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Capture of CO_2

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EXECUTIVE SUMMARY

The purpose of CO_2 capture is to produce a concentrated stream that can be readily transported to a CO_2 storage site. CO_2 capture and storage is most applicable to large, centralized sources like power plants and large industries. Capture technologies also open the way for large-scale production of low-carbon or carbon-free electricity and fuels for transportation, as well as for small-scale or distributed applications. The energy required to operate CO_2 capture systems reduces the overall efficiency of power generation or other processes, leading to increased fuel requirements, solid wastes and environmental impacts relative to the same type of base plant without capture. However, as more efficient plants with capture become available and replace many of the older less efficient plants now in service, the net impacts will be compatible with clean air emission goals for fossil fuel use. Minimization of energy requirements for capture, together with improvements in the efficiency of energy conversion processes will continue to be high priorities for future technology development in order to minimize overall environmental impacts and cost.

At present, CO_2 is routinely separated at some large industrial plants such as natural gas processing and ammonia production facilities, although these plants remove CO_2 to meet process demands and not for storage. CO_2 capture also has been applied to several small power plants. However, there have been no applications at large-scale power plants of several hundred megawatts, the major source of current and projected CO_2 emissions. There are three main approaches to CO_2 capture, for industrial and power plant applications. *Post-combustion* systems separate CO_2 from the flue gases produced by combustion of a primary fuel (coal, natural gas, oil or biomass) in air. *Oxy-fuel combustion* uses oxygen instead of air for combustion, producing a flue gas that is mainly H_2O and CO_2 and which is readily captured. This is an option still under development. *Pre-combustion* systems process the primary fuel in a reactor to produce separate streams of CO_2 for storage and H_2 which is used as a fuel. Other industrial processes, including processes for the production of low-carbon or carbon-free fuels, employ one or more of these same basic capture methods. The monitoring, risk and legal aspects associated with CO_2 capture systems appear to present no new challenges, as they are all elements of long-standing health, safety and environmental control practice in industry.

For all of the aforementioned applications, we reviewed recent studies of the performance and cost of commercial or near-commercial technologies, as well as that of newer CO_2 capture concepts that are the subject of intense R&D efforts worldwide. For power plants, current commercial CO_2 capture systems can reduce CO_2 emissions by 80-90% kWh^{-1} (85-95% capture efficiency). Across all plant types the cost of electricity production (COE) increases by 12-36 US\$ MWh^{-1} (US\$ 0.012-0.036 kWh^{-1}) over a similar type of plant without capture, corresponding to a 40-85% increase for a supercritical pulverized coal (PC) plant, 35-70% for a natural gas combined cycle (NGCC) plant and 20-55% for an integrated gasification combined cycle (IGCC) plant using bituminous coal. Overall the COE for fossil fuel plants with capture, ranges from 43-86 US\$ MWh^{-1}, with the cost per tonne of CO_2 ranging from 11-57 US\$/tCO_2 captured or 13-74 US\$/tCO_2 avoided (depending on plant type, size, fuel type and a host of other factors). These costs include CO_2 compression but not additional transport and storage costs. NGCC systems typically have a lower COE than new PC and IGCC plants (with or without capture) for gas prices below about 4 US\$ GJ^{-1}. Most studies indicate that IGCC plants are slightly more costly without capture and slightly less costly with capture than similarly sized PC plants, but the differences in cost for plants with CO_2 capture can vary with coal type and other local factors. The lowest CO_2 capture costs (averaging about 12 US\$/t CO_2 captured or 15 US\$/tCO_2 avoided) were found for industrial processes such as hydrogen production plants that produce concentrated CO_2 streams as part of the current production process; such industrial processes may represent some of the earliest opportunities for CO_2 Capture and Storage (CCS). In all cases, CO_2 capture costs are highly dependent upon technical, economic and financial factors related to the design and operation of the production process or power system of interest, as well as the design and operation of the CO_2 capture technology employed. Thus, comparisons of alternative technologies, or the use of CCS cost estimates, require a specific context to be meaningful.

New or improved methods of CO_2 capture, combined with advanced power systems and industrial process designs, can significantly reduce CO_2 capture costs and associated energy requirements. While there is considerable uncertainty about the magnitude and timing of future cost reductions, this assessment suggests that improvements to commercial technologies can reduce CO_2 capture costs by at least 20-30% over approximately the next decade, while new technologies under development promise more substantial cost reductions. Realization of future cost reductions, however, will require deployment and adoption of commercial technologies in the marketplace as well as sustained R&D.

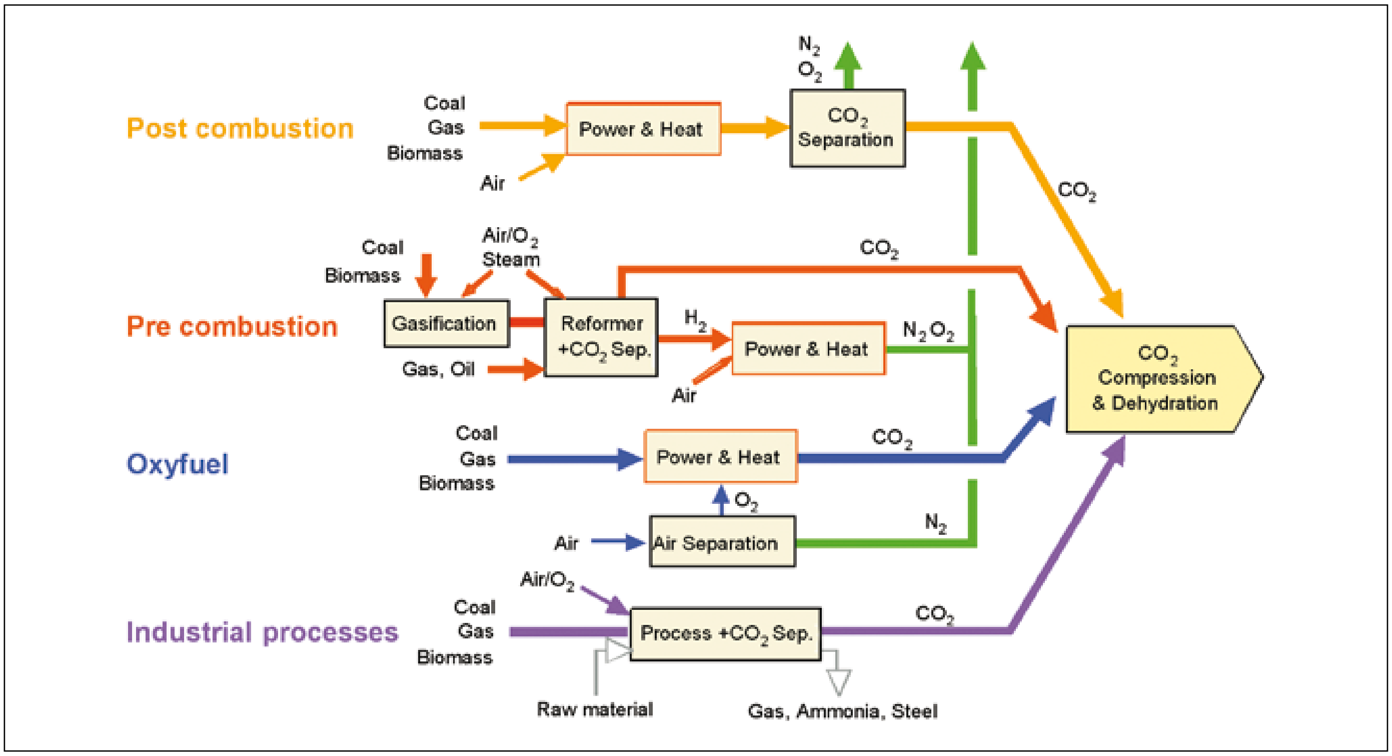

Figure 3.1 CO_2 capture systems (adapted from BP).

3.1 Introduction

3.1.1 *The basis for CO_2 capture*

The main application of CO_2 capture is likely to be at large point sources: fossil fuel power plants, fuel processing plants and other industrial plants, particularly for the manufacture of iron, steel, cement and bulk chemicals, as discussed in Chapter 2.

Capturing CO_2 directly from small and mobile sources in the transportation and residential & commercial building sectors is expected to be more difficult and expensive than from large point sources. Small-scale capture is therefore not further discussed in this chapter. An alternative way of avoiding emissions of CO_2 from these sources would be by use of energy carriers such as hydrogen or electricity produced in large fossil fuel-based plants with CO_2 capture or by using renewable energy sources. Production of hydrogen with CO_2 capture is included in this chapter.

The possibility of CO_2 capture from ambient air (Lackner, 2003) is not discussed in this chapter because the CO_2 concentration in ambient air is around 380 ppm, a factor of 100 or more lower than in flue gas. Capturing CO_2 from air by the growth of biomass and its use in industrial plants with CO_2 capture is more cost-effective based on foreseeable technologies, and is included in this chapter.

In an analysis of possible future scenarios for anthropogenic greenhouse-gas emissions it is implicit that technological innovations will be one of the key factors which determines our future path (Section 2.5.3). Therefore this chapter deals not only with application of existing technology for CO_2 capture, but describes many new processes under development which may result in lower CO_2 capture costs in future.

3.1.2 *CO_2 capture systems*

There are four basic systems for capturing CO_2 from use of fossil fuels and/or biomass:

- Capture from industrial process streams (described in Section 3.2);
- Post-combustion capture (described in Section 3.3);
- Oxy-fuel combustion capture (described in Section 3.4);
- Pre-combustion capture (described in Section 3.5).

These systems are shown in simplified form in Figure 3.1.

3.1.2.1 *Capture from industrial process streams*

CO_2 has been captured from industrial process streams for 80 years (Kohl and Nielsen, 1997), although most of the CO_2 that is captured is vented to the atmosphere because there is no incentive or requirement to store it. Current examples of CO_2 capture from process streams are purification of natural gas and production of hydrogen-containing synthesis gas for the manufacture of ammonia, alcohols and synthetic liquid fuels. Most of the techniques employed for CO_2 capture in the examples mentioned are also similar to those used in pre-combustion capture. Other industrial process streams which are a source of CO_2 that is not captured include cement and steel production, and fermentation processes for food and drink production. CO_2 could be captured from these streams using techniques that are common to post-combustion capture, oxy-fuel combustion capture and pre-combustion capture (see below and Section 3.2).

3.1.2.2 Post-combustion capture

Capture of CO_2 from flue gases produced by combustion of fossil fuels and biomass in air is referred to as post-combustion capture. Instead of being discharged directly to the atmosphere, flue gas is passed through equipment which separates most of the CO_2. The CO_2 is fed to a storage reservoir and the remaining flue gas is discharged to the atmosphere. A chemical sorbent process as described in Section 3.1.3.1 would normally be used for CO_2 separation. Other techniques are also being considered but these are not at such an advanced stage of development.

Besides industrial applications, the main systems of reference for post-combustion capture are the current installed capacity of 2261 GW_e of oil, coal and natural gas power plants (IEA WEO, 2004) and in particular, 155 GW_e of supercritical pulverized coal fired plants (IEA CCC, 2005) and 339 GW_e of natural gas combined cycle (NGCC) plants, both representing the types of high efficiency power plant technology where CO_2 capture can be best applied (see Sections 3.3 and 3.7).

3.1.2.3 Oxy-fuel combustion capture

In oxy-fuel combustion, nearly pure oxygen is used for combustion instead of air, resulting in a flue gas that is mainly CO_2 and H_2O. If fuel is burnt in pure oxygen, the flame temperature is excessively high, but CO_2 and/or H_2O-rich flue gas can be recycled to the combustor to moderate this. Oxygen is usually produced by low temperature (cryogenic) air separation and novel techniques to supply oxygen to the fuel, such as membranes and chemical looping cycles are being developed. The power plant systems of reference for oxy-fuel combustion capture systems are the same as those noted above for post-combustion capture systems.

3.1.2.4 Pre-combustion capture

Pre-combustion capture involves reacting a fuel with oxygen or air and/or steam to give mainly a 'synthesis gas (syngas)' or 'fuel gas' composed of carbon monoxide and hydrogen. The carbon monoxide is reacted with steam in a catalytic reactor, called a shift converter, to give CO_2 and more hydrogen. CO_2 is then separated, usually by a physical or chemical absorption process, resulting in a hydrogen-rich fuel which can be used in many applications, such as boilers, furnaces, gas turbines, engines and fuel cells. These systems are considered to be strategically important (see Section 3.5) but the power plant systems of reference today are 4 GW_e of both oil and coal-based, integrated gasification combined cycles (IGCC) which are around 0.1% of total installed capacity worldwide (3719 GW_e; IEA WEO, 2004). Other reference systems for the application of pre-combustion capture include substantially more capacity than that identified above for IGCC in existing natural gas, oil and coal-based syngas/hydrogen production facilities and other types of industrial systems described in more detail in Sections 3.2 and 3.5.

3.1.3 Types of CO_2 capture technologies

CO_2 capture systems use many of the known technologies for gas separation which are integrated into the basic systems for CO_2 capture identified in the last section. A summary of these separation methods is given below while further details are available in standard textbooks.

3.1.3.1 Separation with sorbents/solvents

The separation is achieved by passing the CO_2-containing gas in intimate contact with a liquid absorbent or solid sorbent that is capable of capturing the CO_2. In the general scheme of Figure 3.2a, the sorbent loaded with the captured CO_2 is transported to a different vessel, where it releases the CO_2 (regeneration) after being heated, after a pressure decrease or after any other change in the conditions around the sorbent. The sorbent resulting after the regeneration step is sent back to capture more CO_2 in a cyclic process. In some variants of this scheme the sorbent is a solid and does not circulate between vessels because the sorption and regeneration are achieved by cyclic changes (in pressure or temperature) in the vessel where the sorbent is contained. A make-up flow of fresh sorbent is always required to compensate for the natural decay of activity and/or sorbent losses. In some situations, the sorbent may be a solid oxide which reacts in a vessel with fossil fuel or biomass producing heat and mainly CO_2 (see Section 3.4.6). The spent sorbent is then circulated to a second vessel where it is re-oxidized in air for reuse with some loss and make up of fresh sorbent.

The general scheme of Figure 3.2 governs many important CO_2 capture systems, including leading commercial options like chemical absorption and physical absorption and adsorption. Other emerging processes based on new liquid sorbents, or new solid regenerable sorbents are being developed with the aim of overcoming the limitations of the existing systems. One common problem of these CO_2 capture systems is that the flow of sorbent between the vessels of Figure 3.2a is large because it has to match the huge flow of CO_2 being processed in the power plant. Therefore, equipment sizes and the energy required for sorbent regeneration are large and tend to translate into an important efficiency penalty and added cost. Also, in systems using expensive sorbent materials there is always a danger of escalating cost related to the purchase of the sorbent and the disposal of sorbent residues. Good sorbent performance under high CO_2 loading in many repetitive cycles is obviously a necessary condition in these CO_2 capture systems.

3.1.3.2 Separation with membranes

Membranes (Figure 3.2b) are specially manufactured materials that allow the selective permeation of a gas through them. The selectivity of the membrane to different gases is intimately related to the nature of the material, but the flow of gas through the membrane is usually driven by the pressure difference across the membrane. Therefore, high-pressure streams are usually preferred for membrane separation. There are many different types of membrane materials (polymeric, metallic, ceramic) that may find application in CO_2 capture systems to

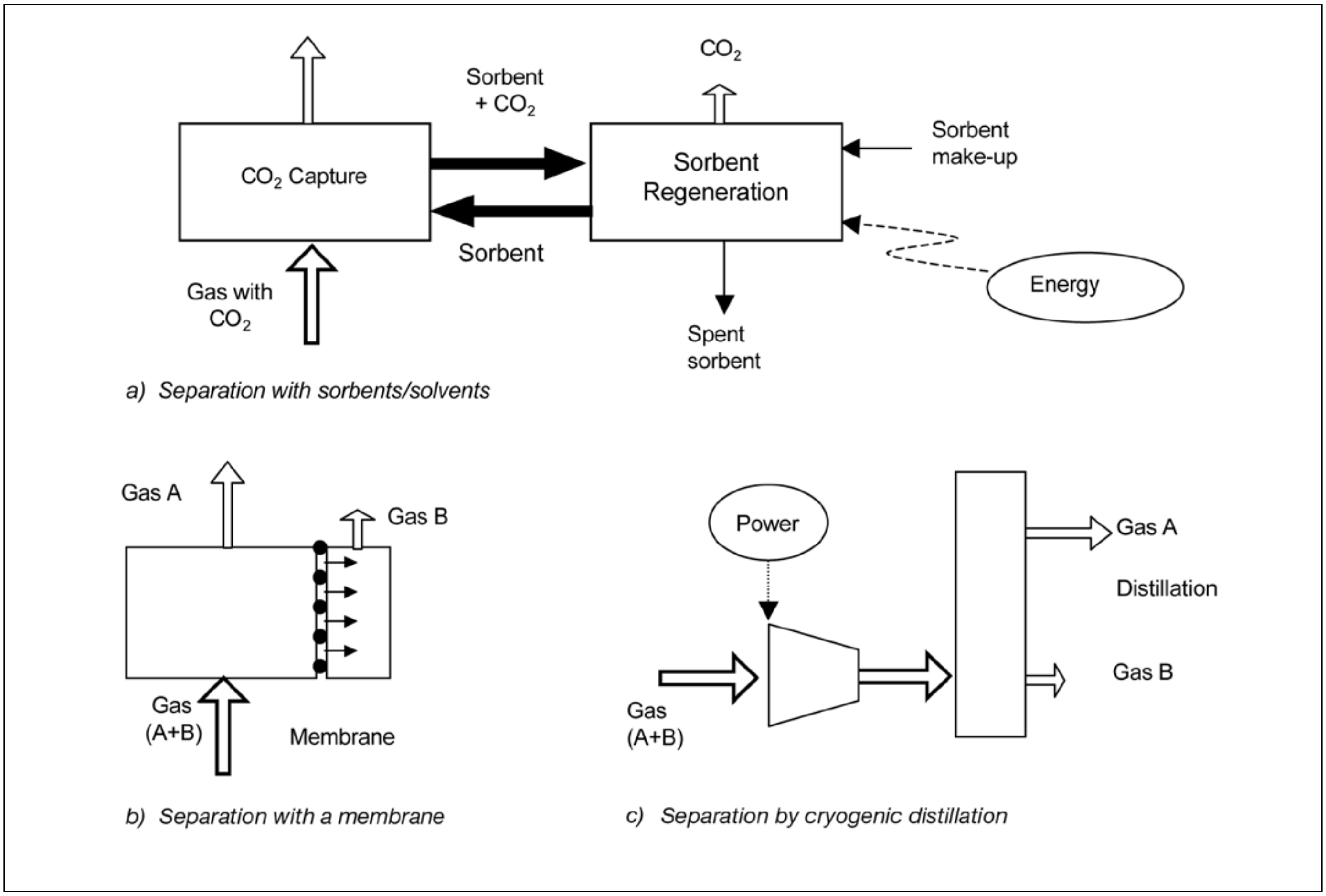

Figure 3.2 General schemes of the main separation processes relevant for CO_2 capture. The gas removed in the separation may be CO_2, H_2 or O_2. In Figures 3.2b and 3.2c one of the separated gas streams (A and B) is a concentrated stream of CO_2, H_2 or O_2 and the other is a gas stream with all the remaining gases in the original gas (A+B).

preferentially separate H_2 from a fuel gas stream, CO_2 from a range of process streams or O_2 from air with the separated O_2 subsequently aiding the production of a highly concentrated CO_2 stream. Although membrane separation finds many current commercial applications in industry (some of a large scale, like CO_2 separation from natural gas) they have not yet been applied for the large scale and demanding conditions in terms of reliability and low-cost required for CO_2 capture systems. A large worldwide R&D effort is in progress aimed at the manufacture of more suitable membrane materials for CO_2 capture in large-scale applications.

3.1.3.3 Distillation of a liquefied gas stream and refrigerated separation

A gas can be made liquid by a series of compression, cooling and expansion steps. Once in liquid form, the components of the gas can be separated in a distillation column. In the case of air, this operation is currently carried out commercially on a large scale. Oxygen can be separated from air following the scheme of Figure 3.2c and be used in a range of CO_2 capture systems (oxy-fuel combustion and pre-combustion capture). As in the previous paragraphs, the key issue for these systems is the large flow of oxygen required. Refrigerated separation can also be used to separate CO_2 from other gases. It can be used to separate impurities from relatively high purity CO_2 streams, for example, from oxy-fuel combustion and for CO_2 removal from natural gas or synthesis gas that has undergone a shift conversion of CO to CO_2.

3.1.4 Application of CO_2 capture

The CO_2 capture systems shown in Figure 3.1 can be cross-referenced with the different separation technologies of Figure 3.2, resulting in a capture toolbox. Table 3.1 gives an overview of both current and emerging technologies in this toolbox. In the next sections of this chapter a more detailed description of all these technological options will be given, with more emphasis on the most developed technologies for which the CO_2 capture cost can be estimated most reliably. These leading commercial options are shown in bold in Table 3.1. An overview of the diverse range of emerging options being investigated worldwide for CO_2 capture applications will also be provided. All of these options are aimed at more efficient and lower cost CO_2-capture systems (compared with the leading options). It is important

Table 3.1 Capture toolbox.

Separation task	**Process streams[a]**		**Post-combustion capture**		**Oxy-fuel combustion capture**		**Pre-combustion capture**	
	CO_2/CH_4		**CO_2/N_2**		**O_2/N_2**		**CO_2/H_2**	
Capture Technologies	**Current**	**Emerging**	**Current**	**Emerging**	**Current**	**Emerging**	**Current**	**Emerging**
Solvents (Absorption)	**Physical solvents** **Chemical solvents**	Improved solvents Novel contacting equipment Improved design of processes	**Chemical solvents**	Improved solvents Novel contacting equipment Improved design of processes	n. a.	Biomimetic solvents, e.g. hemoglobine-derivatives	**Physical solvent** **Chemical solvents**	Improved chemical solvents Novel contacting equipment Improved design of processes
Membranes	**Polymeric**	Ceramic Facilitated transport Carbon Contactors	Polymeric	Ceramic Facilitated transport Carbon Contactors	Polymeric	Ion transport membranes Facilitated transport	Polymeric	Ceramic Palladium Reactors Contactors
Solid sorbents	Zeolites Activated carbon		Zeolites Activated carbon	Carbonates Carbon based sorbents	Zeolites Activated carbon	Adsorbents for O_2/N_2 separation, Perovskites Oxygen chemical looping	Zeolites Activated carbon Alumina	Carbonates Hydrotalcites Silicates
Cryogenic	Ryan-Holmes process		Liquefaction	Hybrid processes	**Distillation**	Improved distillation	Liquefaction	Hybrid processes

[a] Notes: Processes shown in bold are commercial processes that are currently preferred in most circumstances. Some process streams involve CO_2/H_2 or CO_2/N_2 separations but this is covered under pre-combustion capture and post-combustion capture. The key separation processes are outlined in Section 3.1.3 and described in Sections 3.2-3.5.

to understand that this wide variety of approaches for CO_2 capture will tend to settle with time as the expected benefits (and potential weaknesses) in the technological portfolio of Table 3.1 becomes obvious with new results from current and future research and demonstration projects. Only a few of these options will prove truly cost-effective in the medium to long term.

CO_2 capture may be installed in new energy utilization plants or it may be retrofitted to existing plants. In principle, if CO_2 capture is to be introduced rapidly, it may have to be retrofitted to some existing plants or these plants would have to be retired prematurely and replaced by new plants with capture. Disadvantages of retrofits are:

- There may be site constraints such as availability of land for the capture equipment;
- A long remaining plant life may be needed to justify the large expense of installing capture equipment;
- Old plants tend to have low energy efficiencies. Including CO_2 capture will have a proportionally greater impact on the net output than in high efficiency plants.

To minimize the site constraints, new energy utilization plants could be built ‘capture-ready’, that is with the process design initially factoring in the changes necessary to add capture and with sufficient space and facilities made available for simple installation of CO_2 capture at a later date. For some types of capture retrofit, for example pre-combustion capture and oxy-fuel combustion, much of the retrofit equipment could be built on a separate site if necessary.

The other barriers could be largely overcome by upgrading or substantially rebuilding the existing plant when capture is retrofitted. For example, old inefficient boilers and steam turbines could be replaced by modern, high-efficiency supercritical boilers and turbines or IGCC plants. As the efficiencies of power generation technologies are increasing, the efficiency of the retrofitted plant with CO_2 capture could be as high as that of the original plant without capture.

3.2 Industrial process capture systems

3.2.1 Introduction

There are several industrial applications involving process streams where the opportunity exists to capture CO_2 in large quantities and at costs lower than from the systems described in the rest of this chapter. Capture from these sources will not be the complete answer to the needs of climate change, since the volumes of combustion-generated CO_2 are much higher, but it may well be the place where the first capture and storage occurs.

3.2.2 Natural gas sweetening

Natural gas contains different concentration levels of CO_2, depending on its source, which must be removed. Often pipeline specifications require that the CO_2 concentration be lowered to around 2% by volume (although this amount varies in different places) to prevent pipeline corrosion, to avoid excess energy for transport and to increase the heating value of the gas. Whilst accurate figures are published for annual worldwide natural gas production (BP, 2004), none seem to be published on how much of that gas may contain CO_2. Nevertheless, a reasonable assumption is that about half of raw natural gas production contains CO_2 at concentrations averaging at least 4% by volume. These figures can be used to illustrate the scale of this CO_2 capture and storage opportunity. If half of the worldwide production of 2618.5 billion m^3 of natural gas in 2003 is reduced in CO_2 content from 4 to 2% mol, the resultant amount of CO_2 removed would be at least 50 Mt CO_2 yr^{-1}. It is interesting to note that there are two operating natural gas plants capturing and storing CO_2, BP's In Salah plant in Algeria and a Statoil plant at Sleipner in the North Sea. Both capture about 1 $MtCO_2$ yr^{-1} (see Chapter 5). About 6.5 million tCO_2 yr^{-1} from natural gas sweetening is also currently being used in enhanced oil recovery (EOR) in the United States (Beecy and Kuuskraa, 2005) where in these commercial EOR projects, a large fraction of the injected CO_2 is also retained underground (see Chapter 5).

Depending on the level of CO_2 in natural gas, different processes for natural gas sweetening (i.e., H_2S and CO_2 removal) are available (Kohl and Nielsen, 1997 and Maddox and Morgan, 1998):

- Chemical solvents
- Physical solvents
- Membranes

Natural gas sweetening using various alkanolamines (MEA, DEA, MDEA, etc.; See Table 3.2), or a mixture of them, is the most commonly used method. The process flow diagram for CO_2 recovery from natural gas is similar to what is presented for flue gas treatment (see Figure 3.4, Section 3.3.2.1), except that in natural gas processing, absorption occurs at high pressure, with subsequent expansion before the stripper column, where CO_2 will be flashed and separated. When the CO_2 concentration in natural gas is high, membrane systems may be more economical. Industrial application of membranes for recovery of CO_2 from natural gas started in the early 1980s for small units, with many design parameters unknown (Noble and Stern, 1995). It is now a well-established and competitive technology with advantages compared to other technologies, including amine treatment in certain cases (Tabe-Mohammadi, 1999). These advantages include lower capital cost, ease of skid-mounted installation, lower energy consumption, ability to be applied in remote areas, especially offshore and flexibility.

3.2.3 *Steel production*

The iron and steel industry is the largest energy-consuming manufacturing sector in the world, accounting for 10-15% of total industrial energy consumption (IEA GHG, 2000a). Associated CO_2 emissions were estimated at 1442 $MtCO_2$ in 1995. Two types of iron- and steel-making technologies are in operation today. The integrated steel plant has a typical capacity of 3-5 Mtonnes yr^{-1} of steel and uses coal as its basic fuel with, in many cases, additional natural gas and oil. The mini-mill uses electric arc furnaces to melt scrap with a typical output of 1 Mtonnes yr^{-1} of steel and an electrical consumption of 300-350 kWh $tonne^{-1}$ steel. Increasingly mini-mills blend direct-reduced iron (DRI) with scrap to increase steel quality. The production of direct-reduced iron involves reaction of high oxygen content iron ore with H_2 and CO to form reduced iron plus H_2O and CO_2. As a result, many of the direct reduction iron processes could capture a pure CO_2 stream.

An important and growing trend is the use of new iron-making processes, which can use lower grade coal than the coking coals required for blast furnace operation. A good example is the COREX process (von Bogdandy *et. al*, 1989), which produces a large additional quantity of N_2-free fuel gas which can be used in a secondary operation to convert iron ore to iron. Complete CO_2 capture from this process should be possible with this arrangement since the CO_2 and H_2O present in the COREX top gas must be removed to allow the CO plus H_2 to be heated and used to reduce iron oxide to iron in the secondary shaft kiln. This process will produce a combination of molten iron and iron with high recovery of CO_2 derived from the coal feed to the COREX process.

Table 3.2 Common solvents used for the removal of CO_2 from natural gas or shifted syngas in pre-combustion capture processes.

Solvent name	Type	Chemical name	Vendors
Rectisol	Physical	Methanol	Lurgi and Linde, Germany Lotepro Corporation, USA
Purisol	Physical	N-methyl-2-pyrolidone (NMP)	Lurgi, Germany
Selexol	Physical	Dimethyl ethers of polyethylene glycol (DMPEG)	Union Carbide, USA
Benfield	Chemical	Potassium carbonate	UOP
MEA	Chemical	Monoethanolamine	Various
MDEA	Chemical	Methyldiethylamine	BASF and others
Sulfinol	Chemical	Tetrahydrothiophene 1,1-dioxide (Sulfolane), an alkaloamine and water	Shell

Early opportunities exist for the capture of CO_2 emissions from the iron and steel industry, such as:

- CO_2 recovery from blast furnace gas and recycle of CO-rich top gas to the furnace. A minimum quantity of coke is still required and the blast furnace is fed with a mixture of pure O_2 and recycled top gas. The furnace is, in effect, converted from air firing to oxy-fuel firing with CO_2 capture (see Section 3.4). This would recover 70% of the CO_2 currently emitted from an integrated steel plant (Dongke et al., 1988). It would be feasible to retrofit existing blast furnaces with this process.
- Direct reduction of iron ore, using hydrogen derived from a fossil fuel in a pre-combustion capture step (see Section 3.5) (Duarte and Reich, 1998). Instead of the fuel being burnt in the furnace and releasing its CO_2 to atmosphere, the fuel would be converted to hydrogen and the CO_2 would be captured during that process. The hydrogen would then be used as a reduction agent for the iron ore. Capture rates should be 90-95% according to the design of the pre-combustion capture technique (see Section 3.5).

Other novel process routes for steel making to which CO_2 capture can be applied are currently in the research and development phase (Gielen, 2003; IEA, 2004)

3.2.4 Cement production

Emissions of CO_2 from the cement industry account for 6% of the total emissions of CO_2 from stationary sources (see Chapter 2). Cement production requires large quantities of fuel to drive the high temperature, energy-intensive reactions associated with the calcination of the limestone – that is calcium carbonate being converted to calcium oxide with the evolution of CO_2.

At present, CO_2 is not captured from cement plants, but possibilities do exist. The concentration of CO_2 in the flue gases is between 15-30% by volume, which is higher than in flue gases from power and heat production (3-15% by volume). So, in principle, the post-combustion technologies for CO_2 capture described in Section 3.3 could be applied to cement production plants, but would require the additional generation of steam in a cement plant to regenerate the solvent used to capture CO_2. Oxy-fuel combustion capture systems may also become a promising technique to recover CO_2 (IEA GHG, 1999). Another emerging option would be the use of calcium sorbents for CO_2 capture (see Sections 3.3.3.4 and 3.5.3.5) as calcium carbonate (limestone) is a raw material already used in cement plants. All of these capture techniques could be applied to retrofit, or new plant applications.

3.2.5 Ammonia production

CO_2 is a byproduct of ammonia (NH_3) production (Leites *et al.*, 2003); Two main groups of processes are used:

- Steam reforming of light hydrocarbons (natural gas, liquefied petroleum gas, naphtha)
- Partial oxidation or gasification of heavy hydrocarbons (coal, heavy fuel oil, vacuum residue).

Around 85% of ammonia is made by processes in the steam methane reforming group and so a description of the process is useful. Although the processes vary in detail, they all comprise the following steps:

1. Purification of the feed;
2. Primary steam methane reforming (see Section 3.5.2.1);
3. Secondary reforming, with the addition of air, commonly called auto thermal reforming (see Section 3.5.2.3);
4. Shift conversion of CO and H_2O to CO_2 and H_2;
5. Removal of CO_2;
6. Methanation (a process that reacts and removes trace CO and CO_2);
7. Ammonia synthesis.

The removal of CO_2 as a pure stream is of interest to this report. A typical modern plant will use the amine solvent process to treat 200,000 $Nm^3\ h^{-1}$ of gas from the reformer, to produce 72 tonnes h^{-1} of concentrated CO_2 (Apple, 1997). The amount of CO_2 produced in modern plants from natural gas is about 1.27 tCO_2/tNH_3. Hence, with a world ammonia production of about 100 Mtonnes yr^{-1}, about 127 $MtCO_2\ yr^{-1}$ is produced. However, it should be noted that this is not all available for storage, as ammonia plants are frequently combined with urea plants, which are capable of utilizing 70-90% of the CO_2. About 0.7 $MtCO_2\ yr^{-1}$captured from ammonia plants is currently used for enhanced oil recovery in the United States (Beecy and Kuuskraa, 2005) with a large fraction of the injected CO_2 being retained underground (see Chapter 5) in these commercial EOR projects.

3.2.6 Status and outlook

We have reviewed processes – current and potential - that may be used to separate CO_2 in the course of producing another product. One of these processes, natural gas sweetening, is already being used in two industrial plants to capture and store about 2 $MtCO_2\ yr^{-1}$ for the purpose of climate change mitigation. In the case of ammonia production, pure CO_2 is already being separated. Over 7 $MtCO_2\ yr^{-1}$ captured from both natural gas sweetening and ammonia plants is currently being used in enhanced oil recovery with some storage (see also Chapter 5) of the injected CO_2 in these commercial EOR projects. Several potential processes for CO_2 capture in steel and cement production exist, but none have yet been applied. Although the total amount of CO_2 that may be captured from these industrial processes is insignificant in terms of the scale of the climate change challenge, significance may arise in that their use could serve as early examples of solutions that can be applied on larger scale elsewhere.

3.3 Post-combustion capture systems

3.3.1 Introduction

Current anthropogenic CO_2 emissions from stationary sources come mostly from combustion systems such as power plants, cement kilns, furnaces in industries and iron and steel production plants (see Chapter 2). In these large-scale processes, the direct firing of fuel with air in a combustion chamber has been (for centuries, as it is today) the most economic technology to extract and use the energy contained in the fuel. Therefore, the strategic importance of post-combustion capture systems becomes evident when confronted with the reality of today's sources of CO_2 emissions. Chapter 2 shows that any attempt to mitigate CO_2 emissions from stationary sources on a relevant scale using CO_2 capture and storage, will have to address CO_2 capture from combustion systems. All the CO_2 capture systems described in this section are aimed at the separation of CO_2 from the flue gases generated in a large-scale combustion process fired with fossil fuels. Similar capture systems can also be applied to biomass fired combustion processes that tend to be used on a much smaller scale compared to those for fossil fuels.

Flue gases or stack gases found in combustion systems are usually at atmospheric pressure. Because of the low pressure, the large presence of nitrogen from air and the large scale of the units, huge flows of gases are generated, the largest example of which may be the stack emissions coming from a natural gas combined cycle power plant having a maximum capacity of around 5 million normal $m^3 h^{-1}$. CO_2 contents of flue gases vary depending on the type of fuel used (between 3% for a natural gas combined cycle to less than 15% by volume for a coal-fired combustion plant See Table 2.1). In principle post-combustion capture systems can be applied to flue gases produced from the combustion of any type of fuel. However, the impurities in the fuel are very important for the design and costing of the complete plant (Rao and Rubin, 2002). Flue gases coming from coal combustion will contain not only CO_2, N_2, O_2 and H_2O, but also air pollutants such as SO_x, NO_x, particulates, HCl, HF, mercury, other metals and other trace organic and inorganic contaminants. Figure 3.3 shows a general schematic of a coal-fired power plant in which additional unit operations are deployed to remove the air pollutants prior to CO_2 capture in an absorption-based process. Although capture of CO_2 in these flue gases is in principle more problematic and energy intensive than from other gas streams, commercial experience is available at a sufficiently large scale (see Section 3.3.2) to provide the basis for cost estimates for post-combustion CO_2 capture systems (see Section 3.7). Also, a large R&D effort is being undertaken worldwide to develop more efficient and lower cost post-combustion systems (see Section 3.3.3), following all possible approaches for the CO_2 separation step (using sorbents, membranes or cryogenics; see Section 3.1.3).

3.3.2 Existing technologies

There are several commercially available process technologies which can in principle be used for CO_2 capture from flue gases. However, comparative assessment studies (Hendriks, 1994; Riemer and Ormerod, 1995; IEA GHG, 2000b) have shown that absorption processes based on chemical solvents are currently the preferred option for post-combustion CO_2 capture. At this point in time, they offer high capture efficiency and selectivity, and the lowest energy use and costs when compared with other existing post-combustion capture processes. Absorption processes have reached the commercial stage of operation for post-combustion CO_2 capture systems, albeit not on the scale required for power plant flue gases. Therefore, the following paragraphs are devoted to a review of existing knowledge of the technology and the key technical and environmental issues relevant to the application of this currently leading commercial option for CO_2 capture. The fundamentals of the CO_2 separation step using commercial chemical absorption processes are discussed first. The requirements of flue gas pretreatment (removal of pollutants other than CO_2) and the energy requirements for regeneration of the chemical solvent follow.

3.3.2.1 Absorption processes

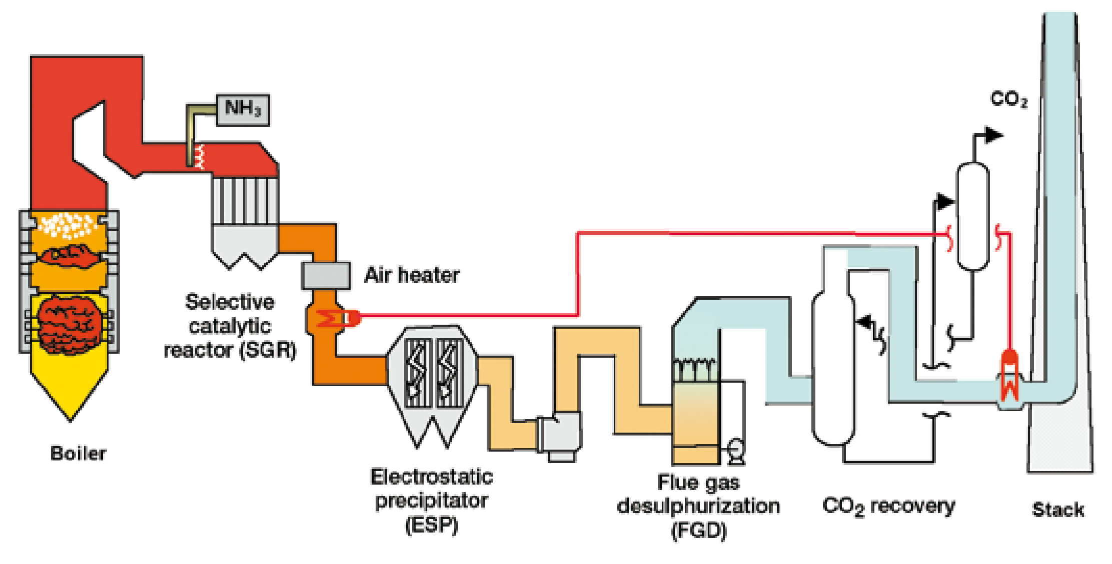

Figure 3.3 Schematic of a pulverized coal-fired power plant with an amine-based CO_2 capture system and other emission controls.

Absorption processes in post-combustion capture make use of the reversible nature of the chemical reaction of an aqueous alkaline solvent, usually an amine, with an acid or sour gas. The process flow diagram of a commercial absorption system is presented in Figure 3.4. After cooling the flue gas, it is brought into contact with the solvent in the absorber. A blower is required to overcome the pressure drop through the absorber. At absorber temperatures typically between 40 and 60°C, CO_2 is bound by the chemical solvent in the absorber. The flue gas then undergoes a water wash section to balance water in the system and to remove any solvent droplets or solvent vapour carried over, and then it leaves the absorber. It is possible to reduce CO_2 concentration in the exit gas down to very low values, as a result of the chemical reaction in the solvent, but lower exit concentrations tend to increase the height of the absorption vessel. The 'rich' solvent, which contains the chemically bound CO_2 is then pumped to the top of a stripper (or regeneration vessel), via a heat exchanger. The regeneration of the chemical solvent is carried out in the stripper at elevated temperatures (100°C–140°C) and pressures not very much higher than atmospheric pressure. Heat is supplied to the reboiler to maintain the regeneration conditions. This leads to a thermal energy penalty as a result of heating up the solvent, providing the required desorption heat for removing the chemically bound CO_2 and for steam production which acts as a stripping gas. Steam is recovered in the condenser and fed back to the stripper, whereas the CO_2 product gas leaves the stripper. The 'lean' solvent, containing far less CO_2 is then pumped back to the absorber via the lean-rich heat exchanger and a cooler to bring it down to the absorber temperature level.

Figure 3.4 also shows some additional equipment needed to maintain the solution quality as a result of the formation of degradation products, corrosion products and the presence of particles. This is generally done using filters, carbon beds and a thermally operated reclaimer. Control of degradation and corrosion has in fact been an important aspect in the development of absorption processes over the past few decades.

The key parameters determining the technical and economic operation of a CO_2 absorption system are:

- *Flue gas flow rate* - The flue gas flow rate will determine the size of the absorber and the absorber represents a sizeable contribution to the overall cost.
- *CO_2 content in flue gas* - Since flue gas is usually at atmospheric pressure, the partial pressure of CO_2 will be as low as 3-15 kPa. Under these low CO_2 partial pressure conditions, aqueous amines (chemical solvents) are the most suitable absorption solvents (Kohl and Nielsen, 1997).
- *CO_2 removal* - In practice, typical CO_2 recoveries are between 80% and 95%. The exact recovery choice is an economic trade-off, a higher recovery will lead to a taller absorption column, higher energy penalties and hence increased costs.
- *Solvent flow rate* - The solvent flow rate will determine the size of most equipment apart from the absorber. For a given solvent, the flow rate will be fixed by the previous parameters and also the chosen CO_2 concentrations within the lean and the rich solutions.
- *Energy requirement* - The energy consumption of the process is the sum of the thermal energy needed to regenerate the solvents and the electrical energy required to operate liquid pumps and the flue gas blower or fan. Energy is also required to compress the CO_2 recovered to the final pressure required for transport and storage.

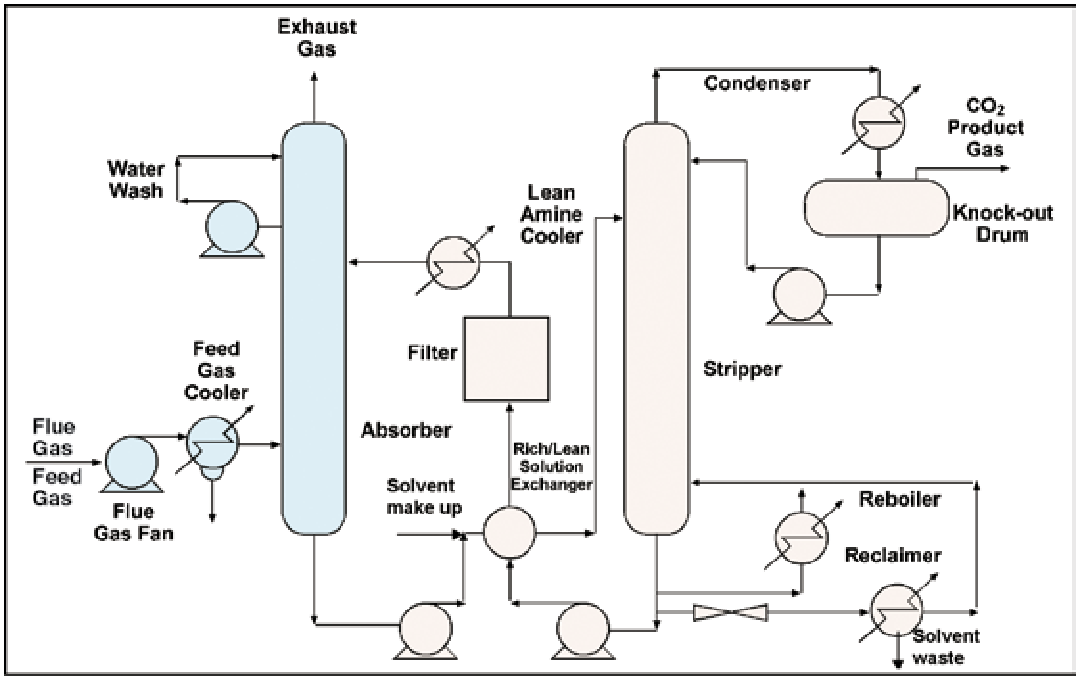

Figure 3.4 Process flow diagram for CO_2 recovery from flue gas by chemical absorption.

- Cooling requirement - Cooling is needed to bring the flue gas and solvent temperatures down to temperature levels required for efficient absorption of CO_2. Also, the product from the stripper will require cooling to recover steam from the stripping process.

The purity and pressure of CO_2 typically recovered from an amine-based chemical absorption process are as follows (Sander and Mariz, 1992):

- CO_2 purity: 99.9% by volume or more (water saturated conditions)
- CO_2 pressure: 50 kPa (gauge)

A further CO_2 purification step makes it possible to bring the CO_2-quality up to food-grade standard. This is required for use in beverages and packaging.

Since combustion flue gases are generally at atmospheric pressure and the CO_2 is diluted, the CO_2 partial pressure is very low. Also, flue gas contains oxygen and other impurities; therefore an important characteristic of an absorption process is in the proper choice of solvent for the given process duty. High CO_2 loading and low heat of desorption energy are essential for atmospheric flue gas CO_2 recovery. The solvents must also have low byproduct formation and low decomposition rates, to maintain solvent performance and to limit the amount of waste materials produced. The important effect of other contaminants on the solvent is discussed in Section 3.3.2.2.

The following three absorption processes are commercially available for CO_2 capture in post-combustion systems:

- The Kerr-McGee/ABB Lummus Crest Process (Barchas and Davis, 1992) - This process recovers CO_2 from coke and coal-fired boilers, delivering CO_2 for soda ash and liquid CO_2 preparations. It uses a 15-20% by weight aqueous MEA (Mono-Ethanolamine) solution. The largest capacity experienced for this process is 800 $tCO_2\ d^{-1}$utilizing two parallel trains (Arnold *et al*., 1982).
- The Fluor Daniel ® ECONAMINE™ Process (Sander and Mariz, 1992, Chapel *et al*., 1999) - This process was acquired by Fluor Daniel Inc. from Dow Chemical Company in 1989. It is a MEA-based process (30% by weight aqueous solution) with an inhibitor to resist carbon steel corrosion and is specifically tailored for oxygen-containing gas streams. It has been used in many plants worldwide recovering up to 320 $tCO_2\ d^{-1}$ in a single train for use in beverage and urea production.
- The Kansai Electric Power Co., Mitsubishi Heavy Industries, Ltd., KEPCO/MHI Process (Mimura *et al*., 1999 and 2003) - The process is based upon sterically-hindered amines and already three solvents (KS-1, KS-2 and KS-3) have been developed. KS-1 was commercialized in a urea production application. In this process, low amine losses and low solvent degradation have been noted without the use of inhibitors or additives. As shown in Figure 3.5, the first commercial plant at 200 $tCO_2\ d^{-1}$ recovery from a flue gas stream has been operating in Malaysia since 1999 for urea production (equivalent to the emissions from a 10 MWt coal-fired power plant)

Figure 3.5 CO_2 capture plant in Malaysia using a 200 tonne d^{-1} KEPCO/MHI chemical solvent process (Courtesy of Mitsubishi).

The performance of the chemical solvent in the operation is maintained by replacement, filtering and reclaiming, which leads to a consumables requirement. Typical values for the solvent consumption are between 0.2 and 1.6 kg/tCO2. In addition, chemicals are needed to reclaim the amine from the heat stable salt (typically 0.03–0.13 kg NaOH/tCO2) and to remove decomposition products (typically 0.03-0.06 kg activated carbon/tCO2). The ranges are primarily dependent on the absorption process, with KS-1 being at the low end of the range and ECONAMINE ™ at the high end.

3.3.2.2. Flue gas pretreatment

Flue gases from a combustion power plant are usually above 100°C, which means that they need to be cooled down to the temperature levels required for the absorption process. This can be done in a cooler with direct water contact, which also acts as a flue gas wash with additional removal of fine particulates.

In addition to the above, flue gas from coal combustion will contain other acid gas components such as NO_x and SO_x. Flue gases from natural gas combustion will normally only contain NO_x. These acidic gas components will, similar to CO_2, have a chemical interaction with the alkaline solvent. This is not desirable as the irreversible nature of this interaction leads to the formation of heat stable salts and hence a loss in absorption capacity of the solvent and the risk of formation of solids in the solution. It also results in an extra consumption of chemicals to regenerate the solvent and the production of a waste stream such as sodium sulphate or sodium nitrate. Therefore, the pre-removal of NO_x and SO_x to very low values before CO_2

recovery becomes essential. For NO_x it is the NO_2 which leads to the formation of heat stable salts. Fortunately, the level of NO_2 is mostly less than 10% of the overall NO_x content in a flue gas (Chapel *et al.*, 1999).

The allowable SO_x content in the flue gas is primarily determined by the cost of the solvent - as this is consumed by reaction with SO_x. SO_2 concentrations in the flue gas are typically around 300-5000 ppm. Commercially available SO_2-removal plants will remove up to 98-99%. Amines are relatively cheap chemicals, but even cheap solvents like MEA (with a price around 1.25 US\$ kg^{-1} (Rao and Rubin, 2002) may require SO_x concentrations of around 10 ppm, to keep solvent consumption (around 1.6 kg of MEA/tCO_2 separated) and make up costs at reasonable values, which often means that additional flue gas desulphurization is needed. The optimal SO_2 content, before the CO_2 absorption process is a cost trade-off between CO_2-solvent consumption and SO_2-removal costs. For the Kerr-Mcgee/ABB Lummus Crest Technology, SO_2-removal is typically not justified for SO_2 levels below 50 ppm (Barchas and Davis, 1992). For the Fluor Daniel Econamine FG process a maximum of 10 ppm SO_2 content is generally set as the feed gas specification (Sander and Mariz, 1992). This can be met by using alkaline salt solutions in a spray scrubber (Chapel *et al.*, 1999). A SO_2 scrubber might also double as a direct contact cooler to cool down the flue gas.

Careful attention must also be paid to fly ash and soot present in the flue gas, as they might plug the absorber if contaminants levels are too high. Often the requirements of other flue gas treatment are such that precautions have already been taken. In the case of CO_2 recovery from a coal-fired boiler flue gas, the plant typically has to be equipped with a $DeNO_x$ unit, an electrostatic precipitator or a bag house filter and a $DeSO_x$ or flue gas desulphurization unit as part of the environmental protection of the power plant facilities. In some cases, these environmental protection facilities are not enough to carry out deep SO_x removal up to the 1-2 ppm level sometimes needed to minimize solvent consumption and its reclamation from sticking of solvent wastes on reclaimer tube surfaces.

3.3.2.3 Power generation efficiency penalty in CO_2 capture

A key feature of post-combustion CO_2 capture processes based on absorption is the high energy requirement and the resulting efficiency penalty on power cycles. This is primarily due to the heat necessary to regenerate the solvent, steam use for stripping and to a lesser extent the electricity required for liquid pumping, the flue gas fan and finally compression of the CO_2 product. Later in this chapter, Sections 3.6 and 3.7 present summaries of CO_2 capture energy requirements for a variety of power systems and discuss the environmental and economic implications of these energy demands.

In principle, the thermal energy for the regeneration process can be supplied by an auxiliary boiler in a retrofit situation. Most studies, however, focus on an overall process in which the absorption process is integrated into the power plant. The heat requirement is at such levels that low-pressure steam, for example condensing at 0.3 MPa(g), can be used in the reboiler. The steam required for the regeneration process is then extracted from the steam cycle in the power plant. For a coal-fired power station, low-pressure steam will be extracted prior to the last expansion stage of the steam turbine. For a natural gas fired combined cycle, low-pressure steam will be extracted from the last stage in the heat recovery steam generator. Some of this heat can be recovered by preheating the boiler feed water (Hendriks, 1994). Values for the heat requirement for the leading absorption technologies are between 2.7 and 3.3 GJ/tCO_2, depending on the solvent process. Typical values for the electricity requirement are between 0.06 and 0.11 GJ/tCO_2 for post-combustion capture in coal- fired power plants and 0.21 and 0.33 GJ/tCO_2 for post-combustion capture in natural gas fired combined cycles. Compression of the CO_2 to 110 bar will require around 0.4 GJ/tCO_2 (IEA GHG, 2004).

Integration of the absorption process with an existing power plant will require modifications of the low-pressure part of the steam cycle, as a sizeable fraction of the steam will be extracted and hence will not be available to produce power (Nsakala *et al.*, 2001, Mimura *et al.*,1995, Mimura *et al.*, 1997). To limit the required modifications, small back-pressure steam turbines using medium pressure steam to drive the flue gas fan and boiler feed water pumps can be used. The steam is then condensed in the reboiler (Mimura *et al.*, 1999). Furthermore, in power plants based on steam cycles more than 50% thermal energy in the steam cycle is disposed off in the steam condenser. If the steam cycle system and CO_2 recovery can be integrated, part of the waste heat disposed by the steam condenser can be utilized for regeneration of the chemical solvent.

The reduction of the energy penalty is, nevertheless, closely linked to the chosen solvent system. The IEA Greenhouse Programme (IEA GHG) has carried out performance assessments of power plants with post-combustion capture of CO_2, taking into consideration the most recent improvements in post-combustion CO_2 capture processes identified by technology licensors (IEA GHG, 2004). In this study, Mitsui Babcock Energy Ltd. and Alstom provided information on the use of a high efficiency, ultra-supercritical steam cycle (29 MPa, 600°C, 620°C reheat) boiler and steam turbine for a coal-fired power plant, while for the NGCC case, a combined cycle using a GE 9FA gas turbine was adopted. Fluor provided information on the Fluor Econamine + process based on MEA, and MHI provided information on KEPCO/MHI process based on the KS-1 solvent for CO_2 capture. CO_2 leaving these systems were compressed to a pressure of 11 MPa. The overall net power plant efficiencies with and without CO_2 capture are shown in Figure 3.6, while Figure 3.7 shows the efficiency penalty for CO_2 capture. Overall, results from this study show that the efficiency penalty for post-combustion capture in coal and gas fired plant is lower for KEPCO/MHI's CO_2 absorption process. For the purpose of comparison, the performance of power plants with pre-combustion and oxy-fuel capture, based on the same standard set of plant design criteria are also shown in Figures 3.6 and 3.7.

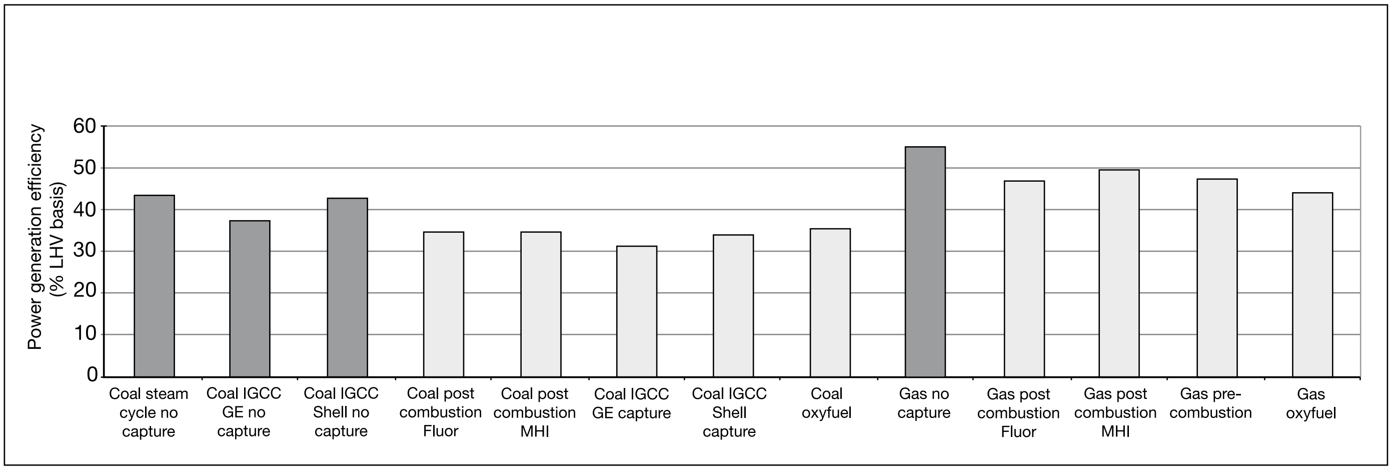

Figure 3.6 Thermal efficiencies of power plants with and without CO_2 capture, % LHV-basis (Source data: Davison 2005, IEA GHG 2004, IEA GHG 2003; IEA GHG, 2000b; Dillon *et al*., 2005).

a. The efficiencies are based on a standard set of plant design criteria (IEA GHG, 2004).
b. The coal steam cycle plants, including the post-combustion capture and oxy-fuel plants, are based on ultra-supercritical steam (29MPa, 600C superheat, 620C reheat). The IGCC and natural gas pre- and post-combustion capture plants are based on GE 9FA gas turbine combined cycles. The natural gas oxy-fuel plant is based on a CO_2 recycle gas turbine, as shown in Figure 3.10, with different operating pressures and temperatures but similar mechanical design criteria to that of the 9FA.
c. Data are presented for two types of post-combustion capture solvent: MEA (Fluor plant designs) and KS-1 (MHI plant designs). The solvent desorption heat consumptions are 3.2 and 2.7 MJ/kgCO_2 captured respectively for the coal plants and 3.7 and 2.7 MJ kg^{-1} for the natural gas plants.
d. Data are presented for IGCC plants based on two types of gasifier: the Shell dry feed/heat recovery boiler type and the GE (formerly Texaco) slurry feed water quench type.
e. The natural gas pre-combustion capture plant is based on partial oxidation using oxygen.
f. The oxy-fuel plants include cryogenic removal of some of the impurities from the CO_2 during compression. Electricity consumption for oxygen production by cryogenic distillation of air is 200 kWh/ tO_2 at atmospheric pressure for the coal plant and 320 kWh/ tO_2 at 40 bar for the natural gas plant. Oxygen production in the IGCC and natural gas pre-combustion capture plants is partially integrated with the gas turbine compressor, so comparable data cannot be provided for these plants.
g. The percentage CO_2 capture is 85–90% for all plants except the natural gas oxy-fuel plant which has an inherently higher percentage capture of 97%.

3.3.2.4 Effluents

As a result of decomposition of amines, effluents will be created, particularly ammonia and heat-stable salts. Rao and Rubin (2002) have estimated these emissions for an MEA-based process based on limited data. In such processes, heat stable salts (solvent decomposition products, corrosion products etc.) are removed from the solution in a reclaimer and a waste stream is created and is disposed of using normal HSE (Health, Safety and Environmental) practices. In some cases, these reclaimer bottoms may be classified as a hazardous waste, requiring special handling (Rao and Rubin, 2002). Also a particle filter and carbon filter is normally installed in the solvent circuit to remove byproducts. Finally, some solvent material will be lost to the environment through evaporation and carry over in the absorber, which is accounted for in the solvent consumption. It is expected that acid gases other than CO_2, which are still present in the flue gas (SO_x and NO_2) will also be absorbed in the solution. This will lower the concentration of these components further and even the net emissions in some cases depending on the amount of additional energy use for CO_2 capture (see Tables 3.4 and 3.5). As SO_2-removal prior to CO_2-removal is very likely in coal-fired plants, this will lead to the production of a waste or byproduct stream containing gypsum and water from the FGD unit.

3.3.3 Emerging technologies

3.3.3.1 Other absorption process

Various novel solvents are being investigated, with the object of achieving a reduced energy consumption for solvent regeneration (Chakma, 1995; Chakma and Tontiwachwuthikul, 1999; Mimura *et al*., 1999; Zheng *et al*., 2003; Cullinane and Rochelle, 2003; Leites, 1998; Erga *et al*., 1995; Aresta and Dibenedetto, 2003; Bai and Yeh, 1997).

Besides novel solvents, novel process designs are also currently becoming available (Leites *et al*. 2003). Research is also being carried out to improve upon the existing practices and packing types (Aroonwilas *et al*., 2003). Another area of research is to increase the concentration levels of aqueous MEA solution used in absorption systems as this tends to reduce the size of equipment used in capture plants (Aboudheir *et al*., 2003). Methods to prevent oxidative degradation of MEA by de-oxygenation of the solvent solutions are also being investigated (Chakravarti *et al*., 2001). In addition to this, the catalytic removal of oxygen in flue gases from coal firing has been suggested (Nsakala *et al*., 2001) to enable operation with promising solvents sensitive to oxygen.

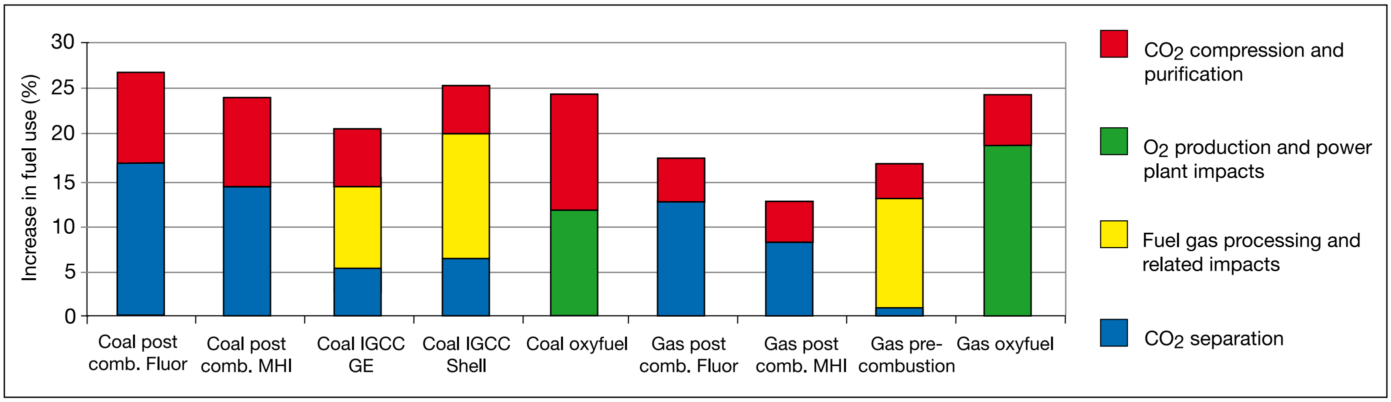

Figure 3.7 Percentage increase in fuel use per kWh of electricity due to CO_2 capture, compared to the same plant without capture (Source data: Davison, 2005; IEA GHG, 2004; IEA GHG, 2003; IEA GHG, 2000b; Dillon *et al.*, 2005).

a. The increase in fuel required to produce a kWh of electricity is calculated by comparing the same type of plant with and without capture. The increase in fuel consumption depends on the type of baseline plant without capture. For example, the increase in energy consumption for a GE IGCC plant with capture compared to a coal steam cycle baseline plant without capture would be 40% as opposed to the lower value shown in the figure that was calculated relative to the same type of baseline plant without capture.

b. The direct energy consumptions for CO_2 separation are lower for pre-combustion capture than for post-combustion capture, because CO_2 is removed from a more concentrated, higher pressure gas, so a physical rather than a chemical solvent can be used.

c. The ‘Fuel gas processing and related impacts’ category for IGCC includes shift conversion of the fuel gas and the effects on the gas turbine combined cycle of removal of CO_2 from the fuel gas and use of hydrogen as a fuel instead of syngas. For natural gas pre-combustion capture this category also includes partial oxidation/steam reforming of the natural gas.

d. The energy consumption for CO_2 compression is lower in pre-combustion capture than in post-combustion capture because some of the CO_2 leaves the separation unit at elevated pressure.

e. The energy consumption for CO_2 compression in the oxy-fuel processes depends on the composition of the extracted product, namely 75% by volume in the coal-fired plant and 93% by volume in the gas fired plant. Impurities are cryogenically removed from the CO_2 during compression, to give a final CO_2 purity of 96% by volume. The energy consumption of the cryogenic CO_2 separation unit is included in the CO_2 compression power consumption.

f. The ‘Oxygen production and power plant impacts’ category for oxy-fuel processes includes the power consumption for oxygen production and the impacts of CO_2 capture on the rest of the power plant, that is excluding CO_2 compression and purification. In the coal-fired oxy-fuel plant, the efficiency of the rest of the power plant increases slightly, for example due to the absence of a flue gas desulphurization (FGD) unit. The efficiency of the rest of the gas fired oxy-fuel plant decreases because of the change of working fluid in the power cycle from air to recycled flue gas.

3.3.3.2 Adsorption process

In the adsorption process for flue gas CO_2 recovery, molecular sieves or activated carbons are used in adsorbing CO_2. Desorbing CO_2 is then done by the pressure swing operation (PSA) or temperature swing operation (TSA). Most applications are associated with pressure swing adsorption (Ishibashi *et al.*, 1999 and Yokoyama, 2003). Much less attention has been focused on CO_2 removal via temperature swing adsorption, as this technique is less attractive compared to PSA due to the longer cycle times needed to heat up the bed of solid particles during sorbent regeneration. For bulk separations at large scales, it is also essential to limit the length of the unused bed and therefore opt for faster cycle times.

Adsorption processes have been employed for CO_2 removal from synthesis gas for hydrogen production (see Section 3.5.2.9). It has not yet reached a commercial stage for CO_2 recovery from flue gases. The following main R&D activities have been conducted:

- Study of CO_2 removal from flue gas of a thermal power plant by physical adsorption (Ishibashi *et al.*, 1999);
- Study of CO_2 removal from flue gas of a thermal power plant by a combined system with pressure swing adsorption and a super cold separator (Takamura *et al.*, 1999);
- Pilot tests on the recovery of CO_2 from a coal and oil fired power plant, using pressure temperature swing adsorption (PTSA) and an X-type zeolite as an adsorbent (Yokoyama, 2003).

Pilot test results of coal-fired flue gas CO_2 recovery by adsorption processes show that the energy consumption for capture (blowers and vacuum pumps) has improved from the original 708 kWh/tCO_2 to 560 kWh/tCO_2. An energy consumption of 560 kWh/tCO_2 is equivalent to a loss corresponding to 21% of the energy output of the power plant. Recovered CO_2 purity is about 99.0% by volume using two stages of a PSA and PTSA system (Ishibashi *et al.*, 1999).

It can be concluded that based on mathematical models and data from pilot-scale experimental installations, the design of a full-scale industrial adsorption process might be feasible. A serious drawback of all adsorptive methods is the necessity to treat the gaseous feed before CO_2 separation in an adsorber. Operation at high temperature with other sorbents (see Section 3.3.3.4) can circumvent this requirement (Sircar and Golden, 2001). In many cases gases have to be also cooled and dried, which limits the attractiveness of PSA, TSA or ESA (electric swing adsorption) vis-à-vis capture by chemical absorption described in previous sections. The development of a new generation of materials that would efficiently adsorb CO_2 will undoubtedly enhance the competitiveness of adsorptive separation in a flue gas application.

3.3.3.3 Membranes

Membrane processes are used commercially for CO_2 removal from natural gas at high pressure and at high CO_2 concentration (see Section 3.2.2). In flue gases, the low CO_2 partial pressure difference provides a low driving force for gas separation. The removal of carbon dioxide using commercially available polymeric gas separation membranes results in higher energy penalties on the power generation efficiency compared to a standard chemical absorption process (Herzog *et al*., 1991, Van der Sluijs *et al*., 1992 and Feron, 1994). Also, the maximum percentage of CO_2 removed is lower than for a standard chemical absorption processes. Improvements can be made if more selective membranes become available, such as facilitated membranes, described below.

The membrane option currently receiving the most attention is a hybrid membrane – absorbent (or solvent) system. These systems are being developed for flue gas CO_2 recovery. Membrane/solvent systems employ membranes to provide a very high surface area to volume ratio for mass exchange between a gas stream and a solvent resulting in a very compact system. This results in a membrane contactor system in which the membrane forms a gas permeable barrier between a liquid and a gaseous phase. In general, the membrane is not involved in the separation process. In the case of porous membranes, gaseous components diffuse through the pores and are absorbed by the liquid; in cases of non-porous membranes they dissolve in the membrane and diffuse through the membrane. The contact surface area between gas and liquid phase is maintained by the membrane and is independent of the gas and liquid flow rate. The selectivity of the partition is primarily determined by the absorbent (solvent). Absorption in the liquid phase is determined either by physical partition or by a chemical reaction.

The advantages of membrane/solvent systems are avoidance of operational problems occurring in conventional solvent absorption systems (see Section 3.3.2.1) where gas and liquid flows are in direct contact. Operational problems avoided include foaming, flooding entrainment and channelling, and result in the free choice of the gas and liquid flow rates and a fixed interface for mass transfer in the membrane/solvent system. Furthermore, the use of compact membranes result in smaller equipment sizes with capital cost reductions. The choice of a suitable combination of solvent and membrane material is very important. The material characteristics should be such that the transfer of solvent through the membrane is avoided at operating pressure gradients of typically 50–100 kPa, while the transfer of gas is not hindered. The overall process configuration in terms of unit operations would be very similar to a conventional chemical absorption/desorption process (see Figure 3.4). Membrane/solvent systems can be both used in the absorption as well as in the desorption step. Feron and Jansen (2002) and Falk-Pedersen *et al*. (1999) give examples of suitable membrane/solvent systems.

Research and development efforts have also been reported in the area of facilitated transport membranes. Facilitated transport membranes rely on the formation of complexes or reversible chemical reactions of components present in a gas stream with compounds present in the membrane. These complexes or reaction products are then transported through the membrane. Although solution and diffusion still play a role in the transport mechanism, the essential element is the specific chemical interaction of a gas component with a compound in the membrane, the so-called carrier. Like other pressure driven membrane processes, the driving force for the separation comes from a difference in partial pressure of the component to be transported. An important class of facilitated transport membranes is the so-called supported liquid membrane in which the carrier is dissolved into a liquid contained in a membrane. For CO_2 separations, carbonates, amines and molten salt hydrates have been suggested as carriers (Feron, 1992). Porous membranes and ion-exchange membranes have been employed as the support. Until now, supported liquid membranes have only been studied on a laboratory scale. Practical problems associated with supported liquid membranes are membrane stability and liquid volatility. Furthermore, the selectivity for a gas decreases with increasing partial pressure on the feed side. This is a result of saturation of the carrier in the liquid. Also, as the total feed pressure is increased, the permeation of unwanted components is increased. This also results in a decrease in selectivity. Finally, selectivity is also reduced by a reduction in membrane thickness. Recent development work has focused on the following technological options that are applicable to both CO_2/N_2 and CO_2/H_2 separations:

- Amine-containing membranes (Teramoto *et al*., 1996);
- Membranes containing potassium carbonate polymer gel membranes (Okabe *et al*., 2003);
- Membranes containing potassium carbonate-glycerol (Chen *et al*., 1999);
- Dendrimer-containing membranes (Kovvali and Sirkar, 2001).
- Poly-electrolyte membranes (Quinn and Laciak, 1997);

Facilitated transport membranes and other membranes can also be used in a preconcentration step prior to the liquefaction of CO_2 (Mano *et al*., 2003).

3.3.3.4 Solid sorbents

There are post-combustion systems being proposed that make use of regenerable solid sorbents to remove CO_2 at relatively high temperatures. The use of high temperatures in the CO_2 separation step has the potential to reduce efficiency penalties with respect to wet-absorption methods. In principle, they all follow the scheme shown in Figure 3.2a, where the combustion flue gas is put in contact with the sorbent in a suitable reactor to allow the gas-solid reaction of CO_2 with the sorbent (usually the carbonation of a metal oxide). The solid can be easily separated from the gas stream and sent for regeneration in a different reactor. Instead of moving the solids, the reactor can also be switched between sorption and regeneration modes of operation in a batch wise, cyclic operation. One key component for the development of these systems is obviously the sorbent itself, that has to have good CO_2 absorption capacity and chemical and mechanical stability for long periods of operation in repeated cycles. In general, sorbent performance and cost are critical issues in all post-combustion systems, and more elaborate sorbent materials are usually more expensive and will have to demonstrate outstanding performance compared with existing commercial alternatives such as those described in 3.3.2.

Solid sorbents being investigated for large-scale CO_2 capture purposes are sodium and potassium oxides and carbonates (to produce bicarbonate), usually supported on a solid substrate (Hoffman *et al.*, 2002; Green *et al.*, 2002). Also, high temperature Li-based and CaO-based sorbents are suitable candidates. The use of lithium-containing compounds (lithium, lithium-zirconia and lithium-silica oxides) in a carbonation-calcination cycle, was first investigated in Japan (Nakagawa and Ohashi, 1998). The reported performance of these sorbents is very good, with very high reactivity in a wide range of temperatures below 700ºC, rapid regeneration at higher temperatures and durability in repeated capture-regeneration cycles. This is essential because lithium is an intrinsically expensive material.

The use of CaO as a regenerable CO_2 sorbent has been proposed in several processes dating back to the 19th century. The carbonation reaction of CaO to separate CO_2 from hot gases ($T > 600$ºC) is very fast and the regeneration of the sorbent by calcining the $CaCO_3$ into CaO and pure CO_2 is favoured at $T > 900$ºC (at a partial pressure of CO_2 of 0.1 MPa). The basic separation principle using this carbonation-calcination cycle was successfully tested in a pilot plant (40 tonne d^{-1}) for the development of the Acceptor Coal Gasification Process (Curran *et al.*, 1967) using two interconnected fluidized beds. The use of the above cycle for a post-combustion system was first proposed by Shimizu *et al.* (1999) and involved the regeneration of the sorbent in a fluidized bed, firing part of the fuel with O_2/CO_2 mixtures (see also Section 3.4.2). The effective capture of CO_2 by CaO has been demonstrated in a small pilot fluidized bed (Abanades *et al.*, 2004a). Other combustion cycles incorporating capture of CO_2 with CaO that might not need O_2 are being developed, including one that works at high pressures with simultaneous capture of CO_2 and SO_2 (Wang *et al.*, 2004). One weak point in all these processes is that natural sorbents (limestones and dolomites) deactivate rapidly, and a large make-up flow of sorbent (of the order of the mass flow of fuel entering the plant) is required to maintain the activity in the capture-regeneration loop (Abanades *et al.*, 2004b). Although the deactivated sorbent may find application in the cement industry and the sorbent cost is low, a range of methods to enhance the activity of Ca-based CO_2 sorbents are being pursued by several groups around the world.

3.3.4 Status and outlook

Virtually all the energy we use today from carbon-containing fuels is obtained by directly burning fuels in air. This is despite many decades of exploring promising and more efficient alternative energy conversion cycles that rely on other fuel processing steps prior to fuel combustion or avoiding direct fuel combustion (see pre-combustion capture – Section 3.5). In particular, combustion-based systems are still the competitive choice for operators aiming at large-scale production of electricity and heat from fossil fuels, even under more demanding environmental regulations, because these processes are reliable and well proven in delivering electricity and heat at prices that often set a benchmark for these services. In addition, there is a continued effort to raise the energy conversion efficiencies of these systems through advanced materials and component development. This will allow these systems to operate at higher temperature and higher efficiency.

As was noted in Section 3.1, the main systems of reference for post-combustion capture are the present installed capacity of coal and natural gas power plants, with a total of 970 GW_e subcritical steam and 155 GW_e of supercritical/ultra-supercritical steam-based pulverized coal fired plants, 339 GW_e of natural gas combined cycle, 333 GW_e natural gas steam-electric power plants and 17 GW_e of coal-fired, circulating, fluidized-bed combustion (CFBC) power plants. An additional capacity of 454 GW_e of oil-based power plant, with a significant proportion of these operating in an air-firing mode is also noted (IEA WEO, 2004 and IEA CCC, 2005). Current projections indicate that the generation efficiency of commercial, pulverized coal fired power plants based on ultra-supercritical steam cycles would exceed 50% lower heating value (LHV) over the next decade (IEA, 2004), which will be higher than efficiencies of between 36 and 45% reported for current subcritical and supercritical steam-based plants without capture (see Section 3.7). Similarly, natural gas fired combined cycles are expected to have efficiencies of 65% by 2020 (IEA GHG, 2002b) and up from current efficiencies between 55 and 58% (see Section 3.7). In a future carbon-constrained world, these independent and ongoing developments in power cycle efficiencies will result in lower CO_2-emissions per kWh produced and hence a lower loss in overall cycle efficiency when post-combustion capture is applied.

There are proven post-combustion CO_2 capture technologies based on absorption processes that are commercially available at present . They produce CO_2 from flue gases in coal and gas-fired installations for food/beverage applications and chemicals production in capacity ranges between 6 and 800 tCO_2 d^{-1}. They require scale up to 20-50 times that of current unit capacities for deployment in large-scale power plants in the 500 MW_e capacity range (see Section 3.3.2). The inherent limitations of currently available absorption technologies when applied to post-combustion capture systems are well known and their impact on system cost can be estimated relatively accurately for a given application (see Section 3.7). Hence, with the dominant role played by air- blown energy conversion processes in the global energy infrastructure, the availability of post-combustion capture systems is important if CO_2 capture and storage becomes a viable climate change mitigation strategy.

The intense development efforts on novel solvents for improved performance and reduced energy consumption during regeneration, as well as process designs incorporating new contacting devices such as hybrid membrane-absorbent systems, solid adsorbents and high temperature regenerable sorbents, may lead to the use of more energy efficient post-combustion capture systems. However, all these novel concepts still need to prove their lower costs and reliability of operation on a commercial scale. The same considerations also apply to other advanced CO_2 capture concepts with oxy-fuel combustion or pre-combustion capture reviewed in the following sections of this chapter. It is generally not yet clear which of these emerging technologies, if any, will succeed as the dominant commercial technology for energy systems incorporating CO_2 capture.

3.4 Oxy-fuel combustion capture systems

3.4.1 Introduction

The oxy-fuel combustion process eliminates nitrogen from the flue gas by combusting a hydrocarbon or carbonaceous fuel in either pure oxygen or a mixture of pure oxygen and a CO_2-rich recycled flue gas (carbonaceous fuels include biomass). Combustion of a fuel with pure oxygen has a combustion temperature of about 3500°C which is far too high for typical power plant materials. The combustion temperature is limited to about 1300-1400°C in a typical gas turbine cycle and to about 1900°C in an oxy-fuel coal-fired boiler using current technology. The combustion temperature is controlled by the proportion of flue gas and gaseous or liquid-water recycled back to the combustion chamber.

The combustion products (or flue gas) consist mainly of carbon dioxide and water vapour together with excess oxygen required to ensure complete combustion of the fuel. It will also contain any other components in the fuel, any diluents in the oxygen stream supplied, any inerts in the fuel and from air leakage into the system from the atmosphere. The net flue gas, after cooling to condense water vapour, contains from about 80-98% CO_2 depending on the fuel used and the particular oxy-fuel combustion process. This concentrated CO_2 stream can be compressed, dried and further purified before delivery into a pipeline for storage (see Chapter 4). The CO_2 capture efficiency is very close to 100% in oxy-fuel combustion capture systems. Impurities in the CO_2 are gas components such as SO_x, NO_x, HCl and Hg derived from the fuel used, and the inert gas components, such as nitrogen, argon and oxygen, derived from the oxygen feed or air leakage into the system. The CO_2 is transported by pipeline as a dense supercritical phase. Inert gases must be reduced to a low concentration to avoid two-phase flow conditions developing in the pipeline systems. The acid gas components may need to be removed to comply with legislation covering co-disposal of toxic or hazardous waste or to avoid operations or environmental problems with disposal in deep saline reservoirs, hydrocarbon formations or in the ocean. The carbon dioxide must also be dried to prevent water condensation and corrosion in pipelines and allow use of conventional carbon-steel materials.

Although elements of oxy-fuel combustion technologies are in use in the aluminium, iron and steel and glass melting industries today, oxy-fuel technologies for CO_2 capture have yet to be deployed on a commercial scale. Therefore, the first classification between *existing technologies* and *emerging technologies* adopted in post-combustion (Section 3.3) and pre-combustion (Section 3.5) is not followed in this section. However, it is important to emphasize that the key separation step in most oxy-fuel capture systems (O_2 from air) is an 'existing technology' (see Section 3.4.5). Current methods of oxygen production by air separation comprise cryogenic distillation, adsorption using multi-bed pressure swing units and polymeric membranes. For oxy-fuel conversions requiring less than 200 tO_2 d^{-1}, the adsorption system will be economic. For all the larger applications, which include power station boilers, cryogenic air separation is the economic solution (Wilkinson *et al.*, 2003a).

In the following sections we present the main oxy-fuel combustion systems classified according to how the heat of combustion is supplied and whether the flue gas is used as a working fluid (Sections 3.4.2, 3.4.3, 3.4.4). A brief overview of O_2 production methods relevant for these systems is given (Section 3.4.5). In Section 3.4.6, the emerging technology of chemical looping combustion is presented, in which pure oxygen is supplied by a metal oxide rather than an oxygen production process. The section on oxy-fuel systems closes with an overview of the status of the technology (Section 3.4.7).

3.4.2 Oxy-fuel indirect heating - steam cycle

In these systems, the oxy-fuel combustion chamber provides heat to a separate fluid by heat transfer through a surface. It can be used for either process heating, or in a boiler with a steam cycle for power generation. The indirect system can be used with any hydrocarbon or carbon-containing fuel.

The application of oxy-fuel indirect heating for CO_2 capture in process heating and power generation has been examined in both pilot-scale trials evaluating the combustion of carbonaceous fuels in oxygen and CO_2-rich recycled flue gas mixtures and engineering assessments of plant conversions as described below.

3.4.2.1 Oxy-fuel combustion trials

Work to demonstrate the application of oxy-fuel recycle combustion in process heating and for steam generation for use in steam power cycles have been mostly undertaken in pilot scale tests that have looked at the combustion, heat transfer and pollutant-forming behaviour of natural gas and coal.

One study carried out (Babcock Energy Ltd. *et al.*, 1995) included an oxy-fuel test with flue gas recycle using a 160kW, pulverized coal, low NO_x burner. The system included a heat-transfer test section to simulate fouling conditions. Test conditions included variation in recycle flow and excess O_2 levels. Measurements included all gas compositions, ash analysis and tube fouling after a 5-week test run. The work also included a case study on oxy-fuel operation of a 660 MW power boiler with CO_2 capture, compression and purification. The main test results were that NO_x levels reduced with increase in recycle rate, while SO_2 and carbon in ash levels were insensitive to the recycle rate. Fouling in the convective test section was greater with oxy-fuel firing than with air. High-slagging UK coal had worse slagging when using oxy-fuel firing, the higher excess O_2 level lowered carbon in ash and CO concentration.

For the combustion of pulverized coal, other pilot-scale tests by Croiset and Thambimuthu (2000) have reported that the flame temperature and heat capacity of gases to match fuel burning in air occurs when the feed gas used in oxy-fuel combustion has a composition of approximately 35% by volume O_2 and 65% by volume of dry recycled CO_2 (c.f. 21% by volume O_2 and the rest nitrogen in air). In practice, the presence of inerts such as ash and inorganic components in the coal, the specific fuel composition and moisture in the recycled gas stream and the coal feed will result in minor adjustments to this feed mixture composition to keep the flame temperature at a value similar to fuel combustion in air.

At conditions that match O_2/CO_2 recycle combustion to fuel burning in air, coal burning is reported to be complete (Croiset and Thambimuthu, 2000), with operation of the process at excess O_2 levels in the flue gas as low as 1-3% by volume O_2, producing a flue gas stream of 95-98% by volume dry CO_2 (the rest being excess O_2, NO_x, SO_x and argon) when a very high purity O_2 stream is used in the combustion process with zero leakage of ambient air into the system. No differences were detected in the fly ash formation behaviour in the combustor or SO_2 emissions compared to conventional air firing conditions. For NO_x on the other hand, emissions were lower due to zero thermal NO_x formation from the absence of nitrogen in the feed gas - with the partial recycling of NO_x also reducing the formation and net emissions originating from the fuel bound nitrogen. Other studies have demonstrated that the level of NO_x reduction is as high as 75% compared to coal burning in air (Chatel-Pelage *et al*., 2003). Similar data for natural gas burning in O_2/CO_2 recycle mixtures report zero thermal NO_x emissions in the absence of air leakage into the boiler, with trace amounts produced as thermal NO_x when residual nitrogen is present in the natural gas feed (Tan *et al*., 2002).

The above and other findings show that with the application of oxy-fuel combustion in modified utility boilers, the nitrogen-free combustion process would benefit from higher heat transfer rates (McDonald and Palkes, 1999), and if also constructed with higher temperature tolerant materials, are able to operate at higher oxygen concentration and lower flue gas recycle flows – both of which will considerably reduce overall volume flows and size of the boiler.

It should be noted that even when deploying a 2/3 flue gas recycle gas ratio to maintain a 35% by volume O_2 feed to a pulverized coal fired boiler, hot recycling of the flue gas prior to CO_2 purification and compression also reduces the size of all unit operations in the stream leaving the boiler to 1/5 that of similar equipment deployed in conventional air blown combustion systems (Chatel-Pelage *et al*., 2003). Use of a low temperature gas purification step prior to CO_2 compression (see Section 3.4.2.2) will also eliminate the need to deploy conventional selective catalytic reduction for NO_x removal and flue gas desulphurization to purify the gas, a practice typically adopted in conventional air-blown combustion processes (see Figure 3.3). The overall reduction in flow volumes, equipment scale and simplification of gas purification steps will thus have the benefit of reducing both capital and operating costs of equipment deployed for combustion, heat transfer and final gas purification in process and power plant applications (Marin *et al*., 2003).

As noted above for pulverized coal, oil, natural gas and biomass combustion, fluidized beds could also be fired with O_2 instead of air to supply heat for the steam cycle. The intense solid mixing in a fluidized bed combustion system can provide very good temperature control even in highly exothermic conditions, thereby minimizing the need for flue gas recycling. In principle, a variety of commercial designs for fluidized combustion boilers exist that could be retrofitted for oxygen firing. A circulating fluidized bed combustor with O_2 firing was proposed by Shimizu *et al*. (1999) to generate the heat required for the calcination of $CaCO_3$ (see also Section 3.3.3.4). More recently, plans for pilot testing of an oxy-fired circulating fluidized bed boiler have been published by Nsakala *et al*. (2003).

3.4.2.2 *Assessments of plants converted to oxy-fuel combustion*

We now discuss performance data from a recent comprehensive design study for an application of oxy-fuel combustion in a new build pulverized coal fired power boiler using a supercritical steam cycle (see Figure 3.8; Dillon *et al*., 2005). The overall thermal efficiency on a lower heating value basis is reduced from 44.2% to 35.4%. The net power output is reduced from 677 MW_e to 532 MW_e.

Important features of the system include:

- Burner design and gas recycle flow rate have been selected to achieve the same temperatures as in air combustion (compatible temperatures with existing materials in the boiler).
- The CO_2-rich flue gas from the boiler is divided into three gas streams: one to be recycled back to the combustor, one to be used as transport and drying gas of the coal feed, and the third as product gas. The first recycle and the product stream are cooled by direct water scrubbing to remove residual particulates, water vapour and soluble acid gases such as SO_3 and HCl. Oxygen and entrained coal dust together with the second recycle stream flow to the burners.
- The air leakage into the boiler is sufficient to give a high enough inerts level to require a low temperature inert gas

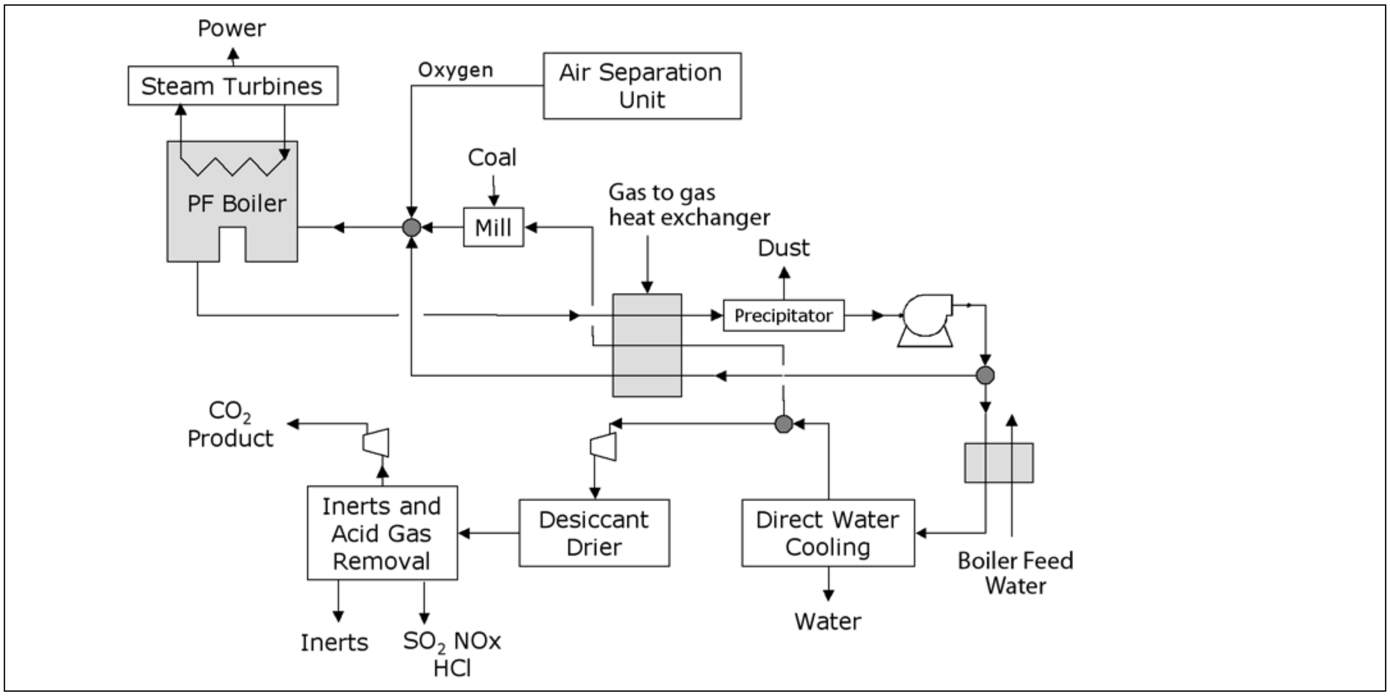

Figure 3.8 Schematic of an oxy-fuel, pulverized coal fired power plant.

removal unit to be installed, even if pure O_2 were used as the oxidant in the boiler. The cryogenic oxygen plant will, in this case, produce 95% O_2 purity to minimize power consumption and capital cost.

- The low temperature (-55°C) CO_2 purification plant (Wilkinson et al., 2003b) integrated with the CO_2 compressor will not only remove excess O_2, N_2, argon but can also remove all NO_x and SO_2 from the CO_2 stream, if high purity CO_2 is required for storage. Significantly, removal of these components before final CO_2 compression eliminates the need to otherwise incorporate upstream NO_x and SO_x removal equipment in the net flue gas stream leaving the boiler. Elimination of N_2 from the flue gas results in higher SO_x concentrations in the boiler and reduced NO_x levels. Suitable corrosion resistant materials of construction must be chosen.
- The overall heat transfer is improved in oxy-fuel firing because of the higher emissivity of the CO_2/H_2O gas mixture in the boiler compared to nitrogen and the improved heat transfer in the convection section. These improvements, together with the recycle of hot flue gas, increase the boiler efficiency and steam generation by about 5%.
- The overall thermal efficiency is improved by running the O_2 plant air compressor and the first and final stages of the CO_2 compressor without cooling, and recovering the compression heat for boiler feed water heating prior to de-aeration.

Engineering studies have also been reported by Simbeck and McDonald (2001b) and by McDonald and Palkes (1999). This work has confirmed that the concept of retrofitting oxy-fuel combustion with CO_2 capture to existing coal-fired power stations does not have any technical barriers and can make use of existing technology systems.

It has been reported (Wilkinson *et al.*, 2003b) that the application of oxy-fuel technology for the retrofit of power plant boilers and a range of refinery heaters in a refinery complex (Grangemouth refinery in Scotland) is technically feasible at a competitive cost compared to other types of CO_2 capture technologies. In this case, the existing boiler is adapted to allow combustion of refinery gas and fuel oil with highly enriched oxygen and with partial flue gas recycling for temperature control. Oxy-fuel boiler conversions only needed minor burner modifications, a new O_2 injection system and controls, and a new flue gas recycle line with a separate blower. These are cheap and relatively simple modifications and result in an increase in boiler/heater thermal efficiency due to the recycle of hot gas. Modifications to a coal-fired boiler are more complex. In this study, it was found to be more economic to design the air separation units for only 95% O_2 purity instead of 99.5% to comply with practical levels of air leakage into boilers and to separate the associated argon and nitrogen in the CO_2 inert gas removal system to produce a purity of CO_2 suitable for geological storage. After conversion of the boiler, the CO_2 concentration in the flue gas increases from 17 to 60% while the water content increases from 10 to 30%. Impurities (SO_x, NO_x) and gases (excess O_2, N_2, argon) representing about 10% of the stream are separated from CO_2 at low temperature (-55°C). After cooling, compression and drying of the separated or non-recycled flue gas, the product for storage comprises 96% CO_2 contaminated with 2% N_2, 1% argon and less than 1% O_2 and SO_2. Production of ultra-pure CO_2 for storage would also be possible if distillation steps are added to the separation process.

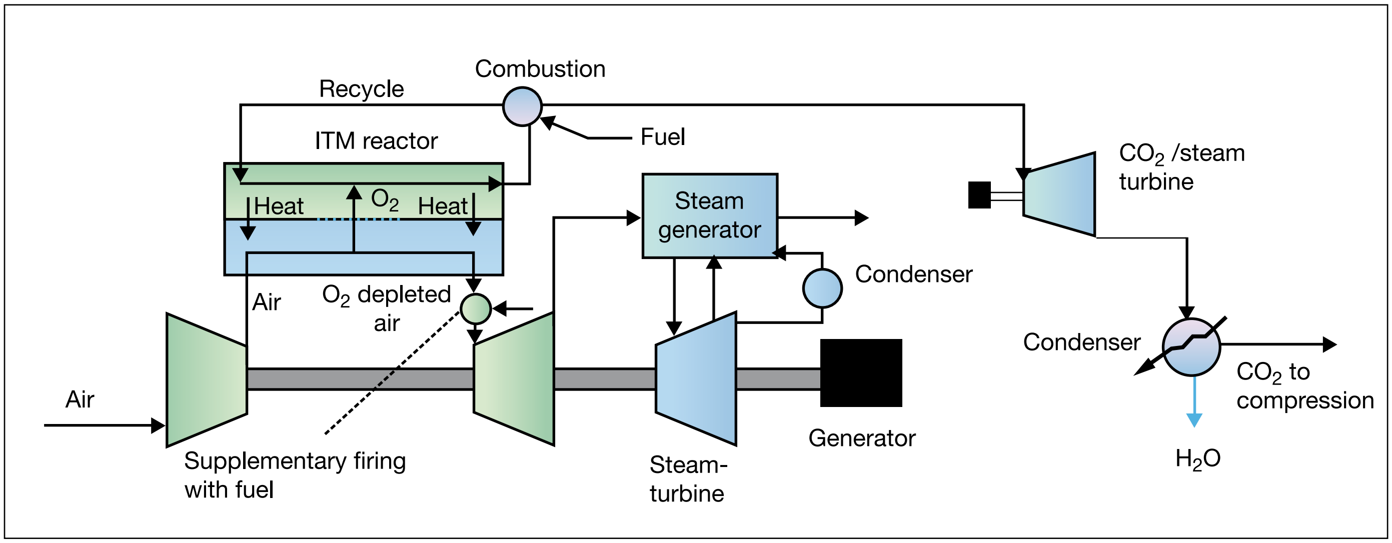

Figure 3.9 Principle flow scheme of the advanced zero emission power plant cycle.

3.4.2.3 Advanced zero emission power plant

The advanced zero emission power plant (or AZEP as outlined in Figure 3.9; Griffin *et al.*, 2003) is an indirect heating gas turbine cycle that incorporates a high-temperature oxygen transport membrane, operating at about 800°C -1000°C (see Section 3.4.5.2). This process uses a standard air-based gas turbine in a combined cycle arrangement. Three process steps take place in a reactor system that replaces the combustion chamber of a standard gas turbine: 1) separation of oxygen from hot air using the membrane and transport to the combustion section; 2) combustion and 3) heat exchange from the combustion products to the compressed air.

A net efficiency for advanced zero emission power cycle of around 49–50% LHV is claimed including CO_2 compression for transport. In order to get full advantage of the potential of the most advanced gas turbines, which have inlet temperatures of 1300°C-1400°C, an afterburner fired with natural gas in air may be added behind the reactor system. The efficiency then climbs up to 52% but now 15% of the CO_2 generated by combustion is released at the stack and is not captured.

3.4.3 *Oxy-fuel direct heating - gas turbine cycle*

Oxy-fuel combustion takes place in a pressurized CO_2-rich recirculating stream in a modified gas turbine. The hot gas is expanded in the turbine producing power. The turbine exhaust is cooled to provide heat for a steam cycle and water vapour is condensed by further cooling. The CO_2-rich gas is compressed in the compressor section. The net CO_2-rich combustion product is removed from the system. Only natural gas, light hydrocarbons and syngas (CO + H_2) can be used as fuel.

3.4.3.1 Cycle description and performance

Figure 3.10 shows how a gas turbine can be adapted to run with oxy-fuel firing using CO_2 as a working fluid. Exhaust gas leaving the heat recovery steam generator is cooled to condense water. The net CO_2 product is removed and the remaining gas is recycled to the compressor. Suitable fuels are natural gas, light to medium hydrocarbons or (H_2 + CO) syngas, which could be derived from coal. The use of CO_2 as the working fluid in the turbine will necessitate a complete redesign of the gas turbine (see Section 3.4.3.2). A recent study (Dillon *et al.*, 2005) gives an overall efficiency including CO_2 compression of 45%.

Two typical variants of this configuration are the so-called Matiant and Graz cycles (Mathieu, 2003; Jericha *et al.*, 2003). The Matiant cycle uses CO_2 as the working fluid, and consists of features like intercooled compressor and turbine reheat. The exhaust gas is preheating the recycled CO_2 in a heat exchanger. The CO_2 generated in combustion is extracted from the cycle behind the compressor. The net overall LHV efficiency is expected to be 45-47% and can increase above 50% in a combined cycle configuration similar to that shown in Figure 3.10. The Graz cycle consists of an integrated gas turbine and steam turbine cycle. A net LHV efficiency of above 50% has been calculated for this cycle (Jericha *et al.*, 2003).

A recent comprehensive review of gas turbine cycles with CO_2 capture provides efficiencies of different cycles on a common basis (Kvamsdal *et al.*, 2004).

3.4.3.2 The CO_2/oxy-fuel gas turbine

In existing gas turbines the molecular weight of the gases in the compressor and turbine are close to that of air (28.8). In the case of oxy-fuel combustion with CO_2-recycle the compressor fluid molecular weight is about 43 and about 40 in the turbine. The change in working fluid from air to a CO_2-rich gas results in a number of changes in properties that are of importance for the design of the compressor, combustor and the hot gas path including the turbine:

- The speed of sound is 80% of air;
- The gas density is 50% higher than air;
- The specific heat ratio is lower than air resulting in a lower temperature change on adiabatic compression or expansion. An oxy-fuel gas turbine in a combined cycle has a higher optimal pressure ratio, typically 30 to 35 compared to 15

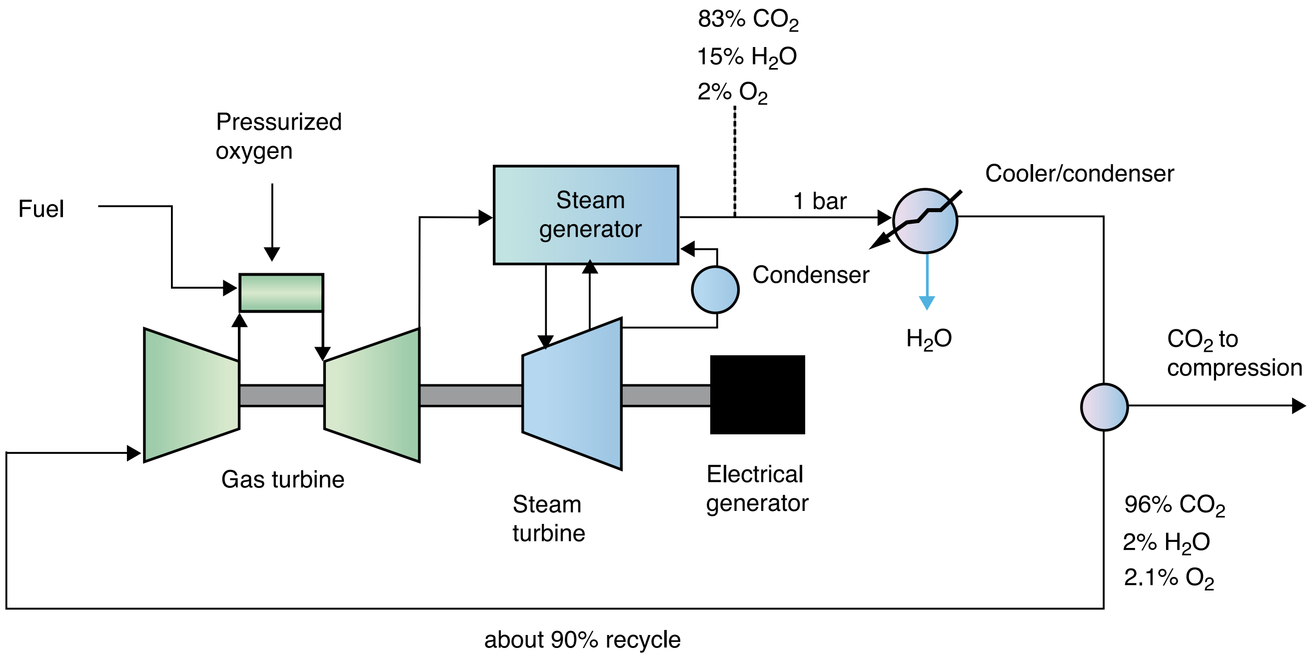

Figure 3.10 Principle of the oxy-fuel gas turbine combined cycle. Exhaust gas is recycled, compressed and used in the combustion chamber to control the temperature entering the turbine.

to 18 used with air in a combined cycle system. With the highest turbine inlet temperature consistent with material limitations, the rather high-pressure ratio results in an exhaust gas temperature of about 600°C, which is optimal for the steam cycle.

These changes in the fundamental properties of the working fluid will have a significant impact on gas turbine components, requiring completely new designs of compressors, combustors (to account for aerodynamic changes and acoustic feedbacks) and hot gas path (O_2 partial pressure must be low in oxy-fuel systems but it is also important to avoid reducing conditions for the materials of the turbine or the change to materials allowing much lower O_2 partial pressures).

3.4.4 *Oxy-fuel direct heating - steam turbine cycle*

In an oxy-fuel steam turbine cycle, water is pressurized as a liquid and is then evaporated, heated by the direct injection and combustion of a fuel with pure oxygen and expanded in a turbine. Most of the water in the low pressure turbine exhaust gas is cooled and condensed, prior to pumping back to a high pressure while the CO_2 produced from combustion is removed and compressed for pipeline transport. A variant of this cycle in which the heat is provided by burning natural gas fuel in-situ with pure oxygen was proposed by Yantovskii *et al.* (1992).

The direct combustion of fuel and oxygen has been practised for many years in the metallurgical and glass industries where burners operate at near stoichiometric conditions with flame temperatures of up to 3500°C. A water quenched H_2/O_2 burner capable of producing 60 tonne h^{-1}, 6 MPa super heated steam was demonstrated in the mid-1980s (Ramsaier *et al.*, 1985). A recent development by Clean Energy Systems incorporating these concepts where a mixture of 90 % by volume superheated steam and 10% CO_2 is produced at high temperature and pressure to power conventional or advanced steam turbines is shown in Figure 3.11. The steam is condensed in a low-pressure condenser and recycled, while CO_2 is extracted from the condenser, purified and compressed. (Anderson *et al.*, 2003 and Marin *et al.*, 2003).

Plants of this type require a clean gaseous or liquid fuel and will operate at 20 to 50 MPa pressure. The steam plus CO_2 generator is very compact. Control systems must be very precise as start-up and increase to full flow in a preheated plant can take place in less than 2 seconds. Precise control of this very rapid start was demonstrated (Ramsaier *et al.*, 1985) in a 60 tonne steam h^{-1} unit. The Clean Energy Systems studies claim efficiencies as high as 55% with CO_2 capture depending on the process conditions used.

The Clean Energy Systems technology can be initially applied with current steam turbines (565°C inlet temperature). The main technical issue is clearly the design of the steam turbines which could be used at inlet temperatures up to 1300°C by applying technology similar to that used in the hot path of gas turbines. The combustor itself (the ‘gas generator’) is adapted from existing rocket engine technology. In 2000, Clean Energy Systems proved the concept with a 110 kW pilot project conducted at the University of California Davis. A 20 MW thermal gas generator was successfully operated in a test run of the order of a few minutes in early 2003. A zero emissions demonstration plant (up to 6 MW electrical) is now on-line. US Department of Energy’s National Energy Technology Laboratory designed the reheater (Richards, 2003) and NASA tested it in 2002. Much more technology development and demonstration

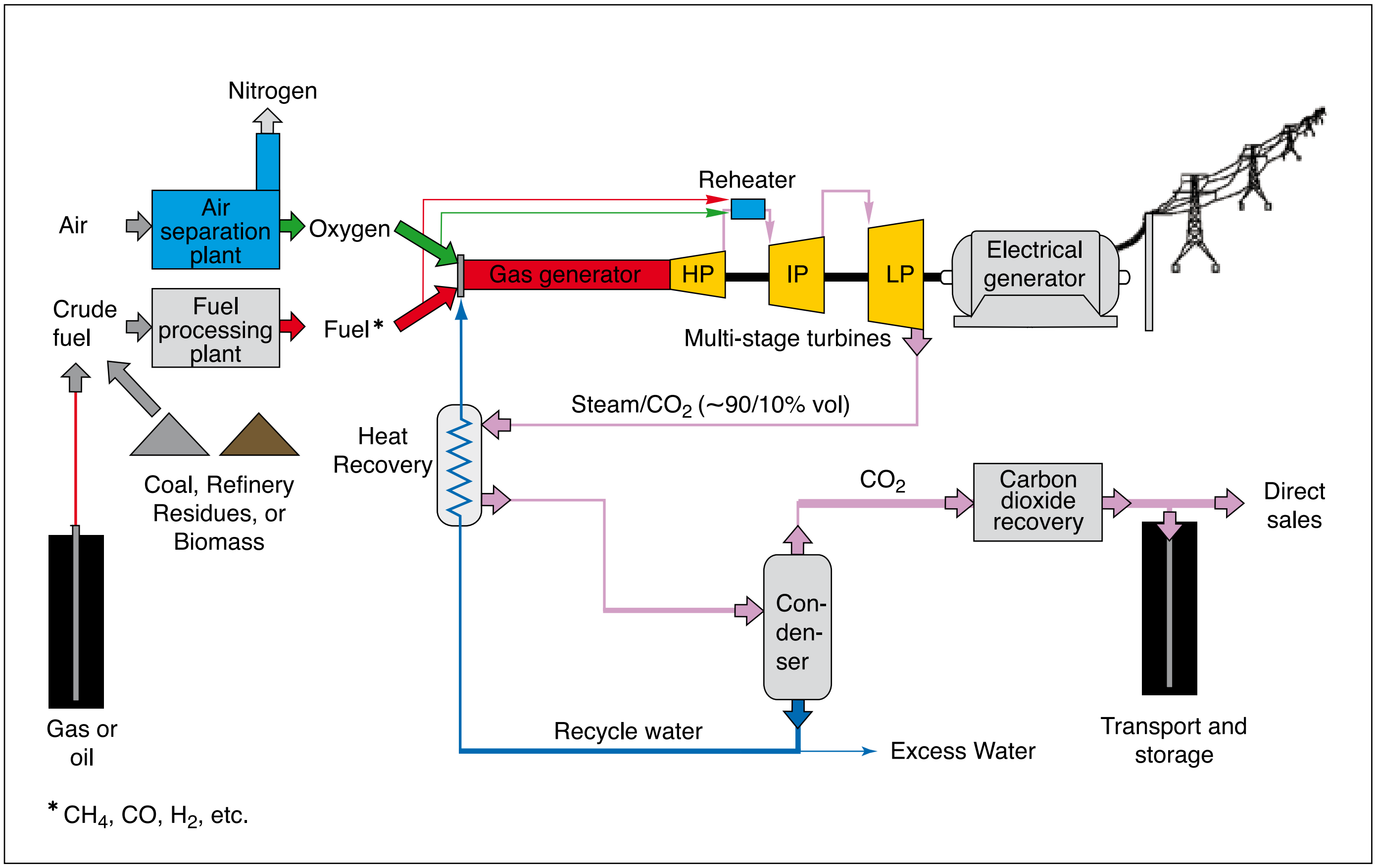

Figure 3.11 Principle of the Clean Energy Systems cycle. The combustion of the fuel and oxygen is cooled by injection of liquid-water, which is recycled in the process.

is needed on this proposed power cycle, but it shows significant potential for low capital cost and high efficiency.

3.4.5 Techniques and improvements in oxygen production

Oxygen is the key requirement for any oxy-fuel combustion system. It is also a key technology for pre-combustion CO_2 capture (see Section 3.5). In the next paragraphs, existing large-scale O_2 production methods are described first, followed by emerging concepts aimed at reducing the energy consumption and cost.

3.4.5.1 Cryogenic oxygen production

The very large quantities of oxygen required for CO_2 capture using the techniques of oxy-fuel combustion and pre-combustion de-carbonization can only be economically produced, at present, by using the established process of oxygen separation from air by distillation at cryogenic temperatures (Latimer, 1967). This is a technology that has been practiced for over 100 years.

In a typical cryogenic air separation plant (Castle, 1991; Figure 3.12), air is compressed to a pressure of 0.5 to 0.6 MPa and purified to remove water, CO_2, N_2O and trace hydrocarbons which could accumulate to dangerous levels in oxygen-rich parts of the plant, such as the reboiler condenser. Two or more switching fixed bed adsorbers are used, which can be regenerated by either temperature or pressure swing, using in each case, a low pressure waste nitrogen stream. The air is cooled against returning products (oxygen and nitrogen) in a battery of aluminium plate-fin heat exchangers and separated into pure oxygen and nitrogen fractions in a double distillation column, which uses aluminium packing.

Oxygen can be pumped as liquid and delivered as a high-pressure gas at up to 10 MPa. Pumped oxygen plants have largely replaced the oxygen gas compression systems. They have virtually identical power consumptions but in a pumped cycle, a high-pressure air booster compressor provides a means of efficiently vaporizing and heating the liquid oxygen stream to ambient temperature. Current plant sizes range up to 3500 $tO_2\ d^{-1}$ and larger single train plants are being designed. Typical power consumption for the delivery of 95% O_2 at low pressure (0.17 MPa, a typical pressure for an oxy-fuel application) is 200 to 240 kWh/tO_2. There are numerous process cycle variations particularly for the production of oxygen at less than 97.5% purity which have been developed to reduce power and capital cost. Note that adsorption and polymeric membrane methods of air separation are only economic for small oxygen production rates.

3.4.5.2 High temperature oxygen ion transport membranes

Ceramic mixed metal oxides have been developed which exhibit simultaneous oxygen ion and electron conduction at

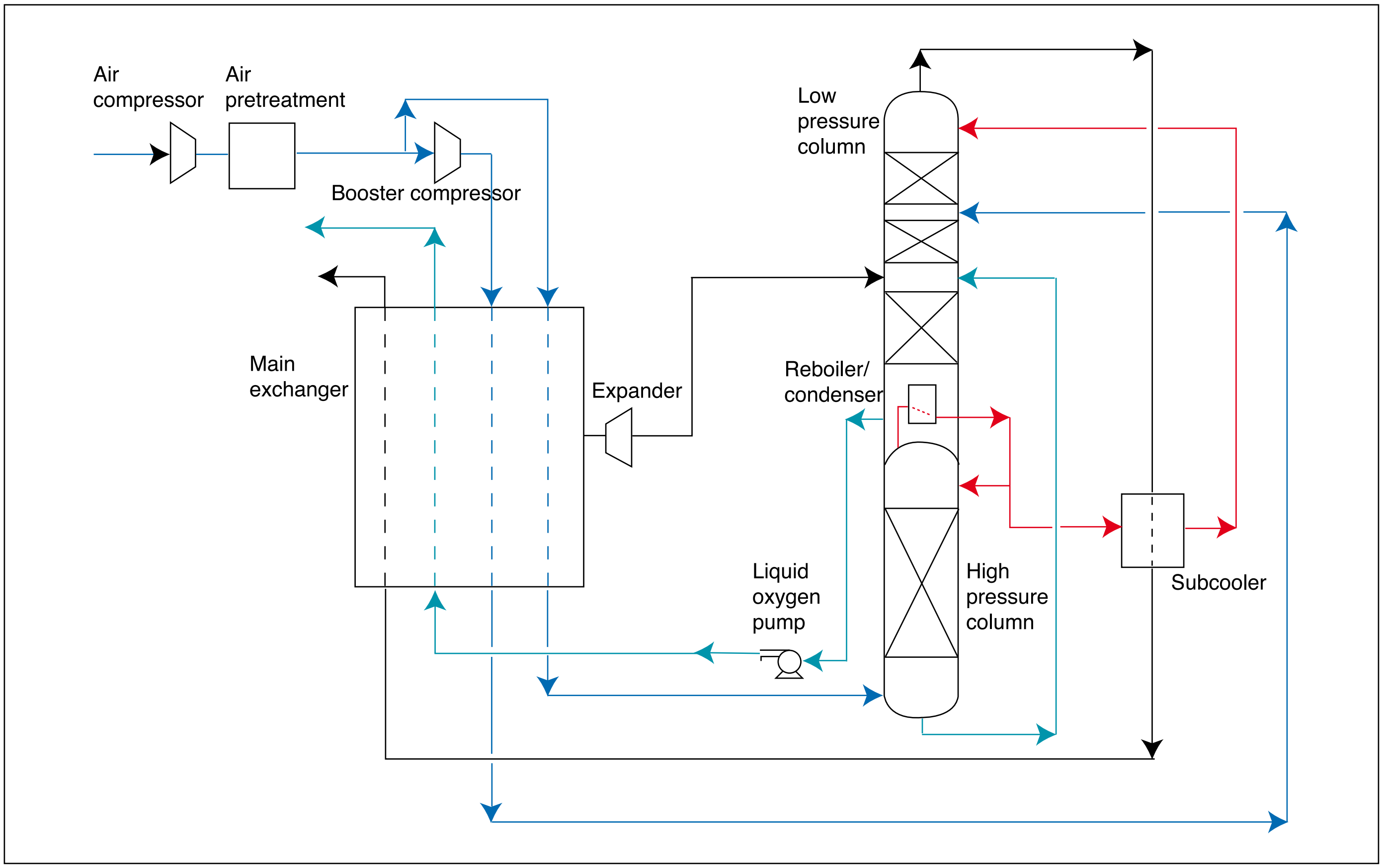

Figure 3.12a Oxygen production by distillation of liquid air.

Figure 3.12b A 3000 t day^{-1} oxygen plant (Courtesy of Air Products).

temperatures above 500°C and preferably above 700°C (Skinner and Kilner 2003; Bouwmeester and Van Laar, 2002; Dyer *et al*., 2000; Bredesen *et al*., 2004). Typical crystal structures which exhibit these properties include the perovskites and the brownmillerites. The selectivity of these materials for oxygen is infinite. The oxygen permeability is primarily controlled by the oxygen ion vacancies in the metal oxide lattice. A difference in oxygen partial pressure across the membrane will cause oxygen molecules to ionize on the ceramic surface and pass into the crystal structure while simultaneously on the permeate side of the membrane, the oxygen ions give up their electrons and leave the ceramic in the region of lower activity. The electron conduction path is through the metal ions in the lattice. Unlike conventional membranes, the flux through the ceramic is a function of the partial pressure ratio. In the technical literature, the engineered structures of these ceramic mixed metal oxides are referred to as *ion transport membranes, ITM* or *oxygen transport membranes, OTM*.

The oxygen transport membrane can be fabricated in the form of plain tubes or as hollow fins on a central collector tube (Armstrong *et al*., 2002). The finned elements are then mounted in tube sheets within a pressure vessel with high-pressure air flowing over the fins. There are several new concepts that have been proposed for using oxygen transport membranes in power cycles with CO_2 capture. A prime example of an oxy-fuel gas turbine cycle that incorporates an oxygen transport membrane for oxygen production is the advanced zero emission power plant described in Section 3.4.2.3. Another example is found in Sundnes (1998).

Development status

Oxygen transport membrane systems for oxygen production are currently in the early stages of development by at least two consortia receiving research funding from the US Department of Energy and the European Commission. The concept has now reached the pilot plant stage and projected cost, manufacturing procedures and performance targets for full size systems have been evaluated. Systems capable of large-scale production are projected to be available after industrial demonstration in about 7 years time (Armstrong *et al.*, 2002).

3.4.6 Chemical looping combustion

Originally proposed by Richter and Knoche (1983) and with subsequent significant contributions by Ishida and Jin (1994), the main idea of chemical looping combustion is to split combustion of a hydrocarbon or carbonaceous fuel into separate oxidation and reduction reactions by introducing a suitable metal oxide as an oxygen carrier to circulate between two reactors (Figure 3.13). Separation of oxygen from air is accomplished by fixing the oxygen as a metal oxide. No air separation plant is required. The reaction between fuel and oxygen is accomplished in a second reactor by the release of oxygen from the metal oxide in a reducing atmosphere caused by the presence of a hydrocarbon or carbonaceous fuel. The recycle rate of the solid material between the two reactors and the average solids residence time in each reactor, control the heat balance and the temperature levels in each reactor. The effect of having combustion in two reactors compared to conventional combustion in a single stage is that the CO_2 is not diluted with nitrogen gas, but is almost pure after separation from water, without requiring any extra energy demand and costly external equipment for CO_2 separation.

Possible metal oxides are some oxides of common transition-state metals, such as iron, nickel, copper and manganese (Zafar *et al.*, 2005). The metal/metal oxide may be present in various forms, but most studies so far have assumed the use of particles with diameter 100-500 µm. In order to move particles between the two reactors, the particles are fluidized. This method also ensures efficient heat and mass transfer between the gases and the particles. A critical issue is the long-term mechanical and chemical stability of the particles that have to undergo repeated cycles of oxidation and reduction, to minimize the make-up requirement. When a chemical looping cycle is used in a gas turbine cycle, the mechanical strength for crushing and the filtration system is important to avoid damaging carry-over to the turbine.

The temperature in the reactors, according to available information in the literature, may be in the range 800°C-1200°C. NO_x formation at these typical operating temperatures will always be low. The fuel conversion in the reduction reactor may not be complete, but it is likely (Cho *et al.*, 2002) that the concentrations of methane and CO when burning natural gas are very small. In order to avoid deposit of carbon in the reduction reactor, it is necessary to use some steam together with the fuel.

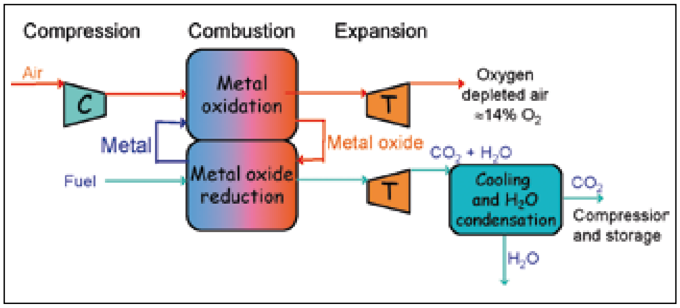

Figure 3.13 The chemical looping combustion principle in a gas turbine cycle.

The chemical looping principle may be applied either in a gas turbine cycle with pressurized oxidation and reduction reactors, or in a steam turbine cycle with atmospheric pressure in the reactors. In the case of a gas turbine cycle, the oxidation reactor replaces the combustion chamber of a conventional gas turbine. The exothermic oxidation reaction provides heat for increasing the air temperature entering the downstream expansion turbine. In addition, the reduction reactor exit stream may also be expanded in a turbine together with steam production for power generation. The cooled low pressure CO_2 stream will then be compressed to pipeline pressure. Another option is to generate steam using heat transfer surfaces in the oxidation reactor. Current circulating fluidized bed combustion technology operating at atmospheric pressure in both the oxidation and reduction stages necessitates the use of a steam turbine cycle for power generation. Using natural gas as fuel in a chemical looping combustion cycle which supplies a gas turbine combined cycle power plant and delivering CO_2 at atmospheric pressure, the potential for natural gas fuel-to-electricity conversion efficiency is estimated to be in the range 45-50% (Brandvoll and Bolland, 2004). Work on chemical looping combustion is currently in the pilot plant and materials research stage.

3.4.7 Status and outlook

Oxy-fuel combustion applied to furnaces, process heaters, boilers and power generation systems is feasible since no technical barriers for its implementation have been identified. Early use of this capture technology is likely to address applications involving indirect heating in power generation and process heating (Section 3.4.2), since these options involve the minimal modification of technologies and infrastructure that have hitherto been already developed for the combustion of hydrocarbon or carbonaceous fuels in air. However, several novel applications proposed for direct heating in steam turbine cycles or gas turbine cycles for power generation (Sections 3.4.3 and 3.4.4) still require the development of new components such as oxy-fuel combustors, higher temperature tolerant components such as CO_2- and H_2O-based turbines with blade cooling, CO_2 compressors and high temperature ion transport membranes for oxygen separation. As for Chemical Looping Combustion, it is currently still at an early stage of development.

The potential for thermal efficiencies for oxy-fuel cycles with CO_2 capture, assuming the current state of development in power plant technology, is depicted in Figures 3.6 and 3.7. Power generation from pulverized coal fired systems, using supercritical steam conditions presently operate at efficiencies around 45% (LHV), while projections to the 2010-2020 time frame are predicting efficiencies above 50% (IEA, 2004) for plants using ultra-supercritical steam conditions. An increase in efficiency of more than 5% can therefore be expected for future oxy-fuel capture systems based on coal firing that could potentially match the best efficiencies realisable today for pulverized coal-fired plants without CO_2 capture. Similarly, natural gas fired combined cycles will have efficiencies of 65% in 2020 (IEA GHG, 2000b and up from current efficiencies between 55 and 58%), which will enable plant efficiencies for natural gas fired oxy-fuel cycles with CO_2 capture above 50%. The energy penalty for producing oxygen is by far the most important cause for reduced efficiency in an oxy-fuel cycle compared to a conventional power plant.

Current technology development envisages very high efficiency separation of NO_x, SO_x, and Hg, as part of the CO_2 compression and purification system. Improved separation efficiencies of these contaminants are possible based on further process and heat integration in the power cycle.

Current cryogenic oxygen technology is showing continuing cost reduction based on improved compressor efficiencies, more efficient process equipment and larger scale plants. The new high temperature oxygen membrane could significantly improve power generation efficiency and reduce capital cost.

Future oxy-fuel demonstration plants could be based on retrofits to existing equipment such as process heaters and boilers, in order to minimize development costs and achieve early market entry. In this respect, power systems of reference for oxy-fuel combustion capture are mainly the steam-based pulverized coal and natural gas fired plants that currently represent up to 1468 GW_e, or 40% (IEA WEO, 2004) of the existing global infrastructure (see also Section 3.1.2.3). Several demonstration units may be expected within the next few years particularly in Europe, USA, Canada and Australia where active research initiatives are currently underway. As these developments proceed and the technologies achieve market penetration they may become competitive relative to alternate options based on pre- and post-combustion CO_2 capture. A significant incentive to the development of oxy-fuel combustion technology, as well as for pre- and post-combustion capture technologies, is the introduction of environmental requirements and/or fiscal incentives to promote CO_2 capture and storage.

3.5 Pre-combustion capture systems

3.5.1 Introduction

A pre-combustion capture process typically comprises a first stage of reaction producing a mixture of hydrogen and carbon monoxide (syngas) from a primary fuel. The two main routes are to add steam (reaction 1), in which case the process is called 'steam reforming', or oxygen (reaction 2) to the primary fuel. In the latter case, the process is often called 'partial oxidation' when applied to gaseous and liquid fuels and 'gasification' when applied to a solid fuel, but the principles are the same.

Steam reforming

$$C_xH_y + xH_2O \leftrightarrow xCO + (x+y/2)H_2 \quad \Delta H \text{ +ve} \qquad (1)$$

Partial oxidation

$$C_xH_y + x/2O_2 \leftrightarrow xCO + (y/2)H_2 \quad \Delta H \text{ –ve} \qquad (2)$$

This is followed by the 'shift' reaction to convert CO to CO_2 by the addition of steam (reaction 3):

Water Gas Shift Reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H \text{ -41 kJ mol}^{-1} \qquad (3)$$

Finally, the CO_2 is removed from the CO_2/H_2 mixture. The concentration of CO_2 in the input to the CO_2/H_2 separation stage can be in the range 15-60% (dry basis) and the total pressure is typically 2-7 MPa. The separated CO_2 is then available for storage.

It is possible to envisage two applications of pre-combustion capture. The first is in producing a fuel (hydrogen) that is essentially carbon-free. Although the product H_2 does not need to be absolutely pure and may contain low levels of methane, CO or CO_2, the lower the level of carbon-containing compounds, the greater the reduction in CO_2 emissions. The H_2 fuel may also contain inert diluents, such as nitrogen (when air is typically used for partial oxidation), depending on the production process and can be fired in a range of heaters, boilers, gas turbines or fuel cells.

Secondly, pre-combustion capture can be used to reduce the carbon content of fuels, with the excess carbon (usually removed as CO_2) being made available for storage. For example, when using a low H:C ratio fuel such as coal it is possible to gasify the coal and to convert the syngas to liquid Fischer-Tropsch fuels and chemicals which have a higher H:C ratio than coal. In this section, we consider both of these applications.

This section reports on technologies for the production of H_2 with CO_2 capture that already exist and those that are currently emerging. It also describes enabling technologies that need to be developed to enhance the pre-combustion capture systems for power, hydrogen or synfuels and chemicals production or combination of all three.

3.5.2 Existing technologies

3.5.2.1 Steam reforming of gas and light hydrocarbons

Steam reforming is the dominant technology for hydrogen production today and the largest single train plants produce up to 480 tH_2 d^{-1}. The primary energy source is often natural gas, Then the process is referred to as steam methane reforming (SMR), but can also be other light hydrocarbons, such as naphtha. The process begins with the removal of sulphur compounds from the feed, since these are poisons to the current nickel-based catalyst and then steam is added. The reforming reaction (1), which is endothermic, takes place over a catalyst at high temperature (800°C-900°C). Heat is supplied to the reactor tubes by burning part of the fuel (secondary fuel). The reformed gas is cooled in a waste heat boiler which generates the steam needed for the reactions and passed into the CO shift system. Shift reactors in one or two stages are used to convert most of the CO in the syngas to CO_2 (Reaction 3, which is exothermic).

The conventional two-stage CO conversion reduces the CO concentration in syngas (or in hydrogen) down to 0.2-0.3%. High temperature shift reactors operating between 400°C and 550°C and using an iron-chromium catalyst leave between 2% and 3% CO in the exit gas (dry basis). Copper-based catalyst can be used at temperatures from 180°C-350°C and leave from 0.2-1% CO in the exhaust. Lower CO content favours higher CO_2 recovery. The gas is then cooled and hydrogen is produced by a CO_2/H_2 separation step. Until about 30 years ago, the CO_2 was removed using a chemical (solvent) absorption process such as an amine or hot potassium carbonate and was rejected to atmosphere as a pure stream from the top of the regenerator. There are many of these plants still in use and the CO_2 could be captured readily.

Modern plants, however, use a pressure swing adsorber (PSA), where gases other than H_2 are adsorbed in a set of switching beds containing layers of solid adsorbent such as activated carbon, alumina and zeolites (see the fuller description of PSA in Section 3.5.2.9). The H_2 exiting the PSA (typically about 2.2 MPa) can have a purity of up to 99.999%, depending on the market need. The CO_2 is contained in a stream, from the regeneration cycle, which contains some methane and H_2. The stream is used as fuel in the reformer where it is combusted in air and the CO_2 ends up being vented to atmosphere in the reformer flue gas. Hence, to capture CO_2 from modern SMR plants would require one of the post-combustion processes described above in Section 3.3. Alternatively, the PSA system could be designed not only for high recovery of pure H_2 but also to recover pure CO_2 and have a fuel gas as the third product stream.

In a design study for a large modern plant (total capacity 720 $tH_2\ d^{-1}$), the overall efficiency of making 6.0 MPa H_2 from natural gas with CO_2 vented that is without CO_2 capture, is estimated to be 76%, LHV basis, with emissions of 9.1 kg CO_2/kg H_2 (IEA GHG, 1996). The process can be modified (at a cost) to provide a nearly pure CO_2 co-product. One possibility is to remove most of the CO_2 from the shifted, cooled syngas in a 'wet' CO_2 removal plant with an appropriate amine solvent. In this case the CO_2-deficient syngas exiting the amine scrubber is passed to a PSA unit from which relatively pure H_2 is recovered and the PSA purge gases are burned along with additional natural gas to provide the needed reformer heat. The CO_2 is recovered from the amine solvent by heating and pressurized for transport. Taking into account the power to compress the CO_2 (to 11.2 MPa) reduces the efficiency to about 73% and the emission rate to 1.4 $kgCO_2/kgH_2$, while the CO_2 removal rate is 8.0 $kgCO_2/kgH_2$.

3.5.2.2 *Partial oxidation of gas and light hydrocarbons*

In the partial oxidation (POX) process (reaction 2), a fuel reacts with pure oxygen at high pressure. The process is exothermic and occurs at high temperatures (typically 1250°C-1400°C). All the heat required for the syngas reaction is supplied by the partial combustion of the fuel and no external heat is required. As with SMR, the syngas will be cooled, shifted and the CO_2 removed from the mixture. The comments made on the separation of CO_2 from SMR syngas above apply equally to the POX process. POX is a technology in common use today, the efficiency is lower than SMR, but the range of fuels that can be processed is much wider.

For large-scale hydrogen production, the oxygen is supplied from a cryogenic air separation unit (ASU). The high investment and energy consumption of the ASU is compensated by the higher efficiency and lower cost of the gasification process and the absence of N_2 (from the air) in the syngas, which reduces the separation costs considerably. However for pre-combustion de-carbonization applications, in which the hydrogen would be used as fuel in a gas turbine, it will be necessary to dilute the H_2 with either N_2 or steam to reduce flame temperature in the gas turbine combustor and to limit NO_x emission levels. In this case the most efficient system will use air as the oxidant and produce a H_2/N_2 fuel mixture (Hufton *et al.* 2005)

3.5.2.3 *Auto-thermal reforming of gas and light hydrocarbons*

The autothermal reforming (ATR) process can be considered as a combination of the two processes described above. The heat required in the SMR reactor is generated by the partial oxidation reaction (2) using air or oxygen, but because steam is supplied to the reactor as well as excess natural gas, the endothermic reforming reaction (1) occurs in a catalytic section of the reactor downstream of the POX burner. The addition of steam enables a high conversion of fuel to hydrogen at a lower temperature. Operating temperatures of the autothermal process are typically 950-1050°C, although this depends on the design of the process. An advantage of the process, compared to SMR, is the lower investment cost for the reactor and the absence of any emissions of CO_2 since all heat release is internal, although this is largely offset by investment and operating cost for the oxygen plant. The range of fuels that can be processed is similar to the SMR process, but the feed gas must be sulphur free. CO_2 capture is accomplished as described above for the steam methane reforming.

3.5.2.4 *Gas heated reformer*

Each of the three syngas generation technologies, SMR, ATR and POX produce high temperature gas which must be cooled, producing in each case a steam flow in excess of that required by the reforming and shift reactions. It is possible to reduce this excess production by, for example, using preheated air and a pre-reformer in an SMR plant. Another technique is to use the hot syngas, leaving the primary reactor, as the shell-side heating fluid in a tubular steam/hydrocarbon reforming reactor which can operate in series, or in parallel, with the primary reactor (Abbott *et al.*, 2002). The addition of a secondary gas heated reformer will increase the hydrogen production by up to 33% and eliminate the excess steam production. The overall efficiency is improved and specific capital cost is typically reduced by 15%. Again, CO_2 capture is accomplished as described previously for steam methane reforming.

3.5.2.5 *Gasification of coal, petroleum residues, or biomass*

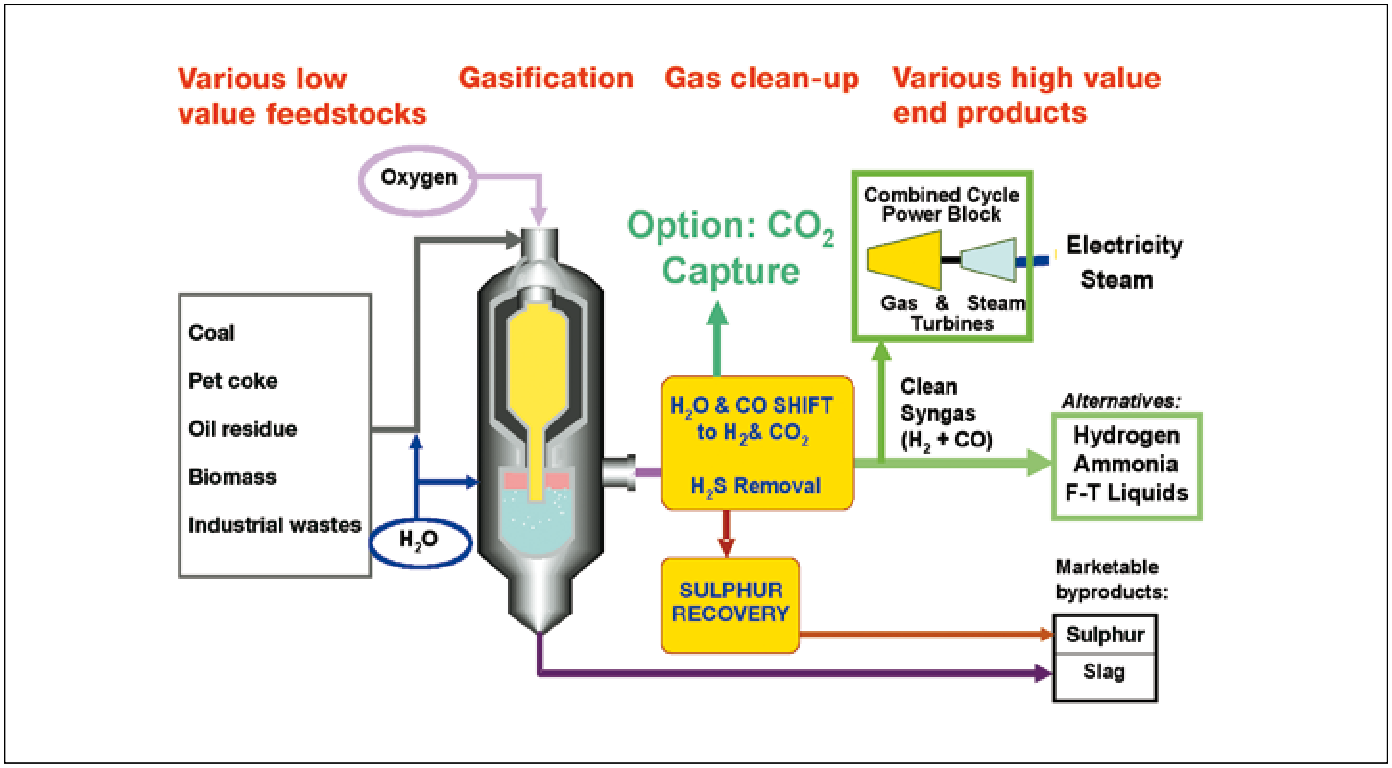

Figure 3.14 Simplified schematic of a gasification process showing options with CO_2 capture and electricity, hydrogen or chemical production.

Gasification (see Figure 3.14) is a chemical process aimed at making high-value products (chemicals, electricity, clean synthetic fuels) out of low-value solid feedstocks such as coal, oil refining residues, or biomass. Gasification is basically partial oxidation (reaction 2), although steam is also supplied to the reactor in most processes. Fixed bed, fluidized bed or entrained flow gasifiers can be used. These can have very different characteristics with respect to oxidant (air or O_2), operating temperature (up to 1350°C), operating pressure (0.1-7 MPa), feed system (dry or water slurry), syngas cooling method (water quench or via radiative and convective heat exchangers) and gas clean-up system deployed. These alternative design options determine the fraction of feedstock converted to syngas, syngas composition and cost. As economics depend strongly on scale, gasification is generally considered to be suitable only for large plants. The gasifier output contains CO, H_2, CO_2, H_2O and impurities (e.g., N_2, COS, H_2S, HCN, NH_3, volatile trace minerals and Hg) that must be managed appropriately.

A worldwide survey of commercial gasification projects identified 128 operating gasification plants with 366 gasifiers producing 42,700 MW_t of syngas (NETL-DOE, 2002 and Simbeck, 2001a). There are also about 24,500 MW_t of syngas projects under development or construction, with 4000-5000 MW_t of syngas added annually. The feedstocks are mainly higher rank coals and oil residues. Most commercial gasification growth for the last 20 years has involved entrained-flow gasifiers, for which there are three competing systems on the market. Recent commercial gasification development has been mainly with industrial ammonia production, industrial polygeneration (in which clean syngas is used to make electricity and steam along with premium syngas chemicals) and IGCC power plants. Commercial experience with biomass gasification and fluidized bed gasification has been limited.

CO_2 capture technology is well established for gasification systems that make chemicals and synthetic fuels (NETL-DOE, 2002). Gasification-based NH_3 plants (many in China) include making pure H_2 and CO_2 separation at rates up to 3500 tCO_2 d^{-1} per plant. South African plants making Fischer-Tropsch fuels and chemicals and a North Dakota plant making synthetic natural gas (SNG) from coal also produce large streams of nearly pure CO_2. Figure 3.15 shows a picture of the North Dakota gasification plant in which 3.3 $MtCO_2$ yr^{-1} is captured using a refrigerated methanol-based, physical solvent scrubbing process (Rectisol process, see Section 3.5.2.11 and Table 3.2). Most of this captured CO_2 is vented and about 1.5 Mtonnes yr^{-1} of this stream is currently pipelined to the Weyburn, Canada enhanced oil recovery and CO_2 storage project (see Chapter 5).

When CO_2 capture is an objective, O_2-blown and high-pressure systems are preferred because of the higher CO_2 partial pressures. De-carbonization via gasification entails lower energy penalties for CO_2 capture than does post-combustion capture when considering only the separation stage, because the CO_2 can be recovered at partial pressures up to 3 orders of magnitude higher. This greatly reduces CO_2 absorber size, solvent circulation rates and CO_2 stripping energy requirements. However, additional energy penalties are incurred in shifting the CO in the syngas to CO_2 and in other parts of the system (see examples for IGCC plant with CO_2 capture in Figures 3.6 and 3.7). Recent analyses for bituminous coals (see, for example, IEA GHG, 2003) suggest using simple high-pressure

Figure 3.15 North Dakota coal gasification plant with 3.3 $MtCO_2$ yr^{-1} capture using a cold methanol, physical solvent process (cluster of 4 tall columns in the middle of the picture represent the H_2S and CO_2 capture processes; part of the captured stream is used for EOR with CO_2 storage in Weyburn, Saskatchewan, Canada).

entrained-flow gasifiers with water slurry feed and direct water quench followed by 'sour' (sulphur-tolerant) shift reactors and finally co-removal of CO_2 and H_2S by physical absorption. With sour shifting, hot raw syngas leaving the gasifier requires only one cooling cycle and less processing. Oxygen requirements increase for slurry fed gasifiers and conversion efficiencies decline with higher cycle efficiency losses with quench cooling. Similar trends are also noted with a shift from bituminous to lower rank sub-bituminous coal and lignite (Breton and Amick, 2002). Some analyses (e.g., Stobbs and Clark, 2005) suggest that the advantages of pre-combustion over post-combustion de-carbonization may be small or disappear for low-rank coals converted with entrained-flow gasifiers. High-pressure, fluidized-bed gasifiers may be better suited for use with low-rank coals, biomass and various carbonaceous wastes. Although there are examples of successful demonstration of such gasifiers (e.g., the high temperature Winkler, Renzenbrink *et al.*, 1998), there has been little commercial-scale operating experience.

The H_2S in syngas must be removed to levels of tens of ppm for IGCC plants for compliance with SO_2 emissions regulations and to levels much less than 1 ppm for plants that make chemicals or synthetic fuels, so as to protect synthesis catalysts. If the CO_2 must be provided for storage in relatively pure form, the common practice would be to recover first H_2S (which is absorbed more readily than CO_2) from syngas (along with a small amount of CO_2) in one recovery unit, followed by reduction of H_2S to elemental sulphur in a Claus plant and tail gas clean-up, and subsequent recovery of most of the remaining CO_2 in a separate downstream unit. An alternative option is to recover sulphur in the form of sulphuric acid (McDaniel and Hormick, 2002). If H_2S/CO_2 co-storage is allowed, however, it would often be desirable to recover H_2S and CO_2 in the same physical absorption unit, which would lead to moderate system cost savings (IEA GHG, 2003; Larson and Ren, 2003; Kreutz *et al.*, 2005) especially in light of the typically poor prospects for selling byproduct sulphur or sulphuric acid. Although co-storage of H_2S and CO_2 is routinely pursued in Western Canada as an acid gas management strategy for sour natural gas projects (Bachu and Gunter, 2005), it is not yet clear that co-storage would be routinely viable at large scales - a typical gasification-based energy project would involve an annual CO_2 storage rate of 1-4 Mtonnes yr^{-1}, whereas the total CO_2 storage rate for all 48 Canadian projects is presently only 0.48 Mtonnes yr^{-1} (Bachu and Gunter, 2005).

3.5.2.6 Integrated gasification combined cycle (IGCC) for power generation

In a coal IGCC, syngas exiting the gasifier is cleaned of particles, H_2S and other contaminants and then burned to make electricity via a gas turbine/steam turbine combined cycle. The syngas is generated and converted to electricity at the same site, both to avoid the high cost of pipeline transport of syngas (with a heating value only about 1/3 of that for natural gas) and to cost-effectively exploit opportunities for making extra power in the combined cycle's steam turbine using steam from syngas cooling. The main drivers for IGCC development were originally the prospects of exploiting continuing advances in gas turbine technology, the ease of realizing low levels of air-pollutant emissions when contaminants are removed from syngas, and greatly reduced process stream volumes compared to flue gas streams from combustion which are at low pressure and diluted with nitrogen from air.

Since the technology was initially demonstrated in the 1980s, about 4 GW_e of IGCC power plants have been built. Most of this capacity is fuelled with oil or petcoke; less than 1 GW_e of the total is designed for coal (IEA CCC, 2005) and 3 out of 4 plants currently operating on coal and/or petcoke. This experience has demonstrated IGCC load-following capability, although the technology will probably be used mainly in base load applications. All coal-based IGCC projects have been subsidized, whereas only the Italian oil-based IGCC projects have been subsidized. Other polygeneration projects in Canada, the Netherlands and the United States, as well as an oil-based IGCC in Japan, have not been subsidized (Simbeck, 2001a).

IGCC has not yet been deployed more widely because of strong competition from the natural gas combined cycle (NGCC) wherever natural gas is readily available at low prices, because coal-based IGCC plants are not less costly than pulverized coal fired steam-electric plants and because of availability (reliability) concerns. IGCC availability has improved in recent years in commercial-scale demonstration units (Wabash River Energy, 2000; McDaniel and Hornick, 2002). Also, availability has been better for industrial polygeneration and IGCC projects at oil refineries and chemical plants where personnel are experienced with the chemical processes involved. The recent rise in natural gas prices in the USA has also increased interest in IGCC.

Because of the advantages for gasification of CO_2 capture at high partial pressures discussed above, IGCC may be attractive for coal power plants in a carbon-constrained world (Karg and Hannemann, 2004). CO_2 capture for pre-combustion systems is commercially ready, however, no IGCC plant incorporating CO_2 capture has yet been built. With current technology, average estimates of the energy penalties and the impact of increased fuel use for CO_2 removal are compared with other capture systems in Figures 3.6 and 3.7 and show the prospective potential of IGCC options. The data in Figures 3.6 and 3.7 also show that some IGCC options may be different from others (i.e., slurry fed and quench cooled versus dry feed and syngas cooling) and their relative merits in terms of the capital cost of plant and the delivered cost of power are discussed in Section 3.7.

3.5.2.7 Hydrogen from coal with CO_2 capture

Relative to intensively studied coal IGCC technology with CO_2 capture, there are few studies in the public domain on making H_2 from coal via gasification with CO_2 capture (NRC, 2004; Parsons 2002a, b; Gray and Tomlinson, 2003; Chiesa *et al*., 2005; Kreutz *et al*., 2005), even though this H_2 technology is well established commercially, as noted above. With commercial technology, H_2 with CO_2 capture can be produced via coal gasification in a system similar to a coal IGCC plant with CO_2 capture. In line with the design recommendations for coal IGCC plants described above (IEA GHG, 2003), what follows is the description from a design study of a coal H_2 system that produces, using best available technology, 1070 MW_t of H_2 from high-sulphur (3.4%) bituminous coal (Chiesa *et al*., 2005; Kreutz *et al*., 2005). In the base case design, syngas is produced in an entrained flow quench gasifier operated at 7 MPa. The syngas is cooled, cleaned of particulate matter, and shifted (to primarily H_2 and CO_2) in sour water gas shift reactors. After further cooling, H_2S is removed from the syngas using a physical solvent (Selexol). CO_2 is then removed from the syngas, again using Selexol. After being stripped from the solvents, the H_2S is converted to elemental S in a Claus unit and a plant provides tail gas clean-up to remove residual sulphur emissions; and the CO_2 is either vented or dried and compressed to 150 atm for pipeline transport and underground storage. High purity H_2 is extracted at 6 MPa from the H_2-rich syngas via a pressure swing adsorption (PSA) unit. The PSA purge gas is compressed and burned in a conventional gas turbine combined cycle, generating 78 MW_e and 39 MW_e of electricity in excess of onsite electricity needs in the without and with CO_2 capture cases, respectively. For this base case analysis, the effective efficiency of H_2 manufacture was estimated to be 64% with CO_2 vented and 61% with CO_2 captured, while the corresponding emission rates are 16.9 $kgCO_2$ and 1.4 $kgCO_2/kgH_2$, respectively. For the capture case, the CO_2 removal rate was 14.8 $kgCO_2/kgH_2$. Various alternative system configurations were explored. It was found that there are no thermodynamic or cost advantages from increasing the electricity/H_2 output ratio, so this ratio would tend to be determined by relative market demands for electricity and H_2. One potentially significant option for reducing the cost of H_2 with CO_2 capture to about the same level as with CO_2 vented involves H_2S/CO_2 co-capture in a single Selexol unit, as discussed above.

3.5.2.8 Carbon-based fluid fuels and multi-products

As discussed in Chapter 2, clean synthetic high H/C ratio fuels can be made from syngas via gasification of coal or other low H/C ratio feedstocks. Potential products include synthetic natural gas, Fischer-Tropsch diesel/gasoline, dimethyl ether, methanol and gasoline from methanol via the Mobil process. A byproduct is typically a stream of relatively pure CO_2 that can be captured and stored.

Coal derived Fischer-Tropsch synfuels and chemicals have been produced on a commercial scale in South Africa; coal methanol is produced in China and at one US plant; and coal SNG is produced at a North Dakota (US) plant (NETL-DOE, 2002). Since 2000, 1.5 $MtCO_2\ yr^{-1}$ from the North Dakota synthetic natural gas plant (see Figure 3.15) have been transported by pipeline, 300 km to the Weyburn oil field in Saskatchewan, Canada for enhanced oil recovery with CO_2 storage.

Synfuel manufacture involves O_2-blown gasification to make syngas, gas cooling, gas clean-up, water gas shift and acid gas (H_2S/CO_2) removal. Subsequently cleaned syngas is converted catalytically to fuel in a synthesis reactor and unconverted syngas is separated from the liquid fuel product. At this point either most unconverted gas is recycled to the synthesis reactor to generate additional liquid fuel and the remaining unconverted gas is used to make electricity for onsite needs, or syngas is passed only once through the synthesis reactor, and all unconverted syngas is used for other purposes, for example, to make electricity for sale to the electric grid as well as for onsite use. The latter *once through* option is often more competitive as a technology option (Williams, 2000; Gray and Tomlinson, 2001; Larson and Ren, 2003; Celik *et al*., 2005).

New slurry-phase synthesis reactors make the once through configuration especially attractive for CO-rich (e.g., coal-derived) syngas by making high once through conversion possible. For once through systems, a water gas shift reactor is often placed upstream of the synthesis reactor to generate the H_2/CO ratio that maximizes synfuel conversion in the synthesis reactor. It is desirable to remove most CO_2 from shifted syngas to maximize synthetic fuel conversion. Also, because synthesis catalysts are extremely sensitive to H_2S and various trace contaminants, these must be removed to very low levels ahead of the synthesis reactor. Most trace metals can be removed at low-cost using an activated carbon filter. CO_2 removal from syngas upstream of the synthesis reactor is a low-cost, partial de-carbonization option, especially when H_2S and CO_2 are co-captured and co-stored as an acid gas management strategy (Larson and Ren, 2003). Further de-carbonization can be realized in once through systems, at higher incremental cost, by adding additional shift reactors downstream of the synthesis reactor, recovering the CO_2, and using the CO_2-depleted, H_2-rich syngas to make electricity or some mix of electricity plus H_2 in a 'polygeneration' configuration (see Figure 3.16). The relative amounts of H_2 and electricity produced would depend mainly on relative demands, as there do not seem to be thermodynamic or cost advantages for particular H_2/electricity production ratios (Chiesa *et al*., 2005; Kreutz *et al*., 2005). When syngas is de-carbonized both upstream and downstream of the synthesis reactor (see Figure 3.16) it is feasible to capture and store as CO_2 up to 90% of the carbon in the original feedstock except

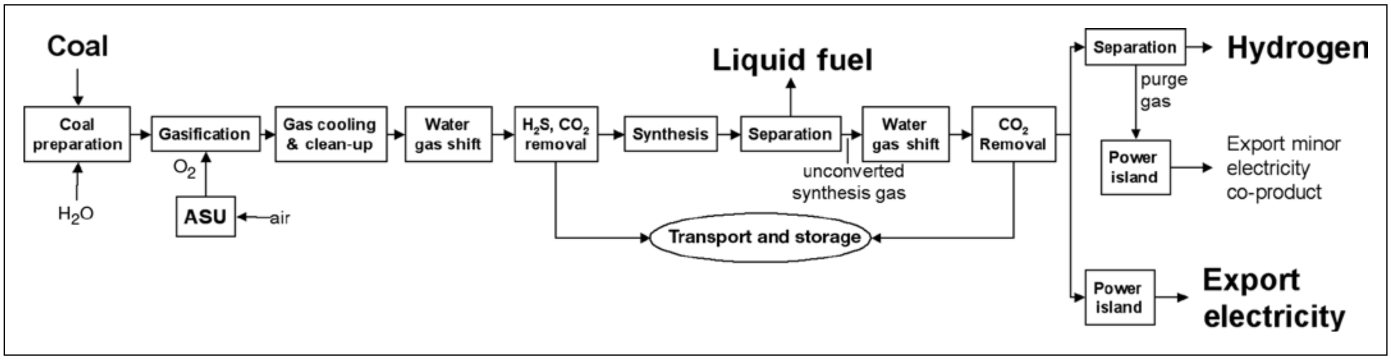

Figure 3.16 Making liquid fuel, electricity and hydrogen from coal via gasification, with CO_2 capture and storage.

that contained in the synthetic fuel produced.

An example of such a system (Celik *et al.*, 2005) is one making 600 MW of dimethyl ether (containing 27% of coal input energy and 20% of coal input carbon) plus 365 MW of electricity (no H_2) from coal. For this system the CO_2 storage rate (equivalent to 74% of C in coal) is 3.8 Mtonnes yr^{-1} (39% from upstream of the synthesis reactor). The estimated fuel cycle-wide GHG emissions for dimethyl ether are 0.9 times those for crude oil-derived diesel and those for electricity are 0.09 times those for a 43% efficient coal-fired power plant with CO_2 vented.

3.5.2.9 Pressure swing adsorption

Pressure Swing Adsorption (PSA) is the system of choice for the purification of syngas, where high purity H_2 is required. However, it does not selectively separate CO_2 from the other waste gases and so for an SMR application the CO_2 concentration in the waste gas would be 40-50% and require further upgrading to produce pure CO_2 for storage. Simultaneous H_2 and CO_2 separation is possible by using an additional PSA section to remove the CO_2 prior to the H_2 separation step, such as the Air Products Gemini Process (Sircar, 1979).

The PSA process is built around adsorptive separations of cyclic character. The cycles consist of two basic steps: adsorption, in which the more adsorbable species are selectively removed from the feed gas and regeneration (desorption), when these species are removed from the adsorbent so that it can be ready for the next cycle. It is possible to obtain useful products during both adsorption and regeneration. The principal characteristic of PSA processes is the use of a decrease in pressure and/or the purge by a less adsorbable gas to clean the adsorbent bed. Apart from adsorption and regeneration, a single commercial PSA cycle consists of a number of additional steps, including co- and counter-current pressurization, pressure equalization and co- and counter-current depressurization. A detailed description of the PSA technique, along with its practical applications can be found elsewhere (Ruthven *et al.*, 1994).

3.5.2.10 Chemical solvent processes

Chemical solvents are used to remove CO_2 from syngas at partial pressures below about 1.5 MPa (Astarita *et al.*, 1983) and are similar to those used in post-combustion capture (see Section 3.3.2.1). The solvent removes CO_2 from the shifted syngas by means of a chemical reaction, which can be reversed by pressure reduction and heating. The tertiary amine methyldiethanolamine (MDEA, see Table 3.2) is widely used in modern industrial processes, due to the high CO_2 loading possible and the low regenerator heating load, relative to other solvents. Hot potassium carbonate (the most common commercial version of which is known as Benfield) was used for CO_2 removal in most hydrogen plants until about 15 years ago.

3.5.2.11 Physical solvent processes

Physical solvent (or absorption) processes are mostly applicable to gas streams which have a high CO_2 partial pressure and/or a high total pressure. They are often used to remove the CO_2 from the mixed stream of CO_2 and H_2 that comes from the shift reaction in pre-combustion CO_2 capture processes, such as product from partial oxidation of coal and heavy hydrocarbons.

The leading physical solvent processes are shown in Table 3.2. The regeneration of solvent is carried out by release of pressure at which CO_2 evolves from the solvent, in one or more stages. If a deeper regeneration is required the solvent would be stripped by heating. The process has low energy consumption, as only the energy for pressurizing the solvent (liquid pumping) is required.

The use of high sulphur fossil fuels in a pre-combustion capture process results in syngas with H_2S. Acid gas components must be removed. If transport and storage of mixed CO_2 and H_2S is possible then both components can be removed together. Sulphinol was developed to achieve significantly higher solubilities of acidic components compared to amine solvents, without added problems of excessive corrosion, foaming, or solution degradation. It consists of a mixture of sulpholane (tetrahydrothiophene 1,1-dioxide), an alkanolamine and water in various proportions depending on the duty. If pure CO_2 is required, then a selective process is required using physical solvents - often Rectisol or Selexol. The H_2S must be separated at sufficiently high concentration (generally >50%) to be treated in a sulphur recovery plant.

3.5.2.12 Effect on other pollutants

Pre-combustion capture includes reforming, partial oxidation or gasification. In order to maintain the operability of the catalyst of reformers, sulphur (H_2S) has to be removed prior to reforming. In gasification, sulphur can be captured from the syngas, and in the case when liquid or solid fuels are gasified, particulates, NH_3, COS and HCN are also present in the system that need to be removed. In general, all of these pollutants can be removed from a high-pressure fuel gas prior to combustion, where combustion products are diluted with nitrogen and excess oxygen. In the combustion of hydrogen or a hydrogen-containing fuel gas, NO_x may be formed. Depending upon combustion technology and hydrogen fraction, the rate at which NO_x is formed may vary. If the volumetric fraction of hydrogen is below approximately 50-60%, NO_x formation is at the same level as for natural gas dry low-NO_x systems (Todd and Battista, 2001).

In general, with the exception of H_2S that could be co-removed with CO_2, other pollutants identified above are separated in additional pretreatment operations, particularly in systems that gasify liquid or solid fuels. High temperature pretreatment operations for these multi-pollutants that avoid cooling of the syngas have the advantage of improving the cycle efficiency of the overall gasification process, but these separation processes have not been commercially demonstrated.

Although it is not yet regulated as a 'criteria pollutant', mercury (Hg), is currently the focus of considerable concern as a pollutant from coal power systems. For gasification systems Hg can be recovered from syngas at ambient temperatures at very low-cost, compared to Hg recovery from flue gases (Klett *et al.*, 2002).

3.5.3 Emerging technologies

Emerging options in both natural gas reforming and coal gasification incorporate novel combined reaction/separation systems such as sorption-enhanced reforming and sorption-enhanced water gas shift, membrane reforming and membrane water gas shift. Finally there is a range of technologies that make use of the carbonation of CaO for CO_2 capture.

3.5.3.1 Sorption enhanced reaction

A concept called Sorption Enhanced Reaction (SER) uses a packed bed containing a mixture of a catalyst and a selective adsorbent to remove CO_2 from a high temperature reaction zone, thus driving the reaction to completion. (Hufton *et al.*, 1999). The adsorbent is periodically regenerated by using a pressure swing, or temperature swing adsorption system with steam regeneration (Hufton *et al.*, 2005).

High temperature CO_2 adsorbents such as hydrotalcites (Hufton *et al.*, 1999) or lithium silicate (Nakagawa and Ohashi, 1998) can be mixed with a catalyst to promote either the steam methane reforming reaction (Reaction 1) or water gas shift reaction (Reaction 3) producing pure hydrogen and pure CO_2 in a single process unit. The continuous removal of the CO_2 from the reaction products by adsorption shifts each reaction towards completion.

The SER can be used to produce hydrogen at 400-600°C to fuel a gas turbine combined cycle power generation system. A design study based on a General Electric 9FA gas turbine with hot hydrogen, produced from an air blown ATR with a sorption enhanced water gas shift reactor, gave a theoretical net efficiency of 48.3% with 90% CO_2 capture at 99% purity and 150 bar pressure (Hufton *et al.*, 2005). The process is currently at the pilot plant stage.

3.5.3.2 Membrane reactors for hydrogen production with CO_2 capture

Inorganic membranes with operating temperatures up to 1000°C offer the possibility of combining reaction and separation of the hydrogen in a single stage at high temperature and pressure to overcome the equilibrium limitations experienced in conventional reactor configurations for the production of hydrogen. The combination of separation and reaction in membrane steam reforming and/or membrane water gas shift offers higher conversion of the reforming and/or shift reactions due to the removal of hydrogen from these equilibrium reactions as shown in Reactions (1) and (3) respectively. The reforming reaction is endothermic and can, with this technique, be forced to completion at lower temperature than normal (typically 500-600°C). The shift reaction being exothermic can be forced to completion at higher temperature (500-600°C).

Another reason to incorporate H_2 separation membranes in the hydrogen production system is that CO_2 is also produced without the need for additional separation equipment. Membrane reactors allow one-step reforming, or a single intermediate water gas shift reaction, with hydrogen separation (the permeate) leaving behind a retentate gas which is predominantly CO_2 and a small amount of non-recovered hydrogen and steam. This CO_2 remains at the relatively high pressure of the reacting system (see Figure 3.17). Condensation of the steam leaves a concentrated CO_2 stream at high pressure, reducing the compression energy for transport and storage. Membrane reforming will benefit from high-pressure operation due to the increased H_2 partial pressure differential across the membrane which is the driving force for hydrogen permeation. Therefore membrane reactors are also seen as a good option for pre-combustion de-carbonization where a low-pressure hydrogen stream for fuel gas and a high-pressure CO_2-rich stream for transport and storage are required. The use of the membrane reformer reactor in a gas turbine combined cycle means that the hydrogen needs to be produced at such pressure that the significant power consumption for the hydrogen compression is avoided. This could be done by increasing the operating pressure of the membrane reactor or by using a sweep gas, for instance steam, at the permeate side of the membrane (Jordal *et al.*, 2003).

For these membrane reactor concepts, a hydrogen selective membrane capable of operating in a high-temperature, high-pressure environment is needed. In the literature a number of membrane types have been reported that have these capabilities and these are listed in Table 3.3. Microporous inorganic membranes based upon surface diffusion separation exhibit rather low separation factors (e.g., H_2/CO_2 separation factor of 15). However, the separation ability of the current commercially available gamma-alumina and silica microporous membranes (which have better separation factors, up to 40) depends upon the stability of the membrane pore size, which is adversely

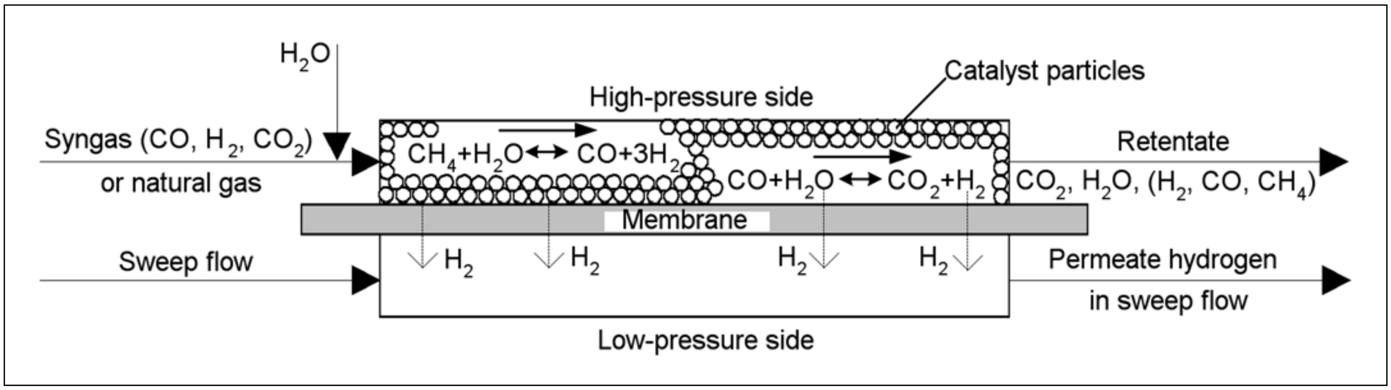

Figure 3.17 Operating principle of a membrane reactor.

Table 3.3 Membrane materials, operating conditions and characteristics for H_2 separation.

	Microporous Ceramic	**Microporous Ceramic**	**Microporous Carbon**	**Zeolites**	**Metal**
Membrane material	Alumina	Silica	Carbon	Silica (Alumina)	Pd/Ag
Temperature range (°C)	<500	<400	<400	<500 - 700	<600
Pressure range (bar)	>100	>100	10	>100	>100
Pore size distribution (nm)	0.7-2	0.7-2	0.7-2	0.3-0.7	no pores
Separation factors (H_2/CO_2)	15	15	15-25	50	100
Permeability (mol $m^{-2}s^{-1}Pa^{-1}$)	10^{-6}	10^{-6}	10^{-7}	10^{-6}	10^{-7}-10^{-6}
Experim. temp. (°C)	200	200	300-400	300-400	300-400
Pre-clean-up requirements				S	S, HCl, HF (?)
Chemical resistance problem		H_2O	O_2	S	S, HCl, HF
Geometry	Top layer tube	Top layer tube	Top layer tube/fibre	Top layer tube	Top layer tube/plate
Configuration	Cascade/recycle/ once through	Cascade/recycle/ once through	Cascade/recycle/ once through	Once through	Once through
Lifetime	+	-	+	+	0
Costs (US\$ m^{-2})	4250	4250	3000?	4000-4250	4000-4250
Scalability	0	0	0	-	0

affected by the presence of steam in the feed streams. The dense ceramic membranes based on inorganic perovskite oxides (also called proton conducting) need high temperatures, higher than 800°C, to achieve practical hydrogen flux rates. Palladium-based dense membranes are also known for their high hydrogen selectivity and permeability over other gases in the temperature range 300°C-600°C that is appropriate for these two reactions. Palladium alloy tubes have been available for several decades, but for CCS applications they are too expensive due to the membrane thickness needed for structural stability and consequently low hydrogen flux rates. In order to be suitable for the target application, a hydrogen separation membrane must have adequate selectivity and flux rate and must be stable in the reducing coal gas or fuel-reforming environment containing steam and hydrogen sulphide.

A number of membrane reactor developments have been reported for hydrogen production with CO_2 capture. Several groups have evaluated methane steam reforming membrane reactors based on palladium alloy membranes (Middleton *et al.*, 2002, Damle and Dorchak, 2001). These evaluations showed that membrane reactors could achieve 90% CO_2 recovery and that at this moment the projected cost is nearly identical to that for a conventional system. However, a cost-reduction can be achieved by either reducing the material cost of the membrane or by increasing the permeability. Similar evaluations of membrane reactors for the shift conversion and separation of CO_2 from syngas produced from heavy feeds by gasification have been reported (Bracht *et al.*, 1997; Middleton 2002; Lowe *et al.*, 2003). For these gasifier systems the membrane reactors could reduce the costs for capturing CO_2 and the cost reduction would be more significant if they could be made sulphur tolerant.

3.5.3.3 Microchannel reformer

Microreactor technology can be used to produce a SMR, or low temperature air-based POX system using a multichannel plate-fin heat exchanger, fabricated in stainless steel or high nickel alloy by vacuum brazing or diffusion bonding.

An SMR reactor consists of alternate passages having fins, which are coated with catalyst or porous catalyst insets. Heat is produced by catalytic combustion of fuel gas premixed with air and transferred by conduction to the adjacent passage fed with the steam/hydrocarbon mixture, where the reforming reaction takes place (Babovic *et al.*, 2001). Very compact high efficiency systems can be produced. Although these units are being currently developed by a number of groups for small-scale H_2 production for fuel cell applications, they also show promise in larger H_2 plants.

3.5.3.4 Conversion to hydrogen and carbon

Thermal cracking or pyrolysis of methane is the reaction where methane reacts to carbon and hydrogen through:

Methane pyrolysis:

$$CH_4 \rightarrow C + 2\ H_2 \qquad (4)$$

The main advantage of the process is that it can potentially yield a clean gas (free of carbon oxides) that could be used directly for power production, but a disadvantage is that the chemical energy from the oxidation of carbon to CO_2 is not released. The cracking reaction is endothermic and so heat has to be supplied to the reaction. If the natural gas is converted fully, the theoretical yield of hydrogen corresponds to 60% of the heating value of the natural gas. The amount of carbon, which can be obtained, corresponds to 49% of the heating value, with the extra 9% of the energy in this calculation being provided as endothermic heat shown by reaction (4) above. Therefore full conversion can be achieved only if heat is supplied from an external source. If full conversion of methane is not achieved, the remaining methane will be combusted to produce heat. There are many different methods under development for reactors based on this principle, including thermal catalytic, thermal non-catalytic and plasma cracking.

In the plasma cracking process natural gas or other hydrocarbons are supplied to a plasma reactor where the hydrocarbons are cracked under pyrolysis conditions (i.e., in absence of oxides, e.g., steam, which can supply oxygen to form CO or CO_2). The plasma arc, for which electricity is used, supplies the heat for the cracking reaction. Advantages of the process are its flexibility with respect to the fuel and the high quality carbon black which can be produced. Two small-scale plasma cracking processes for hydrogen/syngas production have been in development. The Glid Arc process has been developed by the Canadian Synergy Technologies Corporation. The second process is the Kvaerner CB&H process. Kvaerner has reported results for a pilot plant producing 1000 Nm^3 hydrogen per hour and 270 kg or 500 kg carbon black using natural gas and aromatic oil respectively (IEA GHG, 2001).

3.5.3.5 Technologies based on calcium oxide

There is a range of pre-combustion systems that make use of the carbonation reaction of CaO at high pressures and temperatures, to further integrate the gasification of the fuel (if solid), the shift reaction, and in-situ CO_2 removal with CaO. The overall reaction aimed in the system is:

Carbonation of calcium oxide:

$$CaO + C + 2\ H_2O \rightarrow CaCO_3 + 2H_2 \qquad (5)$$

The regeneration of the sorbent produces pure CO_2 when carried out in a separate reactor by calcining $CaCO_3$. A range of systems can be developed under this general reaction scheme depending on the technology adopted for gasification, carbonation-calcination, hydrogen utilization route and storage option for CO_2. The first of these concepts was proposed at the Los Alamos National Laboratory (USA) and is currently under development as the Zero Emission Coal Alliance (ZECA) process. The full system includes (Lackner *et al.*, 2001) a hydro-gasification reactor, solid oxide fuel cell and a technology for mineral carbonation. However, the fuel cell will require more development and mineral carbonation is only at the laboratory investigation stage (see Section 7.2 for a discussion of mineral carbonation).

The HyPrRing process (Lin *et al.*, 2002) is being developed by the Center for Coal Utilization of Japan. It integrates gasification, reforming and *in situ* CO_2 capture in a single reactor at pressures above 12 MPa and temperature above 650ºC. Projects in Norway using natural gas and in Germany using brown coal (Bandi *et al.*, 2002) are also underway developing pre-combustion systems using capture of CO_2 with CaO. Finally, General Electric (Rizeq *et al.*, 2002) is developing an innovative system involving the capture of CO_2 in the gasification reactor by a high temperature sorbent and with calcination in a separate reactor by burning part of the fuel with an oxygen carrier.

All these systems are at an early stage of development. Detailed process simulations show that the efficiencies are potentially high because most of the energy employed for sorbent regeneration is effectively transferred to the H_2 generated in reaction (5). The systems are aimed at very large-scale generation of electricity and/or H_2 and cement production (from the deactivated sorbent, CaO). However, many uncertainties remain concerning the performance of the individual units and their practical integration. The main challenge may be the regeneration of the sorbent at very high temperatures (>900^{0}C), to produce a pure stream of CO_2. Another is the operating conditions to achieve sufficient conversion towards hydrogen, without the use of a catalyst for the shift reaction.

3.5.4 Enabling technologies

The performance and cost of a pre-combustion capture system is linked to the availability of the enabling technologies that complete the system. In this section we consider the availability of industrial systems, to produce heat from the de-carbonized fuel and gas turbines and fuel cells to produce power.

3.5.4.1 Use of de-carbonized fuel in industrial systems

The use of hydrogen as a fuel for conventional fired heaters and boilers is considered to be proven and indeed it is practiced at certain industrial sites. There is a very large stock of capital equipment of this type and so the use of hydrogen as a fuel might be considered a valuable technology option in a carbon-constrained world. A study (IEA GHG, 2000c) has looked at the cost of converting an existing refinery to use hydrogen fuel.

3.5.4.2 Use of de-carbonized fuel in gas turbine systems

There is extensive commercial experience with hydrogen-rich fuel gas firing in gas turbines. For example, General Electric reports over 450,000 hours of operating experience with high hydrogen (52-95% by volume) content fuel gas in gas turbines (Shilling and Jones, 2003). Unfortunately, most of that experience is for 'refinery gas' where methane is the other main component of the fuel gas and is utilized in older lower firing temperature gas turbines, not the state-of-the-art over 1300°C gas turbines normally considered for large de-carbonization power plants.

Norsk Hydro and General Electric collaborated to perform full-scale combustion system testing for modern gas turbines firing hydrogen-rich gas with combustion exit temperatures of above 1400°C (Todd and Battista, 2001). The results showed good combustion conditions with low NO_x emission and acceptable hot metal temperatures for mixtures with 54-77% by volume hydrogen with most of the additional gas being nitrogen. Dilution of the hydrogen with nitrogen or steam reduces the NO_x emission.

For pre-combustion capture of CO_2 from natural gas, air-blown gasification or autothermal reforming is usually preferred (IEA GHG, 2000b; Wilkinson and Clarke, 2002). Nitrogen dilution of the hydrogen required for firing in modern gas turbines comes from the gasification air. High-pressure air is usually extracted from the gas turbine to feed the air-blown gasifier, or autothermal reformer to reduce costs and avoid a separate air compressor. The balance between the amount of air withdrawn from the gas turbine and the amount provided from a separate air compressor is determined by the particular characteristics of the gas turbine used. Some gas turbines can accept a higher ratio of expander to compressor flow, allowing greater volumes of dilution gas or smaller air-side draw flow and giving higher power output.

For pre-combustion capture of CO_2 from coal, oxygen-blown gasification is usually preferred (IEA GHG, 2003). Nitrogen dilution of the hydrogen required for firing in modern gas turbines comes from the cryogenic air separation unit (used to make the oxygen; see Section 3.4.5.1). The nitrogen is added to the hydrogen after the gasification, CO shifting and CO_2 capture to reduce the equipment sizes and cost. High-pressure air is usually extracted from the gas turbine to supply a higher than normal pressure cryogenic air separation unit to reduce costs plus air, oxygen and nitrogen compression power. An alternative IGCC scheme that incorporates newly emerging ion transport membranes for oxygen production is also described below in Section 3.5.4.3.

3.5.4.3 Syngas production using oxygen membranes

Oxygen required for a coal-fired IGCC process (Section 3.5.2.6) can be generated in an oxygen transport membrane system by using a heated, high-pressure air stream produced by heating the discharge air from the compressor section of a gas turbine (Allam *et al.*, 2002), typically at 1.6 MPa or 420°C, to the precise inlet temperature of the oxygen transport membrane module which is above 700°C. The oxygen, which permeates to the low-pressure side passes through a heat recovery section and is compressed to the final pressure of use. The O_2 depleted air leaving the oxygen transport membrane module then enters the gas turbine combustor where it is used to burn fuel before entering the gas turbine expander at the required temperature. Note that due to the necessity to have excess air in a gas turbine to limit turbine inlet temperature, removing one mole of oxygen can be compensated by injection of the equivalent thermal capacity of steam to maintain gas turbine power output. Studies have been carried out (Armstrong *et al.*, 2002) to compare oxygen transport membrane and cryogenic oxygen production in an IGCC power plant using coal as fuel. The oxygen plant projected cost was reduced by 35% and the power consumption by 37%. An LHV efficiency of 41.8% without CO_2 capture and compression is reported for this cycle compared to 40.9% when a conventional cryogenic oxygen plant is used.

For autothermal reforming or the partial oxidation of natural gas, if the permeate side of the oxygen transport membrane is exposed to a natural gas plus water vapour stream in the presence of a reforming catalyst, the oxygen will react as it leaves the membrane in an exothermic reaction (Dyer *et al.*, 2001; Carolan *et al.*, 2001), which will provide heat for the endothermic steam/natural gas reforming reaction. The oxygen partial pressure at these highly-reducing, high temperature conditions is extremely low, allowing heated air at close to atmospheric pressure to be used on the feed side of the membrane while producing a H_2 + CO mixture at high pressure from the permeate side. This system can be used to produce H_2 following CO shift reaction and CO_2 removal.

3.5.4.4 Chemical looping gasification/reforming

The chemical looping concept described in 3.4.6 is being considered for reforming of a fuel to produce H_2 and CO (Zafar *et al.*, 2005). When the amount of oxygen brought by the metal oxide into the reduction reactor is below stoichiometric requirements, the chemical reaction with the fuel produces H_2 and CO. The reaction products may subsequently be shifted with steam to yield CO_2 and more H_2.

3.5.4.5 Use of de-carbonized fuel in fuel cells

Fuel cells offer the possibility for highly efficient power production since the conversion process is not controlled by heat to work Carnot cycle restrictions (Blomen and Mugerwa, 1993). In general fuel cells feature the electrochemical oxidation of gaseous fuels directly into electricity, avoiding the mixture of the air and the fuel flows and thus the dilution with nitrogen and excess oxygen of the oxidized products (Campanari, 2002). As a result, the anode outlet stream of a fuel cell already has a very high CO_2 content that simplifies the CO_2 capture subsystem. The fuel is normally natural gas, though some concepts can also be incorporated into coal gasification systems. The systems concepts can be classified into two main groups (Goettlicher, 1999):

- Systems with pre-fuel cell CO_2 capture;
- Systems with post-fuel cell CO_2 capture.

In pre-fuel cell CO_2 capture systems (see Figure 3.18a) the fuel is first converted into hydrogen using steam reforming or coal gasification, followed by the water gas shift conversion. This system approach has been first proposed both for low temperature and for high temperature fuel cells.

The post-fuel cell capture system (see Figure 3.18b) is proposed for high temperature fuel cell systems (Dijkstra and Jansen, 2003). These systems make use of the internal reforming capabilities of the high temperature fuel cells resulting in an anode off-gas that has a high CO_2-content, but also contains H_2O and unconverted CO and H_2. The water can easily be removed by conventional techniques (cooling, knock-out, additional drying). Oxidizing the H_2 and CO from the (SOFC) anode with air will result in a too high dilution of the stream with nitrogen.

Haines (1999) chooses to use an oxygen-transport membrane reactor placed after the SOFC. The anode off-gas is fed to one side of the membrane, the cathode off-gas is fed to the other side of the membrane. The membrane is selective to oxygen, which permeates from the cathode off-gas stream to the anode-off gas. In the membrane unit the H_2 and CO are oxidized. The retenate of the membrane unit consist of CO_2 and water. Finally a concept using a water gas shift membrane reactor has been proposed (Jansen and Dijkstra, 2003).

3.5.5 *Status and outlook*

This section reviewed a wide variety of processes and fuel conversion routes that share a common objective: to produce a cleaner fuel stream from the conversion of a raw carbonaceous fuel into one that contains little, or none, of the carbon contained in the original fuel. This approach necessarily involves the separation of CO_2 at some point in the conversion process. The resulting H_2-rich fuel can be fed to a hydrogen consuming process, oxidized in a fuel cell, or burned in the combustion chamber of a gas turbine to produce electricity. In systems that operate at high pressure, the energy conversion efficiencies tend to be higher when compared to equivalent systems operating at low pressures following the combustion route, but these efficiency improvements are often obtained at the expense of a higher complexity and capital investment in process plants (see Section 3.7).

In principle, all pre-combustion systems are substantially similar in their conversion routes, allowing for differences that arise from the initial method employed for syngas production from gaseous, liquid or solid fuels and from the subsequent need to remove impurities that originate from the fuel feed to the plant. Once produced, the syngas is first cleaned and then reacted with steam to produce more H_2 and CO_2. The separation of these two gases can be achieved with well-known, commercial absorption-desorption methods, producing a CO_2 stream suitable for storage. Also, intense R&D efforts worldwide are being directed towards the development of new systems that combine CO_2 separation with some of the reaction steps, such as the steam reforming of natural gas or water gas shift reaction stages, but it is not yet clear if these emerging concepts (see Section 3.5.3) will deliver a lower CO_2 capture cost.

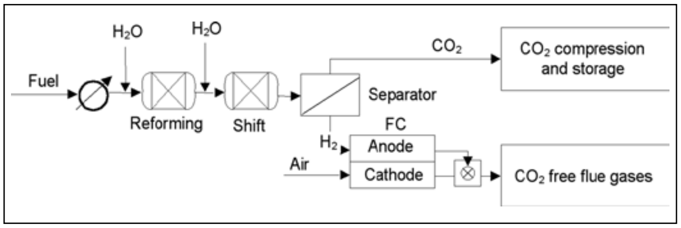

Figure 3.18a Fuel cell system with pre-fuel cell CO_2 capture. The carbon-containing fuel is first completely converted into a mixture of hydrogen and CO_2. Hydrogen and CO_2 are then separated and the H_2-rich fuel is oxidized in the fuel cell to produce electricity. The CO_2 stream is dried and compressed for transport and storage.

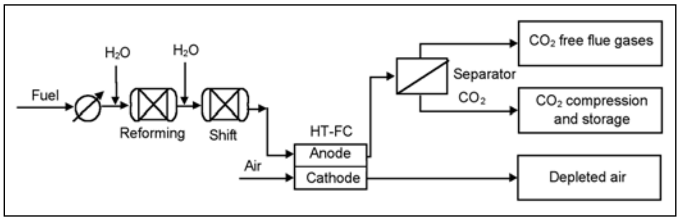

Figure 3.18b Fuel cell system with post-fuel cell CO_2 capture. The carbon-containing fuel is first converted into a syngas. The syngas is oxidized in the fuel cell to produce electricity. At the outlet of the fuel cell CO_2 is separated from the flue gas, dried and compressed for transport and storage.

In power systems, pre-combustion CO_2 capture in natural gas combined cycles has not been demonstrated. However, studies show that based on current state of the art gas turbine combined cycles, pre-combustion CO_2 capture will reduce the efficiency from 56% LHV to 48% LHV (IEA, 2000b). In natural gas combined cycles, the most significant area for efficiency improvement is the gas turbine and it is expected that by 2020, the efficiency of a natural gas combined cycle could be as high as 65% LHV (IEA GHG, 2000d). For such systems the efficiency with CO_2 capture would equal the current state-of-the-art efficiency for plants without CO_2 capture, that is, 56% LHV.

Integrated Gasification Combined Cycles (IGCC) are large scale, near commercial examples of power systems that can be implemented with heavy oil residues and solid fuels like coal and petroleum coke. For the embryonic coal-fired IGCC technology with the largest unit rated at 331 MW_e, future improvements are expected. A recent study describes improvements potentially realisable for bituminous coals by 2020 that could reduce both energy and cost-of-electricity penalties for CO_2 capture to 13% compared to a same base plant without capture. For such systems the generation efficiency with capture would equal the best efficiency realisable today without CO_2 capture (i.e., 43% LHV; IEA GHG, 2003). Notably, all the innovations considered, with the exception of ion transport membrane technology for air separation (which is motivated by many market drivers other than IGCC needs) involve 'non- breakthrough' technologies, with modest continuing improvements in components that are already established commercially - improvements that might emerge as a natural result of growing commercial experience with IGCC technologies.

All fuel cell types are currently in the development phase. The first demonstration systems are now being tested, with the largest units being at the 1 MW scale. However, it will take at least another 5 to 10 years before these units become commercially available. In the longer term, these highly efficient fuel cell systems are expected to become competitive for power generation. Integrating CO_2 capture in these systems is relatively simple and therefore fuel cell power generation systems offer the prospect of reducing the CO_2 capture penalty in terms of efficiency and capture costs. For instance, for high temperature fuel cell systems without CO_2 capture, efficiencies that exceed 67% are calculated with an anticipated 7% efficiency reduction when CO_2 capture is integrated into the system (Jansen and Dijkstra, 2003). However, fuel cell systems are too small to reach a reasonable level of CO_2 transport cost (IEA GHG, 2002a), but in groups of a total of capacity 100MWe, the cost of CO_2 transport is reduced to a more acceptable level.

Most studies agree that pre-combustion systems may be better suited to implement CO_2 capture at a lower incremental cost compared to the same type of base technology without capture (Section 3.7), but with a key driver affecting implementation being the absolute cost of the carbon emission-free product, or service provided. Pre-combustion systems also have a high strategic importance, because their capability to deliver, in a large scale and at high thermal efficiencies, a suitable mix of electricity, hydrogen and lower carbon-containing fuels or chemical feedstocks in an increasingly carbon-constrained world.

3.6 Environmental, monitoring, risk and legal aspects of capture systems

The previous sections of this chapter focused on each of the major technologies and systems for CO_2 capture. Here we summarize the major environmental, regulatory and risk issues associated with the use of CO_2 capture technology and the handling of carbon dioxide common to all of these systems. Issues related to the subsequent transport and storage of carbon dioxide are discussed in Chapters 4 to 7.

3.6.1 Emissions and resource use impacts of CO_2 capture systems

3.6.1.1 Overview of emissions from capture systems

Plants with CO_2 capture would produce a stream of concentrated CO_2 for storage, plus in most cases a flue gas or vent gas emitted to the atmosphere and liquid wastes. In some cases solid wastes will also be produced.

The captured CO_2 stream may contain impurities which would have practical impacts on CO_2 transport and storage systems and also potential health, safety and environmental impacts. The types and concentrations of impurities depend on the type of capture process, as shown in Table 3.4, and detailed plant design. The major impurities in CO_2 are well known but there is little published information on the fate of any trace impurities in the feed gas such as heavy metals. If substances are captured along with the CO_2 then their net emissions to the atmosphere will be reduced, but impurities in the CO_2 may result in environmental impacts at the storage site.

CO_2 from most capture processes contains moisture, which has to be removed to avoid corrosion and hydrate formation during transportation. This can be done using conventional

Table 3.4 Concentrations of impurities in dried CO_2, % by volume (Source data: IEA GHG, 2003; IEA GHG, 2004; IEA GHG, 2005).

	SO_2	NO	H_2S	H_2	CO	CH_4	$N_2/Ar/O_2$	Total
COAL FIRED PLANTS								
Post-combustion capture	<0.01	<0.01	0	0	0	0	0.01	0.01
Pre-combustion capture (IGCC)	0	0	0.01-0.6	0.8-2.0	0.03-0.4	0.01	0.03-0.6	2.1-2.7
Oxy-fuel	0.5	0.01	0	0	0	0	3.7	4.2
GAS FIRED PLANTS								
Post-combustion capture	<0.01	<0.01	0	0	0	0	0.01	0.01
Pre-combustion capture	0	0	<0.01	1.0	0.04	2.0	1.3	4.4
Oxy-fuel	<0.01	<0.01	0	0	0	0	4.1	4.1

a. The SO_2 concentration for oxy-fuel and the maximum H_2S concentration for pre-combustion capture are for cases where these impurities are deliberately left in the CO_2, to reduce the costs of capture (see Section 3.6.1.1). The concentrations shown in the table are based on use of coal with a sulphur content of 0.86%. The concentrations would be directly proportional to the fuel sulphur content.

b. The oxy-fuel case includes cryogenic purification of the CO_2 to separate some of the N_2, Ar, O_2 and NO_x. Removal of this unit would increase impurity concentrations but reduce costs.

c. For all technologies, the impurity concentrations shown in the table could be reduced at higher capture costs.

processes and the costs of doing so are included in published costs of CO_2 capture plants.

CO_2 from post-combustion solvent scrubbing processes normally contains low concentrations of impurities. Many of the existing post-combustion capture plants produce high purity CO_2 for use in the food industry (IEA GHG, 2004).

CO_2 from pre-combustion physical solvent scrubbing processes typically contains about 1-2% H_2 and CO and traces of H_2S and other sulphur compounds (IEA GHG, 2003). IGCC plants with pre-combustion capture can be designed to produce a combined stream of CO_2 and sulphur compounds, to reduce costs and avoid the production of solid sulphur (IEA GHG, 2003). Combined streams of CO_2 and sulphur compounds (primarily hydrogen sulphide, H_2S) are already stored, for example in Canada, as discussed in Chapter 5. However, this option would only be considered in circumstances where the combined stream could be transported and stored in a safe and environmentally acceptable manner.

The CO_2-rich gas from oxy-fuel processes contains oxygen, nitrogen, argon, sulphur and nitrogen oxides and various other trace impurities. This gas will normally be compressed and fed to a cryogenic purification process to reduce the impurities concentrations to the levels required to avoid two-phase flow conditions in the transportation pipelines. A 99.99% purity could be produced by including distillation in the cryogenic separation unit. Alternatively, the sulphur and nitrogen oxides could be left in the CO_2 fed to storage in circumstances where that is environmentally acceptable as described above for pre-combustion capture and when the total amount of all impurities left in the CO_2 is low enough to avoid two-phase flow conditions in transportation pipelines.

Power plants with CO_2 capture would emit a CO_2-depleted flue gas to the atmosphere. The concentrations of most harmful substances in the flue gas would be similar to or lower than in the flue gas from plants without CO_2 capture, because CO_2 capture processes inherently remove some impurities and some other impurities have to be removed upstream to enable the CO_2 capture process to operate effectively. For example, post-combustion solvent absorption processes require low concentrations of sulphur compounds in the feed gas to avoid excessive solvent loss, but the reduction in the concentration of an impurity may still result in a higher rate of emissions per kWh of product, depending upon the actual amount removed upstream and the capture system energy requirements. As discussed below (Section 3.6.1.2), the latter measure is more relevant for environmental assessments. In the case of post-combustion solvent capture, the flue gas may also contain traces of solvent and ammonia produced by decomposition of solvent.

Some CO_2 capture systems produce solid and liquid wastes. Solvent scrubbing processes produce degraded solvent wastes, which would be incinerated or disposed of by other means. Post-combustion capture processes produce substantially more degraded solvent than pre-combustion capture processes. However, use of novel post-combustion capture solvents can significantly reduce the quantity of waste compared to MEA solvent, as discussed in Section 3.3.2.1. The waste from MEA scrubbing would normally be processed to remove metals and then incinerated. The waste can also be disposed of in cement kilns, where the waste metals become agglomerated in the clinker (IEA GHG, 2004). Pre-combustion capture systems periodically produce spent shift and reforming catalysts and these would be sent to specialist reprocessing and disposal facilities.

3.6.1.2 Framework for evaluating capture system impacts

As discussed in Chapter 1, the framework used throughout this report to assess the impacts of CO_2 capture and storage is based on the material and energy flows needed to produce a unit of product from a particular process. As seen earlier in this chapter, CO_2 capture systems require an increase in energy use for their operation. As defined in this report (see Section 1.5 and Figure 1.5), the energy requirement associated with CO_2 capture is expressed as the additional energy required to produce a unit of useful product, such as a kilowatt-hour of electricity (for the case of a power plant). As the energy and resource requirement for CO_2 capture (which includes the energy needed to compress CO_2 for subsequent transport and storage) is typically much larger than for other emission control systems, it has important implications for plant resource requirements and environmental emissions when viewed from the 'systems' perspective of Figure 1.5.

In general, the CCS energy requirement per unit of product can be expressed in terms of the change in net plant efficiency (η) when the reference plant without capture is equipped with a CCS system:[1]

$$\Delta E = (\eta_{ref} / \eta_{ccs}) - 1 \qquad (6)$$

where ΔE is the fractional increase in plant energy input per unit of product and η_{ccs} and η_{ref} are the net efficiencies of the capture plant and reference plant, respectively. The CCS energy requirement directly determines the increases in plant-level resource consumption and environmental burdens associated with producing a unit of useful product (like electricity) while capturing CO_2. In the case of a power plant, the larger the CCS energy requirement, the greater the increases per kilowatt-hour of in-plant fuel consumption and other resource requirements (such as water, chemicals and reagents), as well as environmental releases in the form of solid wastes, liquid wastes and air pollutants not captured by the CCS system. The magnitude of ΔE also determines the magnitude of additional upstream environmental impacts associated with the extraction, storage and transport of additional fuel and other resources consumed at the plant. However, the additional energy for these upstream activities is not normally included in the reported

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[1] A different measure of the 'energy penalty' commonly reported in the literature is the fractional decrease in plant output (plant derating) for a fixed energy input. This value can be expressed as: $\Delta E^* = 1 - (\eta_{ccs}/\eta_{ref})$. Numerically, ΔE^* is smaller than the value of ΔE given by Equation (6). For example, a plant derating of $\Delta E^* = 25\%$ corresponds to an increase in energy input per kWh of $\Delta E = 33\%$.

energy requirements for CO_2 capture systems.[2]

Recent literature on CO_2 capture systems applied to electric power plants quantifies the magnitude of CCS energy requirements for a range of proposed new plant designs with and without CO_2 capture. As elaborated later in Section 3.7 (Tables 3.7 to 3.15), those data reveal a wide range of ΔE values. For new supercritical pulverized coal (PC) plants using current technology, these ΔE values range from 24-40%, while for natural gas combined cycle (NGCC) systems the range is 11%–22% and for coal-based gasification combined cycle (IGCC) systems it is 14%–25%. These ranges reflect the combined effects of the base plant efficiency and capture system energy requirements for the same plant type with and without capture.

3.6.1.3 Resource and emission impacts for current systems

Only recently have the environmental and resource implications of CCS energy requirements been discussed and quantified for a variety of current CCS systems. Table 3.5 displays the assumptions and results from a recent comparison of three common fossil fuel power plants employing current technology to capture 90% of the CO_2 produced (Rubin *et al.*, 2005). Increases in specific fuel consumption relative to the reference plant without CO_2 capture correspond directly to the ΔE values defined above. For these three cases, the plant energy requirement per kWh increases by 31% for the PC plant, 16% for the coal-based IGCC plant and 17% for the NGCC plant. For the specific examples used in Table 3.5, the increase in energy consumption for the PC and NGCC plants are in the mid-range of the values for these systems reported later in Tables 3.7 to 3.15 (see also Section 3.6.1.2), whereas the IGCC case is nearer the low end of the reported range for such systems. As a result of the increased energy input per kWh of output, additional resource requirements for the PC plant include proportionally greater amounts of coal, as well as limestone (consumed by the FGD system for SO_2 control) and ammonia (consumed by the SCR system for NO_x control). All three plants additionally require more sorbent make-up for the CO_2 capture units. Table 3.5 also shows the resulting increases in solid residues for these three cases. In contrast, atmospheric emissions of CO_2 decrease sharply as a result of the CCS systems, which also remove residual amounts of other acid gases, especially SO_2 in flue gas streams. Thus, the coal combustion system shows a net reduction in SO_2 emission rate as a result of CO_2 capture. However, because of the reduction in plant efficiency, other air emission rates per kWh increase relative to the reference plants without capture. For the PC and NGCC systems, the increased emissions of ammonia are a result of chemical reactions in the amine-based capture process. Not included in this analysis are the incremental impacts of upstream operations such as mining, processing and transport of fuels and other resources. Other studies, however, indicate that these impacts, while not insignificant, tend to be small relative to plant-level impacts (Bock *et al.*, 2003).

For the most part, the magnitude of impacts noted above - especially impacts on fuel use and solid waste production - is directly proportional to the increased energy per kWh resulting from the reduction in plant efficiency, as indicated by Equation (6). Because CCS energy requirements are one to two orders of magnitude greater than for other power plant emission control technologies (such as particulate collectors and flue gas desulphurization systems), the illustrative results above emphasize the importance of maximizing overall plant efficiency while controlling environmental emissions.

3.6.1.4 Resource and emission impacts of future systems

The analysis above compared the impacts of CO_2 capture for a given plant type based on current technology. The magnitude of actual future impacts, however, will depend on four important factors: (1) the performance of technologies available at the time capture systems are deployed; (2) the type of power plants and capture systems actually put into service; (3) the total capacity of each plant type that is deployed; and, (4) the characteristics and capacity of plants they may be replacing.

Analyses of both current and near-future post-combustion, pre-combustion and oxy-fuel combustion capture technology options reveal that some of the advanced systems currently under development promise to significantly reduce the capture energy requirements - and associated impacts - while still reducing CO_2 emissions by 90% or more, as shown in Figure 3.19. Data in this figure was derived from the studies previously reported in Figures 3.6 and 3.7.

The timetable for deploying more efficient plants with CO_2 capture will be the key determinant of actual environmental changes. If a new plant with capture replaces an older, less efficient and higher-emitting plant currently in service, the net change in plant-level emission impacts and resource requirements would be much smaller than the values given earlier (which compared identical new plants with and without

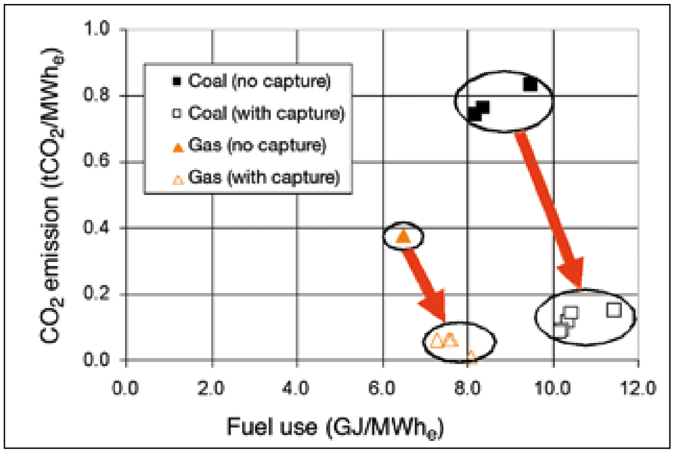

Figure 3.19 Fuel use for a reduction of CO_2 emissions from capture plants (data presented from design studies for power plants with and without capture shown in Figures 3.6 and 3.7).

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[2] Those additional energy requirements, if quantified, could be included by re-defining the system boundary and system efficiency terms in Equation (6) to apply to the full life cycle, rather than only the power plant. Such an analysis would require additional assumptions about the methods of fuel extraction, processing, transport to the power plant, and the associated energy requirements of those activities; as well as the CO_2 losses incurred during storage.

Table 3.5 Illustrative impacts of CCS energy requirements on plant-level resource consumption and non-CO_2 emission rates for three current power plant systems. Values shown are mass flow rates in kg per MWh for the capture plant, plus increases over the reference plant rates for the same plant type. See footnotes for additional details. (Source: Rubin *et al.*, 2005)

Capture Plant Parameter [a]	**PC** [b]		**IGCC** [c]		**NGCC** [d]	
	Rate	**Increase**	**Rate**	**Increase**	**Rate**	**Increase**
Resource consumption	**(All values in kg MWh^{-1})**					
Fuel	390	93	361	49	156	23
Limestone	27.5	6.8	-	-	-	-
Ammonia	0.80	0.19	-	-	-	-
CCS Reagents	2.76	2.76	0.005	0.005	0.80	0.80
Solid Wastes/byproduct						
Ash/slag	28.1	6.7	34.2	4.7	-	-
FGD residues	49.6	12.2	-	-	-	-
Sulfur	-	-	7.53	1.04	-	-
Spent CCS sorbent	4.05	4.05	0.005	0.005	0.94	0.94
Atmospheric emissions						
CO_2	107	*–704*	97	*-720*	43	*–342*
SO_x	0.001	*–0.29*	0.33	0.05	-	-
NO_x	0.77	0.18	0.10	0.01	0.11	0.02
NH_3	0.23	0.22	-	-	0.002	0.002

[a] Net power output of all plants is approximately 500 MW. Coal plants use Pittsburgh #8 coal with 2.1%S, 7.2% ash, 5.1% moisture and 303.2 MJ kg^{-1} lower heating value basis (LHV). Natural gas LHV = 59.9 MJ kg^{-1}. All plants capture 90% of potential CO_2 emissions and compress to 13.7 MPa.

[b] PC= Pulverized coal-fired plant; based on a supercritical unit with SCR, ESP and FGD systems, followed by an amine system for CO_2 capture. SCR system assumes 2 ppmv ammonia slip. SO_2 removal efficiency is 98% for reference plant and 99% for capture plant. Net plant efficiency (LHV basis) is 40.9% without CCS and 31.2% with CCS.

[c] IGCC=integrated gasification combined cycle system based on Texaco quench gasifiers (2 + 1 spare), two GE 7FA gas turbines, 3-pressure reheat HRSG. Sulfur removal efficiency is 98% via hydrolyzer plus Selexol system; Sulfur recovery via Claus plant and Beavon-Stretford tailgas unit. Net plant efficiency (LHV basis) is 39.1% without CCS and 33.8% with CCS.

[d] NGCC=natural gas combined cycle plant using two GE 7FA gas turbines and 3-pressure reheat HRSG, with an amine system for CO_2 capture. Net plant efficiency (LHV basis) is 55.8% without CCS and 47.6% with CCS.

capture). For example, the efficiency of a modern coal-based plant with capture is close to many older coal-burning plants currently in service. Replacing the latter with the former would thus reduce CO_2 emissions significantly with little or no net change in plant coal consumption or related solid waste impacts. In some cases, there could in fact be net reductions in other plant emissions, in support of clean air goals. If, however, the deployment of new CCS plants is delayed significantly, older existing plants could well be replaced by modern high-efficiency plants without capture. Such plants also would be built to provide additional capacity in regions with high electricity growth rates, such as in China and other parts of Asia today. A decade or two from now, the fleet of 'existing' plants in those regions would thus look very different from the present. Accordingly, the environmental and resource impacts of additional new plants with CO_2 capture would have to be assessed in the context of the future situation.

Because comparisons of different plant types require a specific context (or scenario) to be meaningful, this chapter has only focused on characterizing the effects of CO_2 capture systems relative to the same type of power plant and not the type of infrastructure it would replace (either currently, or in a future carbon-constrained world). If other systems such as the use of renewable energy, or electricity and synfuels cogenerated from coal, find significant applications, those systems too would require more comprehensive comparative life-cycle assessments of resource use and impacts that are not currently available. Chapter 8, however, assesses overall energy use impacts for illustrative scenarios of CCS deployment in competition with other carbon mitigation options.

3.6.2 Issues related to the classification of carbon dioxide as a product

As a current commercial product, carbon dioxide is subject to classification and regulations. The classification of carbon dioxide is dependent on its physical state (gas, liquid or solid), its concentration, impurities present and other criteria established by national legislative classification in different regions of the world. During the capture and concentration process, the quality properties can change the classification of the substance. A detailed assessment of carbon dioxide physical and chemical properties is provided in Annex I.

The environmental, monitoring, risk and legal aspects associated with carbon dioxide handling and storage are well established in the processing industry. However, much larger volumes are targeted for carbon dioxide processing for purposes of CCS than the volumes handled at present. On a local and regional level, additional emergency response and other regulatory measures can be expected in the future, depending on the rate of development of CCS. It is anticipated that human capacity will be developed to assess the monitoring, risk and legal aspects as required by the market.

At present, carbon dioxide typically occurs and is mainly traded as a non-flammable gas (US Department of Transportation classification class 2.2). The classification system of Transport Dangerous Goods, International Maritime Organization/ International Maritime Dangerous Goods and International Civil Aviation Organization / International Air Transport Association, all classify carbon dioxide in class 2.2, non-flammable, non-corrosive and non-poisonous gases. In US federal regulations, carbon dioxide is not listed as a product in the Clean Water Act (CWA 307 and 311), Clean Air Act (CAA 112) or the Toxics Release Inventory. In other international regulations carbon dioxide is not classified in the European Inventory of Existing Commercial Chemical Substance or other international lists, but in Canada is classified as a compressed gas (class A) on the Canadian Energy Pipeline Association Dangerous Substances List (Hazardous Substances Data Bank, 2002).

3.6.3 Health and safety risks associated with carbon dioxide processing

The effects of exposure to carbon dioxide are described in Annex I. However, a risk assessment that includes an understanding of both exposure and effects is required to characterize the risk for various situations associated with carbon dioxide processing (European Chemicals Bureau, 2003); see the following two sections for established risk management practices. The most probable routes of human exposure to carbon dioxide are inhalation or skin contact. The need for a risk-based approach is clear from the following two descriptions. Carbon dioxide and its products of degradation are not legally classified as a toxic substance; is non-hazardous on inhalation, is a non-irritant and does not sensitize or permeate the skin. However, chronic effects on humans follow from long-term exposure to airborne carbon dioxide concentrations of between 0.5 and 1% resulting in metabolic acidosis and increased calcium deposits in soft tissues. The substance is toxic to the cardiovascular system and upper respiratory tract at concentrations above 3%. Sensitive populations to elevated carbon dioxide levels are described in Annex I. The product risk assessment process is therefore necessary as with any other chemical use to determine the risk and establish the necessary risk management processes.

As an asphyxiate carbon dioxide presents the greatest danger. If atmospheric oxygen is displaced such that oxygen concentration is 15-16%, signs of asphyxia will be noted. Skin contact with dry ice has caused serious frostbites and blisters (Hazardous Substances Data Bank, 2002). Protective equipment and clothing required in the processing industries include full face-piece respirators to prevent eye contact and appropriate personal protective clothing to protect the skin from becoming frozen by the liquid.

3.6.4 Plant design principles and guidelines used by governments, industries and financiers

New plant facilities like those envisioned for carbon dioxide are subject to design guidelines for the petrochemical industry as determined by relevant authorities. One example is the European Unions' Integrated Pollution Prevention and Control (IPPC) directive requiring the application of the principles of Best Available Technology Not Entailing Excessive Cost (BATNEEC). Carbon dioxide capture and compression processes are listed in several guidelines as gas-processing facilities. Typically the World Bank guidelines and other financial institutions have specific requirements to reduce risk and these require monitoring (World Bank, 1999) which is part of routine plant monitoring to detect accidental releases. Investor guidelines like the World Bank guidelines are particularly important for developing countries where there is less emphasis on monitoring and legislation. National and regional legislation for plant design and specifications from organizations like the US Environmental Protection Agency are available to guide the development of technology.

3.6.5 Commissioning, good practice during operations and sound management of chemicals

The routine engineering design, commissioning and start-up activities associated with petrochemical facilities are applicable to the capture and compression of carbon dioxide; for example Hazard Operability studies are conducted on a routine basis for new facilities (Sikdar and Diwekar, 1999).

The management of carbon dioxide and reagents inside factory battery limits will be in accordance with the relevant practices in use for carbon dioxide. For carbon dioxide, US Occupational Health and Safety Act standards and National Institute for Occupational Safety and Health recommendations exist, which are applied widely in industry to guide safe handling of carbon dioxide and the same applies to reagents and catalysts used. Well established and externally audited management systems such as International Standards Organization's ISO 14001 (environment) and ISO 9001 (quality) and Occupational Health and Safety (OHSAS 18000) exist to provide assurance that environment, safety, health and quality management systems are in place (American Institute of Chemical Engineers, 1995). Tools like life-cycle assessment (ISO 14040 series) with the necessary boundary expansion methodology are useful to determine the overall issues associated with a facility and assist with selection of parameters such as energy carriers, operational conditions and materials used in the process. The life-cycle assessment will also indicate if a trouble-free capture system does generate environmental concerns elsewhere in the product life cycle.

3.6.6 Site closure and remediation

It is not anticipated that carbon dioxide capture will result in a legacy of polluted sites requiring remediation after plant closure, assuming that standard operating procedures and management practices in the previous section are followed. However, depending on the technology used and the materials procured for operations, waste disposal at the facilities and operation according to a formal management system from construction, operation to the development of site closure plans will largely assist to reduce the risk of a polluted site after closure of operations.

3.7 Cost of CO_2 capture

This section of the report deals with the critical issue of CO_2 capture costs. We begin with an overview of the many factors that affect costs and the ability to compare published estimates on a consistent basis. Different measures of CO_2 capture cost also are presented and discussed. The literature on CO_2 capture costs for currently available technologies is then reviewed, along with the outlook for future costs over the next several decades.

3.7.1 Factors affecting CO_2 capture cost

Published estimates for CO_2 capture costs vary widely, mainly as a result of different assumptions regarding technical factors related to plant design and operation (e.g., plant size, net efficiency, fuel properties and load factor), as well as key economic and financial factors such as fuel cost, interest rates and plant lifetime. A number of recent papers have addressed this issue and identified the principal sources of cost differences and variability (Herzog, 1999; Simbeck, 1999; Rubin and Rao, 2003). This section draws heavily on Rubin and Rao (2003) to highlight the major factors affecting the cost of CO_2 capture.

3.7.1.1 Defining the technology of interest

Costs will vary with the choice of CO_2 capture technology and the choice of power system or industrial process that generates the CO_2 emissions. In engineering-economic studies of a single plant or CO_2 capture technology, such definitions are usually clear. However, where larger systems are being analyzed, such as in regional, national or global studies of CO_2 mitigation options, the specific technologies assumed for CO_2 production and capture may be unclear or unspecified. In such cases, the context for reported cost results also may be unclear.

3.7.1.2 Defining the system boundary

Any economic assessment should clearly define the 'system' whose CO_2 emissions and cost is being characterized. The most common assumption in studies of CO_2 capture is a single facility (most often a power plant) that captures CO_2 and transports it to an off-site storage area such as a geologic formation. The CO_2 emissions considered are those released at the facility before and after capture. Reported costs may or may not include CO_2 transport and storage costs. *The system boundary of interest in this section of the report includes only the power plant or other process of interest and does not include CO_2 transport and storage systems, whose costs are presented in later chapters. CO_2 compression, however, is assumed to occur within the facility boundary and therefore the cost of compression is included in the cost of capture.*[3]

In some studies the system boundary includes emissions of

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[3] Alternatively, compression costs could be attributed wholly or in part to CO_2 transport and storage. Most studies, however, include compression with capture cost. This also facilitates comparisons of capture technologies that operate at different pressures, and thus incur different costs to achieve a specified final pressure.

CO_2 and other greenhouse gases such as methane (expressed as equivalent CO_2) over the complete fuel cycle encompassing not only the power plant or facility in question, but also the 'upstream' processes of extraction, refining and transport of fuel used at the facility, plus any 'downstream' emissions from the use or storage of captured CO_2. Still larger system boundaries might include all power plants in a utility company's system; all plants in a regional or national grid; or a national economy where power plant and industrial emissions are but one element of the overall energy system being modelled. In each of these cases it is possible to derive a mitigation cost for CO_2, but the results are not directly comparable because they reflect different system boundaries and considerations. Chapter 8 discusses such differences in more detail and presents results for alternative systems of interest.

3.7.1.3 Defining the technology time frame and maturity

Another factor that is often unclear in economic evaluations of CO_2 capture is the assumed time frame and/or level of maturity for the technology under study. Does the cost estimate apply to a facility that would be built today, or at some future time? This is especially problematic in studies of 'advanced' technologies that are still under development and not currently commercial. In most cases, studies of advanced technologies assume that costs apply to an 'nth plant' to be built sometime in the future when the technology is mature. Such estimates reflect the expected benefits of technological learning, but may or may not adequately account for the increased costs that typically occur in the early stages of commercialization. The choice of technology time frame and assumed rate of cost improvements and can therefore make a big difference in CO_2 capture cost estimates.

3.7.1.4 Different cost measures and assumptions

The literature reveals a number of different measures used to characterize CO_2 capture and storage costs, including capital cost, cost of electricity, cost of CO_2 avoided and others. Because some of these measures are reported in the same units (e.g., US dollars per tonne of CO_2) there is great potential for misunderstanding. Furthermore, for any given cost measure, different assumptions about the technical, economic and financial parameters used in cost calculations can also give rise to large differences in reported capture costs. Section 3.7.2 elaborates on some of the common metrics of cost and the parameters they employ.

3.7.2 Measures of CO_2 capture cost

We define four common measures of CO_2 capture cost here: capital cost, incremental product cost (such as the cost of electricity), cost of CO_2 avoided and cost of CO_2 captured or removed. Each of these measures provides a different perspective on CO_2 capture cost for a particular technology or system of interest. All of them, however, represent an 'engineering economic' perspective showing the added cost of capturing CO_2 in a particular application. Such measures are required to address larger questions such as which options or strategies to pursue - a topic addressed later in Chapter 8.

3.7.2.1 Capital cost

Capital cost (also known as investment cost or first cost) is a widely used, albeit incomplete, metric of the cost of a technology. It is often reported on a normalized basis (e.g., cost per kW). For CO_2 capture systems, the capital cost is generally assumed to represent the total expenditure required to design, purchase and install the system of interest. It may also include the additional costs of other plant components not needed in the absence of a CO_2 capture device, such as the costs of an upstream gas purification system to protect the capture device. Such costs often arise in complex facilities like a power plant. Thus, the total incremental cost of CO_2 capture for a given plant design is best determined as the difference in total cost between plants with and without CO_2 capture, producing the same amounts of useful (primary) product, such as electricity.

Different organizations employ different systems of accounts to specify the elements of a capital cost estimate. For electric power plants, one widely used procedure is that defined by the Electric Power Research Institute (EPRI, 1993). However, because there is no universally employed nomenclature or system of accounts, capital costs reported by different organizations or authors may not always include the same items. The terms used to report capital costs may further disguise such differences and lead to misunderstandings about what is and is not included. For example, power plant cost studies often report a value of capital cost that does not include the cost of interest during construction or other so-called 'owners costs' that typically add at least 10-20% (sometimes substantially more) to the 'total capital requirement' of a system. Only if a capital cost breakdown is reported can such omissions be discovered. Studies that fail to report the year of a cost estimate introduce further uncertainty that may affect cost comparisons.

3.7.2.2 Incremental product cost

The effect of CO_2 capture on the cost of electricity (or other product) is one of the most important measures of economic impact. Electric power plants, a major source of CO_2 emissions, are of particular interest in this regard. The cost electricity (COE) for a power plant can be calculated as:[4]

$$\mathrm{COE} = [(\mathrm{TCR})(\mathrm{FCF}) + (\mathrm{FOM})]/[(\mathrm{CF})(8760)(\mathrm{kW})] + \mathrm{VOM} + (\mathrm{HR})(\mathrm{FC}) \qquad (7)$$

where, COE = levelized cost of electricity (US\$ kWh^{-1}), TCR = total capital requirement (US\$), FCF = fixed charge factor (fraction yr^{-1}), FOM = fixed operating costs (US\$ yr^{-1}), VOM = variable operating costs (US\$ kWh^{-1}), HR = net plant heat rate (kJ kWh^{-1}), FC = unit fuel cost (US\$ kJ^{-1}), CF = capacity

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[4] For simplicity, the value of FCF in Equation (7) is applied to the total capital requirement. More detailed calculations of COE based on a year-by-year analysis apply the FCF to the total capital cost excluding owner's costs (such as interest during construction), which are separately accounted for in the years prior to plant start-up.

factor (fraction), 8760 = total hours in a typical year and kW = net plant power (kW). In this chapter, the costs in Equation (7) include only the power plant and capture technologies and not the additional costs of CO_2 transport and storage that are required for a complete system with CCS. The incremental COE is the difference in electricity cost with and without CO_2 capture.[5] Again, the values reported here exclude transport and storage costs. Full CCS costs are reported in Chapter 8.

Equation (7) shows that many factors affect this incremental cost. For example, just as the total capital cost includes many different items, so too do the fixed and variable costs associated with plant operation and maintenance (O&M). Similarly, the fixed charge factor (FCF, also known as the capital recovery factor) reflects assumptions about the plant lifetime and the effective interest rate (or discount rate) used to amortize capital costs.[6] Assumptions about any of the factors in Equation (7) can have a pronounced effect on overall cost results. Nor are these factors all independent of one another. For example, the design heat rate of a new power plant may affect the total capital requirement since high-efficiency plants usually are more costly than lower-efficiency designs.

Finally, because several of the parameter values in Equation (7) may change over the operating life of a facility (such as the capacity factor, unit fuel cost, or variable operating costs), the value of COE also may vary from year to year. To include such effects, an economic evaluation would calculate the net present value (NPV) of discounted costs based on a schedule of year-to-year cost variations, in lieu of the simpler formulation of Equation (7). However, most engineering-economic studies use Equation (7) to calculate a single value of 'levelized' COE over the assumed life of the plant. The levelized COE is the cost of electricity, which, if sustained over the operating life of the plant, would produce the same NPV as an assumed stream of variable year-to-year costs. In most economic studies of CO_2 capture, however, all parameter values in Equation (7) are held constant, reflecting (either implicitly or explicitly) a levelized COE over the life of the plant.[7]

3.7.2.3 Cost of CO_2 avoided

One of the most widely used measures for the cost of CO_2 capture and storage is the 'cost of CO_2 avoided.' This value reflects the average cost of reducing atmospheric CO_2 mass emissions by one unit while providing the same amount of useful product as a 'reference plant' without CCS. For an electric power plant the avoidance cost can be defined as:

$$\text{Cost of } CO_2 \text{ avoided (US\$/t}CO_2) =$$

$$[(\text{COE})_{\text{capture}} - (\text{COE})_{\text{ref}}] / [(CO_2 \text{ kWh}^{-1})_{\text{ref}} - (CO_2 \text{ kWh}^{-1})_{\text{capture}}] \qquad (8)$$

where, COE = levelized cost of electricity (US\$ kWh^{-1}) as given by Equation (7) and CO_2 kWh^{-1} = CO_2 mass emission rate (in tonnes) per kWh generated, based on the net plant capacity for each case. The subscripts 'capture' and 'ref' refer to the plant with and without CO_2 capture, respectively. Note that while this equation is commonly used to report a cost of CO_2 avoided for the capture portion of a full CCS system, strictly speaking it should be applied only to a complete CCS system including transport and storage costs (since all elements are required to avoid emissions to the atmosphere).

The choice of the reference plant without CO_2 capture plays a key role in determining the CO_2 avoidance cost. *Here the reference plant is assumed to be a plant of the same type and design as the plant with CO_2 capture*. This provides a consistent basis for reporting the incremental cost of CO_2 capture for a particular type of facility.

Using Equation (8), a cost of CO_2 avoided can be calculated for any two plant types, or any two aggregates of plants. Thus, special care should be taken to ensure that the basis for a reported cost of CO_2 avoided is clearly understood or conveyed. For example, the avoidance cost is sometimes taken as a measure of the cost to society of reducing GHG emissions.[8] In that case, the cost per tonne of CO_2 avoided reflects the average cost of moving from one situation (e.g., the current mix of power generation fuels and technologies) to a different mix of technologies having lower overall emissions. Alternatively, some studies compare individual plants with and without capture (as we do), but assume different types of plants for the two cases. Such studies, for example, might compare a coal-fired plant with capture to an NGCC reference plant without capture. Such cases reflect a different choice of system boundaries and address very different questions, than those addressed here. However, the data presented in this section (comparing the same type of plant with and without capture) can be used to estimate a cost of CO_2 avoided for any two of the systems of interest in a particular situation (see Chapter 8).

3.7.2.4 Cost of CO_2 captured or removed

Another cost measure frequently reported in the literature is based on the mass of CO_2 captured (or removed) rather than emissions avoided. For an electric power plant it can be defined as:

$$\text{Cost of } CO_2 \text{ Captured (US\$/t}CO_2) =$$
$$[(\text{COE})_{\text{capture}} - (\text{COE})_{\text{ref}}] / (CO_{2,\text{ captured}} \text{ kWh}^{-1}) \qquad (9)$$

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[5] For CO_2 capture systems with large auxiliary energy requirements, the magnitude of incremental cost also depends on whether the plant with capture is assumed to be a larger facility producing the same net output as the reference plant without capture, or whether the reference plant is simply derated to supply the auxiliary energy. While the latter assumption is most common, the former yields a smaller incremental cost due to economy-of-scale effects.

[6] In its simplest form, FCF can be calculated from the project lifetime, n (years), and annual interest rate, i (fraction), by the equation: $FCF = i / [1 - (1 + i)^{-n}]$.

[7] Readers not familiar with these economic concepts and calculations may wish to consult a basic economics text, or references such as (EPRI, 1993) or (Rubin, 2001) for more details.

[8] As used here, 'cost' refers only to money spent for technology, fuels and related materials, and not to broader societal measures such as macroeconomic costs or societal damage costs associated with atmospheric emissions. Further discussions and use of the term 'cost of CO_2 avoided' appear in Chapter 8 and in the references cited earlier.

where, $CO_{2,\ captured}\ kWh^{-1}$ = total mass of CO_2 captured (in tonnes) per net kWh for the plant with capture. This measure reflects the economic viability of a CO_2 capture system given a market price for CO_2 (as an industrial commodity). If the CO_2 captured at a power plant can be sold at this price (e.g., to the food industry, or for enhanced oil recovery), the COE for the plant with capture would be the same as for the reference plant having higher CO_2 emissions. Numerically, the cost of CO_2 captured is lower than the cost of CO_2 avoided because the energy required to operate the CO_2 capture systems increases the amount of CO_2 emitted per unit of product.

3.7.2.5 Importance of CCS energy requirements

As the energy requirement for CCS is substantially larger than for other emission control systems, it has important implications for plant economics as well as for resource requirements and environmental impacts. The energy 'penalty' (as it is often called) enters cost calculations in one of two ways. Most commonly, all energy needed to operate CCS absorbers, compressors, pumps and other equipment is assumed to be provided within the plant boundary, thus lowering the net plant capacity (kW) and output (kWh, in the case of a power plant). The result, as shown by Equation (7), is a higher unit capital cost (US\$ kW^{-1}) and a higher cost of electricity production (US\$ kWh^{-1}). Effectively, these higher unit costs reflect the expense of building and operating the incremental capacity needed to operate the CCS system.

Alternatively, some studies - particularly for industrial processes such as hydrogen production - assume that some or all of the energy needed to operate the CCS system is purchased from outside the plant boundary at some assumed price. Still other studies assume that new equipment is installed to generate auxiliary energy on-site. In these cases, the net plant capacity and output may or may not change and may even increase. However, the COE in Equation (7) again will rise due to the increases in VOM costs (for purchased energy) and (if applicable) capital costs for additional equipment. The assumption of purchased power, however, does not guarantee a full accounting of the replacement costs or CO_2 emissions associated with CCS. In all cases, however, the larger the CCS energy requirement, the greater the difference between the costs of CO_2 captured and avoided.

3.7.2.6 Other measures of cost

The cost measures above characterize the expense of adding CO_2 capture to a single plant of a given type and operating profile. A broader modelling framework is needed to address questions involving multiple plants (e.g., a utility system, regional grid, or national network), or decisions about what type of plant to build (and when). Macroeconomic models that include emission control costs as elements of a more complex framework typically yield cost measures such as the change in gross domestic product (GDP) from the imposition of a carbon constraint, along with changes in the average cost of electricity and cost per tonne of CO_2 abated. Such measures are often useful for policy analysis, but reflect many additional assumptions about the structure of an economy as well as the cost of technology. Chapter 8 provides a discussion of macroeconomic modelling as it relates to CO_2 capture costs.

3.7.3 The context for current cost estimates

Recall that CO_2 capture, while practiced today in some industrial applications, is not currently a commercial technology used at large electric power plants, which are the focus of most CCS studies. Thus, cost estimates for CO_2 capture systems rely mainly on studies of hypothetical plants. Published studies also differ significantly in the assumptions used for cost estimation. Equation (7), for example, shows that the plant capacity factor has a major impact on the cost of electric power generation, as do the plant lifetime and discount rate used to compute the fixed charge factor. The COE, in turn, is a key element of CO_2 avoidance cost, Equation (8). Thus, a high plant capacity factor or a low fixed charge rate will lower the cost of CO_2 capture per kWh. The choice of other important parameters, such as the plant size, efficiency, fuel type and CO_2 removal rate will similarly affect the CO_2 capture cost. Less apparent, but often equally important, are assumptions about parameters such as the 'contingency cost factors' embedded in capital cost estimates to account for unspecified costs anticipated for technologies at an early stage of development, or for commercial systems that have not yet been demonstrated for the application, location, or plant scale under study.

Because of the variability of assumptions employed in different studies of CO_2 capture, a systematic comparison of cost results is not straightforward (or even possible in most cases). Moreover, there is no universally 'correct' set of assumptions that apply to all the parameters affecting CO_2 capture cost. For example, the quality and cost of natural gas or coal delivered to power plants in Europe and the United States may differ markedly. Similarly, the cost of capital for a municipal or government-owned utility may be significantly lower than for a privately-owned utility operating in a competitive market. These and other factors lead to real differences in CO_2 capture costs for a given technology or power generation system. Thus, we seek in this report to elucidate the key assumptions employed in different studies of similar systems and technologies and their resulting impact on the cost of CO_2 capture. Analyses comparing the costs of alternative systems on an internally consistent basis (within a particular study) also are highlighted. Nor are all studies equally credible, considering their vintage, data sources, level of detail and extent of peer review. Thus, the approach adopted here is to rely as much as possible on recent peer-reviewed literature, together with other publicly-available studies by governmental and private organizations heavily involved in the field of CO_2 capture. Later, in Chapter 8, the range of capture costs reported here are combined with cost estimates for CO_2 transport and storage to arrive at estimates of the overall cost of CCS for selected power systems and industrial processes.

Table 3.6 Confidence levels for technology and system cost estimates.

Confidence Level	Description
Very High	Mature technology with multiple commercial replications for this application and scale of operation; considerable operating experience and data under a variety of conditions.
High	Commercially deployed in applications similar to the system under study, but at a smaller scale and/or with limited operating experience; no major problems or issues anticipated in this application; commercial guarantees available.
Moderate	No commercial application for the system and/or scale of interest, but technology is commercially deployed in other applications; issues of scale-up, operability and reliability remain to be demonstrated for this application.
Low	Experience and data based on pilot plant or proof-of-concept scale; no commercial applications or full-scale demonstrations; significant technical issues or cost-related questions still to be resolved for this application.
Very Low	A new concept or process not yet tested, or with operational data limited to the laboratory or bench-scale level; issues of large-scale operability, effectiveness, reliability and manufacturability remain to be demonstrated.

3.7.4 Overview of technologies and systems evaluated

Economic studies of CO_2 capture have focused mainly on electric power generation, a major source of CO_2 emissions. To a lesser extent, CO_2 capture from industrial processes also has been subject to economic evaluations, especially processes producing hydrogen, often in combination with other products.

The sections below review and summarize recent estimates of CO_2 capture costs for major systems of interest. Sections 3.7.5 to 3.7.8 focus first on the cost of current CO_2 capture technologies, while Sections 3.7.10 to 3.7.12 go on to discuss improved or 'advanced' technologies promising lower costs in the future. In all cases the system boundary is defined as a single facility at which CO_2 is captured and compressed for delivery to a transport and storage system. To reflect different levels of confidence (or uncertainty) in cost estimates for technologies at different stages of development, the qualitative descriptors shown in Table 3.6 are applied in summarizing published cost estimates.[9] The studies reviewed typically report costs in US dollars for reference years ranging from 2000 to early 2004. Because inflation effects generally have been small during this period no adjustments have been made in summarizing ranges of reported costs.

3.7.5 Post-combustion CO_2 capture cost for electric power plants (current technology)

Most of the world's electricity is currently generated from the combustion of fossil fuels, especially coal and (to an increasing extent) natural gas. Hence, the ability to capture and store the CO_2 emitted by such plants has been a major focus of investigation. This section of the report focuses on the cost of currently available technology for CO_2 capture. Because of the relatively low CO_2 concentration in power plant flue gases, chemical absorption systems have been the dominant technology of interest for post-combustion capture (see Section 3.3.2). However, the cost of CO_2 capture depends not only on the choice of capture technology, but also - and often more importantly - on the characteristics and design of the overall power plant. For purposes of cost reporting, we distinguish between coal-fired and gas-fired plant designs and between new and existing facilities.

3.7.5.1 New coal-fired power plants

Table 3.7 summarizes the key assumptions and results of recent studies of post-combustion CO_2 capture at new coal-fired power plants. Assumed plant sizes with CO_2 capture range from approximately 300-700 MW net power output. In all cases, CO_2 capture is accomplished using an amine-based absorption system, typically MEA. Capture efficiencies range from 85-95% with the most common value being 90%. The studies employ different assumptions about other key parameters such as the base power plant efficiency, coal properties, coal cost, plant capacity factor, CO_2 product pressure and financial parameters such as the fixed charge factor. All of these factors have a direct influence on total plant cost and the cost of CO_2 capture.

Table 3.7 summarizes several measures of CO_2 capture cost, both in absolute and relative terms. Across the full set of studies, CO_2 capture adds 44-87% to the capital cost of the reference plant (US\$ kW^{-1}) and 42-81% to the cost of electricity (US\$ MWh^{-1}), while achieving CO_2 reductions of approximately 80-90% per net kWh produced. The cost of CO_2 avoided for these cases varies from 29-51 US\$/tCO_2. The absolute values of capital cost, COE and incremental cost of electricity in Table 3.7 reflect the different assumptions employed in each study. The result is an incremental COE of 18-38 US\$ MWh^{-1} (or US\$ 0.018-0.038 kWh^{-1}) for CO_2 capture. The total COE for plants with capture ranges from 62-87 US\$ MWh^{-1}. In all cases, a significant portion of the total CO_2 capture cost is due to the energy requirement for CO_2 capture and compression. For the studies in Table 3.7, the plants with CO_2 capture require 24-42% more fuel input per MWh of plant output relative to a similar reference plant without capture. Roughly half the energy is required for solvent regeneration and a third for CO_2 compression.

While many factors contribute to the cost differences observed in Table 3.7, systematic studies of the influence of different factors indicate that the most important sources of variability in reported cost results are assumptions about the

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[9] These descriptions are used in subsequent tables to characterize systems with CO_2 capture. In most cases the cost estimates for reference plants (without capture) would rank as high (e.g., IGCC power plants) or very high (e.g., PC and NGCC power plants).

Table 3.7 CO_2 capture costs: new pulverized-coal power plants using current technology.

Study Assumptions and Results	Parsons	Parsons	Simbeck	IEA GHG	IEA GHG	Rubin *et al.*	Range		NETL	Rao & Rubin	Stobbs & Clark
	2002b	2002b	2002	2004	2004	2005	min	max	2002	2002	2005
	SUPERCRITICAL UNITS / BITUMINOUS COALS								SUBCRIT UNITS / LOW RANK COALS		
Reference Plant (without capture)			*			*			*	*	
Boiler type (subcritical, super, ultra)	super	ultra	ultra	ultra	ultra	super			subcritical	subcritical	super
Coal type (bit, sub-bit, lig) and %S	bit, 2.5% S	bit, 2.5% S	bit, 1% S	bit, 1% S	bit, 1% S	bit, 2.1% S			bit, 2.5%S	sub-bit, 0.5%S	lignite
Emission control technologies (SO_2/NO_x)	FGD, SCR	FGD, SCR	FGD, SCR	FGD, SCR	FGD, SCR	FGD, SCR			FGD	FGD, SCR	FGD, SCR, LoTOx
Reference plant net output (MW)	462	506	520	758	754	524	**462**	**758**	397	462	424
Plant capacity factor (%)	65	65	80	85	85	75	**65**	**85**	85	75	90
Net plant efficiency, LHV (%)	42.2	44.8	44.5	44.0	43.7	40.9	**41**	**45**	38.9	36.1	43.4
Coal cost, LHV (US$ GJ^{-1})	1.29		0.98	1.50	1.50	1.25	**0.98**	**1.50**	1.03	1.25	0.88
Reference plant emission rate (t CO_2 MWh^{-1})	0.774	0.736	0.76	0.743	0.747	0.811	**0.74**	**0.81**	0.835	0.941	0.883
Capture Plant Design											
CO_2 capture technology	MEA	MEA	MEA	MEA	KS-1	MEA			MEA	MEA	MEA
Net plant output with capture (MW)	329	367	408	666	676	492	**329**	**676**	283	326	311.0
Net plant efficiency, LHV (%)	30.1	32.5	34.9	34.8	35.4	31.1	**30**	**35**	27.7	25.4	31.8
CO_2 capture system efficiency (%)	90	90	85	87.5	90	90	**85**	**90**	95	90	95
CO_2 emission rate after capture (t MWh^{-1})	0.108	0.101	0.145	0.117	0.092	0.107	**0.09**	**0.15**	0.059	0.133	0.060
CO_2 captured (Mt yr^{-1})	1.830	2.350	2.360	4.061	4.168	3.102	**1.83**	**4.17**	2.346	2.580	2.795
CO_2 product pressure (MPa)	8.4	8.4	13.7	11.0	11.0	13.9	**8**	**14**	10.3	13.9	13.9
CCS energy requirement (% more input MWh^{-1})	40	38	28	26	24	31	**24**	**40**	40	42	36
CO_2 reduction per kWh (%)	**86**	**86**	**81**	**84**	**88**	**87**	**81**	**88**	**93**	**86**	**93**
Cost Results			***	**	**						***
Cost year basis (constant dollars)	2000	2000	2000	2004	2004	2002			2002	2000	2003
Fixed charge factor (%)	15.5	15.5	12.7	11.0	11.0	14.8	**11.0**	**15.5**	14.8	15.0	
Reference plant TCR (US$ kW^{-1})	1281	1161	1486	1319	1265	1205	**1161**	**1486**	1268	1236	1891
Capture plant TCR (US$ kW^{-1})	2219	1943	2578	1894	2007	1936	**1894**	**2578**	2373	2163	3252
Incremental TCR for capture (US$ kW^{-1})	938	782	1092	575	742	731	**575**	**1092**	1105	927	1361
Reference plant COE (US$ MWh^1)	**51.5**	**51.0**	**42.9**	**43.9**	**42.8**	**46.1**	**43**	**52**	**42.3**	**49.2**	**44.5**
Capture plant COE (US$ MWh^1)	**85.6**	**82.4**	**70.9**	**62.4**	**63.0**	**74.1**	**62**	**86**	**76.6**	**87.0**	**74.3**
Incremental COE for capture (US$ MWh^1)	**34.1**	**31.4**	**28**	**18.5**	**20.2**	**28**	**18**	**34**	**37.8**	**37.8**	**29.8**
% increase in capital cost (over ref. plant)	73	67	74	44	59	61	**44**	**74**	87	75	72
% increase in COE (over ref. plant)	**66**	**62**	**65**	**42**	**47**	**61**	**42**	**66**	**81**	**77**	**67**
Cost of CO_2 captured (US$/$tCO_2$)	35	28	34	23	24	29	**23**	**35**	31	31	26
Cost of CO_2 avoided (US$/$tCO_2$)	51	49	43	29	31	40	**29**	**51**	43	47	36
Capture cost confidence level (see Table 3.6)	moderate								moderate		

Notes: 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. * Reported HHV values converted to LHV assuming LHV/HHV = 0.96 for coal. ** Reported capital costs increased by 8% to include interest during construction. ***Reported capital costs increased by 15% to estimate interest during construction and other owners' costs.

CO_2 capture system energy requirement, power plant efficiency, fuel type, plant capacity factor and fixed charge rate (Rao and Rubin, 2002). In this regard, it is useful to note that the lowest-cost capture systems in Table 3.7 (in terms of COE and cost of CO_2 avoided) come from a recent study (IEA GHG, 2004) that combines an efficient supercritical power plant design using bituminous coal, with high plant utilization, lowest fixed charge rate and more energy-efficient amine system designs, as recently announced by two major vendors (but not yet demonstrated on coal-fired power plants). In contrast, the highest reported COE values are for less efficient subcritical plant designs using low rank coal, combined with lower capacity factors, higher fixed charge rates and employing amine system designs typical of units currently in operation at small power plants.

Recent increases in world coal prices, if sustained, also would affect the levelized COE values reported here. Based on one recent study (IEA GHG, 2004), each 1.00 US\$ GJ^{-1} increase in coal price would increase the COE by 8.2 US\$ MWh^{-1} for a new PC plant without capture and by 10.1 US\$ MWh^{-1} for a plant with capture.

These results indicate that new power plants equipped with CO_2 capture are likely to be high-efficiency supercritical units, which yield lowest overall costs. The worldwide use of supercritical units (without capture) with current usage at 155 GW_e (Section 3.1.2.2), is rapidly increasing in several regions of the world and, as seen in Table 3.7, the preponderance of recent studies of CO_2 capture are based on supercritical units using bituminous coals. For these plants, Table 3.7 shows that capture systems increase the capital cost by 44-74% and the COE by 42-66% (18-34 US\$ MWh^{-1}). The major factors contributing to these ranges were differences in plant size, capacity factor and fixed charge factor. New or improved capture systems and power plant designs that promise to further reduce the costs of CO_2 capture are discussed later in Section 3.7.7. First, however, we examine CO_2 capture costs at existing plants.

3.7.5.2 Existing coal-fired plants

Compared to the study of new plants, CO_2 capture options for existing power plants have received relatively little study to date. Table 3.8 summarizes the assumptions and results of several studies estimating the cost of retrofitting an amine-based CO_2 capture system to an existing coal-fired power plant. Several factors significantly affect the economics of retrofits, especially the age, smaller sizes and lower efficiencies typical of existing plants relative to new builds. The energy requirement for CO_2 capture also is usually higher because of less efficient heat integration for sorbent regeneration. All of these factors lead to higher overall costs. Existing plants not yet equipped with a flue gas desulphurization (FGD) system for SO_2 control also must be retrofitted or upgraded for high-efficiency sulphur capture in addition to the CO_2 capture device. For plants with high NO_x levels, a NO_2 removal system also may be required to minimize solvent loss from reactions with acid gases. Finally, site-specific difficulties, such as land availability, access to plant areas and the need for special ductwork, tend to further increase the capital cost of any retrofit project relative to an equivalent new plant installation. Nonetheless, in cases where the capital cost of the existing plant has been fully or substantially amortized, Table 3.8 shows that the COE of a retrofitted plant with capture (including all new capital requirements) can be comparable to or lower than that of a new plant, although the incremental COE is typically higher because of the factors noted above.

Table 3.8 further shows that for comparable levels of about 85% CO_2 reduction per kWh, the average cost of CO_2 avoided for retrofits is about 35% higher than for the new plants analyzed in Table 3.7. The incremental capital cost and COE depend strongly on site-specific assumptions, including the degree of amortization and options for providing process energy needs. As with new plants, heat and power for CO_2 capture are usually assumed to be provided by the base (reference) plant, resulting in a sizeable (30 to 40%) plant output reduction. Other studies assume that an auxiliary gas-fired boiler is constructed to provide the CO_2 capture steam requirements and (in some cases) additional power. Low natural gas prices can make this option more attractive than plant output reduction (based on COE), but such systems yield lower CO_2 reductions (around 60%) since the emissions from natural gas combustion are typically not captured. For this reason, the avoided cost values for this option are not directly comparable to those with higher CO_2 reductions.

Also reflected in Table 3.8 is the option of rebuilding an existing boiler and steam turbine as a supercritical unit to gain efficiency improvements in conjunction with CO_2 capture. One recent study (Gibbins *et al.*, 2005) suggests this option could be economically attractive in conjunction with CO_2 capture since the more efficient unit minimizes the cost of capture and yields a greater net power output and a lower COE compared to a simple retrofit. The use of a new and less energy-intensive capture unit yields further cost reductions in this study. Another recent study similarly concluded that the most economical approach to CO_2 capture for an existing coal-fired plant was to combine CO_2 capture with repowering the unit with an ultra-supercritical steam system (Simbeck, 2004). One additional option, repowering an existing unit with a coal gasifier, is discussed later in Section 3.7.6.2.

3.7.5.3 Natural gas-fired power plants

Power plants fuelled by natural gas may include gas-fired boilers, simple-cycle gas turbines, or natural gas combined cycle (NGCC) units. The current operating capacity in use globally is 333 GW_e for gas-fired boilers, 214 GW_e for simple cycle gas turbines and 339 GW_e for NGCC (IEA WEO, 2004). The absence of sulphur and other impurities in natural gas reduces the capital costs associated with auxiliary flue gas clean-up systems required for amine-based CO_2 capture technology. On the other hand, the lower concentration of CO_2 in gas-fired units tends to increase the cost per tonne of CO_2 captured or avoided relative to coal-fired units.

Table 3.9 summarizes the assumptions and cost results of several recent studies of CO_2 capture at gas-fired combined cycle power plants ranging in size from approximately 300-700 MW. Relative to reference plants without capture, to achieve net

Table 3.8 CO$_2$ capture costs: existing pulverized-coal power plants using current technology.

Study Assumptions and Results	**Simbeck & McDonald**	**Alstom *et al.***	**Rao & Rubin**	**Rao & Rubin**	**Chen *et al.***	**Chen *et al.***	**Chen *et al.***	**Singh *et al.***	**Gibbins *et al.***	**Range**		**Gibbins *et al.***	**Gibbins *et al.***	**Chen *et al.***
	2000	**2001**	**2002**	**2002**	**2003**	**2003**	**2003**	**2003**	**2005**	**min**	**max**	**2006**	**2006**	**2003**
	AMINE SYSTEM RETROFITS TO EXISTING BOILERS											**REPOWERING + CO$_2$ CAPTURE**		
Reference Plant (without capture)		*	*	*	*	*	*							
Boiler type (subcritical, super, ultra)	sub	sub	sub	sub	sub	sub	sub		sub			super	super	sub
Coal type (bit, sub-bit, lig) and %S	sub-bit, 0.5%	bit, 2.7%S	sub-bit, 0.5%	sub-bit, 0.5%	sub-bit, 1.1%S	sub-bit, 1.1%S	sub-bit, 1.1%S	sub-bit						
Emission control technologies (SO$_2$/NO$_x$)	none	FGD	none	FGD	FGD	FGD	FGD	not reported	not reported			not reported	not reported	FGD
Reference plant size (MW)	292	434	470	470	248	248	248	400		**248**	**470**			248
Plant capacity factor (%)	80	67	75	75	80	76 (Capture= 80)	76 (Capture=80)	91.3	80	**67**	**91**	80	80	80
Net plant efficiency, LHV (%)	36.2	36.2	36.6		33.1	33.1	33.1		36.0	**33**	**37**	43.5	43.5	
Coal cost, LHV (US$ GJ^{-1})	0.98	1.30	1.25	1.25	1.20	1.20	1.20		3.07	**0.98**	**3.07**	3.07	3.07	1.20
Reference plant emission rate (t CO$_2$ MWh^{-1})	0.901	0.908	0.941	0.95	1.004	1.004	1.004	0.925		**0.90**	**1.00**			1.004
Capture Plant Design														
CO$_2$ capture technology	MEA	MEA	MEA	MEA	MEA	MEA	MEA	MEA	MEA			MEA	KS	Selexol
Other equipment included	new FGD	FGD upgrade	New FGD	FGD upgrade	FGD upgrade	FGD upgrade	FGD upgrade	FGD				Advanced supercrit boiler retrofit	Advanced supercrit boiler retrofit	IGCC (Texaco Q) repower +current steam turbine
Net plant size with capture (MW)	294	255	275	275	140	282	282	400		**140**	**400**			590
Auxilary boiler/fuel used? (type, LHV cost)	NG. $4.51 GJ^{-1}	none	none	none	none	NG. $2.59 GJ^{-1}	NG. $5.06 GJ^{-1}	NG. $3.79 GJ^{-1}	none			none	none	none
Net plant efficiency, LHV (%)	25.3	21.3	21.4	21.4	18.7				24.0	**19**	**25**	31.5	34.5	32.6
CO$_2$ capture system efficiency (%)	90	96	90	90	90	90	90	90		**90**	**96**			90
CO$_2$ emission rate after capture (t MWh^{-1})	0.113	0.059	0.155	0.16	0.177	0.369	0.369	0.324		**0.06**	**0.37**			0.099
CO$_2$ captured (Mt yr^{-1})	2.090	2.228			1.480	1.480	1.480	2.664		**1.48**	**2.66**			3.684
CO$_2$ product pressure (MPa)	13.7	13.9	13.9	13.9	13.9	13.9	13.9		10.0	**10**	**14**	10.0	10.0	14.5
CCS energy requirement (% more input MWh^{-1})	43	70	71		77				50	**43**	**77**	38	26	
CO$_2$ reduction per kWh (%)	**87**	**94**	**84**	**83**	**82**	**63**	**63**	**65**		**63**	**94**			
Cost Results	**							**						
Cost year basis (constant dollars)	1999	n/a	2000	2000	2000	2000	2000	2001						
Fixed charge factor (%)	12.8	13.0	15.0	15.0	14.8	14.8	14.8	9.4	11.8	**9.4**	**15.0**	11.8	11.8	15
Reference plant TCR (US$ kW^{-1})	112				0	0	0	0	160	**0**	**160**	480	480	0
Capture plant TCR (US$ kW^{-1})	1059	1941			837	647	654	846	1028	**647**	**1941**	1282	1170	1493
Incremental TCR for capture (US$ kW^{-1})	947	1602			837	647	654	846	868	**647**	**1602**	802	690	1493
Reference plant COE (US$ MWh^{-1})	**18.8**		**18.0**	**18.0**	**20.6**	**20.6**	**20.6**		**26.0**	**18**	**26**	**27.0**	**27.0**	**21**
Capture plant COE (US$ MWh^{-1})	**54.3**		**70.4**	**66.7**	**66.8**	**51.1**	**62.2**		**65.0**	**51**	**70**	**58.0**	**53.0**	**62.2**
Incremental COE for capture (US$ MWh^{-1})	**35.5**	**61.7**	**52.4**	**48.7**	**46.2**	**30.6**	**41.7**	**33.2**	**39.0**	**31**	**62**	**31.0**	**26.0**	**41.2**
% increase in capital cost (over ref. plant)														
% increase in COE (over ref. plant)	**189**		**291**	**271**	**225**	**149**	**203**		**150**	**149**	**291**	**115**	**96**	**196**
Cost of CO$_2$ captured (US$/tCO$_2$)	35	42			31	41	56	40		**31**	**56**			
Cost of CO$_2$ avoided (US$/tCO$_2$)	45	73	67	59	56	48	66	55		**45**	**73**			46
Capture cost confidence level (see Table 3.6)	moderate											moderate		

Notes: 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. * Reported HHV values converted to LHV assuming LHV/HHV = 0.96 for coal and 0.90 for natural gas. **Reported capital costs increased by 15% to estimate interest during construction and other owners' costs.

Table 3.9 CO_2 capture costs: natural gas-fired power plants using current technology.

Study Assumptions and Results	**Parsons**	**NETL**	**IEA GHG**	**IEA GHG**	**CCP**	**Rubin *et al.***	**Rubin *et al.***	**Range**	
	2002(b)	**2002**	**2004**	**2004**	**2005**	**2005**	**2005**	**min**	**max**
Reference Plant (without capture)	*					*	*		
Plant type (boiler, gas turbine, comb.cycle)	comb.cycle	comb.cycle	comb.cycle	comb.cycle	comb.cycle	comb.cycle	comb.cycle		
Reference plant size (MW)	509	379	776	776	392	507	507	**379**	**776**
Plant capacity factor (%)	65	85	85	85	95	75	50	**50**	**95**
Net plant efficiency, LHV (%)	55.1	57.9	55.6	55.6	57.6	55.8	55.8	**55**	**58**
Fuel cost, LHV (US$ GJ^{-1})	2.82	3.55	3.00	3.00	2.96	4.44	4.44	**2.82**	**4.44**
Reference plant emission rate (tCO_2 MWh^{-1})	0.364	0.344	0.379	0.379	0.37	0.367	0.367	**0.344**	**0.379**
Capture Plant Design									
CO_2 capture technology	MEA	MEA	MEA	KS-1	MEA	MEA	MEA		
Net plant size with capture (MW)	399	327	662	692	323	432	432	**323**	**692**
Net plant efficiency, LHV (%)	47.4	49.9	47.4	49.6	47.4	47.6	47.6	**47**	**50**
CO_2 capture system efficiency (%)	90	90	85	85	86	90	90	**85**	**90**
CO_2 emission rate after capture (t MWh^{-1})	0.045	0.040	0.066	0.063	0.063	0.043	0.043	**0.040**	**0.066**
CO_2 captured (Mt yr^{-1})	0.949	0.875	1.844	1.844	1.09	1.099	0.733	**0.733**	**1.844**
CO_2 product pressure (MPa)	8.4	10.3	11.0	11.0		13.7	13.7	**8**	**14**
CCS energy requirement (% more input MWh^{-1})	16	16	15	11	22	17	17	**11**	**22**
CO_2 reduction per kWh (%)	**88**	**88**	**83**	**83**	**83**	**88**	**88**	**83**	**88**
Cost Results									
Cost year basis (constant dollars)	2000	2002	2004	2004		2001	2001		
Fixed charge factor (%)			11.0	11.0	11.0	14.8	14.8	**11.0**	**14.8**
Reference plant TCR (US$ kW^{-1})	549	515	539	539	724	554	554	**515**	**724**
Capture plant TCR (US$ kW^{-1})	1099	911	938	958	1261	909	909	**909**	**1261**
Incremental TCR for capture (US$ kW^{-1})	550	396	399	419	537	355	355	**355**	**550**
Reference plant COE (US$ MWh^{-1})	**34.2**	**34.7**	**31.3**	**31.3**	**34.2**	**43.1**	**50**	**31**	**50**
Capture plant COE (US$ MWh^{-1})	**57.9**	**48.3**	**44**	**43.1**	**51.8**	**58.9**	**72**	**43**	**72**
Incremental COE for capture (US$ MWh^{-1})	**23.7**	**13.6**	**12.7**	**11.8**	**17.6**	**15.8**	**22**	**12**	**24**
% increase in capital cost (over ref. plant)	100	77	74	78	74	64	64	**64**	**100**
% increase in COE (over ref. plant)	**69**	**39**	**41**	**38**	51	**37**	**44**	**37**	**69**
Cost of CO_2 captured (US$/$tCO_2$)	57	38	34	33	46	41	57	**33**	**57**
Cost of CO_2 avoided (US$/$tCO_2$)	74	45	41	37	57	49	68	**37**	**74**
Capture cost confidence level (see Table 3.6)	moderate								

Notes: 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. * Reported HHV values converted to LHV assuming LHV/HHV = 0.90 for natural gas.

CO_2 reductions (per kWh) of the order of 83-88%, the capital cost per kW increases by 64-100%, while the COE increases by 37-69%, or by 12-24 US$ MWh^{-1} on an absolute basis. The corresponding cost of CO_2 avoided ranges from 37-74 US$/$tCO_2$, while the CCS energy requirement increases plant fuel consumption per kWh by 11-22%.

As seen earlier in Equations (7) to (9), assumptions about the plant fuel cost have an especially important influence on the COE for gas-fired plants because the contribution of capital costs is relatively low compared to coal plants. The studies in Table 3.9 assume stable gas prices of 2.82-4.44 US$ GJ^{-1} (LHV basis) over the life of the plant, together with high capacity factors (65-95%) representing base load operation. These assumptions result in relatively low values of COE for both the reference plant and capture plant. Since about 2002, however, natural gas prices have increased significantly in many parts of the world, which has also affected the outlook for future prices. Based on the assumptions of one recent study (IEA GHG, 2004), the COE for an NGCC plant without capture would increase by 6.8 US$ MWh^{-1} for each 1.00 US$ GJ^{-1} increase in natural gas price (assuming no change in plant utilization or other factors of production). An NGCC plant with CCS would see a slightly higher increase of 7.3 US$ MWh^{-1}. The price of natural gas, and its relation to the price of competing fuels like coal, is an important determinant of which type of power plant will provide the lowest cost electricity in the context of a particular situation. However, across a twofold increase in gas price (from 3-6 US$ GJ^{-1}), the incremental cost of CO_2 capture changed by only 2 US$ MWh^{-1} (US$ 0.002 kWh^{-1}) with all other factors held constant.

In countries like the US, higher gas prices have also resulted in lower utilization rates (averaging 30-50%) for plants originally designed for base-load operation, but where lower-cost coal plants are available for dispatch. This further raises the average cost of electricity and CO_2 capture for those NGCC plants, as reflected in one case in Table 3.9 with a capacity factor of 50%. In other parts of the world, however, lower-cost coal plants may not be available, or gas supply contracts might limit the ability to curtail gas use. Such situations again illustrate that options for power generation with or without CO_2 capture should be evaluated in the context of a particular situation or scenario.

Studies of commercial post-combustion CO_2 capture applied to simple-cycle gas turbines have been conducted for the special case of retrofitting an auxiliary power generator in a remote location (CCP, 2005). This study reported a relatively high cost of 88 US$/$tCO_2$ avoided. Studies of post-combustion capture for gas-fired boilers have been limited to industrial applications, as discussed later in Section 3.7.8.

3.7.5.4 Biomass-firing and co-firing systems

Power plants can be designed to be fuelled solely by biomass, or biomass can be co-fired in conventional coal-burning plants. The requirement to reduce net CO_2 emissions could lead to an increased use of biomass fuel, because plants that utilize biomass as a primary or supplemental fuel may be able to take credit for the carbon removed from the atmosphere during the biomass growth cycle. If the biomass carbon released during combustion (as CO_2) is then captured and stored, the net quantity of CO_2 emitted to the atmosphere could in principle be negative.

The most important factor affecting the economics of biomass use is the cost of the biomass. This can range from a negative value, as in the case of some biomass wastes, to costs substantially higher than coal, as in the case of some purposely-grown biomass fuels, or wastes that have to be collected from diffuse sources. Power plants that use only biomass are typically smaller than coal-fired plants because local availability of biomass is often limited and biomass is more bulky and hence more expensive to transport than coal. The smaller sizes of biomass-fired plants would normally result in lower energy efficiencies and higher costs of CO_2 capture. Biomass can be co-fired with coal in larger plants (Robinson *et al.*, 2003). In such circumstances the incremental costs of capturing biomass-derived CO_2 should be similar to costs of capturing coal-derived CO_2. Another option is to convert biomass into pellets or refined liquid fuels to reduce the cost of transporting it over long distances. However, there are costs and emissions associated with production of these refined fuels. Information on costs of CO_2 capture at biomass-fired plants is sparse but some information is given in Section 3.7.8.4. The overall economics of CCS with biomass combustion will depend very much on local circumstances, especially biomass availability and cost and (as with fossil fuels) proximity to potential CO_2 storage sites.

3.7.6 Pre-combustion CO_2 capture cost for electric power plants (current technology)

Studies of pre-combustion capture for electric power plants have focused mainly on IGCC systems using coal or other solid fuels such as petroleum coke. This section of the report focuses on currently available technology for CO_2 capture at such plants. As before, the cost of CO_2 capture depends not only on the choice of capture technology, but more importantly on the characteristics and design of the overall power plant, including the fuel type and choice of gasifier. Because IGCC is not widely used for electric power generation at the present time, economic studies of IGCC power plants typically employ design assumptions based on the limited utility experience with IGCC systems and the more extensive experience with gasification in industrial sectors such as petroleum refining and petrochemicals. For oxygen-blown gasifiers, the high operating pressure and relatively high CO_2 concentrations achievable in IGCC systems makes physical solvent absorption systems the predominant technology of interest for pre-combustion CO_2 capture (see Section 3.5.2.11). For purposes of cost reporting, we again distinguish between new plant designs and the retrofitting of existing facilities.

3.7.6.1 New coal gasification combined cycle power plants

Table 3.10 summarizes the key assumptions and results of several recent studies of CO_2 capture costs for new IGCC power plants ranging in size from approximately 400-800 MW

Table 3.10 CO_2 capture costs: new IGCC power plants using current technology.

Study Assumptions and Results	**NETL**	**NETL**	**NETL**	**Parsons**	**Simbeck**	**Nsakala, *et al.***	**IEA GHG**	**IEA GHG**	**IEA GHG**	**Rubin *et al.***	**Rubin *et al.***	**Range**	
	2002	**2002**	**2002**	**2002b**	**2002**	**2003**	**2003**	**2003**	**2003**	**2005**	**2005**	**min**	**max**
	PLANTS WITH BITUMINOUS COAL FEEDSTOCK												
Reference Plant without capture)	*	*	*	*		*							
Gasifier name or type	Shell, O_2 blown, CGCU	E-gas, O_2 blown, CGUC	Texaco quench, O_2 blown	E-gas, O_2 blown	Texaco quench, O_2 blown	Texaco syngas cooler, O_2 blown	Texaco quench, O_2 blown	Texaco quench, O_2 blown	Shell, O_2 blown	Texaco quench, O_2 blown	Texaco quench, O_2 blown		
Fuel type (bit, subbit, lig; other) and %S	Illinois #6	Illinois #6	Illinois #6	bit, 2.5% S	bit, 1% S	bit	bit, 1%S	bit, 1%S	bit, 1%S	bit, 2.1%S	bit, 2.1%S		
Reference plant size (MW)	413	401	571	425	521		827	827	776	527	527	**401**	**827**
Plant capacity factor (%)	85	85	65	65	80	80	85	85	85	75	65	**65**	**85**
Net plant efficiency, LHV (%)	47.4	46.7	39.1	44.8	44.6		38.0	38.0	43.1	39.1	39.1	**38**	**47**
Fuel cost, LHV (US\$ GJ^{-1})	1.03	1.03	1.28	1.29	0.98	1.23	1.50	1.50	1.50	1.25	1.25	**0.98**	**1.50**
Reference plant emission rate (tCO_2 MWh^{-1})	0.682	0.692	0.846	0.718	0.725		0.833	0.833	0.763	0.817	0.817	**0.68**	**0.85**
Capture Plant Design													
CO_2 capture technology	Selexol	Selexol	Selexol	Selexol	Selexol	Selexol	Selexol	Selexol. NS	Selexol	Selexol	Selexol		
Net plant size, with capture (MW)	351	359	457	404	455		730	742	676	492	492	**351**	**742**
Net plant efficiency, LHV (%)	40.1	40.1	31.3	38.5	39.0	31.5	31.5	32.0	34.5	33.8	33.8	**31**	**40**
CO_2 capture system efficiency (%)	89.2	87.0	89.0	91.0	91.2		85	85	85	90	90	**85**	**91**
CO_2 emission rate after capture (t MWh^{-1})	0.087	0.105	0.116	0.073	0.065	0.104	0.152	0.151	0.142	0.097	0.097	**0.07**	**0.15**
CO_2 captured (Mt/yr)	1.803	1.870	2.368	1.379	2.151		4.682	4.728	4.050	2.749	2.383	**1.38**	**4.73**
CO_2 product pressure (MPa)	14.5	14.5	8.3	8.3			11.0	11.0	11.0	13.7	13.7	**8**	**14**
CCS energy requirement (% more input MWh^{-1})	18	16	25	16	14		21	19	25	16	16	**14**	**25**
CO_2 reduction per kWh (%)	**87**	**85**	**86**	**90**	**91**		**82**	**82**	**81**	**88**	**88**	**81**	**91**
Cost Results							**	**	**				
Cost year basis (constant dollars)	2002	2002	2002	2000	2000		2002	2002	2002	2001	2001		
Fixed charge factor (%)	14.8	14.8	15.0	13.8	13.0		11.0	11.0	11.0	14.8	17.3	**11**	**17**
Reference plant TCR (US\$ kW^{-1})	1370	1374	1169	1251	1486	1565	1187	1187	1371	1311	1311	**1169**	**1565**
Capture plant TCR (US\$ kW^{-1})	2270	1897	1549	1844	2067	2179	1495	1414	1860	1748	1748	**1414**	**2270**
Incremental TCR for capture (US\$ kW^{-1})	900	523	380	593	581	614	308	227	489	437	437	**227**	**900**
Reference plant COE (US\$ MWh^{-1})	**40.6**	**40.9**	**43.4**	**47.7**	**43.0**	**53.0**	**45.0**	**45.0**	**48.0**	**48.3**	**61**	**41**	**61**
Capture plant COE (US\$ MWh^{-1})	**62.9**	**54.4**	**59.9**	**65.8**	**57.7**	**71.5**	**56.0**	**54.0**	**63.0**	**62.6**	**79**	**54**	**79**
Incremental COE for capture (US\$ MWh^{-1})	**22.3**	**13.5**	**16.5**	**18.1**	**14.7**	**18.5**	**11**	**9**	**15**	**14.3**	**18.2**	**9**	**22**
% increase in capital cost (over ref. plant)	66	38	33	47	39	39	26	19	36	33	33	**19**	**66**
% increase in COE (over ref. plant)	55	33	38	38	34	**35**	**24**	**20**	**31**	30	30	**20**	**55**
Cost of CO_2 captured (US\$/tCO_2)	32	19	18	30	21		13	11	19	17	21	**11**	**32**
Cost of CO_2 avoided (US\$/tCO_2)	37	23	23	28	22	23	16	13	24	20	25	**13**	**37**
Capture cost confidence level (see Table 3.6)	moderate												

Notes: 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. * Reported HHV values converted to LHV assuming LHV/HHV = 0.96 for coal. ** Reported capital costs increased by 8% to include interest during construction. **Reported capital costs increased by 15% to estimate interest during construction and other owners' costs.

Table 3.10. *Continued.*

Study Assumptions and Results	Stobbs & Clark	Stobbs & Clark	Stobbs & Clark	IEA GHG
	2005	**2005**	**2005**	**2000b**
	PLANTS WITH OTHER FEEDSTOCKS			
Reference Plant without capture)				
Gasifier name or type		Texaco quench, O_2 blown	Shell, O_2 blown	O_2 blown, partial oxidation
Fuel type (bit, subbit, lig; other) and %S	bit	Sub-bit	Lignite	Natural gas
Reference plant size (MW)	[No IGCC Reference Plants]			790
Plant capacity factor (%)	90	90	90	90
Net plant efficiency, LHV (%)				56.2
Fuel cost, LHV (US\$ GJ^{-1})	1.90	0.48	0.88	2.00
Reference plant emission rate (tCO_2 MWh^{-1})				0.370
Capture Plant Design				
CO_2 capture technology	Selexol	Selexol	Selexol	Selexol
Net plant size, with capture (MW)	445	437	361	820
Net plant efficiency, LHV (%)	32.8	27.0	28.3	48.3
CO_2 capture system efficiency (%)	87	92	86	85
CO_2 emission rate after capture (t MWh^{-1})	0.130	0.102	0.182	0.065
CO_2 captured (Mt/yr)	3.049	4.040	3.183	2.356
CO_2 product pressure (MPa)	13.9	13.9	13.9	11.0
CCS energy requirement (% more input MWh^{-1})				14
CO_2 reduction per kWh (%)				**82**
Cost Results	***	***	***	**
Cost year basis (constant dollars)	2003	2003	2003	2000
Fixed charge factor (%)				11.0
Reference plant TCR (US\$ kW^{-1})				447
Capture plant TCR (US\$ kW^{-1})	2205	2518	3247	978
Incremental TCR for capture (US\$ kW^{-1})				531
Reference plant COE (US\$ MWh^{-1})				21.6
Capture plant COE (US\$ MWh^{-1})	68.4	62.1	83.9	34.4
Incremental COE for capture (US\$ MWh^{-1})				12.8
% increase in capital cost (over ref. plant)				119
% increase in COE (over ref. plant)				**59**
Cost of CO_2 captured (US\$/tCO_2)				35
Cost of CO_2 avoided (US\$/tCO_2)	31	33	56	42
Capture cost confidence level (see Table 3.6)	moderate			moderate

Notes: 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. * Reported HHV values converted to LHV assuming LHV/HHV = 0.96 for coal. ** Reported capital costs increased by 8% to include interest during construction. ***Reported capital costs increased by 15% to estimate interest during construction and other owners' costs.

net power output. While several gasifiers and coal types are represented, most studies focus on the oxygen-blown Texaco quench system,[10] and all but one assume bituminous coals. CO_2 capture efficiencies across these studies range from 85-92% using commercially available physical absorption systems. The energy requirements for capture increase the overall plant heat rate (energy input per kWh) by 16-25%, yielding net CO_2 reductions per kWh of 81-88%. Other study variables that influence total plant cost and the cost of CO_2 capture include the fuel cost, CO_2 product pressure, plant capacity factor and fixed charge factor. Many of the recent studies also include the cost of a spare gasifier to ensure high system reliability.

Table 3.10 indicates that for studies based on the Texaco or E-Gas gasifiers, CO_2 capture adds approximately 20-40% to both the capital cost (US\$ kW^{-1}) and the cost of electricity (US\$ MWh^{-1}) of the reference IGCC plants, while studies using the Shell gasifier report increases of roughly 30-65%. The total COE reported for IGCC systems ranges from 41-61 US\$ MWh^{-1} without capture and 54-79 US\$ MWh^{-1} with capture. With capture, the lowest COE is found for gasifier systems with quench cooling designs that have lower thermal efficiencies than the more capital-intensive designs with heat recovery systems. Without capture, however, the latter system type has the lowest COE in Table 3.10. Across all studies, the cost of CO_2 avoided ranges from 13-37 US\$/tCO_2 relative to an IGCC without capture, excluding transport and storage costs. Part of the reason for this lower incremental cost of CO_2 capture relative to coal combustion plants is the lower average energy requirement for IGCC systems. Another key factor is the smaller gas volume treated in oxygen-blown gasifier systems, which substantially reduces equipment size and cost.

As with PC plants, Table 3.10 again emphasizes the importance of plant financing and utilization assumptions on the calculated cost of electricity, which in turn affects CO_2-capture costs. The lowest COE values in this table are for plants with a low fixed charge rate and high capacity factor, while

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[10] In 2004, the Texaco gasifier was re-named as the GE gasifier following acquisition by GE Energy (General Electric). However, this report uses the name Texaco, as it is referred to in the original references cited.

substantially higher COE values result from high financing costs and lower plant utilization. Similarly, the type and properties of coal assumed has a major impact on the COE, as seen in a recent Canadian Clean Power Coalition study, which found substantially higher costs for low-rank coals using a Texaco-based IGCC system (Stobbs and Clark, 2005, Table 3.10). EPRI also reports higher IGCC costs for low-rank coals (Holt *et al*., 2003). On the other hand, where plant-level assumptions and designs are similar across studies, there is relatively little difference in the estimated costs of CO_2 capture based on current commercial technology. Similarly, the several studies in Tables 3.7 and 3.10 that estimate costs for both IGCC and PC plants on an internally consistent basis, all find that IGCC plants with capture have a lower COE than PC plants with capture. There is not yet a high degree of confidence in these cost estimates, however (see Table 3.6).

The costs in Table 3.10 also reflect efforts in some studies to identify least-cost CO_2 capture options. For example, one recent study (IEA GHG, 2003) found that capture and disposal of hydrogen sulphide (H_2S) along with CO_2 can reduce overall capture costs by about 20% (although this may increase transport and storage costs, as discussed in Chapters 4 and 5). The feasibility of this approach depends in a large part on applicable regulatory and permitting requirements. Advanced IGCC designs that may further reduce future CO_2 capture costs are discussed in Section 3.7.7.

3.7.6.2 Repowering of existing coal-fired plants with IGCC

For some existing coal-fired power plants, an alternative to the post-combustion capture systems discussed earlier is repowering with an IGCC system. In this case - depending on site-specific circumstances - some existing plant components, such as the steam turbine, might be refurbished and utilized as part of an IGCC plant. Alternatively, the entire combustion plant might be replaced with a new IGCC system while preserving other site facilities and infrastructure.

Although repowering has been widely studied as an option to improve plant performance and increase plant output, there are relatively few studies of repowering motivated by CO_2 capture. Table 3.8 shows results from one recent study (Chen et *al*., 2003) which reports CO_2 capture costs for IGCC repowering of a 250 MW coal-fired unit that is assumed to be a fully amortized (hence, a low COE of 21 US\$ MWh^{-1}). IGCC repowering yielded a net plant capacity of 600 MW with CO_2 capture and a COE of 62-67 US\$ MWh^{-1} depending on whether or not the existing steam turbine can be reused. The cost of CO_2 avoided was 46-51 US\$/tCO_2. Compared to the option of retrofitting the existing PC unit with an amine-based capture system and retaining the existing boiler (Table 3.8), the COE for IGCC repowering was estimated to be 10-30% lower. These findings are in general agreement with earlier studies by Simbeck (1999). Because the addition of gas turbines roughly triples the gross plant capacity of a steam-electric plant, candidates for IGCC repowering are generally limited to smaller existing units (e.g., 100-300 MW). Taken together with the post-combustion retrofit studies in Table 3.8, the most cost-effective options for existing plants involve combining CO_2 capture with plant upgrades that increase overall efficiency and net output. Additional studies would be needed to systematically compare the feasibility and cost of IGCC repowering to supercritical boiler upgrades at existing coal-fired plants.

3.7.7 CO_2 capture cost for hydrogen production and multi-product plants (current technology)

While electric power systems have been the dominant technologies of interest for CO_2 capture studies, other industrial processes, including hydrogen production and multi-product plants producing a mix of fuels, chemicals and electricity also are of interest. Because CO_2 capture cost depends strongly on the production process in question, several categories of industrial processes are discussed below.

3.7.7.1 Hydrogen production plants

Section 3.5 discussed the potential role of hydrogen as an energy carrier and the technological options for its production. Here we examine the cost of capturing CO_2 normally released during the production of hydrogen from fossil fuels. Table 3.11 shows the key assumptions and cost results of recent studies of CO_2 capture costs for plants with hydrogen production rates of 155,000-510,000 $Nm^3\ h^{-1}$ (466-1531 MW_t), employing either natural gas or coal as a feedstock. The CO_2 capture efficiency for the hydrogen plant ranges from 87-95% using commercially available chemical and physical absorption systems. The CO_2 reduction per unit of product is lower, however, because of the process energy requirements and because of additional CO_2 emitted by an offsite power plant assumed in some of these studies. As hydrogen production requires the separation of H_2 from CO_2, the incremental cost of capture is mainly the cost of CO_2 compression.

At present, hydrogen is produced mainly from natural gas. Two recent studies (see Table 3.11) indicate that CO_2 capture would add approximately 18-33% to the unit cost of hydrogen while reducing net CO_2 emissions per unit of H_2 product by 72-83% (after accounting for the CO_2 emissions from imported electricity). The total cost of hydrogen is sensitive to the cost of feedstock, so different gas prices would alter both the absolute and relative costs of CO_2 capture.

For coal-based hydrogen production, a recent study (NRC,2004) projects an 8% increase in the unit cost of hydrogen for an 83% reduction in CO_2 emissions per unit of product. Again, this figure includes the CO_2 emissions from imported electricity.

3.7.7.2 Multi-product plants

Multi-product plants (also known as polygeneration plants) employ fossil fuel feedstocks to produce a variety of products such as electricity, hydrogen, chemicals and liquid fuels. To calculate the cost of any particular product (for a given rate of return), economic analyses of multi-product plants require that the selling price of all other products be specified over the operating life of the plant. Such assumptions, in addition to

Table 3.11. CO_2 capture costs: Hydrogen and multi-product plants using current or near-commercial technology. (Continued on next page)

Study Assumptions and Results	HYDROGEN AND ELECTRICITY PRODUCTS								
	Simbeck	**NRC**	**NRC**	**Parsons**	**Mitretek**	**Kreutz *et al.***	**Kreutz *et al.***	**Range**	
	2005	**2004**	**2004**	**2002a**	**2003**	**2005**	**2005**	**min**	**max**
Reference Plant (without capture)	*			*	*				
Plant products (primary/secondary)	H_2	H_2	H_2	H_2+ electricity	H_2+ electricity	H_2+ electricity	H_2+ electricity		
Production process or type	Steam reforming	Steam reforming	Texaco quench, CGCU	Conv E-Gas, CGCU, H_2SO_4 co-product	Texaco quench, CGCU, Claus/Scot sulphur co-product	Texaco quench	Texaco quench		
Feedstock	Natural gas	Natural gas	Coal	Pgh #8 Coal	Coal	Coal	Coal		
Feedstock cost, LHV (US\$ GJ^{-1})	5.26	4.73	1,20	0.89	1.03	1.26	1.26	**0.89**	**5.26**
Ref. plant input capacity, LHV (GJ h^{-1})	9848	7235	8861	2627	2954	6706	6706	**2627**	**9848**
Ref plant output capacity, LHV: Fuels (GJ h^{-1})	7504	5513	6004	1419	1579	3853	3853	**1419**	**7504**
Electricity (MW)	-44	-32	-121	38	20	78	78	**-121**	**78**
Net plant efficiency, LHV (%)	74.6	74.6	62.9	59.2	55.9	61.7	61.7	**55.9**	**74.6**
Plant capacity factor (%)	90	90	90	80	85	80	80	**80**	**90**
CO_2emitted (MtCO$_2$ yr^{-1})	4.693	3.339	7.399	1.795	2.148	4.215	4.215	**1.80**	**7.40**
Carbon exported in fuels (MtC yr^{-1})	0	0	0	0	0	0	0	**0**	**0**
Total carbon released (kg CO$_2$ GJ^{-1} products)	81	78	168	164	174	145	145	**78**	**174**
Capture Plant Design									
CO_2 capture/separation technology	Amine scrubber, SMR flue gas	MEA scrubber	Not reported	Selexol	Not reported	Selexol	CO_2 H_2S co-capture, Selexol		
Capture plant input capacity, LHV (GJ h^{-1})	11495	8339	8861	2627	2954	6706	6706	**2627**	**11495**
Capture plant output capacity, LHV: Fuels (GJ h^{-1})	7504	6004	6004	1443	1434	3853	3853	**1434**	**7504**
Electricity (MW)	-129	-91	-187	12	27	39	35	**-187**	**39**
Net plant efficiency, LHV (%)	61.2	68.1	60.2	56.6	51.8	59.5	59.3	**51.8**	**68.1**
CO_2 capture efficiency (%)**	90	90	90	92	87	91	95	**87**	**95**
CO_2 emitted (MtCO$_2$ yr^{-1})***	1.280	0.604	1.181	0.143	0.279	0.338	0.182	**0.14**	**1.280**
Carbon exported in fuels (MtC yr^{-1})	0	0	0	0	0	0	0	**0.0**	**0**
Total carbon released (kgCO$_2$ GJ^{-1} products)	23.0	13.5	28.1	13.7	24.5	12.1	6.5	**6.5**	**28.1**
CO_2 captured (MtCO$_2$ yr^{-1})	4.658	3.378	6.385	1.654	1.869	3.882	4.037	**1.7**	**6.4**
CO_2 product pressure (MPa)	13.7	13.7	13.7	13.4	20	15	15	**13.4**	**20.0**
CCS energy requirement (% more input/GJ plant output)	21.8	9.5	4.5	4.7	7.9	3.6	3.9	**3.6**	**21.8**
CO_2 reduction per unit product (%)	72	83	83	92	86	92	96	**72**	**96**
Cost Results									
Cost year basis (constant dollars)	2003	2000	2000	2000	2000	2002	2002		
Fixed charge rate (%)	20.0	16.0	16.0	14.3	13.0	15.0	15.0	**13.0**	**20.0**
Reference plant TCR (million US\$)****	668	469	1192	357	365	887	887	**357**	**1192**
Capture plant TCR (million US\$)****	1029	646	1218	415	409	935	872	**409**	**1218**
% increase in capital cost (%)	54.1	37.7	2.2	16.5	11.9	5.4	-1.7	**-1.7**	**54.1**
Ref. plant electricity price (US\$ MWh^{-1})	50.0	45.0	45.0	30.8	35.6	46.2	46.2	**30.8**	**50.0**
Capture plant electricity price (US\$ MWh^{-1})	50.0	45.0	45.0	30.8	53.6	62.3	60.5	**30.8**	**62.3**
% increase in assumed electricity price	0.0	0.0	0.0	0.0	50.6	34.8	31.0	**0.0**	**50.6**
Ref. plant fuel product cost, LHV (US\$ GJ^{-1})	**10.03**	**8.58**	**7.99**	**6.51**	**7.29**	**7.19**	**7.19**	**6.51**	**10.03**
Capture plant fuel product cost, LHV (US\$ GJ^{-1})	**13.29**	**10.14**	**8.61**	**7.90**	**8.27**	**7.86**	**7.52**	**7.52**	**13.29**
Increase in fuel product cost (US\$ GJ^{-1})	**3.26**	**1.56**	**0.62**	**1.38**	**0.98**	**0.67**	**0.32**	**0.32**	**3.26**
% increase in fuel product cost	**32.5**	**18.2**	**7.7**	**21.1**	**13.4**	**9.3**	**4.5**	**4.5**	**32.5**
Cost of CO_2 captured (US\$/tCO$_2$)	38.9	20.7	4.1	8.7	6.0	4.8	2.2	**2.2**	**38.9**
Cost of CO_2 avoided (US\$/tCO$_2$)	56.3	24.1	4.4	9.2	6.5	5.0	2.3	**2.3**	**56.3**
Confidence level (see Table 3.6)	high		high	moderate					

Notes: 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. * Reported HHV values converted to LHV assuming LHV/HHV = 0.96 for coal, 0.846 for hydrogen, and 0.93 for F-T liquids. ** CO_2 capture efficiency = (C in CO_2 captured) /(C in fossil fuel input to plant - C in carbonaceous fuel products of plant) x100; C associated with imported electricity is not included. ***Includes CO_2 emitted in the production of electricity imported by the plant. ****Reported total plant investment values increased by 3.5% to estimate total capital requirement.

those discussed earlier, can significantly affect the outcome of cost calculations when there is not one dominant product at the facility.

Several of the coal-based hydrogen production plants in Table 3.11 also produce electricity, albeit in small amounts (in fact, smaller than the electricity quantities purchased by the stand-alone plants). Most of these studies assume that the value of the electricity product is higher under a carbon capture regime than without CO_2 capture. The result is a 5-33% increase in hydrogen production cost for CO_2 reductions of 72-96% per unit of product. The case with the lowest incremental product cost and highest CO_2 reduction assumes co-disposal of H_2S with CO_2, thus eliminating the costs of sulphur capture and recovery. As noted earlier (Section 3.7.6.1), the feasibility of this option depends strongly on local regulatory requirements; nor are higher costs for transport and storage reflected in the Table 3.11 cost estimate for this case.

Table 3.11 also presents examples of multi-product plants

Table 3.11. *Continued.*

Study Assumptions and Results	**LIQUID FUEL AND ELECTRICITY PRODUCTS**										
	Mitretek	**Larson/Ren**	**Larson/Ren**	**Larson/Ren**	**Larson/Ren**	**Celik *et al.***	**Celik *et al.***	**Celik *et al.***	**Celik *et al.***	**Range**	
	2003	**2003**	**2003**	**2003**	**2003**	**2005**	**2005**	**2005**	**2005**	**min**	**max**
Reference Plant (without capture)	*										
Plant products (primary/secondary)	F-T liquids + electricity	MeOH +electricity	MeOH +electricity	DME +electricity	DME +electricity	DME + electricity	DME + electricity	DME + electricity	DME + electricity		
Production process or type	Unspecified O_2-blown gasifier, unspecified synthesis reactor	Texaco quench, Liquid phase reactor, Once-through config,	Texaco quench, Liquid phase reactor, Once-through config,	Texaco quench, Liquid phase reactor, Once-through config,	Texaco quench, Liquid phase reactor, Once-through config,	Texaco quench, Liquid phase reactor, Once-through config,	Texaco quench, Liquid phase reactor, Once-through config,	Texaco quench, Liquid phase reactor, Once-through config,	Texaco quench, Liquid phase reactor, Once-through config,		
Feedstock	Coal	Coal	Coal	Coal	Coal	Coal	Coal	Coal	Coal		
Feedstock cost, LHV (US\$ GJ^{-1})	1,09	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	**1.00**	**1.09**
Ref. plant input capacity, LHV (GJ h^{-1})	16136	9893	9893	8690	8690	7931	7931	7931	7931	**7931**	**16136**
Ref plant output capacity, LHV: Fuels (GJ h^{-1})	7161	2254	2254	2160	2160	2161	2161	2161	2161	**2160**	**7161**
Electricity (MW)	697	625	625	552	552	490	490	490	490	**490**	**697**
Net plant efficiency, LHV (%)	59.9	45.5	45.5	47.7	47.7	49.5	49.5	49.5	49.5	**45.5**	**59.9**
Plant capacity factor (%)	90	85	85	85	85	80	80	80	80	**80**	**90**
CO_2 emitted ($MtCO_2$ yr^{-1})	8.067	5.646	5.646	4.895	4.895	4.077	4.077	4.077	4.077	**4.08**	**8.07**
Carbon exported in fuels (MtC yr^{-1})	1.190	0.317	0.317	0.334	0.334	0.274	0.274	0.274	0.274	**0.27**	**1.19**
Total carbon released ($kgCO_2$ GJ^{-1} products)	163	203	203	198	198	185	185	185	185	**163**	**203**
Capture Plant Design											
CO_2 capture/separation technology	Amine scrubber	Selexol	CO_2 H_2S co-capture. Selexol	Selexol	CO_2 H_2S co-capture. Selexol	CO_2 H_2S co-capture. Rectisol	CO_2 H_2S co-capture. Rectisol	CO_2 H_2S co-capture. Rectisol	CO_2 H_2S co-capture. Rectisol		
Capture plant input capacity, LHV (GJ h^{-1})	16136	9893	9893	8690	Coal	7931	7931	7931	7931	**7931**	**16136**
Capture plant output capacity LHV: Fuels (GJ h^{-1})	7242	2254	2254	2160	2160	2161	2160	2160	2160	**2160**	**7242**
Electricity (MW)	510	582	577	531	527	469	367	365	353	**353**	**582**
Net plant efficiency, LHV (%)	56.3	44.0	43.8	46.9		48.5	43.9	43.8	43.2	**43**	**56**
CO_2 capture efficiency (%)**	91	58	63	32	37	36	89	92	97	**32**	**97**
CO_2 emitted ($MtCO_2$ yr^{-1})***	0.733	2.377	2.099	3.320	3.076	2.598	0.390	0.288	0.028	**0.03**	**3.32**
Carbon exported in fuels (MtC yr^{-1})	1.2	0.317	0.317	0.294	0.294	0.274	0.274	0.274	0.274	**0.274**	**1.200**
Total carbon released ($kgCO_2$ GJ^{-1} products)	71.7	109.2	101.0	144.9	137.4	134	57	53	43	**43**	**145**
CO_2 captured ($MtCO_2$ yr^{-1})	7.260	3.269	3.547	1.574	1.819	1.479	3.692	3.790	4.021	**1.48**	**7.26**
CO_2 product pressure (MPa)	13.8	15	15	15	15	15	15	15	15	**14**	**15**
CCS energy requirement. (% more input/GJ plant output)	6.5	3.6	4.0	1.9		2.0	12.8	13.0	14.5	**1.9**	**14.5**
CO_2 reduction/unit product (%)	56	46	50	27	31					**27**	**56**
Cost Results											
Cost year basis (constant dollars)						2003	2003	2003	2003		
Fixed charge rate (%)	12.7	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	**12.7**	**15.0**
Reference plant TCR (million US\$)****	2160	1351	1351	1215	1215	1161	1161	1161	1161	**1161**	**2160**
Capture plant TCR (million US\$)****	2243	1385	1220	1237	1090	1066	1128	1164	1172	**1066**	**2243**
% increase in capital cost (%)	3.8	2.6	-9.7	1.8	-10.3	-8.1	-2.8	0.2	0.9	**-10.3**	**3.8**
Ref. plant electricity price (US\$ MWh^{-1})	35.6	42.9	42.9	42.9	42.9	44.1	44.1	44.1	44.1	**35.6**	**44.1**
Capture plant electricity price (US\$ MWh^{-1})	53.6	42.9	42.9	42.9	42.9	58.0	58.0	58.0	58.0	**42.9**	**58.0**
% increase in assumed elec. price	50.5	0.0	0.0	0.0	0.0	31.5	31.5	31.5	31.5	**0.0**	**50.5**
Ref. plant fuel product cost, LHV (US\$ GJ^{-1})	**5.58**	**9.12**	**9.12**	**8.68**	**8.68**	**7.41**	**7.41**	**7.41**	**7.41**	**5.6**	**9.1**
Capture plant fuel product cost, LHV (US\$ GJ^{-1})	**5.43**	**10.36**	**8.42**	**9.37**	**7.57**	**6.73**	**7.18**	**7.65**	**8.09**	**5.4**	**10.4**
Increase in fuel product cost (US\$ GJ^{-1})	**-0.15**	**1.24**	**-0.70**	**0.69**	**-1.11**	**-0.68**	**-0.23**	**0.24**	**0.68**	**-1.1**	**1.2**
% increase in fuel product cost	**-5.7**	**13.6**	**-7.7**	**7.9**	**-12.8**	**-9.2**	**-3.1**	**3.2**	**9.2**	**-12.8**	**13.6**
Cost of CO_2 captured (US\$/tCO_2)		12.3	-6.4	13.3	-18.4	-12.4	-1.5	1.5	4.1	**-18.4**	**13.3**
Cost of CO_2 avoided (US\$/tCO_2)		13.2	-6.9	13.0	-18.3	-13.3	-1.8	1.8	4.8	**-18.3**	**13.2**
Confidence level (see Table 3.6)	moderate	moderate	moderate	low to moderate							

Notes: 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. * Reported HHV values converted to LHV assuming LHV/HHV = 0.96 for coal, 0.846 for hydrogen, and 0.93 for F-T liquids. ** CO_2 capture efficiency = (C in CO_2 captured)/(C in fossil fuel input to plant - C in carbonaceous fuel products of plant) x100; C associated with imported electricity is not included. ***Includes CO_2 emitted in the production of electricity imported by the plant. ****Reported total plant investment values increased by 3.5% to estimate total capital requirement.

producing liquid fuels plus electricity. In these cases the amounts of electricity produced are sizeable compared to the liquid products, so the assumed selling price of electricity has a major influence on the product cost results. So too does the assumption in two of the cases of co-disposal of H_2S with CO_2 (as described above). For these reasons, the incremental cost of CO_2 capture ranges from a 13% decrease to a 13% increase in fuel product cost relative to the no-capture case. Note too that the overall level of CO_2 reductions per unit of product is only 27-56%. This is because a significant portion of carbon in the coal feedstock is exported with the liquid fuel products. Nonetheless, an important benefit of these fuel-processing schemes is a reduction (of 30-38%) in the carbon content per unit of fuel energy relative to the feedstock fuel. To the extent these liquid fuels displace other fuels with higher carbon per unit of energy, there is a net benefit in end-use CO_2 emissions when the fuels are burned. However, no credit for such reductions is taken in Table 3.11 because the system boundary considered is confined to the fuel production plant.

3.7.8 Capture costs for other industrial processes (current technology)

CO_2 can be captured in other industrial processes using the techniques described earlier for power generation. While the costs of capture may vary considerably with the size, type and location of industrial processes, such costs will be lowest for processes or plants having: streams with relatively high CO_2 concentrations; process plants that normally operate at high load factors; plants with large CO_2 emission rates; and, processes that can utilize waste heat to satisfy the energy requirements of CO_2 capture systems. Despite these potential advantages, little detailed work has been carried out to estimate costs of CO_2 capture at industrial plants, with most work focused on oil refineries and petrochemical plants. A summary of currently available cost studies appears in Table 3.12.

3.7.8.1 Oil refining and petrochemical plants

Gas-fired process heaters and steam boilers are responsible for the bulk of the CO_2 emitted from typical oil refineries and petrochemical plants. Although refineries and petrochemical plants emit large quantities of CO_2, they include multiple emission sources often dispersed over a large area. Economies of scale can be achieved by using centralized CO_2 absorbers or amine regenerators but some of the benefits are offset by the cost of pipes and ducts. Based on Table 3.14, the cost of capturing and compressing CO_2 from refinery and petrochemical plant heaters using current technology is estimated to be 50-60 US\$/tCO_2 captured. Because of the complexity of these industrial facilities, along with proprietary concerns, the incremental cost of plant products is not normally reported.

High purity CO_2 is currently vented to the atmosphere by some gas processing and petrochemical plants, as described in Chapter 2. The cost of CO_2 capture in such cases would be simply the cost of drying and compressing the CO_2 to the pressure required for transport. The cost would depend on various factors, particularly the scale of operation and the electricity price. Based on 2 MtCO_2 yr^{-1} and an electricity price of US\$ 0.05 kWh^{-1}, the cost is estimated to be around 10 US\$/tCO_2 emissions avoided. Electricity accounts for over half of the total cost.

3.7.8.2 Cement plants

As noted in Chapter 2, cement plants are the largest industrial source of CO_2 apart from power plants. Cement plants normally burn lower cost high-carbon fuels such as coal, petroleum coke and various wastes. The flue gas typically has a CO_2 concentration of 14-33% by volume, significantly higher than at power plants, because CO_2 is produced in cement kilns by decomposition of carbonate minerals as well as by fuel combustion. The high CO_2 concentration would tend to reduce the specific cost of CO_2 capture from flue gas. Pre-combustion capture, if used, would only capture the fuel-related CO_2, so would be only a partial solution to CO_2 emissions. Oxy-fuel combustion and capture using calcium sorbents are other options, which are described in Sections 3.2.4 and 3.7.11.

3.7.8.3 Integrated steel mills

Integrated steel mills are some of the world's largest emitters of CO_2, as described in Chapter 2. About 70% of the carbon introduced into an integrated steel mill is contained in the blast furnace gas in the form of CO_2 and CO, each of which comprise about 20% by volume of the gas. The cost of capturing CO_2 from blast furnace gas was estimated to be 35 US\$/tCO_2 avoided (Farla *et al.*, 1995) or 18 US\$/tCO_2 captured (Gielen, 2003).

Iron ore can be reacted with synthesis gas or hydrogen to produce iron by direct reduction (Cheeley, 2000). Direct reduction processes are already used commercially but further development work would be needed to reduce their costs so as to make them more widely competitive with conventional iron production processes. The cost of capturing CO_2 from a direct reduction iron (DRI) production processes was estimated to be 10 US\$/tCO_2 (Gielen, 2003). CO_2 also could be captured from other gases in iron and steel mills but costs would probably be higher as they are more dilute or smaller in scale.

3.7.8.4 Biomass plants

The main large point sources of biomass-derived CO_2 are currently wood pulp mills, which emit CO_2 from black liquor recovery boilers and bark-fired boilers, and sugar/ethanol mills, which emit CO_2 from bagasse-fired boilers. Black liquor is a byproduct of pulping that contains lignin and chemicals used in the pulping process. The cost of post-combustion capture was estimated to be 34 US\$/tCO_2 avoided in a plant that captures about 1 MtCO_2 yr^{-1} (Möllersten *et al.*, 2003). Biomass gasification is under development as an alternative to boilers.

CO_2 could be captured from sucrose fermentation and from combustion of sugar cane bagasse at a cost of about 53 US\$/tCO_2 avoided for a plant capturing 0.6 MtCO_2 yr^{-1} avoided (Möllersten *et al.*, 2003). CO_2 from sugar cane fermentation has a high purity, so only drying and compression is required. The overall cost is relatively high due to an annual load factor that is lower than that of most power stations and large industrial

Table 3.12. Capture costs: Other industrial processes using current or advanced technology.

Study Assumptions and Cost Results	**CURRENT TECHNOLOGY**									**ADVANCED TECHNOLOGY**			
	Farla *et al.*	**IEA GHG**	**IEA GHG**	**IEA GHG**	**Möllersten *et al.***	**Möllersten *et al.***	**Möllersten *et al.***	**CCP**	**CCP**	**CCP**	**CCP**	**CCP**	**CCP**
	1995	**2000c**	**2000c**	**2002b**	**2003**	**2003**	**2003**	**2005**	**2005**	**2005**	**2005**	**2005**	**2005**
Reference Plant (without capture)													
Industrial process	Iron production												
Oil refining petrochemical	Oil refining petrochemical	High purity CO_2 sources	Pulp mill	Pulp mill	Ethanol fermentation	Refinery heaters & boilers	Small gas turbines		Refinery heaters & boilers	Small gas turbines	Small gas turbines		
Feedstock type	Coke	Refinery gas/ natural gas	Refinery gas/ natural gas		Black liquor and bark	Black liquor	Sugar cane	Mixed	NG	Mixed	Mixed	Natural gas	Natural gas
Plant size (specify units)	168 kg s^{-1} iron	315 kg s^{-1} crude oil	315 kg s^{-1} crude oil		17.9 kg s^{-1} pulp	17.9 kg s^{-1} pulp	9.1 kg s^{-1} ethanol	1351 MWt	358 MWt	1351 MWt	1351 MWt	358 MWt	358 MWt
Plant capacity factor (%)	95.3	90	90	90	90.4	90.4	49.3	90.4	98.5	90.4	90.4	98.5	98.5
Feedstock cost (US$ per unit specified)					US$3 GJ^{-1} LHV	US$3 GJ^{-1} LHV							
Ref. plant emission rate ($kgCO_2$ MWh^{-1})								0.22	0.82	0.22	0.22	0.82	0.82
Capture Plant Design													
CO_2 capture/separation technology	MDEA	MEA	Pre-combustion	Compression only	Amine	Physical solvent							
Location of CO_2 capture	Blast furnace gas	Fired heaters and H_2 plant	Fired heaters and H_2 plant		Boiler	IGCC	Fermentation and bagasse boiler	MEA Baseline (post-comb.)	MEA Baseline (post-comb.)	Membrane Water Gas Shift (pre-comb.)	Flue Gas Recycle & ITM (oxy-fuel)	Very Large-scale ATR (pre-comb.)	Sorption Enhanced Water Gas Shift (pre-comb.)
Capture unit size (specify units)					392 MW fuel	338 MW fuel		1351 MWt	358 MWt	1351 MWt	1351 MWt	358 MWt	358 MWt
CO_2capture system efficiency (%)	90	95	91		90	90	100/90						
Energy source(s) for capture (type +onsite or offsite)													
Are all energy-related CO_2 emissions included?								yes	yes	yes	yes	yes	yes
CO_2emission rate after capture ($kgCO_2$ MWh^{-1})								0.09	0.19	0.09	0.05	0.10	0.14
CO_2 captured (Mt yr^{-1})	2.795	1.013	1.175	1.970	0.969	0.399	0.560						
CO_2product pressure (MPa)	11.0	11.0	11.0	8.0	10.0	10.0	10.0						
CO_2 reduction per unit of product (%)								60.3	76.5	58.4	75.8	87.4	82.2
Cost Results													
Cost year basis (constant dollars)													
Fixed charge factor (%)					15	15	15	11.0	11.0	11.0	11.0	11.0	11.0
Ref. plant capital cost (US$ per unit capacity)													
Capture plant capital cost (US$ per unit capacity)													
Incremental capital cost (million US$ per kg s^{-1} CO_2)*	3.8	4.1	4.9	0.3	3.2	1.9	2.6						
Ref. plant cost of product (US$/unit)													
Capture plant cost of product (US$/unit)								10.2	55.1	6.1	6.8	54.2	48.2
Incremental cost of product (US$/ unit)								10.2	55.1	6.1	6.8	54.2	48.2
% increase in capital cost (over ref. plant)													
% increase in unit cost of product (over ref. plant)													
Cost of CO_2 captured (US$/$tCO_2$)		50	60					55.3	90.9	36.4	38.2	59.0	60.5
Cost of CO_2 avoided (US$/$tCO_2$)	35	74	116	10	34	23	53	78.1	88.2	48.1	41.0	76.0	71.8
Capture cost confidence level (see Table 3.6)	moderate									low			

Notes: 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. *Capital costs are incremental costs of capture, excluding cost of make-up steam and power generation and also excluding interest during construction and other owner's costs.

plants.

CO_2 could be captured at steam-generating plants or power plants that use other biomass byproducts and/or purpose-grown biomass. At present most biomass plants are relatively small. The cost of capturing 0.19 $MtCO_2$ yr^{-1} in a 24 MW biomass-powered IGCC plant, compared to a biomass IGCC plant without capture, is estimated to be about 70 US\$/tCO_2 (Audus and Freund, 2005). Larger plants using purpose-grown biomass may be built in the future and biomass can be co-fired with fossil fuels to give economies of scale, as discussed in Chapter 2. Biomass fuels produce similar or slightly greater quantities of CO_2 per unit of fuel energy as bituminous coals; thus, the CO_2 concentration of flue gases from these fuels will be broadly similar. This implies that the cost of capturing CO_2 at large power plants using biomass may be broadly similar to the cost of capturing CO_2 in large fossil fuel power plants in cases where plant size, efficiency, load factor and other key parameters are similar. The costs of avoiding CO_2 emissions in power plants that use biomass are discussed in more detail in Chapter 8.

3.7.9 *Outlook for future CO_2 capture costs*

The following sections focus on 'advanced' technologies that are not yet commercial available, but which promise to lower CO_2 capture costs based on preliminary data and design studies. Earlier sections of Chapter 3 discussed some of the efforts underway worldwide to develop lower-cost options for CO_2 capture. Some of these developments are based on new process concepts, while others represent improvements to current commercial processes. Indeed, the history of technology innovation indicates that incremental technological change, sustained over many years (often decades), is often the most successful path to substantial long-term improvements in performance and reductions in cost of a technology (Alic *et al*., 2003). Such trends are commonly represented and quantified in the form of a 'learning curve' or 'experience curve' showing cost reductions as a function of the cumulative adoption of a particular technology (McDonald and Schrattenholzer, 2001). One recent study relevant to CO_2 capture systems found that over the past 25 years, capital costs for sulphur dioxide (SO_2) and nitrogen oxides (NO_x) capture systems at US coal-fired power plants have decreased by an average of 12% for each doubling of installed worldwide capacity (a surrogate for cumulative experience, including investments in R&D) (Rubin *et al*., 2004a). These capture technologies bear a number of similarities to current systems for CO_2 capture. Another recent study (IEA, 2004) suggests a 20% cost reduction for a doubling of the unit capacity of engineered processes due to technological learning. For CCS systems the importance of costs related to energy requirements is emphasized, since reductions in such costs are required to significantly reduce the overall cost of CO_2 capture.

At the same time, a large body of literature on technology innovation also teaches us that learning rates are highly uncertain,[11] and that cost estimates for technologies at the early stages of development are often unreliable and overly optimistic (Merrow *et al*., 1981). Qualitative descriptions of cost trends for advanced technologies and energy systems typically show costs increasing from the research stage through full-scale demonstration; only after one or more full-scale commercial plants are deployed do costs begin to decline for subsequent units (EPRI, 1993; NRC, 2003). Case studies of the SO_2 and NO_x capture systems noted above showed similar behaviour, with large (factor of two or more) increases in the cost of early full-scale FGD and SCR installations before costs subsequently declined (Rubin *et al*., 2004b). Thus, cost estimates for CO_2 capture systems should be viewed in the context of their current stage of development. Here we try to provide a perspective on potential future costs that combines qualitative judgments with the quantitative cost estimates offered by technology developers and analysts. The sections below revisit the areas of power generation and other industrial processes to highlight some of the major prospects for CO_2 capture cost reductions.

3.7.10 *CO_2 capture costs for electric power plants (advanced technology)*

This section first examines oxy-fuel combustion, which avoids the need for CO_2 capture by producing a concentrated CO_2 stream for delivery to a transport and storage system. Following this we examine potential advances in post-combustion and pre-combustion capture.

3.7.10.1 Oxy-fuel combustion systems

It is first important to distinguish between two types of oxy-fuel systems: an oxy-fuel boiler (either a retrofit or new design) and oxy-fuel combustion-based gas turbine cycles. The former are close to demonstration at a commercial scale, while the latter (such as chemical looping combustion systems and novel power cycles using CO_2/water as working fluid) are still at the design stage. Table 3.13 summarizes the key assumptions and cost results of several recent studies of CO_2 capture costs for oxy-fuel combustion systems applied to new or existing coal-fired units. As discussed earlier in Section 3.4, oxygen combustion produces a flue gas stream consisting primarily of CO_2 and water vapour, along with smaller amounts of SO_2, nitrogen and other trace impurities. These designs eliminate the capital and operating costs of a post-combustion CO_2 capture system, but new costs are incurred for the oxygen plant and other system design modifications. Because oxy-fuel combustion is still under development and has not yet been utilized or demonstrated for large-scale power generation, the design basis and cost estimates for such systems remain highly variable and uncertain. This is reflected in the wide range of oxy-fuel cost estimates in Table 3.13. Note, however, that cost estimates for advanced design

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[11] In their study of 42 energy-related technologies, McDonald and Schrattenholzer (2001) found learning rates varying from -14% to 34%, with a median value of 16%. These rates represent the average reduction in cost for each doubling of installed capacity. A negative learning rate indicates that costs increased rather than decreased over the period studied.

Table 3.13 Capture costs: Advanced technologies for electric power plants. (continued on next page)

Study Assumptions and Results	**OXY-FUEL COMBUSTION**							**ADVANCED PC**	
	Alstom *et al.*	**Singh *et al.***	**Stobbs &Clark**	**Dillon *et al.***	**Nsakala *et al.***	**Nsakala *et al.***	**Nsakala *et al.***	**Gibbins *et al.***	**Gibbins *et al.***
	2001	**2003**	**2005**	**2005**	**2003**	**2003**	**2003**	**2005**	**2005**
Reference Plant (without capture)	*				*	*	*		
Power plant type	RETROFIT subcrit PC	RETROFIT PC + aux NGCC	RETROFIT PC	New PC	Air-fired CFB	Air-fired CFB	Air-fired CFB	Double reheat supercrit PC	Double reheat supercrit PC
Fuel type (bit, sub-bit, lig; NG, other) and %S	bit, 2.7%S	sub-bit	lignite	bit	bit, 2.3%S	bit, 2.3%S	bit, 2.3%S		
Reference plant net size (MW)	434	400	300	677	193	193	193		
Plant capacity factor (%)	67	91		85	80	80	80	85	85
Net plant efficiency, LHV (%)				44.2	37.0	37.0	37.0	45.6	45.6
Fuel cost, LHV (US$ GJ^{-1})	1.30			1.50	1.23	1.23	1.23	1.50	1.50
Reference plant emission rate (tCO$_2$ MWh^{-1})	0.908	0.925	0.883	0.722	0.909	0.909	0.909		
Capture Plant Design									
CO$_2$ capture technology	oxy-fuel	oxy-fuel	oxy-fuel	oxy-fuel	oxy-fuel	oxy-fuel with CMB	chemical looping with CMB	MEA	KS-1
Net plant size with capture (MW)	273	400		532	135	197	165		
Net plant efficiency, LHV (%)	23.4			35.4	25.8	31.3	32.2	34.3	36.5
CO$_2$ capture system efficiency (%)				about 91					
CO$_2$ emission rate after capture (t MWh^{-1})		0.238	0.145	0.085	0.086	0.073	0.005		
CO$_2$ captured (Mt yr^{-1})		2.664							
CO$_2$ product pressure (MPa)	13.9	15	13.7	11				11.0	11.0
CCS energy requirement (% more input MWh^{-1})				25	43	18	15	33	25
CO$_2$ reduction per kWh (%)		**74**		**88.2**	**90.5**	**92.0**	**99.5**		
Cost Results	**	**							
Cost year basis (constant dollars)		2001	2000		2003	2003	2003		
Fixed charge factor (%)	13.0	9.4		11				11.0	11.0
Reference plant TCR (US$ kW^{-1})		0		1260	1500	1500	1500	1022	1022
Capture plant TCR (US$ kW^{-1})	1527	909	4570	1857	2853	2731	1912	1784	1678
Incremental TCR for capture (US$ kW^{-1})	1198	909		597	1354	1232	413	762	656
Reference plant COE (US$ MWh^{-1})			**44.5**	**44**	**45.3**	**45.3**	**45.3**	**37**	**37**
Capture plant COE (US$ MWh^{-1})			**97.5**	**61.2**	**82.5**	**70.5**	**58.4**	**61**	**57**
Incremental COE for capture (US$ MWh^{-1})	44.5	23.9	53	17.2	37.2	25.2	13.1	24	20
% increase in capital cost (over ref. plant)				47	90	82	28	75	64
% increase in COE (over ref. plant)			**119**	**39**	**82**	**56**	**29**	**65**	**54**
Cost of CO$_2$ captured (US$/tCO$_2$)		29							
Cost of CO$_2$ avoided (US$/tCO$_2$)	54	35	72	27	45	30	14		
Capture cost confidence level (see Table 3.6)	low					very low	very low	low to moderate	

Notes: 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. * Reported HHV values converted to LHV assuming LHV/HHV = 0.96 for coal. ** Reported value increased by 15% to estimate interest during construction and other owners' costs.

Table 3.13 *Continued.*

Study Assumptions and Results	ADVANCED NGCC								ADVANCED IGCC					ADVANCED HYBRIDS	
	Simbeck	**Parsons**	**Parsons**	**CCP**	**CCP**	**CCP**	**CCP**	**Dillon *et al.***	**Parsons**	**NETL**	**NETL**	**CCP**	**CCP**	**NETL**	**Parsons**
	2002	**2002b**	**2002b**	**2005**	**2005**	**2005**	**2005**	**2005**	**2002b**	**2002**	**2002**	**2005**	**2005**	**2002**	**2002b**
Reference Plant (without capture)									*	*	*			*	
Power plant type	comb. cycle H-class turbine	comb. cycle H-class turbine	comb. cycle H-class turbine					NGCC	E-gas, O_2, water scrubber; H-class turbine	E-gas, O_2, CGCU, Hydraulic air compression	E-gas, O_2, CGCU, Hydraulic air compression with open loop water system	Canada coke gasification	Canada coke gasification	E-gas, O_2, HGCU, "G" GT, SOFC	CHAT SOFC
Fuel type (bit, sub-bit, lig; NG, other) and %S	Nat. gas	Nat. gas	Nat. gas	NG	NG	NG	NG	NG	Illinois #6	Illinois #6	Illinois #6	Coke	Coke	Illinois #6	Nat. gas
Reference plant net size (MW)	480	384	384	392	392	392	507	388	425	326	408	588	588	644	557
Plant capacity factor (%)	80	65	80	95	95	95	95	85	80	85	85	91.3	91.3	85	80
Net plant efficiency, LHV (%)	60.0	59.5	59.5	57.6%	57.6%	57.6%	57.6%	56.0	41.1	43.8	54.9			56.4	66.2
Fuel cost, LHV (US\$ GJ^{-1})	4.86	2.82	2.82	2.96	2.96	2.96	2.96	3.00	1.23	1.03	1.03	2.96	2.96	1.03	2.82
Reference plant emission rate															
(tCO_2 MWh^{-1})	0.342	0.338	0.338	0.37	0.37	0.37	0.37	0.371	0.720	0.712	0.568	0.95	0.95	0.572	0.302
Capture Plant Design															
CO_2 capture technology	MEA	MEA	MEA	MEA low-cost/ CCGT-integrated (post-comb.)	Membrane Contactor; KS-1 (post-comb.)	Hydrogen Membrane Reformer (pre-comb.)	Sorption Enhanced Water Gas Shift- Air ATR (pre-comb.)	Oxy-fuel	Selexol	Selexol		IGCC with capture (pre-comb.)	IGCC with advanced capture (pre-comb.)	Selexol	
Net plant size with capture (MW)	413	311	311	345	335	361	424	440	387	312	404	699	734	755	517
Net plant efficiency, LHV (%)	51.7	48.1	48.1	50.6	49.2	53.0	48.2	44.7	33.8	35.2	45.4			49.7	46.1
CO_2capture system efficiency (%)	85	90	90	86	86	100	90		91.5	92.7	92.7			90	86.8
CO_2 emission rate after capture (t/MWh)	0.06	0.042	0.042	0.06	0.06	0.00	0.04	0.011	0.074	0.065	0.050	0.27	0.28	0.046	0.043
CO_2 captured (Mt yr–1)	0.980	0.669	0.823	1.09	1.09	1.27	1.47		2.074	1.984	1.984	6.80	6.44	3.390	
CO_2 product pressure (MPa)	13.7	8.3	8.3					11	8.3	14.5	14.5			14.5	8.3
CCS energy requirement(% more input MWh–1)	16	24	24					25	22	24	21			13	44
CO_2 reduction per kWh (%)	82	88	88	84.1	83.6	100	87.9	97.0	90	91	91	71.2	71.1	92	86
Cost Results															
Cost year basis (constant dollars)	2001	2000	2000						2000	2002	2002			2002	2000
Fixed charge factor (%)	15.0			11.0	11.0	11.0	11.0	11	15.0	14.8	14.8	11.0	11.0	14.8	
Reference plant TCR (US\$ kW^{-1})	582	539	496	724	724	724	724	559	1249	1436	881.4	1398	1398	1508	623
Capture plant TCR (US\$ kW^{-1})	1216	1026	943	1002	1225	1058	1089	1034	1698	2189	1450	1919	1823	1822	
Incremental TCR for capture															
(US\$ kW^{-1})	634	487	447	278	501	334	365	475	449	753	568	521	425	314	
Reference plant COE (US\$ MWh^{-1})	42.9	33.5	30.7	34.2	34.2	34.2	34.2	33.5	41.0	47.0	28.5	32.3	32.3	41.1	
Capture plant COE (US\$ MWh^{-1})	65.9	54.1	48.8	45.1	48.9	43.2	45.4	50.3	53.6	65.5	41.8	42.1	40.5	48.8	
Incremental COE for capture															
(US\$ MWh^{-1})	23	20.6	18.1	10.9	14.7	9.0	11.2	16.8	12.6	18.5	13.3	9.8	8.2	7.7	
% increase in capital cost (over ref. plant)	109	90	90	38	69	46	50	85	36	52	64	37	30	21	
% increase in COE (over ref. plant)	54	61	59	32	43	26	33	50	31	39	47	30	25	19	
Cost of CO_2 captured (US\$/tCO_2)		48		30.2	39.5	22.5	28.2		16	22	20	11	10	13	
Cost of CO_2 avoided (US\$/tCO_2)	82	70	61	35.1	47.5	24.4	34.4	47	19	29	26	14	12	15	
Capture cost confidence level (see Table 3.6)	low to moderate				low to very low				low					very low	

Notes: 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. * Reported HHV values converted to LHV assuming LHV/HHV = 0.96 for coal and LHV/HHV = 0.90 for natural gas. **Reported value increased by 15% to estimate interest during construction and other owners' costs.

concepts based on oxy-fuel combustion gas turbine cycles are more uncertain at this time than cost estimates for new or retrofitted boilers employing oxy-fuel combustion.

For new plant applications, the data in Table 3.13 indicate that oxy-fuel combustion adds about 30-90% to the capital cost and 30-150% to the COE of a conventional plant, while reducing CO_2 emissions per kWh by 75-100%. Retrofit applications exhibit higher relative costs in cases where the existing plant is wholly or partially amortized. The lowest-cost oxy-fuel system in Table 3.13 is one that employs chemical looping to achieve nearly a 100% reduction in CO_2 emissions. While this concept thus appears promising (see Section 3.4.6), it has yet to be tested and verified at a meaningful scale. Thus cost estimates based on conceptual designs remain highly uncertain at this time.

To judge the potential cost savings of oxy-fuels relative to current CO_2 capture systems, it is useful to compare the costs of alternative technologies evaluated within a particular study based on a particular set of premises. In this regard, the COE for the oxy-fuel retrofit system reported by Alstom *et al.* (2001) in Table 3.13 is 20% lower than the cost of an amine system retrofit (Table 3.13) for the same 255 MW plant, while the cost of CO_2 avoided is 26% lower. In contrast, a recent study by the Canadian Clean Power Coalition (Stobbs and Clark, 2005) reports that the COE for an oxy-fuel system at a large lignite-fired plant (Table 3.13) is 36% higher than for an amine CO_2 capture system, while the cost of CO_2 avoided is more than twice as great. The major source of that cost difference was a specification in the CCPC study that the oxy-fuelled unit also be capable of full air firing. This resulted in a much higher capital cost than for a new unit designed solely for oxy-fuel operation. A more recent study sponsored by IEA GHG (Dillon *et al.*, 2005) found that a large new supercritical coal-fired boiler with oxy-fuel combustion had a COE slightly (2-3%) lower than a state-of-the-art coal plant with post-combustion analyzed in a separate study employing similar assumptions (IEA GHG, 2004). Further cost reductions could be achieved with the successful development of new lower-cost oxygen production technology (see Section 3.4.5). At the current time, the optimum designs of oxy-fuel combustion systems are not yet well established and costs of proposed commercial designs remain uncertain. This is especially true for advanced design concepts that employ components which are not yet available or still in the development stage, such as CO_2 gas turbines or high temperature ceramic membranes for oxygen production.

3.7.10.2 Advanced systems with post-combustion capture

Improvements to current amine-based systems for post-combustion CO_2 capture are being pursued by a number of process developers (Mimura *et al.*, 2003; Muramatsu and Iijima, 2003; Reddy *et al.*, 2003) and may offer the nearest-term potential for cost reductions over the systems currently in use. The newest systems summarized earlier in Table 3.7 reportedly reduce the cost of CO_2 avoided by approximately 20-30% (IEA GHG, 2004). Table 3.13 indicates that additional advances in plant heat integration could further reduce the COE of capture plants by about 5%. These results are consistent with a recent study by Rao *et al.* (2003), who used expert elicitations and a plant simulation model to quantify the improvements likely achievable by 2015 for four key process parameters: sorbent concentration, regeneration energy requirements, sorbent loss and sorbent cost. The 'most likely' improvement was an 18% reduction in COE, while the 'optimistic' estimates yielded a 36% cost reduction from improvements in just these four parameters. The cost of CO_2 avoided was reduced by similar amounts. Advances in more efficient heat integration (for sorbent regeneration) and higher power plant efficiency could lead to even greater reductions in CO_2 capture cost.

Advances in gas turbine technology produce similar benefits for NGCC systems. Table 3.13 shows several cases based on the H-turbine design. Relative to the cases in Table 3.9, these systems offer higher efficiency and greater CO_2 reductions per kWh. The higher COEs for the advanced NGCC systems reflects the higher natural gas prices assumed in more recent studies.

Table 3.13 indicates that other advanced technologies for post-combustion applications, such as membrane separation systems, may also lower the future cost of CO_2 capture (see Section 3.3.3). Reliable cost estimates for such technologies should await their further development and demonstration.

3.7.10.3 Advanced systems with pre-combustion capture

The cost of gasification-based systems with CO_2 capture also can be expected to fall as a result of continued improvements in gas turbine technology, gasifier designs, oxygen production systems, carbon capture technology, energy management and optimization of the overall facility. One recent study (IEA GHG, 2003) estimates a 20% reduction in the cost of electricity generation from a coal-based IGCC plant with CO_2 capture by 2020. This takes into account improvements in gasification, oxygen production, physical solvent scrubbing and combined cycle processes, but does not take into account any possible radical innovations in CO_2 separation technology. The additional IGCC cases shown in Table 3.13, including recent results of the CO_2 Capture Project (CCP, 2005), foresee similar reductions in the COE of advanced IGCC systems compared to the systems in Table 3.10.

3.7.11 CO_2 capture costs for hydrogen production and multi-product plants (advanced technology)

Table 3.14 shows results of several recent studies that have projected the performance and cost of new or improved ways of producing hydrogen and electricity from fossil fuels.

Compared to the current commercial plants in Table 3.11, the advanced single-product systems with CO_2 capture have hydrogen cost reductions of 16% (for natural gas feedstock) to 26% (for coal feedstock). Additional cases in Table 3.14 show multi-product systems producing hydrogen and electricity. These cases indicate the potential for substantial reductions in the future cost of hydrogen production with CO_2 capture. As before, the results are sensitive to the assumed selling price of co-product electricity. More importantly, these cases assume

Table 3.14 CO_2 capture costs: Multi-product plants using advanced technology.

Study Assumptions and Results	Simbeck	NRC	NRC	Parsons	Mitretek	Mitretek	Mitretek	Range	
	2005	2004	2004	2002a	2003	2003	2003	min	max
Capture Plant Design	*			*	*	*	*		
Plant products (primary/secondary)	H_2	H_2	H_2	H_2+electricity	H_2+electricity	H_2+electricity	H_2+electricity		
Production process or type	Autothermal reforming with O_2 provided by ITM	78% efficient ATR/SMR, adv CO_2 compressor	Gasifier LHV= 75-->80%, Adv ASU, membrane sep, adv CO_2 compressor	High-pressure E-gas, HGCU, HTMR, H_2SO_4 co-product	Advanced E-gas, HGCU, HTMR	Advanced E-gas, HGCU, HTMR, large elec. co-product	Advanced E-gas, HGCU, HTMR, SOFC, large elec. co-product		
Feedstock	Natural gas	Natural gas	Coal	Pgh #8 Coal	Coal	Coal	Coal		
Feedstock cost, LHV (US$ GJ$^{-1)}$	5.26	4.73	1.20	0.89	1.03	1.03	1.03	1	5
Plant capacity factor (%)	90	90	90	80	85	85	85	80	90
CO_2 capture/separation technology	Oxy-fuel			Oxy-fuel	Oxy-fuel	Oxy-fuel	Oxy-fuel		
Capture plant input capacity, LHV (GJ h^{-1})	9527	7697	8121	2794	3020	6051	6051	2794	9527
Capture plant output capacity, LHV: Fuels (GJ h^{-1})	7504	6004	6004	1956	1904	1844	1808	1808	7504
Electricity (MW)	–13	–66	–88	7	25	416	519	-88	519
Net plant efficiency, LHV (%)	78.3	74.9	70.0	70.9	66.0	55.2	60.7	55	78
CO_2 capture efficiency (%)**	95	90	90	94	100	100	95	90	100
CO_2 emitted ($MtCO_2$ yr^{-1})***	0.086	0.505	0.873	0.117	0.000	0.000	0.191	0.000	0.873
Carbon exported in fuels (MtC yr^{-1})	0	0	0	0	0	0	0	0	0
Total carbon released ($kgCO_2$ GJ^{-1} products)	1.46	11.10	19.45	8.45	0.00	0.00	6.96	0.0	19.5
CO_2 captured ($MtCO_2$ yr^{-1})	4.074	3.119	5.853	1.855	1.918	3.846	3.652	1.9	5.9
CO_2 product pressure (MPa)	13.7	13.7	13.7	13.4	20	20	20	13.4	20.0
Cost Results									
Cost year basis (constant dollars)	2003	2000	2000	2000	2000	2000	2000		
Fixed charge rate (%)	20	16	16	14.3	12.7	12.7	12.7	12.7	20.0
Capture plant TCR (million US$)****	725	441	921	398	441	950	1023	398	1023
Capture plant electricity price (US$ MWh^{-1})	50.0	45.0	45.0	30.8	53.6	53.6	53.6	31	54
Capture plant fuel product cost, LHV (US$ GJ^{-1})	9.84	8.53	6.39	5.79	6.24	3.27	1.13	1.13	9.84
Capture cost confidence level (see Table 3.6)	low	low	low	low to very low			very low		

Notes: 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. * Reported HHV values converted to LHV assuming LHV/HHV = 0.96 for coal and 0.846 for hydrogen. **CO_2 capture efficiency = (C in CO_2 captured)/(C in fossil fuel input to plant - C in carbonaceous fuel products of plant) x100; C associated with imported electricity is not included. ***Includes CO_2 emitted in the production of electricity imported by the plant. ****Reported total plant investment values increased by 3.5% to estimate total capital requirement.

the successful scale-up and commercialization of technologies that have not yet been demonstrated, or which are still under development at relatively small scales, such as solid oxide fuel cells (SOFC). Published cost estimates for these systems thus have a very high degree of uncertainty.

3.7.12 CO_2 capture costs for other industrial processes (advanced technology)

As noted earlier, CO_2 capture for industrial processes has not been widely studied. The most extensive analyses have focused on petroleum refineries, especially CO_2 capture options for heaters and other combustion-based processes (see Table 3.12). The use of oxy-fuel combustion offers potential cost savings in several industrial applications. The CO_2 Capture Project reports the cost of capturing CO_2 in refinery heaters and boilers, with an ion transport membrane oxygen plant, to be 31 US\$/tCO_2 avoided. The cost of pre-combustion capture based on shift and membrane gas separation was predicted to be 41 US\$/tCO_2 avoided (CCP, 2005).

It also may be possible to apply oxy-fuel combustion to cement plants, but the CO_2 partial pressure in the cement kiln would be higher than normal and the effects of this on the calcination reactions and the quality of the cement product would need to be investigated. The quantity of oxygen required per tonne of CO_2 captured in a cement plant would be only about half as much as in a power plant, because only about half of the CO_2 is produced by fuel combustion. This implies that the cost of CO_2 capture by oxy-fuel combustion at large cement plants would be lower than at power plants, but a detailed engineering cost study is lacking. Emerging technologies that capture CO_2 using calcium-based sorbents, described in Section 3.3.3.4, may be cost competitive in cement plants in the future.

3.7.13 Summary of CO_2 capture cost estimates

Table 3.15 summarizes the range of current CO_2 capture costs for the major electric power systems analyzed in this report. These costs apply to case studies of large new plants employing current commercial technologies. For the PC and IGCC systems, the data in Table 3.15 apply only to plants using bituminous coals and the PC plants are for supercritical units only. The cost ranges for each of the three systems reflect differences in the technical, economic and operating assumptions employed in different studies. While some differences in reported costs can be attributed to differences in the CO_2 capture system design, the major sources of variability are differences in the assumed design, operation and financing of the reference plant to which the capture technology is applied (i.e., factors such as plant size, location, efficiency, fuel type, fuel cost, capacity factor and cost of capital). Because no single set of assumptions applies to all situations or all parts of the world, we display the ranges of cost represented by the studies in Tables 3.8, 3.10, 3.11 and 3.12.

For the power plant studies reflected in Table 3.15, current CO_2 capture systems reduce CO_2 emissions per kilowatt-hour by approximately 85-90% relative to a similar plant without capture. The cost of electricity production attributed to CO_2 capture increases by 35-70% for a natural gas combined cycle plant, 40-85% for a new pulverized coal plant and 20-55% for an integrated gasification combined cycle plant. Overall, the COE for fossil fuel plants with capture ranges from 43-86 US\$ MWh^{-1}, as compared to 31-61 US\$ MWh^{-1} for similar plants without capture. These costs include CO_2 compression but not transport and storage costs. In most studies to date, NGCC systems typically have a lower COE than new PC and IGCC plants (with or without capture) for large base load plants with high capacity factors (75% or more) and gas prices below about 4 US\$ GJ^{-1} over the life of the plant. However, for higher gas prices and/or lower capacity factors, NGCC plants typically have higher COEs than coal-based plants, with or without capture. Recent studies also found that IGCC plants were on average slightly more costly without capture and slightly less costly with capture than similarly sized PC plants. However, the difference in cost between PC and IGCC plants with or without CO_2 capture can vary significantly with coal type and other local factors, such as the cost of capital. Since neither PC nor IGCC systems have yet been demonstrated with CO_2 capture and storage for a large modern power plant (e.g., 500 MW), neither the absolute or relative costs of these systems (nor comparably sized NGCC systems with capture and storage) can be stated with a high degree of confidence at this time, based on the criteria of Table 3.6.

Table 3.15 also shows that the lowest CO_2 capture costs with current technology (as low as 2 US\$/tCO_2 captured or avoided) were found for industrial processes such as coal-based hydrogen production plants that produce concentrated CO_2 streams as part of the production process. Such industrial processes may represent some of the earliest opportunities for CCS.

Figure 3.20 displays the normalized power plant cost and emissions data from Table 3.15 in graphical form. On this graph, the cost of CO_2 avoided corresponds to the slope of a line connecting any two plants (or points) of interest. While Table 3.15 compares a given capture plant to a similar plant without capture, in some cases comparisons may be sought between a given capture plant and a different type of reference plant. Several cases are illustrated in Figure 3.20 based on either a PC or NGCC reference plant. In each case, the COE and CO_2 emission rate are highly dependent upon technical, economic and financial factors related to the design and operation of the power systems of interest at a particular location. The cost of CO_2 avoided is especially sensitive to these site-specific factors and can vary by an order of magnitude or more when different types of plants are compared. Comparisons of different plant types, therefore, require a specific context and geographical location to be meaningful and should be based on the full COE including CO_2 transport and storage costs. Later, Chapter 8 presents examples of full CCS costs for different plant types and storage options.

In contrast to new plants, CO_2 capture options and costs for existing power plants have not been extensively studied. Current studies indicate that these costs are extremely site-specific and fall into two categories (see Table 3.8). One is the retrofitting of a post-combustion capture system to the existing unit.

Table 3.15 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.***	**Range**		***Rep.***	**Range**		***Rep.***	**Range**		***Rep.***	
	low	**high**	***Value***	**low**	**high**	***Value***	**low**	**high**	***Value***	**low**	**high**	***Value***	
Emission rate without capture ($kgCO_2$ MWh^{-1})	344 -	379	*367*	736 -	811	*762*	682 -	846	*773*	78 -	174	*137*	$kgCO_2$ GJ^{-1} (without capture)
Emission rate with capture ($kgCO_2$ MWh^{-1})	40 -	66	*52*	92 -	145	*112*	65 -	152	*108*	7 -	28	*17*	$kgCO_2$ 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 GJ^{-1} 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$/$tCO_2$)	33 -	57	*44*	23 -	35	*29*	11 -	32	*20*	2 -	39	*12*	US$/$tCO_2$ captured
Cost of CO_2 avoided (US$/$tCO_2$)	37 -	74	*53*	29 -	51	*41*	13 -	37	*23*	2 -	56	*15*	US$/$tCO_2$ avoided
Capture cost confidence level (see Table 3.6)	moderate			moderate			moderate			moderate to high			Confidence Level (see Table 3.6)

Notes: See Section 3.6.1 for calculation of energy requirement for capture plants. Values in italics were adjusted from original reported values as explained below.(a) Ranges and representative values are based on data from Tables 3.8, 3.11, 3.11 and 3.12. 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 US$1.0-1.5 GJ^{-1} (LHV); all PC plants are supercritical units. (c) NGCC data based on natural gas prices of US$2.8-4.4 GJ^{-1} (LHV basis). (d) Cost are in constant US dollars (approx. year 2002 basis). (e) Power plant sizes range from approximately 400-800 MW without capture and 300-700 MW with capture. (f) Capacity factors vary from 65-85% for coal plants and 50-95% for gas plants (average for each = 80%). (g) Hydrogen plant feedstocks are natural gas (US$ 4.7-5.3 GJ^{-1}) or coal (US$ 0.9-1.3 GJ^{-1}); some plants in data set 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 (see Chapter 8 for full CCS costs).

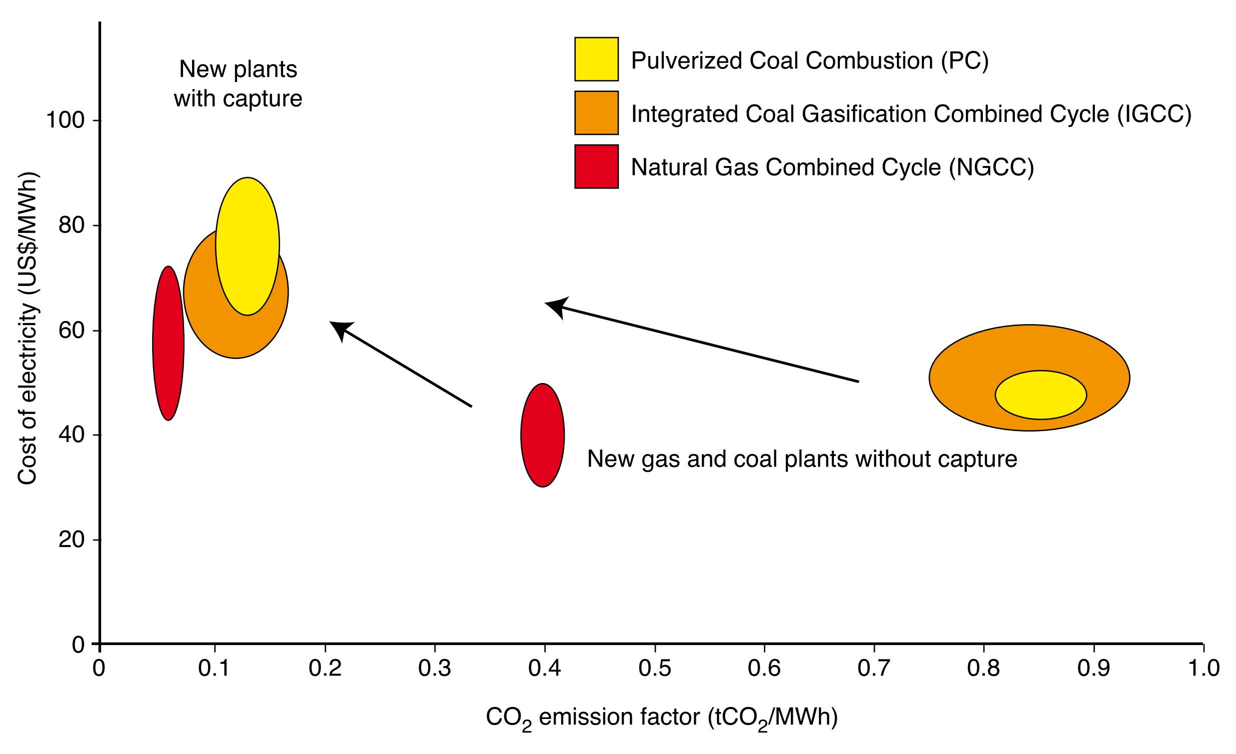

Figure 3.20 Cost of electricity (excluding transport and storage costs) compared to CO_2 emission rate for different reference and capture plants based on current technology. The shaded areas show the Table 3.15 ranges of CO_2 emission rates and levelized cost of electricity (COE) for new PC, IGCC and NGCC plants with and without CO_2 capture. All coal plant data are for bituminous coals only. PC plants are supercritical units only (see Tables 3.7, 3.9, 3.10 and 3.15 for additional assumptions). The cost of CO_2 avoided corresponds to the slope of a line connecting a plant with capture and a reference plant without capture (i.e., the change in electricity cost divided by the change in emission rate). Avoidance costs for the same type of plant with and without capture plant are given in Table 3.15. When comparing different plant types, 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. The cost per tonne of CO_2 avoided can be highly variable and depends strongly on the costs and emissions of new plants being considered in a particular situation. See Chapter 8 for the full COE and full cost of CO_2 avoided for different plant types.

The other category combines CO_2 capture with upgrading or repowering the existing plant to significantly improve its efficiency and net power output (see Sections 3.7.4.2 and 3.7.5.2). In general, the latter option appears to be more cost-effective. However, further site-specific studies are required to systematically assess the feasibility and cost of alternative repowering options in conjunction with CO_2 capture for existing power plants.

New or improved methods of CO_2 capture, combined with advanced power systems and industrial process designs, promise to significantly reduce CO_2 capture costs and associated energy requirements. Tables 3.12 to 3.14 summarize the results from recent studies that examine future options. As discussed earlier, there is considerable uncertainty about the magnitude and timing of future cost reductions, as well as the potential for costs to rise above current estimates, especially for technologies still in the early stages of research and development. The current assessment is based on studies of the specific technologies in Tables 3.12 to 3.14 (and the supporting discussions and literature cited in Sections 3.7.9 to 3.7.12), as well as analyses of historical cost trends for related energy and environmental technologies. This assessment suggests that improvements to current commercial technologies can reduce CO_2 capture costs by at least 20-30% over approximately the next decade, while new technologies under development promise more substantial cost reductions. Achieving future cost reductions, however, will require deployment and adoption of commercial technologies in the marketplace as well as sustained R&D.

3.8 Gaps in knowledge

Gaps in knowledge are related to differences in the stages of development of component technologies for the capture systems reviewed in Sections 3.2 to 3.5. For CO_2 capture from industrial processes, a number of technologies that are commonly used in natural gas sweetening and ammonia production are already used on a commercial scale. For other types of industrial systems capturing CO_2 from steel and cement production, further work is still needed. For CO_2 capture that might be reliant on post-combustion capture or oxy-fuel combustion, options are less well developed, or are available at a smaller scale than those required for applications such as in power generation, where much larger gas flows are handled. For pre-combustion capture many of the required systems have been developed and applied in industry already.

Although many of the component and/or enabling technologies required for CO_2 capture in post-combustion, pre-combustion and oxy-fuel combustion are well known, gaps in knowledge are in the practical and/or commercial demonstration of integrated systems. This demonstration is essential to prove the cost of CO_2 capture and its use on a large scale, particularly in power generation applications, but also for cement, steel and other large industries. Operating experience is also needed to test system reliability, improved methods of system integration, methods to reduce the energy requirements for CO_2 capture, improved process control strategies and the use of optimized functional materials for the implementation of capture processes with advanced, higher efficiency power cycles. As such developments are realized, environmental issues associated with the capture of CO_2 and other deleterious pollutants in these systems should also be re-assessed from a perspective involving the whole capture-transport-storage operation.

In an ongoing search to implement existing, new or improved methods of CO_2 capture, most capture systems also rely on the application of a range of enabling technologies that influence the attractiveness of a given system. These enabling technologies have their own critical gaps of knowledge. For example, improved processes for the effective removal of sulphur, nitrogen, chlorine, mercury and other pollutants are needed for the effective performance of unit operations for CO_2 separation in post- and pre-combustion capture systems, especially when coal is used as the primary fuel. Improved gasification reactors for coals and biomass, the availability of hydrogen-burning gas turbines and fuel cells for stationary power generation also need further development in the pre-combustion route. Combustors and boilers operating at higher temperatures, or a new class of CO_2 turbines and compressors, are important requirements for oxy-fuel systems.

With reference to the development of novel CO_2 capture and/or other enabling technologies, a wide range of options are currently being investigated worldwide. However, many technical details of the specific processes proposed or under development for these emerging technologies are still not well understood. This makes the assessment of their performance and cost highly uncertain. This is where intense R&D is needed to develop and bring to pilot scale testing the most promising concepts for commercial application. Membranes for H_2, CO_2 or O_2 separation, new sorbents, O_2 or CO_2 solid carriers and materials for advanced combustors, boilers and turbines all require extensive performance testing. Multi-pollutant emission controls in these novel systems and the impact of fuel impurities and temperature on the functional materials, should also be an area of future work.

References

Abanades, J.C., E.J. Anthony, D. Alvarez, D.Y. Lu, and C. Salvador, 2004a: Capture of CO_2 from Combustion Gases in a Fluidised Bed of CaO. *AIChE J*, **50**, No. 7, 1614-1622.

Abanades, J.C., E.S. Rubin and E.J. Anthony, 2004b: Sorbent cost and performance in CO_2 capture systems. *Industrial and Engineering Chemistry Research,* **43**, 3462-3466.

Abbot, J., B. Crewdson, and K. Elhius, 2002: Efficient cost effective and environmentally friendly synthesis gas technology for gas to liquids production. IBC Gas to Liquids Conference, London.

Aboudheir, A., P. Tontiwachwuthikul, A. Chakma, and R. Idem, 2003: Kinetics of the reactive absorption of carbon dioxide in high CO_2-loaded, concentrated aqueuous monoethanolamine solutions. *Chemical Engineering Science* **58**, 5195-5210.

Alic, J.A., D.C. Mowery, and E.S. Rubin, 2003: *U.S. Technology and Innovation Policies: Lessons for Climate Change*. Pew Center on Global Climate Change, Arlington, VA, November.

Allam, R.J., E.P. Foster, V.E. Stein, 2002: Improving Gasification Economics through ITM Oxygen Integration. Proceedings of the Fifth Institution of Chemical Engineers (UK) European Gasification Conference, Noordwijk, The Netherlands.

Alstom Power Inc., ABB Lummus Global Inc., Alstom Power Environmental Systems and American Electric Power, 2001: *Engineering feasibility and economics of CO_2 capture on an existing coal-fired power plant*. Report no. PPL-01-CT-09 to Ohio Department of Development, Columbus, OH and US Department of Energy/NETL, Pittsburgh, PA.

American Institute of Chemical Engineers, 1995: Centre for Chemical Process Safety. Guidelines for Technical Planning for On-site Emergencies *Wiley*, New York.

Anderson, R., H. Brandt, S. Doyle, K. Pronske, and F. Viteri, 2003: Power generation with 100% carbon capture and sequestration. Second Annual Conference on Carbon Sequestration, Alexandria, VA.

Apple, M. 1997: Ammonia. Methanol. Hydrogen. Carbon Monoxide. Modern Production Technologies. A Review. Published by *Nitrogen - The Journal of the World Nitrogen and Methanol Industries*. CRU Publishing Ltd.

Aresta, M.A. and A. Dibenedetto, 2003: New Amines for the reversible absorption of carbon dioxide from gas mixtures. *Greenhouse Gas Control Technologies*, Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), 1-4 Oct. 2002, Kyoto, Japan, J. Gale and Y. Kaya (eds.), Elsevier Science Ltd, Oxford, UK. 1599-1602.

Armstrong, P.A., D.L. Bennett, E.P. Foster, and V.E. Stein, 2002: Ceramic membrane development for oxygen supply to gasification applications. Proceedings of the Gasification Technologies Conference, San Francisco, CA, USA.

Arnold, D.S., D.A. Barrett and R.H. Isom, 1982: CO_2 can be produced from flue gas. *Oil & Gas Journal*, November, 130-136.

Aroonwilas, A., A. Chakma, P. Tontiwachwuthikul, and A. Veawab, 2003: Mathematical Modeling of Mass-Transfer and Hydrodynamics in CO_2 Absorbers Packed with Structured Packings, *Chemical Engineering Science,* **58**, 4037-4053.

Astarita, G., D.W. Savage, and A. Bisio, 1983: Gas Treating with Chemical Solvents, Chapter 9 Removal of Carbon Dioxide. *Wiley*, New York.

Audus, H. and P. Freund, 2005: Climate change mitigation by biomass gasification combined with CO_2 capture and storage. Proceedings of 7th International Conference on Greenhouse Gas Control Technologies. E.S. Rubin, D.W. Keith, and C.F. Gilboy (eds.), Vol. 1: Peer-Reviewed Papers and Overviews, E.S. Rubin, D.W. Keith and C.F. Gilboy (eds.), Elsevier Science, Oxford, UK, 187-200.

Babcock Energy Ltd, Air Products Ltd, University of Naples and University of Ulster, 1995: Pulverised coal combustion system for CO_2 capture. Final report 2.1.1, European Commission JOULE II Clean Coal Technology Programme - Powdered Coal Combustion Project.

Babovic, M., A. Gough, P. Leveson, and C. Ramshaw, 2001: Catalytic Plate Reactors for Endo- and Exothermic Reactions. 4th International Conference on Process Intensification for the Chemical Industry, Brugge, Belgium, 10-12 September.

Bachu, S., and W. Gunter, 2005: Overview of Acid Gas Injection in Western Canada. In E.S.Rubin, D.W. Keith, and C.F. Gilboy (eds.), Proceedings of 7th International Conference on Greenhouse Gas Control Technologies. Volume I: Peer Reviewed Papers and Overviews, *Elsevier Science*, Oxford, UK, 443-448.

Bai, H., A.C. Yeh, 1997: Removal of CO_2 Greenhouse Gas by Ammonia Scrubbing. Ind. Eng. Chem. Res, **36** (6), 2490-2493.

Bandi, A., M. Specht, P. Sichler, and N. Nicoloso, 2002: In situ Gas Conditioning in Fuel Reforming for Hydrogen Generation. 5th International Symposium on Gas Cleaning at High Temperature. U.S. DOE National Energy Technology Laboratory, Morgantown, USA.

Barchas, R., R. Davis, 1992: The Kerr-McGee / ABB Lummus Crest Technology for the Recovery of CO_2 from Stack Gases. *Energy Conversion and Management*, **33**(5-8), 333-340.

Beecy, D.J. and Kuuskraa, V.A., 2005: Basic Strategies for Linking CO_2 enhanced oil recovery and storage of CO_2 emissions. In E.S.Rubin, D.W. Keith and C.F. Gilboy (eds.), Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5-9, 2004, Vancouver, Canada. Volume I: Peer Reviewed Papers and Overviews, *Elsevier Science*, Oxford, UK, 351-360.

Blomen, L.J.N.J. and M.N. Mugerwa, 1993: Fuel Cell systems, Plenum Press, New York, 1993, ISBN 0-36-44158-6.

Bock, B., R. Rhudy, H. Herzog, M. Klett, J. Davison, D. De la Torre Ugarte, and D.Simbeck, 2003: Economic Evaluation of CO_2 Storage and Sink Options, DOE Research Report DE-FC26-00NT40937, U.S. Department of Energy, Pittsburgh Energy Technology Center, Pittsburgh, PA.

Bouwmeester, H.J.M., L.M.Van Der Haar, 2002: Oxygen permeation through mixed-conducting perovskite oxide membranes. *Ceramic Transactions*, **127**, Materials for Electrochemical Energy Conversion and Storage, 49-57.

BP, 2004: *Statistical Review of World Energy.* Http:\www.bp.com.

Bracht, M, Alderliesten P.T., R. Kloster, R. Pruschek, G. Haupt, E. Xue, J.R.H. Ross, M.K. Koukou, and N. Papayannakos, 1997: Water gas shift membrane reactor for CO_2 control in IGCC systems: techno-economic feasibility study, *Energy Conversion and Management,* **38** (Suppl.), S159-S164, 1997.

Brandvoll, Ø. and O. Bolland, 2004: Inherent CO_2 capture using chemical looping combustion in a natural gas fired power cycle. ASME Paper No. GT-2002-30129, *ASME Journal of Engineering for Gas Turbines and Power*, **126**, 316-321.

Bredesen, R., K. Jordal and O. Bolland, 2004: High-Temperature Membranes in Power Generation with CO_2 capture. *Journal of Chemical Engineering and Processing*, **43**, 1129-1158.

Breton, D.L. and P. Amick, 2002: Comparative IGCC Cost and Performance for Domestic Coals, Preceedings of the 2002 Gasification Technology Conference, San Francisco, October.

Campanari, S., 2002: Carbon dioxide separation from high temperature fuel cell power plants. *Journal of Power Sources,* **112** (2002), 273-289.

Carolan, M.F., P.N. Dyer, E. Minford, T.F. Barton, D.R. Peterson, A.F. Sammells, D.L. Butt, R.A. Cutler, and D.M. Taylor, 2001: Development of the High Pressure ITM Syngas Process, Proceedings of the 6th Natural Gas Conversion Symposium, Alaska, 17-22 June.

Castle, W.F., 1991: Modern liquid pump oxygen plants: Equipment and performance, Cryogenic Processes and Machinery, AIChE Series No: 294; 89:14-17, 8th Intersociety Cryogenic Symposium, Houston, Texas, USA.

CCP, 2005: Economic and Cost Analysis for CO_2 Capture Costs in the CO_2 Capture Project, Scenarios. In D.C. Thomas (Ed.), Volume 1 - Capture and Separation of Carbon Dioxide from Combustion Sources, Elsevier Science, Oxford, UK.

Celik, F., E.D. Larson, and R.H. Williams, 2005: Transportation Fuel from Coal with Low CO_2 Emissions, Wilson, M., T. Morris, J. Gale and K. Thambimuthu (eds.), Proceedings of 7th International Conference on Greenhouse Gas Control Technologies. Volume II: Papers, Posters and Panel Discussion, *Elsevier Science*, Oxford UK, 1053-1058.

Chakma, A., P. Tontiwachwuthikul, 1999: Designer Solvents for Energy Efficient CO_2 Separation from Flue Gas Streams. Greenhouse Gas Control Technologies. Riemer, P., B. Eliasson, A. Wokaun (eds.), *Elsevier Science, Ltd.*, United Kingdom, 35-42.

Chakma, A., 1995: An Energy Efficient Mixed Solvent for the Separation of CO_2. *Energy Conversion and Management*, **36**(6-9), 427-430.

Chakravarty, S., A. Gupta, B. Hunek, 2001: Advanced technology for the capture of carbon dioxide from flue gases, Presented at First National Conference on Carbon Sequestration, Washington, DC.

Chapel, D.G., C.L. Mariz, and J. Ernest, 1999: Recovery of CO_2 from flue gases: commercial trends, paper No. 340 at the Annual Meeting of the Canadian Society of Chemical Engineering, Saskatoon, Canada, October.

Chatel-Pelage, F., M. Ovidiu, R. Carty, G. Philo, H. Farzan, S. Vecci, 2003: A pilot scale demonstration of oxy-fuel combustion with flue gas recirculation in a pulverised coal-fired boiler, Proceedings 28th International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, Florida, March 10-13.

Cheeley, R., 2000: Combining gasifiers with the MIDREX® direct reduction process, Gasification 4 Conference, Amsterdam, Netherlands, 11-13 April.

Chen, C., A.B. Rao, and E.S. Rubin, 2003: Comparative assessment of

CO_2 capture options for existing coal-fired power plants, presented at the Second National Conference on Carbon Sequestration, Alexandria, VA, USA, 5-8 May.

Chen, H., A.S. Kovvali, S. Majumdar, K.K. Sirkar, 1999: Selective CO_2 separation from CO_2-N_2 mixtures by immobilised carbonate-glycerol membranes, *Ind. Eng. Chem.,* **38**, 3489-3498.

Chiesa, P., S. Consonni, T. Kreutz, and R. Williams, 2005: Co-production of hydrogen, electricity and CO_2 from coal with commercially ready technology. Part A: Performance and emissions, *International Journal of Hydrogen Energy,* **30** (7): 747-767.

Cho, P., T. Mattisson, and A. Lyngfelt, 2002: Reactivity of iron oxide with methane in a laboratory fluidised bed - application of chemical-looping combustion, 7th International Conference on Circulating Fluidised Beds, Niagara Falls, Ontario, May 5-7, 2002, 599-606.

Croiset, E. and K.V. Thambimuthu, 2000: Coal combustion in O_2/CO_2 Mixtures Compared to Air. *Canadian Journal of Chemical Engineering*, **78**, 402-407.

Cullinane, J.T. and G. T. Rochelle, 2003: Carbon Dioxide Absorption with Aqueous Potassium Carbonate Promoted by Piperazine, Greenhouse Gas Control Technologies, Vol. II, J. Gale, Y. Kaya, *Elsevier Science, Ltd*., United Kingdom, 1603-1606.

Curran, G P., C.E. Fink, and E. Gorin, 1967: Carbon dioxide-acceptor gasification process. Studies of acceptor properties. *Adv. Chem. Ser.,* **69**, 141-165.

Damle, A.S. and T.P. Dorchak, 2001: Recovery of Carbon Dioxide in Advanced Fossil Energy Conversion Processes Using a Membrane Reactor, First National Conference on Carbon Sequestration, Washington, DC.

Davison, J.E., 2005: CO_2 capture and storage and the IEA Greenhouse Gas R&D Programme. Workshop on CO_2 issues, Middelfart, Denmark, 24 May, IEA Greenhouse Gas R&D Programme, Cheltenham, UK.

Dijkstra, J.W. and D. Jansen, 2003: Novel Concepts for CO_2 capture with SOFC, Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6) Volume I, Page 161-166, 1-4 Oct. 2002, Kyoto, Japan, Gale J. and Y. Kaya (eds.), *Elsevier Science Ltd*, Kidlington, Oxford, UK.

Dillon, D.J., R.S. Panesar, R.A.Wall, R.J. Allam, V. White, J. Gibbins, and M.R. Haines, 2005: Oxy-combustion processes for CO_2 capture from advanced supercritical PF and NGCC power plant, In: Rubin, E.S., D.W. Keith, and C.F. Gilboy (eds.), Proceedings of 7th International Conference on Greenhouse Gas Control Technologies. Volume I: Peer Reviewed Papers and Overviews, Elsevier Science, Oxford, UK, 211-220.

Dongke, M.A., L. Kong, and W.K. Lu, 1988: Heat and mass balance of oxygen enriched and nitrogen free blast furnace operations with coal injection. I.C.S.T.I. Iron Making Conference Proceedings.

Duarte, P.E. and E. Reich, 1998: A reliable and economic route for coal based D.R.I. production. I.C.S.T.I Ironmaking Conference Proceedings 1998.

Dyer, P.N., C.M. Chen, K.F. Gerdes, C.M. Lowe, S.R. Akhave, D.R. Rowley, K.I. Åsen and E.H. Eriksen, 2001: An Integrated ITM Syngas/Fischer-Tropsch Process for GTL Conversion, 6th Natural Gas Conversion Symposium, Alaska, 17-22 June 2001.

Dyer, P.N., R.E. Richards, S.L. Russek, D.M. Taylor, 2000: Ion transport membrane technology for oxygen separation and syngas production, *Solid State Ionics*, **134** (2000) 21-33.

EPRI, 1993: Technical Assessment Guide, Volume 1: Electricity Supply-1993 (Revision 7), Electric Power Research Institute, Palo Alto, CA, June.

Erga, O., O. Juliussen, H. Lidal, 1995: Carbon dioxide recovery by means of aqueous amines, *Energy Conversion and Management,* **36**(6-9), 387-392.

European Chemicals Bureau, 2003: Technical Guidance Document on Risk Assessment. European Communities. EUR 20418, http://ecb.jrc.it/.

Falk-Pedersen, O., H. Dannström, M. Grønvold, D.-B. Stuksrud, and O. Rønning, 1999: Gas Treatment Using Membrane Gas/Liquid Contractors, Greenhouse Gas Control Technologies. B. Eliasson, P. Riemer and A. Wokaun (eds.), Elsevier Science, Ltd., United Kingdom 115-120.

Farla, J.C., C.A. Hendriks, and K. Blok, 1995: Carbon dioxide recovery from industrial processes, *Climate Change,* **29**, (1995), 439-61.

Feron, P.H.M and A.E. Jansen, 2002: CO_2 Separation with polyolefin membrane contactors and dedicated absorption liquids: Performances and prospects, *Separation and Purification Technology,* **27**(3), 231-242.

Feron, P.H.M., 1992: Carbon dioxide capture: The characterisation of gas separation/removal membrane systems applied to the treatment of flue gases arising from power plant generation using fossiel fuel. IEA/92/08, IEA Greenhouse Gas R&D programme, Cheltenham, UK.

Feron, P.H.M., 1994: Membranes for carbon dioxide recovery from power plants. In Carbon Dioxide Chemistry: Environmental Issues. J. Paul, C.M. Pradier (eds.), The Royal Society of Chemistry, Cambridge, United Kingdom, 236-249.

Gibbins, J., R.I. Crane, D. Lambropoulos, C. Booth, C.A. Roberts, and M. Lord, 2005: Maximising the effectiveness of post-combustion CO_2 capture systems. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies. Volume I: Peer Reviewed Papers and Overviews, E.S. Rubin, D.W. Keith, and C.F.Gilboy (eds.), Elsevier Science, Oxford, UK, 139-146.

Gielen, D.J., 2003: CO_2 removal in the iron and steel industry, *Energy Conversion and Management*, **44** (7), 1027-1037.

Göttlicher, G., 1999: Energetik der Kohlendioxidrückhaltung in Kraftwerken, Fortschritt-Berichte VDI, Reihe 6: Energietechnik Nr. 421, VDI Düsseldorf, Dissertation Universität Essen 1999, ISBN 3-18-342106-2.

Gray, D. and G. Tomlinson, 2001: Coproduction of Ultra Clean Transportation Fuels, Hydrogen, and Electric Power from Coal, Mitretek Technical Report MTR 2001-43, prepared for the National Energy Technology Laboratory, US DOE, July.

Gray, D. and G. Tomlinson, 2003: Hydrogen from Coal. Mitretek Technical Paper MTR-2003-13, prepared for the National Energy Technology Laboratory, US DOE, April.

Green, D.A., B.S. Turk, R.P. Gupta, J.W. Portzer, W.J. McMichael, and D.P. Harrison, 2002: Capture of Carbon Dioxide from flue gas using regenerable sorbents. 19th Annual International Pittsburgh Coal Conference. September 23-27, Pittsburgh, Pennsylvania, USA.

Griffin, T., S.G. Sundkvist, K. Aasen, and T. Bruun, 2003: Advanced Zero Emissions Gas Turbine Power Plant, ASME Turbo Expo Conference, paper# GT-2003-38120, Atlanta, USA.

Haines, M.R., 1999: Producing Electrical Energy from Natural Gas using a Solid Oxide Fuel Cell. Patent WO 99/10945, 1-14.

Hazardous Substances Data Bank, 2002: US National Library of Medicine, Specialized Information Services: Hazardous Substances Data Bank. Carbon dioxide. 55 pp.

Hendriks, C., 1994: Carbon dioxide removal from coal-fired power plants, Dissertation, Utrecht University, Netherlands, 259 pp.

Herzog, H.J., 1999: The economics of CO_2 capture. Proceedings of the Fourth International Conference on Greenhouse Gas Control Technologies, B. Eliasson, P. Riemer, and A. Wokaun (eds.), 30 August-2 September 1998, Interlaken, Switzerland, Elsevier Science Ltd., Oxford, UK, 101-106.

Herzog, H., D. Golomb, S. Zemba, 1991: Feasibility, modeling and economics of sequestering power plant CO_2 emissions in the deep ocean, *Environmental Progress*, **10**(1), 64-74.

Hoffman, J.S., D.J. Fauth., and H.W. Pennline, 2002: Development of novel dry regenerable sorbents for CO_2 capture. 19th Annual International Pittsburgh Coal Conference. September 23-27, 2002 Pittsburgh, Pennsylvania, USA.

Holt, N., G. Booras, and D. Todd, 2003: Summary of recent IGCC studies of CO_2 for sequestration, Proceedings of Gasification Technologies Conference, October 12-15, San Francisco.

Hufton, J.R., R.J. Allam, R. Chiang, R.P. Middleton, E.L. Weist, and V. White, 2005: Development of a Process for CO_2 Capture from Gas Turbines using a Sorption Enhanced Water Gas Shift Reactor System. Proceedings of 7th International Conference on Greenhouse Gas Control Technologies. Volume I: Peer Reviewed Papers and Overviews, E.S. Rubin, D.W. Keith, and C.F. Gilboy (eds.), Elsevier Science, Oxford, UK, 2005, 253-262.

Hufton, J.R., S. Mayorga, S. Sircar, 1999: Sorption Enhanced Reaction Process for Hydrogen Production *AIChE J*, **45**, 248-254.

IEA WEO, 2004: IEA World Energy Outlook 2004, International Energy Agency, Paris France.

IEA, 2004: Prospects for CO_2 capture and storage, ISBN 92-64-10881-5.

IEA CCC, 2005: IEA CCC (IEA Clean Coal Centre) The World Coal-fired Power Plants Database, Gemini House, Putney, London, United Kingdom.

IEA GHG, 1996: De-carbonisation of fossil fuels, Report PH2/2, March 1996, IEA Greenhouse Gas R&D Programme, Cheltenham, UK.

IEA GHG, 1999: The reduction of greenhouse gas emissions from the cement industry. Report PH3/7, May 1999, IEA Greenhouse Gas R&D Programme, Cheltenham, UK.

IEA GHG, 2000a: Greenhouse gas emissions from major industrial sources III - Iron and Steel Production Report PH3/30, IEA Greenhouse Gas R&D Programme, Cheltenham, UK.

IEA GHG, 2000b: Leading options for the capture of CO_2 emissions at power stations, report PH3/14, Feb. 2000, IEA Greenhouse Gas R&D Programme, Cheltenham, UK.

IEA GHG, 2000c: CO_2 abatement in oil refineries: fired heaters, report PH3/31, Oct. 2000, IEA Greenhouse Gas R&D Programme, Cheltenham, UK.

IEA GHG, 2000d: Key Components for CO_2 abatement: Gas turbines, report PH3/12 July 2000, IEA Greenhouse Gas R&D Programme, Cheltenham, UK.

IEA GHG, 2001: CO_2 abatement by the use of carbon-rejection processes, report PH3/36, February 2001, IEA Greenhouse Gas R&D Programme, Cheltenham, UK.

IEA GHG, 2002a: Transmission of CO_2 and Energy, report PH4/6, March 2002, IEA Greenhouse Gas R&D Programme, Cheltenham, UK.

IEA GHG, 2002b: Opportunities for early application of CO_2 sequestration technologies, report PH4/10, Sept. 2002, IEA Greenhouse Gas R&D Programme, Cheltenham, UK.

IEA GHG, 2003: Potential for improvements in gasification combined cycle power generation with CO_2 Capture, report PH4/19, IEA Greenhouse Gas R&D Programme, Cheltenham, UK.

IEA GHG, 2004: Improvements in power generation with post-combustion capture of CO_2, report PH4/33, Nov. 2004, IEA Greenhouse Gas R&D Programme, Cheltenham, UK.

IEA GHG, 2005: Retrofit of CO_2 capture to natural gas combined cycle power plants, report 2005/1, Jan. 2005, IEA Greenhouse Gas R&D Programme, Cheltenham, UK.

Ishibashi, M., K. Otake, S. Kanamori, and A. Yasutake, 1999: Study on CO_2 Removal Technology from Flue Gas of Thermal Power Plant by Physical Adsorption Method, Greenhouse Gas Control Technologies. P. Riemer, B. Eliasson, and A. Wokaun (eds.), Elsevier Science, Ltd., United Kingdom, 95-100.

Ishida, M. and H. Jin, 1994: A New Advanced Power-Generation System Using Chemical-Looping Combustion, *Energy*, **19**(4), 415-422.

Jansen, D. and J.W. Dijkstra, 2003: CO_2 capture in SOFC-GT systems, Second Annual Conference on Carbon Sequestration, Alexandria, Virginia USA, May 5-7.

Jericha, H., E. Göttlich, W. Sanz, F. Heitmeir, 2003: Design optimisation of the Graz cycle power plant, ASME Turbo Expo Conference, paper GT-2003-38120, Atlanta, USA.

Jordal, K., R. Bredesen, H.M. Kvamsdal, O. Bolland, 2003: Integration of H_2-separating membrane technology in gas turbine processes for CO_2 sequestration. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), Vol 1, 135-140, 1-4 Oct. 2002, Kyoto, Japan, J. Gale and Y. Kaya (eds.), Elsevier Science Ltd, Oxford, UK.

Karg, J. and F. Hannemann, 2004: IGCC - Fuel-Flexible Technology for the Future, Presented at the Sixth European Gasification Conference, Brighton, UK, May 2004.

Klett, M.G., R.C. Maxwell, and M.D. Rutkowski, 2002: The Cost of Mercury Removal in an IGCC Plant. Final Report for the US Department of Energy National Energy Technology Laboratory, by Parsons Infrastructure and Technology Group Inc., September.

Kohl, A.O. and R.B. Nielsen, 1997: Gas purification, Gulf Publishing Co., Houston, TX, USA.

Kovvali, A.S. and K.K. Sirkar, 2001: Dendrimer liquid membranes: CO_2 separation from gas mixtures, *Ind. Eng. Chem.,* **40**, 2502-2511.

Kreutz, T., R. Williams, P. Chiesa, and S. Consonni, 2005: Co-production of hydrogen, electricity and CO_2 from coal with commercially ready technology. Part B: Economic analysis, *International Journal of Hydrogen Energy*, **30** (7): 769-784.

Kvamsdal, H., O. Maurstad, K. Jordal, and O. Bolland, 2004: Benchmarking of gas-turbine cycles with CO_2 capture. Proceedings of 7th International Conference on Greenhouse Gas Control Technologies. Volume I: Peer Reviewed Papers and Overviews, E.S. Rubin, D.W. Keith, and C.F. Gilboy (eds.), Elsevier Science, Oxford, UK, 2005, 233-242.

Lackner, K.S., 2003: Climate change: a guide to CO_2 sequestration, *Science*, **300**, issue 5626, 1677-1678, 13 June.

Lackner, K., H.J. Ziock, D.P. Harrison, 2001: Hydrogen Production from carbonaceous material. United States Patent WO 0142132.

Larson, E.D., and T. Ren, 2003: Synthetic fuels production by indirect coal liquefaction, *Energy for Sustainable Development*, **VII**(4), 79-102.

Latimer, R.E., 1967: Distillation of air. *Chem Eng Progress,* **63**(2), 35-59.

Leites, I.L., D.A. Sama, and N. Lior, 2003: The theory and practice of energy saving in the chemical industry: some methods for reducing thermodynamic irreversibility in chemical technology processes. *Energy,* **28**, N 1, 55-97.

Leites, I.L., 1998: The Thermodynamics of CO_2 solubility in mixtures monoethanolamine with organic solvents and water and commercial experience of energy saving gas purification technology. *Energy Conversion and Management*, **39**, 1665-1674.

Lin, S.Y., Y. Suzuki, H. Hatano, and M. Harada, 2002: Developing an innovative method, HyPr-RING, to produce hydrogen from hydrocarbons, *Energy Conversion and Management,* **43**, 1283-1290.

Lowe, C., V. Francuz, and C. Behrens, 2003: Hydrogen Membrane Selection for a Water Gas Shift Reactor. Second DoE Annual Conference on Carbon Sequestration. May, Arlington, VA.

Maddox, R.N. and D.J. Morgan, 1998: Gas Conditioning and Processing. Volume 4: Gas treating and sulfur recovery. Campbell Petroleum Series, Norman, OK, USA.

Mano, H., S. Kazama, and K. Haraya, 2003: Development of CO_2 separation membranes (1) Polymer membrane, In Greenhouse Gas Control Technologies. J. Gale and Y. Kaya (eds.), Elsevier Science, Ltd., United Kingdom, 1551-1554.

Marin, O., Y. Bourhis, N. Perrin, P. DiZanno, F. Viteri, and R. Anderson, 2003: High efficiency Zero Emission Power Generation based on a high temperature steam cycle, 28th Int. Technical Conference On Coal Utilization and Fuel Systems, Clearwater, FL, March.

Mathieu, P., 2003**:** Mitigation of CO_2 emissions using low and near zero CO_2 emission power plants. Clean Air, *International Journal on Energy for a Clean Environment*, **4**, 1-16.

McDaniel, J.E. and M.J. Hornick, 2002: Tampa Electric Polk Power Station Integrated Gasification Combined Cycle Project, Final Technical Report to the National Energy Technology Laboratory, US Department of Energy, August.

McDonald, A. and L. Schrattenholzer, 2001: Learning rates for energy technologies. *Energy Policy* **29**, pp. 255-261.

McDonald, M. and M. Palkes, 1999: A design study for the application of CO_2/O_2 combustion to an existing 300 MW coal-fired boiler, Proceedings of Combustion Canada 99 Conference-Combustion and Global Climate Change, Calgary, Alberta.

Merrow, E.W., K.E. Phillips and L.W. Myers, 1981: Understanding cost growth and performance shortfalls in pioneer process plants, Rand Publication No. R-2569-DOE, Report to the U.S. Department of Energy by Rand Corporation, Santa Monica, California, September.

Middleton, P., H. Solgaard-Andersen, T. Rostrup-Nielsen T. 2002: Hydrogen Production with CO_2 Capture Using Membrane Reactors. 14th World Hydrogen Energy Conference, June 9-14, Montreal, Canada.

Mimura, T., H. Simayoshi, T. Suda, M. Iijima, S. Mitsuoka, 1997: Development of Energy Saving Technology for Flue Gas Carbon Dioxide Recovery in Power Plant by Chemical Absorption Method and Steam System. *Energy Conversion and Management,* **38**, S57-S62.

Mimura, T., S. Satsumi, M. Iijima, S. Mitsuoka, 1999: Development on Energy Saving Technology for Flue Gas Carbon Dioxide Recovery by the Chemical Absorption Method and Steam System in Power Plant, Greenhouse Gas Control Technologies. P. Riemer, B. Eliasson, A. Wokaun (eds.), Elsevier Science, Ltd., United Kingdom, 71-76.

Mimura, T., S. Shimojo, T. Suda, M. Iijima, S. Mitsuoka, 1995: Research and Development on Energy Saving Technology for Flue Gas Carbon Dioxide Recovery and Steam System in Power Plant, *Energy Conversion and Management*, **36**(6-9), 397-400.

Mimura, T., T. Nojo, M. Iijima, T. Yoshiyama and H. Tanaka, 2003: Recent developments in flue gas CO_2 recovery technology. Greenhouse Gas Control Technologies, Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), 1-4 Oct. 2002, Kyoto, Japan, J. Gale and Y. Kaya (eds.), Elsevier Science Ltd, Oxford, UK.

Mitretek, 2003: Hydrogen from Coal, Technical Paper MTR-2003-13, Prepared by D. Gray and G. Tomlinson for the National Energy Technology Laboratory, US DOE, April.

Möllersten, K., J. Yan, and J. Moreira, 2003: Potential market niches for biomass energy with CO_2 capture and storage – opportunities for energy supply with negative CO_2 emissions, *Biomass and Bioenergy,* **25**(2003), 273-285.

Möllersten, K., L. Gao, J. Yan, and M. Obersteiner, 2004: Efficient energy systems with CO_2 capture and storage from renewable biomass in pulp and paper mills, *Renewable Energy,* **29**(2004), 1583-1598.

Muramatsu, E. and M. Iijima, 2003: Life cycle assessment for CO_2 capture technology from exhaust gas of coal power plant. Greenhouse Gas Control Technologies. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), 1-4 Oct. 2002, Kyoto, Japan, J. Gale and Y. Kaya (eds.), Elsevier Science Ltd, Oxford, UK.

Nakagawa, K., T. Ohashi 1998: A novel method of CO_2 capture from high temperature gases, *Journal Electrochem. Soc*., **145**(4): 1344-1346.

NETL, 2002: Advanced fossil power systems comparison study, Final report prepared for NETL by E.L. Parsons (NETL, Morgantown, WV), W.W. Shelton and J.L. Lyons (EG&G Technical Services, Inc., Morgantown, WV), December.

NETL-DOE, 2002: Worldwide Gasification Database online, Pittsburgh, PA, USA. http://www.netl.doe.gov/coalpower/gasification/models/dtbs(excel.pdf.

Noble, R. and Stern (eds.), 1995: Membrane Separations Technology, Elsevier Science, Amsterdam, The Netherlands, 718 pp.

NRC, 2003: Review of DOE's Vision 21 Research and Development Program - Phase I, Board on Energy and Environmental Systems of the National Research Council, The National Academies Press, Washington, DC, 97 p.

NRC, 2004: The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs, Prepared by the Committee on Alternatives and Strategies for Future Hydrogen Production and Use, Board on Energy and Environmental Systems of the National Research Council, The National Academies Press, Washington, DC.

Nsakala, N., G. Liljedahl, J. Marion, C. Bozzuto, H. Andrus, and R. Chamberland, 2003: Greenhouse gas emissions control by oxygen firing in circulating fluidised bed boilers. Presented at the Second Annual National Conference on Carbon Sequestration. Alexandria, VA May 5-8, USA.

Nsakala, Y.N., J. Marion, C. Bozzuto, G. Liljedahl, M. Palkes, D. Vogel, J.C. Gupta, M. Guha, H. Johnson, and S. Plasynski, 2001: Engineering feasibility of CO_2 capture on an existing US coal-fired power plant, Paper presented at First National Conference on Carbon Sequestration, Washington DC, May 15-17.

Okabe, K., N. Matsumija, H. Mano, M. Teramoto, 2003: Development of CO_2 separation membranes (1) Facilitated transport membrane, In Greenhouse Gas Control Technologies. J. Gale and Y. Kaya (eds.), Elsevier Science, Ltd., United Kingdom, 1555-1558.

Parsons Infrastructure & Technology Group, Inc., 2002b: *Updated cost and performance estimates for fossil fuel power plants with CO_2 removal*. Report under Contract No. DE-AM26-99FT40465 to U.S.DOE/NETL, Pittsburgh, PA, and EPRI, Palo Alto, CA., December.

Parsons Infrastructure and Technology Group, Inc., 2002a: *Hydrogen Production Facilities: Plant Performance and Cost Comparisons*, Final Report, prepared for the National Energy Technology Laboratory, US DOE, March.

Quinn, R., D.V. Laciak, 1997: Polyelectrolyte membranes for acid gas separations, *Journal of Membrane Science*, **131**, 49-60.

Ramsaier, M., H.J. Sternfeld, K. Wolfmuller, 1985: European Patent 0197 555 A2.

Rao, A.B. and E.S. Rubin, 2002: A technical, economic, and environmental assessment of amine-based CO_2 capture technology for power plant greenhouse gas control. *Environmental Science and Technology,* **36,** 4467-4475.

Rao, A.B., E.S. Rubin and M. Morgan, 2003: Evaluation of potential cost reductions from improved CO_2 capture systems. 2nd Annual Conference on Carbon Sequestration, Alexandria, VA, USA, 5-8 May, U.S. Department of Energy, NETL, Pittsburgh, PA.

Reddy, S., J. Scherffius, S. Freguia and C. Roberts, 2003: Fluor's Econamine FG Plus^{SM} technology - an enhanced amine-based CO_2 capture process, 2nd Annual Conference on Carbon Sequestration, Alexandria, VA, USA, 5-8 May, U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA.

Renzenbrink, W., R. Wischnewski, J. Engelhard, A. Mittelstadt, 1998: High Temperature Winkler (HTW) Coal Gasification: A Fully Developed Process for Methanol and Electricity Production, paper presented at the Gasification Technology Conference, October 1998, San Francisco, CA, USA.

Richards, D., 2003: Dilute oxy-fuel technology for zero emmission power, First International Conference on Industrial Gas Turbine Technologies, Brussels (available on www.came-gt.com).

Richter, H.J., K. Knoche 1983: Reversibility of Combustion processes, Efficiency and Costing - Second Law Analysis of Processes, *ACS Symposium series,* **235**, p. 71-85.

Riemer, P.W.F. and W.G. Ormerod, 1995: International perspectives and the results of carbon dioxide capture disposal and utilisation studies, *Energy Conversion and Management,* **36**(6-9), 813-818.

Rizeq, G., R. Subia, J. West, A. Frydman, and V. Zamansky, 2002: Advanced-Gasification Combustion: Bench-Scale Parametric Study. 19th Annual International Pittsburgh Coal Conference September 23-27, 2002, Pittsburgh, PA, USA.

Robinson, A.L., J.S. Rhodes, and D.W. Keith, 2003: Assessment of potential carbon dioxide reductions due to biomass-coal cofiring in the United States, *Environmental Science and Technology*, **37**(22), 5081-5089.

Rubin, E.S. and A.B. Rao, 2003: Uncertainties in CO_2 capture and sequestration costs, Greenhouse Gas Control Technologies, Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), 1-4 Oct. 2002, Kyoto, Japan, J. Gale and Y. Kaya (eds.), Elsevier Science Ltd, Oxford, UK.

Rubin, E.S., 2001: *Introduction to Engineering and the Environment*. McGraw-Hill, Boston, MA, 701 p.

Rubin, E.S., A.B. Rao, and C. Chen, 2005: Comparative Assessments of Fossil Fuel Power Plants with CO_2 Capture and Storage. Proceedings of 7th International Conference on Greenhouse Gas Control Technologies, Volume 1: Peer-Reviewed Papers and Overviews, E.S. Rubin, D.W. Keith and C.F. Gilboy (eds.), Elsevier Science, Oxford, UK, 285-294.

Rubin, E.S., D.A. Hounshell, S. Yeh, M. Taylor, L. Schrattenholzer, K. Riahi, L. Barreto, and S. Rao, 2004b: The Effect of Government Actions on Environmental Technology Innovation: Applications to the Integrated Assessment of Carbon Sequestration Technologies, Final Report of Award No. DE-FG02-00ER63037 from Carnegie Mellon University, Pittsburgh, PA to Office of Biological and Environmental Research, U.S. Department of Energy, Germantown, MD, January, 153 p.

Rubin, E.S., S. Yeh, D.A. Hounshell, and M.R. Taylor, 2004a: Experience Curves for Power Plant Emission Control Technologies, *International Journal of Energy Technology and Policy*, **2**, No.1/2, 52-68, 2004.

Ruthven, D.M., S. Farooq, and K.S. Knaebel, 1994: Pressure Swing Adsorption. VCH, New York, 352 pp.

Sander, M.T., C.L. Mariz, 1992: The Fluor Daniel® Econamine™ FG Process: Past Experience and Present Day Focus, *Energy Conversion Management*, **33**(5-8), 341-348.

Shilling, N. and R. Jones, 2003: The Response of Gas Turbines to a CO_2 Constrained Environment Paper Presented at the Gasification Technology Conference, October 2003, San Francisco, CA, USA, Available at www.gasfication.org.

Shimizu, T, T. Hirama, H. Hosoda, K. Kitano, M. Inagaki, and K. Tejima, 1999: A Twin Fluid-Bed Reactor for removal of CO_2 from combustion processes. *IChemE.*, **77**- A, 62-70.

Sikdar, S.K. and U. Diwekar (eds.), 1999: Tools and Methods for

Pollution Prevention. Proceedings of NATO Advanced Research Workshop. NATO Science Series, No. 2: Environmental Security - Vol. 62. Dordrecht: Kluwer. 12-14 October 1998, Prague, Czech Republic.

Simbeck, D.R., 1999: A portfolio selection approach for power plant CO_2 capture, separation and R&D options. Proceedings of the 4th International Conference on Greenhouse Gas Control Technologies, 30 Aug. - 2 Sept. 1998, Interlaken, Switzerland, B. Eliasson, P. Riemer and A. Wokaun (eds.), Elsevier Science Ltd., Oxford, UK.

Simbeck, D.R., 2001a: World Gasification Survey: Industrial Trends and Developments. Paper presented at the Gasification Technology Conference, San Francisco, CA, USA, October.www.gasfication.org.

Simbeck, D. R. and M. McDonald, 2001b: Existing coal power plant retrofit CO_2 control options analysis, Greenhouse Gas Control Technologies, Proceedings of the 5th International Conference on Greenhouse Gas Control Technologies, 13-16 Aug. 2000, Cairns, Australia, D. Williams et al. (eds.), CSIRO Publishing, Collingwood, Vic., Australia.

Simbeck, D.R., 2002: New power plant CO_2 mitigation costs, SFA Pacific, Inc., Mountain View, California, April.

Simbeck, D.R., 2004: Overview and insights on the three basic CO_2 capture options, Third Annual Conference on Carbon Capture and Sequestration, Alexandria, Virginia, May.

Simbeck, D.R., 2005: Hydrogen Costs with CO_2 Capture. M. Wilson, T. Morris, J. Gale and K. Thambimuthu (eds.): Proceedings of 7th International Conference on Greenhouse Gas Control Technologies. Volume II: Papers, Posters and Panel Discussion, Elsevier Science, Oxford UK, 1059-1066.

Singh, D., E. Croiset, P.L. Douglas and M.A. Douglas, 2003: Techno-economic study of CO_2 capture from an existing coal-fired power plant: MEA scrubbing vs. O_2/CO_2 recycle combustion. *Energy Conversion and Management*, **44,** p. 3073-3091.

Sircar, S., 1979: Separation of multi-component gas mixtures, US Patent No. 4171206, October 16th.

Sircar, S., C.M.A. Golden, 2001: PSA process for removal of bulk carbon dioxide from a wet high-temperature gas. US Patent No. 6322612.

Skinner, S.J.and J.A. Kilner, 2003: Oxygen ion conductors. *Materials Today*, **6**(3), 30-37.

Stobbs, R. and Clark, P., 2005: Canadian Clean Power Coalition: The Evaluation of Options for CO_2 Capture From Existing and New Coal-Fired Power Plants, In, Wilson, M., T. Morris, J. Gale and K. Thambimuthu (eds.), Proceedings of 7th International Conference on Greenhouse Gas Control Technologies. Volume II: Papers, Posters and Panel Discussion, Elsevier Science, Oxford, UK, 1187-1192.

Sundnes, A., 1998: Process for generating power and/or heat comprising a mixed conducting membrane reactor. International patent number WO98/55394 Dec. 1998.

Tabe-Mohammadi, A., 1999**:** A review of the application of membrane separation technology in natural gas treatment, *Sep. Sci. & Tech.*, **34**(10), 2095-2111.

Takamura, Y. Y. Mori, H. Noda, S. Narita, A. Saji, S. Uchida, 1999: Study on CO_2 Removal Technology from Flue Gas of Thermal Power Plant by Combined System with Pressure Swing Adsorption and Super Cold Separator. Proceedings of the 5th International Conference on Greenhouse Gas Control Technologies, 13-16 Aug. 2000, Cairns, Australia, D. Williams et al. (eds.), CSIRO Publishing, Collingwood, Vic., Australia.

Tan, Y., M.A., Douglas, E. Croiset, and K.V. Thambimuthu, 2002: CO_2 Capture Using Oxygen Enhanced Combustion Strategies for Natural Gas Power Plants, *Fuel*, **81**, 1007-1016.

Teramoto, M., K. Nakai, N. Ohnishi, Q. Huang, T. Watari, H. Matsuyama, 1996: Facilitated transport of carbon dioxide through supported liquid membranes of aqueous amine solutions, *Ind. Eng. Chem.,* **35**, 538-545.

Todd, D.M. and Battista, R.A., 2001: Demonstrated Applicability of Hydrogen Fuel for Gas Turbines, 4th European Gasification Conference 11-13th April, Noordwijk Netherlands.

Van der Sluijs, J.P, C.A. Hendriks, and K. Blok, 1992: Feasibility of polymer membranes for carbon dioxide recovery from flue gases, *Energy Conversion Management,* **33**(5-8), 429-436.

Von Bogdandy, L., W. Nieder, G. Schmidt, U. Schroer, 1989: Smelting reduction of iron ore using the COREX process in power compound systems. *Stahl und Eisen,* **109**(9,10), p 445.

Wabash River Energy Ltd., 2000: Wabash River Coal Gasification Repowering Project, Final Technical Report to the National Energy Technology Laboratory, US Department of Energy, August.

Wang, J., E.J. Anthony, J.C. Abanades, 2004: Clean and efficient use of petroleum coke for combustion and power generation. *Fuel,* **83**, 1341-1348.

Wilkinson, M.B. and Clarke, S.C., 2002: Hydrogen Fuel Production: Advanced Syngas Technology Screening Study.14th World Hydrogen Energy Conference, June 9-14, 2002, Montreal, Canada.

Wilkinson, M.B., J.C. Boden, T. Gilmartin, C. Ward, D.A. Cross, R.J. Allam, and N.W. Ivens, 2003b: CO_2 capture from oil refinery process heaters through oxy-fuel combustion, Greenhouse Gas Control Technologies, Proc. of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), 1-4 Oct. 2002, Kyoto, Japan, J. Gale and Y. Kaya (eds.), Elsevier Science Ltd, Oxford, UK. 69-74.

Wilkinson, M.B., M. Simmonds, R.J. Allam, and V. White, 2003a: Oxy-fuel conversion of heaters and boilers for CO_2 capture, 2nd Annual Conf on Carbon Sequestration, Virginia (USA), May 2003.

Williams, R.H. (Convening Lead Author), 2000: Advanced energy supply technologies, Chapter 8, 274-329, in *Energy and the Challenge of Sustainability - the World Energy Assessment World Energy Assessment*, 508 pp., UN Development Programme, New York.

World Bank, 1999: Pollution Prevention and Abatement Handbook: Toward Cleaner Production. Washington: The World Bank Group in collaboration with United Nations Industrial Development Organization and United Nations Environment Programme.

Yantovskii, E.I., K.N. Zvagolsky, and V.A. Gavrilenko**,** 1992**:** Computer exergonomics of power plants without exhaust gases *Energy Conversion and Management,* **33**, No. 5-8, 405-412.

Yokoyama, T., 2003: Japanese R&D on CO_2 Capture. Greenhouse Gas Control Technologies, Proc. of the 6th International Conference on

Greenhouse Gas Control Technologies (GHGT-6), 1-4 Oct. 2002, Kyoto, Japan, J. Gale and Y. Kaya (eds.), Elsevier Science Ltd, Oxford, UK. 13-18.

Zafar, Q., T. Mattisson, and B. Gevert, 2005: Integrated Hydrogen and Power Production with CO_2 Capture Using Chemical-Looping Reforming-Redox Reactivity of Particles of CuO, Mn_2O_3, NiO, and Fe_2O_3 Using SiO_2 as a Support, *Industrial and Engineering Chemistry Research,* **44**(10), 3485-3496.

Zheng, X.Y, Y.-F. Diao, B.-S. He, C.-H. Chen, X.-C. Xu, and W. Feng, 2003: Carbon Dioxide Recovery from Flue Gases by Ammonia Scrubbing. Greenhouse Gas Control Technologies, Proc. of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), 1-4 Oct. 2002, Kyoto, Japan, J. Gale and Y. Kaya (eds.), Elsevier Science Ltd, Oxford, UK. 193-200.

4

Transport of CO_2

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Contents

EXECUTIVE SUMMARY

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

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

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

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

4.1 Introduction

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

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

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

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

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

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

4.2 Pipeline systems

4.2.1 *Pipeline transportation systems*

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

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

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

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

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

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

4.2.2 *Existing experience*

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

4.2.2.1 Canyon Reef

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

4.2.2.2 Bravo Dome Pipeline

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

4.2.2.3 Cortez Pipeline

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

Box 4.1 Specimen CO_2 quality specifications

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

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

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

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

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

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

4.2.2.4 Sheep Mountain Pipeline

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

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

4.2.2.5 Weyburn Pipeline

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

4.2.3 Design

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

Conceptual design

The conceptual design includes the following components:

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

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

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

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

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

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

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

4.2.4 Construction of land pipelines

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

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

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

4.2.5 Underwater pipelines

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

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

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

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

4.2.6 Operations

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

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

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

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

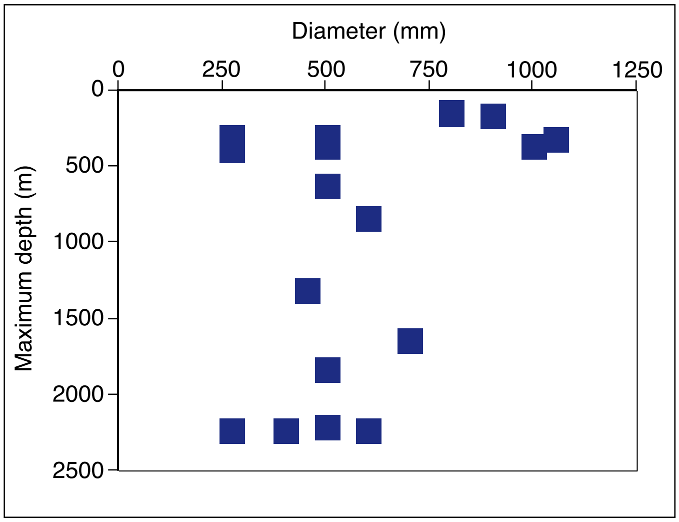

Figure 4.2 Pipelines in deep water.

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

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

4.3 Ships for CO_2 transportation

4.3.1 Marine transportation system

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

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

4.3.2 Existing experience

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

4.3.3 Design

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

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

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

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

4.3.4 Construction

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

4.3.5 Operation

4.3.5.1 Loading

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

4.3.5.2 Transport to the site

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

4.3.5.3 Unloading

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

4.3.5.4 Return to port in ballast, and dry-docking

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

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

4.4 Risk, safety and monitoring

4.4.1 Introduction

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

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

4.4.2 Land pipelines

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

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

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

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

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

Gale and Davison (2002) quote incident statistics for CO_2

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

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

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

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

4.4.3 Marine pipelines

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

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

4.4.4 Ships

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

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

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

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

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

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

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

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

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

4.5 Legal issues, codes and standards

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

4.5.1 International conventions

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

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

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

4.5.2 National codes and standards

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

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

4.6 Costs

4.6.1 Costs of pipeline transport

The costs of pipelines can be categorized into three items

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

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

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

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

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

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

4.6.2 Costs of marine transportation systems

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

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

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

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

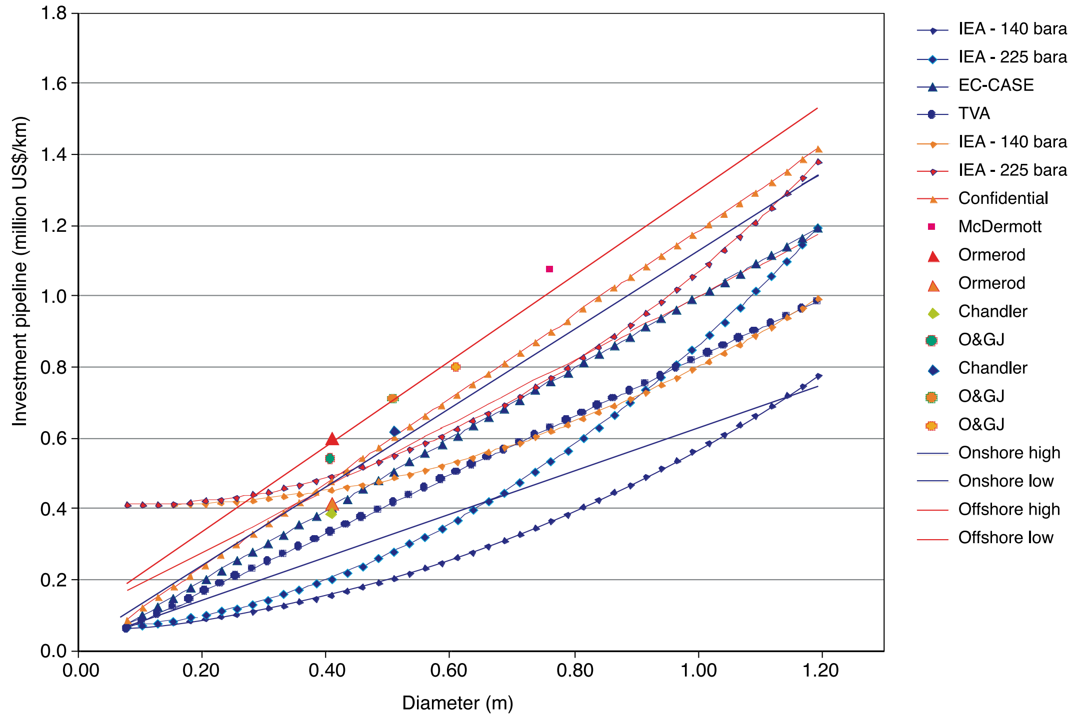

Figure 4.3 Total investment costs for pipelines from various information sources for offshore and onshore pipelines. Costs exclude possible booster stations (IEA GHG, 2002; Hendriks et al., 2005; Bock, 2003; Sarv, 2000; 2001a; 2001b; Ormerod, 1994; Chandler, 2000; O&GJ, 2000).

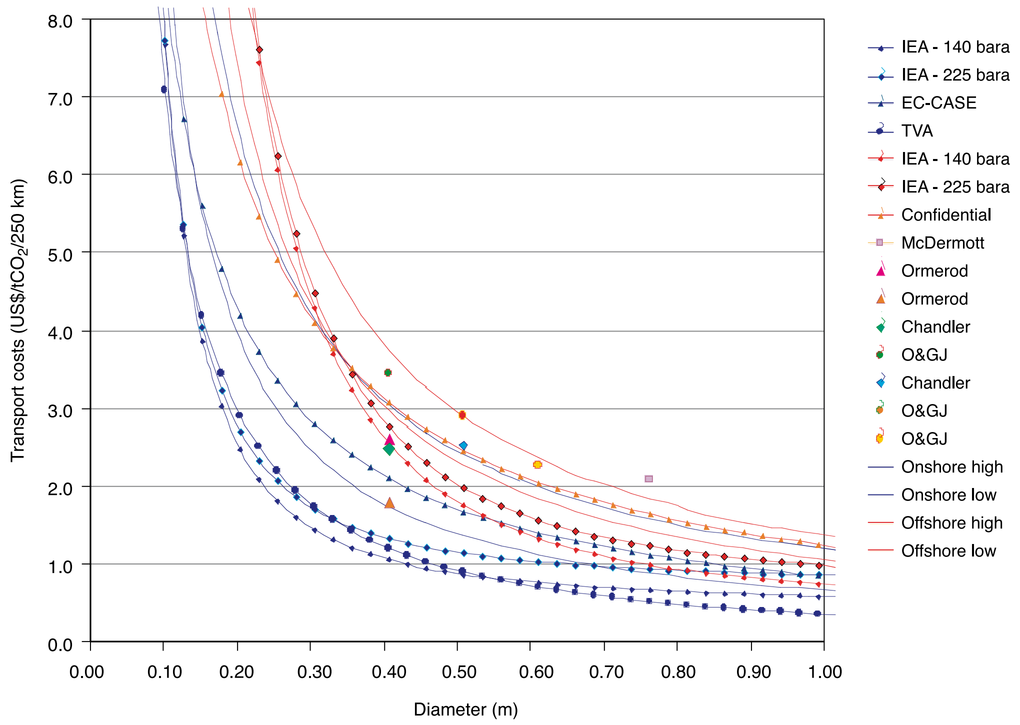

Figure 4.4 Transport costs derived from various information sources for offshore and onshore pipelines. Costs exclude possible booster stations, applying a capital charge rate of 15% and a load factor of 100% (IEA GHG, 2002; Hendriks et al., 2005; Bock, 2003; Sarv, 2000; 2001a; 2001b; Ormerod, 1994;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

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

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

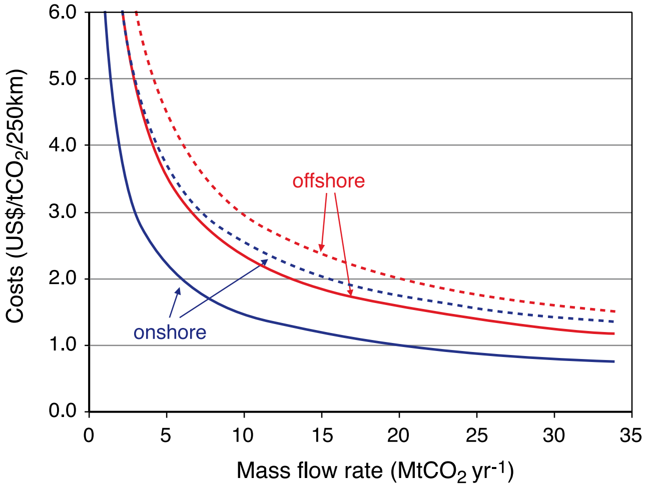

Figure 4.5 Transport costs for onshore and offshore pipelines per 250 km. High (broken lines) and low range (continuous lines) are indicated.

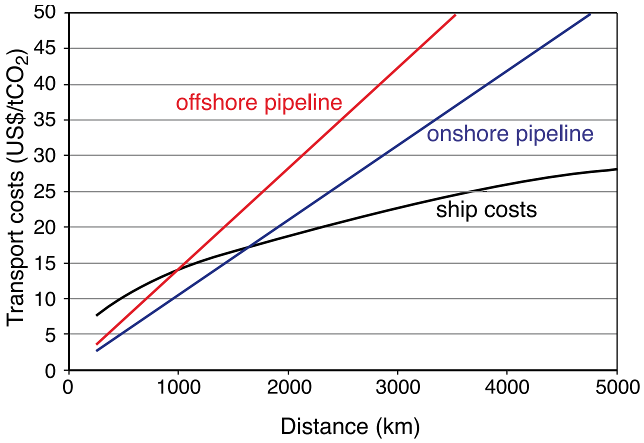

Figure 4.6 Costs, plotted as transportation cost in US$/t$CO_2$ against distance, for onshore and offshore pipelines, and ship transport. The costs include intermediate storage facilities, harbour fees, fuel costs and loading/unloading activities. Costs also include additional costs for liquefaction compared to compression. There is a capital charge factor of 11% for all transport options.

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

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

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

References

Bock, B.R., R. Rhudy, H. Herzog, M. Klett, J. Davison, D.G. de la Torre Ugarte, and D. Simbeck, 2003: Economic Evaluation of CO_2 Storage and Sink Enhancement Options. TVA Public Power Institute, February 2003.

Chandler, H.M. 2000: Heavy Construction Cost Data - 14th Annual Editions. R.S. Means Company, Inc. Kingston, MA, USA.

Concawe, 2002: Western European cross-country oil pipelines 30-year performance statistics, CONCAWE report.

European Gas Pipeline Incident Data Group, 2002: 5th EGIG report 1970-2001 Gas Pipeline Incidents, document EGIG 02.R.0058.

Ffooks, R., 1993: *Natural gas by sea, the development of a new technology.* Royal Institution of Naval Architects, London.

Gale, J. and J. Davison, 2002: Transmission of CO_2 - safety and economic considerations. GHGT-6.

Gottschalch, H. and M. Stadler, 1990: Seefahrtspsychologie (Psychology of navigation). Kasing, Bielefeld.

Guijt, W., 2004: Analyses of incident data show US, European pipelines becoming safer. *Oil and Gas Journal,* January 26, pp.68-73.

Hendriks, C.A., T. Wildenborg, P. Feron, and W. Graus, 2005: Capture and Storage, prepared for EC, DG-ENV, Ecofys Energy and Environment, report nr. M70066.

IEA GHG, 2002: Transmission of CO_2 and Energy, IEA Greenhouse Gas R&D Programme, Report PH4/6, IEA GHG, Cheltenham, UK (March).

IEA GHG, 2003a: Review of International Conventions having Implications for the Storage of Carbon Dioxide in the Ocean and Beneath the Seabed, Report PH4/16, IEA GHG, Cheltenham, UK, 1641 pp.

IEA GHG, 2003b: Barriers to Overcome in Implementation of CO_2 Capture and Storage (2): Rules and Standards for Transmission and Storage of CO_2, Report PH4/23, IEA GHG, Cheltenham, UK, 165 pp.

IEA GHG, 2004: Ship Transport of CO_2, Report PH4/30, IEA GHG, Cheltenham, UK, July 2004-11-16.

Katz, D.L., 1959: Handbook of natural gas engineering. McGraw-Hill, New York, 802 pp.

Lelieveld, J., S. Lechtenböhmer, S.S. Assonov, C.A.M. Brenninkmeijer, C. Dienst, M. Fischedick, and T. Hanke, 2005: Low methane leakage from gas pipelines. *Nature*, **434**, 841-842.

Morris, D. and K. Breaux, 1995: Proceedings of the International Workshop on Damage to Underwater Pipelines, New Orleans, LA, Minerals Management Service.

O&GJ, 2000: Pipeline Economics. *Oil and Gas Journal*, **98**(36), 68-86.

Ormerod, B., 1994: The disposal of carbon dioxide from fossil fuel fired power stations. IEA Greenhouse Gas R&D Programme, Cheltenham, Technical Rep. IEAGHG/SR3, June 1994.

Palmer, A.C. and R.A. King, 2004: Subsea pipeline engineering. Pennwell, Tulsa, OK.

Perrow, C., 1984: Normal accidents. Basic Books, 386 pp.

Rogers, G.F.C. and Y.R. Mayhew, 1980: Engineering thermodynamics and heat transfer. Longman, New York.

Sarv, H. and J. John, 2000: Deep ocean sequestration of captured CO_2. *Technology,* **7S**, 125-135.

Sarv, H., 2001a: Further Technological Evaluation of CO_2 Storage in Deep Oceans. Presented at the 26th International Technical Conference on Coal Utilisation & Fuel Systems, March 5-8, 2001, Clearwater, Florida.

Sarv, H., 2001b: Large-scale CO_2 transportation and deep ocean sequestration - Phase II final report. McDermott Technology Inc., Ohio. Technology Report DE-AC26-98FT40412, 2001.

Seiersten, M., 2001: Material selection for separation, transportation and disposal of CO_2. Proceedings Corrosion 2001, National Association of Corrosion Engineers, paper 01042.

Statoil, 2004: Written communication – O. Kaarstad, Trondheim, Norway, January.

UK Department of Trade and Industry, 2002: Carbon Capture and Storage, report of DTI International Technology Service Mission to the USA and Canada, Advanced Power Generation Technology Forum.

United Nations Environment Programme (UNEP), 2000: Text of the Basel Convention and Decisions of the Conference of the Parties (COP 1 to 5), United Nations Publications, Switzerland.

United Nations, 2001: Recommendations on the Transport of Dangerous Goods: Model Regulations, Twelfth Edition, United Nations Publications ST/SG/AC.10/Rev12, United Nations, New York and Geneva, 732 pp.

Van Bernem, C. and T. Lubbe, 1997: Ől im Meer (Oil in the sea) Wissenschaftliche Buchgesellschaft, Darmstadt.

Vendrig, M., J. Spouge, A. Bird, J. Daycock, and O. Johnsen, 2003: Risk analysis of the geological sequestration of carbon dioxide, Report no. R, Department of Trade and Industry, London, UK.

Veritec, 1988: On-bottom stability design of submarine pipelines. Recommended Practice E305.

West, J.M., 1974: Design and operation of a supercritical CO_2 pipeline-compression system, SACROC unit, Scurry County, Texas. Society of Petroleum Engineers Permian Basin Oil and Gas Recovery Conference, paper SPE 4804.

5

Underground geological storage

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EXECUTIVE SUMMARY

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

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

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

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

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

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

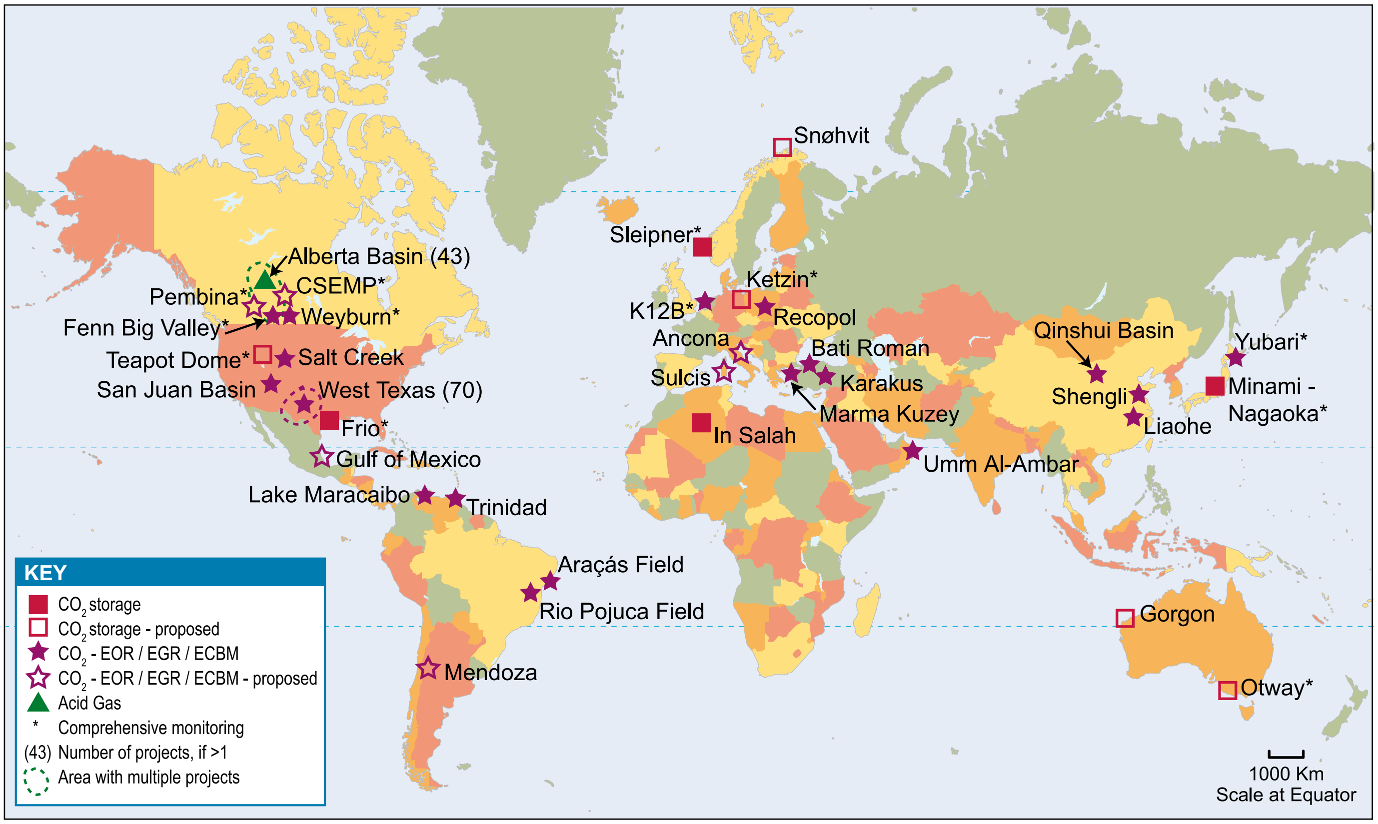

Figure 5.1 Location of sites where activities relevant to CO_2 storage are planned or under way.

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

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

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

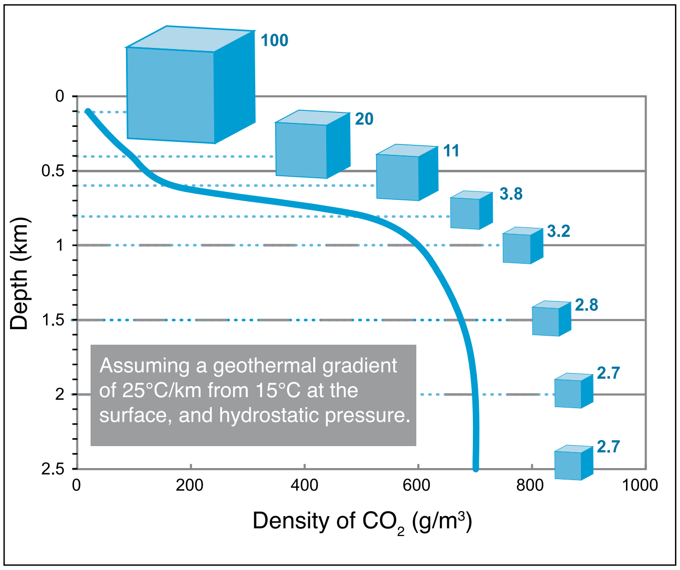

Figure 5.2 Variation of CO_2 density with depth, assuming hydrostatic pressure and a geothermal gradient of 25°C km^{-1} from 15°C at the surface (based on the density data of Angus *et al.*, 1973). Carbon dioxide density increases rapidly at approximately 800 m depth, when the CO_2 reaches a supercritical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

5.1 Introduction

5.1.1 *What is geological storage?*

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

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

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

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

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

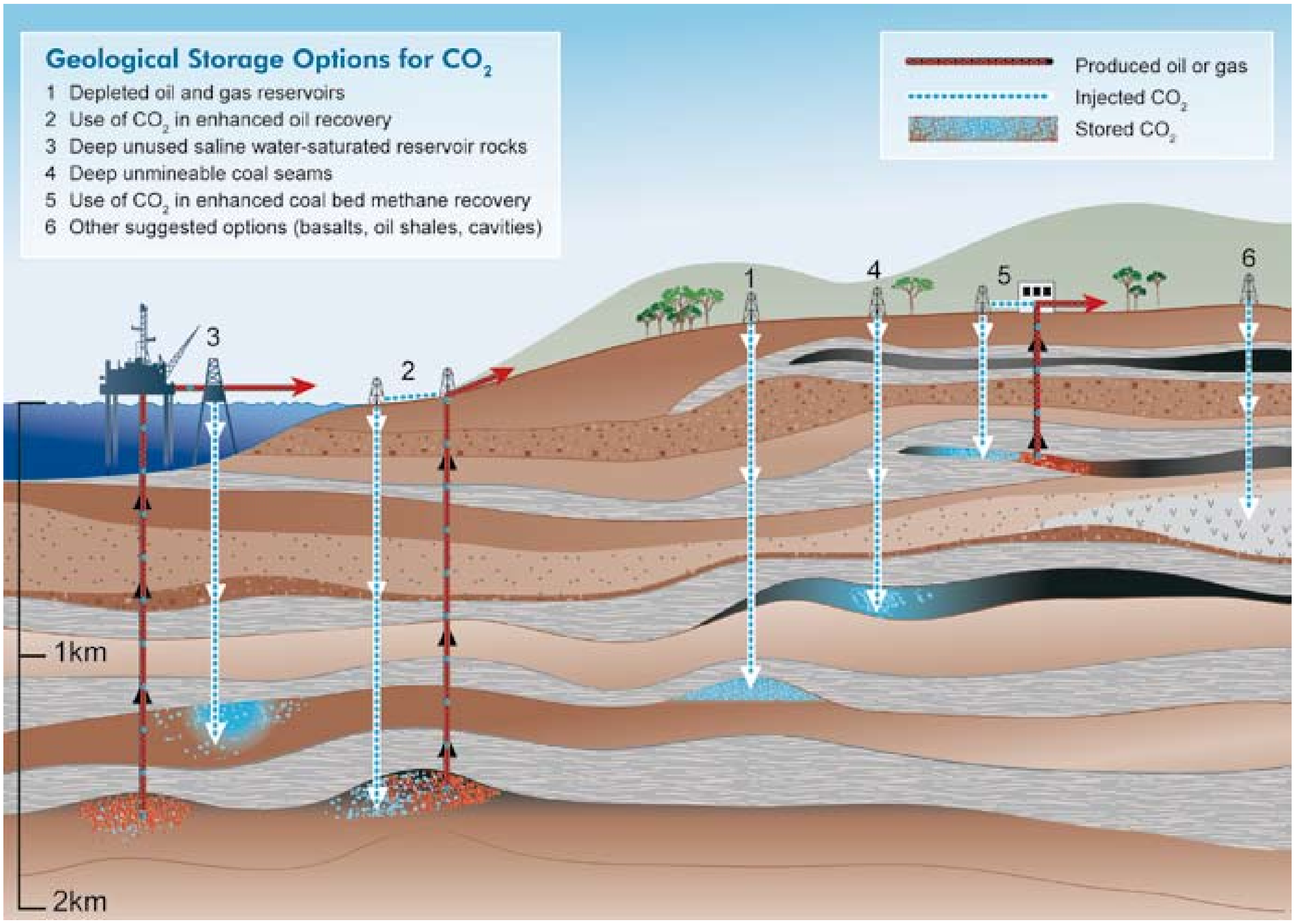

Figure 5.3 Options for storing CO_2 in deep underground geological formations (after Cook, 1999).

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

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

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

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

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

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

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

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

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

5.1.2 Existing and planned CO_2 projects

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

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

Project	Country	Scale of Project	Lead organizations	Injection start date	Approximate average daily injection rate	Total storage	Storage type	Geological storage formation	Age of formation	Lithology	Monitoring
Sleipner	Norway	Commercial	Statoil, IEA	1996	3000 t day^{-1}	20 Mt planned	Aquifer	Utsira Formation	Tertiary	Sandstone	4D seismic plus gravity
Weyburn	Canada	Commercial	EnCana, IEA	May 2000	3-5000 t day^{-1}	20 Mt planned	CO$_2$-EOR	Midale Formation	Mississippian	Carbonate	Comprehensive
Minami-Nagoaka	Japan	Demo	Research Institute of Innovative Technology for the Earth	2002	Max 40 t day^{-1}	10,000 t planned	Aquifer (Sth. Nagoaka Gas Field)	Haizume Formation	Pleistocene	Sandstone	Crosswell seismic + well monitoring
Yubari	Japan	Demo	Japanese Ministry of Economy, Trade and Industry	2004	10 t day^{-1}	200 t Planned	CO$_2$-ECBM	Yubari Formation (Ishikari Coal Basin)	Tertiary	Coal	Comprehensive
In Salah	Algeria	Commercial	Sonatrach, BP, Statoil	2004	3-4000 t day^{-1}	17 Mt planned	Depleted hydrocarbon reservoirs	Krechba Formation	Carboniferous	Sandstone	Planned comprehensive
Frio	USA	Pilot	Bureau of Economic Geology of the University of Texas	4-13 Oct. 2004	Approx. 177 t day^{-1} for 9 days	1600t	Saline formation	Frio Formation	Tertiary	Brine-bearing sandstone-shale	Comprehensive
K12B	Netherlands	Demo	Gaz de France	2004	100-1000 t day^{-1} (2006+)	Approx 8 Mt	EGR	Rotleigendes	Permian	Sandstone	Comprehensive
Fenn Big Valley	Canada	Pilot	Alberta Research Council	1998	50 t day^{-1}	200 t	CO$_2$-ECBM	Mannville Group	Cretaceous	Coal	P, T, flow
Recopol	Poland	Pilot	TNO-NITG (Netherlands)	2003	1 t day^{-1}	10 t	CO$_2$-ECBM	Silesian Basin	Carboniferous	Coal	
Qinshui Basin	China	Pilot	Alberta Research Council	2003	30 t day^{-1}	150 t	CO$_2$-ECBM	Shanxi Formation	Carboniferous-Permian	Coal	P, T, flow
Salt Creek	USA	Commercial	Anadarko	2004	5-6000 t day^{-1}	27 Mt	CO$_2$-EOR	Frontier	Cretaceous	Sandstone	Under development
Planned Projects (2005 onwards)											
Snøhvit	Norway	Decided Commercial	Statoil	2006	2000 t day^{-1}		Saline formation	Tubaen Formation	Lower Jurassic	Sandstone	Under development
Gorgon	Australia	Planned Commercial	Chevron	Planned 2009	Approx. 10,000 t day^{-1}		Saline formation	Dupuy Formation	Late Jurassic	Massive sandstone with shale seal	Under development
Ketzin	Germany	Demo	GFZ Potsdam	2006	100 t day^{-1}	60 kt	Saline formation	Stuttgart Formation	Triassic	Sandstone	Comprehensive
Otway	Australia	Pilot	CO2CRC	Planned late 2005	160 t day^{-1} for 2 years	0.1 Mt	Saline fm and depleted gas field	Waarre Formation	Cretaceous	Sandstone	Comprehensive
Teapot Dome	USA	Proposed Demo	RMOTC	Proposed 2006	170 t day^{-1} for 3 months	10 kt	Saline fm and CO$_2$-EOR	Tensleep and Red Peak Fm	Permian	Sandstone	Comprehensive
CSEMP	Canada	Pilot	Suncor Energy	2005	50 t day^{-1}	10 kt	CO$_2$-ECBM	Ardley Fm	Tertiary	Coal	Comprehensive
Pembina	Canada	Pilot	Penn West	2005	50 t day^{-1}	50 kt	CO$_2$-EOR	Cardium Fm	Cretaceous	Sandstone	Comprehensive

storage projects are also listed in Table 5.1.

At the In Salah Gas Field in Algeria, Sonatrack, BP and Statoil inject CO$_2$ stripped from natural gas into the gas reservoir outside the boundaries of the gas field (Box 5.2). Statoil is planning another project in the Barents Sea, where CO$_2$ from the Snohvit field will be stripped from the gas and injected into a geological formation below the gas field. Chevron is proposing to produce gas from the Gorgon field off Western Australia, containing approximately 14% CO$_2$. The CO$_2$ will be injected into the Dupuy Formation at Barrow Island (Oen, 2003). In The Netherlands, CO$_2$ is being injected at pilot scale into the almost depleted K12-B offshore gas field (van der Meer *et al*., 2005).

Forty-four CO$_2$-rich acid gas injection projects are currently operating in Western Canada, ongoing since the early 1990s (Bachu and Haug, 2005). Although they are mostly small scale, they provide important examples of effectively managing injection of CO$_2$ and hazardous gases such as H$_2$S (Section 5.2.4.2).

Box 5.1 The Sleipner Project, North Sea.

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

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

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

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

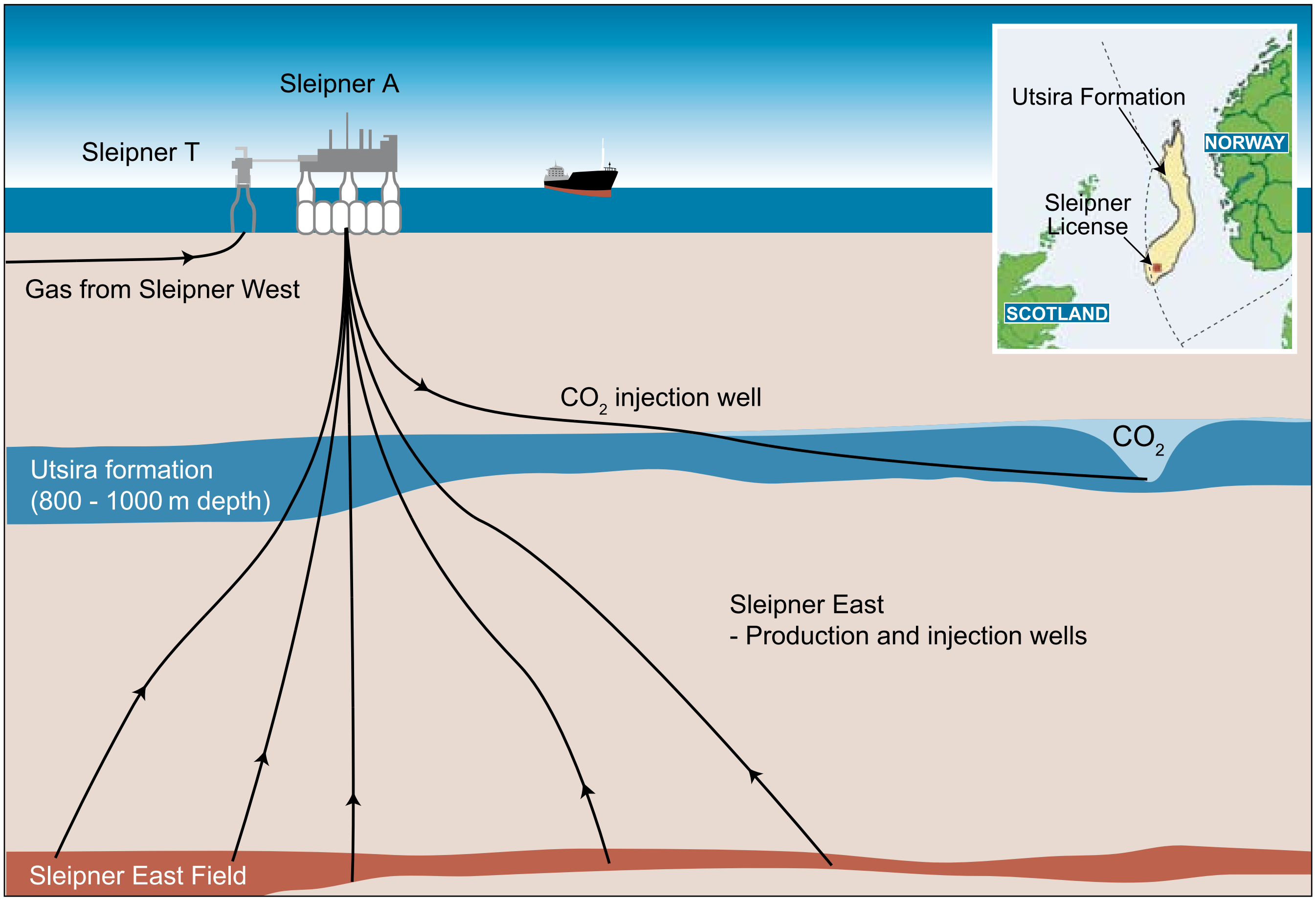

Figure 5.4 Simplified diagram of the Sleipner CO_2 Storage Project. Inset: location and extent of the Utsira formation.

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

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

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

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

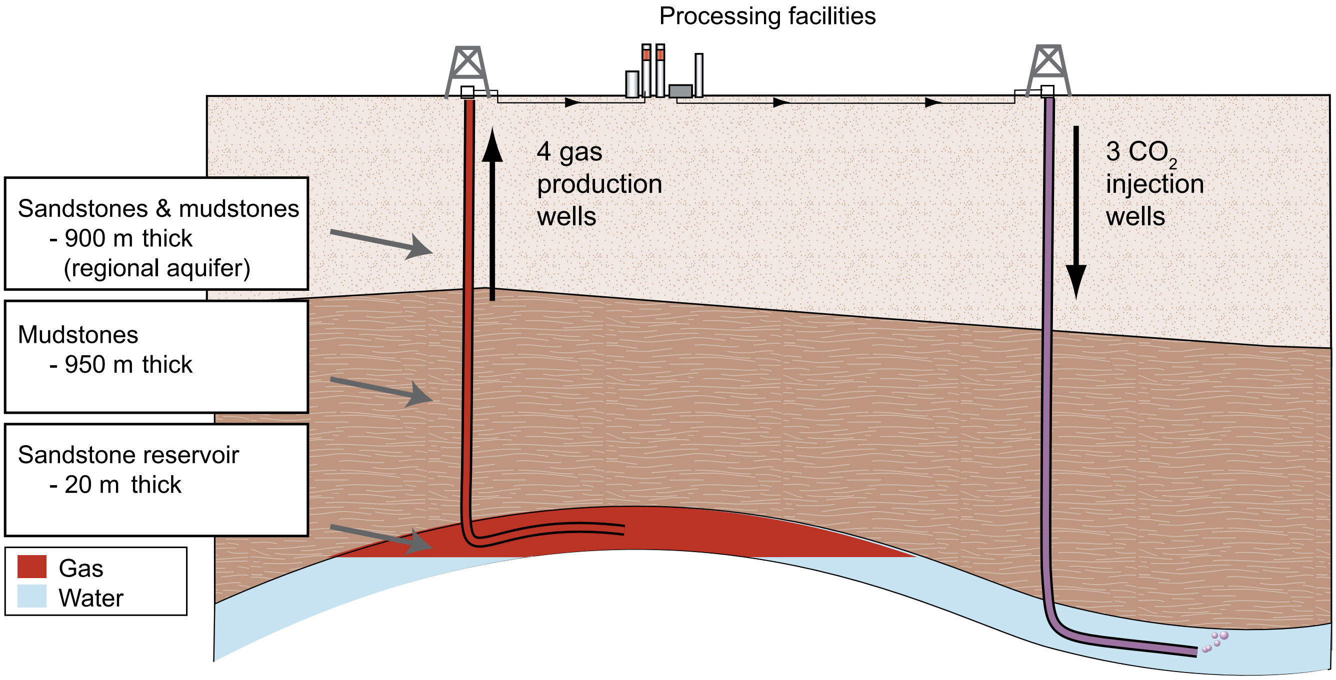

Figure 5.5 Schematic of the In Salah Gas Project, Algeria. One $MtCO_2$ will be stored annually in the gas reservoir. Long-reach horizontal wells with slotted intervals of up to 1.5 km are used to inject CO_2 into the water-filled parts of the gas reservoir.

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

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

Box 5.3 The Weyburn CO_2-EOR Project.

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

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

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

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

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

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

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

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

5.1.3 Key questions

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

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

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

The remainder of this chapter seeks to address these questions.

5.2 Storage mechanisms and storage security

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

5.2.1 CO_2 flow and transport processes

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

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

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

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

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

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

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

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

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

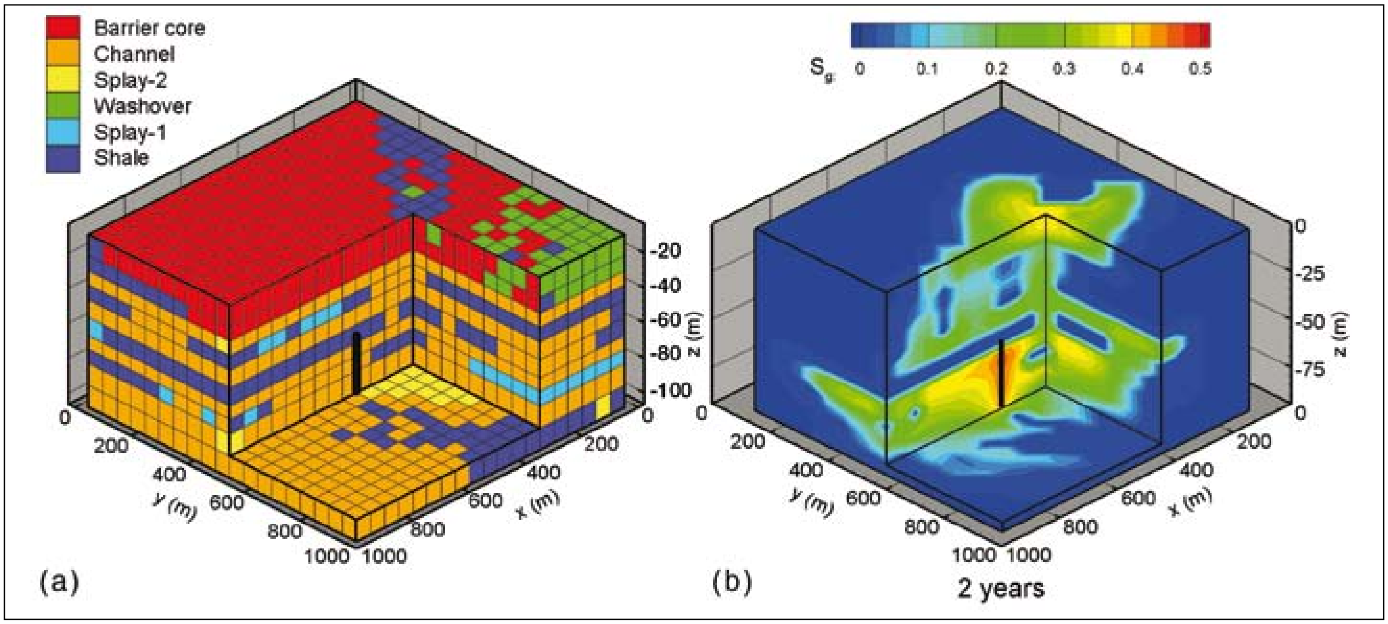

Figure 5.6 Simulated distribution of CO_2 injected into a heterogeneous formation with low-permeability layers that block upward migration of CO_2. (a) Illustration of a heterogeneous formation facies grid model. The location of the injection well is indicated by the vertical line in the lower portion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

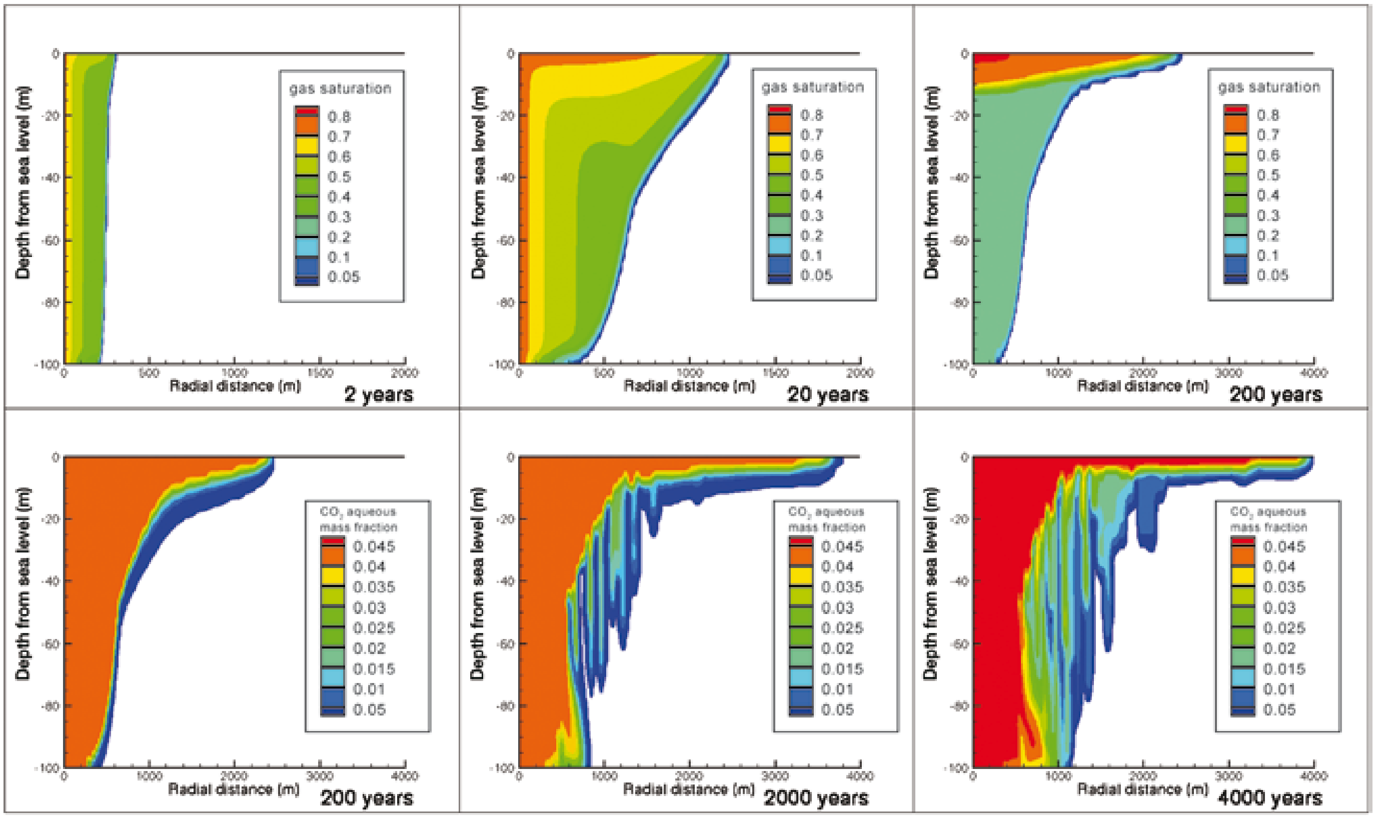

Figure 5.7 Radial simulations of CO_2 injection into a homogeneous formation 100 m thick, at a depth of 1 km, where the pressure is 10 MPa and the temperature is 40°C. The injection rate is 1 $MtCO_2\ yr^{-1}$ for 20 years, the horizontal permeability is $10^{-13}\ m^2$ (approximately 100 mD) and the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

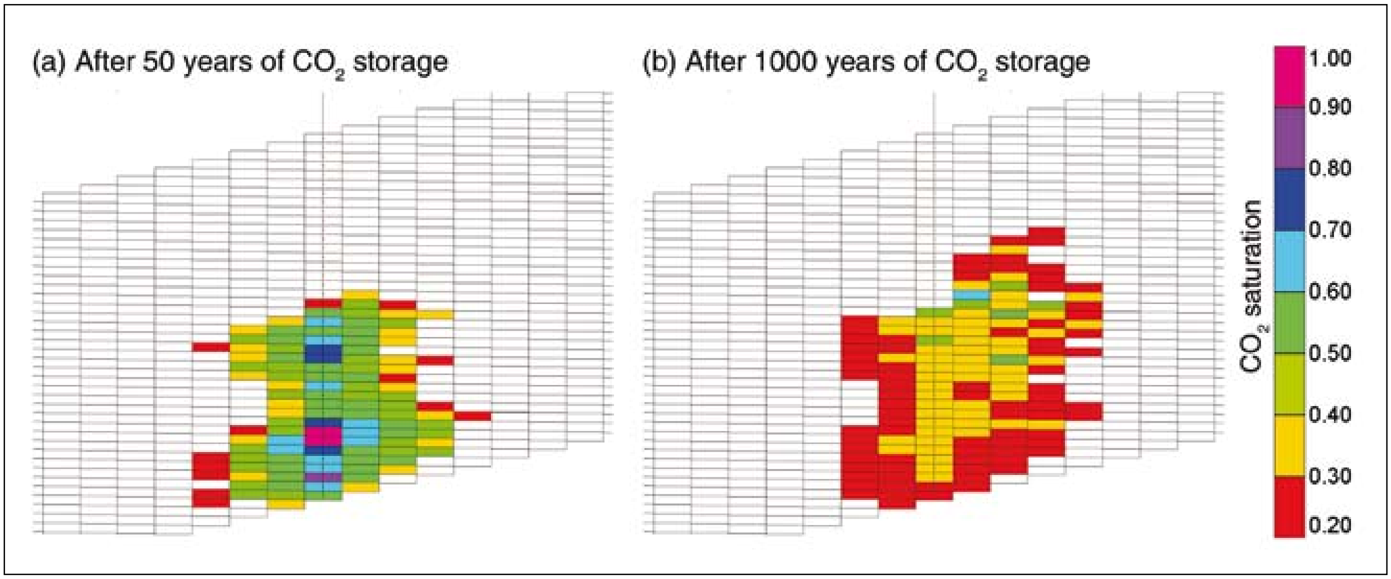

Figure 5.8 Simulation of 50 years of injection of CO_2 into the base of a saline formation. Capillary forces trap CO_2 in the pore spaces of sedimentary rocks. (a) After the 50-year injection period, most CO_2 is still mobile, driven upwards by buoyancy forces. (b) After 1000 years, buoyancy-driven flow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

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

5.2.2 CO_2 storage mechanisms in geological formations

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

5.2.2.1 Physical trapping: stratigraphic and structural

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

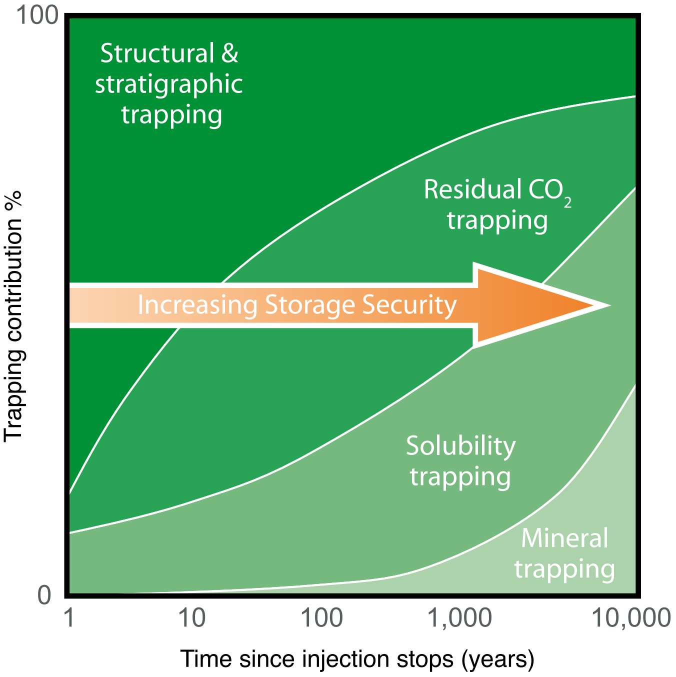

Figure 5.9 Storage security depends on a combination of physical and geochemical trapping. Over time, the physical process of residual CO_2 trapping and geochemical processes of solubility trapping and mineral trapping increase.

5.2.2.2 Physical trapping: hydrodynamic

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

5.2.2.3 Geochemical trapping

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

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

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

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

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

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

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

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

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

Box 5.4 Storage security mechanisms and changes over time.

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

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

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

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

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

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

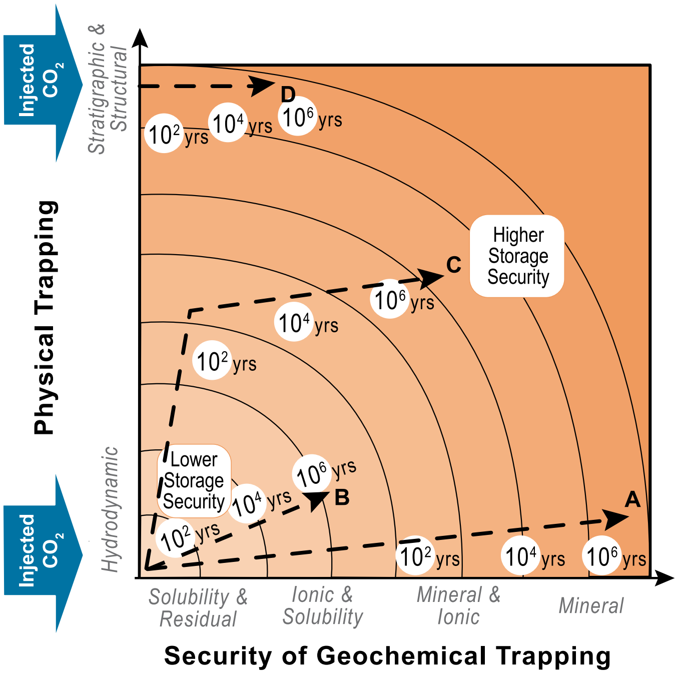

Figure 5.10 Storage expressed as a combination of physical and geochemical trapping. The level of security is proportional to distance from the origin. Dashed lines are examples of million-year pathways, discussed in Box 5.4.

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

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

5.2.3 Natural geological accumulations of CO_2

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

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

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

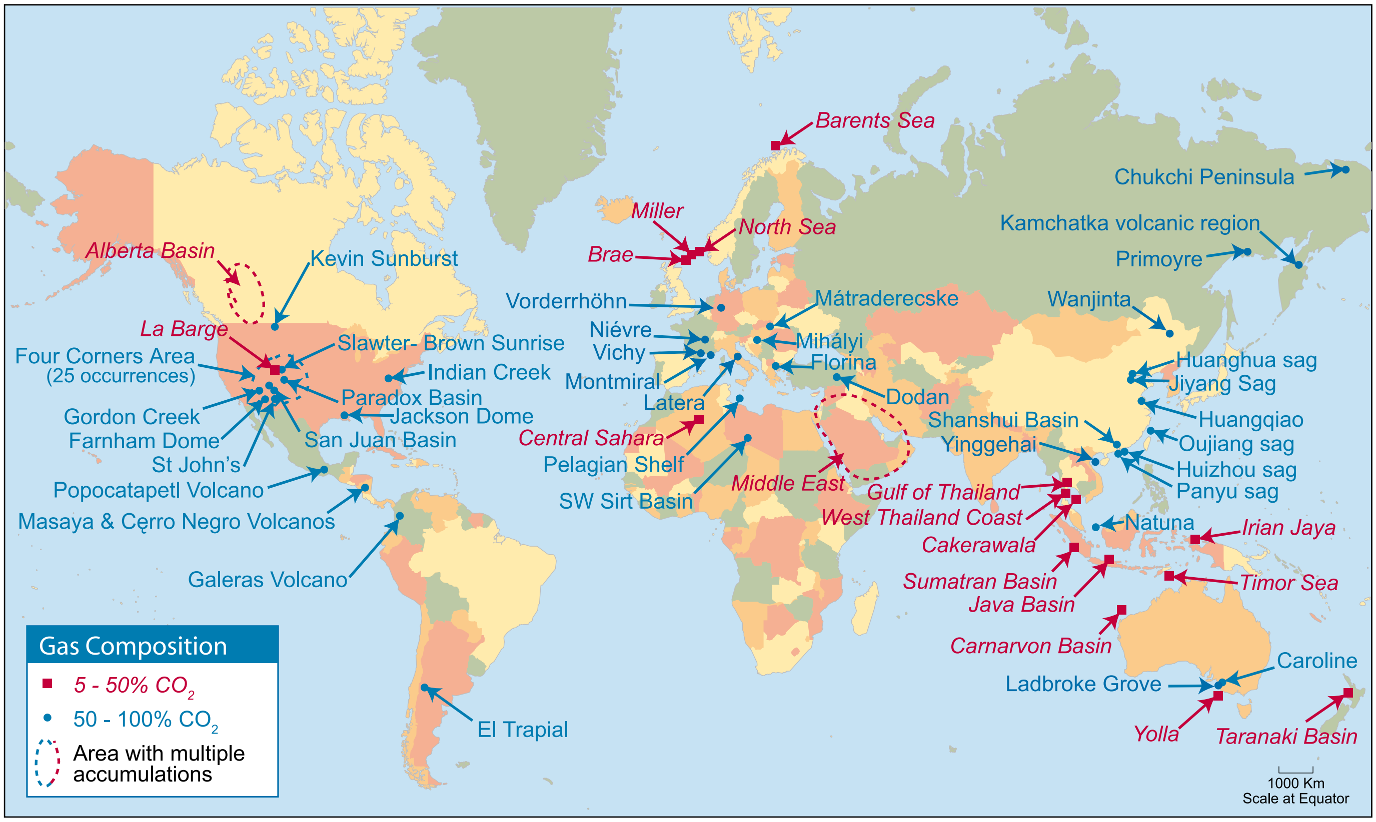

Figure 5.11 Examples of natural accumulations of CO_2 around the world. Regions containing many occurrences are enclosed by a dashed line. Natural accumulations can be useful as analogues for certain aspects of storage and for assessing the environmental impacts of leakage. Data quality is variable and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

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

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

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

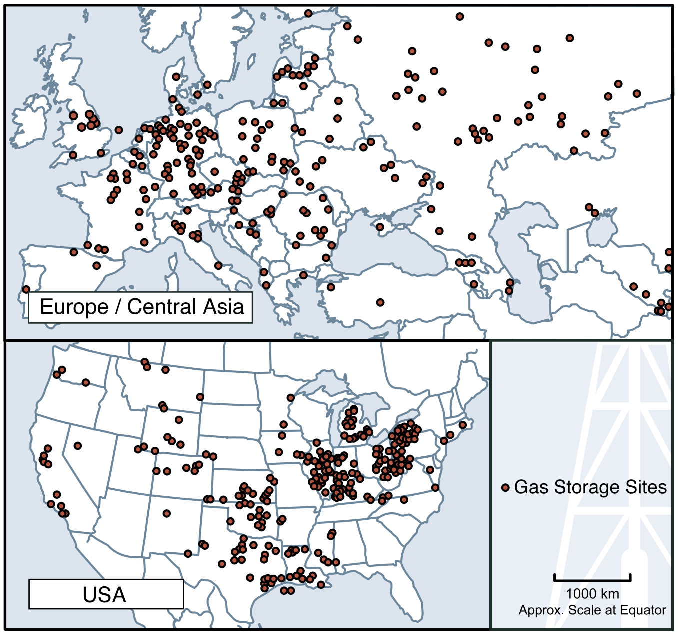

Figure 5.12 Location of some natural gas storage projects.

5.2.4 Industrial analogues for CO_2 storage

5.2.4.1 *Natural gas storage*

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

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

Box 5.5 The Berlin Natural Gas Storage Facility.

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

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

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

5.2.4.2 Acid gas injection

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

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

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

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

5.2.4.3 Liquid waste injection

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

5.2.5 Security and duration of CO_2 storage in geological formations

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

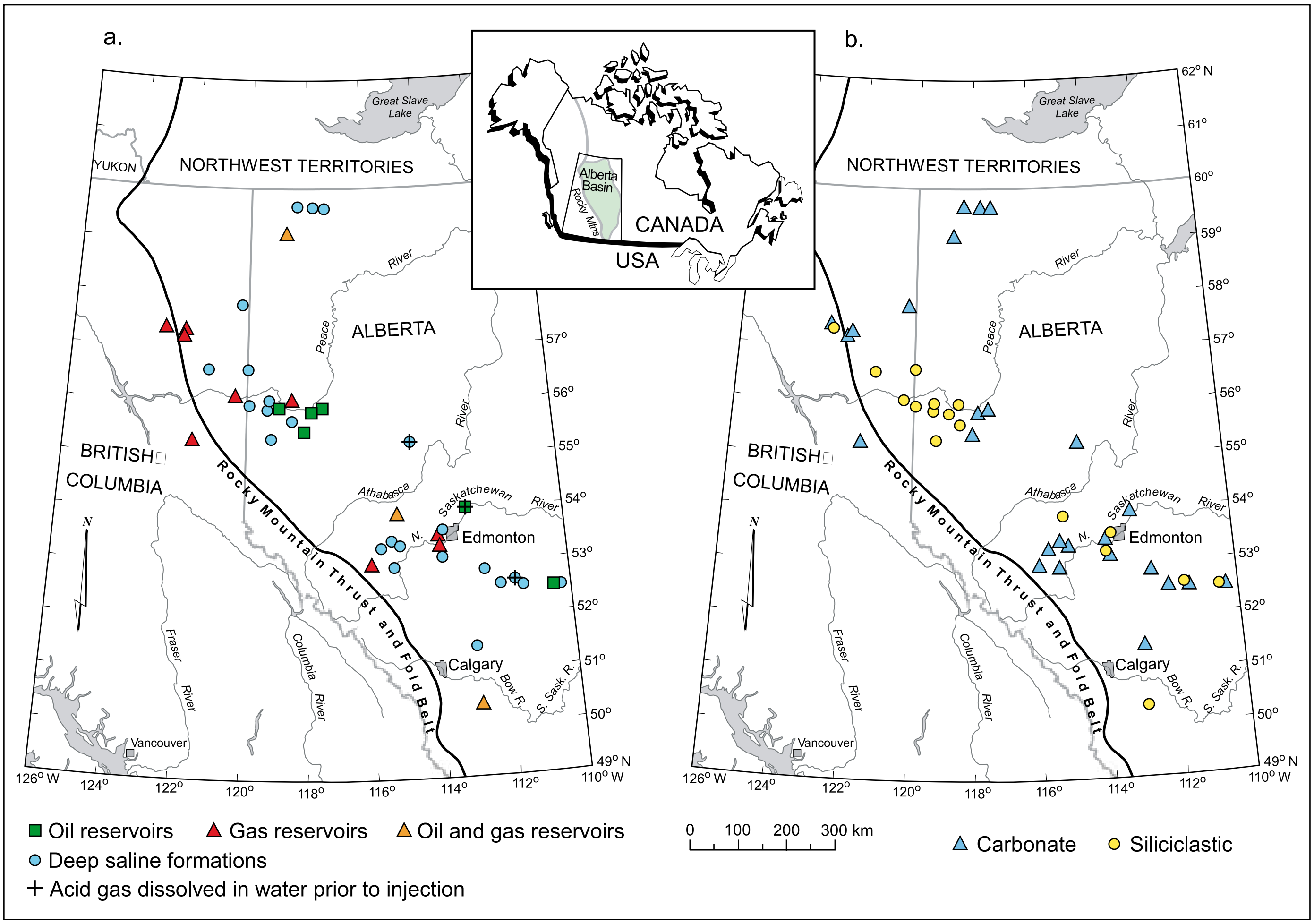

Figure 5.13 Locations of acid gas injection sites in the Alberta Basin, Canada: (a) classified by injection unit; (b) the same locations classified by rock type (from Bachu and Haug, 2005).

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

5.3 Storage formations, capacity and geographical distribution

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

5.3.1 General site-selection criteria

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

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

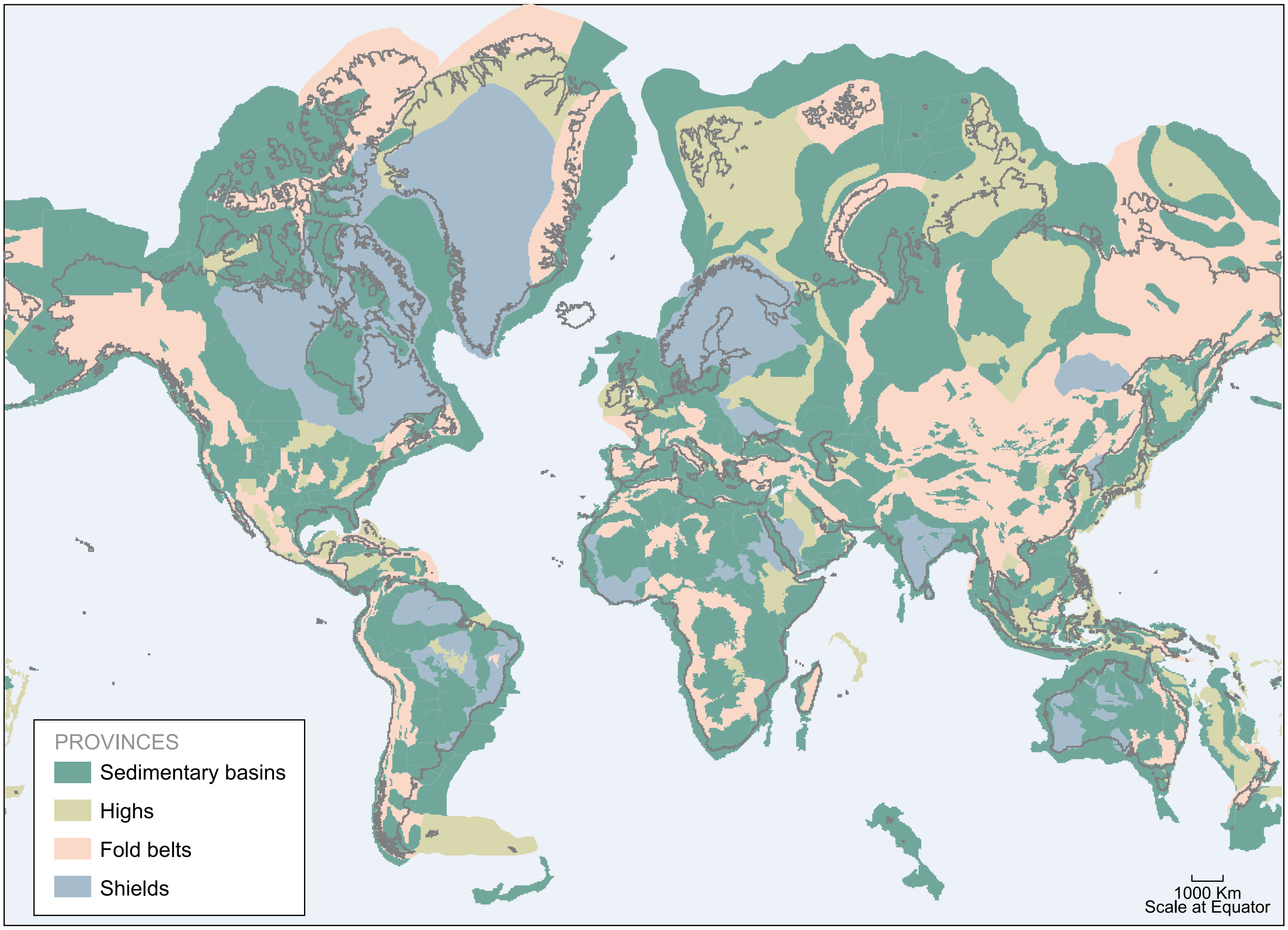

Figure 5.14 Distribution of sedimentary basins around the world (after Bradshaw and Dance, 2005; and USGS, 2001a). In general, sedimentary basins are likely to be the most prospective areas for storage sites. However, storage sites may also be found in some areas of fold belts and in some of the highs.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

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

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

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

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

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

5.3.2 Oil and gas fields

5.3.2.1 Abandoned oil and gas fields

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

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

5.3.2.2 Enhanced oil recovery

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

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

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

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

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

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

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

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

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

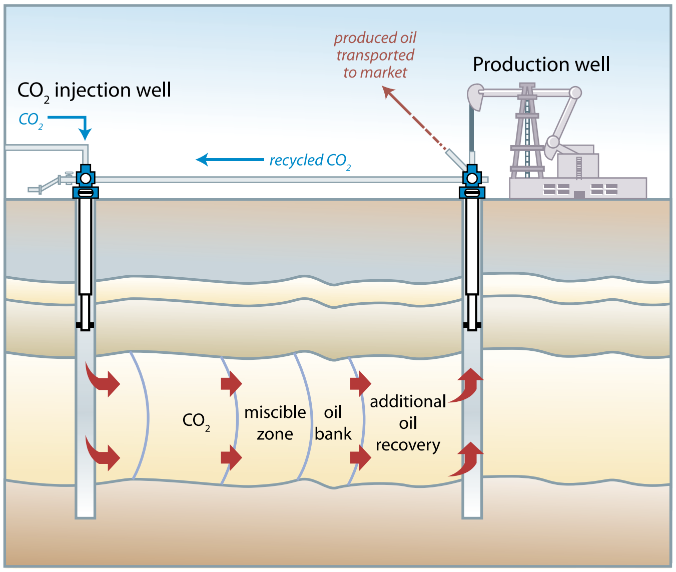

Figure 5.15 Injection of CO_2 for enhanced oil recovery (EOR) with some storage of retained CO_2 (after IEA Greenhouse Gas R&D Programme). The CO_2 that is produced with the oil is separated and re-injected back into the formation. Recycling of produced CO_2 decreases the amount of CO_2 that must be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

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

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

5.3.2.3 Enhanced gas recovery

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

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

5.3.3 Saline formations

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

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

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

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

5.3.4 Coal seams

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

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

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

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

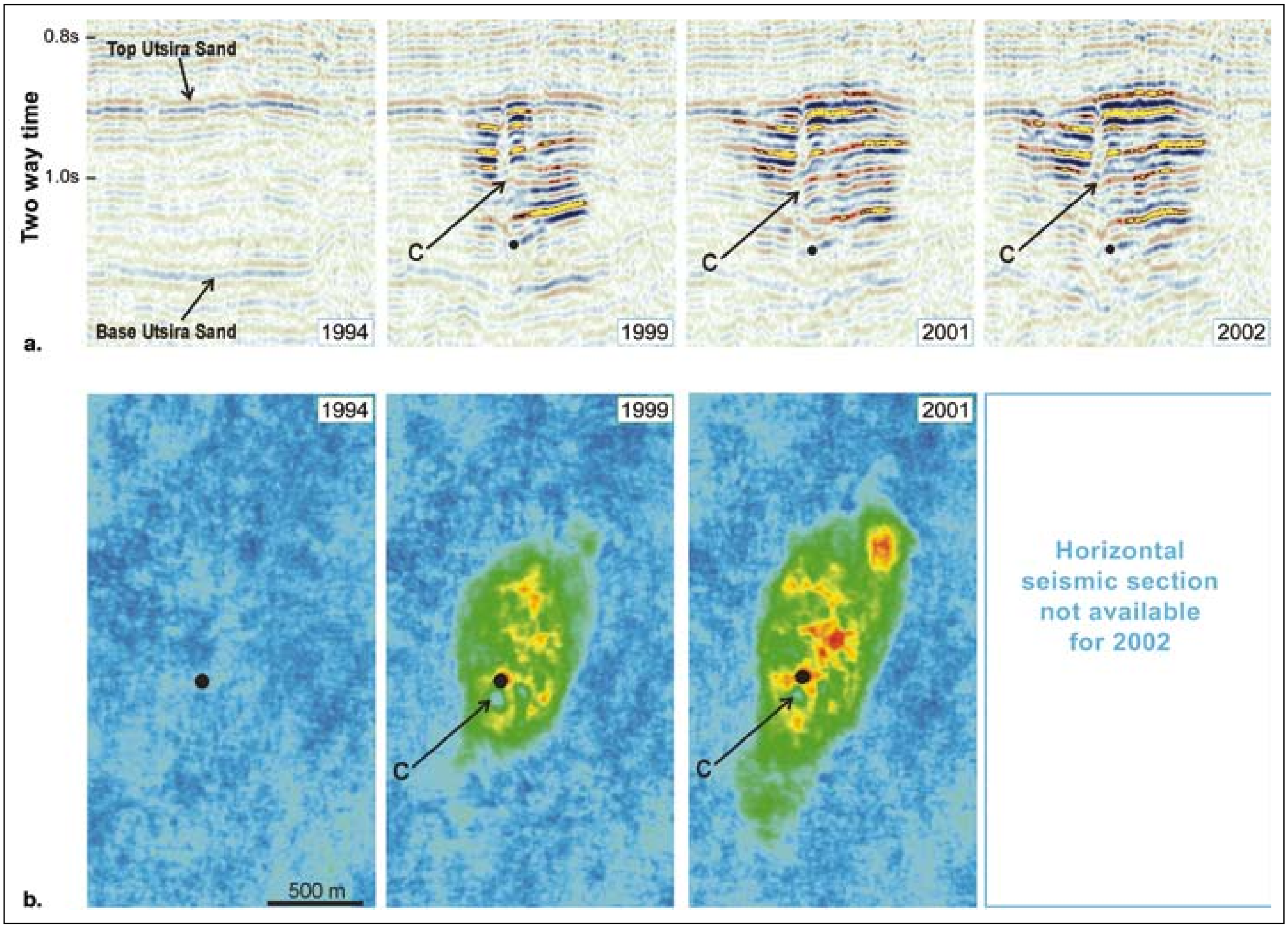

Figure 5.16 (a) Vertical seismic sections through the CO_2 plume in the Utsira Sand at the Sleipner gas field, North Sea, showing its development over time. Note the chimney of high CO_2 saturation (c) above the injection point (black dot) and the bright layers corresponding to high acoustic response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

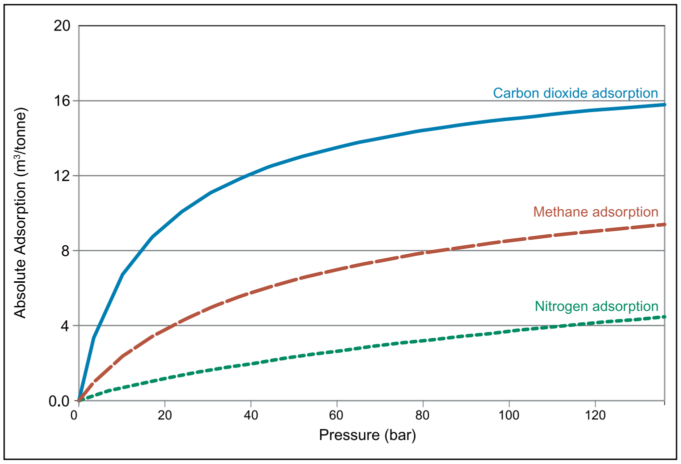

Figure 5.17 Pure gas absolute adsorption in standard cubic feet per tonne (SCF per tonne) on Tiffany Coals at 55°C (after Gasem et al., 2002).

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

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

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

Box 5.7 The Allison Unit CO_2-ECBM Pilot.

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

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

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

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

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

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

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

5.3.5 Other geological media

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

5.3.5.1 Basalts

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

5.3.5.2 Oil or gas rich shale

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

5.3.5.3 Salt caverns

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

5.3.5.4 Abandoned mines

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

5.3.6 Effects of impurities on storage capacity

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

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

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

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

5.3.7 Geographical distribution and storage capacity estimates

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

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

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

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

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

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

5.3.7.1 Storage in oil and gas reservoirs

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

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

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

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

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

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

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

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

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

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

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

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

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

5.3.7.2 Storage in deep saline formations

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

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

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

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

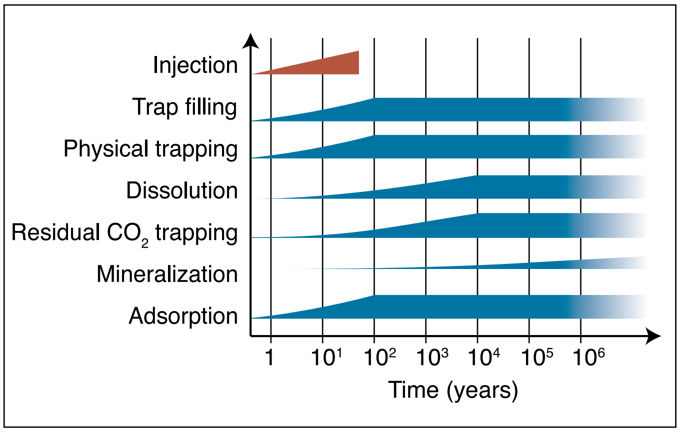


Figure 5.18 Schematic showing the time evolution of various CO_2 storage mechanisms operating in deep saline formations, during and after injection. Assessing storage capacity is complicated by the different time and spatial scales over which these processes occur.

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

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

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

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

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

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

5.3.7.3 Storage in coal

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

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

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

5.3.8 Matching of CO_2 sources and geological storage sites

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

5.3.8.1 Regional studies

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

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

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

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

5.3.8.2 Methodology and assessment criteria

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

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

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

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

5.4 Characterization and performance prediction for identified sites

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

5.4.1 Characterization of identified sites

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

5.4.1.1 Data types

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

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

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

5.4.1.2 Assessment of stratigraphic factors affecting site integrity

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

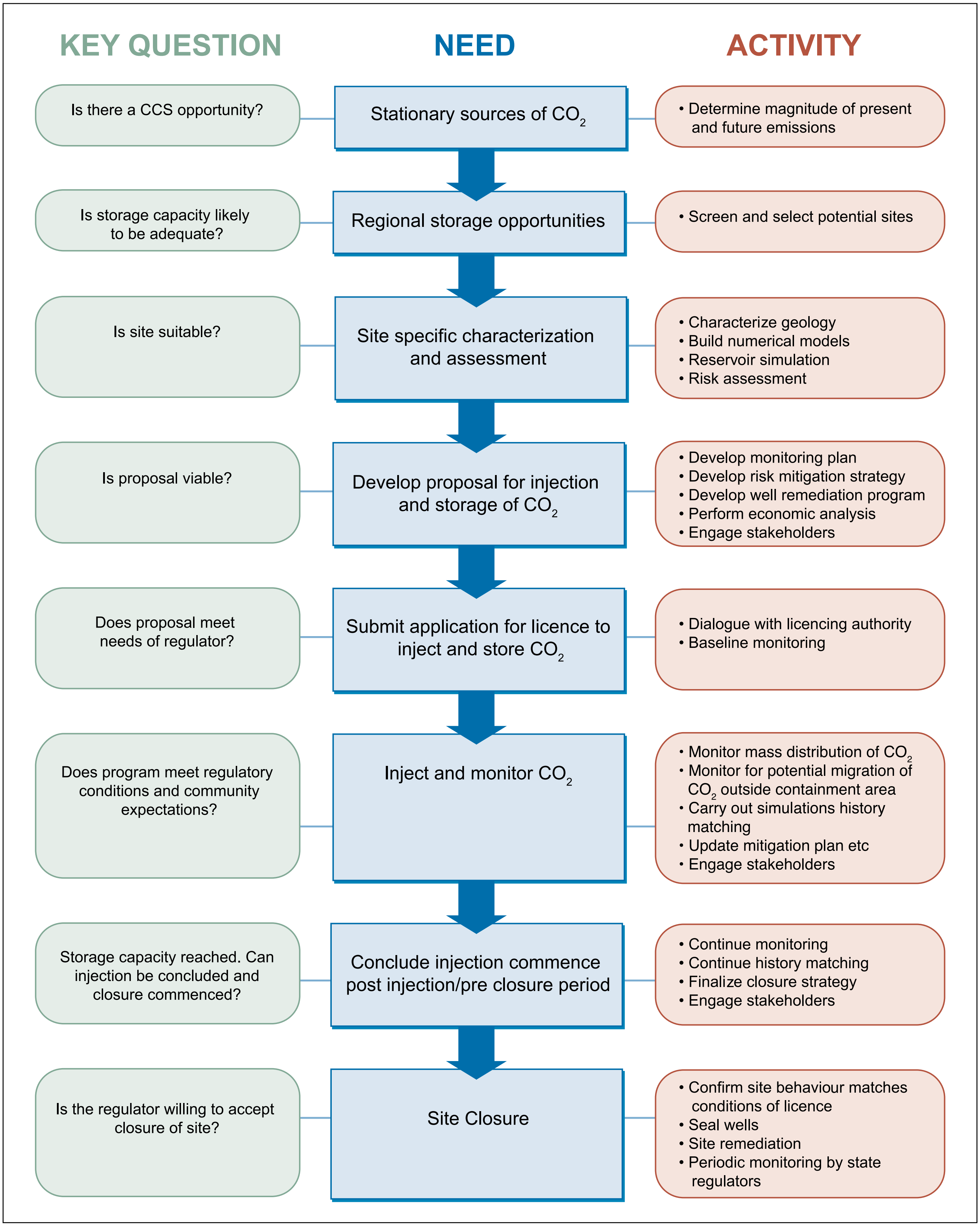


Figure 5.19 Life cycle of a CO_2 storage project showing the importance of integrating site characterization with a range of regulatory, monitoring, economic, risking and engineering issues.

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

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

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

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

5.4.1.3 Geomechanical factors affecting site integrity

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

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

5.4.1.4 Geochemical factors affecting site integrity

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

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

5.4.1.5 Anthropogenic factors affecting storage integrity

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

5.4.2 Performance prediction and optimization modelling

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

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

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

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

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

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

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

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

5.4.3 *Examples of storage site characterization and performance prediction*

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

5.4.3.1 Sleipner

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

5.4.3.2 Petrel Sub-basin

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

5.5 Injection well technology and field operations

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

5.5.1 Injection well technologies

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

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

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

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

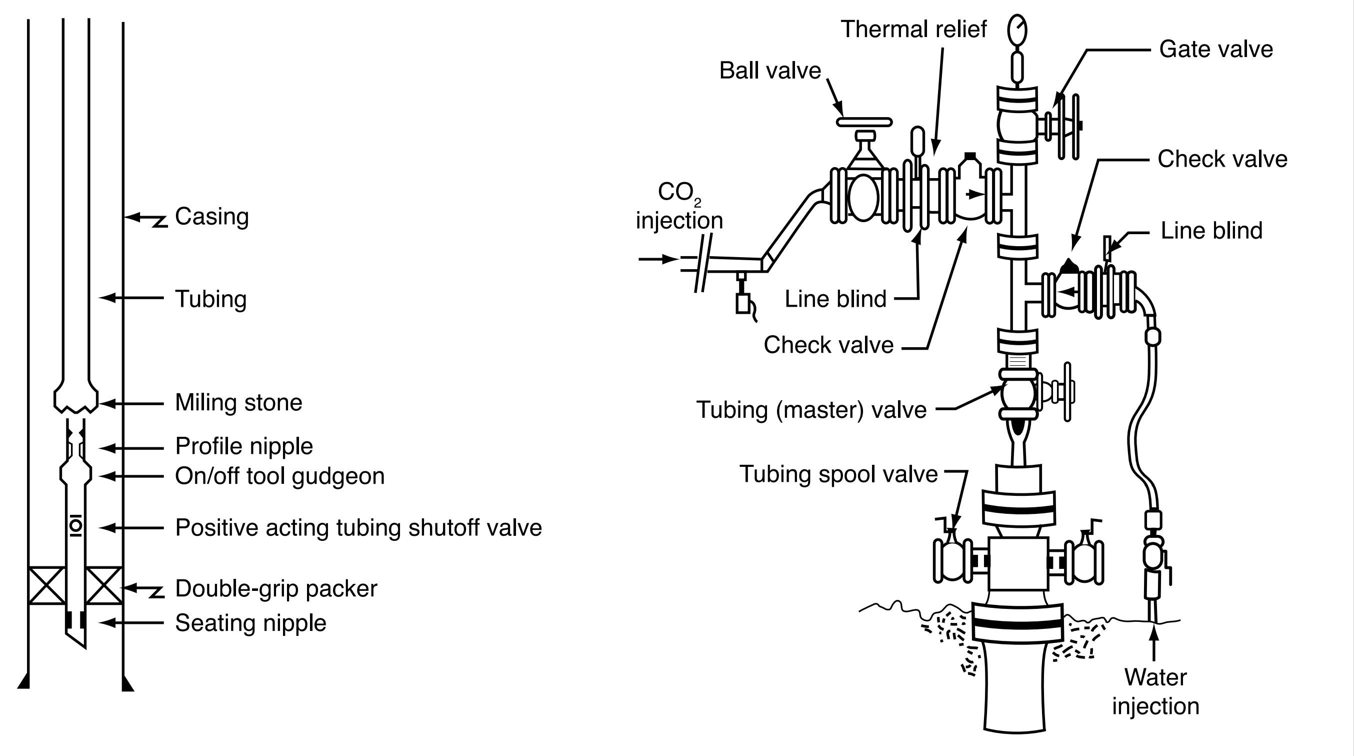


Figure 5.20 Typical CO_2 injection well and wellhead configuration.

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

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

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

5.5.2 *Well abandonment procedures*

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

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

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

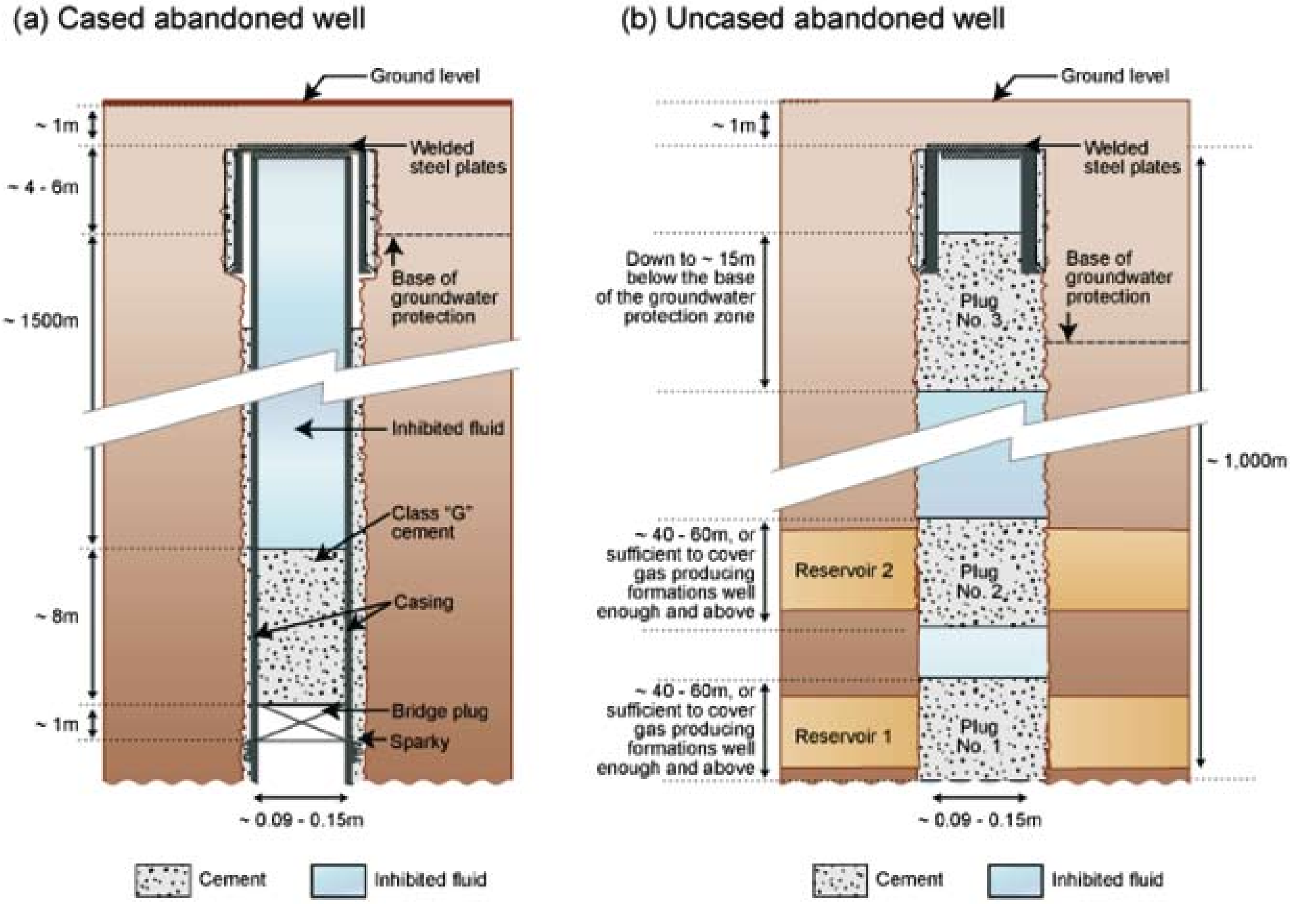


Figure 5.21 Examples of how cased and uncased wells are abandoned today. Special requirements may be developed for abandoning CO_2 storage wells, including use of corrosion-resistant cement plugs and removing all or part of the casing in the injection interval and caprock.

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

5.5.3 Injection well pressure and reservoir constraints

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

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

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

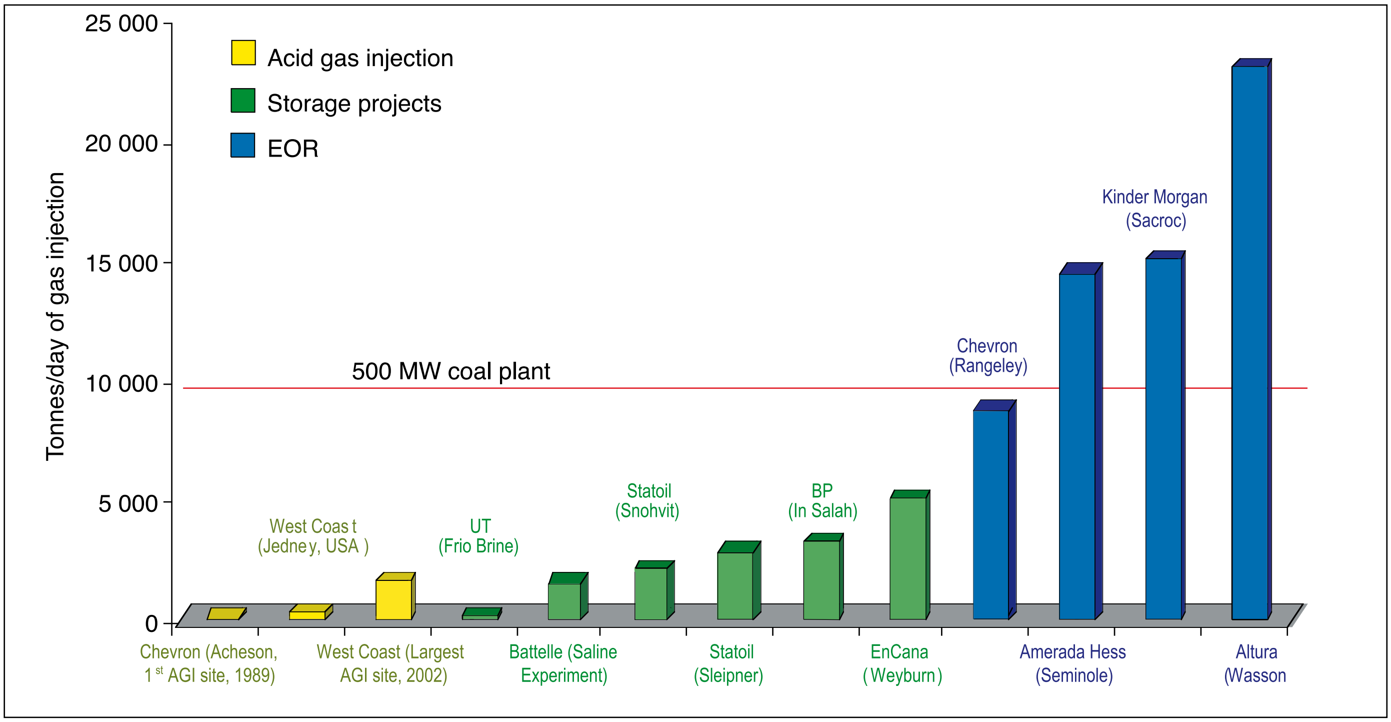


Figure 5.22 Comparison of the magnitude of CO_2 injection activities illustrating that the storage operations from a typical 500-MW coal plant will be the same order of magnitude as existing CO_2 injection operations (after Heinrich *et al.*, 2003).

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

5.5.4 *Field operations and surface facilities*

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

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

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

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

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

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

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

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

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

5.6 Monitoring and verification technology

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

5.6.1 Purposes for monitoring

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

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

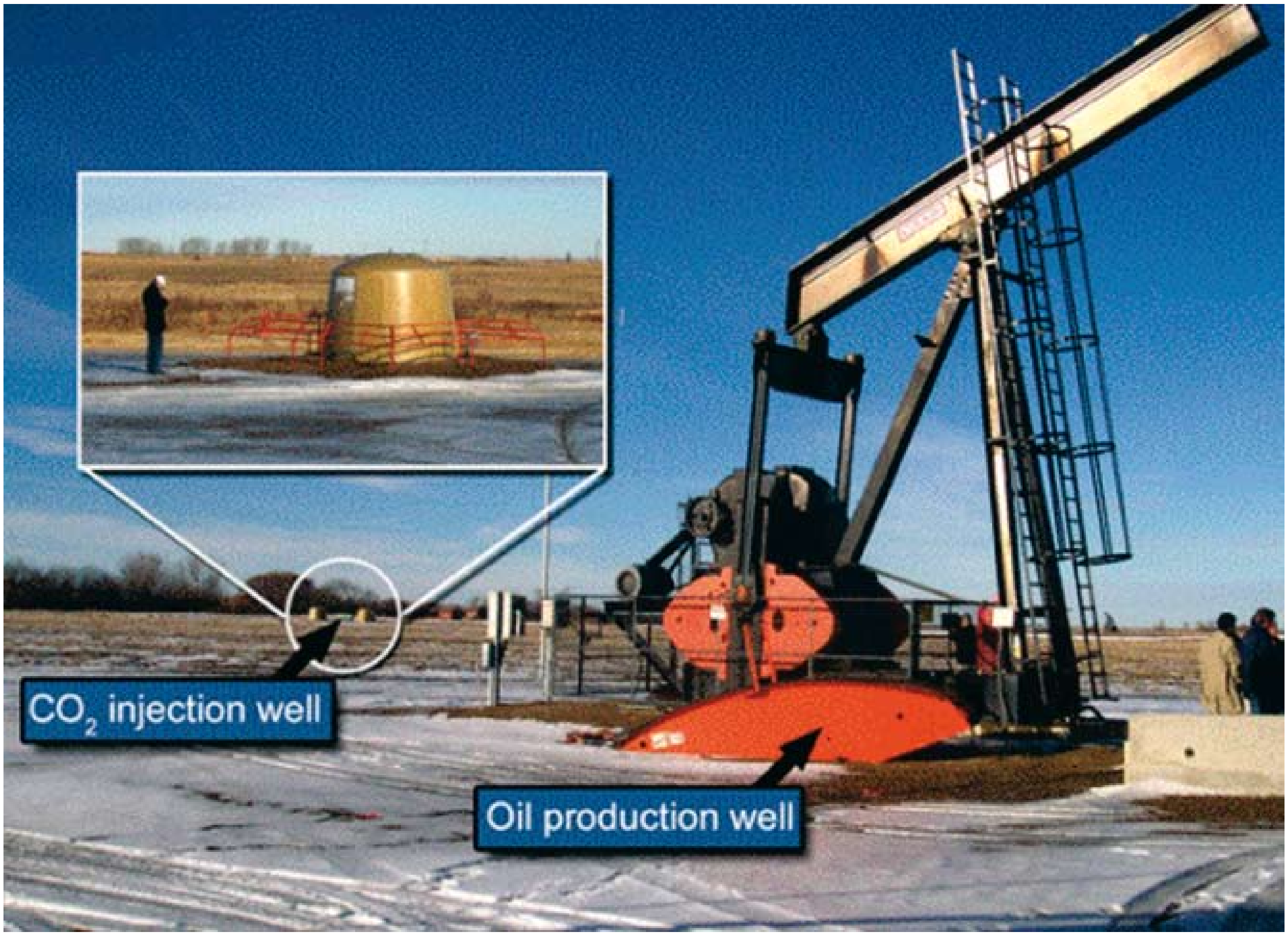


Figure 5.23 Typical CO_2 field operation setup: Weyburn surface facilities.

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

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

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

5.6.2 Technologies for monitoring injection rates and pressures

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

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

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

5.6.3 Technologies for monitoring subsurface distribution of CO_2

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

5.6.3.1 Direct techniques for monitoring CO_2 migration

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

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

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

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

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

5.6.3.2 Indirect techniques for monitoring CO_2 migration

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

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

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

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

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

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

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

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

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

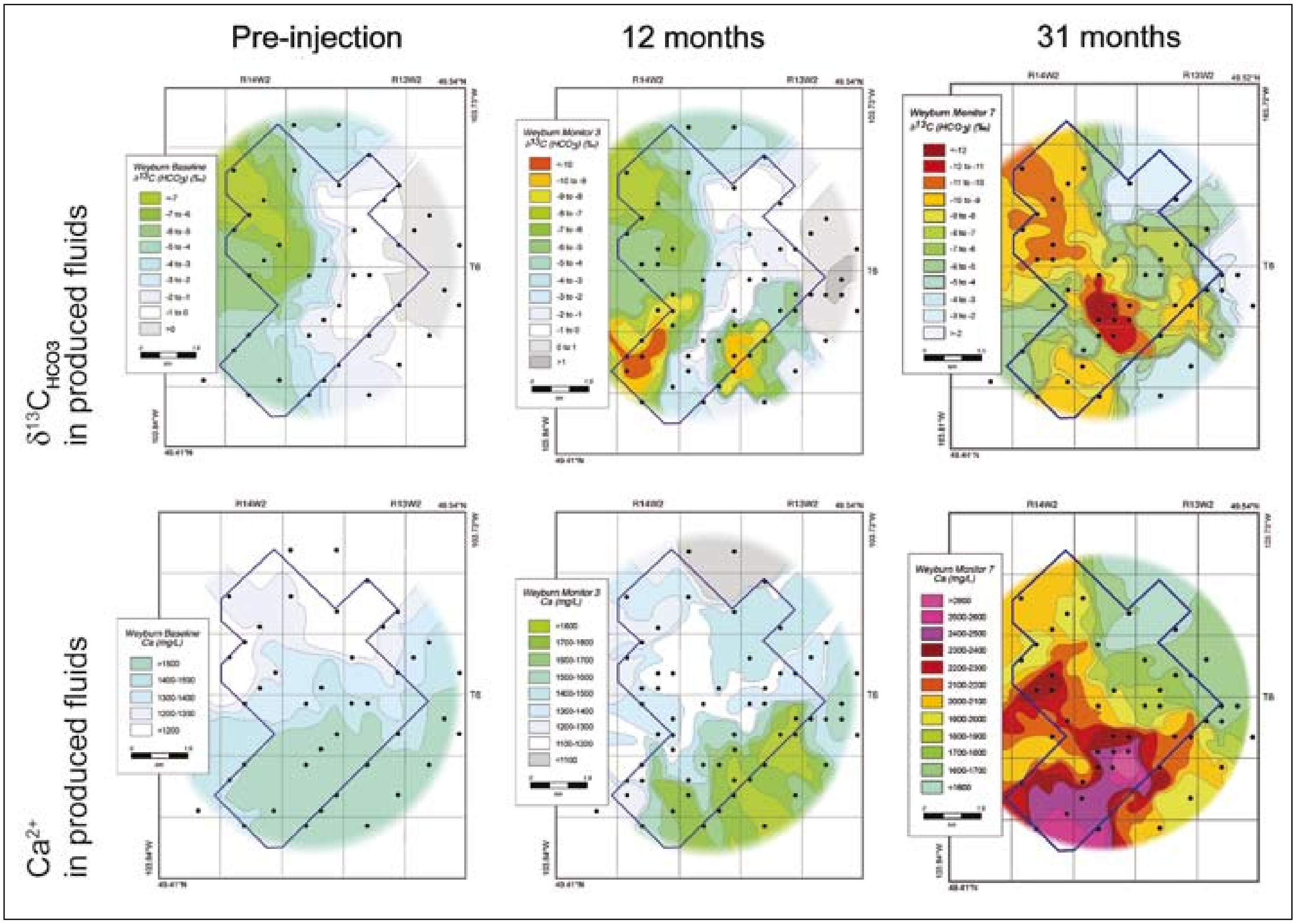


Figure 5.24 The produced water chemistry before CO_2 injection and the produced water chemistry after 12 months and 31 months of injection at Weyburn has been contoured from fluid samples taken at various production wells. The black dots show the location of the sample wells: (a) $\delta^{13}C_{HCO3}$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

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

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

5.6.4 Technologies for monitoring injection well integrity

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

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

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

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

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

5.6.5 Technologies for monitoring local environmental effects

5.6.5.1 Groundwater

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

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

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

5.6.5.2 Air quality and atmospheric fluxes

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

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

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

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

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

5.6.5.3 Ecosystems

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

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

5.6.6 Monitoring network design

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

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

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

5.6.7 Long-term stewardship monitoring

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

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

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

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

5.6.8 Verification of CO_2 injection and storage inventory

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

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

5.7 Risk management, risk assessment and remediation

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

5.7.1 Framework for assessing environmental risks

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

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

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

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

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

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

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

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

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

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

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

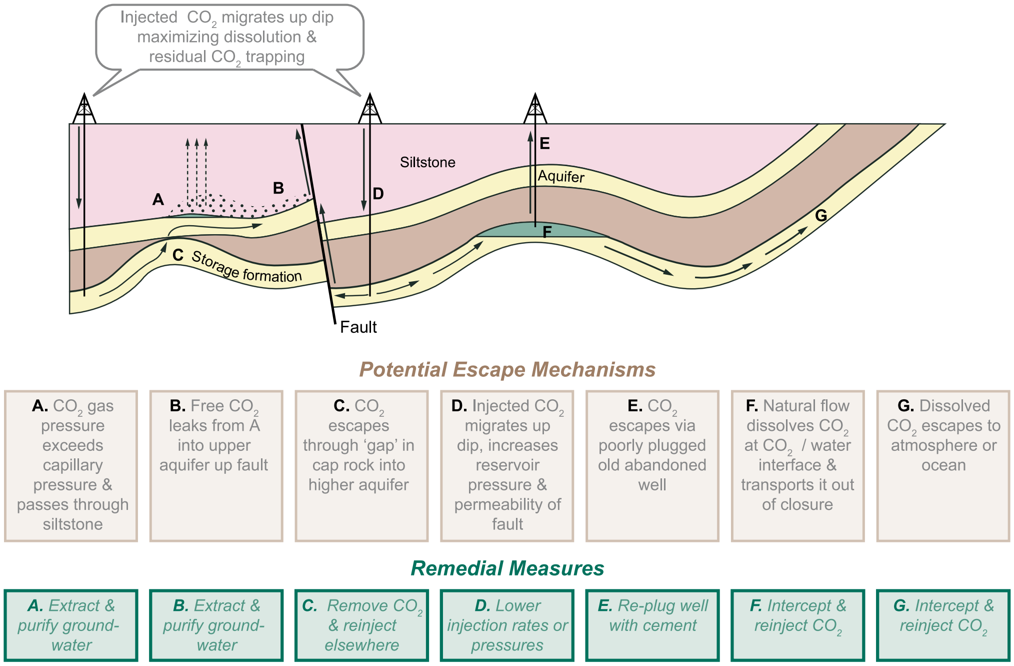
For onshore storage sites, CO_2 that has leaked may reach the water table and migrate into the overlying vadose zone. This occurrence would likely include CO_2 contact with drinking-water aquifers. Depending on the mineral composition of the rock matrix within the groundwater aquifer or vadose zone,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

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

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

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

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



Potential Escape Mechanisms

A. CO_2 gas pressure exceeds capillary pressure & passes through siltstone	**B.** Free CO_2 leaks from A into upper aquifer up fault	**C.** CO_2 escapes through 'gap' in cap rock into higher aquifer	**D.** Injected CO_2 migrates up dip, increases reservoir pressure & permeability of fault	**E.** CO_2 escapes via poorly plugged old abandoned well	**F.** Natural flow dissolves CO_2 at CO_2 / water interface & transports it out of closure	**G.** Dissolved CO_2 escapes to atmosphere or ocean

Remedial Measures

***A.** Extract & purify ground-water*	***B.** Extract & purify ground-water*	***C.** Remove CO_2 & reinject elsewhere*	***D.** Lower injection rates or pressures*	***E.** Re-plug well with cement*	***F.** Intercept & reinject CO_2*	***G.** Intercept & reinject CO_2*

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

as coal mines or mining-induced subsidence cracks.

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

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

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

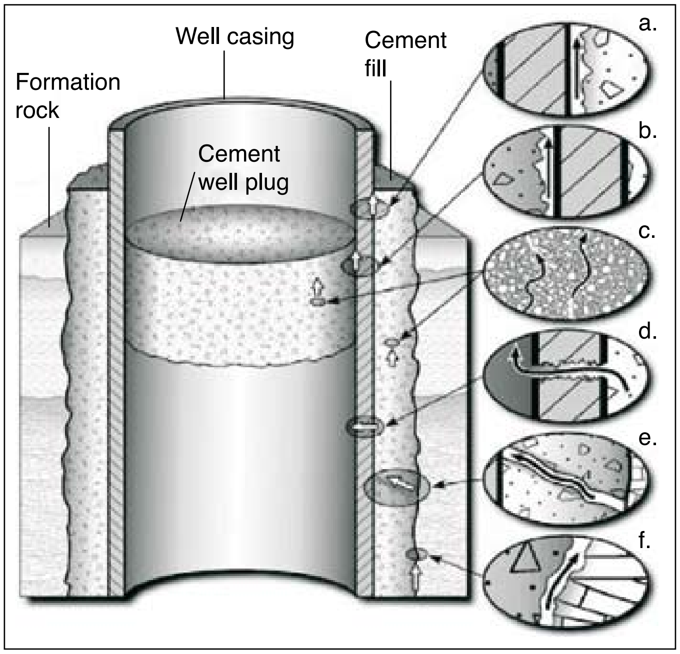


Figure 5.26 Possible leakage pathways in an abandoned well: (a) and (b) between casing and cement wall and plug, respectively; (c) through cement plugs; (d) through casing; (e) through cement wall; and (f) between the cement wall and rock (after Gasda *et al.*, 2004).

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

5.7.3 *Probability of release from geological storage sites*

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

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

5.7.3.1 *Natural systems*

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

5.7.3.2 Engineered systems

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

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

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

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

5.7.3.4 Numerical simulations of long-term storage performance

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

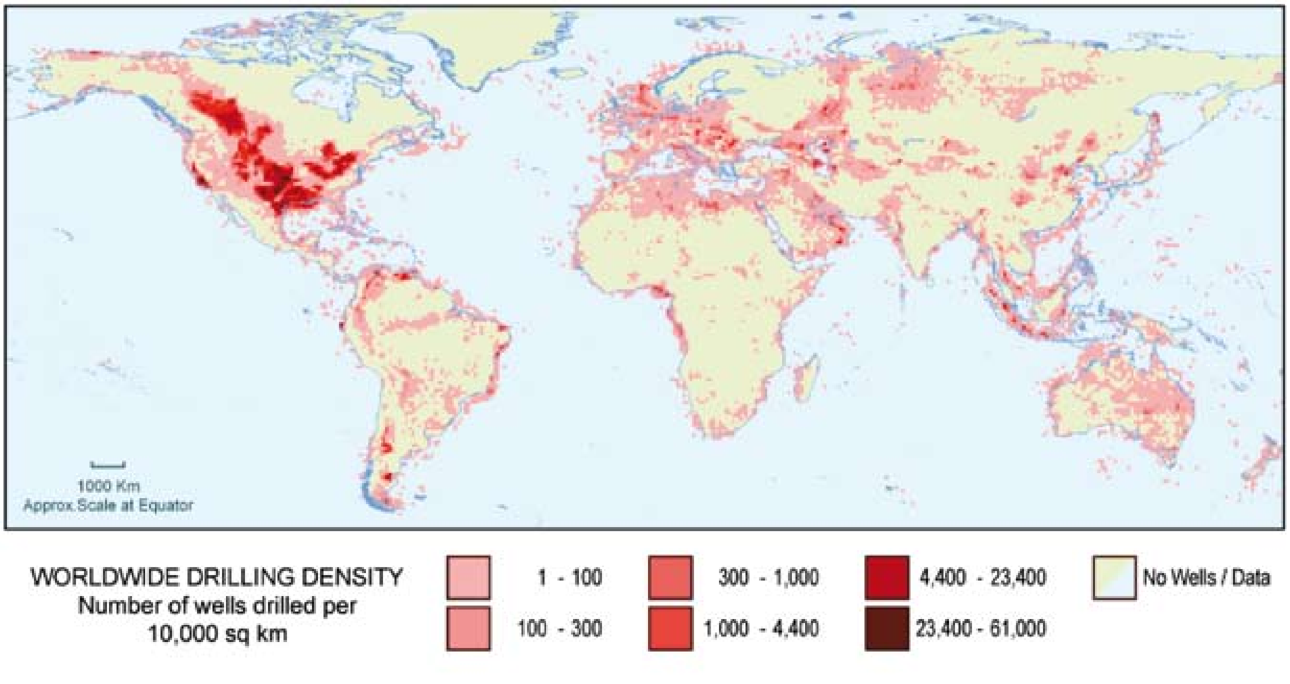


Figure 5.27 World oil and gas well distribution and density (courtesy of IHS Energy).

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

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

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

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

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

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

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

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

5.7.4 *Possible local and regional environmental hazards*

5.7.4.1 *Potential hazards to human health and safety*

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

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

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

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

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

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

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

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

5.7.4.2 *Hazards to groundwater from CO_2 leakage and brine displacement*

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

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

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

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

5.7.4.3 Hazards to terrestrial and marine ecosystems

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

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

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

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

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

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

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

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

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

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

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

5.7.4.4 Induced seismicity

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

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

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

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

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

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

5.7.4.5 Implications of gas impurity

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

5.7.5 Risk assessment methodology

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

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

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

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

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

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

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

Table 5.6 Representative selection of risk assessment models and efforts.

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

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

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

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

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

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

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

5.7.6 *Risk management*

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

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

- Careful site selection, including performance and risk

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

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

5.7.7 Remediation of leaking storage projects

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

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

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

5.8 Legal issues and public acceptance

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

5.8.1 International law

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

5.8.1.1 Sources and nature of international obligations

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

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

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

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

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

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

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

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

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

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

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

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

5.8.1.3 Literature on geological storage under international law

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

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

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

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

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

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

5.8.2 National regulations and standards

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

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

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

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

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

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

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

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

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

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

5.8.3 *Subsurface property rights*

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

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

5.8.4 *Long-term liability*

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

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

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

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

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

5.8.5 Public perception and acceptance

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

5.8.5.1 Survey research

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

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

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

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

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

5.8.5.2 Focus-group research

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

5.8.5.3 Implications of the research

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

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

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

5.8.5.4 Underground storage of other fluids

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

5.9 Costs of geological storage

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

5.9.1 Cost elements for geological storage

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

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

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

5.9.2 Cost estimates

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

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

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

Option type	On or offshore	Location	US$/t$CO_2$ stored Low	 Mid	 High	Comments	Nature of Midpoint value
Saline formation	Onshore	Australia	0.2	0.5	5.1	Statistics for 20 sites[a]	Median
Saline formation	Onshore	Europe	1.9	2.8	6.2	Representative range[b]	Most likely value
Saline formation	Onshore	USA	0.4	0.5	4.5	Low/base/high cases for USA[c]	Base case for average parameters
Saline formation	Offshore	Australia	0.5	3.4	30.2	Statistics for 34 sites[a]	Median
Saline formation	Offshore	N. Sea	4.7	7.7	12.0	Representative range[b]	Most likely value
Depleted oil field	Onshore	USA	0.5	1.3	4.0	Low/base/high cases for USA[c]	Base case for average parameters
Depleted gas field	Onshore	USA	0.5	2.4	12.2	Low/base/high cases for USA[c]	Base case for average parameters
Disused oil or gas field	Onshore	Europe	1.2	1.7	3.8	Representative range[b]	Most likely value
Disused oil or gas field	Offshore	N. Sea	3.8	6.0	8.1	Low/base/high cases for USA[c]	Most likely value

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

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

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

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

Table 5.10 Investment costs for industry CO_2 storage projects.

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

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

5.9.3 Cost estimates for CO_2 geological storage

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

5.9.3.1 Saline formations

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

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

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

5.9.3.2 Disused oil and gas reservoirs

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

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

5.9.3.3 Representative storage costs

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

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

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

5.9.3.4 Investment costs for storage projects

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

5.9.4 Cost estimates for storage with enhanced oil and gas recovery

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

5.9.4.1 Enhanced oil recovery

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

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

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

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

5.9.4.2 Cost of CO_2 storage with enhanced oil recovery

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

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

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

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

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

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

5.9.4.3 Cost of CO_2 storage with enhanced gas recovery

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

5.9.4.4 Cost of CO_2 storage with enhanced coal bed methane

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

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

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

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

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

5.9.5 Cost of monitoring

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

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

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

5.9.6 Cost of remediation of leaky storage projects

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

5.9.7 Cost reduction

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

5.10 Knowledge gaps

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

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

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

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

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

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

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

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

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

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

References

Ahmad, M.U. and J.A. Smith, 1988: Earthquakes, injection wells and the Perry Nuclear Power Plant, Cleveland, Ohio. *Geology*, **16**, 739–742.

Akimoto, K., H. Kotsubo, T. Asami, X. Li, M. Uno, T. Tomoda and T. Ohsumi, 2003: Evaluation of carbon sequestrations in Japan with a mathematical model. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1-4 October 2002, Kyoto, Japan, v.I, 913–918.

Alberta Energy and Utilities Board, 1994: Injection and disposal wells, Guide #51, Calgary, AB, http://eub.gov.ab.ca/bbs/products/guides/g51-1994.pdf.

Alberta Energy and Utilities Board, 2003: Well abandonment guide, August 2003 incorporating errata to August 2004, http://www.eub.gov.ab.ca/bbs/products/guides/g20.pdf.

Allinson, W.G, D.N. Nguyen and J. Bradshaw, 2003: The economics of geological storage of CO_2 in Australia, *APPEA Journal*, **623**.

Allis, R., T. Chidsey, W. Gwynn, C. Morgan, S. White, M. Adams and J. Moore, 2001: Natural CO_2 reservoirs on the Colorado Plateau and southern Rocky Mountains: Candidates for CO_2 sequestration. Proceedings of the First National Conference on Carbon Sequestration, 14–17 May 2001, DOE NETL, Washington, DC.

Alston, R.B., G.P. Kokolis and C.F. James, 1985: CO_2 minimum miscibility pressure: A correlation for impure CO_2 streams and live oil systems. *Society of Petroleum Engineers Journal*, **25**(2), 268–274.

Amadeo, N., H. Bajano, J. Comas, J.P. Daverio, M.A. Laborde, J.A. Poggi and D.R. Gómez, 2005: Assessment of CO_2 capture and storage from thermal power plants in Argentina. Proceedings of the 7th International Conference on Greenhouse Gas Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 243-252.

Angus, S., B. Armstrong and K.M. de Reuck, 1973: International Thermodynamic Tables of the Fluid State Volume 3. Carbon Dioxide. IUPAC Division of Physical Chemistry, Pergamon Press, London, pp. 266–359.

Anheden, M., A. Andersson, C. Bernstone, S. Eriksson, J. Yan, S. Liljemark and C. Wall, 2005: CO_2 quality requirement for a system with CO_2 capture, transport and storage. Proceedings of the 7th International Conference on Greenhouse Gas Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.II, 2559-2566.

Apps, J., 2005: The Regulatory Climate Governing the Disposal of Liquid Wastes in Deep Geologic Formations: a Paradigm for Regulations for the Subsurface Disposal of CO_2, Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results from the CO_2 Capture Project, v.2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson (ed.), *Elsevier Science*, London, pp. 1163–1188.

Arts, R. and P. Winthaegen, 2005: Monitor options for CO_2 storage, Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results from the CO_2 Capture Project, v.2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson (ed.), Elsevier Science, London. pp. 1001–1013.

Arts, R., A. Chadwick and O. Eiken, 2005: Recent time-lapse seismic data show no indication of leakage at the Sleipner CO_2-injection site. Proceedings of the 7th International Conference on Greenhouse Gas Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 653-662.

Bachu, S., 2000: Sequestration of carbon dioxide in geological media: Criteria and approach for site selection. *Energy Conservation and Management*, **41**(9), 953–970.

Bachu, S., 2003: Screening and ranking of sedimentary basins for sequestration of CO_2 in geological media. *Environmental Geology*, **44**(3), 277–289.

Bachu, S. and J.J. Adams, 2003: Sequestration of CO_2 in geological media in response to climate change: Capacity of deep saline aquifers to sequester CO_2 in solution. *Energy Conversion and Management*, **44**(20), 3151–3175.

Bachu, S. and M. Dusseault, 2005: Underground injection of carbon dioxide in salt beds. Proceedings of the Second International Symposium on Deep Well Injection, C-F. Tsang and J. Apps (eds.), 22–24 October 2003, Berkeley, CA, In press.

Bachu, S. and K. Haug, 2005: In-situ characteristics of acid -gas injection operations in the Alberta basin, western Canada: Demonstration of CO_2 geological storage, Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results from the CO_2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson (ed.), Elsevier, London, pp. 867–876.

Bachu, S. and J.C. Shaw, 2003: Evaluation of the CO_2 sequestration capacity in Alberta's oil and gas reservoirs at depletion and the effect of underlying aquifers. *Journal of Canadian Petroleum Technology*, **42**(9), 51–61.

Bachu, S. and J.C. Shaw, 2005: CO_2 storage in oil and gas reservoirs in western Canada: Effect of aquifers, potential for CO_2-flood enhanced oil recovery and practical capacity. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 361-370.

Bachu, S., W.D. Gunter and E.H. Perkins, 1994: Aquifer disposal of CO_2: hydrodynamic and mineral trapping, *Energy Conversion and Management*, **35**(4), 269–279.

Bachu, S., J.C. Shaw and R.M. Pearson, 2004: Estimation of oil recovery and CO_2 storage capacity in CO_2 EOR incorporating the effect of underlying aquifers. SPE Paper 89340, presented at the Fourteenth SPE/DOE Improved Oil Recovery Symposium, Tulsa, OK, April 17–21, 2004, 13 pp.

Baes, C.F., S.E. Beall, D.W. Lee and G. Marland, 1980: The collection, disposal and storage of carbon dioxide. In: Interaction of Energy and Climate, W. Bach, J. Pankrath and J. William (eds.), 495–519, D. Reidel Publishing Co.

Baines, S.J. and R.H. Worden, 2001: Geological CO_2 disposal: Understanding the long-term fate of CO_2 in naturally occurring accumulations. Proceedings of the 5th International Conference on Greenhouse Gas Control Technologies (GHGT-5), D.J. Williams, R.A. Durie, P. McMullan, C.A.J. Paulson and A. Smith (eds.), 13–16 August 2000, Cairns, Australia, CSIRO Publishing, Collingwood, Victoria, Australia, pp. 311–316.

Beecy, D. and V.A. Kuuskra, 2005: Basin strategies for linking CO_2 enhanced oil recovery and storage of CO_2 emissions. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 351-360.

Benson, S.M., 2005: Lessons learned from industrial and natural analogs for health, safety and environmental risk assessment for geologic storage of carbon dioxide. Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results from the CO_2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson (ed.), Elsevier, London, pp. 1133–1141.

Benson, S.M. and R.P. Hepple, 2005: Prospects for early detection and options for remediation of leakage from CO_2, storage projects, Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results from the CO_2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson (ed.), Elsevier, London, pp. 1189–1204.

Benson, S.M., E. Gasperikova and G.M. Hoversten, 2004: Overview of monitoring techniques and protocols for geologic storage projects, IEA Greenhouse Gas R&D Programme Report.

Benson, S.M., E. Gasperikova and G.M. Hoversten, 2005: Monitoring protocols and life-cycle costs for geologic storage of carbon dioxide. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.II, 1259-1266.

Bøe, R., C. Magnus, P.T. Osmundsen and B.I. Rindstad, 2002: CO_2 point sources and subsurface storage capacities for CO_2 in aquifers in Norway. Norsk Geologische Undersogelske, Trondheim, Norway, NGU Report 2002.010, 132 pp.

Bergfeld, D., F. Goff and C.J. Janik, 2001: Elevated carbon dioxide flux at the Dixie Valley geothermal field, Nevada; relations between surface phenomena and the geothermal reservoir. *Chemical Geology*, **177**(1–2), 43–66.

Bergman, P.D. and E.M. Winter, 1995: Disposal of carbon dioxide in aquifers in the US. *Energy Conversion and Management*, **36**(6), 523–526.

Bergman, P.D., E.M. Winter and Z-Y. Chen, 1997: Disposal of power plant CO_2 in depleted oil and gas reservoirs in Texas. *Energy Conversion and Management*, **38**(Suppl.), S211–S216.

Bewers, M., 2003: Review of international conventions having implications for ocean storage of carbon dioxide. International Energy Agency, Greenhouse Gas Research and Development Programme, Cheltenham, UK, March 2003.

Bock, B., R. Rhudy, H. Herzog, M. Klett, J. Davison, D. De la Torre Ugarte and D. Simbeck, 2003: Economic Evaluation of CO_2 Storage and Sink Options. DOE Research Report DE-FC26-00NT40937.

Bondor, P.L., 1992: Applications of carbon dioxide in enhanced oil recovery. *Energy Conversion and Management*, **33**(5), 579–586.

Bossie-Codreanu, D., Y. Le-Gallo, J.P. Duquerroix, N. Doerler and P. Le Thiez, 2003: CO_2 sequestration in depleted oil reservoirs. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.I, 403–408.

Bradshaw, J.B. and T. Dance, 2005: Mapping geological storage prospectivity of CO_2 for the world sedimentary basins and regional source to sink matching. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 583-592.

Bradshaw, J.B., E. Bradshaw, G. Allinson, A.J. Rigg, V. Nguyen and A. Spencer, 2002: The potential for geological sequestration of CO_2 in Australia: preliminary findings and implications to new gas field development. *Australian Petroleum Production and Exploration Association Journal*, **42**(1), 24–46.

Bradshaw, J., G. Allinson, B.E. Bradshaw, V. Nguyen, A.J. Rigg, L. Spencer and P. Wilson, 2003: Australia's CO_2 geological storage potential and matching of emissions sources to potential sinks. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.I, 633–638.

Bradshaw, J., C. Boreham and F. la Pedalina, 2005: Storage retention time of CO_2 in sedimentary basins: Examples from petroleum systems. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 541-550.

Brennan, S.T. and R.C. Burruss, 2003: Specific Sequestration Volumes: A Useful Tool for CO_2 Storage Capacity Assessment. USGS OFR 03-0452 available at http://pubs.usgs.gov/of/2003/of03-452/.

Bryant, S. and L. Lake, 2005: Effect of impurities on subsurface CO_2 storage processes, Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results from the CO_2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson (ed.), Elsevier, London. pp. 983–998.

Buschbach, T.C. and D.C. Bond, 1974: Underground storage of natural gas in Illinois - 1973, *Illinois Petroleum*, 101, Illinois State Geological Survey.

Carapezza, M. L., B. Badalamenti, L. Cavarra and A. Scalzo, 2003: Gas hazard assessment in a densely inhabited area of Colli Albani Volcano (Cava dei Selci, Roma). *Journal of Volcanology and Geothermal Research*, **123**(1–2), 81–94.

Cawley, S., M. Saunders, Y. Le Gallo, B. Carpentier, S. Holloway, G.A. Kirby, T. Bennison, L. Wickens, R. Wikramaratna, T. Bidstrup, S.L.B. Arkley, M.A.E. Browne and J.M. Ketzer, 2005, The NGCAS Project - Assessing the potential for EOR and CO_2 storage at the Forties Oil field, Offshore UK - Results from the CO_2 Capture Project, v.2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson (ed.), Elsevier Science, London, pp. 1163–1188.

Celia, M.A. and S. Bachu, 2003: Geological sequestration of CO_2: Is leakage avoidable and acceptable? Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October, Kyoto Japan, Pergamon, v. 1, pp. 477–482.

Celia, M.A., S. Bachu, J.M. Nordbotten, S.E. Gasda and H.K. Dahle, 2005: Quantitative estimation of CO_2 leakage from geological storage: Analytical models, numerical models and data needs. Proceedings of 7th International Conference on Greenhouse Gas Control Technologies. (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 663-672.

Chadwick, R.A., P. Zweigel, U. Gregersen, G.A. Kirby, S. Holloway and P.N. Johannesen, 2003: Geological characterization of CO_2 storage sites: Lessons from Sleipner, northern North Sea. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.I, 321–326.

Chadwick, R.A., R. Arts and O. Eiken, 2005: 4D seismic quantification of a growing CO_2 plume at Sleipner, North Sea. In: A.G. Dore and B. Vining (eds.), Petroleum Geology: North West Europe and Global Perspectives - Proceedings of the 6th Petroleum Geology Conference. Petroleum Geology Conferences Ltd. Published by the Geological Society, London, 15pp (in press).

Chalaturnyk, R. and W.D. Gunter, 2005: Geological storage of CO_2: Time frames, monitoring and verification. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 623-632.

Chikatamarla, L. and M.R. Bustin, 2003: Sequestration potential of acid gases in Western Canadian Coals. Proceedings of the 2003 International Coalbed Methane Symposium, University of Alabama, Tuscaloosa, AL, May 5–8, 2003, 16 pp.

Chiodini, G., F. Frondini, C. Cardellini, D. Granieri, L. Marini and G. Ventura, 2001: CO_2 degassing and energy release at Solfatara volcano, Campi Flegrei, Italy. *Journal of Geophysical Research*, **106**(B8), 16213–16221.

Christman, P.G. and S.B. Gorell, 1990: Comparison of laboratory and field-observed CO_2 tertiary injectivity. *Journal of Petroleum Technology*, February 1990.

Chow, J.C., J.G. Watson, A. Herzog, S.M. Benson, G.M. Hidy, W.D. Gunter, S.J. Penkala and C.M. White, 2003: Separation and capture of CO_2 from large stationary sources and sequestration in geological formations. Air and Waste Management Association (AWMA) *Critical Review Papers,* **53**(10), October 2003.http://www.awma.org/journal/past-issue.asp?month=10&year=2003.

Clarkson, C.R. and R.M. Bustin, 1997: The effect of methane gas concentration, coal composition and pore structure upon gas transport in Canadian coals: Implications for reservoir characterization. Proceedings of International Coalbed Methane Symposium, 12–17 May 1997, University of Alabama, Tuscaloosa, AL, pp. 1–11.

Clemens, T. and K. Wit, 2002: CO_2 enhanced gas recovery studied for an example gas reservoir, SPE 77348, presented at the SPE Annual Technical Meeting and Conference, San Antonio, Texas, 29 September - 2 October 2002.

Clesceri, L.S., A.E. Greenberg and A.D. Eaton (eds.), 1998: Standard Methods for the Examination of Water and Wastewater, 20th Edition. American Public Health Association, Washington, DC, January 1998.

Cook, P.J., 1999: Sustainability and nonrenewable resources. *Environmental Geosciences*, **6**(4), 185–190.

Cook, P.J. and C.M. Carleton (eds.), 2000: Continental Shelf Limits: The Scientific and Legal Interface. Oxford University Press, New York, 360 pp.

Cook, A.C., L. J. Hainsworth, M.L. Sorey, W.C. Evans and J.R. Southon, 2001: Radiocarbon studies of plant leaves and tree rings from Mammoth Mountain, California: a long-term record of magmatic CO_2 release. *Chemical Geology*, **177**(1–2),117–131.

Crolet, J.-L., 1983: Acid corrosion in wells (CO_2, H_2S): Metallurgical aspects. *Journal of Petroleum Technology*, August 1983, 1553–1558.

CRUST Legal Task Force, 2001: Legal aspects of underground CO_2 storage. Ministry of Economic Affairs, the Netherlands. Retrieved from www.CO_2-reductie.nl. on August 19, 2003.

Curry, T., D. Reiner, S. Ansolabehere and H. Herzog, 2005: How aware is the public of carbon capture and storage? In E.S. Rubin, D.W. Keith and C.F. Gilboy (Eds.), Proceedings of 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 1001-1010.

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

D'Hondt, S., S. Rutherford and A.J. Spivack, 2002: Metabolic activity of subsurface life in deep-sea sediments. *Science*, **295**, 2067–2070.

DOGGR (California Department of Oil, Gas and Geothermal Resources), 1974: Sixtieth Annual Report of the State Oil and Gas Supervisor. Report No. PR06, pp. 51–55.

Dooley, J.J., R.T. Dahowski, C.L. Davidson, S. Bachu, N. Gupta and J. Gale, 2005: A CO_2 storage supply curve for North America and its implications for the deployment of carbon dioxide capture and storage systems. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 593-602.

Doughty, C. and K. Pruess, 2004: Modeling Supercritical Carbon Dioxide Injection in Heterogeneous Porous Media, *Vadose Zone Journal,* **3**(3), 837–847.

Doughty, C., K. Pruess, S.M. Benson, S.D. Hovorka, P.R. Knox and C.T. Green, 2001: Capacity investigation of brine-bearing sands of the Frio Formation for geologic sequestration of CO_2. Proceedings of First National Conference on Carbon Sequestration, 14–17 May 2001, Washington, D.C., United States Department of Energy, National Energy Technology Laboratory, CD-ROM USDOE/NETL-2001/1144, Paper P.32, 16 pp.

Ducroux, R. and J.M. Bewers, 2005: Acceptance of CCS under international conventions and agreements, IEA GHG Weyburn CO_2 Monitoring and Storage Project Summary Report 2000-2004, M. Wilson and M. Monea (eds.), Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.II, 1467-1474.

Dusseault, M.B., S. Bachu and L. Rothenburg, 2004: Sequestration of CO_2 in salt caverns. *Journal of Canadian Petroleum Technology*, **43**(11), 49–55.

Emberley, S., I. Hutcheon, M. Shevalier, K. Durocher, W.D. Gunter and E.H. Perkins, 2002: Geochemical monitoring of rock-fluid interaction and CO_2 storage at theWeyburn CO_2 - injection enhanced oil recovery site, Saskatchewan, Canada. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.I, pp. 365–370.

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

Ennis-King, J. and L. Paterson, 2001: Reservoir engineering issues in the geological disposal of carbon dioxide. Proceedings of the 5th International Conference on Greenhouse Gas Control Technologies (GHGT-5), D. Williams, D. Durie, P. McMullan, C. Paulson and A. Smith (eds.), 13–16 August 2000, Cairns, Australia, CSIRO Publishing, Collingwood, Victoria, Australia, pp. 290–295.

Ennis-King, J.P. and L. Paterson, 2003: Role of convective mixing in the long-term storage of carbon dioxide in deep saline formations. Presented at Society of Petroleum Engineers Annual Technical Conference and Exhibition, Denver, Colorado, 5–8 October 2003, SPE paper no. 84344.

Ennis-King, J, C.M. Gibson-Poole, S.C. Lang and L. Paterson, 2003: Long term numerical simulation of geological storage of CO_2 in the Petrel sub-basin, North West Australia. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.I, 507–511.

Espie, A.A, P.J Brand, R.C. Skinner, R.A. Hubbard and H.I. Turan, 2003: Obstacles to the storage of CO_2 through EOR in the North Sea. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.I, 213–218.

EU, 2000: White Paper on Environmental Liability. COM(2000) 66 final, 9 February 2000. European Union Commission, Brussels. http://http://aei.pitt.edu/archive/00001197/01/environment_liability_wp_COM_2000_66.pdf

Eurobarometer, 2003: Energy Issues, Options and Technologies: A Survey of Public Opinion in Europe. Energy DG, European Commission, Brussels, Belgium.

Farrar, C.D., J.M. Neil and J.F. Howle, 1999: Magmatic carbon dioxide emissions at Mammoth Mountain, California. U.S. Geological Survey Water-Resources Investigations Report 98-4217, Sacramento, CA.

Figueiredo, M.A. de, H.J. Herzog and D.M. Reiner, 2005: Framing the long-term liability issue for geologic storage carbon storage in the United States. *Mitigation and Adaptation Strategies for Global Change*. In press.

Fischer, M.L., A.J. Bentley, K.A. Dunkin, A.T. Hodgson, W.W. Nazaroff, R.G. Sextro and J.M. Daisy, 1996: Factors affecting indoor air concentrations of volatile organic compounds at a site of subsurface gasoline contamination, *Environmental Science and Technology*, **30**(10), 2948–2957.

Flett, M.A., R.M. Gurton and I.J. Taggart, 2005: Heterogeneous saline formations: Long-term benefits for geo-sequestration of greenhouse gases. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 501-510.

Flower, F.B., E.F. Gilman and I.A.Leon, 1981: Landfill Gas, What It Does To Trees And How Its Injurious Effects May Be Prevented. *Journal of Arboriculture*, **7**(2), 43–52.

Freund, P., 2001: Progress in understanding the potential role of CO_2 storage. Proceedings of the 5th International Conference on Greenhouse Gas Control Technologies (GHGT-5), D.J. Williams, R.A. Durie, P. McMullan, C.A.J. Paulson and A.Y. Smith (eds.), 13–16 August 2000, Cairns, Australia, pp. 272–278.

Gadgil, A.J., Y.C. Bonnefous and W.J. Fisk, 1994: Relative effectiveness of sub-slab pressurization and depressurization systems for indoor radon mitigation: Studies with an experimentally verified numerical model, *Indoor Air,* **4**, 265–275.

Gale, J., 2003: Geological storage of CO_2: what's known, where are the gaps and what more needs to be done. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.I, 207–212.

Gale, J.J., 2004: Using coal seams for CO_2 sequestration. Geologica Belgica, 7(1–2), In press.

Gale, J. and P. Freund, 2001: Coal-bed methane enhancement with CO_2 sequestration worldwide potential. *Environmental Geosciences*, **8**(3), 210–217.

Garg, A., D. Menon-Choudhary, M. Kapshe and P.R. Shukla, 2005: Carbon dioxide capture and storage potential in India. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada.

Gasda, S.E., S. Bachu and M.A. Celia, 2004: The potential for CO_2 leakage from storage sites in geological media: analysis of well distribution in mature sedimentary basins. *Environmental Geology*, **46**(6–7), 707–720.

Gasem, K.A.M., R.L. Robinson and S.R. Reeves, 2002: Adsorption of pure methane, nitrogen and carbon dioxide and their mixtures on San Juan Basin coal. U.S. Department of Energy Topical Report, Contract No. DE-FC26-OONT40924, 83 pp.

Gerlach, T.M., M.P. Doukas, K.A. McGee and R. Kessler, 1999: Soil efflux and total emission rates of magmatic CO_2 at the Horseshoe Lake tree kill, Mammoth Mountain, California, 1995–1999. *Chemical Geology*, **177**, 101–116.

Gibbs, J.F., J.H. Healy, C.B. Raleigh and J. Coakley, 1973: Seismicity in the Rangely, Colorado area: 1962–1970, *Bulletin of the Seismological Society of America*, **63**, 1557–1570.

Gibson-Poole, C.M., S.C. Lang, J.E. Streit, G.M. Kraishan and R.R Hillis, 2002: Assessing a basin's potential for geological sequestration of carbon dioxide: an example from the Mesozoic of the Petrel Sub-basin, NW Australia. In: M. Keep and S.J. Moss (eds.) The Sedimentary Basins of Western Australia 3, Proceedings of the Petroleum Exploration Society of Australia Symposium, Perth, Western Australia, 2002, pp. 439–463.

Gough, C., I. Taylor and S. Shackley, 2002: Burying carbon under the sea: an initial exploration of public opinion. *Energy & Environment*, **13**(6), 883–900.

Granieri, D., G. Chiodini, W. Marzocchi and R. Avino, 2003: Continuous monitoring of CO_2 soil diffuse degassing at Phlegraean Fields (Italy): influence of environmental and volcanic parameters. *Earth and Planetary Science Letters*, **212**(1–2), 167–179.

Grigg, R.B., 2005: Long-term CO_2 storage: Using petroleum industry experience, Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results from the CO_2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson (ed.), Elsevier, London, pp. 853–866.

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

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

Gunter, W.D., S. Wong, D.B. Cheel and G. Sjostrom, 1998: Large CO_2 sinks: their role in the mitigation of greenhouse gases from an international, national (Canadian) and provincial (Alberta) perspective. *Applied Energy*, **61**, 209–227.

Gunter, W.D., E.H. Perkins and I. Hutcheon, 2000: Aquifer disposal of acid gases: Modeling of water-rock reactions for trapping acid wastes. *Applied Geochemistry*, **15**, 1085–1095.

Gunter, W.D., S. Bachu and S. Benson, 2004: The role of hydrogeological and geochemical trapping in sedimentary basins for secure geological storage for carbon dioxide. In: Geological Storage of Carbon Dioxide: Technology. S. Baines and R.H. Worden (eds.), Special Publication of Geological Society, London, UK. Special Publication 233, pp. 129–145.

Gunter, W.D., M.J. Mavor and J.R. Robinson, 2005: CO_2 storage and enhanced methane production: field testing at Fenn-Big Valley, Alberta, Canada, with application. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 413-422.

Gupta, N., B. Sass, J. Sminchak and T. Naymik, 1999: Hydrodynamics of CO_2 disposal in a deep saline formation in the midwestern United States. Proceedings of the 4th International Conference on Greenhouse Gas Control Technologies (GHGT-4), B. Eliasson, P.W.F. Riemer and A. Wokaun (eds.), 30 August to 2 September 1998, Interlaken, Switzerland, Pergamon, 157–162.

Gurevich, A.E., B.L. Endres, J.O. Robertson Jr. and G.V. Chilingar, 1993: Gas migration from oil and gas fields and associated hazards. *Journal of Petroleum Science and Engineering*, **9**, 223–238.

Haidl, F.M., S.G. Whittaker, M. Yurkowski, L.K. Kreis, C.F. Gilboy and R.B. Burke, 2005: The importance of regional geological mapping in assessing sites of CO_2 storage within intracratonic basins: Examples from the IEA Weyburn CO_2 monitoring and storage project, Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 751-760.

Hantush, M.S., 1960: Modifications to the theory of leaky aquifers, *Journal of Geophysical Research*, **65**(11), 3713–3725.

Hantush, M.S. and C.E. Jacobs, 1955: Non-steady radial flow to an infinite leaky aquifer. *Transactions of the American Geophysical Union*, **2**, 519–524.

Haveman, S.A. and K. Pedersen, 2001: Distribution of culturable microorganisms in Fennoscandian Shield groundwater. *FEMS Microbiology Ecology*, **39**(2), 129–137.

Healy, J.H., W.W. Ruby, D.T. Griggs and C.B. Raleigh, 1968: The Denver earthquakes, *Science*, **161**, 1301–1310.

Hefner, T. A. and K.T. Barrow, 1992: AAPG Treatise on Petroleum Geology. Structural Traps VII, pp. 29–56.

Heinrich, J.J., H.J. Herzog and D.M. Reiner, 2003: Environmental assessment of geologic storage of CO_2. Second National Conference on Carbon Sequestration, 5–8 May 2003, Washington, DC.

Hendriks, C., W. Graus and F. van Bergen, 2002: Global carbon dioxide storage potential and costs. Report Ecofys & The Netherland Institute of Applied Geoscience TNO, Ecofys Report EEP02002, 63 pp.

Hobbs, P.V., L.F. Radke, J.H. Lyons, R.J. Ferek and D.J. Coffman, 1991: Airborne measurements of particle and gas emissions from the 1990 volcanic eruptions of Mount Redoubt. *Journal of Geophysical Research*, **96**(D10), 18735–18752.

Hodgkinson, D.P. and T.J. Sumerling, 1990: A review of approaches to scenario analysis for repository safety assessment. Proceedings of the Paris Symposium on Safety Assessment of Radioactive Waste Repositories, 9–13 October 1989, OECD Nuclear Energy Agency: 333–350.

Holloway, S. (ed.), 1996: The underground disposal of carbon dioxide. Final report of Joule 2 Project No. CT92-0031. British Geological Survey, Keyworth, Nottingham, UK, 355 pp.

Holloway, S., 1997: Safety of the underground disposal of carbon dioxide. *Energy Conversion and Management*, **38**(Suppl.), S241–S245.

Holloway, S. and D. Savage, 1993: The potential for aquifer disposal of carbon dioxide in the UK. *Energy Conversion and Management*, **34**(9–11), 925–932.

Holt, T., J. L. Jensen and E. Lindeberg, 1995: Underground storage of CO_2 in aquifers and oil reservoirs. *Energy Conversion and Management*, **36**(6–9), 535–538.

Holtz, M.H., 2002: Residual gas saturation to aquifer influx: A calculation method for 3-D computer reservoir model construction. SPE Paper 75502, presented at the SPE Gas Technologies Symposium, Calgary, Alberta, Canada. April 2002.

Holtz, M.H., P.K. Nance and R.J. Finley, 2001: Reduction of greenhouse gas emissions through CO_2 EOR in Texas. *Environmental Geosciences*, **8**(3) 187–199.

Hoversten, G.M. and E. Gasperikova, 2005: Non Seismic Geophysical Approaches to Monitoring, Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results from the CO_2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson (ed.), Elsevier Science, London. pp. 1071–1112.

Hoversten, G. M., R. Gritto, J. Washbourne and T.M. Daley, 2003: Pressure and Fluid Saturation Prediction in a Multicomponent Reservoir, using Combined Seismic and Electromagnetic Imaging. *Geophysics*, (in press Sept–Oct 2003).

Hovorka, S.D., C. Doughty and M.H. Holtz, 2005: Testing Efficiency of Storage in the Subsurface: Frio Brine Pilot Experiment, Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), Vancouver, Canada. September 5–9, 2004, v.II, 1361-1366.

Huijts, N. 2003: Public Perception of Carbon Dioxide Storage, Masters Thesis, Eindhoven University of Technology, The Netherlands.

IEA-GHG, 1998: Enhanced Coal Bed Methane Recovery with CO_2 Sequestration, IEA Greenhouse Gas R&D Programme, Report No. PH3/3, August, 139 pp.

IEA-GHG, 2003: Barriers to Overcome in Implementation of CO_2 Capture and Storage (2):Rules and Standards for the Transmission and Storage of CO_2, IEA Greenhouse Gas R&D Programme, Report No. PH4/23. Cheltenham, U.K.

IEA-GHG, 2004: A Review of Global Capacity Estimates for the Geological Storage of Carbon Dioxide, IEA Greenhouse Gas R&D Programme Technical Review (TR4), March 23, 2004, 27 pp.

IOGCC (Interstate Oil and Gas Compact Commission), 2005: Carbon Capture and Storage: A Regulatory Framework for States. Report to USDOE, 80 pp.

Ispen, K.H. and F.L. Jacobsen, 1996: The Linde structure, Denmark: an example of a CO_2 depository with a secondary chalk cap rock. *Energy and Conversion and Management*, **37**(6–8), 1161–1166.

Itaoka, K., A. Saito and M. Akai, 2005: Public acceptance of CO_2 capture and storage technology: A survey of public opinion to explore influential factors. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, p.1011.

Jarrell, P.M., C.E. Fox, M.H. Stein and S.L. Webb, 2002: Practical Aspects of CO_2 Flooding. SPE Monograph Series No. 22, Richardson, TX, 220 pp.

Jimenez, J.A and R.J. Chalaturnyk, 2003: Are disused hydrocarbon reservoirs safe for geological storage of CO_2? Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.I, 471–476.

Johnson, J.W., J.J. Nitao and J.P. Morris, 2005: Reactive transport modeling of cap rock integrity during natural and engineered CO_2 storage, Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results from the CO_2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson, (ed.), Elsevier, London, pp. 787–814.

Kaarstad, O., 1992: Emission-free fossil energy from Norway. *Energy Conversion and Management*, **33**(5–8), 619–626.

Kaarstad, O., 2002: Geological storage including costs and risks, in saline aquifers, Proceedings of workshop on Carbon Dioxide Capture and Storage, Regina Canada, 2002.

Katzung, G., P. Krull and F. Kühn, 1996: Die Havarie der UGS-Sonde Lauchstädt 5 im Jahre 1988 - Auswirkungen und geologische Bedingungen. *Zeitschrift für Angewandte Geologie*, **42**, 19–26.

Keith, D.W. and M. Wilson, 2002: Developing recommendations for the management of geologic storage of CO_2 in Canada. University of Regina, PARC, Regina, Saskatchewan.

Keith, D., H. Hassanzadeh and M. Pooladi-Darvish, 2005: Reservoir Engineering To Accelerate Dissolution of Stored CO_2 In Brines. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.II, 2163-2168.

Kempton, W., J. Boster and J. Hartley, 1995: Environmental Values in American Culture. MIT Press, Boston, MA, 320 pp.

Kling, G.W., M.A. Clark, H.R. Compton, J.D. Devine, W.C. Evans, A.M. Humphrey, E.J. Doenigsberg, J.P. Lockword, M.L. Tuttle and G.W. Wagner, 1987: The lake gas disaster in Cameroon, West Africa, *Science*, **236**, 4798, 169–175.

Klins, M.A., 1984: Carbon Dioxide Flooding, D. Reidel Publishing Co., Boston, MA, 267 pp.

Klins, M.A. and S.M. Farouq Ali, 1982: Heavy oil production by carbon dioxide injection. *Journal of Canadian Petroleum Technology*, **21**(5), 64–72.

Klusman, R.W., 2003: A geochemical perspective and assessment of leakage potential for a mature carbon dioxide-enhanced oil recovery project and as a prototype for carbon dioxide sequestration; Rangely field, Colorado. *American Association of Petroleum Geologists Bulletin*, **87**(9), 1485–1507.

Knauss, K.G., J.W. Johnson and C.I Steefel, 2005: Evaluation of the impact of CO_2, co-contaminant gas, aqueous fluid and reservoir rock interactions on the geologic sequestration of CO_2. *Chemical Geology,* Elsevier, **217**, 339–350.

Koide, H. and K. Yamazaki, 2001: Subsurface CO_2 disposal with enhanced gas recovery and biogeochemical carbon recycling. *Environmental Geosciences*, **8**(3), 218–224.

Koide, H.G., Y. Tazaki, Y. Noguchi, S. Nakayama, M. Iijima, K. Ito and Y. Shindo, 1992: Subterranean containment and long-term storage of carbon dioxide in unused aquifers and in depleted natural gas reservoirs. *Energy Conversion and Management*, **33**(5–8), 619–626.

Koide, H.G., M. Takahashi and H. Tsukamoto, 1995: Self-trapping mechanisms of carbon dioxide. *Energy Conversion and Management*, **36**(6–9), 505–508.

Koide, H., M. Takahashi, Y. Shindo, Y. Tazaki, M. Iijima, K. Ito, N. Kimura and K. Omata, 1997: Hydrate formation in sediments in the sub-seabed disposal of CO_2. *Energy-The International Journal*, **22**(2/3), 279–283.

Korbol, R. and A. Kaddour, 1994: Sleipner West CO_2 disposal: injection of removed CO_2 into the Utsira formation. *Energy Conversion and Management*, **36**(6–9), 509–512.

Kovscek, A.R., 2002: Screening criteria for CO_2 storage in oil reservoirs. *Petroleum Science and Technology*, **20**(7–8), 841–866.

Krom, T.D., F.L. Jacobsen and K.H. Ipsen, 1993: Aquifer based carbon dioxide disposal in Denmark: capacities, feasibility, implications and state of readiness. *Energy Conversion and Management*, **34**(9–11), 933–940.

Krooss, B.M., F. van Bergen, Y. Gensterblum, N. Siemons, H.J.M. Pagnier and P. David, 2002: High-pressure methane and carbon dioxide adsorption on dry and moisture-equilibrated Pennsylvanian coals. *International Journal of Coal Geology*, **51**(2), 69–92.

Kumar, A., M.H. Noh, K. Sepehrnoori, G.A. Pope, S.L. Bryant and L.W. Lake, 2005: Simulating CO_2 storage in deep saline aquifers, Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results from the CO_2 Capture Project, v.2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson, (ed.), Elsevier, London. pp. 977–898.

Larsen, J.W., 2003: The effects of dissolved CO_2 on coal structure and properties. *International Journal of Coal Geology*, **57**, 63–70.

Larsen, M., N.P. Christensen, B. Reidulv, D. Bonijoly, M. Dusar, G. Hatziyannis, C. Hendriks, S. Holloway, F. May and A. Wildenborg, 2005: Assessing European potential for geological storage of CO_2 - the GESTCO project. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada.

Law, D. (ed.), 2005: Theme 3: CO_2 Storage Capacity and Distribution Predictions and the Application of Economic Limits. In: IEA GHG Weyburn CO_2 Monitoring and Storage Project Summary Report 2000–2004, M. Wilson and M. Monea (eds.), Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT7), Volume III, p 151–209.

Law, D.H.-S., L.G.H. van der Meer and W.D. Gunter, 2003: Comparison of numerical simulators for greenhouse gas storage in coal beds, Part II: Flue gas injection. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.I, 563–568.

Lee, A.M., 2001: The Hutchinson Gas Explosions: Unravelling a Geologic Mystery, Kansas Bar Association, 26th Annual KBA/KIOGA Oil and Gas Law Conference, v1, p3-1 to 3-29.

Lenstra, W.J. and B.C.W. van Engelenburg, 2002: Legal and policy aspects: impact on the development of CO_2 storage. Proceedings of IPCC Working Group III: Mitigation of Climate Change Workshop on Carbon Dioxide Capture and Storage, Regina, Canada, 18–21, November, 2002.

Leone, I.A., F.B. Flower, J.J. Arthur and E.F. Gilman, 1977: Damage To Woody Species By Anaerobic Landfill Gases. *Journal of Arboriculture*, **3**(12), 221–225.

Lichtner, P.C., 2001: FLOTRAN User's Manual. Los Alamos National Laboratory Report LA-UR-01-2349, Los Alamos, NM, 2001.

Lindeberg, E. and P. Bergmo, 2003: The long-term fate of CO_2 injected into an aquifer. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.I, 489–494.

Lindeberg, E. and D. Wessel-Berg, 1997: Vertical convection in an aquifer column under a gas cap of CO_2. *Energy Conversion and Management*, **38**(Suppl.), S229–S234.

Lindeberg, E., A. Ghaderi, P. Zweigel and A. Lothe, 2001: Prediction of CO_2 dispersal pattern improved by geology and reservoir simulation and verified by time lapse seismic, Proceedings of 5th International Conference on Greenhouse Gas Control Technologies, D.J. Williams, R.A. Durie, P. McMullan, C.A.J. Paulson and A.Y. Smith (eds.), CSIRO, Melbourne, Australia. pp. 372–377.

Lippmann, M.J. and S.M. Benson, 2003: Relevance of underground natural gas storage to geologic sequestration of carbon dioxide. Department of Energy's Information Bridge, http://www.osti.gov/dublincore/ecd/servlets/purl/813565-MVm7Ve/native/813565.pdf, U.S. Government Printing Office (GPO).

Looney, B. and R. Falta, 2000: Vadose Zone Science and Technology Solutions: Volume II, Batelle Press, Columbus, OH.

Magoon, L.B. and W.G. Dow, 1994: The petroleum system. American Association of Petroleum Geologists, *Memoir* **60**, 3–24.

Marchetti, C., 1977: On Geoengineering and the CO_2 Problem. Climatic Change, 1, 59–68.

Martin, F.D. and J. J. Taber, 1992: Carbon dioxide flooding. *Journal of Petroleum Technology*, **44**(4), 396–400.

Martini, B. and E. Silver, 2002: The evolution and present state of tree-kills on Mammoth Mountain, California: tracking volcanogenic CO_2 and its lethal effects. Proceedings of the 2002 AVIRIS Airborne Geoscience Workshop, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA.

May, F., 1998: Thermodynamic modeling of hydrothermal alteration and geoindicators for CO_2-rich waters. *Zeitschrift der Deutschen Geologischen Gesellschaft*, **149**, 3, 449–464.

McGrail, B.P., S.P. Reidel and H.T. Schaef, 2003: Use and features of basalt formations for geologic sequestration. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.II, 1637–1641.

McKelvey, V.E., 1972: Mineral resource estimates and public policy. *American Scientist*, **60**(1), 32–40.

McKinnon, R.J., 1998: The interplay between production and underground storage rights in Alberta, *The Alberta Law Review*, **36**(400).

McPherson, B.J.O.L. and B.S. Cole, 2000: Multiphase CO_2 flow, transport and sequestration in the Powder River basin, Wyoming, USA. *Journal of Geochemical Exploration*, **69–70**(6), 65–70.

Menzies, R.T., D.M., Tratt, M.P. Chiao and C.R. Webster, 2001: Laser absorption spectrometer concept for globalscale observations of atmospheric carbon dioxide. 11th Coherent Laser Radar Conference, Malvern, United Kingdom.

Metcalfe, R.S., 1982: Effects of impurities on minimum miscibility pressures and minimum enrichment levels for CO_2 and rich gas displacements. *SPE Journal*, **22**(2), 219–225.

Miles, N., K. Davis and J. Wyngaard, 2005: Detecting Leaks from CO_2 Reservoirs using Micrometeorological Methods, Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results from the CO_2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson (ed.), Elsevier Science, London. pp.1031–1044.

Moberg, R., D.B. Stewart and D. Stachniak, 2003: The IEA Weyburn CO_2 Monitoring and Storage Project. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, 219–224.

Morgan, M.G. and M. Henrion, 1999: Uncertainty: A guide to dealing with uncertainty in quantitative risk and policy analysis. Cambridge University Press, New York, NY.

Moritis, G., 2002: Enhanced Oil Recovery, *Oil and Gas Journal,* **100**(15), 43–47.

Moritis, G., 2003: CO_2 sequestration adds new dimension to oil, gas production. *Oil and Gas Journal*, **101**(9), 71–83.

Morner, N.A. and G. Etiope, 2002: Carbon degassing from the lithosphere. *Global and Planetary Change*, **33**, 185–203.

Morrow, T.B., D.L. George and M.G. Nored, 2003: Operational factors that affect orifice meter accuracy: Key findings from a multi-year study. Flow Control Network.

Myer, L.R., G.M. Hoversten and E. Gasperikova, 2003: Sensitivity and cost of monitoring geologic sequestration using geophysics. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan. *Pergamon*, **1**, 377–382.

NETL, 2004: Carbon Sequestration Technology Roadmap and Program Plan – 2004. US Department of Energy – National Energy Technology Laboratory Report, April 2004, http://www.fe.doe.gov/programs/sequestration/publications/programplans/2004/SequestrationRoadmap4-29-04.pdf

Nimz, G.J. and G.B. Hudson, 2005: The use of noble gas isotopes for monitoring leakage of geologically stored CO_2, Carbon Dioxide Capture for Storage in Deep Geologic Formations—Results from the CO_2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification S.M. Benson (ed.), Elsevier Science, London,. pp. 1113–1130.

Nitao, J.J., 1996: The NUFT code for modeling nonisothermal, multiphase, multicomponent flow and transport in porous media. EOS, *Transactions of the American Geophysical Union*, **74**(3), 3.

Nordbotten, J.M., M.A. Celia and S. Bachu, 2005a: Injection and storage of CO_2 in deep saline aquifers: Analytical solution for CO_2 plume evolution during injection. *Transport in Porous Media,* **58**, 339–360, DOI 10.1007/s11242-004-0670-9.

Nordbotten, J.M., M.A. Celia and S. Bachu, 2005b: Semi-analytical solution for CO_2 leakage through an abandoned well. *Environmental Science and Technology*, **39**(2), 602–611.

North, D.W., 1999: A perspective on nuclear waste. *Risk Analysis*, **19**, 751–758.

Obdam, A., L.G.H. van der Meer, F. May, C. Kervevan, N. Bech and A. Wildenborg, 2003: Effective CO_2 storage capacity in aquifers, gas fields, oil fields and coal fields. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.I, 339–344.

Oen, P. M., 2003: The development of the Greater Gorgon Gas Fields. *The APPEA Journal 2003*, **43**(2), 167–177.

Oil and Gas Conservation Regulations, 1985 (with amendments through 2000): Saskatchewan Industry and Resources, 70 pp.

Oldenburg, C.M. and A.J. Unger, 2003: On leakage and seepage from geologic carbon sequestration sites: unsaturated zone attenuation. *Vadose Zone Journal*, **2**, 287–296.

Oldenburg, C.M. and A.J.A. Unger, 2004: Coupled subsurface-surface layer gas transport for geologic carbon sequestration seepage simulation. *Vadose Zone Journal*, **3**, 848–857.

Oldenburg, C.M., K. Pruess and S. M. Benson, 2001: Process modeling of CO_2 injection into natural gas reservoirs for carbon sequestration and enhanced gas recovery. *Energy and Fuels*, **15**, 293–298.

Oldenburg, C.M., S.H. Stevens and S.M. Benson, 2002: Economic Feasibility of Carbon Sequestration with Enhanced Gas Recovery (CSEGR). Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.I, 691–696.

Onstott, T., 2005: Impact of CO_2 injections on deep subsurface microbial ecosystems and potential ramifications for the surface biosphere, Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results from the CO_2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson (ed.), Elsevier Science, London, pp. 1217–1250.

Orphan, V.J., L.T. Taylor, D. Hafenbradl and E.F. Delong, 2000: Culture-dependent and culture-independent characterization of microbial assemblages associated with high-temperature petroleum reservoirs. *Applied and Environmental Microbiology*, **66**(2), 700–711.

Oskarsson, N., K. Palsson, H. Olafsson and T. Ferreira, 1999: Experimental monitoring of carbon dioxide by low power IR-sensors; Soil degassing in the Furnas volcanic centre, Azores. *Journal of Volcanology and Geothermal Research*, **92**(1–2), 181–193.

OSPAR Commission, 2004: Report from the Group of Jurists and Linguists on the placement of carbon dioxide in the OSPAR maritime area. Annex 12 to 2004 Summary Record.

Palmer, I. and J. Mansoori, 1998: How permeability depends on stress and pore pressure in coalbeds: a new model. *SPE Reservoir Evaluation & Engineering*, **1**(6), 539–544.

Palmgren, C., M. Granger Morgan, W. Bruine de Bruin and D. Keith, 2004: Initial public perceptions of deep geological and oceanic disposal of CO_2. *Environmental Science and Technology*. In press.

Parkes, R.J., B.A. Cragg and P. Wellsbury, 2000: Recent studies on bacterial populations and processes in subseafloor sediments: a review. *Hydrogeology Journal*, **8**(1), 11–28.

Pearce, J.M., S. Holloway, H. Wacker, M.K. Nelis, C. Rochelle and K. Bateman, 1996: Natural occurrences as analogues for the geological disposal of carbon dioxide. *Energy Conversion and Management*, **37**(6–8), 1123–1128.

Pearce, J.M., J. Baker, S. Beaubien, S. Brune, I. Czernichowski-Lauriol, E. Faber, G. Hatziyannis, A. Hildebrand, B.M. Krooss, S. Lombardi, A. Nador, H. Pauwels and B.M. Schroot, 2003: Natural CO_2 accumulations in Europe: Understanding the long-term geological processes in CO_2 sequestration. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.I, 417–422

Perkins, E., I. Czernichowski-Lauriol, M. Azaroual and P. Durst, 2005: Long term predictions of CO_2 storage by mineral and solubility trapping in the Weyburn Midale Reservoir. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.II, 2093-2096.

Perry, K.F., 2005: Natural gas storage industry experience and technology: Potential application to CO_2 geological storage, Carbon Dioxide Capture for Storage in Deep Geologic Formations—Results from the CO_2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson (ed.), Elsevier Science, London, pp. 815–826.

Pickles, W.L., 2005: Hyperspectral geobotanical remote sensing for CO_2, Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results from the CO_2 Capture Project, v.2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson (ed.), Elsevier Science, London, pp. 1045–1070.

Piessens, K. and M. Dusar, 2004: Feasibility of CO_2 sequestration in abandoned coal mines in Belgium. *Geologica Belgica*, **7**-3/4. In press.

Pizzino, L., G. Galli, C. Mancini, F. Quattrocchi and P. Scarlato, 2002: Natural gas hazard (CO_2, ^{222}Rn) within a quiescent volcanic region and its relations with tectonics; the case of the Ciampino-Marino area, Alban Hills Volcano, Italy. *Natural Hazards*, **27**(3), 257–287.

Poortinga, W. and N. Pidgeon, 2003: Public Perceptions of Risk, Science and Governance. Centre for Environmental Risk, University of East Anglia, Norwich, UK, 60 pp.

Pruess, K., C. Oldenburg and G. Moridis, 1999: TOUGH2 User's Guide, Version 2.0, Lawrence Berkeley National Laboratory Report LBNL-43134, Berkeley, CA, November, 1999.

Pruess, K., J. García, T. Kovscek, C. Oldenburg, J. Rutqvist, C. Steefel and T. Xu, 2004: Code Intercomparison Builds Confidence in Numerical Simulation Models for Geologic Disposal of CO_2. *Energy*, 2003.

Purdy, R. and R. Macrory, 2004: Geological carbon sequestration: critical legal issues. Tyndall Centre Working Paper 45.

Raleigh, C.B., J.D. Healy and J.D. Bredehoeft, 1976: An experiment in earthquake control of Rangely, Colorado. *Science*, **191**, 1230–1237.

Reeves, S., 2003a: Coal-Seq project update: field studies of ECBM recovery/CO_2 sequestration in coal seams. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.I, 557–562.

Reeves, S.R., 2003b: Assessment of CO_2 Sequestration and ECBM Potential of US Coalbeds, Topical Report for US Department of Energy by Advanced Resources International, Report No. DE-FC26-00NT40924, February 2003.

Reeves, S.R., 2005: The Coal-Seq project: Key results from field, laboratory and modeling studies. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.II, 1399-1406.

Reeves, S., A. Taillefert, L. Pekot and C. Clarkson, 2003: The Allison Unit CO_2-ECBM Pilot: A Reservoir Modeling Study. DOE Topical Report, February, 2003.

Reeves, S., D. Davis and A. Oudinot, 2004: A Technical and Economic Sensitivity Study of Enhanced Coalbed Methane Recovery and Carbon Sequestration in Coal. DOE Topical Report, March, 2004.

Reiner, D.M. and H.J. Herzog, 2004: Developing a set of regulatory analogs for carbon sequestration. *Energy*, **29**(9/10): 1561–1570.

Riddiford, F.A., A. Tourqui, C.D. Bishop, B. Taylor and M. Smith, 2003: A cleaner development: The In Salah Gas Project, Algeria. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya, (eds.), 1–4 October 2002, Kyoto, Japan, v.I, 601–606.

Rigg, A., G. Allinson, J. Bradshaw, J. Ennis-King, C.M. Gibson-Poole, R.R. Hillis, S.C. Lang and J.E. Streit, 2001: The search for sites for geological sequestration of CO_2 in Australia: A progress report on GEODISC. *APPEA Journal,* **41**, 711–725.

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

Rochelle, C.A., I. Czernichowski-Lauriol and A.E. Milodowski, 2004: The impact of chemical reactions on CO_2 storage in geological formations, a brief review. In: Geological Storage of Carbon Dioxide for Emissions Reduction: Technology, S.J. Baines and R.H. Worden (eds.). Geological Society Special Publication, Bath, UK.

Rogie, J.D., D.M. Kerrick, M.L. Sorey, G. Chiodini and D.L. Galloway, 2001: Dynamics of carbon dioxide emission at Mammoth Mountain, California. *Earth and Planetary Science Letters*, **188**, 535–541.

Rutqvist, J. and C-F. Tsang, 2002: A study of caprock hydromechanical changes associated with CO_2 injection into a brine formation. *Environmental Geology*, **42**, 296–305.

Salvi, S., F. Quattrocchi, M. Angelone, C.A. Brunori, A. Billi, F. Buongiorno, F. Doumaz, R. Funiciello, M. Guerra, S. Lombardi, G. Mele, L. Pizzino and F. Salvini, 2000: A multidisciplinary approach to earthquake research: implementation of a Geochemical Geographic Information System for the Gargano site, Southern Italy. Natural Hazard, 20(1), 255–278.

Saripalli, K.P., N.M. Mahasenan and E.M. Cook, 2003: Risk and hazard assessment for projects involving the geological sequestration of CO_2. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.I, 511–516.

Scherer, G.W., M.A. Celia, J-H. Prevost, S. Bachu, R. Bruant, A. Duguid, R. Fuller, S.E. Gasda, M. Radonjic and W. Vichit-Vadakan, 2005: Leakage of CO_2 through Abandoned Wells: Role of Corrosion of Cement, Carbon Dioxide Capture for Storage in Deep Geologic Formations—Results from the CO_2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, Benson, S.M. (Ed.), Elsevier Science, London, pp. 827–850.

Schremp, F.W. and G.R. Roberson, 1975: Effect of supercritical carbon dioxide (CO_2) on construction materials. *Society of Petroleum Engineers Journal,* June 1975, 227–233.

Schreurs, H.C.E., 2002: Potential for geological storage of CO_2 in the Netherlands. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.I, 303–308.

Sebastian, H.M., R.S. Wenger and T.A. Renner, 1985: Correlation of minimum miscibility pressure for impure CO_2 streams. *Journal of Petroleum Technology,* **37**(12), 2076–2082.

Sedlacek, R., 1999: Untertage Erdgasspeicherung in Europa. Erdol, Erdgas, Kohle 115, 573–540.

Shackley, S., C. McLachlan and C. Gough, 2004: The public perception of carbon dioxide capture and storage in the UK: Results from focus groups and a survey, *Climate Policy.* In press.

Shapiro, S.A., E. Huenges and G. Borm, 1997: Estimating the crust permeability from fluid-injection-induced seismic emission at the KTB site. *Geophysical Journal International,* 131, F15–F18.

Shaw, J. C. and S. Bachu, 2002: Screening, evaluation and ranking of oil reserves suitable for CO_2 flood EOR and carbon dioxide sequestration. *Journal of Canadian Petroleum Technology,* **41**(9), 51–61.

Shi, J-Q. and S. Durucan, 2005: A numerical simulation study of the Allison Unit CO_2-ECBM pilot: the effect of matrix shrinkage and swelling on ECBM production and CO_2 injectivity. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 431-442.

Shuler, P. and Y. Tang, 2005: Atmospheric CO_2 monitoring systems, Carbon Dioxide Capture for Storage in Deep Geologic Formations—Results from the CO_2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson (ed.), Elsevier Science, London, pp. 1015–1030.

Skinner, L., 2003: CO_2 blowouts: An emerging problem. World Oil, 224(1).

Sleipner Best Practice Manual, 2004: S. Holloway, A. Chadwick, E. Lindeberg, I. Czernichowski-Lauriol and R. Arts (eds.), Saline Aquifer CO_2 Storage Project (SACS). 53 pp.

Sminchak, J., N. Gupta, C. Byrer and P. Bergman, 2002: Issues related to seismic activity induced by the injection of CO_2 in deep saline aquifers. *Journal of Energy & Environmental Research,* **2,** 32–46.

Sorey, M. L., W.C. Evans, B.M. Kennedy, C.D. Farrar, L.J. Hainsworth and B. Hausback, 1996: Carbon dioxide and helium emissions from a reservoir of magmatic gas beneath Mammoth Mountain, California. *Journal of Geophysical Research,* **103**(B7), 15303–15323.

Steefel C. I., 2001: CRUNCH. Lawrence Livermore National Laboratory, Livermore, CA. 76 pp.

Stenhouse, M., M. Wilson, H. Herzog, M. Kozak and W. Zhou, 2004: Regulatory Issues Associated with Long-term Storage and Sequestration of CO_2. IEA Greenhouse Gas Report, 34–35.

Stenhouse, M., W. Zhou, D. Savage and S. Benbow, 2005: Framework methodology for long-term assessment of the fate of CO_2 in the Weyburn Field, Carbon Dioxide Capture for Storage in Deep Geologic Formations—Results from the CO_2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, Benson, S.M. (Ed.), Elsevier Science, London, pp. 1251–1262.

Stevens, S. H., J.A. Kuuskraa and R.A. Schraufnagel, 1996: Technology spurs growth of U.S. coalbed methane. *Oil and Gas Journal,* **94**(1), 56–63.

Stevens, S.H., V.K. Kuuskraa and J. Gale, 2000: Sequestration of CO_2 in depleted oil and gas fields: Global capacity and barriers to overcome. Proceedings of the 5th International Conference on Greenhouse Gas Control Technologies (GHGT5), Cairns, Australia, 13–16 August, 2000.

Stevens, S.H., C.E. Fox and L.S. Melzer, 2001a: McElmo dome and St. Johns natural CO_2 deposits: Analogs for geologic sequestration. Proceedings of the 5th International Conference on Greenhouse Gas Control Technologies (GHGT-5), D.J. Williams, R.A. Durie, P. McMullan, C.A.J. Paulson and A.Y. Smith (eds.), 13–16 August 2000, Cairns, Australia, CSIRO Publishing, Collingwood, Victoria, Australia, 317–321.

Stevens, S. H., V.A. Kuuskra and J.J. Gale, 2001b: Sequestration of CO_2 in depleted oil and gas fields: global capacity, costs and barriers. Proceedings of the 5th International Conference on Greenhouse Gas Control Technologies (GHGT-5), D.J. Williams, R.A. Durie, P. McMullan, C.A.J. Paulson and A.Y. Smith (eds.), 13–16 August 2000, Cairns, Australia, CSIRO Publishing, Collingwood, Victoria, Australia, pp. 278–283.

Stevens, S.H., V.A. Kuuskra, J. Gale and D. Beecy, 2001c: CO_2 injection and sequestration in depleted oil and gas fields and deep coal seams: worldwide potential and costs. *Environmental Geosciences,* **8**(3), 200–209.

Stevens, S.H., C. Fox, T. White, S. Melzer and C. Byrer, 2003: Production operations at natural CO_2 Fields: Technologies for geologic sequestration. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon,.v.I, 429–433.

Streit, J.E. and R.R. Hillis, 2003: Building geomechanical models for the safe underground storage of carbon dioxide in porous rock. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, Amsterdam, v.I., 495–500.

Streit, J., A. Siggins and B. Evans, 2005: Predicting and monitoring geomechanical effects of CO_2 injection, Carbon Dioxide Capture for Storage in Deep Geologic Formations—Results from the CO_2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson (ed.), Elsevier Science, London, pp. 751–766.

Strutt, M.H, S.E. Beaubien, J.C. Beabron, M. Brach, C. Cardellini, R. Granieri, D.G. Jones, S. Lombardi, L. Penner, F. Quattrocchi and N. Voltatorni, 2003: Soil gas as a monitoring tool of deep geological sequestration of carbon dioxide: preliminary results from the EnCana EOR project in Weyburn, Saskatchewan (Canada). Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, Amsterdam, v.I., 391–396.

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

Taber, J.J., F.D. Martin and R.S. Seright, 1997: EOR screening criteria revisited - part 1: introduction to screening criteria and enhanced recovery fields projects. *SPE Reservoir Engineering,* **12**(3), 189–198.

Talebi, S., T.J. Boone and J.E. Eastwood, 1998: Injection induced microseismicity in Colorado shales. *Pure and Applied Geophysics,* **153**, 95–111.

Tamura, S., N. Imanaka, M. Kamikawa and G. Adachi, 2001: A CO_2 sensor based on a Sc^{3+} conducting $Sc_{1/3}Zr_2(PO_4)_3$ solid electrolyte. *Sensors and Actuators B,* **73**, 205–210.

Tanaka, S., H. Koide and A. Sasagawa, 1995: Possibility of underground CO_2 sequestration in Japan. *Energy Conversion and Management,* **36**(6–9), 527–530.

Torp, T. and K.R. Brown, 2005: CO_2 underground storage costs as experienced at Sleipner and Weyburn. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 531-540.

Torp, T.A. and J. Gale, 2003: Demonstrating storage of CO_2 in geological reservoirs: the Sleipner and SACS projects. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, Amsterdam, v.I, 311–316.

USEPA, 1994: Determination of Maximum Injection Pressure for Class I Wells. Region 5 -- Underground Injection Control Section Regional Guidance #7.

U.S. Geological Survey, 2001a: U.S. Geological Survey World Petroleum Assessment 2000 - Description and Results. U.S. Geological Survey Digital Data Series - DDS-60. http://greenwood.cr.usgs.gov/energy/WorldEnergy/DDS-60/.

U.S. Geological Survey, 2001b: U.S. Geological Survey, On-line factsheet 172-96 Version 2. Invisible Gas Killing Trees at Mammoth Mountain California. http://wrgis.wr.usgs.gov/fact-sheet/fs172-96/.

Van Bergen, F., H.J.M. Pagnier, L.G.H. van der Meer, F.J.G. van den Belt, P.L.A. Winthaegen and R.S. Westerhoff, 2003a: Development of a field experiment of CO_2 storage in coal seams in the Upper Silesian Basin of Poland (RECOPOL). Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.I, 569–574.

Van Bergen, F., A.F.B. Wildenborg, J. Gale and K.J. Damen, 2003b: Worldwide selection of early opportunities for CO_2-EOR and CO_2-ECBM. Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6), J. Gale and Y. Kaya (eds.), 1–4 October 2002, Kyoto, Japan, Pergamon, v.I, 639–644.

Van der Burgt, M.J., J. Cantle and V.K. Boutkan, 1992: Carbon dioxide disposal from coal-based IGCC's in depleted gas fields. *Energy Conversion and Management,* **33**(5–8), 603–610.

Van der Meer, L.G.H., 1992: Investigation regarding the storage of carbon dioxide in aquifers in the Netherlands. *Energy Conversion and Management,* **33**(5–8), 611–618.

Van der Meer, L.G.H., 1995: The CO_2 storage efficiency of aquifers. *Energy Conversion and Management,* **36**(6–9), 513–518.

Van der Meer L.G.H., 1996: Computer modeling of underground CO_2 storage. *Energy Conversion and Management,* **37**(6–8), 1155–1160.

Van der Meer, L.G.H., R.J. Arts and L. Paterson, 2001: Prediction of migration of CO_2 after injection into a saline aquifer: reservoir history matching of a 4D seismic image with a compositional gas/water model. Proceedings of the 5th International Conference on Greenhouse Gas Control Technologies (GHGT-5), D.J. Williams, R.A. Durie, P. McMullan, C.A.J. Paulson and A.Y. Smith (eds.), 2001, CSIRO, Melbourne, Australia, 378–384.

Van der Meer, L.G.H., J. Hartman, C. Geel and E. Kreft, 2005: Re-injecting CO_2 into an offshore gas reservoir at a depth of nearly 4000 metres sub-sea. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 521-530.

Vavra, C.L., J.G. Kaldi and R.M. Sneider, 1992: Geological applications of capillary pressure: a review. *American Association of Petroleum Geologists Bulletin,* **76**(6), 840–850.

Vine, E., 2004: Regulatory constraints to carbon sequestration in terrestrial ecosystems and geological formations: a California perspective. *Mitigation and Adaptation Strategies for Global Change,* **9,** 77–95.

Wall, C., C. Bernstone. and M. Olvstam, 2005: International and European legal aspects on underground geological storage of CO_2, Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), v.I, 971-978.

Walton, F.C., J.C Tait, D. LeNeveu and M.I. Sheppard, 2005: Geological storage of CO_2: A statistical approach to assessing performance and risk. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 693-700.

Wang, S. and P.R. Jaffé, 2004: Dissolution of Trace Metals in Potable Aquifers due to CO_2 Releases from Deep Formations. Energy Conversion and Management. In press.

Watson, M.N., C.J. Boreham and P.R. Tingate, 2004: Carbon dioxide and carbonate elements in the Otway Basin: implications for geological storage of carbon dioxide. *The APPEA Journal*, **44**(1), 703–720.

White, C.M., B.R. Strazisar, E.J. Granite, J.S. Hoffman and H.W. Pennline, 2003: Separation and capture of CO_2 from large stationary sources and sequestration in geological formations--coalbeds and deep saline aquifers, Air and Waste Management Association (AWMA) Critical Review Papers, http://www.awma.org/journal/ShowAbstract.asp?Year=2003&PaperID=1066, June 2003.

White, D. (ed.), 2005: Theme 2: Prediction, Monitoring and Verification of CO_2 Movements. In: IEA GHG Weyburn CO_2 Monitoring and Storage Project Summary Report 2000-2004, M. Wilson and M. Monea (eds.), Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), Volume III, p 73–148.

White, D.J., G. Burrowes, T. Davis, Z. Hajnal, K. Hirsche, I. Hutcheon, E. Majer, B. Rostron and S. Whittaker, 2004: Greenhouse gas sequestration in abandoned oil reservoirs: The International Energy Agency Weyburn pilot project. *GSA Today*, **14**, 4–10.

White, M.D. and M. Oostrom, 1997: STOMP, Subsurface Transport Over Multiple Phases. Pacific Northwest National Laboratory Report PNNL-11218, Richland, WA, October 1997.

White, S.P.,1995: Multiphase Non-Isothermal Transport of Systems of Reacting Chemicals. *Water Resources Research,* **32**(7), 1761–1772.

Whitman, W.B., D.C. Coleman and W.J. Wiebe, 2001: Prokaryotes: The unseen majority. *Proceedings of the National Academy of Sciences U.S.A.*, **95**(12), 6578–6583.

Wildenborg, A.F.B., A.L. Leijnse, E. Kreft, M.N. Nepveu, A.N.M. Obdam, B. Orlic, E.L. Wipfler, B. van der Grift, W. van Kesteren, I. Gaus, I. Czernichowski-Lauriol, P. Torfs and R. Wojcik, 2005a: Risk assessment methodology for CO_2 sequestration scenario approach, Carbon Dioxide Capture for Storage in Deep Geologic Formations—Results from the CO_2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson (ed.), Elsevier Science, London, pp. 1293–1316.

Wildenborg, T., J. Gale, C. Hendriks, S. Holloway, R. Brandsma, E. Kreft and A. Lokhorst, 2005b: Cost curves for CO_2 storage: European sector. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 603-610.

Wilson, E., 2004: Managing the Risks of Geologic Carbon Sequestration: A Regulatory and Legal Analysis. Doctoral Dissertation, Engineering and Public Policy, Carnegie Mellon, Pittsburgh, PA, U.S.A.

Wilson, E., T. Johnson and D. Keith, 2003: Regulating the ultimate sink: managing the risks of geologic CO_2 Storage. Environmental Science and Technology, 37, 3476–3483.

Wilson, M. and M. Monea, 2005: IEA GHG Weyburn Monitoring and Storage Project, Summary Report, 2000-2004. Petroleum Technology Research Center, Regina SK, Canada. In: Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), Vol. III, September 5–9, Vancouver, Canada

Winter, E.M. and P.D. Bergman, 1993: Availability of depleted oil and gas reservoirs for disposal of carbon dioxide in the United States. Energy Conversion and Management, **34**(9–11), 1177–1187.

Witherspoon, P.A., I. Javendal, S.P. Neuman and R.A. Freeze, 1968: Interpretation of aquifer gas storage conditions from water pumping tests. American Gas Association.

Wo, S. and J-T. Liang, 2005: CO_2 storage in coalbeds: CO_2/N_2 injection and outcrop seepage modeling, Carbon Dioxide Capture for Storage in Deep Geologic Formations—Results from the CO_2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson (ed.), Elsevier Science, London, pp. 897–924.

Wo, S., J-T. Liang and L.R. Myer, 2005: CO_2 storage in coalbeds: Risk assessment of CO_2 and methane leakage, Carbon Dioxide Capture for Storage in Deep Geologic Formations—Results from the CO_2 Capture Project, v. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, S.M. Benson (ed.), Elsevier Science, London. pp. 1263–1292.

Wong, S., W.D. Gunter and J. Gale, 2001: Site ranking for CO_2-enhanced coalbed methane demonstration pilots. Proceedings of the 5th International Conference on Greenhouse Gas Control Technologies (GHGT-5), D.J. Williams, R.A. Durie, P. McMullan, C.A.J. Paulson and A. Smith (eds.), 13–16 August 2000, Cairns, Australia, CSIRO Publishing, Collingwood, Victoria, Australia, pp. 543–548.

Wright, G. and Majek, 1998: Chromatograph, RTU Monitoring of CO_2 Injection. *Oil and Gas Journal,* July 20, 1998.

Wyss, M. and P. Molnar, 1972: Efficiency, stress drop, apparent stress, effective stress and frictional stress of Denver, Colorado, earthquakes. *Journal of Geophysical Research,* **77**, 1433–1438.

Xu, T., J.A. Apps and K. Pruess, 2003: Reactive geochemical transport simulation to study mineral trapping for CO_2 disposal in deep arenaceous formations. *Journal of Geophysical Research,* **108**(B2), 2071–2084.

Yamaguchi, S., K. Ohga, M. Fujioka and S. Muto, 2005: Prospect of CO_2 sequestration in Ishikari coal mine, Japan. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), 5–9 September 2004, Vancouver, Canada, v.I, 423-430.

Zarlenga F., R. Vellone, G.P. Beretta, C. Calore, M.A. Chiaramonte, D. De Rita, R. Funiciello, G. Gambolati, G. Gianelli, S. Grauso, S. Lombardi, I. Marson, S. Persoglia, G. Seriani and S. Vercelli, 2004: Il confinamento geologico della CO_2: Possibilità e problematiche aperte in Italia. Energia e Innovazione, In press (In Italian).

Zhang, C.J., M. Smith, M. and B.J. McCoy, 1993: Kinetics of supercritical fluid extraction of coal: Physical and chemical processes. In: Supercritical Fluid Engineering Science: Fundamentals and Applications, E. Kiran and J.F. Brennecke (eds.), American Chemical Society, Washington, DC, pp. 363–379.

Zhou, W., M.J. Stenhouse, R. Arthur, S. Whittaker, D.H.-S. Law, R. Chalaturnyk and W. Jazwari, 2005: The IEA Weyburn CO_2 monitoring and storage project—Modeling of the long-term migration of CO_2 from Weyburn. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September 5–9, 2004, Vancouver, Canada, v.I, 721-730. Volume 1: Peer-Reviewed Papers and Plenary Presentations, Elsevier, UK.

Zoback, M.D. and H.P. Harjes, 1997: Injection-induced earthquakes and crustal stress at 9 km depth at the KTB deep drilling site, Germany. *Journal of Geophysical Research,* **102**, 18477–18491.