80-220
PC	70-270	260-980	30-70	110-260
IGCC	40-220	150-790	20-70	80-260
Power plant with capture and EOR				
NGCC	20-70	70-250	1-30	4-130
PC	50-240	180-890	10-40	30-160
IGCC	20 – 190	80 – 710	1 – 40	4 – 160

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[8] Capture costs represent range from Table 3.11. Transport costs range from 0–5 US\$/tCO_2. Geological storage costs (including monitoring) range from 0.6–8.3 US\$/tCO_2.

[9] Capture costs represent range from Table 3.11. Transport costs range from 0–5 US\$/tCO_2. EOR credits range from 10–16 US\$/tCO_2.

8.3.1.1 Description of bottom-up and top-down models

The component and systems level costs provided in Section 8.2 are based on technology-based bottom-up models. These models can range from technology-specific, engineering-economic calculations embodied in a spreadsheet to broader, multi-technology, integrated, partial-equilibrium models. This may lead to two contrasting approaches: an engineering-economic approach and a least-cost equilibrium one. In the first approach, each technology is assessed independently, taking into account all its parameters; partial-equilibrium least-cost models consider all technologies simultaneously and at a higher level of aggregation before selecting the optimal mix of technologies in all sectors and for all time periods.

Top-down models evaluate the system using aggregate economic variables. Econometric relationships between aggregated variables are generally more reliable than those between disaggregated variables, and the behaviour of the models tends to be more stable. It is therefore common to adopt high levels of aggregation for top-down models; especially when they are applied to longer-term analyses. Technology diffusion is often described in these top-down models in a more stylized way, for example using aggregate production functions with price-demand or substitution elasticities.

Both types of models have their strengths and weaknesses. Top-down models are useful for, among other things, calculating gross economic cost estimates for emissions mitigation. Most of these top-down macro-economic models tend to overstate costs of meeting climate change targets because, among other reasons, they do not take adequate account of the potential for no-regret measures and they are not particularly adept at estimating the benefits of climate change mitigation. On the other hand, many of these models – and this also applies to bottom-up models – are not adept at representing economic and institutional inefficiencies, which would lead to an underestimation of emissions mitigation costs.

Technologically disaggregated bottom-up models can take some of these benefits into account but may understate the costs of overcoming economic barriers associated with their deployment in the market. Recent modelling efforts have focused on the coupling of top-down and bottom-up models in order to develop scenarios that are consistent from both the macroeconomic and systems engineering perspectives. Readers interested in a more detailed discussion of these modelling frameworks and their application to understanding future energy, economic and emission scenarios are encouraged to consult the IPCC's Working Group III's assessment of the international work on both bottom-up and top-down analytical approaches (Third Assessment Report; IPCC, 2001).

8.3.1.2 Assumptions embodied in emissions baselines

Integrated Assessment Models (IAMs) constitute a particular category of energy and economic models and will be used here to describe the importance of emissions baselines before examining model projections of potential future CCS use. IAMs integrate the simulation of climate change dynamics with the modelling of the energy and economic systems. A common and illuminating type of analysis conducted with IAMs, and with other energy and economic models, involves the calculation of the cost differential or the examination of changes in the portfolio of energy technologies used when moving from a baseline (i.e., no climate policy) scenario to a control scenario (i.e., a case where a specific set of measures designed to constrain GHG emissions is modelled). It is therefore important to understand what influences the nature of these baseline scenarios. A number of parameters spanning economic, technological, natural and demographic resources shape the energy use and resulting emissions trajectories of these baseline cases. How these parameters change over time is another important aspect driving the baseline scenarios. A partial list of some of the major parameters that influence baseline scenarios include, for example, modelling assumptions centring on:

- global and regional economic and demographic developments;
- costs and availability of
  1) global and regional fossil fuel resources;
  2) fossil-based energy conversion technologies (power generation, H_2 production, etc.), including technology-specific parameters such as efficiencies, capacity factors, operation and maintenance costs as well as fuel costs;
  3) zero-carbon energy systems (renewables and nuclear), which might still be non-competitive in the baseline but may play a major role competing for market shares with CCS if climate policies are introduced;
- rates of technological change in the baseline and the specific way in which technological change is represented in the model;
- the relative contribution of CO_2 emissions from different economic sectors.

Modelling all of these parameters as well as alternative assumptions for them yields a large number of 'possible futures'. In other words, they yield a number of possible baseline scenarios. This is best exemplified by the Special Report on Emission Scenarios (SRES, 2000): it included four different narrative storylines and associated scenario families, and identified six 'illustrative' scenario groups – labelled A1FI, A1B, A1T, A2, B1, B2 – each representing different plausible combinations of socio-economic and technological developments in the absence of any climate policy (for a detailed discussion of these cases, see SRES, 2000). The six scenario groups depict alternative developments of the energy system based on different assumptions about economic and demographic change, hydrocarbon resource availability, energy demand and prices, and technology costs and their performance. They lead to a wide range of possible future worlds and CO_2 emissions consistent with the full uncertainty range of the underlying literature (Morita and Lee, 1998). The cumulative emissions from 1990 to 2100 in the scenarios range from less than 2930 to 9170 $GtCO_2$ (800 to 2500 GtC). This range is divided into four intervals, distinguishing between scenarios

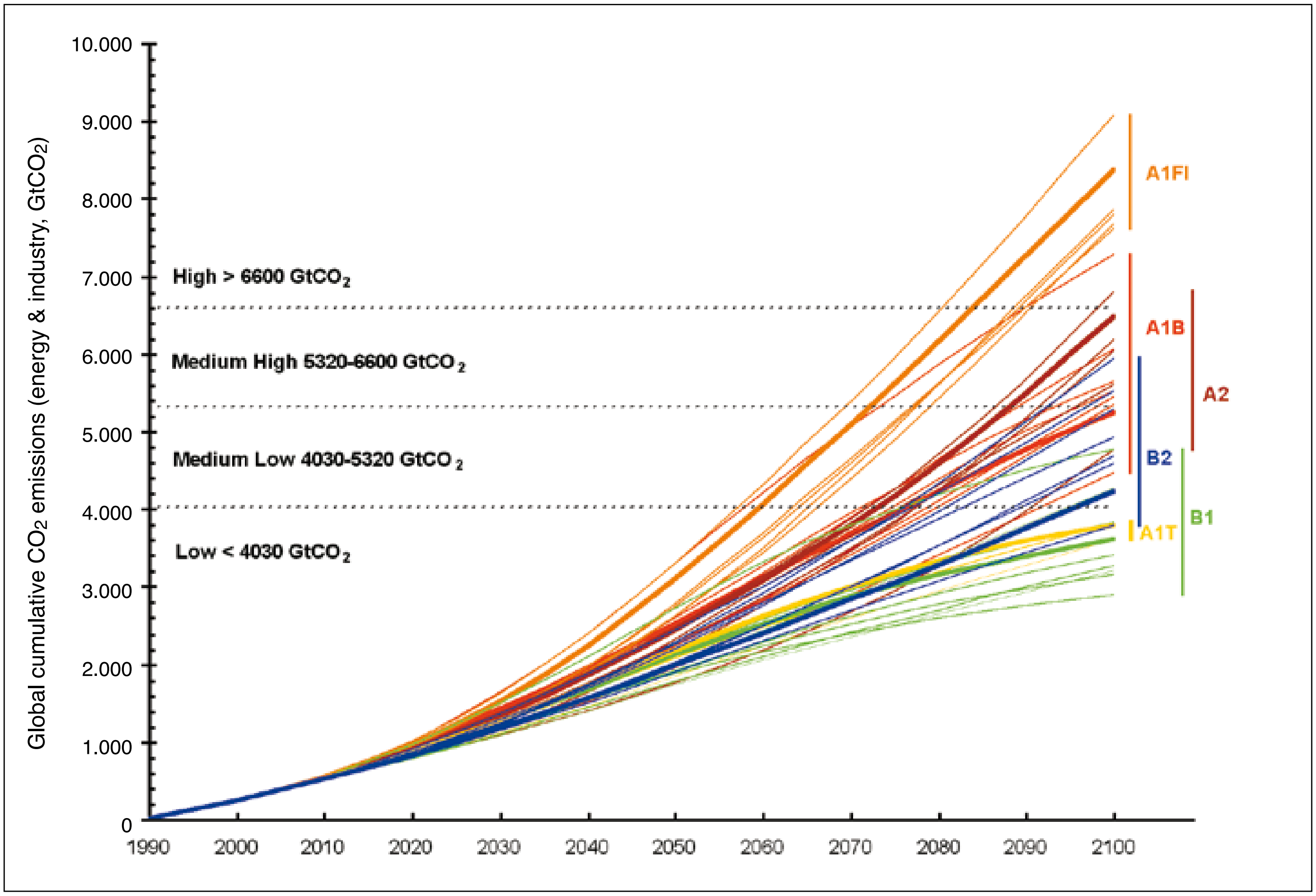

Figure 8.3 Annual and cumulative global emissions from energy and industrial sources in the SRES scenarios ($GtCO_2$). Each interval contains alternative scenarios from the six SRES scenario groups that lead to comparable cumulative emissions. The vertical bars on the right-hand side indicate the ranges of cumulative emissions (1990–2100) of the six SRES scenario groups.

with high, medium-high, medium-low, and low emissions:

- high (≥6600 $GtCO_2$ or ≥1800 GtC);
- medium-high (5320–6600 $GtCO_2$ or 1450–1800 GtC);
- medium-low (4030–5320 $GtCO_2$ or 1100–1450 GtC);
- low (≤4030 $GtCO_2$ or ≤1100 GtC).

As illustrated in Figure 8.3, each of the intervals contains multiple scenarios from more than one of the six SRES scenario groups (see the vertical bars on the right side of Figure 8.3, which show the ranges for cumulative emissions of the respective SRES scenario group). Other scenario studies, such as the earlier set of IPCC scenarios developed in 1992 (Pepper *et al.*, 1992) project similar levels of cumulative emissions over the period 1990 to 2100, ranging from 2930 to 7850 $GtCO_2$ (800 to 2,140 GtC). For the same time horizon, the IIASA-WEC scenarios (Nakicenovic *et al.*, 1998) report 2,270–5,870 $GtCO_2$ (620–1,600 GtC), and the Morita and Lee (1998) database – which includes more than 400 emissions scenarios – report cumulative emissions up to 12,280 $GtCO_2$ (3,350 GtC).

The SRES scenarios illustrate that similar future emissions can result from very different socio-economic developments, and that similar developments in driving forces can nonetheless result in wide variations in future emissions. The scenarios also indicate that the future development of energy systems will play a central role in determining future emissions and suggests that technological developments are at least as important a driving force as demographic change and economic development. These findings have major implications for CCS, indicating that the pace at which these technologies will be deployed in the future – and therefore their long-term potential – is affected not so much by economic or demographic change but rather by the choice of the technology path of the energy system, the major driver of future emissions. For a detailed estimation of the technical potential of CCS by sector for some selected SRES baseline scenarios, see Section 2.3.2. In the next section we shall discuss the economic potential of CCS in climate control scenarios.

8.3.2 CCS economic potential and implications

As shown by the SRES scenarios, uncertainties associated with alternative combinations of socio-economic and technological developments may lead to a wide range of possible future emissions. Each of the different baseline emissions scenarios has different implications for the potential use of CCS technologies in emissions control cases.[10] Generally, the size of the future market for CCS depends mostly on the carbon intensity of the baseline scenario and the stringency of the assumed climate stabilization target. The higher the CO_2 emissions in the baseline, the more emissions reductions are required to achieve a given level of allowable emissions, and the larger the markets for CCS. Likewise, the tighter the modelled constraint on CO_2 emissions, the more CCS deployment there is likely to be. This section will examine what the literature says about possible CCS deployment rates, the timing of CCS deployment, the total deployment of these systems under various scenarios, the economic impact of CCS systems and how CCS systems interact with other emissions mitigation technologies.

8.3.2.1 Key drivers for the deployment of CCS

Energy and economic models are increasingly being employed to examine how CCS technologies would deploy in environments where CO_2 emissions are constrained (i.e., in control cases). A number of factors have been identified that drive the rate of CCS deployment and the scale of its ultimate deployment in modelled control cases:[11]

1. The policy regime; the interaction between CCS deployment and the policy regime in which energy is produced and consumed cannot be overemphasized; the magnitude and timing of early deployment depends very much on the policy environment; in particular, the cumulative extent of deployment over the long term depends strongly on the stringency of the emissions mitigation regime being modelled; comparatively low stabilization targets (e.g., 450 ppmv) foster the relatively faster penetration of CCS and the more intensive use of CCS (where 'intensity of use' is measured both in terms of the percentage of the emissions reduction burden shouldered by CCS as well as in terms of how many cumulative gigatonnes of CO_2 is to be stored) (Dooley *et al*., 2004b; Gielen and Podanski, 2004; Riahi and Roehrl, 2000);
2. The reference case (baseline); storage requirements for stabilizing CO_2 concentrations at a given level are very sensitive to the choice of the baseline scenario. In other words, the assumed socio-economic and demographic trends, and particularly the assumed rate of technological change, have a significant impact on CCS use (see Section 8.3.1, Riahi and Roehrl, 2000; Riahi *et al*., 2003);
3. The nature, abundance and carbon intensity of the energy resources / fuels assumed to exist in the future (e.g., a future world where coal is abundant and easily recoverable would use CCS technologies more intensively than a world in which natural gas or other less carbon-intensive technologies are inexpensive and widely available). See Edmonds and Wise (1998) and Riahi and Roehrl (2000) for a comparison of two alternative regimes of fossil fuel availability and their interaction with CCS;
4. The introduction of flexible mechanisms such as emissions trading can significantly influence the extent of CCS deployment. For example, an emissions regime with few, or significantly constrained, emissions trading between nations entails the use of CCS technologies sooner and more extensively than a world in which there is efficient global emissions trading and therefore lower carbon permit prices (e.g., Dooley *et al*., 2000 and Scott *et al*., 2004). Certain regulatory regimes that explicitly emphasize CCS usage can also accelerate its deployment (e.g., Edmonds and Wise, 1998).
5. The rate of technological change (induced through learning or other mechanisms) assumed to take place with CCS and other salient mitigation technologies (e.g., Edmonds *et al*., 2003, or Riahi *et al*., 2003). For example, Riahi *et al*. (2003) indicate that the long-term economic potential of CCS systems would increase by a factor of 1.5 if it assumed that technological learning for CCS systems would take place at rates similar to those observed historically for sulphur removal technologies when compared to the situation where no technological change is specified.[12]

The marginal value of CO_2 emission reduction permits is one of the most important mechanisms through which these factors impact CCS deployment. CCS systems tend to deploy quicker and more extensively in cases with higher marginal carbon values. Most energy and economic modelling done to date suggests that CCS systems begin to deploy at a significant level when carbon dioxide prices begin to reach approximately 25–30 US\$/tCO_2 (90–110 US\$/tC) (IEA, 2004; Johnson and Keith, 2004; Wise and Dooley, 2004; McFarland *et al*., 2004). The only caveat to this carbon price as a lower limit for the deployment of these systems is the 'early opportunities' literature discussed below.

Before turning to a specific focus on the possible contribution of CCS in various emissions mitigation scenarios, it is worth reinforcing the point that there is a broad consensus in the

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[10] As no climate policy is assumed in SRES, there is also no economic value associated with carbon. The potential for CCS in SRES is therefore limited to applications where the supplementary benefit of injecting CO_2 into the ground exceeds its costs (e.g., EOR or ECBM). The potential for these options is relatively small as compared to the long-term potential of CCS in stabilization scenarios. Virtually none of the global modelling exercises in the literature that incorporate SRES include these options and so there is also no CCS system deployment assumed in the baseline scenarios.

[11] Integrated assessment models represent the world in an idealized way, employing different methodologies for the mathematical representation of socio-economic and technological developments in the real world. The representation of some real world factors, such as institutional barriers, inefficient legal frameworks, transaction costs of carbon permit trading, potential free-rider behaviour of geopolitical agents and the implications of public acceptance has traditionally been a challenge in modelling. These factors are represented to various degrees (often generically) in these models

[12] The factor increase of 1.5 corresponds to about 250 to 360 GtCO_2 of additional capture and storage over the course of the century.

technical literature that no single mitigation measure will be adequate to achieve a stable concentration of CO_2. This means that the CO_2 emissions will most likely be reduced from baseline scenarios by a portfolio of technologies in addition to other social, behavioural and structural changes (Edmonds *et al.*, 2003; Riahi and Roehrl, 2000). In addition, the choice of a particular stabilization level from any given baseline significantly affects the technologies needed for achieving the necessary emissions reduction (Edmonds *et al.*, 2000; Roehrl and Riahi, 2000). For example, a wider range of technological measures and their widespread diffusion, as well as more intensive use, are required for stabilizing at 450 ppmv compared with stabilization at higher levels (Nakicenovic and Riahi, 2001). These and other studies (e.g., IPCC, 2001) have identified several classes of robust mitigation measures: reductions in demand and/or efficiency improvements; substitution among fossil fuels; deployment of non-carbon energy sources (i.e., renewables and nuclear); CO_2 capture and storage; and afforestation and reforestation.

8.3.3 The share of CCS in total emissions mitigation

When used to model energy and carbon markets, the aim of integrated assessment models is to capture the heterogeneity that characterizes energy demand, energy use and the varying states of development of energy technologies that are in use at any given point in time, as well as over time. These integrated

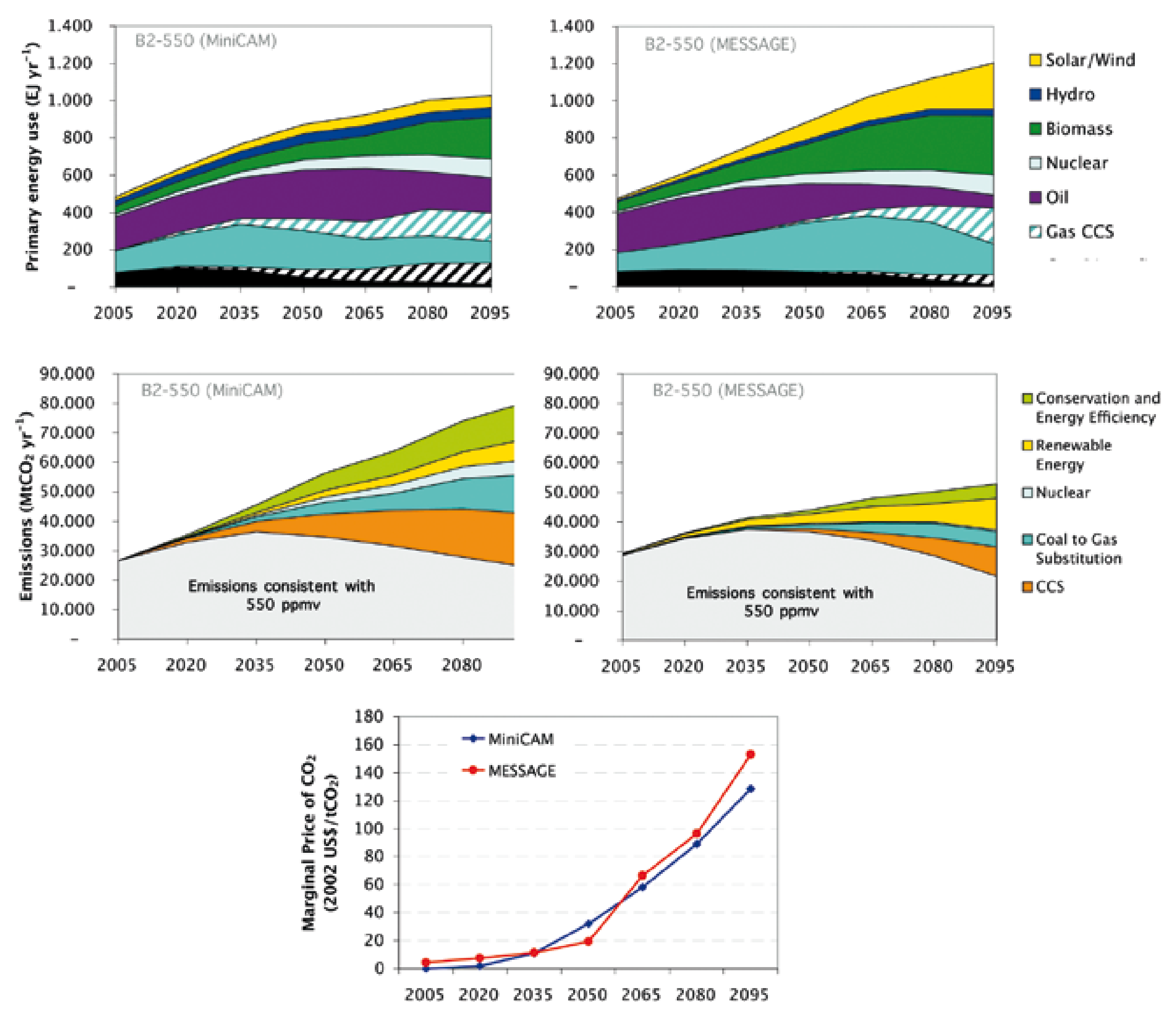

Figure 8.4 The set of graphs shows how two different integrated assessment models (MiniCAM and MESSAGE) project the development of global primary energy (upper panels) and the corresponding contribution of major mitigation measures (middle panels). The lower panel depicts the marginal carbon permit price in response to a modelled mitigation regime that seeks to stabilize atmospheric concentrations of CO_2 at 550 ppmv. Both scenarios adopt harmonized assumptions with respect to the main greenhouse gas emissions drivers in accordance with the IPCC-SRES B2 scenario (Source: Dooley et al., 2004b; Riahi and Roehrl, 2000).

Box 8.2 Two illustrative 550 ppmv stabilization scenarios based on IPCC SRES B2

The MESSAGE and MiniCAM scenarios illustrated in Figure 8.4 represent two alternative quantifications of the B2 scenario family of the IPCC SRES. They are used for subsequent CO_2 mitigation analysis and explore the main measures that would lead to the stabilization of atmospheric concentrations at 550 ppmv.

The scenarios are based on the B2 storyline, a narrative description of how the world will evolve during the twenty-first century, and share harmonized assumptions concerning salient drivers of CO_2 emissions, such as economic development, demographic change, and final energy demand.

In accordance with the B2 storyline, gross world product is assumed to grow from US$ 20 trillion in 1990 to about US$ 235 trillion in 2100 in both scenarios, corresponding to a long-term average growth rate of 2.2%. Most of this growth takes place in today's developing countries. The scenarios adopt the UN median 1998 population projection (UN, 1998), which assumes a continuation of historical trends, including recent faster-than-expected fertility declines, towards a completion of the demographic transition within the next century. Global population increases to about 10 billion by 2100. Final energy intensity of the economy declines at about the long-run historical rate of about one per cent per year through 2100. On aggregate, these trends constitute 'dynamics-as-usual' developments, corresponding to middle-of-the-road assumptions compared to the scenario uncertainty range from the literature (Morita and Lee, 1999).

In addition to the similarities mentioned above, the MiniCAM and MESSAGE scenarios are based on alternative interpretations of the B2 storyline with respect to a number of other important assumptions that affect the potential future deployment of CCS. These assumptions relate to fossil resource availability, long-term potentials for renewable energy, the development of fuel prices, the structure of the energy system and the sectoral breakdown of energy demand, technology costs, and in particular technological change (future prospects for costs and performance improvements for specific technologies and technology clusters).

The two scenarios therefore portray alternative but internally consistent developments of the energy technology portfolio, associated CO_2 emissions, and the deployment of CCS and other mitigation technologies in response to the stabilization target of 550 ppmv CO_2, adopting the same assumptions for economic, population, and aggregated demand growth. Comparing the scenarios' portfolio of mitigation options (Figure 8.4) illustrates the importance of CCS as part of the mitigation portfolio. For more details, see Dooley *et al.* (2004b) and Riahi and Roehrl (2000).

assessment tools are also used to model changes in market conditions that would alter the relative cost-competitiveness of various energy technologies. For example, the choice of energy technologies would vary as carbon prices rise, as the population grows or as a stable population increases its standard of living.

The graphs in Figure 8.4 show how two different integrated assessment models (MiniCAM and MESSAGE) project the development of global primary energy (upper panels), the contribution of major mitigation measures (middle panels), and the marginal carbon permit price in response to a modelled policy that seeks to stabilize atmospheric concentrations of CO_2 at 550 ppmv in accordance with the main greenhouse gas emissions drivers of the IPCC-SRES B2 scenario (see Box 8.2). As can be seen from Figure 8.4, CCS coupled with coal and natural-gas-fired electricity generation are key technologies in the mitigation portfolio in both scenarios and particularly in the later half of the century under this particular stabilization scenario. However, solar/wind, biomass, nuclear power, etc. still meet a sizeable portion of the global demand for electricity. This demonstrates that the world is projected to continue to use a multiplicity of energy technologies to meet its energy demands and that, over space and time, a large portfolio of these technologies will be used at any one time.

When assessing how various technologies will contribute to the goal of addressing climate change, these technologies are modelled in such a way that they all compete for market share to provide the energy services and emissions reduction required by society, as this is what would happen in reality. There are major uncertainties associated with the potential and costs of these options, and so the absolute deployment of CCS depends on various scenario-specific assumptions consistent with the underlying storyline and the way they are interpreted in the different models. In the light of this competition and the wide variety of possible emissions futures, the contribution of CCS to total emissions reduction can only be assessed within relatively wide margins.

The uncertainty with respect to the future deployment of CCS and its contribution to total emissions reductions for achieving stabilization of CO_2 concentrations between 450 and 750 ppmv is illustrated by the IPCC TAR mitigation scenarios (Morita *et al.*, 2000; 2001). The TAR mitigation scenarios are based upon SRES baseline scenarios and were developed by nine different modelling teams. In total, 76 mitigation scenarios were developed for TAR, and about half of them (36 scenarios from three alternative models: DNE21, MARIA, and MESSAGE) consider CO_2 capture and storage explicitly as a mitigation option. An overview of the TAR scenarios is presented in Morita *et al.* (2000). It includes eleven publications from individual modelling teams about their scenario assumptions and results.

As illustrated in Figure 8.5, which is based upon the TAR mitigation scenarios, the average share of CCS in total emissions reductions may range from 15% for scenarios aiming

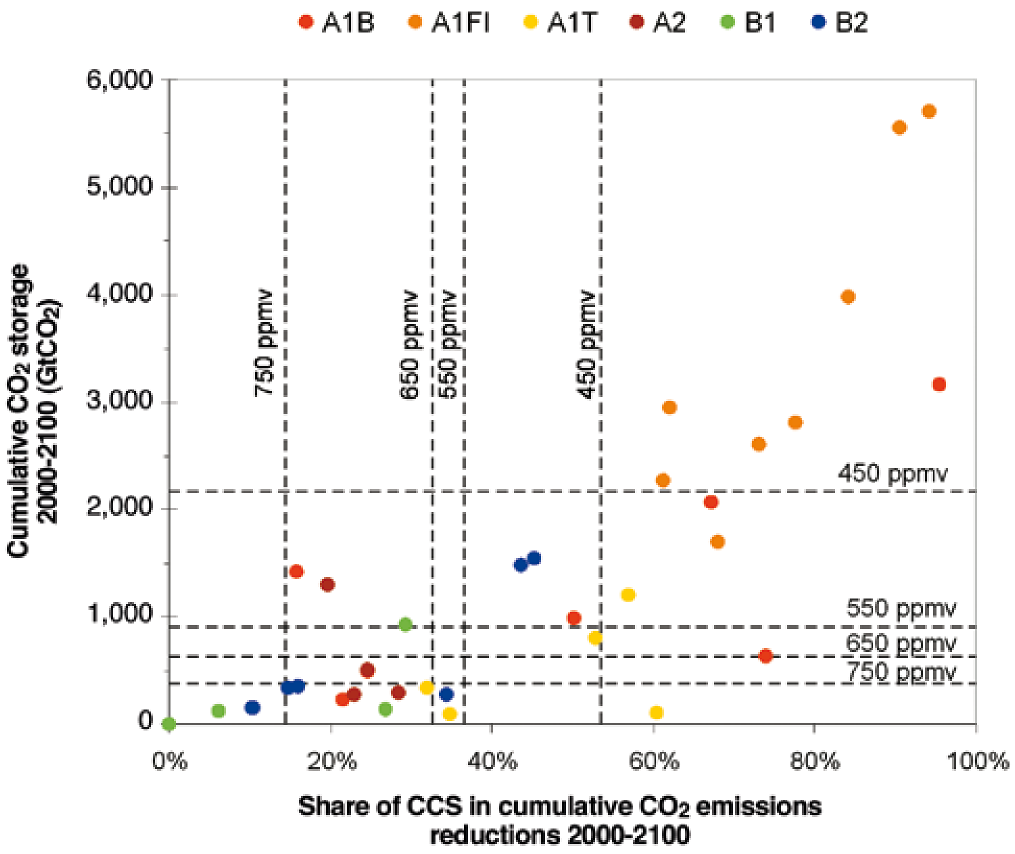

Figure 8.5 Relationship between (1) the imputed share of CCS in total cumulative emissions reductions in per cent and (2) total cumulative CCS deployment in $GtCO_2$ (2000–2100). The scatter plots depict values for individual TAR mitigation scenarios for the six SRES scenario groups. The vertical dashed lines show the average share of CCS in total emissions mitigation across the 450 to 750 ppmv stabilization scenarios, and the dashed horizontal lines illustrate the scenarios' average cumulative storage requirements across 450 to 750 ppmv stabilization.

at the stabilization of CO_2 concentrations at 750 ppmv to 54% for 450 ppmv scenarios.[13] However, the full uncertainty range of the set of TAR mitigation scenarios includes extremes on both the high and low sides, ranging from scenarios with zero CCS contributions to scenarios with CCS shares of more than 90% in total emissions abatement.

8.3.3.1 Cumulative CCS deployment

Top-down and bottom-up energy-economic models have been used to examine the likely total deployment of CCS technologies (expressed in GtC). These analyses reflect the fact that the future usage of CCS technologies is associated with large uncertainties. As illustrated by the IPCC-TAR mitigation scenarios, global cumulative CCS during the 21st century could range – depending on the future characteristics of the reference world (i.e., baselines) and the employed stabilization target (450 to 750 ppmv) – from zero to more than 5500 $GtCO_2$ (1500 GtC) (see Figure 8.6). The average cumulative CO_2 storage (2000–2100) across the six scenario groups shown in Figure 8.6 ranges from 380 $GtCO_2$ (103 GtC) in the 750 ppmv stabilization scenarios to 2160 $GtCO_2$ (590 GtC) in the 450 ppmv scenarios (Table 8.5).[14] However, it is important to note that the majority of the six individual TAR scenarios (from the 20th to the 80th percentile) tend to cluster in the range of 220–2200 $GtCO_2$ (60–600 GtC) for the four stabilization targets (450–750 ppmv).

The deployment of CCS in the TAR mitigation scenarios is comparable to results from similar scenario studies projecting storage of 576–1370 $GtCO_2$ (157–374 GtC) for stabilization scenarios that span 450 to 750 ppmv (Edmonds *et al.*, 2000) and storage of 370 to 1250 $GtCO_2$ (100 to 340 GtC) for stabilization scenarios that span 450 to 650 ppmv (Dooley and Wise, 2003). Riahi *et al.* (2003) project 330–890 $GtCO_2$ (90–243 GtC) of stored CO_2 over the course of the current century for various

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[13] The range for CCS mitigation in the TAR mitigation scenarios is calculated on the basis of the cumulative emissions reductions from 1990 to 2100, and represents the average contribution for 450 and 750 ppmv scenarios across alternative modelling frameworks and SRES baseline scenarios. The full range across all scenarios for 450 ppmv is 20 to 95% and 0 to 68% for 750 ppmv scenarios respectively.

[14] Note that Table 8.5 and Figure 8.6 show average values of CCS across alternative modelling frameworks used for the development of the TAR mitigation scenarios. The deployment of CCS over time, as well as cumulative CO_2 storage in individual TAR mitigation scenarios, are illustrated in Figures 8.5 and 8.7.

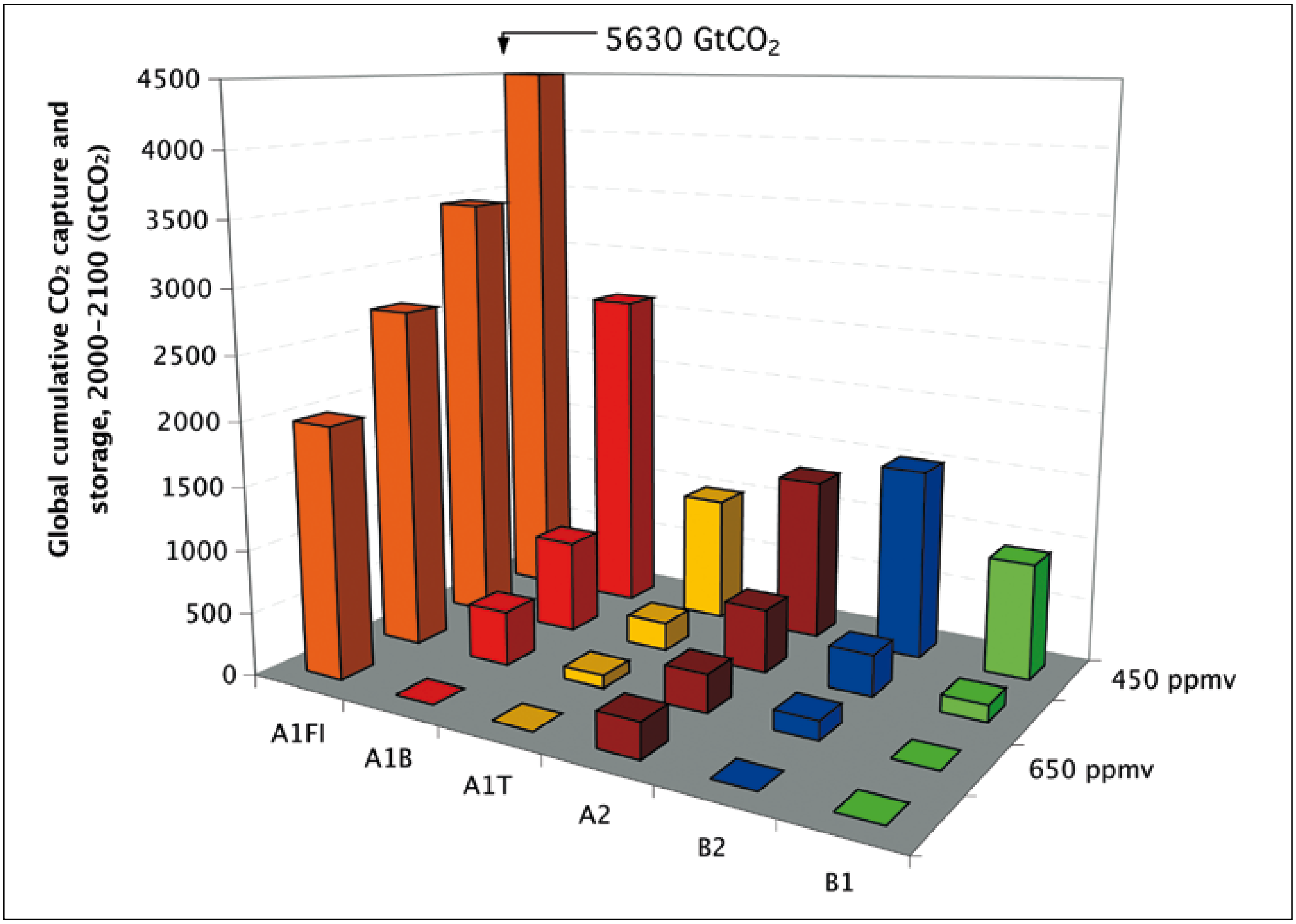

Figure 8.6 Global cumulative CO_2 storage (2000–2100) in the IPCC TAR mitigation scenarios for the six SRES scenario groups and CO_2 stabilization levels between 450 and 750 ppmv. Values refer to averages across scenario results from different modelling teams. The contribution of CCS increases with the stringency of the stabilization target and differs considerably across the SRES scenario groups.

550 ppmv stabilization cases. Fujii and Yamaji (1998) have also included ocean storage as an option. They calculate that, for a stabilization level of 550 ppmv, 920 $GtCO_2$ (250 GtC) of the emissions reductions could be provided by the use of CCS technologies and that approximately one-third of this could be stored in the ocean. This demand for CO_2 storage appears to be within global estimates of total CO_2 storage capacity presented in Chapters 5 and 6.

8.3.3.2 Timing and deployment rate

Recently, two detailed studies of the cost of CO_2 transport and storage costs have been completed for North America (Dooley *et al.*, 2004a) and Western Europe (Wildenborg *et al.*, 2004). These studies concur about the large potential of CO_2 storage capacity in both regions. Well over 80% of the emissions from current CO_2 point sources could be transported and stored in candidate geologic formations for less than 12–15 US\$/tCO_2 in North America and 25 US\$/tCO_2 in Western Europe. These studies are the first to define at a continental scale a 'CO_2 storage supply curve', conducting a spatially detailed analysis in order to explore the relationship between the price of CO_2 transport and storage and the cumulative amount of CO_2 stored. Both studies conclude that, at least for these two regions, the CO_2 storage supply curves are dominated by a very large single plateau (hundreds to thousands of gigatonnes of CO_2), implying roughly constant costs for a wide range of storage capacity[15]. In other words, at a practical level, the cost of CO_2 transport and storage in these regions will have a cap. These studies and a handful of others (see, for example, IEA GHG, 2002) have also shown that early (i.e., low cost) opportunities for CO_2 capture and storage hinge upon a number of factors: an inexpensive (e.g., high-purity) source of CO_2; a (potentially) active area of advanced hydrocarbon recovery (either EOR or ECBM); and the relatively close proximity of the CO_2 point source to the candidate storage reservoir in order to minimize transportation costs. These bottom-up studies provide some of the most detailed insights into the graded CCS resources presently available, showing that the set of CCS opportunities likely to be encountered in the real world will be very heterogeneous. These

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[15] See Chapter 5 for a full assessment of the estimates of geological storage capacity.

Table 8.5 Cumulative CO_2 storage (2000 to 2100) in the IPCC TAR mitigation scenarios in $GtCO_2$. CCS contributions for the world and for the four SRES regions are shown for four alternative stabilization targets (450, 550, 650, and 750 ppmv) and six SRES scenario groups. Values refer to averages across scenario results from different modelling teams.

	All scenarios (average)	A1			A2	B2	B1
		A1FI	A1B	A1T			
WORLD							
450 ppmv	2162	5628	2614	1003	1298	1512	918
550 ppmv	898	3462	740	225	505	324	133
650 ppmv	614	2709	430	99	299	149	0
750 ppmv	377	1986	0	0	277	0	0
OECD90*							
450 ppmv	551	1060	637	270	256	603	483
550 ppmv	242	800	202	82	174	115	80
650 ppmv	172	654	166	54	103	55	0
750 ppmv	100	497	0	0	104	0	0
REF*							
450 ppmv	319	536	257	152	512	345	110
550 ppmv	87	233	99	42	55	79	16
650 ppmv	55	208	56	0	31	37	0
750 ppmv	36	187	0	0	28	0	0
ASIA*							
450 ppmv	638	2207	765	292	156	264	146
550 ppmv	296	1262	226	47	153	67	20
650 ppmv	223	1056	162	20	67	33	0
750 ppmv	111	609	0	0	57	0	0
ROW*							
450 ppmv	652	1825	955	289	366	300	179
550 ppmv	273	1167	214	54	124	63	17
650 ppmv	164	791	45	24	99	25	0
750 ppmv	130	693	0	0	89	0	0

* The OECD90 region includes the countries belonging to the OECD in 1990. The REF ('reforming economies') region aggregates the countries of the Former Soviet Union and Eastern Europe. The ASIA region represents the developing countries on the Asian continent. The ROW region covers the rest of the world, aggregating countries in sub-Saharan Africa, Latin America and the Middle East. For more details see SRES, 2000.

studies, as well as those based upon more top-down modelling approaches, also indicate that, once the full cost of the complete CCS system has been accounted for, CCS systems are unlikely to deploy on a large scale in the absence of an explicit policy or regulatory regime that substantially limits greenhouse gas emissions to the atmosphere. The literature and current industrial experience indicate that, in the absence of measures to limit CO_2 emissions, there are only small, niche opportunities for the deployment of CCS technologies. These early opportunities could provide experience with CCS deployment, including the creation of parts of the infrastructure and the knowledge base needed for the future large-scale deployment of CCS systems.

Most analyses of least-cost CO_2 stabilization scenarios indicate that, while there is significant penetration of CCS systems over the decades to come, the majority of CCS deployment will occur in the second half of this century (Edmonds *et al*., 2000, 2003; Edmonds and Wise, 1998; Riahi *et al*., 2003). One of the main reasons for this trend is that the stabilization of CO_2 concentrations at relatively low levels (<650 ppmv) generally leads to progressively more constraining mitigation regimes over time, resulting in carbon permit prices that start out quite low and steadily rise over the course of this century. The TAR mitigation scenarios (Morita *et al*., 2000) based upon the SRES baselines report cumulative CO_2 storage due to CCS ranging from zero to 1100 $GtCO_2$ (300 GtC) for the first half of the century, with the majority of the scenarios clustering below 185 $GtCO_2$ (50 GtC). By comparison, the cumulative contributions of CCS range from zero to 4770 $GtCO_2$ (1300 GtC) in the second half of the century, with the majority of the scenarios stating figures below 1470 $GtCO_2$ (400 GtC). The deployment of CCS over time in the TAR mitigation scenarios is illustrated in Figure 8.7. As can be seen, the use

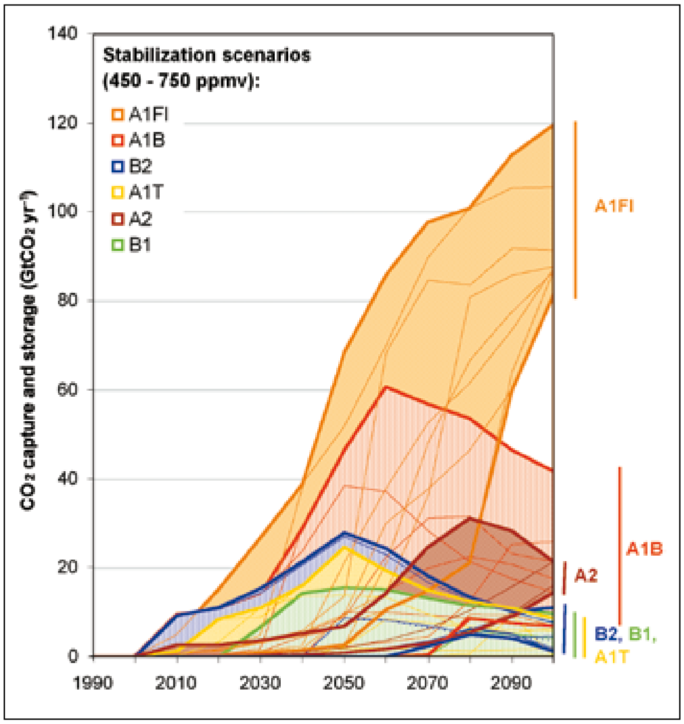

Figure 8.7 Deployment of CCS systems as a function of time from 1990 to 2100 in the IPCC TAR mitigation scenarios where atmospheric CO_2 concentrations stabilize at between 450 to 750 ppmv. Coloured thick lines show the minimum and maximum contribution of CCS for each SRES scenario group, and thin lines depict the contributions in individual scenarios. Vertical axes on the right-hand side illustrate the range of CCS deployment across the stabilization levels for each SRES scenario group in the year 2100.

of CCS is highly dependent upon the underlying base case. For example, in the high economic growth and carbon-intensive baseline scenarios (A1FI), the development path of CCS is characterized by steadily increasing contributions, driven by the rapidly growing use of hydrocarbon resources. By contrast, other scenarios (e.g., A1B and B2) depict CCS deployment to peak during the second half of the century. In a number of these scenarios, the contribution of CCS declines to less than 11 $GtCO_2$ per year (3 GtC per year) until the end of the century. These scenarios reflect the fact that CCS could be viewed as a transitional mitigation option (bridging the transition from today's fossil-intensive energy system to a post-fossil system with sizable contributions from renewables).

Given these models' relatively coarse top-down view of the world, there is less agreement about when the first commercial CCS units will become operational. This is – at least in part – attributable to the importance of policy in creating the context in which initial units will deploy. For example, McFarland *et al.* (2003) foresee CCS deployment beginning around 2035. Other modelling exercises have shown CCS systems beginning to deploy – at a lower level of less than 370 $MtCO_2$ a year (100 MtC a year) – in the period 2005–2020 (see, for example, Dooley *et al.*, 2000). Moreover, in an examination of CCS deployment in Japan, Akimoto *et al.* (2003) show CCS deployment beginning in 2010–2020. In a large body of literature (Edmonds *et al.* 2003; Dooley and Wise, 2003; Riahi *et al.* 2003; IEA, 2004), there is agreement that, in a CO_2-constrained world, CCS systems might begin to deploy in the next few decades and that this deployment will expand significantly after the middle of the century. The variation in the estimates of the timing of CCS-system deployment is attributable to the different ways energy and economic models parameterize CCS systems and to the extent to which the potential for early opportunities – such as EOR or ECBM – is taken into account. Other factors that influence the timing of CCS diffusion are the rate of increase and absolute level of the carbon price.

8.3.3.3 Geographic distribution

McFarland *et al.* (2003) foresee the eventual deployment of CCS technologies throughout the world but note that the timing of the entry of CCS technologies into a particular region is influenced by local conditions such as the relative price of coal and natural gas in a region. Dooley *et al.* (2002) show that the policy regime, and in particular the extent of emissions trading, can influence where CCS technologies are deployed. In the specific case examined by this paper, it was demonstrated that, where emissions trading was severely constrained (and where the cost of abatement was therefore higher), CCS technologies tended to deploy more quickly and more extensively in the US and the EU. On the other hand, in the absence of an efficient emissions-trading system spanning all of the Annex B nations, CCS was used less intensively and CCS utilization was spread more evenly across these nations as the EU and US found it cheaper to buy CCS-derived emission allowances from regions like the former Soviet Union.

Table 8.5 gives the corresponding deployment of CCS in the IPCC TAR mitigation scenarios for four world regions. All values are given as averages across scenario results from different modelling teams. The data in this table (in particular the far left-hand column which summarizes average CO_2 storage across all scenarios) help to demonstrate a common and consistent finding of the literature: over the course of this century, CCS will deploy throughout the world, most extensively in the developing nations of today (tomorrow's largest emitters of CO_2). These nations will therefore be likely candidates for adopting CCS to control their growing emissions.[16]

Fujii *et al.* (2002) note that the actual deployment of CCS technologies in any given region will depend upon a host of geological and geographical conditions that are, at present, poorly represented in top-down energy and economic models. In an attempt to address the shortcomings noted by Fujii *et al.* (2002) and others, especially in the way in which the cost of CO_2 transport and storage are parameterized in top-down models, Dooley *et al.* (2004b) employed graded CO_2 storage supply curves for all regions of the world based upon a preliminary assessment of the literature's estimate of regional CO_2 storage

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[16] This trend can be seen particularly clearly in the far left-hand column of Table 8.5, which gives the average CCS deployment across all scenarios from the various models. Note, nevertheless, a few scenarios belonging to the B1 and B2 scenario family, which suggest larger levels of deployment for CCS in the developed world.

capacity. In this framework, where the cost of CO_2 storage varies across the globe depending upon the quantity, quality (including proximity) and type of CO_2 storage reservoirs present in the region, as well as upon the demand for CO_2 storage (driven by factors such as the size of the regional economy, the stringency of the modelled emissions reduction regime), the authors show that the use of CCS across the globe can be grouped into three broad categories: (1) countries in which the use of CCS does not appear to face either an economic or physical constraint on CCS deployment given the large potential CO_2 storage resource compared to projected demand (e.g., Australia, Canada, and the United States) and where CCS should therefore deploy to the extent that it makes economic sense to do so; (2) countries in which the supply of potential geological storage reservoirs (the authors did not consider ocean storage) is small in comparison to potential demand (e.g., Japan and South Korea) and where other abatement options must therefore be pressed into service to meet the modelled emissions reduction levels; and (3) the rest of the world in which the degree to which CCS deployment is constrained is contingent upon the stringency of the emission constraint and the useable CO_2 storage resource. The authors note that discovering the true CO_2 storage potential in regions of the world is a pressing issue; knowing whether a country or a region has 'sufficient' CO_2 storage capacity is a critical variable in these modelling analyses because it can fundamentally alter the way in which a country's energy infrastructure evolves in response to various modelled emissions constraints.

8.3.3.4 Long-term economic impact

An increasing body of literature has been analyzing short- and long-term financial requirements for CCS. The World Energy Investment Outlook 2003 (IEA, 2003) estimates an upper limit for investment in CCS technologies for the OECD of about US$ 350 to 440 billion over the next 30 years, assuming that all new power plant installations will be equipped with CCS. Similarly, Riahi *et al.* (2004) estimate that up-front investments for initial niche market applications and demonstration plants could amount to about US$ 70 billion or 0.2% of the total global energy systems costs over the next 20 years. This would correspond to a market share of CCS of about 3.5% of total installed fossil-power generation capacities in the OECD countries by 2020, where most of the initial CCS capacities are expected to be installed.

Long-term investment requirements for the full integration of CCS in the electricity sector as a whole are subject to major uncertainties. Analyses with integrated assessment models indicate that the costs of decarbonizing the electricity sector via CCS might be about three to four per cent of total energy-related systems costs over the course of the century (Riahi *et al.*, 2004). Most importantly, these models also point out that the opportunity costs of CCS not being part of the CO_2 mitigation portfolio would be significant. Edmonds *et al.* (2000) indicate that savings over the course of this century associated with the wide-scale deployment of CCS technologies when compared to a scenario in which these technologies do not exist could be in the range of tens of billions of 1990 US dollars for high CO_2 concentrations limits such as 750 ppmv, to trillions of dollars for more stringent CO_2 concentrations such as 450 ppm [17]. Dooley *et al.* (2002) estimate cost savings in excess of 36% and McFarland *et al.* (2004) a reduction in the carbon permit price by 110 US$/t$CO_2$ in scenarios where CCS technologies are allowed to deploy when compared to scenarios in which they are not.

8.3.3.5 Interaction with other technologies

As noted above, the future deployment of CCS will depend on a number of factors, many of which interact with each other. The deployment of CCS will be impacted by factors such as the development and deployment of renewable energy and nuclear power (Mori, 2000). Edmonds *et al.* (2003) report that CCS technologies can synergistically interact with other technologies and in doing so help to lower the cost and therefore increase the overall economic potential of less carbon-intensive technologies. The same authors note that these synergies are perhaps particularly important for the combination of CCS, H_2 production technologies and H_2 end-use systems (e.g., fuel cells). On the other hand, the widespread availability of CCS technologies implies an ability to meet a given emissions reduction at a lower marginal cost, reducing demand for substitute technologies at the margin. In other words, CCS is competing with some technologies, such as energy-intensity improvements, nuclear, fusion, solar power options, and wind. The nature of that interaction depends strongly on the climate policy environment and the costs and potential of alternative mitigation options, which are subject to large variations depending on site-specific, local conditions (IPCC, 2001). At the global level, which is spatially more aggregated, this variation translates into the parallel deployment of alternative options, taking into account the importance of a diversified technology portfolio for addressing emissions mitigation in a cost-effective way.

An increasing body of literature (Willams, 1998; Obersteiner *et al.*, 2001; Rhodes and Keith, 2003; Makihira *et al.*, 2003; Edmonds *et al.*, 2003, Möllersten *et al.*, 2003) has begun to examine the use of CCS systems with biomass-fed energy systems to create useful energy (electricity or transportation fuels) as well as excess emissions credits generated by the system's resulting 'negative emissions'. These systems can be fuelled solely by biomass, or biomass can be co-fired in conventional coal-burning plants, in which case the quantity is normally limited to about 10–15% of the energy input. Obersteiner *et al.* (2001) performed an analysis based on the SRES scenarios, estimating that 880 to 1650 GtCO_2 (240 to 450 GtC) of the scenario's cumulative emissions that are vented during biomass-based energy-conversion processes could potentially be available for capture and storage over the course of the century. Rhodes and Keith (2003) note that, while this coupled bio-energy CCS system would generate expensive

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[17] Savings are measured as imputed gains of GDP due to CCS deployment, in contrast to a world where CCS is not considered to be part of the mitigation portfolio.

electricity in a world of low carbon prices, this system could produce competitively priced electricity in a world with carbon prices in excess of 54.5 US$/t$CO_2$ (200 US$/tC). Similarly, Makihira *et al.* (2003) estimate that CO_2 capture during hydrogen production from biomass could become competitive at carbon prices above 54.5 to 109 US$/t$CO_2$ (200 to 400 US$/tC).

8.4 Economic impacts of different storage times

As discussed in the relevant chapters, geological and ocean storage might not provide permanent storage for all of the CO_2 injected. The question arises of how the possibility of leakage from reservoirs can be taken into account in the evaluation of different storage options and in the comparison of CO_2 storage with mitigation options in which CO_2 emissions are avoided.

Chapters 5 and 6 discuss the expected fractions of CO_2 retained in storage for geological and ocean reservoirs respectively. For example, Box 6.7 suggests four types of measures for ocean storage: storage efficiency, airborne fraction, net present value, and global warming potential. Chapter 9 discusses accounting issues relating to the possible impermanence of stored CO_2. Chapter 9 also contains a review of the broader literature on the value of delayed emissions, primarily focusing on sequestration in the terrestrial biosphere. In this section, we focus specifically on the economic impacts of differing storage times in geological and ocean reservoirs.

Herzog *et al.* (2003) suggest that CO_2 storage and leakage can be looked upon as two separate, discrete events. They represent the value of temporary storage as a familiar economic problem, with explicitly stated assumptions about the discount rate and carbon prices. If someone stores a tonne of CO_2 today, they will be credited with today's carbon price. Any future leakage will have to be compensated by paying the carbon price in effect at that time. Whether non-permanent storage options will be economically attractive depends on assumptions about the leakage rate, discount rate and relative carbon permit prices. In practice, this may turn out to be a difficult issue since the commercial entity that undertakes the storage may no longer exist when leakage rates have been clarified (as Baer (2003) points out), and hence governments or society at large might need to cover the leakage risk of many storage sites rather than the entity that undertakes the storage.

Ha-Duong and Keith (2003) explore the trade-offs between discounting, leakage, the cost of CO_2 storage and the energy penalty. They use both an analytical approach and an integrated assessment numerical model in their assessment. In the latter case, with CCS modelled as a backstop technology, they find that, for an optimal mix of CO_2 abatement and CCS technologies, 'an (annual) leakage rate of 0.1% is nearly the same as perfect storage while a leakage rate of 0.5% renders storage unattractive'.

Some fundamental points about the limitations of the economic valuation approaches presented in the literature have been raised by Baer (2003). He argues that financial efficiency, which is at the heart of the economic approaches to the valuation of, and decisions about, non-permanent storage is only one of a number of important criteria to be considered. Baer points out that at least three risk categories should to be taken into account as well:

- ecological risk: the possibility that 'optimal' leakage may preclude future climate stabilization;
- financial risk: the possibility that future conditions will cause carbon prices to greatly exceed current expectations, with consequences for the maintenance of liability and distribution of costs; and
- political risk: the possibility that institutions with an interest in CO_2 storage may manipulate the regulatory environment in their favour.

As these points have not been extensively discussed in the literature so far, the further development of the scientific debate on these issues must be followed closely.

In summary, within this purely economic framework, the few studies that have looked at this topic indicate that some CO_2 leakage can be accommodated while still making progress towards the goal of stabilizing atmospheric concentrations of CO_2. However, due to the uncertainties of the assumptions, the impact of different leakage rates and therefore the impact of different storage times are hard to quantify.

8.5 Gaps in knowledge

Cost developments for CCS technologies are now estimated based on literature, expert views and a few recent CCS deployments. Costs of large-scale integrated CCS applications are still uncertain and their variability depends among other things on many site-specific conditions. Especially in the case of large-scale CCS biomass based applications, there is a lack of experience and therefore little information in the literature about the costs of these systems.

There is little empirical evidence about possible cost decreases related to 'learning by doing' for integrated CCS systems since the demonstration and commercial deployment of these systems has only recently begun. Furthermore, the impact of targeted research, development and deployment (RD&D) of CCS investments on the level and rate of CCS deployment is poorly understood at this time. This lack of knowledge about how technologies will deploy in the future and the impact of RD&D on the technology's deployment is a generic issue and is not specific to CCS deployment.

In addition to current and future CCS technological costs, there are other possible issues that are not well known at this point and that would affect the future deployment of CCS systems: for example, costs related to the monitoring and regulatory framework, possible environmental damage costs, costs associated with liability and possible public-acceptance issues.

There are at present no known, full assessments of life-cycle costs for deployed CCS systems, and in particular the economic impact of the capture, transport and storage of non-pure CO_2 streams.

The development of bottom-up CCS deployment cost curves that take into account the interplay between large CO_2 point sources and available storage capacity in various regions of the world should continue; these cost curves would help to show how CCS technologies will deploy in practice and would also help improve the economic modelling of CCS deployment in response to various modelled scenarios.

Recent changes in energy prices and changes in policy regimes related to climate change are not fully reflected in the literature available as this chapter was being written. This suggests a need for a continuous effort to update analyses and perhaps draft a range of scenarios with a wider range of assumptions (e.g., fuel prices, climate policies) in order to understand better the robustness and sensitivity of the current outcomes.

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9

Implications of carbon dioxide capture and storage for greenhouse gas inventories and accounting

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EXECUTIVE SUMMARY

This chapter addresses how methodologies to estimate and report reduced or avoided greenhouse gas emissions from the main options for CO_2 capture and storage (CCS) systems could be included in national greenhouse gas inventories, and in accounting schemes such as the Kyoto Protocol.

The *IPCC Guidelines* and Good Practice Guidance reports (*GPG2000* and *GPG-LULUCF*) [1]are used in preparing national inventories under the UNFCCC. These guidelines do not specifically address CO_2 capture and storage, but the general framework and concepts could be applied for this purpose. The IPCC guidelines give guidance for reporting on annual emissions by gas and by sector. The amount of CO_2 captured and stored can be measured, and could be reflected in the relevant sectors and categories producing the emissions, or in new categories created specifically for CO_2 capture, transportation and storage in the reporting framework. In the first option, CCS would be treated as a mitigation measure and, for example, power plants with CO_2 capture or use of decarbonized fuels would have lower emissions factors (kgCO_2/kg fuel used) than conventional systems. In the second option, the captured and stored amounts would be reported as removals (sinks) for CO_2. In both options, emissions from fossil fuel use due to the additional energy requirements in the capture, transportation and injection processes would be covered by current methodologies. But under the current framework, they would not be allocated to the CCS system.

Methodologies to estimate, monitor and report physical leakage from storage options would need to be developed. Some additional guidance specific to the systems would need to be given for fugitive emissions from capture, transportation and injection processes. Conceptually, a similar scheme could be used for mineral carbonation and industrial use of CO_2. However, detailed methodologies would need to be developed for the specific processes.

Quantified commitments, emission trading or other similar mechanisms need clear rules and methodologies for accounting for emissions and removals. There are several challenges for the accounting frameworks. Firstly, there is a lack of knowledge about the rate of physical leakage from different storage options including possibilities for accidental releases over a very long time period (issues of permanence and liability). Secondly, there are the implications of the additional energy requirements of the options; and the issues of liability and economic leakage where CO_2 capture and storage crosses the traditional accounting boundaries.

The literature on accounting for the potential impermanence of stored CO_2 focuses on sequestration in the terrestrial biosphere. Although notably different from CCS in oceans or in geological reservoirs (with respect to ownership, the role of management, measurement and monitoring, expected rate of physical leakage; modes of potential physical leakage; and assignment of liability), there are similarities. Accounting approaches, such as discounting, the ton-year approach, and rented or temporary credits, are discussed. Ultimately, political processes will decide the value of temporary storage and allocation of responsibility for stored carbon. Precedents set by international agreements on sequestration in the terrestrial biosphere provide some guidance, but there are important differences that will have to be considered.

9.1 Introduction

CO_2 capture and storage (CCS) can take a variety of forms. This chapter discusses how the main CCS systems as well as mineral carbonation and industrial uses of CO_2, described in the previous chapters could be incorporated into national greenhouse gas inventories and accounting schemes. However, inventory or accounting issues specific to enhanced oil recovery or enhanced coal bed methane are not addressed here.

The inclusion of CCS systems in national greenhouse gas inventories is discussed in Section 9.2 (Greenhouse gas inventories). The section gives an overview of the existing framework, the main concepts and methodologies used in preparing and reporting national greenhouse gas emissions and removals with the aim of identifying inventory categories for reporting CCS systems. In addition, areas are identified where existing methodologies could be used to include these systems in the inventories, and areas where new methodologies (including emission/removal factors and uncertainty estimates) would need to be developed. Treatment of CCS in corporate or company reporting is beyond the scope of the chapter.

Issues related to accounting[2] under the Kyoto Protocol; or under other similar accounting schemes that would limit emissions, provide credits for emission reductions, or encourage emissions trading; are addressed in Section 9.3 (Accounting issues). The section addresses issues that could warrant special rules and modalities in accounting schemes because of specific features of CCS systems, such as permanence of CO_2 storage and liability issues related to transportation and storage in international territories and across national borders. Specific consideration is also given to CCS systems in relation to the mechanisms of the Kyoto Protocol (Emission Trading, Joint Implementation and the Clean Development Mechanism).

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[1] Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC 1997) – abbreviated as IPCC Guidelines in this chapter; IPCC Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories (IPCC 2000) – abbreviated as GPG2000; and IPCC Good Practice Guidance for Land Use, Land-Use Change and Forestry (IPCC 2003) – abbreviated as GPG-LULUCF.

[2] 'Accounting' refers to the rules for comparing emissions and removals as reported with commitments. In this context, 'estimation' is the process of calculating greenhouse gas emissions and removals, and 'reporting' is the process of providing the estimates to the UNFCCC (IPCC 2003).

9.2 National greenhouse gas inventories

Information on pollutant emissions is usually compiled in 'emission inventories'. Emissions are listed according to categories such as pollutants, sectors, and source and compiled per geographic area and time interval. Many different emission inventories have been prepared for different purposes. Among the commitments in the United Nations Framework Convention on Climate Change (UNFCCC, 1992) all Parties, taking into account their common but differentiated responsibilities, and their specific national and regional development priorities, objectives and circumstances, shall: 'Develop, periodically update, publish and make available to the Conference of the Parties, national inventories of anthropogenic emissions by sources and removals by sinks of all greenhouse gases not controlled by the Montreal Protocol, using comparable methodologies to be agreed upon by the Conference of the Parties'.[3]

Industrialized countries (Annex I Parties) are required to report annually and developing countries (non-Annex I Parties) to report on greenhouse gas emissions and removals to the Convention periodically, as part of their National Communications to the UNFCCC. National greenhouse gas inventories are prepared using the methodologies in the *IPCC Guidelines* as complemented by the *GPG2000* and G*PGLULUCF*, or methodologies consistent with these. These inventories should include all anthropogenic greenhouse gas emissions by sources and removals by sinks not covered by the Montreal Protocol. To ensure high quality and accuracy, inventories by Annex I Parties are reviewed by expert review teams coordinated by the UNFCCC Secretariat. The review reports are published on the UNFCCC website[4].

The rules and modalities for accounting are elaborated under the Kyoto Protocol (UNFCCC, 1997) and the Marrakech Accords[5] (UNFCCC, 2002). The Kyoto Protocol specifies emission limitation or reduction commitments by the Annex I Parties for six gases/gas groups: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulphur hexafluoride (SF_6).

At present, CCS is practiced on a very small scale. CCS projects have not generally been described in the national inventory reports of the countries where they take place. An exception is the Sleipner CCS project, which is included in Norway's inventory report.[6] Norway provides information on the annual captured and stored amounts, as well as on the amounts of CO_2 that escape to the atmosphere during the injection process (amounts have varied from negligible to about 0.8% of the captured amount). The escaping CO_2 emissions are included in the total emissions of Norway. The spread of the CO_2 in the storage reservoir has been monitored by seismic methods. No physical leakage has been detected. An uncertainty estimate has not been performed but it is expected to be done when more information is available from the project's monitoring programme.

The scarce reporting of current CCS projects is due largely to the small number and size of industrial CCS projects in operation, as well as to the lack of clarity in the reporting methodologies.

9.2.1 Revised 1996 IPCC Guidelines and IPCC Good Practice Guidance

The reporting guidelines under the UNFCCC[7], and under the Kyoto Protocol as specified in the Marrakech Accords require Annex I Parties to use the *IPCC Guidelines*[1], as elaborated by the *GPG2000*[1], in estimating and reporting national greenhouse gas inventories. The use of the *GPG-LULUCF*[1] will start in 2005 with a one-year trial period[8]. Non-Annex I Parties also use the *IPCC Guidelines* in their reporting, and use of *GPG2000* and *GPG-LULUCF* reports is encouraged.[9] The main reporting framework (temporal, spatial and sectoral) and the guiding principles of the *IPCC Guidelines* and good practice guidance reports are given in Box 9.1.

The IPCC Guidelines will be revised and updated by early 2006[10]. In the draft outline for the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, CCS is mentioned in a footnote in the Energy Sector: 'It is recognized that CO_2 capture and storage is an important emerging issue in inventory development. The coverage of CO_2 storage in this report will be closely coordinated with progress on IPCC SR on CO_2 capture and storage. CO_2 capture activities will be integrated as appropriate into the methods presented for source categories where it may occur.'

9.2.2 Methodological framework for CO_2 capture and storage systems in national greenhouse gas inventories

The two main options for including CCS in national greenhouse gas inventories have been identified and analysed using the current methodological framework for total chain from capture to storage (geological and ocean storage). These options are:

- Source reduction: To evaluate the CCS systems as mitigation options to reduce emissions to the atmosphere;

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[3] Commitment related to the Articles 4.1 (a) and 12.1 (a) of the United Nations Framework Convention of Climate Change (UNFCCC).

[4] http://unfccc.int

[5] The Marrakech Accords refer to the Report of the Conference of the Parties of the UNFCCC on its seventh session (COP7), held in Marrakech 29 October to 10 November 2001.

[6] Norway's inventory report can be found at http://cdr.eionet.eu.int/no/un/UNFCCC/envqh6rog.

[7] FCCC/CP2002/7/Add.2: Annexes to Decision 17/CP.8 Guidelines for the preparation of national communications from Parties not included in Annex I to the Convention and 18/CP.8 Guidelines for the preparation of national communications by Parties included in Annex I to the Convention, part I: UNFCCC reporting guidelines on annual inventories.

[8] FCCC/SBSTA/2003/L.22 and FCCC/SBSTA/2003/L.22/Add.1.

[9] FCCC/CP/2002/7/Add.2.

[10] http://www.ipcc.ch/meet/session21.htm: IPCC XXI/Doc.10.

Box 9.1 Main reporting framework (temporal, spatial and sectoral) and guiding principles of the IPCC Guidelines and good practice guidance reports.

The IPCC methodologies for estimating and reporting **national** greenhouse gas inventories are based on **sectoral** guidance for reporting of actual emissions and removals of greenhouse gases by gas and **by year**. The *IPCC Guidelines* give the framework for the reporting (sectors, categories and sub-categories), default methodologies and default emission/removal factors (the so called Tier 1 methodologies) for the estimation. Higher tier methodologies are based on more sophisticated methods for estimating emissions/removals and on the use of national or regional parameters that accommodate the specific national circumstances. These methodologies are not always described in detail in the IPCC Guidelines. Use of transparent and well-documented national methodologies consistent with those in the *IPCC Guidelines* is encouraged.

The Good Practice Guidance (GPG) reports facilitate the development of inventories in which the emissions/removals are not over- or under-estimated, so far as can be judged, and in which the uncertainties are reduced as far as practicable. Further aims are to produce transparent, documented, consistent, complete, comparable inventories, which are i) assessed for uncertainties, ii) subject to quality assurance and quality control, and iii) efficient in the use of resources. The GPG reports give guidance on how to choose the appropriate methodologies for specific categories in a country, depending on the importance of the category (key category analysis is used to determine the importance) and on availability of data and resources for the estimation. Decision trees guide the choice of estimation method most suited to the national circumstances. The category-specific guidance linked to the decision trees also provides information on the choice of emission factors and activity data. The GPG reports give guidance on how to meet the requirements of transparency, consistency, completeness, comparability, and accuracy required by the national greenhouse gas inventories.

The **Sectors** covered in the *IPCC Guidelines* are: (i) Energy, (ii) Industrial Processes, (iii) Solvent and Other Product Use, (iv) Agriculture, (v) Land Use Change and Forestry, (vi) Waste and (vii) Other. The use of the seventh sector 'Other' is discouraged: 'Efforts should be made to fit all emission sources/sinks into the six categories described above. If it is impossible to do so, however, this category can be used, accompanied by a detailed explanation of the source/sink activity'' (IPCC 1997).

- Sink enhancement: To evaluate the CCS systems using an analogy with the treatment made to CO_2 removals by sinks in the sector Land Use, Land-Use Change and Forestry. A balance is made of the CO_2 emissions and removals to obtain the net emission or removal. In this option, removals by sinks are related to CO_2 storage.

In both options, estimation methodologies could be developed to cover most of the emissions in the CCS system (see Figure 9.1), and reporting could use the current framework for preparation of national greenhouse gas inventories.

In the first option, reduced emissions could be reported in the category where capture takes place. For instance, capture in power plants could be reported using lower emission factors than for plants without CCS. But this could reduce transparency of reporting and make review of the overall impact on emissions more difficult, especially if the capture process and emissions from transportation and storage are not linked. This would be emphasized where transportation and storage includes captured CO_2 from many sources, or when these take place across national borders. An alternative would be to track CO_2 flows through the entire capture and storage system making transparent how much CO_2 was produced, how much was emitted to the atmosphere at each process stage, and how much CO_2 was transferred to storage. This latter approach, which appears fully transparent and consistent with earlier UNFCCC agreements, is described in this chapter.

The second option is to report the impact of the CCS system as a sink. For instance, reporting of capture in power plants would not alter the emissions from the combustion process but the stored amount of CO_2 would be reported as a removal in the inventory. Application of the second option would require adoption of new definitions not available in the UNFCCC or in the current methodological framework for the preparation of inventories. UNFCCC (1992) defines a sink as 'any process, activity or mechanism which removes a greenhouse gas, an aerosol, or a precursor of a greenhouse gas *from the atmosphere*'. Although 'removal' was not included explicitly in the UNFCCC definitions, it appears associated with the 'sink' concept. CCS[11] systems do not meet the UNFCCC definition for a sink, but given that the definition was agreed without having CCS systems in mind, it is likely that this obstacle could be solved (Torvanger *et al.*, 2005).

General issues of relevance to CCS systems include system boundaries (sectoral, spatial and temporal) and these will vary in importance with the specific system and phases of the system. The basic methodological approaches for system components, together with the status of the methods and availability of data for these are discussed below. Mineral carbonation and industrial use of CO_2 are addressed separately.

- Sectoral boundaries: The draft outline for the *2006 IPCC Guidelines* (see Section 9.2.1) states that: 'CO_2 capture activities will be integrated as appropriate into the methods presented for source/sink categories where they may

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[11] Few cases are nearer to the 'sink' definition. For example, mineralization can also include fixation from the atmosphere.

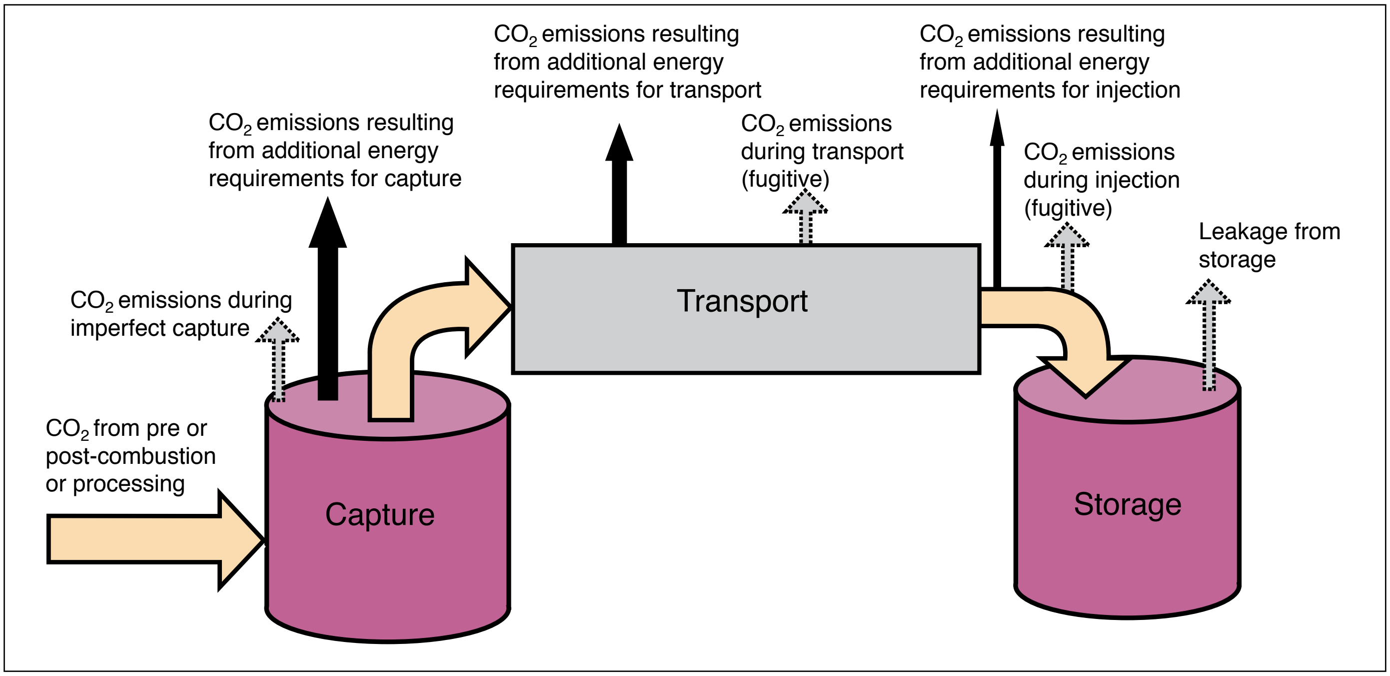

Figure 9.1 Simplified flow diagram of possible CO_2 emission sources during CCS

occur'. This approach is followed here when addressing the sectors under which the specific phases of the CCS systems could be reported. The reporting of emissions/removals associated with CO_2 capture, transportation, injection and storage processes should be described clearly to fulfil the requirement of transparent reporting.

- Spatial boundaries: National inventories include greenhouse gas emissions and removals taking place within national (including administered) territories and offshore areas over which that country has jurisdiction. Some of the emissions and removals of CCS systems could occur outside the areas under the jurisdiction of the reporting country, an aspect that requires additional consideration and is addressed mainly in Section 9.3.
- Temporal boundaries: Inventories are prepared on a calendar year basis. Some aspects of CCS systems (such as the amount of CO_2 captured or fugitive emissions from transportation) could easily be incorporated into an annual reporting system (yearly estimates would be required). However, other emissions (for example, physical leakage of CO_2 from geological storage) can occur over a very long period after the injection has been completed - time frames range from hundreds to even millions of years (see further discussion in Section 9.3).

Table 9.1 lists potential sources and emissions of greenhouse gases in the different phases of a CCS system and their relationship with the framework for the reporting (sectors, categories and sub-categories) of the *IPCC Guidelines*. The relative importance of these potential sources for the national greenhouse inventory can vary from one CCS project to another, depending on factors such as capture technologies and storage site characteristics. Emissions from some of these sources are probably very small, sometimes even insignificant, but to guarantee an appropriate completeness[12] of the national inventory, it is necessary to evaluate their contribution.

Some important considerations relative to the source categories and emissions included in Table 9.1 are the following:

- Capture, transportation and injection of CO_2 into storage requires energy (the additional energy requirements have been addressed in previous chapters). Greenhouse gas emissions from this energy use are covered by the methodologies and reporting framework in the *IPCC Guidelines* and *GPG2000*. Additional methodologies and emission factors can be found in other extensive literature, such as EEA (2001) and US EPA (1995, 2000). Where capture processes take place at the fuel production site, the emissions from the fuel used in the capture process may not be included in the national statistics. Additional methods to cover emissions from this source may be needed. In the current reporting framework, emissions from the additional energy requirements would not be linked to the CCS system.
- Fugitive emissions from CCS systems can occur during capture, compression, liquefaction, transportation and injection of CO_2 to the storage reservoir. A general framework for estimation of fugitive emissions is included in the *IPCC Guidelines* in the Energy sector. The estimation and reporting of fugitive emissions from CCS need further

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[12] Completeness means that an inventory covers all sources and sinks, as well as all gases included in the IPCC Guidelines and also other existing relevant source/sink categories specific to individual Parties, and therefore may not be included in the IPCC Guidelines. Completeness also means full geographic coverage of sources and sinks of a Party (FCCC/CP/1999/7).

Table 9.1 Potential sources and emissions of greenhouse gases (GHG) in the general phases of a CCS system.

IPCC guidelines			**Emissions**	**Capture**	**Transportation** (b)	**Injection**	**Storage** (c)
Sector (a)	**Source category** (a)						
1 Energy	GHG emissions from stationary combustion 1A1; 1A2		CO_2, CH_4, N_2O, NO_x, CO, NMVOCs, SO_2	●		●	
1 Energy	GHG emissions from mobile combustion	Water-borne navigation 1A3di (d) 1A3dii (e)	CO_2, CH_4, N_2O, NO_x, CO, NMVOCs, SO_2		●		
		Other transportation (pipeline transportation) 1A3ei	CO_2, CH_4, N_2O, NO_x, CO, NMVOCs, SO_2		●		
1 Energy	Fugitive emissions from fuels 1B	Oil and natural gas 1B2 (f)	CO_2; CH_4; N_2O NMVOCs	●		●	
2 Industrial processes (excluding emissions from fuel combustion)	Mineral products 2A	(e.g., cement)	CO_2, SO_2	●		●	
	Chemical industry 2B	(e.g., ammonia)	CO_2, NMVOCs, CO, SO_2	●		●	
	Metal production 2C	(e.g., iron and steel)	CO_2, NO_x, NMVOCs, CO, SO_2	●		●	
	Other production 2D	(e.g. food and drink)	CO_2, NMVOCs	●		●	
6 Waste	Industrial wastewater handling 6B1		CH_4	●			
	Fugitive CO_2 emissions from capture, transportation and injection processes (g)	Normal operations	CO_2	●	●	●	
		Repair and maintenance	CO_2	●	●	●	
		Systems upsets and accidental discharges	CO_2	●	●	●	

a) IPCC source/sink category numbering (see also IPCC (1997), Vol.1, Common Reporting Framework).

b) Emissions from transportation include both GHG emissions from fossil fuel use and fugitive emissions of CO_2 from pipelines and other equipment/processes. Besides ships and pipelines, limited quantities of CO_2 could be transported by railway or by trucks, source categories identified in the IPCC Guidelines/GPG2000.

c) Long-term physical leakage of stored CO_2 is not covered by the existing framework for reporting of emissions in the *IPCC Guidelines*. Different potential options exist to report these emissions in the inventories (for example, in the relevant sectors/categories producing the emissions, creating a separate and new category for the capture, transportation and/or storage industry). No conclusion can yet be made on the most appropriate reporting option taking into account the different variants adopted by the CCS systems.

d) International Marine (Bunkers). Emissions based on fuel sold to ships engaged in international transport should not be included in national totals but reported separately under Memo Items.

e) National Navigation.

f) Emissions related to the capture (removal) of CO_2 in natural gas processing installations to improve the heating valued of the gas or to meet pipeline specifications.

g) A general framework for estimation of fugitive emissions is included in the *IPCC Guidelines* in the Energy sector. However, estimation and reporting of fugitive emissions from CCS needs further elaboration of the methodologies.

elaboration in methodologies.

- The long-term physical leakage of stored CO_2 (escape of CO_2 from a storage reservoir) is not covered by the existing framework for reporting emissions in the *IPCC Guidelines*. Different options exist to report these emissions in the inventories (for example, in the relevant sectors/categories producing the emissions initially, by creating a separate and new category under fugitive emissions, or by creating a new category for the capture, transportation and/or storage industry).
- Application of CCS to CO_2 emissions from biomass combustion, and to other CO_2 emissions of biological origin (for example, fermentation processes in the production of food and drinks) would require specific treatment in inventories. It is generally assumed that combustion of biomass fuels results in zero net CO_2 emissions if the biomass fuels are produced sustainably. In this case, the CO_2 released by combustion is balanced by CO_2 taken up during photosynthesis. In greenhouse gas inventories, CO_2 emissions from biomass combustion are, therefore, not reported under Energy. Any unsustainable production should be evident in the calculation of CO_2 emissions and removals in Land Use, Land-Use Change and Forestry Sector. Thus, CCS from biomass sources would be reported as negative CO_2 emissions.

9.2.2.1 Capture

The capture processes are well defined in space and time, and their emissions (from additional energy use, fugitives, etc.) could be covered by current national and annual inventory systems. The capture processes would result in reduced emissions from industrial plants, power plants and other sites of fuel combustion. For estimation purposes, the reduced CO_2 emissions could be determined by measuring the amount of CO_2 captured and deducting this from the total amount of CO_2 produced (see Figure 8.2 in Chapter 8).

The total amount of CO_2, including emissions from the additional energy consumption necessary to operate the capture process, could be estimated using the methods and guidance in the *IPCC Guidelines* and *GPG2000*. The capture process could produce emissions of other greenhouse gases, such as CH_4 from treatment of effluents (for example, from amine decomposition). These emissions are not included explicitly in the *IPCC Guidelines* and *GPG2000*. Estimates on the significance of these emissions are not available, but are likely to be small or negligible compared to the amount of captured CO_2.

Although not all possible CCS systems can be considered here, it is clear that some cases would require different approaches. For example, pre-combustion decarbonization in fuel production units presents some important differences compared to the post-combustion methods, and the simple estimation process described above might not be applicable. For example, the capture of CO_2 may take place in a different country than the one in which the decarbonized fuel is used. This would mean that emissions associated with the capture process (possible fugitive CO_2 emissions) would need to be estimated and reported separately to those resulting from the combustion process (see also Section 9.3 on issues relating to accounting and allocation of the emissions and emissions reductions).

9.2.2.2 Transportation

Most research on CCS systems focuses on the capture and storage processes and fugitive emissions from CO_2 transportation are often overlooked (Gale and Davison, 2002). CO_2 transportation in pipelines and ships is discussed in Chapter 4. Limited quantities of CO_2 could also be transported via railway or by trucks (Davison *et al.*, 2001). The additional energy required for pipeline transport is mostly covered by compression at the capture site. Additional compression may be required when CO_2 is transported very long distances. The emissions from fossil fuel in transportation by ships, rail or trucks would be covered under the category on mobile combustion and other subcategories in the Energy sector. However, according to the current IPCC guidelines, emissions from fuels sold to any means of international transport should be excluded from the national total emissions and be reported separately as emissions from international bunkers. These emissions are not included in national commitments under the Kyoto Protocol (e.g., IPCC 1997 and 2000, see also Section 9.3).

Any fugitive emissions or accidental releases from transportation modes could be covered in the Energy sector under the category 'Fugitive Emissions'. CO_2 emissions from a pipeline can occur at the intake side during pumping and compression, at the pipeline joints, or at the storage site. Emission rates can differ from surface, underground and sub-sea pipelines. Explicit guidance for CO_2 transportation in pipelines is not given in the current IPCC methodologies, but a methodology for natural gas pipelines is included. A distinction is to be made between leakage during normal operation and CO_2 losses during accidents or other physical disruptions. As described in Chapter 4, statistics on the incident rate in pipelines for natural gas and CO_2 varied from 0.00011 to 0.00032 incidents km^{-1} $year^{-1}$ (Gale and Davison, 2002). However, as an analogy of CO_2 transportation to natural gas transportation, Gielen (2003) reported that natural gas losses during transportation can be substantial.

Total emissions from pipelines could be calculated on the basis of the net difference between the intake and discharge flow rates of the pipelines. Because CO_2 is transported in pipelines as a supercritical or dense phase fluid, the effect of the surrounding temperature on the estimated flow rate would need to be taken into account. Volumetric values would need to be corrected accordingly when CO_2 is transmitted from a cooler climate to a moderate or hot climate, and vice versa. In some cases, fugitive losses could be lower than metering accuracy tolerances. Hence, all metering devices measuring CO_2 export and injection should be to a given standard and with appropriate tolerances applied. But metering uncertainties may prohibit measurement of small quantities of losses during transportation. For transportation by CO_2 pipeline across the borders of several countries, emissions would need to be allocated to the countries where they occur.

No methodologies for estimation of fugitive emission from ship, rail or road transportation are included in the IPCC Guidelines.

9.2.2.3 Storage

Some estimates of CO_2 emissions (physical leakage rates) from geological and ocean storage are given in Chapters 5 and 6. Physical leakage rates are estimated to be very small for geological formations chosen with care. In oil reservoirs and coal seams, storage times could be significantly altered if exploitation or mining activities in these fields are undertaken after CO_2 storage. Some of the CO_2 injected into oceans would be released to the atmosphere over a period of hundreds to thousands of years, depending on the depth and location of injection.

The amount of CO_2 injected or stored could be easily measured in many CCS systems. Estimation of physical leakage rates would require the development of new methodologies. Very limited data are available in relation to the physical leakage of CO_2.

Despite the essential differences in the nature of the physical processes of CO_2 retention in oceans, geological formations, saline aquifers and mineralized solids, the mass of CO_2 stored over a given time interval can be defined by the Equation 1.

$$CO_2\ stored = \int_{O}^{T} (CO_2\ injected(t) - CO_2\ emitted(t)dt \qquad (1)$$

where t is time and T is the length of the assessment time period.

Use of this simple equation requires estimates or measurements of the injected CO_2 mass and either default values of the amount of CO_2 emitted from the different storage types, or rigorous source-specific evaluation of mass escaped CO_2. This approach would be possible when accurate measurements of mass of injected and escaped CO_2 are applied on site. Thus, for monitoring possible physical leakage of CO_2 from geological formations, direct measurement methods for CO_2 detection, geochemical methods and tracers, or indirect measurement methods for CO_2 plume detection could be applied (see Section 5.6, Monitoring and verification technology).

Physical leakage of CO_2 from storage could be defined as follows (Equation 2):

$$Emissions\ of\ CO_2\ from\ storage = \int_{O}^{T} m(t)dt \qquad (2)$$

where m(t) is the mass of CO_2 emitted to the atmosphere per unit of time and T is the assessment time period.

This addresses physical leakage that might occur in a specific timeframe after the injection, perhaps far into the future. The issue is discussed further in Section 9.3.

9.2.2.4 Mineral carbonation

Mineral carbonation of CO_2 captured from power plants and industrial processes is discussed in Chapter 7. These processes are still under development and aim at permanent fixation of the CO_2 in a solid mineral phase. There is no discussion in the literature about possible modes and rates of physical leakage of CO_2 from mineral carbonation, probably because investigations in this field have been largely theoretical character (for example, Goldberg *et al.*, 2000). However, the carbonate produced would be unlikely to release CO_2. Before and during the carbonation process, some amount of gas could escape into the atmosphere.

The net benefits of mineral carbonation processes would depend on the total energy use in the chain from capture to storage. The general framework discussed above for CCS systems can also be applied in preparing inventories of emissions from these processes. The emissions from the additional energy requirements would be seen in the energy sector under the current reporting framework. The amount of CO_2 captured and mineralized could be reported in the category where the capture takes place, or as a specific category addressing mineral carbonation, or in the sector ‘Other’.

9.2.2.5 Industrial uses

Most industrial uses of CO_2 result in release of the gas to the atmosphere, often after a very short time period. Because of the short ‘storage times’, no change may be required in the inventory systems provided they are robust enough to avoid possible double counting or omission of emissions. The benefits of these systems are related to the systems they substitute for, and the relative net efficiencies of the alternate systems. Comparison of the systems would need to take into account the whole cycle from capture to use of CO_2. As an example, methanol production by CO_2 hydrogenation could be a substitute for methanol production from fossil fuels, mainly natural gas. The impacts of the systems are in general covered by current inventory systems, although they are not addressed explicitly, because the emissions and emission reductions are related to relative energy use (reduction or increase depending on the process alternatives).

In cases where industrial use of CO_2 would lead to more long-term carbon storage in products, inventory methodologies would need to be tailored case by case.

9.2.3 Monitoring, verification and uncertainties

The IPCC Guidelines and good practice reports give guidance on monitoring, verification and estimation of uncertainties, as well as on quality assurance and quality control measures. General guidance is given on how to plan monitoring, what to monitor and how to report on results. The purpose of verifying national inventories is to establish their reliability and to check the accuracy of the reported numbers by independent means.

Section 5.6, on monitoring and verification technology, assesses the current status of monitoring and verification techniques for CCS systems. The applicability of monitoring techniques as well as associated detection limits and uncertainties vary greatly depending on the type and specific characteristics of the CCS projects. There is insufficient experience in monitoring CCS projects to allow conclusions to be drawn on physical leakage rates.

Reporting of uncertainties in emission and removal estimates, and how they have been derived, is an essential part of national greenhouse gas inventories. Uncertainty estimates can be based on statistical methods where measured data are available, or on expert judgement. No information on uncertainties related to emissions from different phases of CCS systems was available. In Section 5.7.3, the probability of release from geological storage is assessed based on data from analogous natural or engineered systems, fundamental physical and chemical processes, as well as from experience with current geological storage projects. The probabilities of physical leakage are estimated to be small and the risks are mainly associated with leakage from well casings of abandoned wells.

9.3 Accounting issues

One of the goals of an accounting system is to ensure that CCS projects produce real and quantifiable environmental benefits. One ton of CO_2 permanently stored has the same benefit in terms of atmospheric CO_2 concentrations as one ton of CO_2 emissions avoided. But one ton of CO_2 temporarily stored has less value than one ton of CO_2 emissions avoided. This difference can be reflected in the accounting system. Accounting for CCS may have to go beyond measuring the amount of CO_2 stored in order to ensure the credibility of storage credits and that credits claimed are commensurate with benefits gained. CO_2 storage should not avoid properly accounting for emissions that have been moved to other times, other places, or other sectors. Yet, Kennett (2003) notes that if there is benefit to potentially permanent or even to known temporary storage, accounting systems should contribute to their credibility and transparency while minimizing transaction costs.

In a political environment where only some parties have commitments to limit greenhouse gas emissions and where emissions from all sources are not treated the same, the amount by which emissions are reduced may not be equal to the amount of CO_2 stored. Differences can occur because CO_2 can be captured in one country but released in another country or at a later time. Also, CCs requires energy and likely additional emissions of CO_2 to produce this additional energy. Yoshigahara *et al*. (2004) note that emission reduction through CCS technology differs from many other modes of emission reduction. Although the former avoids CO_2 release to the atmosphere, it creates the long-term possibility that stored CO_2 could eventually flow to the atmosphere through physical leakage.

In this Chapter, the general term 'leakage' is used in the economist's sense, to describe displacement of greenhouse gas emissions beyond the boundaries of the system under discussion. The term 'physical leakage' refers to escape of CO_2 from a storage reservoir. As discussed above, some physical leakage effects and the additional energy requirements will be reported within standard, national reporting procedures for greenhouse gas emissions. Additional complexities arise when new or unexpected sources of emissions occur, for example, if CO_2 injected into an uneconomic coal seam forces the release of methane from that seam. Complexities also arise when new or unexpected sources of emissions occur in different countries, for example, if CO_2 is captured in one country but released in another, or at later times, for example, if CO_2 is captured during one time period and physically leaked to the atmosphere at a later time.

The problems of economic leakage are not unique to CCS systems, but the problems of physical leakage are unique to CCS. In particular, when emission inventories are done by country and year they may fail to report emissions that are delayed in time, displaced to other countries or to international waters, or that stimulate emissions of other greenhouse gases not identified as sources or for which methodologies have not been developed.

In this section, ideas on the issues involved in accounting are summarized for the stored CO_2 of CCS systems. The consequences for mitigating greenhouse gas emissions are discussed, and ideas on alternative accounting strategies to address them are presented. Figure 9.2 provides a simple flow diagram of how CCS emissions can create flows of greenhouse gases that transcend traditional accounting boundaries. The diagram also shows how emissions might escape reporting because they occur outside normal system boundaries (sectoral, national, or temporal) of reporting entities.

Concern about displacement of emissions across national boundaries is a consequence of the political and economic constructs being developed to limit greenhouse gas emissions. Most notably, the Kyoto Protocol imposes limits on greenhouse gas emissions from developed countries and from countries with economies in transition, but no such limits on emissions from developing countries or international transport.

Concern about displacement of emissions across temporal boundaries is essentially the widely posed question: 'if we store carbon away from the atmosphere, how long must it be stored?' The same question is phrased by Herzog *et al*. (2003) as 'What is the value of temporary storage?'

Concern about leakage among countries, sectors, or gases; or physical leakage from reservoirs is largely about the completeness and accuracy of emissions accounting. Kennett (2003), for example, emphasizes the importance of 'establishing general rules and procedures to simplify transactions, and increasing certainty by defining legal rights and by providing dispute resolution and enforcement procedures' and of ensuring the credibility of sinks-based emissions offsets or storage-based emissions reductions. The operation of a market requires clearly defined rights (i.e. who has the rights to the carbon stored), what those rights entail, how those rights can be transferred, and liability and remedies in the event of unanticipated release (Kennett, 2003). The core of establishing rights, liabilities, and markets will be the accounting and certification systems. Yet, a well-designed accounting system should not lead to transaction costs that unnecessarily discourage meritorious activities.

9.3.1 Uncertainty, non-permanence and discounting methodology

9.3.1.1 Dealing with the impermanence of carbon dioxide storage

CO_2 storage is not necessarily permanent. Physical leakage from storage reservoirs is possible via (1) gradual and long-term release or (2) sudden release of CO_2 caused by disruption of the reservoir. There is very little literature on accounting for the potential impermanence of CCS. There are, however, a significant number of publications on accounting for the impermanence of CO_2 sequestration in the terrestrial biosphere. Although sequestration in the terrestrial biosphere is notably different from CO_2 storage in the ocean or in geological reservoirs, there are also similarities. [13]CO_2 stored in the terrestrial biosphere is subject to potential future release if, for example, there is a wildfire, change in land management practices, or climate change renders the vegetative cover unsustainable. Although the risks of CO_2 loss from well-chosen geological reservoirs are very different, such risks do exist. The literature suggests various accounting strategies so that sequestration in the biosphere could be treated as the negative equivalent of emissions. Sequestration could be shown in national emission accounts and trading of emissions credits, and debits between parties could occur for sequestration activities in the terrestrial biosphere. Whether CCS is treated as a CO_2 sink or as a reduction in emissions, the issues of accounting for physical leakage from storage are similar.

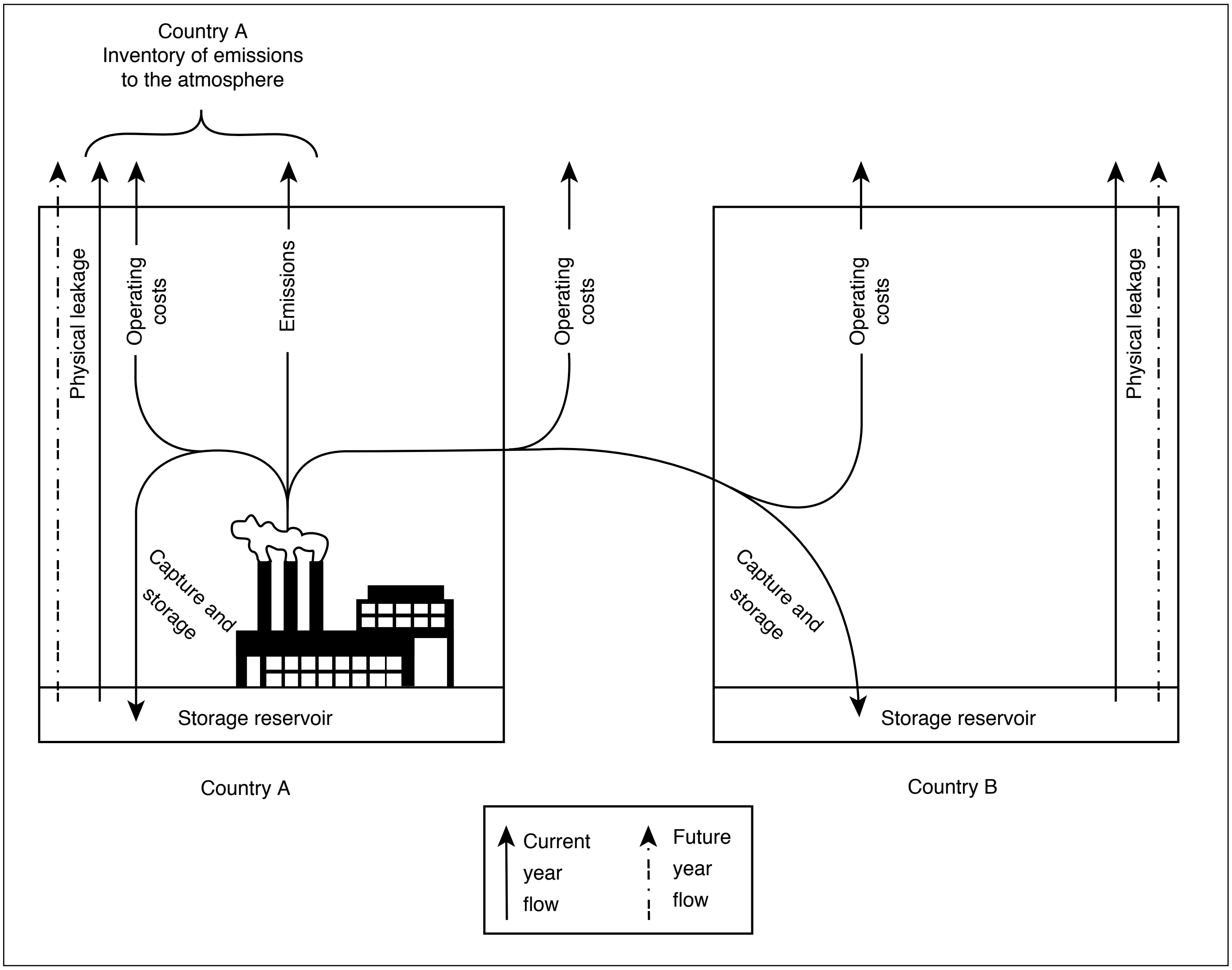

Figure 9.2 Simplified flow diagram showing how CCS could transcend traditional accounting boundaries[13]

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[13] The operating cost shown are the CO_2 emitted as a result of the additional energy required to operate the system, plus fugitive emissions from separation, transport and injection.

Chomitz (2000) suggests two primary approaches to accounting for stored CO_2: (1) acknowledge that CO_2 storage is likely not permanent, assess the environmental and economic benefits of limited-term storage, and allot credits in proportion to the time period over which CO_2 is stored, and (2) provide reasonable assurance of indefinite storage. Examples discussed for sequestration in the terrestrial biosphere include (under the first approach) ton-year accounting (described below); and (under the second approach) various combinations of reserve credits and insurance replacing lost CO_2 by sequestration reserves or other permanent emissions reductions. For further discussion on these issues, see Watson *et al.*, 2000; Marland *et al.*, 2001; Subak, 2003; Aukland *et al.*, 2003; Wong and Dutschke, 2003; and Herzog *et al.*, 2003. There are also proposals to discount credits so that there is a margin of conservativeness in the number of credits acknowledged. With this kind of discussion and uncertainty, negotiations toward the Kyoto Protocol have chosen to place limits on the number of credits that can be claimed for some categories of terrestrial CO_2 sequestration during the Protocol's first commitment period (UNFCCC, 2002).

To illustrate the concept of allotting credits in proportion to storage time, one alternative, the ton-year approach is described. The ton-year alternative for accounting defines an artificial equivalence so that capture and storage for a given time interval (for example, t years) are equated with permanent storage. Availability of credits can be defined in different ways but typically capture and storage for one year would result in a number of credits equal to 1/t, and thus storage for t years would result in one full credit (Watson *et al.*, 2000). A variety of constructs have been proposed for defining the number of storage years that would be equated with permanent storage (see, for example, Marland *et al.*, 2001). But as Chomitz (2000) points out, despite being based on scientific and technical considerations, this equivalence is basically a political decision. Although ton-year accounting typifies the first approach, it has been subject to considerable discussion. Another derivative of Chomitz's first approach that has been further developed within negotiations on the Kyoto Protocol (Columbia, 2000; UNFCCC, 2002; UNFCCC, 2004) is the idea of expiring credits or rented temporary credits (Marland et el., 2001; Subak, 2003). Temporary or rented credits would have full value over a time period defined by rule or by contract, but would result in debits or have to be replaced by permanent credits at expiration. In essence, credit for stored CO_2 would create liability for the possible subsequent CO_2 release or commitment to storage was ended.

UNFCCC (2002), Marland et al. (2001), Herzog et al. (2003), and others agree that the primary issue for stored CO_2 is liability. They argue that if credit is given for CO_2 stored, there should be debits if the CO_2 is subsequently released. Physical leakage from storage and current emissions produce the same result for the atmosphere. Accounting problems arise if ownership is transferred or stored CO_2 is transferred to a place or party that does not accept liability (for example, if CO_2 is stored in a developing country without commitments under the Kyoto protocol). Accounting problems also arise if potential debits are transferred sufficiently far into the future with little assurance that the systems and institutions of liability will still be in place if and when CO_2 is released. The system of expiring credits in the Marrakech Accords for sequestration in the terrestrial biosphere fulfils the requirement of continuing liability. Limiting these credits to five years provides reasonable assurance that the liable institutions will still be responsible. This arrangement also addresses an important concern of those who might host CO_2 storage projects, that they might be liable in perpetuity for stored CO_2. Under most proposals, the hosts for CO_2 storage would be liable for losses until credits expire and then liability would return to the purchaser/renter of the expiring credits. Kennett (2003) suggests that long-term responsibility for regulating, monitoring, certifying, and supporting credits will ultimately fall to governments (see also section 5.8.4). With this kind of ultimate responsibility, governments may wish to establish minimum requirements for CCS reservoirs and projects (see Torvanger *et al.*, 2005).

The published discussions on 'permanence' have largely been in the context of sequestration in the terrestrial biosphere. It is not clear whether the evolving conclusions are equally appropriate for CCS in the ocean or in geological reservoirs. Important differences between modes of CCS may influence the accounting scheme chosen (see Table 9.2). An apparent distinction is that sequestration in the terrestrial biosphere involves initial release of CO_2 to the atmosphere and subsequent removal by growing plants. But as storage in geological reservoirs does not generally involve release to the atmosphere, it might be envisioned as a decrease in emissions rather than as balancing source with sink. In either case, a mass of CO_2 must be managed and isolated from the atmosphere. Storage in the terrestrial biosphere leaves open the possibility that sequestration will be reversed because of decisions on maintenance or priorities for resource management. Ocean and geological storage have very different implications for the time scale of commitments and for the role of physical processes versus decisions in potential physical releases.

An important question for crediting CCS is whether future emissions have the same value as current emissions. Herzog *et al.* (2003) define 'sequestration effectiveness' as the net benefit from temporary storage compared to the net benefit of permanent storage, but this value cannot be known in advance. They go one step further and argue that while CO_2 storage is not permanent, reducing emissions may not be permanent either, unless some backstop energy technology assures all fossil fuel resources are not eventually consumed. According to Herzog *et al.* (2003), stored CO_2 emissions are little different, to fossil fuel resources left in the ground. Most analysts, however, assume that all fossil fuels will never be consumed so that refraining from emitting fossil-fuel CO_2 does not, like CO_2 storage, give rise directly to a risk of future emissions. Wigley *et al.* (1996) and Marland *et al.* (2001) argue that there is value in delaying emissions. If storage for 100 years were to be defined as permanent, then virtually all carbon injected below 1500 m in the oceans would be considered to be permanent storage (Herzog *et al.*, 2003).

Table 9.2 Differences between forms of carbon storage with potential to influence accounting method.

Property	**Terrestrial biosphere**	**Deep ocean**	**Geological reservoirs**
CO_2 sequestered or stored	Stock changes can be monitored over time.	Injected carbon can be measured	Injected carbon can be measured
Ownership	Stocks will have a discrete location and can be associated with an identifiable owner.	Stocks will be mobile and may reside in international waters.	Stocks may reside in reservoirs that cross national or property boundaries and differ from surface boundaries.
Management decisions	Storage will be subject to continuing decisions about land-use priorities.	Once injected, no further human decisions on maintenance.	Once injected, human decisions to influence continued storage involve monitoring and perhaps maintenance, unless storage interferes with resource recovery.
Monitoring	Changes in stocks can be monitored.	Changes in stocks will be modelled.	Release of CO_2 might be detected by physical monitoring but because of difficulty in monitoring large areas may also require modelling.
Time scale with expected high values for fraction CO_2 retained	Decades, depending on management decisions.	Centuries, depending on depth and location of injection.	Very small physical leakage from well-designed systems expected, barring physical disruption of the reservoir.
Physical leakage	Losses might occur due to disturbance, climate change, or land-use decisions.	Losses will assuredly occur as an eventual consequence of marine circulation and equilibration with the atmosphere.	Losses are likely to be small for well-designed systems except where reservoir is physically disrupted.
Liability	A discrete land-owner can be identified with the stock of sequestered carbon.	Multiple parties may contribute to the same stock of stored carbon and the carbon may reside in international waters.	Multiple parties may contribute to the same stock of stored carbon lying under several countries.

At the other temporal extreme, Kheshgi *et al*. (1994) point out that over the very long term of equilibration between the ocean and atmosphere (over 1000 years), capture and storage in the ocean will lead to higher CO_2 levels in the atmosphere than without emissions controls, because of the additional energy requirements for operating the system. It is also true that chronic physical leakage over long time periods could increase the difficulty of meeting targets for net emissions at some time in the future (see Hawkins, 2003; Hepple and Benson, 2003; and Pacala, 2003).

The fundamental question is then, how to deal with impermanent storage of CO_2. Although Findsen *et al*. (2003) detail many circumstances where accounting for CCS is beginning or underway, and although the rates of physical leakage for well-designed systems may sometimes be in the range of the uncertainty of other components of emissions, the risks of physical leakage need to be acknowledged. A number of questions remains to be answered: how to deal with liability and continuity of institutions in perpetuity, how to quantify the benefits of temporary storage; the needs in terms of monitoring and verification, whether or not there is a need for a reserve of credits or other ways to assure that losses will be replaced, whether or not there is need for a system of discounting to consider expected or modelled duration of storage, the utility of expiring, temporary, or rented credits over very long time periods, whether there is a need to consider different accounting practices as a function of expected duration of storage or mode of storage. The implications if storage in the terrestrial biosphere and in geological formations are sufficiently different that the former might be considered carbon management and the latter CO_2 waste disposal.

Ultimately, the political process will decide the value of temporary storage and the allocation of responsibility for stored CO_2. Some guidance is provided by precedents set by international agreements on sequestration in the terrestrial biosphere. But there are important differences to be considered. The reason for rules and policies is presumably to influence behaviour. Accounting rules for CO_2 storage can best influence permanence if they are aimed accordingly: at liability for CO_2 stored in the terrestrial biosphere but at the initial design and implementation requirements for CCS in the oceans or geological reservoirs.

9.3.1.2 Attribution of physical leakage from storage in international/regional territories or shared facilities and the use of engineering standards to limit physical leakage

The previous section deals largely with the possibility that CO_2 emissions stored now will be released at a later time. It also introduces the possibility that emissions stored now will result in additional, current emissions in different countries or in different sectors. CO_2 injected into the ocean could leak physically from international waters. Accounting for stored CO_2 raises questions such as responsibility for the emissions from energy used in CO_2 transport and injection, especially if transport and/or storage is in a developing country or in international waters. Similarly, questions about physical leakage of stored CO_2 will need to address liability for current year physical leakage that occurs in developing countries or from international waters. These questions may be especially complex when multiple countries have injected CO_2 into a common reservoir such as the deep Atlantic Ocean, or into a deep aquifer under multiple countries, or if multiple countries share a common pipeline for CO_2 transport.

There may also be a need for international agreement on certification of CCS credits or performance standards for CCS projects. Standards would minimize the risk of leakage and maximize the time for CO_2 storage. Performance standards could minimize the possibility of parties looking for the least cost, lowest quality storage opportunities - opportunities most susceptible to physical leakage - when liability for spatial or temporal leakage is not clear. Performance standards could be used to limit the choice of technologies, quality of operations, or levels of measurement and monitoring.

9.3.2 Accounting issues related to Kyoto mechanisms (JI[14], CDM[15], and ET[16])

CCS is not currently addressed in the decisions of the COP to the UNFCCC in relation to the Kyoto mechanisms. Little guidance has been provided so far by international negotiations regarding the methodologies to calculate and account for project-related CO_2 reductions from CCS systems under the various project-based schemes in place or in development. The only explicit reference to CCS in the Kyoto Protocol states that Annex I countries need to "research, promote, develop and increasingly use CO_2 sequestration technologies"[17]. The Marrakech Accords further clarify the Protocol regarding technology cooperation, stating that Annex I countries should indicate how they give priority to cooperation in the development and transfer of technologies relating to fossil fuel that capture and store greenhouse gases (Paragraph 26, Decision 5/CP.7). No text referring explicitly to CCS project-based activities can be found in the CDM and JI-related decisions (Haefeli *et al*., 2004).

Further, Haefeli *et al*. (2004) note that CCS is not explicitly addressed in any form in CO_2 reporting schemes that include projects (i.e., the Chicago Climate Exchange and the EU Directive for Establishing a Greenhouse Gas Emissions Trading Scheme (implemented in 2005) along with the EU Linking Directive (linking the EU Emissions Trading Scheme with JI and the CDM). At present, it is unclear how CCS will be dealt with in practice. According to Haines *et al*. (2004), the eligibility of CCS under CDM could be resolved in a specific agreement similar to that for land use, land-use change and forestry (LULUCF) activities. As with biological sinks, there will be legal issues as well as concerns about permanence and economic leakage, or emissions outside a system boundary. At the same time, CCS could involve a rather less complex debate because of the geological time scales involved. Moreover, Haefeli *et al*. (2004) noted that guidelines on how to account for CO_2 transfers between countries would need to be agreed either under the UNFCCC or the Kyoto Protocol. Special attention would need to be given to CO_2 exchange between an Annex I country and a non-Annex I country, and between an Annex I country party to the Kyoto Protocol and an Annex I country that has not ratified the Kyoto Protocol.

9.3.2.1 Emission baselines

The term 'baseline', used mostly in the context of project-based accounting, is a hypothetical scenario for greenhouse gas emissions in the absence of a greenhouse gas reduction project or activity (WRI, 2004). Emission baselines are the basis for calculation of net reductions (for example, storage) of emissions from any project-based activity. Baselines need to be established to show the net benefits of emissions reductions. The important issue is to determine which factors need to be taken into account when developing an emissions baseline. At present, there is little guidance on how to calculate net reductions in CO_2 emissions through CCS project-based activities. An appropriate baseline scenario could minimize the risk that a project receives credits for avoiding emissions that would have been avoided in the absence of the project (Haefeli *et al*., 2004).

9.3.2.2 Leakage in the context of the Kyoto mechanisms

The term 'Leakage' is defined according to Marrakech Accords as 'the net change of anthropogenic emissions by sources and/or removals by sinks of greenhouse gases which occurs outside

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[14] Kyoto Protocol Article 6.1 'For the purpose of meeting its commitments under Article 3, any Party included in Annex I may transfer to, or acquire from, any other such Party emission reduction units resulting from projects aimed at reducing anthropogenic emissions by sources or enhancing anthropogenic removals by sinks of greenhouse gases in any sector of the economy…'

[15] Kyoto Protocol Article 12.2 'The purpose of the clean development mechanism shall be to assist Parties not included in Annex I in achieving sustainable development and in contributing to the ultimate objective of the Convention, and to assist Parties included in Annex I in achieving compliance with their quantified emission limitation and reduction commitments under Article 3.'

[16] Kyoto Protocol Article 17 'The Conference of the Parties shall define the relevant principles, modalities, rules and guidelines, in particular for verification, reporting and accountability for emissions trading. The Parties included in Annex B may participate in emissions trading for the purpose of fulfilling their commitments under Article 3. Any such trading shall be supplemental to domestic actions for the purpose of meeting quantified emission limitation and reduction commitments under that Article.'

[17] Article 2, 1(a) (iv) of the Kyoto Protocol.

Table 9.3 Accounting issues related to Kyoto Mechanisms.

Mechanism	**Article in the Kyoto Protocol**	**Principle**	**Requirements in relation to CCS**	**Basic considerations**
Joint Implementation (JI)	Article 6.1	As a general principle, any Annex I party may transfer to or obtain from another Annex I party Emission Reduction Units (ERUs) that shall result from projects that seek to reduce GHG emissions by sources and/or enhance removals by sinks.	• Set modalities and procedures to set the project in a transparent manner • Procedures for verification and certification of ERU.	Important to ensure that credits received from projects in Annex I countries result from emission reductions that are real and additional to what would have happened in the absence of the project i.e. are measured against baselines.
Clean Development Mechanism (CDM)	Article 12.2	• Intended to promote sustainable develop-ment in developing countries through the allowance of trade between developed and developing countries. • Refers to the establishment of a CDM with the objective of assisting Annex I parties to achieve part of their Article 3 KP emission reduction commitments through the implementation of project-based activities generating emission cut/backs and/or enhanced sink removals.	Highly detailed set of modalities and procedures regarding issues such as: • project level versus national level obligations • modelled versus actual amounts of credits • timing of storage and liabilities in the long term.	• Overall baseline methodology • Annex I parties shall be able to acquire Certified Emission Reductions (CERs) from projects implemented in non Annex I countries. • Should provide real, measurable and long-term benefits related to the mitigation of climate change, i.e. will be measured against baselines.
Emission Trading (ET)	Article 17	Allows for trading between developed countries that have targets and assigned amount units (AAUs) allocated to them through the KP, it endorses the basic principle of the use of ET as a mean available to Annex I parties to achieve their emission commitment.	• Cap (emission trading) i.e. the maximum amount of allowable emission offsets between Annex I countries; • Net versus gross accounting (measures in non-Annex I).	• Trade is based on national Assigned Amounts (AAUs) to individual countries. • The proposed guidelines for ET contain provisions on the amount of AAUs that may be traded between Annex I parties so as to avoid overselling of quotas. It also contains several options that would impose a quantified upper limit on the amount of AAUs that a transferring party could trade. • A successful carbon trading system must accurately measure the offsets and credits to assure companies that they will receive the reductions.

the project boundary, and that is measurable and attributable to the Article 6 project'. The term has been proposed for leakage of emissions resulting from capture, transport and injection, which should not be confused with releases of CO_2 from a geological reservoir (escaped CO_2). According to Haefeli *et al*. (2004), current legislation does not deal with cross-border CCS projects and would need further clarification. Guidance would be especially needed to deal with cross-border projects involving CO_2 capture in an Annex I country that is party to the Kyoto Protocol and storage in a country not party to the Kyoto Protocol or in an Annex I country not bound by the Kyoto Protocol.

Table 9.3 provides an overview of the Kyoto mechanisms and the general principles and requirements of each (practical indices and specific accounting rules and procedures) for developing CCS accounting systems that can be employed for emissions control and reduction within these mechanisms. Although the political process has not yet decided how CCS systems will be accepted under the Kyoto mechanisms, these general procedures could be applicable to them as well as to other similar schemes on emission trading and projects.

9.4 Gaps in knowledge

Methodologies for incorporating CCS into national inventories and accounting schemes are under development. CCS (see Sections 9.2 and 9.3) can be incorporated in different ways and data requirements may differ depending on the choices made. The following gaps in knowledge and need for decisions by the political process have been identified:

- Methodologies to estimate physical leakage from storage, and emission factors (fugitive emissions) for estimating emissions from capture systems and from transportation and injection processes are not available.
- Geological and ocean storage open new challenges regarding a) uncertainty on the permanence of the stored emissions, b) the need for protocols on transboundary transport and storage, c) accounting rules for CCS and, d) insight on issues such as emission measurement, long term monitoring, timely detection and liability/responsibility.
- Methodologies for reporting and verification of reduced emission under the Kyoto Mechanisms have not been agreed upon.
- Methodologies for estimating and dealing with potential emissions resulting from system failures, such as sudden geological faults and seismic activities or pipeline disruptions have not been developed.

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Annexes

Annex I

Properties of CO_2 and carbon-based fuels

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AI.1 Introduction

This Annex presents data about the relevant physical and chemical properties of CO_2 together with an outline of the effects of CO_2 on human health and a summary of some of the typical recommendations for avoiding harm to humans. Established uses for CO_2 are listed and some common conversion factors relevant to this report are presented. An introduction is also provided to the main types of fossil fuels and other carbon-containing fuels, as background to considering how their use produces CO_2.

AI.2 Carbon dioxide

Carbon dioxide is a chemical compound of two elements, carbon and oxygen, in the ratio of one to two; its molecular formula is CO_2. It is present in the atmosphere in small quantities (370 ppmv) and plays a vital role in the Earth's environment as a necessary ingredient in the life cycle of plants and animals. During photosynthesis plants assimilate CO_2 and release oxygen. Anthropogenic activities which cause the emission of CO_2 include the combustion of fossil fuels and other carbon-containing materials, the fermentation of organic compounds such as sugar and the breathing of humans. Natural sources of CO_2, including volcanic activity, dominate the Earth's carbon cycle.

CO_2 gas has a slightly irritating odour, is colourless and is denser than air. Although it is a normal, if minor, constituent of air, high concentrations of CO_2 can be dangerous.

AI.2.1 Physical properties of CO_2

AI.2.1.1 General

At normal temperature and pressure, carbon dioxide is a gas. The physical state of CO_2 varies with temperature and pressure as shown in Figure AI.1 – at low temperatures CO_2 is a solid; on warming, if the pressure is below 5.1 bar, the solid will sublime directly into the vapour state. At intermediate temperatures (between –56.5°C, the temperature of the triple point, and 31.1°C, the critical point), CO_2 may be turned from a vapour into a liquid by compressing it to the corresponding liquefaction pressure (and removing the heat produced).

At temperatures higher than 31.1°C (if the pressure is greater than 73.9 bar, the pressure at the critical point), CO_2 is said

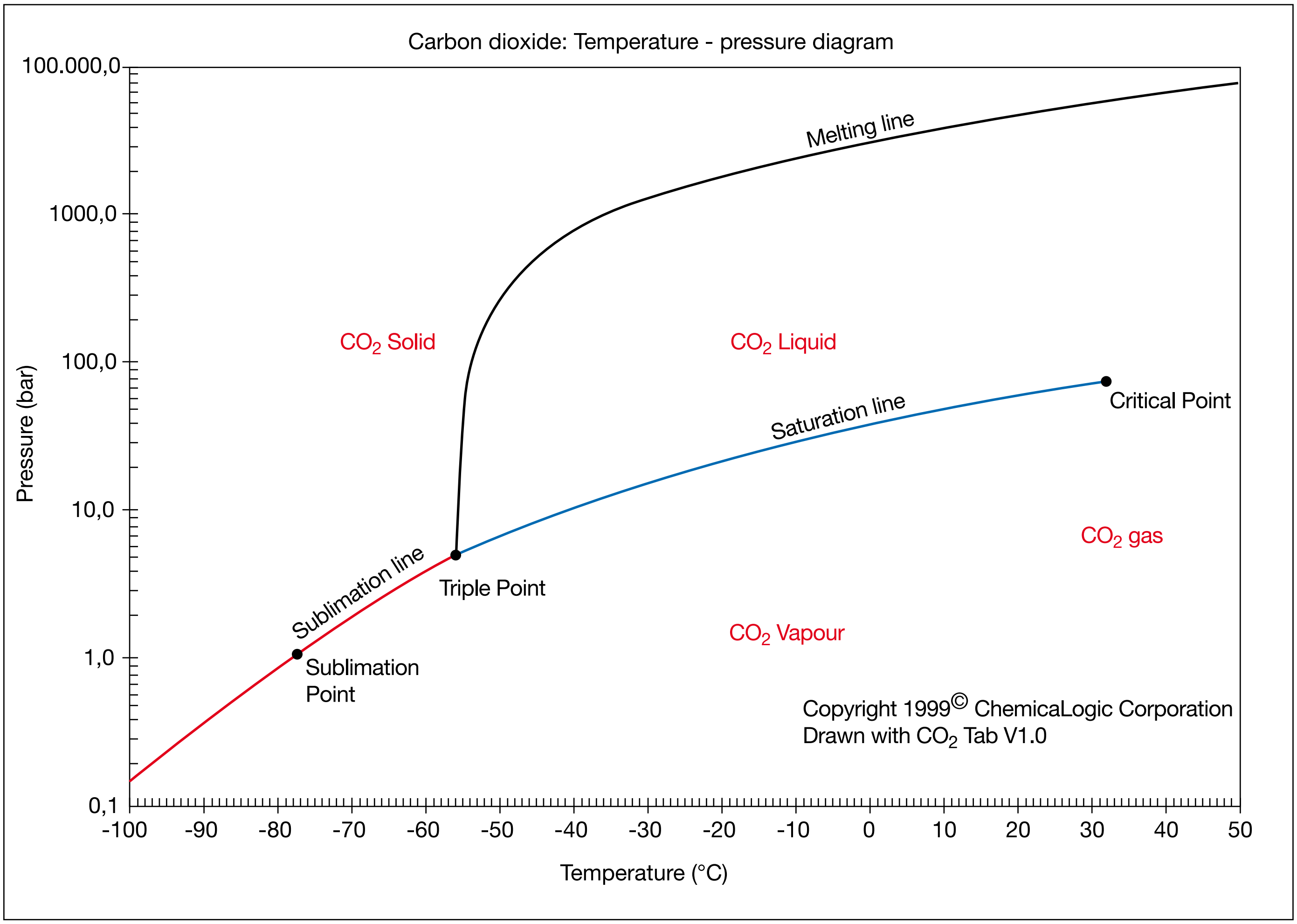

Figure AI.1 Phase diagram for CO_2. Copyright © 1999 ChemicaLogic Corporation, 99 South Bedford Street, Suite 207, Burlington, MA 01803 USA. All rights reserved.

to be in a supercritical state where it behaves as a gas; indeed under high pressure, the density of the gas can be very large, approaching or even exceeding the density of liquid water (also see Figure AI.2). This is an important aspect of CO_2's behaviour and is particularly relevant for its storage.

Heat is released or absorbed in each of the phase changes across the solid-gas, solid-liquid and liquid-gas boundaries (see Figure AI.1). However, the phase changes from the supercritical condition to liquid or from supercritical to gas do not require or release heat. This property is useful for the design of CO_2 compression facilities since, if this can be exploited, it avoids the need to handle the heat associated with the liquid-gas phase change.

AI.2.1.2 Specific physical properties

There is a substantial body of scientific information available on the physical properties of CO_2. Selected physical properties of CO_2 are given in Table AI.1 The phase diagram for CO_2 is shown in Figure AI.1 Many authors have investigated the equation of state for CO_2 (e.g., Span and Wagner, 1996). The variation of the density of CO_2 as a function of temperature and pressure is shown in Figure AI.2, the variation of vapour pressure of CO_2 with temperature in Figure AI.3, and the variation of viscosity with temperature and pressure in Figure AI.4 Further information on viscosity can be found in Fenghour *et al*. (1998). The pressure-enthalpy chart for CO_2 is shown in Figure AI.5. The solubility of CO_2 in water is described in Figure AI.6.

AI.2.2 Chemical properties of CO_2

AI.2.2.1 General

Some thermodynamic data for CO_2 and a few related compounds are given in Table AI.2.

In an aqueous solution CO_2 forms carbonic acid, which is too unstable to be easily isolated. The solubility of CO_2 in water (Figure AI.6) decreases with increasing temperature and increases with increasing pressure. The solubility of CO_2 in

Table AI.1 Physical properties of CO_2.

Property	Value
Molecular weight	44.01
Critical temperature	31.1°C
Critical pressure	73.9 bar
Critical density	467 kg m^{-3}
Triple point temperature	-56.5 °C
Triple point pressure	5.18 bar
Boiling (sublimation) point (1.013 bar)	-78.5 °C
Gas Phase	
Gas density (1.013 bar at boiling point)	2.814 kg m^{-3}
Gas density (@ STP)	1.976 kg m^{-3}
Specific volume (@ STP)	0.506 m^3 kg^{-1}
Cp (@ STP)	0.0364 kJ (mol^{-1} K^{-1})
Cv (@ STP)	0.0278 kJ (mol^{-1} K^{-1})
Cp/Cv (@ STP)	1.308
Viscosity (@ STP)	13.72 µN.s m^{-2} (or µPa.s)
Thermal conductivity (@ STP)	14.65 mW (m K^{-1})
Solubility in water (@ STP)	1.716 vol vol^{-1}
Enthalpy (@ STP)	21.34 kJ mol^{-1}
Entropy (@ STP)	117.2 J mol K^{-1}
Entropy of formation	213.8 J mol K^{-1}
Liquid Phase	
Vapour pressure (at 20 °C)	58.5 bar
Liquid density (at -20 °C and 19.7 bar)	1032 kg m^{-3}
Viscosity (@ STP)	99 µN.s m^{-2} (or µPa.s)
Solid Phase	
Density of carbon dioxide snow at freezing point	1562 kg m^{-3}
Latent heat of vaporisation (1.013 bar at sublimation point)	571.1 kJ kg^{-1}

Where STP stands for Standard Temperature and Pressure, which is 0°C and 1.013 bar.
Sources: Air Liquide gas data table; Kirk-Othmer (1985); NIST (2003).

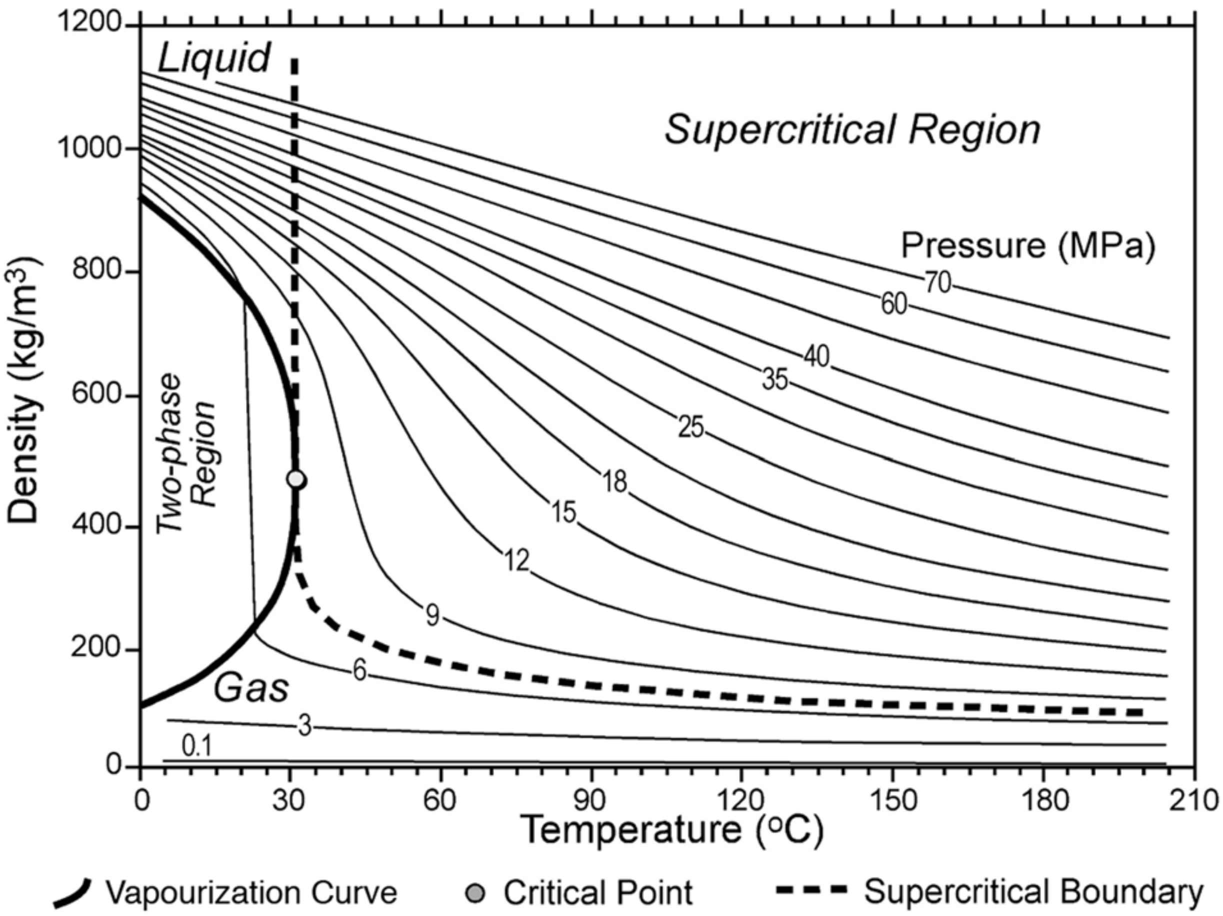

Figure AI.2 Variation of CO_2 density as a function of temperature and pressure (Bachu, 2003).

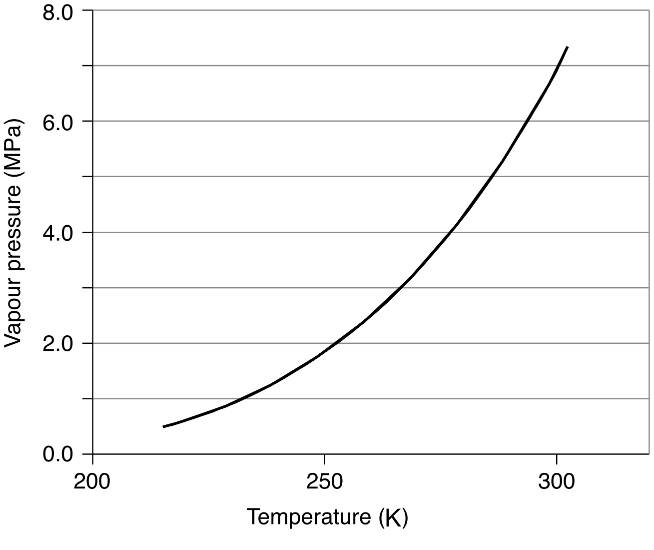

Figure AI.3 Vapour pressure of CO_2 as a function of temperature (Span and Wagner, 1996).

water also decreases with increasing water salinity by as much as one order of magnitude (Figure AI.7). The following empirical relation (Enick and Klara, 1990) can be used to estimate CO_2 solubility in brackish water and brine:

$$w_{CO2,\,b} = w_{CO2,\,w} \cdot (1.0 - 4.893414 \cdot 10^{-2} \cdot S + 0.1302838 \cdot 10^{-2} \cdot S^2 - 0.1871199 \cdot 10^{-4} \cdot S^3) \qquad (1)$$

where w_{CO2} is CO_2 solubility, S is water salinity (expressed as total dissolved solids in % by weight) and the subscripts *w* and *b* stand for pure water and brine, respectively. A solid hydrate separates from aqueous solutions of CO_2 that are chilled (below about 11°C) at elevated pressures. A hydrate is a crystalline compound consisting of the host (water) plus guest molecules. The host is formed from a tetrahedral hydrogen-bonding network of water molecules; this network is sufficiently open to create pores (or cavities) that are large enough to contain a variety of other small molecules (the guests). Guest molecules can include CH_4 and CO_2. CO_2 hydrates have similar (but not identical) properties to methane hydrates, which have been extensively studied due to their effects on natural gas production and their potential as future sources of hydrocarbons.

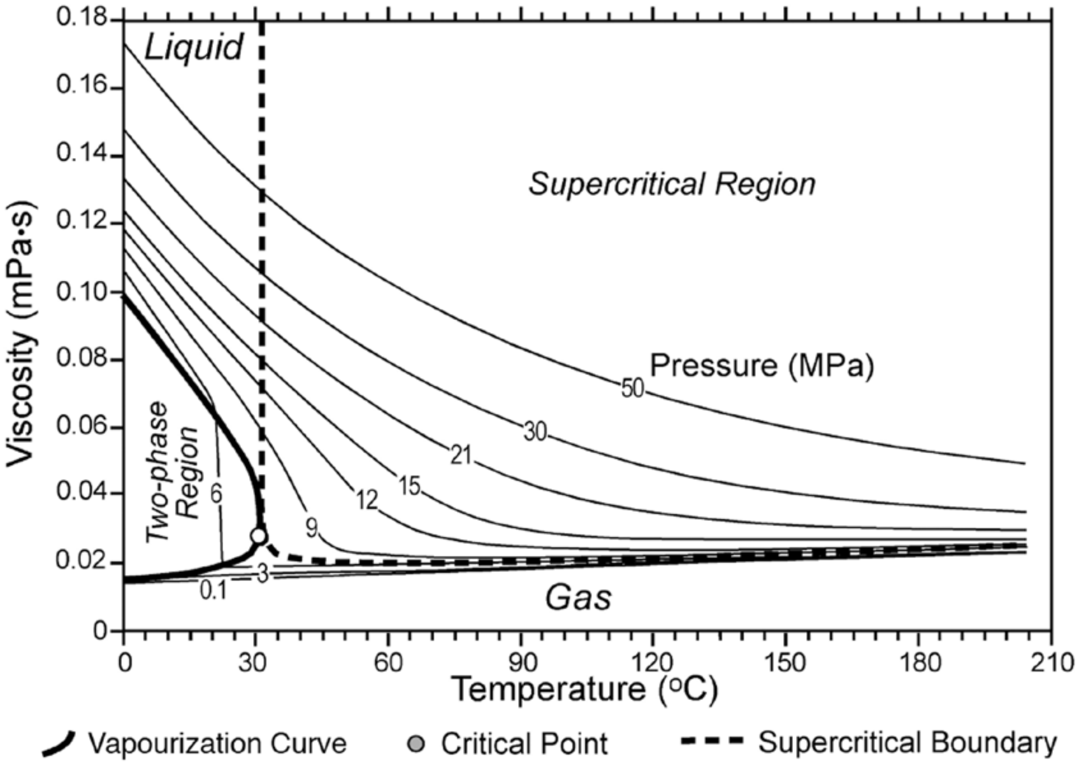

Figure AI.4 Variation of CO_2 viscosity as a function of temperature and pressure (Bachu, 2003).

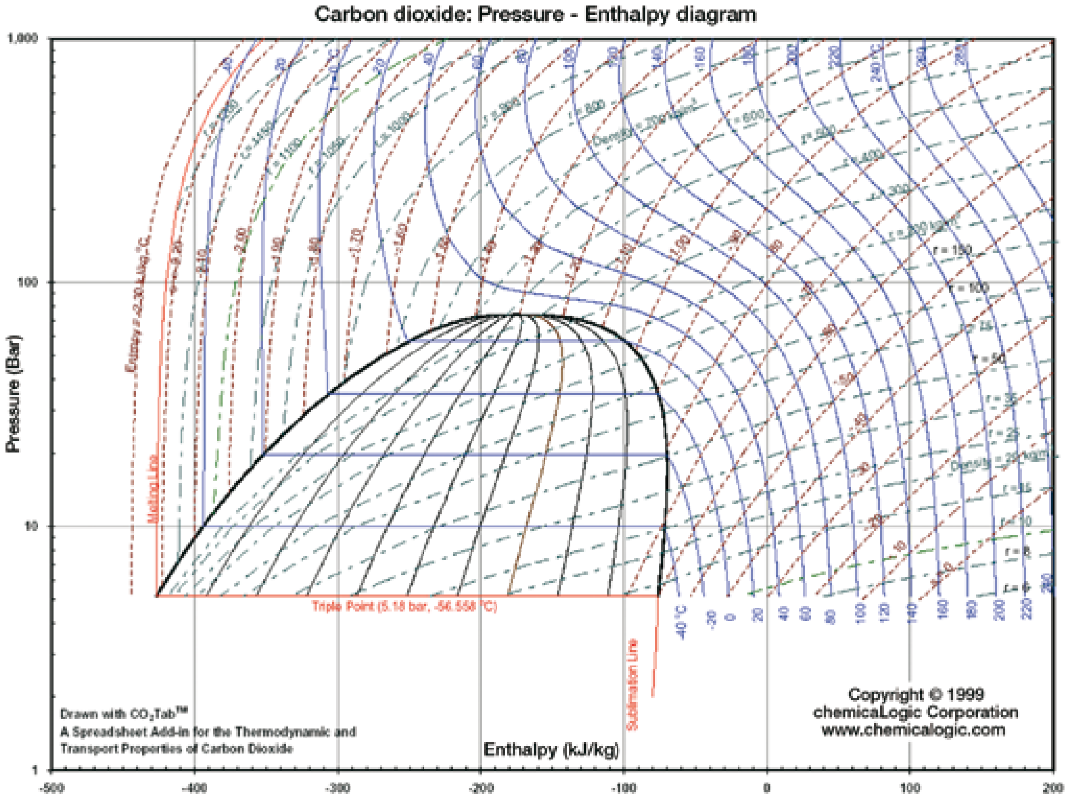

Figure AI.5 Pressure-Enthalpy chart for CO_2. Copyright © 1995-2003 ChemicaLogic Corporation, 99 South Bedford Street, Suite 207, Burlington, MA 01803 USA. All rights reserved.

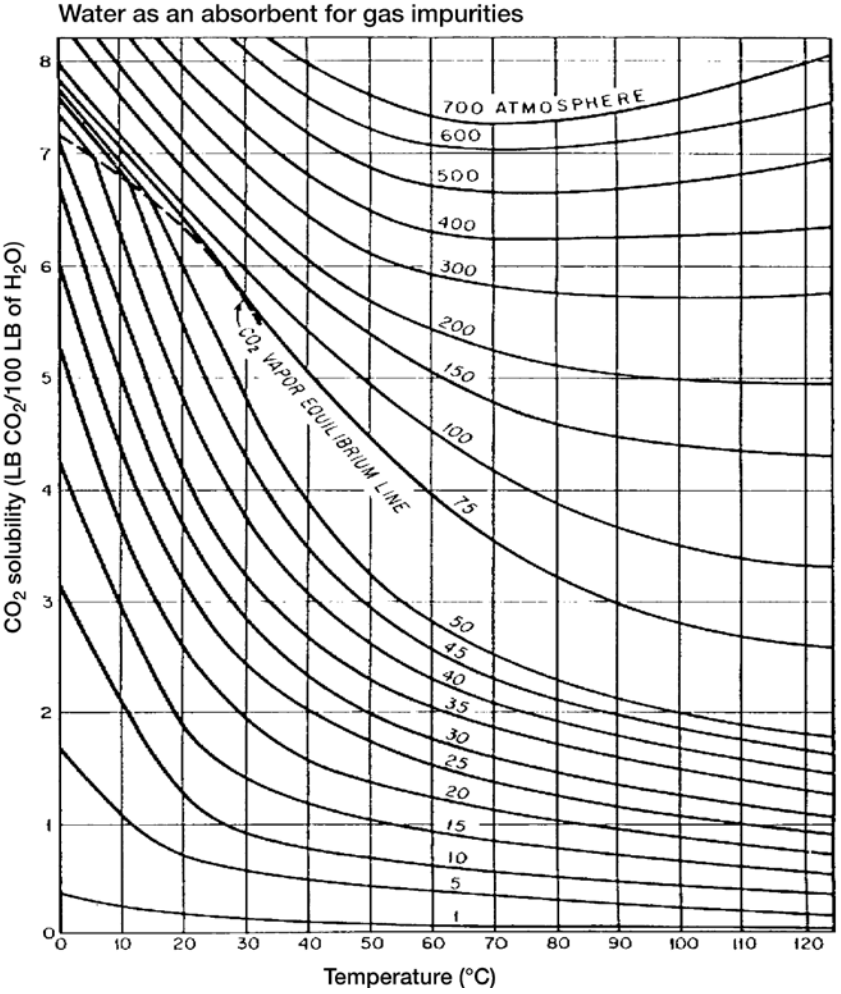

Figure AI.6 Solubility of CO_2 in water (Kohl and Nielsen, 1997).

Table AI.2 Thermodynamic data for selected carbon-containing compounds (ref. Cox *et al*., 1989 and other sources).

Compound	**Heat of Formation $\Delta H_f°$ (kJ mol^{-1})**	**Gibbs free energy of formation $\Delta G_f°$ (kJ mol^{-1})**	**Standard molar entropy $S_f°$ (J mol^{-1} K^{-1})**
CO (g)	–110.53	–137.2	197.66
CO_2 (g)	–393.51	–394.4	213.78
CO_2 (l)		–386	
CO_2 (aq)	–413.26		119.36
CO_3^{2-} (aq)	–675.23		–50.0
CaO (s)	–634.92		38.1
HCO_3^- (aq)	–689.93	–603.3	98.4
H_2O (l)	–285.83		69.95
H_2O (g)	–241.83		188.84
$CaCO_3$ (s)	–1207.6 (calcite) –1207.8 (aragonite)	–1129.1 –1128.2	91.7 88
$MgCO_3$ (s)	–1113.28 (magnesite)	–1029.48	65.09
CH_4 (g)	–74.4	–50.3	186.3
CH_3OH (l)	–239.1	–166.6	126.8
(g)	–201.5	–162.6	239.8

CO_2 hydrates have not been studied as extensively.

AI.2.2.2 Impact of CO_2 on pH of water

The dissolution of CO_2 in water (this may be sea water, or the saline water in geological formations) involves a number of chemical reactions between gaseous and dissolved carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}) which can be represented as follows:

$$CO_{2\,(g)} \leftrightarrow CO_{2\,(aq)} \tag{2}$$

$$CO_{2\,(aq)} + H_2O \leftrightarrow H_2CO_{3\,(aq)} \tag{3}$$

$$H_2CO_{3\,(aq)} \leftrightarrow H^+_{(aq)} + HCO_3^-{}_{(aq)} \tag{4}$$

$$HCO_3^-{}_{(aq)} \leftrightarrow H^+_{(aq)} + CO_3^{2-}{}_{(aq)} \tag{5}$$

Addition of CO_2 to water initially leads to an increase in the amount of dissolved CO_2. The dissolved CO_2 reacts with water to form carbonic acid. Carbonic acid dissociates to form bicarbonate ions, which can further dissociate into carbonate ions. The net effect of dissolving *anthropogenic* CO_2 in water is the removal of carbonate ions and production of bicarbonate ions, with a lowering in *pH*.

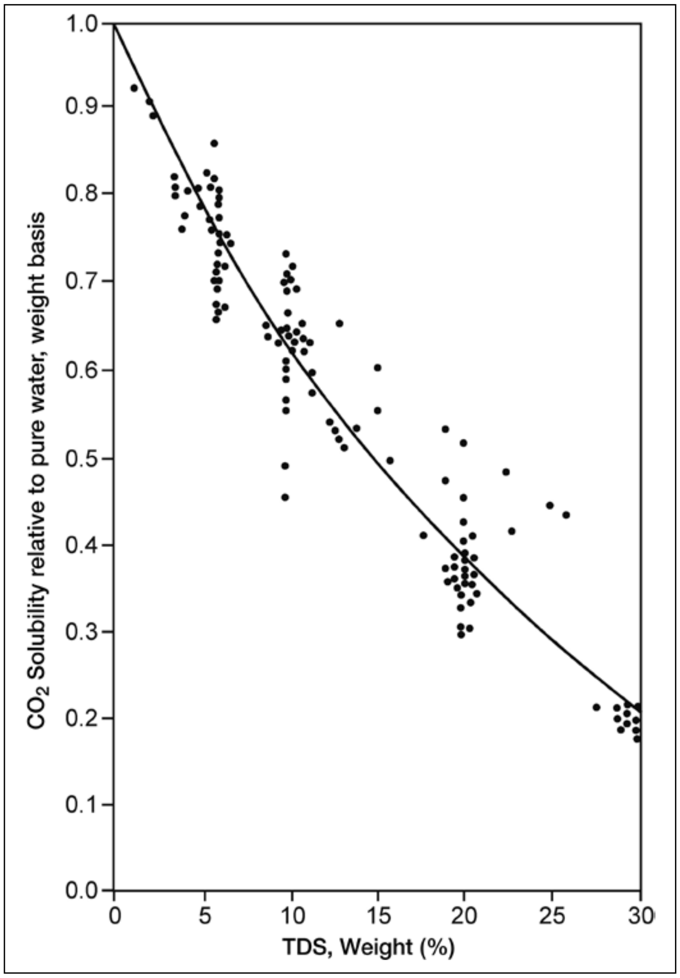

Figure AI.7 Solubility of CO_2 in brine relative to that in pure water, showing experimental points reported by Enick and Klara (1990) and correlation developed by those authors (TDS stands for total dissolved solids).

Figure AI.8 shows the dependence of *p*H on the extent to which CO_2 dissolves in sea water at temperatures of 0ºC and 25ºC based on theoretical calculations (IEA Greenhouse Gas R&D Programme, 2000) by iterative solution of the relationships (Horne, 1969) for the carbonic acid/bicarbonate/carbonate equilibria combined with activity coefficients for the bicarbonate and carbonate ions in sea water. The temperature dependence of the ionization of water and the bicarbonate equilibria were also included in this calculation. This gives values for the *p*H of typical sea water of 7.8–8.1 at 25ºC and 8.1–8.4 at 0ºC. These values, which are strongly dependent on carbonate/bicarbonate buffering, are in line with typical data for sea water (Figure AI.8 shows 2 experimental data points reported by Nishikawa *et al.*, 1992).

Figure AI.8 also shows that there is a small effect of temperature on the reduction in *p*H that results from dissolution of CO_2. A minor pressure dependence of water ionization is also reported (Handbook of Chemistry and Physics, 2000). The effect on water ionization of an increase in pressure from atmospheric to 250 bar (equivalent to 2500 m depth) is minor and about the same as would result from increasing temperature by about 2ºC. The effect of pressure can therefore be ignored.

AI.2.3 Health and safety aspects of exposure to CO_2

As a normal constituent of the atmosphere, where it is present in low concentrations (currently 370 ppmv), CO_2 is considered harmless. CO_2 is non-flammable.

As it is 1.5 times denser than air at normal temperature and pressure, there will be a tendency for any CO_2 leaking from pipework or storage to collect in hollows and other low-lying confined spaces which could create hazardous situations. The hazardous nature of the release of CO_2 is enhanced because the gas is colourless, tasteless and is generally considered odourless

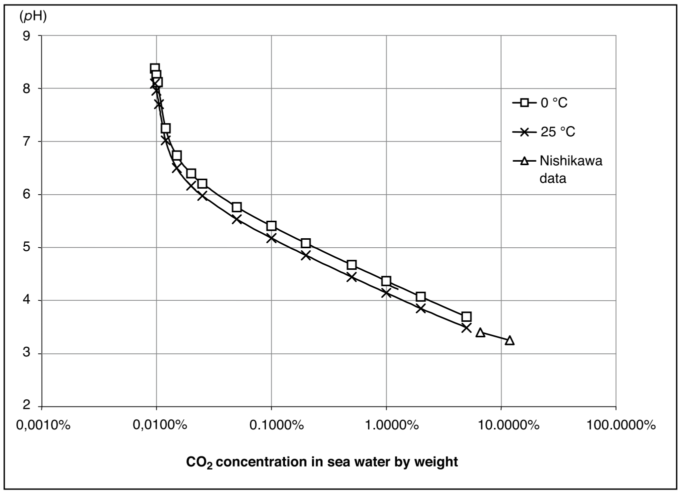

Figure AI.8 Dependence of *p*H on CO_2 concentration in sea water.

unless present in high concentrations.

When contained under pressure, escape of CO_2 can present serious hazards, for example asphyxiation, noise level (during pressure relief), frostbite, hydrates/ice plugs and high pressures (Jarrell *et al.*, 2002). The handling and processing of CO_2 must be taken into account during the preparation of a health, safety and environment plan for any facility handling CO_2.

AI.2.3.1 Effects of exposure to CO_2

At normal conditions, the atmospheric concentration of CO_2 is 0.037%, a non-toxic amount. Most people with normal cardiovascular, pulmonary-respiratory and neurological functions can tolerate exposure of up to 0.5–1.5% CO_2 for one to several hours without harm.

Higher concentrations or exposures of longer duration are hazardous – either by reducing the concentration of oxygen in the air to below the 16% level required to sustain human life[1], or by entering the body, especially the bloodstream, and/or altering the amount of air taken in during breathing; such physiological effects can occur faster than the effects resulting from the displacement of oxygen, depending on the concentration of CO_2. This is reflected in, for example, the current US occupational exposure standard of 0.5% for the maximum allowable concentration of CO_2 in air for eight hours continuous exposure; the maximum concentration to which operating personnel may be exposed for a short period of time is 3.0%.

The impact of elevated CO_2 concentrations on humans depends on the concentration and duration of exposure. At concentrations up to 1.5%, there are no noticeable physical consequences for healthy adults at rest from exposure for an hour or more (Figure AI.9); indeed, exposure to slightly elevated concentrations of CO_2, such as in re-breathing masks on aeroplanes at high altitude, may produce beneficial effects (Benson *et al.*, 2002). Increased activity or temperature may affect how the exposure is perceived. Longer exposure, even to less than 1% concentration, may significantly affect health. Noticeable effects occur above this level, particularly changes in respiration and blood *p*H level that can lead to increased heart rate, discomfort, nausea and unconsciousness.

It is noted (Rice, 2004) that most studies of the effects of CO_2 have involved healthy young male subjects, especially in controlled atmospheres such as submarines. Carbon dioxide tolerance in susceptible subgroups, such as children, the elderly, or people with respiratory deficiency, has not been studied to such an extent.

Acute exposure to CO_2 concentrations at or above 3% may significantly affect the health of the general population. Hearing loss and visual disturbances occur above 3% CO_2. Healthy young adults exposed to more than 3% CO_2 during exercise experience adverse symptoms, including laboured breathing, headache, impaired vision and mental confusion. CO_2 acts as an asphyxiant in the range 7–10% and can be fatal at this concentration; at concentrations above 20%, death can occur in 20 to 30 minutes (Fleming *et al.*, 1992). The effects of CO_2 exposure are summarized in Table AI.3, which shows the consequences at different concentrations.

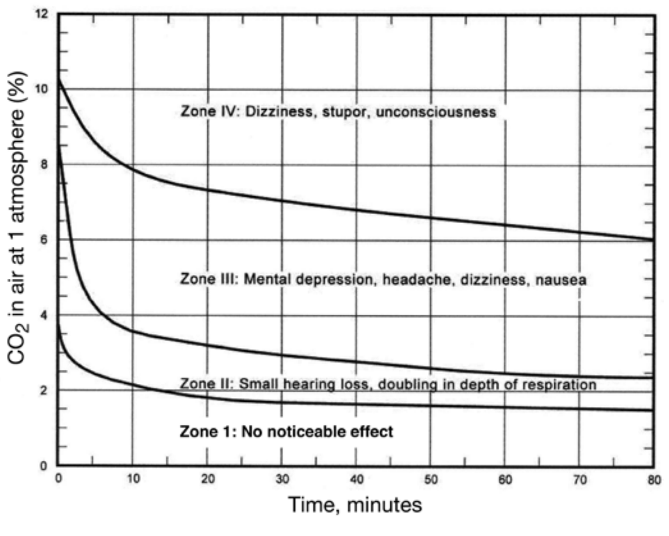

Figure AI.9 Effects of CO_2 exposure on humans (Fleming *et al.*, 1992).

Health risks to the population could therefore occur if a release of CO_2 were to produce:

- relatively low ambient concentrations of CO_2 for prolonged periods;
- or intermediate concentrations of CO_2 in relatively anoxic environments;
- or high concentrations of CO_2.

CO_2 intoxication is identified by excluding other causes, as exposure to CO_2 does not produce unique symptoms.

AI.2.3.2 Occupational standards

Protective standards have been developed for workers who may be exposed to CO_2 (Table AI.4 shows US standards but similar standards are understood to apply in other countries). These standards may or may not be relevant for protection of the general population against exposure to CO_2. Nevertheless, the occupational standards exist and provide a measure of the recommended exposure levels for this class of individual.

Site-specific risk assessments using these and other health data are necessary to determine potential health risks for the general population or for more sensitive subjects.

AI.2.3.3 Sensitive populations

Rice (2004) has indicated that there may be certain specific groups in the population which are more sensitive to elevated CO_2 levels than the general population. Such groups include those suffering from certain medical conditions including cerebral disease as well as patients in trauma medicated patients and those experiencing panic disorder, as well as individuals

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[1] Signs of asphyxia will be noted when atmospheric oxygen concentration falls below 16%. Unconsciousness, leading to death, will occur when the atmospheric oxygen concentration is reduced to ≤ 8% although, if strenuous exertion is being undertaken, this can occur at higher oxygen concentrations (Rice, 2004).

Table AI.3 Some reports of reactions to exposure to elevated concentrations of CO_2.

CO_2 **Concentration**	**Exposure reactions** **Air Products (2004)**	**Rice (2004)**
1%	Slight increase in breathing rate.	Respiratory rate increased by about 37%.
2%	Breathing rate increases to 50% above normal level. Prolonged exposure can cause headache, tiredness.	Ventilation rate raised by about l00%. Respiratory rate raised by about 50%; increased brain blood flow.
3%	Breathing increases to twice normal rate and becomes laboured. Weak narcotic effect. Impaired hearing, headache, increase in blood pressure and pulse rate.	Exercise tolerance reduced in workers when breathing against inspiratory and expiratory resistance.
4-5%	Breathing increases to approximately four times normal rate; symptoms of intoxication become evident and slight choking may be felt.	Increase in ventilation rate by ~200%; Respiratory rate doubled, dizziness, headache, confusion, dyspnoea.
5-10%	Characteristic sharp odour noticeable. Very laboured breathing, headache, visual impairment and ringing in the ears. Judgment may be impaired, followed within minutes by loss of consciousness.	At 8-10%, severe headache, dizziness, confusion, dyspnoea, sweating, dim vision. At 10%, unbearable dyspnoea, followed by vomiting, disorientation, hypertension, and loss of consciousness.
50-100%	Unconsciousness occurs more rapidly above 10% level. Prolonged exposure to high concentrations may eventually result in death from asphyxiation.	

with pulmonary disease resulting in acidosis, children and people engaged in complex tasks.

CO_2 is a potent cerebrovascular dilator and significantly increases the cerebral blood flow. CO_2 exposure can seriously compromise patients in a coma or with a head injury, with increased intra-cranial pressure or bleeding, or with expanding lesions. An elevated partial pressure of CO_2 in arterial blood can further dilate cerebral vessels already dilated by anoxia.

Anoxia and various drugs (Osol and Pratt, 1973) can depress the stimulation of the respiratory centre by CO_2. In such patients, as well as patients with trauma to the head, the normal compensatory mechanisms will not be effective against exposure to CO_2 and the symptoms experienced will not necessarily alert the individuals or their carers to the presence of high CO_2 levels.

Patients susceptible to panic disorder may experience an increased frequency of panic attacks at 5% CO_2 (Woods *et al.*, 1988). Panic attack and significant anxiety can affect the ability of the individual to exercise appropriate judgment in dangerous situations.

CO_2 exposure can increase pulmonary pressure as well as systemic blood pressure and should be avoided in individuals with systemic or pulmonary hypertension. The rise in cardiac work during CO_2 inhalation could put patients with coronary artery disease or heart failure in jeopardy (Cooper *et al.*, 1970).

Infants and children breathe more air than adults relative to their body size and they therefore tend to be more susceptible to respiratory exposures (Snodgrass, 1992). At moderate to high CO_2 concentrations, the relaxation of blood vessels and enhanced ventilation could contribute to rapid loss of body heat in humans of any age. Carbon dioxide can significantly diminish an individual's performance in carrying out complex tasks.

AI.2.3.4 CO_2 control and response procedures

Suitable control procedures have been developed by industries which use CO_2, for example, minimizing any venting of CO_2 unless this cannot be avoided for safety or other operational reasons. Adequate ventilation must be provided when CO_2 is discharged into the air to ensure rapid dispersion.

Due its high density, released CO_2 will flow to low-levels and collect there, especially under stagnant conditions. High concentrations can persist in open pits, tanks and buildings. For this reason, monitors should be installed in areas where CO_2 might concentrate, supplemented by portable monitors. If CO_2 escapes from a vessel, the consequent pressure drop can cause a hazardous cold condition with danger of frostbite from contact with cold surfaces, with solid CO_2 (dry ice) or with escaping liquid CO_2. Personnel should avoid entering a CO_2 vapour

Table AI.4 Occupational exposure standards.

	Time-weighted average (8 hour day/40 hour week)	**Short-term exposure limit (15 minute)**	**Immediately dangerous to life and health**
OSHA permissible exposure limit[a]	5000 ppm (0.5%)	30,000 ppm (3%)	40,000 ppm (5%)
NIOSH recommended exposure limit[b]	5000 ppm (0.5%)		
ACGIH threshold limit value[c]	5000 ppm (0.5%)		

[a] OSHA - US Occupational Safety and Health Administration (1986).

[b] NIOSH - US National Institute of Occupational Safety and Health (1997).

[c] ACGIH - American Conference of Governmental Industrial Hygienists.

cloud not only because of the high concentration of CO_2 but also because of the danger of frostbite.

Hydrates, or ice plugs, can form in the piping of CO_2 facilities and flowlines, especially at pipe bends, depressions and locations downstream of restriction devices. Temperatures do not have to fall below 0°C for hydrates to form; under elevated pressures this can occur up to a temperature of 11°C.

AI.2.4 Established uses for CO_2

A long-established part of the industrial gases market involves the supply of CO_2 to a range of industrial users (source: Air Liquide). In several major industrial processes, CO_2 is manufactured on site as an intermediate material in the production of chemicals. Large quantities of CO_2 are used for enhanced oil recovery. Other uses of CO_2 include:

- Chemicals
    - Carbon dioxide is used in synthesis chemistry and to control reactor temperatures. CO_2 is also employed to neutralize alkaline effluents.
    - The main industrial use of CO_2 is in the manufacture of urea, as a fertilizer.
    - Large amounts of CO_2 are also used in the manufacture of inorganic carbonates and a lesser amount is used in the production of organic monomers and polycarbonates.
    - Methanol is manufactured using a chemical process which makes use of CO_2 in combination with other feedstocks.
    - CO_2 is also used in the manufacture of polyurethanes.
- Pharmaceuticals
    - CO_2 is used to provide an inert atmosphere, for chemical synthesis, supercritical fluid extraction and for acidification of waste water and for product transportation at low temperature (–78°C).
- Food and Beverage
    - CO_2 is used in the food business in three main areas: Carbonation of beverages; packaging of foodstuffs and as cryogenic fluid in chilling or freezing operations or as dry ice for temperature control during the distribution of foodstuffs.
- Health care
    - Intra-abdominal insufflation during medical procedures to expand the space around organs or tissues for better visualization.
- Metals industry
    - CO_2 is typically used for environmental protection; for example for red fume suppression during scrap and carbon charging of furnaces, for nitrogen pick-up reduction during tapping of electric arc furnaces and for bottom stirring.
    - In non-ferrous metallurgy, carbon dioxide is used for fume suppression during ladle transfer of matte (Cu/Ni production) or bullion (Zn/Pb production).
    - A small amount of liquid CO_2 is used in recycling waters from acid mine drainage.
- Pulp and paper
    - CO_2 enables fine-tuning of the *p*H of recycled mechanical or chemical pulps after an alkaline bleaching. CO_2 can be used for increasing the performance of paper production machines.
- Electronics
    - CO_2 is used in waste water treatment and as a cooling medium in environmental testing of electronic devices. CO_2 can also be used to add conductivity to ultra-pure water and, as CO_2 snow, for abrasive cleaning of parts or residues on wafers; CO_2 can also be used as a supercritical fluid for removing photoresist from wafers, thus avoiding use of organic solvents.
- Waste treatment
    - Injection of CO_2 helps control the *p*H of liquid effluents.
- Other applications
    - CO_2 snow is used for fire extinguishers, for *p*H control and for regulation of waste waters in swimming pools.

AI.3 Conversion factors

Some conversion factors relevant to CO_2 capture and storage are given in Table AI.5 Other, less precise conversions and some approximate equivalents are given in Table AI.6.

AI.4 Fuels and emissions

AI.4.1 Carbonaceous fuels

Carbonaceous fuels can be defined as materials rich in carbon and capable of producing energy on oxidation. From a historical perspective, most of these fuels can be viewed as carriers of solar energy, having been derived from plants which depended on solar energy for growth. Thus, these fuels can be distinguished by the time taken for their formation, which is millions of years for fossil fuels, hundreds of years for peat and months-to-years for biofuels. On the scale of the human lifespan, fossil fuels are regarded as non-renewable carbonaceous fuels while biofuels are regarded as renewable. Coal, oil and natural gas are the major fossil fuels. Wood, agro-wastes, etcetera are the main biofuels for stationary uses but, in some parts of the world, crops such as soya, sugar cane and oil-seed plants are grown specifically to produce biofuels, especially transport fuels such as bioethanol and biodiesel. Peat is close to being a biofuel in terms of its relatively short formation time compared with fossil fuels.

AI.4.1.1 Coal

Coal is the most abundant fossil fuel present on Earth. Coal originated from the arrested decay of the remains of plant life which flourished in swamps and bogs many millions of years ago in a humid, tropical climate with abundant rainfall.

Table AI.5 Some conversion factors.

To convert:	Into the following units:	Multiply by:
US gallon	litre	3.78541
barrels (bbl)	m^3	0.158987
ton (Imperial)	tonne	1.01605
short ton (US)	tonne	0.907185
lbf	N	4.44822
kgf	N	9.80665
lbf in^{-2}	Bar	0.0689476
Bar	MPa	0.1
Btu	MJ	0.00105506
Btu	kWh	0.000293071
kWh	MJ	3.60000
Btu lb^{-1}	MJ kg^{-1}	0.00232600
Btu ft^{-3}	MJ m^{-3}	0.0372589
Btu/h	kW	0.000293071
Btu (lb.°F) $^{-1}$	kJ (kg.°C) $^{-1}$	4.18680
Btu (ft^2.h) $^{-1}$	kW m^{-2}	0.00315459
Btu (ft^3.h) $^{-1}$	kW m^{-3}	0.0103497
Btu (ft^2.h.°F) $^{-1}$	W (m^2.°C) $^{-1}$	5.67826
1 MMT[a]	million tonnes	0.907185
°F	°C	$°C = \frac{(°F - 32)}{1.8}$

[a] The abbreviation MMT is used in the literature to denote both Millions of short tons and Millions of metric tonnes. The conversion given here is for the former.

Table AI.6 Approximate equivalents and other definitions.

To convert	Into the following units	Multiply by
1 tC	tCO_2	3.667
1 tCO_2	m^3 CO_2 (at 1.013 bar and 15 °C)	534
1 t crude oil	Bbl	7.33
1 t crude oil	m^3	1.165

Fractions retained			
Release rate (fraction of stored amount released per year)	**Fraction retained over 100 years**	**Fraction retained over 500 years**	**Fraction retained over 5000 years**
0.001	90%	61%	1%
0.0001	99%	95%	61%
0.00001	100%	100%	95%

Other definitions	
Standard Temperature and Pressure	0 °C and 1.013 bar

Subsequent action of heat and pressure and other physical phenomena metamorphosed it into coal. Because of various degrees of metamorphic change during the process, coal is not a uniform substance; no two coals are the same in every respect. The composition of coal is reported in two different ways: The proximate analysis and the ultimate analysis, both expressed in % by weight. In a proximate analysis, moisture, volatile matter, fixed carbon and ash are measured using prescribed methods, which enable the equipment designer to determine how much air is to be supplied for efficient combustion, amongst other things. An ultimate analysis determines the composition in terms of the elements that contribute to the heating value, such as carbon, hydrogen, nitrogen, sulphur, the oxygen content (by difference), as well as ash. Along with these analyses, the heating value (expressed as kJ kg^{-1}) is also determined.

Carpenter (1988) describes the various coal classification systems in use today. In general, these systems are based on hierarchy and rank. The rank of a coal is the stage the coal has reached during the coalification[2] process – that is its degree of metamorphism or maturity. Table AI.7 shows the classification system adopted by the American Society for Testing Materials (ASTM), D388-92A (Carpenter, 1988; Perry and Green, 1997). This rank-based system is extensively used in North America and many other parts of the world. This system uses two parameters to classify coals by rank, fixed carbon (dry, mineral-matter-free) for the higher rank coals and gross calorific value (moist, mineral-matter-free) for the lower rank coals. The agglomerating character of the coals is used to differentiate between adjacent coal groups.

AI.4.1.2 Oil and petroleum fuels

During the past 600 million years, the remains of incompletely decayed plant have become buried under thick layers of rock and, under high pressure and temperature, have been converted to petroleum which may occur in gaseous, liquid or solid form. The fluid produced from petroleum reservoirs may be crude oil (a mixture of light and heavy hydrocarbons and bitumen) or natural gas liquids. Hydrocarbons can also be extracted from tar sands or oil shales; this takes place in several parts of the world.

Fuels are extracted from crude oil through fractional distillation, with subsequent conversion and upgrading. Such fuels are used for vehicles (gasoline, jet fuel, diesel fuel and liquefied petroleum gases (LPG)), heating oils, lighting oils, solvents, lubricants and building materials such as asphalts, plus a variety of other products. The compositions of heating fuels may differ in their composition, density, etcetera but general categories are recognized worldwide: kerosene-type vaporizing fuel, distillate (or 'gas oil') and more viscous blends and residuals. Tables AI.8 and AI.9 provide typical specifications of some common fuels (Perry and Green, 1997; Kaantee *et al.*, 2003).

AI.4.1.3 Natural gas

Natural gas is combustible gas that occurs in porous rock of the Earth's crust; it is often found with or near accumulations of crude oil. It may occur in separate reservoirs but, more commonly, it forms a gas cap entrapped between the petroleum and an impervious, capping rock layer in a petroleum reservoir. Under high-pressure conditions, it becomes partially mixed with or dissolved in the crude oil. Methane (CH_4) is the main component of natural gas, usually making up more than 80% of the constituents by volume. The remaining constituents are ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), hydrogen sulphide (H_2S) and inerts (N_2, CO_2 and He). The amounts of these compounds can vary greatly depending on location. Natural gas is always treated prior to use, mainly by drying, and by removing H_2S and, depending on the amount present, CO_2. There are no universally accepted specification systems for marketed natural gas; however a typical composition of natural gas is given in Table AI.10 (Spath and Mann, 2000).

AI.4.1.4 Biofuels

Biofuels may be defined as fuels produced from organic matter or combustible oils produced by plants (IPCC, 2001). Dedicated energy crops, including short-rotation woody crops such as hardwood trees and herbaceous crops such as switch grass, are agricultural crops that are solely grown for use as biofuels. These crops have very fast growth rates and can therefore provide a regular supply of fuel. The category of biofuels also includes wood from trees and wood waste products (e.g., sawdust, wood chips, etc.), crop residues (e.g., rice husks, bagasse, corn husks, wheat chaff, etc.). This category of fuel is often taken to include some types of municipal, animal and industrial wastes (e.g., sewage sludge, manure, etc.). These would be combusted in stationary plants. Chemical properties of typical biofuels, including peat, are given in Table AI.11 (Sami *et al.*, 2001; Hower, 2003).

Biomass-derived fuels can also be manufactured for use as transport fuels, for example ethanol from fermentation of plant material or biodiesel produced by transesterification of vegetable oils. The energy efficiency of fermentation systems can be improved by combustion of the solid residues to produce electricity.

AI.4.2 Examples of emissions from carbonaceous fuels

Depending on the fuel type and application, the utilization of carbonaceous fuels causes direct and indirect emissions of one or more of the following: SO_x, NO_x, particulate matter, trace metals and elements, volatile organic carbons and greenhouse gases (e.g., CO_2, CH_4, N_2O). Direct emissions are usually confined to the point of combustion of the fuel. Indirect emissions include those that arise from the upstream recovery, processing and distribution of the fuel. Life cycle analysis (LCA) can be used to account for all emissions (direct as well as indirect) arising from the recovery, processing, distribution and end-use of a fuel. Table AI.12 (Cameron, 2002) and Table AI.13 (EPA, 2004) give an idea of some direct and indirect emissions anticipated, but these should only be viewed as examples due to the considerable variation there can be in many of these values.

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[2] Coalification refers to the progressive transformation of peat through lignite/brown coal, to sub-bituminous, bituminous and anthracite coals.

Table AI.7 Characterization of coals by rank (according to ASTM D388-92A).

	Fixed Carbon Limits (dmmf basis)[a] %		**Volatile Matter Limits (dmmf basis)[a] %**		**Gross Calorific Value Limits (mmmf basis)[b] MJ kg^{-1}**		
Class Group	**Equal to or greater than**	**Less than**	**Greater than**	**Equal to or less than**	**Equal to or greater than**	**Less than**	**Agglomerating Character**
Anthracite							Non-agglomerating
Meta-anthracite	98	-	-	2	-	-	
Anthracite	92	98	2	8	-	-	
Semi-anthracite [c]	86	92	8	14	-	-	
Bituminous coal							Commonly agglomerating
Low volatile	78	86	14	22	-	-	
Medium volatile	69	78	22	31	-	-	
High volatile A	-	69	31	-	32.6 [d]	-	
High volatile B	-	-	-	-	30.2 [d]	32.6	
High volatile C	-	-	-	-	26.7	30.2	
					24.4	26.7	Agglomerating
Sub-bituminous coal							Non-agglomerating
A	-	-	-	-	24.4	26.7	
B	-	-	-	-	22.1	24.4	
C	-	-	-	-	19.3	22.1	
Lignite							
A	-	-	-	-	14.7	19.3	
B	-	-	-	-	-	14.7	

[a] Indicates dry-mineral-matter-free basis (dmmf).

[b] mmmf indicates moist mineral-matter-free basis; moist refers to coal containing its natural inherent moisture but not including visible water on the surface of the coal.

[c] If agglomerating, classified in the low volatile group of the bituminous class.

[d] Coals having 69% or more fixed carbon (dmmf) are classified according to fixed carbon, regardless of gross calorific value.

Table AI.8 Typical specifications of petroleum-based heating fuels.

Specifier	**Number**	**Category**
Canadian Government Specification Board, Department of Defense Production, Canada	3-GP-2	Fuel oil, heating
Deutsches Institut fur Normung e.V., Germany	DIN 51603	Heating (fuel) oils
British Standards Institution, UK	B.S. 2869	Petroleum fuels for oil engines and burners
Japan	JIS K2203	Kerosene
	JIS K2204	Gas oil
	JIS K2205	Fuel oil
Federal Specifications, United States	ASTM D 396	Fuel oil, burner

Table AI.9 Typical ultimate analysis of petroleum-based heating fuels.

Composition %	**No. 1 fuel oil (41.5°API[a])**	**No. 2 fuel oil (33°API[a])**	**No. 4 fuel oil (23.2°API[a])**	**Low sulphur, No. 6 fuel oil (33°API[a])**	**High sulphur, No. 6 fuel oil (15.5o APIa)**	**Petroleum coke[b]**
Carbon	86.4	87.3	86.47	87.26	84.67	89.5
Hydrogen	13.6	12.6	11.65	10.49	11.02	3.08
Oxygen	0.01	0.04	0.27	0.64	0.38	1.11
Nitrogen	0.003	0.006	0.24	0.28	0.18	1.71
Sulphur	0.09	0.22	1.35	0.84	3.97	4.00
Ash	<0.01	<0.01	0.02	0.04	0.02	0.50
C/H Ratio	6.35	6.93	7.42	8.31	7.62	29.05

[a] Degree API = (141.5/s) -131.5; where s is the specific density at 15°C.

[b] Reference: Kaantee *et al*. (2003).

Table AI.10 Typical natural gas composition.

Component	**Pipeline composition used in analysis**	**Typical range of wellhead components (mol%)**	
	Mol% (dry)	**Low value**	**High value**
Carbon dioxide CO^2	0.5	0	10
Nitrogen N_2	1.1	0	15
Methane CH_4	94.4	75	99
Ethane C_2H_6	3.1	1	15
Propane C_3H_8	0.5	1	10
Isobutane $C4H_{10}$	0.1	0	1
N-butane C_4H_{10}	0.1	0	2
Pentanes + (C_5+)	0.2	0	1
Hydrogen sulphide (H_2S)	0.0004	0	30
Helium (He)	0.0	0	5
Heat of combustion (LHV)	48.252 MJ kg^{-1}	-	-
Heat of combustion (HHV)	53.463 MJ kg^{-1}	-	-

Table AI.11 Chemical analysis and properties of some biomass fuels (Sami *et al*., 2001; Hower, 2003).

	Peat	**Wood (saw dust)**	**Crop residues (sugar cane bagasse)**	**Municipal solid waste**	**Energy crops (Eucalyptus)**
Proximate Analysis					
Moisture	70–90	7.3	-	16–38	-
Ash	-	2.6	11.3	11–20	0.52
Volatile matter	45–75	76.2	-	67–78	-
Fixed carbon	-	13.9	14.9	6–12	16.9
Ultimate Analysis					
C	45–60	46.9	44.8	-	48.3
H	3.5–6.8	5.2	5.4	-	5.9
O	20–45	37.8	39.5	-	45.1
N	0.75–3	0.1	0.4	-	0.2
S	-	0.04	0.01	-	0.01
Heating Value, MJ $kg^{-1,}$ (HHV)	**17–22**	**18.1**	**17.3**	**15.9–17.5**	**19.3**

Table AI.12 Direct emissions of non-greenhouse gases from two examples of coal and natural gas plants based on best available control technology, burning specific fuels (Cameron, 2002).

Emissions	**Coal** **(supercritical PC with best available emission controls)**	**Natural gas** **(NGCC with SCR)**
NO_x, g GJ^{-1}	4-5	5
SO_x, g GJ^{-1}	4.5-5	0.7
Particulates, g GJ^{-1}	2.4-2.8	2
Mercury, mg GJ^{-1}	0.3-0.5	N/A

Table AI.13 Direct CO_2 emission factors for some examples of carbonaceous fuels.

Carbonaceous Fuel	**Heat Content (HHV)** **MJ kg^{-1} [a]**	**Emission Factor** **gCO_2 MJ^{-1} [a]**
Coal		
Anthracite	26.2	96.8
Bituminous	27.8	87.3
Sub-bituminous	19.9	90.3
Lignite	14.9	91.6
Biofuel		
Wood (dry)	20.0	78.4
Natural Gas	**kJ m^{-3}**	
	37.3	50
Petroleum Fuel	**MJ m^{-3}**	
Distillate Fuel Oil (#1, 2 & 4)	38,650	68.6
Residual Fuel Oil (#5 & 6)	41,716	73.9
Kerosene	37,622	67.8
LPG (average for fuel use	25,220	59.1
Motor Gasoline	-	69.3

[a] Reported values converted to SI units (NIES, 2003).

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Annex II

Glossary, acronyms and abbreviations

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Note: the definitions in this Annex refer to the use of the terms in the context of this report. It provides an explanation of specific terms as the authors intend them to be interpreted in this report.

Abatement
Reduction in the degree or intensity of emissions or other pollutants.

Absorption
Chemical or physical take-up of molecules into the bulk of a solid or liquid, forming either a solution or compound.

Acid gas
Any gas mixture that turns to an acid when dissolved in water (normally refers to $H_2S + CO_2$ from sour gas (q.v.)).

Adiabatic
A process in which no heat is gained or lost by the system.

Adsorption
The uptake of molecules on the surface of a solid or a liquid.

Afforestation
Planting of new forests on lands that historically have not contained forests.

Aluminium silicate mineral
Natural mineral – such as feldspar, clays, micas, amphiboles – composed of Al_2O_3 and SiO_2 plus other cations.

Amine
Organic chemical compound containing one or more nitrogens in $-NH_2$, -NH or -N groups.

Anaerobic condition
Reducing condition that only supports life which does not require free oxygen.

Anhydrite
Calcium sulphate: the common hydrous form is called gypsum.

Antarctic Treaty
Applies to the area south of 60 degrees South, and declares that Antarctica shall be used for peaceful purposes only.

Anthracite
Coal with the highest carbon content and therefore the highest rank (q.v.).

Anthropogenic source
Source which is man-made as opposed to natural.

Anticline
Folded geological strata that is convex upwards.

API
American Petroleum Institute; degree API is a measure of oil density given by (141.5/specific gravity) -131.5.

Aquifer
Geological structure containing water and with significant permeability to allow flow; it is bound by seals.

Assessment unit
A geological province with high petroleum potential.

Assigned amount
The amount by which a Party listed in Annex B of the Kyoto Protocol agrees to reduce its anthropogenic emissions.

ATR
Auto thermal reforming: a process in which the heat for the reaction of CH_4 with steam is generated by partial oxidation of CH_4.

Autoproduction
The production of electricity for own use.

Basalt
A type of basic igneous rock which is typically erupted from a volcano.

Basel Convention
UN Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal, which was adopted at Basel on 22 March 1989.

Baseline
The datum against which change is measured.

Basin
A geological region with strata dipping towards a common axis or centre.

Bathymetric
Pertaining to the depth of water.

Benthic
Pertaining to conditions at depth in bodies of water.

Bicarbonate ion
The anion formed by dissolving carbon dioxide in water, HCO_3^-.

Biomass
Matter derived recently from the biosphere.

Biomass-based CCS
Carbon capture and storage in which the feedstock (q.v.) is biomass

Bituminous coal
An intermediate rank of coal falling between the extremes of peat and anthracite, and closer to anthracite.

Blow-out
Refers to catastrophic failure of a well when the petroleum fluids or water flow unrestricted to the surface.

Bohr effect
The *p*H-dependent change in the oxygen affinity of blood.

Bottom-up model
A model that includes technological and engineering details in the analysis.

Boundary
In GHG accounting, the separation between accounting units, be they national, organizational, operational, business units or sectors.

Break-even price
The price necessary at a given level of production to cover all costs.

Buoyancy
Tendency of a fluid or solid to rise through a fluid of higher density.

Cap rock
Rock of very low permeability that acts as an upper seal to prevent fluid flow out of a reservoir.

Capillary entry pressure
Additional pressure needed for a liquid or gas to enter a pore and overcome surface tension.

Capture efficiency
The fraction of CO_2 separated from the gas stream of a source

Carbon credit
A convertible and transferable instrument that allows an organization to benefit financially from an emission reduction.

Carbon trading
A market-based approach that allows those with excess emissions to trade that excess for reduced emissions elsewhere.

Carbonate
Natural minerals composed of various anions bonded to a CO_3^{2-} cation (e.g. calcite, dolomite, siderite, limestone).

Carbonate neutralization
A method for storing carbon in the ocean based upon the reaction of CO_2 with a mineral carbonate such as limestone to produce bicarbonate anions and soluble cations.

Casing
A pipe which is inserted to stabilize the borehole of a well after it is drilled.

CBM
Coal bed methane

CCS
Carbon dioxide capture and storage

CDM
Clean development mechanism: a Kyoto Protocol mechanism to assist non-Annex 1 countries to contribute to the objectives of the Protocol and help Annex I countries to meet their commitments.

Certification
In the context of carbon trading, certifying that a project achieves a quantified reduction in emissions over a given period.

Chemical looping combustion
A process in which combustion of a hydrocarbon fuel is split into separate oxidation and reduction reactions by using a metal oxide as an oxygen carrier between the two reactors.

Chlorite
A magnesium-iron aluminosilicate sheet silicate clay mineral.

Class “x” well
A regulatory classification for wells used for the injection of fluids into the ground.

Claus plant
A plant that transforms H_2S into elemental sulphur.

Cleats
The system of joints, cleavage planes, or planes of weakness found in coal seams along which the coal fractures.

CO_2 avoided
The difference between CO_2 captured, transmitted and/or stored, and the amount of CO_2 generated by a system without capture, net of the emissions not captured by a system with CO_2 capture.

CO_2 equivalent
A measure used to compare emissions of different greenhouse gases based on their global warming potential.

Co-benefit
The additional benefits generated by policies that are implemented for a specific reason.

COE
Cost of electricity, value as calculated by Equation 1 in Section 3.7.

Co-firing
The simultaneous use of more than one fuel in a power plant or industrial process.
Completion of a well
Refers to the cementing and perforating of casing and stimulation to connect a well bore to reservoir.

Congruence
The quality of agreement between two entities.

Conservative values
Parameter values selected so that a parameter, such as CO_2 leakage, is over-estimated.

Containment
Restriction of movement of a fluid to a designated volume (e.g. reservoir).

Continental shelf
The extension of the continental mass beneath the ocean.

COREX
A process for producing iron.

Cryogenic
Pertaining to low temperatures, usually under about -100°C.

D, Darcy
A non-SI unit of permeability, abbreviated D, and approximately = $1\mu m^2$.

Dawsonite
A mineral: dihydroxide sodium aluminium carbonate.

Deep saline aquifer
A deep underground rock formation composed of permeable materials and containing highly saline fluids.

Deep sea
The sea below 1000m depth.

Default emissions factor
An approximate emission factor that may be used in the absence of precise or measured values of an Emissions Factor.

Demonstration phase
Demonstration phase means that the technology is implemented in a pilot project or on a small scale, but not yet economically feasible at full scale.

Dense phase
A gas compressed to a density approaching that of the liquid.

Dense fluid
A gas compressed to a density approaching that of the liquid.

Depleted
Of a reservoir: one where production is significantly reduced.

Diagenesis
Processes that cause changes in sediment after it has been deposited and buried under another layer.

DIC
Dissolved Inorganic Carbon.

Dip
In geology, the angle below the horizontal taken by rock strata.

Discharge
The amount of water issuing from a spring or in a stream that passes a specific point in a given period of time.

Discordant sequence
In geology, sequence of rock strata that is markedly different from strata above or below.

Dolomite
A magnesium-rich carbonate sedimentary rock. Also, a magnesium-rich carbonate mineral ($CaMgCO_3$).

Double-grip packer
A device used to seal a drill string equipped with two gripping mechanisms.

Down-hole log
Record of conditions in a borehole.

Drill cuttings
The solid particles recovered during the drilling of a well.

Drill string
The assembly of drilling rods that leads from the surface to the drilling tool.

Drive
Fluid flow created in formations by pressure differences arising from borehole operations.

Dry ice
Solid carbon dioxide

Dynamic miscibility
The attainment of mixing following the prolonged injection of gas into an oilfield.

ECBM
Enhanced coal bed methane recovery; the use of CO_2 to enhance the recovery of the methane present in unminable coal beds through the preferential adsorption of CO_2 on coal.

Economic potential
The amount of greenhouse gas emissions reductions from a specific option that could be achieved cost-effectively, given prevailing circumstances (i.e. a market value of CO_2 reductions and costs of other options).

Economically feasible under specific conditions
A technology that is well understood and used in selected commercial applications, such as in a favourable tax regime or a niche market, processing at least 0.1 $MtCO_2$/yr, with a few (less than 5) replications of the technology.

EGR
Enhanced gas recovery: the recovery of gas additional to that produced naturally by fluid injection or other means.

Emission factor
A normalized measure of GHG emissions in terms of activity, e.g., tonnes of GHG emitted per tonne of fuel consumed.

Emissions credit
A commodity giving its holder the right to emit a certain quantity of GHGs (q.v.).

Emissions trading
A trading scheme that allows permits for the release of a specified number of tonnes of a pollutant to be sold and bought.

Endothermic
Concerning a chemical reaction that absorbs heat, or requires heat to drive it.

Enhanced gas recovery
See EGR.

Enhanced oil recovery
See EOR

Entrained flow
Flow in which a solid or liquid, in the form of fine particles, is transported in diluted form by high velocity gas.

Entrainment gas
The gas employed in entrained flow (q.v.).

EOR
Enhanced oil recovery: the recovery of oil additional to that produced naturally by fluid injection or other means.

Euphotic zone
The zone of the ocean reached by sunlight.

Evaporite
A rock formed by evaporation.

Exothermic
Concerning a chemical reaction that releases heat, such as combustion.

Ex-situ mineralization
A process where minerals are mined, transferred to an industrial facility, reacted with carbon dioxide and processed.

Exsolution
The formation of different phases during the cooling of a homogeneous fluid.

Extended reach well
Borehole that is diverted into a more horizontal direction to extend its reach.

Extremophile
Microbe living in environments where life was previously considered impossible.

Far field
A region remote from a signal source.

Fault
In geology, a surface at which strata are no longer continuous, but displaced.

Fault reactivation
The tendency for a fault to become active, i.e. for movement to occur.

Fault slip
The extent to which a fault has slipped in past times.

FBC
Fluidized bed combustion: – combustion in a fluidized bed (q.v.).

Feldspar
A group of alumino-silicate minerals that makes up much of the Earth’s crust.

Feedstock
The material that is fed to a process

FGD
Flue gas desulphurization.

Fischer-Tropsch
A process that transforms a gas mixture of CO and H_2 into liquid hydrocarbons and water.

Fixation
The immobilization of CO_2 by its reaction with another material to produce a stable compound

Fixed bed
A gas-solid contactor or reactor formed by a bed of stationary solid particles that allows the passage of gas between the particles.

Flood
The injection of a fluid into an underground reservoir.

Flue gas
Gases produced by combustion of a fuel that are normally emitted to the atmosphere.

Fluidized bed
A gas-solid contactor or reactor comprising a bed of fine solid particles suspended by passing a gas through the bed at sufficiently high velocity.

Folding
In geology, the bending of rock strata from the plane in which they were formed.

Formation
A body of rock of considerable extent with distinctive characteristics that allow geologists to map, describe, and name it.

Formation water
Water that occurs naturally within the pores of rock formations.

Fouling
Deposition of a solid on the surface of heat or mass transfer equipment that has the effect of reducing the heat or mass transfer.

Fracture
Any break in rock along which no significant movement has occurred.

Fuel cell
Electrochemical device in which a fuel is oxidized in a controlled manner to produce an electric current and heat directly.

Fugitive emission
Any releases of gases or vapours from anthropogenic activities such as the processing or transportation of gas or petroleum.

FutureGen Project
US Government initiative for a new power station with low CO_2 emissions.

Gas turbine
A machine in which a fuel is burned with compressed air or oxygen and mechanical work is recovered by the expansion of the hot products.

Gasification
Process by which a carbon-containing solid fuel is transformed into a carbon- and hydrogen-containing gaseous fuel by reaction with air or oxygen and steam.

Geochemical trapping
The retention of injected CO_2 by geochemical reactions.

Geological setting
The geological environment of various locations.

Geological time
The time over which geological processes have taken place.

Geomechanics
The science of the movement of the Earth's crust.

Geosphere
The earth, its rocks and minerals, and its waters.

Geothermal
Concerning heat flowing from deep in the earth.

GHG
Greenhouse gases: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydroflurocarbons (HFCs), perfluorocarbons (PFCs), and sulphur hexafluoride (SF_6).

Hazardous and non-hazardous waste
Potentially harmful and non-harmful substances that have been released or discarded into the environment.

Hazardous waste directive
European directive in force to regulate definitions of waste classes and to regulate the handling of the waste classes.

HAZOP
HAZard and OPerability, a process used to assess the risks of operating potentially hazardous equipment.

Helsinki Convention
International legal convention protecting the Baltic water against pollution.

Henry's Law
States that the solubility of a gas in a liquid is proportional to the partial pressure of the gas in contact with the liquid.

HHV
Higher heating value: the energy released from the combustion of a fuel that includes the latent heat of water.

Host rock
In geology, the rock formation that contains a foreign material.

Hybrid vehicle
Vehicle that combines a fossil fuel internal combustion engine and an alternative energy source, typically batteries.

Hydrate
An ice-like compound formed by the reaction of water and CO_2, CH_4 or similar gases.

Hydrodynamic trap
A geological structure in which fluids are retained by low levels of porosity in the surrounding rocks.

Hydrogeological
Concerning water in the geological environment.

Hydrostatic
Pertaining to the properties of a stationary body of water.

Hypercapnia
Excessively high CO_2 levels in the blood.

Hypoxia
Having low rates of oxygen transfer in living tissue.

Hysteresis
The phenomenon of a lagging recovery from deformation or other disturbance.

IEA GHG
International Energy Agency – Greenhouse Gas R&D Programme.

IGCC
Integrated gasification combined cycle: power generation in which hydrocarbons or coal are gasified (q.v.) and the gas is used as a fuel to drive both a gas and a steam turbine.

Igneous
Rock formed when molten rock (magma) has cooled and solidified (crystallized).

Immature basin
A basin in which the processes leading to oil or gas formation have started but are incomplete.

Infrared spectroscopy
Chemical analysis using infrared spectroscope method.

Injection
The process of using pressure to force fluids down wells.

Injection well
A well in which fluids are injected rather than produced.

Injectivity
A measure of the rate at which a quantity of fluid can be injected into a well.

***In-situ* mineralization**
A process where minerals are not mined: carbon dioxide is injected in the silicate formation where it reacts with the minerals, forming carbonates and silica.

International Seabed Authority
An organization established under the 1982 UN Convention on the Law of the Sea, headquartered in Kingston, Jamaica.

Ion
An atom or molecule that has acquired a charge by either gaining or losing electrons.

IPCC
Intergovernmental Panel on Climate Change

JI
Joint Implementation: under the Kyoto Protocol, it allows a Party with a GHG emission target to receive credits from other Annex 1 Parties.

Kyoto Protocol
Protocol to the United Nations Framework Convention on Climate Change, which was adopted at Kyoto on 11 December 1997.

Leach
To dissolve a substance from a solid.

Leakage
In respect of carbon trading, the change of anthropogenic emissions by sources or removals by sinks which occurs outside the project boundary.

Leakage
In respect of carbon storage, the escape of injected fluid from storage.

Levellized cost
The future values of an input or product that would make the NPV (q.v.) of a project equal to zero.

LHV
Lower heating value: energy released from the combustion of a fuel that excludes the latent heat of water.

Lignite/sub-bituminous coal
Relatively young coal of low rank with a relatively high hydrogen and oxygen content.

Limestone
A sedimentary rock made mostly of the mineral calcite (calcium carbonate), usually formed from shells of dead organisms.

LNG
Liquefied natural gas

Lithology
Science of the nature and composition of rocks

Lithosphere
The outer layer of the Earth, made of solid rock, which includes the crust and uppermost mantle up to 100 km thick.

Log
Records taken during or after the drilling of a well.

London Convention
On the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, which was adopted at London, Mexico City, Moscow and Washington on 29 December 1972.

London Protocol
Protocol to the Convention adopted in London on 2 November 1996 but which had not entered into force at the time of writing.

Low-carbon energy carrier
Fuel that provides low fuel-cycle-wide emissions of $CO_{2,}$ such as methanol.

Macro-invertebrate
Small creature living in the seabed and subsoil, like earthworms, snails and beetles.

Madrid Protocol
A protocol to the 11th Antarctic Treaty to provide for Antarctica's environmental protection.

Mafic
Term used for silicate minerals, magmas, and rocks, which are relatively high in the heavier elements.

Magmatic activity
The flow of magma (lava).

Marginal cost
Additional cost that arises from the expansion of activity. For example, emission reduction by one additional unit.

Maturation
The geological process of changing with time. For example, the alteration of peat into lignite, then into sub-bituminous and bituminous coal, and then into anthracite.

Mature sedimentary basins
Geological provinces formed by the deposition of particulate matter under water when the deposits have matured into hydrocarbon reserves.

MEA
Mono-ethanolamine

Medium-gravity oil
Oil with a density of between about 850 and 925kg/m^3 (between 20 and 30 API).

Membrane
A sheet or block of material that selectively separates the components of a fluid mixture.

Metamorphic
Of rocks that have been altered by heat or pressure.

Mica
Class of silicate minerals with internal plate structure.

Microseismicity
Small-scale seismic tremors.

Migration
The movement of fluids in reservoir rocks.

Mineral trap
A geological structure in which fluids are retained by the reaction of the fluid to form a stable mineral.

Miscible displacement
Injection process that introduces miscible gases into the reservoir, thereby maintaining reservoir pressure and improving oil displacement.

Mitigation
The process of reducing the impact of any failure.

Monitoring
The process of measuring the quantity of carbon dioxide stored and its location.

Monte Carlo
A modelling technique in which the statistical properties of outcomes are tested by random inputs.

Mudstone
A very fine-grained sedimentary rock formed from mud.

MWh
Megawatt-hour

National Greenhouse Gas Inventory
An inventory of anthropogenic emissions by sources and removals by sinks of greenhouse gases prepared by Parties to the UNFCCC.

Natural analogue
A natural occurrence that mirrors in most essential elements an intended or actual human activity.

Natural underground trap
A geological structure in which fluids are retained by natural processes.

Navier-Stokes equations
The general equations describing the flow of fluids.

Near-field
The region close to a signal source.

NGCC
Natural gas combined cycle: natural-gas-fired power plant with gas and steam turbines.

Non-hazardous waste
Non-harmful substances that have been released or discarded into the environment.

NPV
Net present value: the value of future cash flows discounted to the present at a defined rate of interest.

Numerical approximation
Representation of physico-mathematical laws through linear approximations.

Observation well
A well installed to permit the observation of subsurface conditions.

OECD
Organization for Economic Co-operation and Development

OSPAR
Convention for the Protection of the Marine Environment of the North-East Atlantic, which was adopted at Paris on 22 September 1992.

Outcrop
The point at which a particular stratum reaches the earth's surface.

Overburden
Rocks and sediments above any particular stratum.

Overpressure
Pressure created in a reservoir that exceeds the pressure inherent at the reservoir's depth.

Oxidation
The loss of one or more electrons by an atom, molecule, or ion.

Oxyfuel combustion
Combustion of a fuel with pure oxygen or a mixture of oxygen, water and carbon dioxide.

Packer
A device for sealing off a section of a borehole or part of a borehole.

Partial oxidation
The oxidation of a carbon-containing fuel under conditions that produce a large fraction of CO and hydrogen.

Partial pressure
The pressure that would be exerted by a particular gas in a mixture of gases if the other gases were not present.

$p\mathrm{CO}_2$
The partial pressure (q.v.) of CO_2.

PC
Pulverized coal: usually used in connection with boilers fed with finely ground coal.

Pejus level
The level in the ocean below which the functioning of animals deteriorates significantly.

Pelagic
Relating to, or occurring, or living in, or frequenting, the open ocean.

Perfluorocarbon
Synthetically produced halocarbons containing only carbon and fluorine atoms. They are characterized by extreme stability, non-flammability, low toxicity and high global warming potential.

Permeability
Ability to flow or transmit fluids through a porous solid such as rock.

Permian
A geological age between 290 and 248 million years ago.

Phytotoxic
Poisonous to plants.

Piezo-electric transducer
Crystals or films that are able to convert mechanical energy in electrical energy or vice-versa.

Pig
A device that is driven down pipelines to inspect and/or clean them.

Point source
An emission source that is confined to a single small location

Polygeneration
Production of more than one form of energy, for example synthetic liquid fuels plus electricity.

Pore space
Space between rock or sediment grains that can contain fluids.

Poroelastic
Elastic behaviour of porous media.

Porosity
Measure for the amount of pore space in a rock.

Post-combustion capture
The capture of carbon dioxide after combustion.

POX
Partial oxidation (q.v.)

Pre-combustion capture
The capture of carbon dioxide following the processing of the fuel before combustion.

Primary legal source
Legal source not depending on authority given by others.

Probability density function
Function that describes the probability for a series of parameter values.

Prospectivity
A qualitative assessment of the likelihood that a suitable storage location is present in a given area based on the available information

Proven reserve
For oil declared by operator to be economical; for gas about which a decision has been taken to proceed with development and production; see Resource.

Province
An area with separate but similar geological formations.

PSA
Pressure swing adsorption: a method of separating gases using the physical adsorption of one gas at high pressure and releasing it at low pressure.

Rank
Quality criterion for coal.

Reduction
The gain of one or more electrons by an atom, molecule, or ion

Reduction commitment
A commitment by a Party to the Kyoto Protocol to meet its quantified emission limit.

Reforestation
Planting of forests on lands that have previously contained forests but that have been converted to some other use.

Regional scale
A geological feature that crosses an entire basin.

Remediation
The process of correcting any source of failure.

Renewables
Energy sources that are inherently renewable such as solar energy, hydropower, wind, and biomass.

Rep. Value
Representative value

Reproductive dysfunction
Inability to reproduce.

Reserve
A resource (q.v.) from which it is generally economic to produce valuable minerals or hydrocarbons.

Reservoir
A subsurface body of rock with sufficient porosity and permeability to store and transmit fluids.

Residual saturation
The fraction of the injected CO_2 that is trapped in pores by capillary forces.

Resource
A body of a potentially valuable mineral or hydrocarbon.

Retrofit
A modification of the existing equipment to upgrade and incorporate changes after installation.

Risk assessment
Part of a risk-management system.

Root anoxia
Lack, or deficiency, of oxygen in root zone.

Root zone
Part of the soil in which plants have their roots.

Safe Drinking Water Act
An Act of the US Congress originally passed in 1974. It regulates, among other things, the possible contamination of underground water.

Saline formation
Sediment or rock body containing brackish water or brine.

Saline groundwater
Groundwater in which salts are dissolved.
Sandstone
Sand that has turned into a rock due to geological processes.

Saturated zone
Part of the subsurface that is totally saturated with groundwater.

Scenario
A plausible description of the future based on an internally consistent set of assumptions about key relationships and driving forces. Note that scenarios are neither predictions nor forecasts.

SCR
Selective catalytic reduction

Scrubber
A gas-liquid contacting device for the purification of gases or capture of a gaseous component.

Seabed
Borderline between the free water and the top of the bottom sediment.

Seal
An impermeable rock that forms a barrier above and around a reservoir such that fluids are held in the reservoir.

Secondary recovery
Recovery of oil by artificial means, after natural production mechanisms like overpressure have ceased.

Sedimentary basin
Natural large-scale depression in the earth's surface that is filled with sediments.

Seismic profile
A two-dimensional seismic image of the subsurface.

Seismic technique
Measurement of the properties of rocks by the speed of sound waves generated artificially or naturally.

Seismicity
The episodic occurrence of natural or man-induced earthquakes.

Selexol
A commercial physical absorption process to remove CO_2 using glycol dimethylethers.

Shale
Clay that has changed into a rock due to geological processes.

Shift convertor
A reactor in which the water-gas shift reaction, $CO + H_2O = CO_2 + H_2$, takes place.

Simplex orifice fitting
An apparatus for measuring the flow rate of gases or liquids.

Sink
The natural uptake of CO_2 from the atmosphere, typically in soils, forests or the oceans.

SMR
Steam methane reforming: a catalytic process in which methane reacts with steam to produce a mixture of H_2, CO and CO_2.

SNG
Synthetic natural gas: fuel gas with a high concentration of methane produced from coal or heavy hydrocarbons.

SOFC
Solid oxide fuel cell: a fuel cell (q.v.) in which the electrolyte is a solid ceramic composed of calcium- or yttrium-stabilized zirconium oxides.

Soil gas
Gas contained in the space between soil grains

Solubility trapping
A process in which fluids are retained by dissolution in liquids naturally present.

Sour gas
Natural gas containing significant quantities of acid gases like H_2S and CO_2.

Source
Any process, activity or mechanism that releases a greenhouse gas, an aerosol, or a precursor thereof into the atmosphere.

Speciation
The determination of the number of species into which a single species will divide over time.

Spill point
The structurally lowest point in a structural trap (q.v.) that can retain fluids lighter than background fluids.

Spoil pile
Heap of waste material derived from mining or processing operations.

SRES
Special Report on Emissions Scenarios; used as a basis for the climate projections in the TAR (q.v.).

Stabilization
Relating to the stabilization atmospheric concentrations of greenhouse gases.

Stable geological formation
A formation (q.v.) that has not recently been disturbed by tectonic movement.

Steam reforming
A catalytic process in which a hydrocarbon is reacted with steam to produce a mixture of H_2, CO and CO_2.

Storage
A process for retaining captured CO_2 so that it does not reach the atmosphere.

Strain gauge
Gauge to determine the deformation of an object subjected to stress.

Stratigraphic
The order and relative position of strata.

Stratigraphic column
A column showing the sequence of different strata.

Stratigraphic trap
A sealed geological container capable of retaining fluids, formed by changes in rock type, structure or facies.

Stimulation
The enhancement of the ability to inject fluids into, or recover fluids from, a well.

Stripper
A gas-liquid contacting device, in which a component is transferred from liquid phase to the gas phase.

Structural trap
Geological structure capable of retaining hydrocarbons, sealed structurally by a fault or fold.

Structure
Geological feature produced by the deformation of the Earth's crust, such as a fold or a fault; a feature within a rock such as a fracture; or, more generally, the spatial arrangement of rocks.

Structure contour map
Map showing the contours of geological structures.

Subsoil
Term used in London and OSPAR conventions, meaning the sediments below the seabed.

Sub-bituminous coal
Coal of a rank between lignite (q.v.) and bituminous (q.v.) coal.

Sustainable
Of development, that which is sustainable in ecological, social and economic areas.

Supercritical
At a temperature and pressure above the critical temperature and pressure of the substance concerned. The critical point represents the highest temperature and pressure at which the substance can exist as a vapour and liquid in equilibrium

Syngas
Synthesis gas (q.v.)

Synthesis gas
A gas mixture containing a suitable proportion of CO and H_2 for the synthesis of organic compounds or combustion.

Synfuel
Fuel, typically liquid fuel, produced by processing fossil fuel.

Tail gas
Effluent gas at the end of a process.

Tailing
The waste resulting from the extraction of value from ore.

TAR
Third Assessment Report of the Intergovernmental Panel on Climate Change

TCR
Total capital requirement

Technical Potential
The amount by which it is possible to reduce greenhouse gas emissions by implementing a technology or practice that has reached the demonstration phase.

Tectonically active area
Area of the Earth where deformation is presently causing structural changes.

Tertiary
Geological age about 65 to 2 million years ago.

Tertiary recovery
Oil generated by a third method; the first is by pressure release or depletion, and the second by oil driven out by the injection of water.

Thermocline
The ocean phenomenon characterized by a sharp change in temperature with depth.

Thermohaline
The vertical overturning of water masses due to seasonal heating, evaporation, and cooling.

Top-down model
A model based on applying macro-economic theory and econometric techniques to historical data about consumption, prices, etc.

Toxemia
Poisoning, usually of the blood.

Toxicology
Scientific study of poisons and their effects.

Tracer
A chemical compound or isotope added in small quantities to trace flow patterns.

Transaction cost
The full cost of transferring property or rights between parties.

Trap
A geological structure that physically retains fluids that are lighter than the background fluids, e.g. an inverted cup.

Ultramafic rocks
An igneous rock consisting almost entirely of iron- and magnesium-rich minerals with a silica content typically less than 45%.

UNCLOS
United Nations Convention on the Law of the Sea, which was adopted at Montego Bay on 10 December 1982.

Unconformity
A geological surface separating older from younger rocks and representing a gap in the geological record.

Under-saturated
A solution that could contain more solute than is presently dissolved in it.

UNFCCC
United Nations Framework Convention on Climate Change, which was adopted at New York on 9 May 1992.

Unminable
Extremely unlikely to be mined under current or foreseeable economic conditions

Updip
Inclining upwards following a structural contour of strata.

Upper ocean
The ocean above 1000m depth.

Vacuum residue
The heavy hydrocarbon mixture that is produced at the bottom of vacuum distillation columns in oil refineries.

Vadose zone
Region from the water table to the ground surface, also called the unsaturated zone because it is partially water-saturated.

Validation
In the context of CDM (q.v.), the process of the independent evaluation of a project by a designated operational entity on the basis of set requirements.

Ventilation
The exchange of gases dissolved in sea-water with the atmosphere, or gas exchange between an animal and the environment.

Verification
The proving, to a standard still to be decided, of the results of monitoring (q.v.). In the context of CDM, the independent review by a designated operational entity of monitored reductions in anthropogenic emissions.

Viscous fingering
Flow phenomenon arising from the flow of two largely immiscible fluids through a porous medium.

Well
Manmade hole drilled into the earth to produce liquids or gases, or to allow the injection of fluids.

Well with multiple completions
Well drilled with multiple branching holes and more than one hole being made ready for use.

Well-bore annulus
The annulus between the rock and the well casing.

Wellhead pressure
Pressure developed on surface at the top of the well.

Wettability
Surface with properties allowing water to contact the surface intimately.

Zero-carbon energy carrier
Carbon-free energy carrier, typically electricity or hydrogen.

Annex III

Units

Table AIII.1 Basic SI units

Physical Quantity	Unit	
	Name	**Symbol**
Length	meter	m
Mass	kilogram	kg
Time	second	s
Thermodynamic temperature	kelvin	K
Amount of substance	mole	mol

Table AIII.2 Multiplication factors

Multiple	Prefix	Symbol	Multiple	Prefix	Symbol
10^{-1}	deci	d	10	deca	da
10^{-2}	centi	c	10^{2}	hecto	h
10^{-3}	milli	m	10^{3}	kilo	k
10^{-6}	micro	μ	10^{6}	mega	M
10^{-9}	nano	n	10^{9}	giga	G
10^{-12}	pico	p	10^{12}	tera	T
10^{-15}	femto	f	10^{15}	peta	P

Table AIII.3 Special names and symbols for certain SI-derived units

Physical Quantity	Unit		
	Name	**Symbol**	**Definition**
Force	newton	N	$kg\ m\ s^{-2}$
Pressure	pascal	Pa	$kg\ m^{-1}\ s^{-2}$ (= $N\ m^{-2}$)
Energy	joule	J	$kg\ m^{2}\ s^{-2}$
Power	watt	W	$kg\ m^{2}\ s^{-3}$ (= $J\ s^{-1}$)
Frequency	hertz	Hz	s^{-1} (cycles per second)

Table AIII.4 Decimal fractions and multiples of SI units having special names

	Unit		
Physical quantity	**Name**	**Symbol**	**Definition**
Length	micron	μm	10^{-6} m
Area	hectare	ha	$10^{4}\ m^{2}$
Volume	litre	L	$10^{-3}\ m^{3}$
Pressure	bar	bar	$10^{5}\ N\ m^{-2} = 10^{5}$ Pa
Pressure	millibar	mb	$10^{2}\ N\ m^{-2} = 1$ hPa
Mass	tonne	t	10^{3} kg
Mass	gram	g	10^{-3} kg

Table AIII.5 Other units

Symbol	Description
°C	Degree Celsius (0°C = 273 K approximately) Temperature differences are also given in ºC (= K) rather than the more correct form of 'Celsius degrees'
D	Darcy, unit for permeability, $10^{-12}\ m^{2}$
ppm	Parts per million (10^{6}), mixing ratio (μmol mol^{-1})
ppb	Parts per billion (10^{9}), mixing ratio (nmol mol^{-1})
h	Hour
yr	Year
kWh	Kilowatt hour
MWh	Megawatt hour
$MtCO_2$	Megatonnes (1 Mt = 10^{9} kg = 1 Tg) CO_2
$GtCO_2$	Gigatonnes (1 Gt = 10^{12} kg = 1 Pg) CO_2
$tCO_2\ MWh^{-1}$	tonne CO_2 per megawatt hour
US$ kWh^{-1}	US dollar per kilowatt hour

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Annex V

List of major IPCC reports

LIST OF MAJOR IPCC REPORTS

Climate Change - The IPCC Scientific Assessment
The 1990 report of the IPCC Scientific Assessment Working Group

Climate Change - The IPCC Impacts Assessment
The 1990 report of the IPCC Impacts Assessment Working Group

Climate Change - The IPCC Response Strategies
The 1990 report of the IPCC Response Strategies Working Group

Emissions Scenarios
Prepared by the IPCC Response Strategies Working Group, 1990

Assessment of the Vulnerability of Coastal Areas to Sea Level Rise - A Common Methodology, 1991

Climate Change 1992 - The Supplementary Report to the IPCC Scientific Assessment
The 1992 report of the IPCC Scientific Assessment Working Group

Climate Change 1992 - The Supplementary Report to the IPCC Impacts Assessment
The 1992 report of the IPCC Impacts Assessment Working Group

Climate Change: The IPCC 1990 and 1992 Assessments
IPCC First Assessment Report Overview and Policymaker Summaries, and 1992 IPCC Supplement

Global Climate Change and the Rising Challenge of the Sea
Coastal Zone Management Subgroup of the IPCC Response Strategies Working Group, 1992

Report of the IPCC Country Study Workshop, 1992

Preliminary Guidelines for Assessing Impacts of Climate Change, 1992

IPCC Guidelines for National Greenhouse Gas Inventories (3 volumes), 1994

Climate Change 1994 - Radiative Forcing of Climate Change and An Evaluation of the IPCC IS92 Emission Scenarios

IPCC Technical Guidelines for Assessing Climate Change Impacts and Adaptations
1995

Climate Change 1995 - The Science of Climate Change
– Contribution of Working Group I to the Second Assessment Report

Climate Change 1995 - Scientific-Technical Analyses of Impacts, Adaptations and Mitigation of Climate Change
- Contribution of Working Group II to the Second Assessment Report

Climate Change 1995 - The Economic and Social Dimensions of Climate Change - Contribution of Working Group III to the Second Assessment Report

The IPCC Second Assessment Synthesis of Scientific-Technical Information Relevant to Interpreting Article 2 of the UN Framework Convention on Climate Change, 1995

Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories (3 volumes), 1996

Technologies, Policies and Measuares for Mitigating Climate Change - IPCC Technical Paper 1, 1996

An Introduction to Simple Climate Models Used in the IPCC Second Assessment Report - IPCC Technical Paper 2, 1997

Stabilisation of Atmospheric Greenhouse Gases: Physical, Biological and Socio-Economic Implications - IPCC Technical Paper 3, 1997

Implications of Proposed Co2 Emissions Limitations IPCC Technical Paper 4, 1997

The Regional Impacts of Climate Change: An Assessment of Vulnerability
IPCC Special Report, 1997

Aviation and the Global Atmosphere
IPCC Special Report, 1999

Methodological and Technological Issues in Technology Transfer
IPCC Special Report, 2000

Emissions Scenarios
IPCC Special Report, 2000

Land Use, Land Use Change and Forestry
IPCC Special Report, 2000

Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories
IPCC National Greenhouse Gas Inventories Programme, 2000

Climate Change and Biodiversity - IPCC Technical Paper V, 2002

Climate Change 2001: The Scientific Basis - Contribution of Working Group I to the Third Assessment Report

Climate Change 2001: Impacts, Adaptation & Vulnerability - Contribution of Working Group II to the Third Assessment Report

Climate Change 2001: Mitigation - Contribution of Working Group III to the Third Assessment Report

Climate Change 2001: Synthesis Report

Good Practice Guidance for Land Use, Land-use Change and Forestry
IPCC National Greenhouse Gas Inventories Programme, 2003

Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons
IPCC/TEAP Special Report, 2005