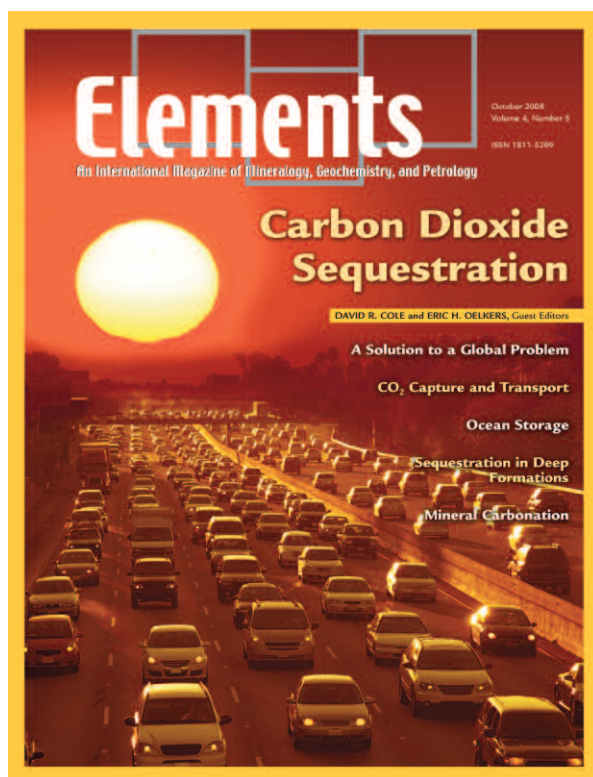


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CO₂ Sequestration in Deep Sedimentary Formations

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Carbon dioxide capture and sequestration (CCS) in deep geological formations has recently emerged as an important option for reducing greenhouse emissions. If CCS is implemented on the scale needed to make noticeable reductions in atmospheric CO₂, a billion metric tons or more must be sequestered annually—a 250 fold increase over the amount sequestered today. Securing such a large volume will require a solid scientific foundation defining the coupled hydrologic–geochemical–geomechanical processes that govern the long-term fate of CO₂ in the subsurface. Also needed are methods to characterize and select sequestration sites, subsurface engineering to optimize performance and cost, approaches to ensure safe operation, monitoring technology, remediation methods, regulatory overview, and an institutional approach for managing long-term liability.

KEYWORDS: sequestration, CO₂ properties, fluid migration, monitoring, risks

INTRODUCTION

Twelve years ago, Statoil began to inject a million metric tons per year of carbon dioxide into an aquifer 800 meters beneath the North Sea (Torp and Gale 2003). The CO₂ was stripped from natural gas to meet specifications for sale in Europe. Statoil could have emitted the CO₂ into the atmosphere and paid a \$50 per ton tax, but they opted instead to inject it into a subseabed aquifer, thus beginning an entirely new approach for reducing emissions: carbon dioxide capture and sequestration (CCS). Since then, two other commercial CCS projects have started, one in Canada and another in Algeria, and today over 20 million tons (Mt) CO₂ have been sequestered (Riddiford et al. 2003; White et al. 2004).

Hailed by some as a silver bullet for meeting the climate-change challenge and by others as ludicrous, CCS is in fact neither. With over 60% of worldwide emissions coming from point sources that are potentially amenable to CO₂ capture, the prospects for CCS to significantly reduce CO₂ emissions are great (IPCC 2005). Technical and economic assessments suggest that over the coming century, CCS may contribute up to 20% of CO₂-emission reductions, equivalent to reductions expected from efficiency improvements and large-scale deployment of renewable energy resources (IPCC 2005). So what is CCS technology? Why have experts concluded that it will work? And why have others expressed concern? Here we address what is known, and what is not known, to answer these questions.

WHERE COULD CO₂ BE SEQUESTERED?

To significantly reduce global emissions to preindustrial levels, huge volumes of CO₂ must be sequestered. For example, a large coal-fired power plant emits about 8 million tons of CO₂ annually. At the pressures and temperatures expected for sequestration reservoirs, the volume required to sequester CO₂ as a supercritical fluid is about 10 million cubic meters (Mm³) per year. Sequestering the CO₂ emissions from a power plant with a 50-year lifetime would require a volume of about 500 Mm³. Such large volumes make some CCS critics skeptical.

Where could we potentially sequester these large volumes of CO₂? Large sedimentary basins are best suited, because they have tremendous pore volume and connectivity and they are widely distributed (Bachu 2003) (Fig. 1). Vast formations of sedimentary rocks with various textures and compositions provide both the volume to sequester the CO₂ and the seals to trap it underground. Possible repositories include depleted oil and gas reservoirs, saline (salt-water filled) aquifers, and coal beds (Fig. 2).

Suitable formations should be deeper than 800 m, have a thick and extensive seal, have sufficient porosity for large volumes, and be sufficiently permeable to permit injection at high flow rates without requiring overly high pressure. Sequestering CO₂ below depths of 800 meters provides two advantages, both a result of the high pressures encountered at these depths: CO₂ density is high enough to allow efficient pore filling and to decrease the buoyancy difference compared with in situ fluids (Fig. 3). To protect groundwater resources, CO₂ will not be injected into shallow aquifers with total dissolved solid concentrations less than 10,000 ppm. Other important aspects include knowing the condition of active and abandoned wells and whether secondary seals are present in the overburden.

Estimates of worldwide sequestration capacity based on these criteria are large. Depleted oil and gas reservoirs are estimated to have the capacity to sequester between 675 and 900 billion tons of carbon (Gt C), saline aquifers between 1000 and 10,000 Gt C, and deep, unmineable coal beds between 3 and 200 Gt C (IPCC 2005). Sequestration capacity estimates for saline aquifers and coal beds are highly uncertain, although in the past several years, there has been some progress in developing standard methods for capacity estimation and improving regional estimates (Bachu et al. 2007; DOE 2007). In a recent assessment of

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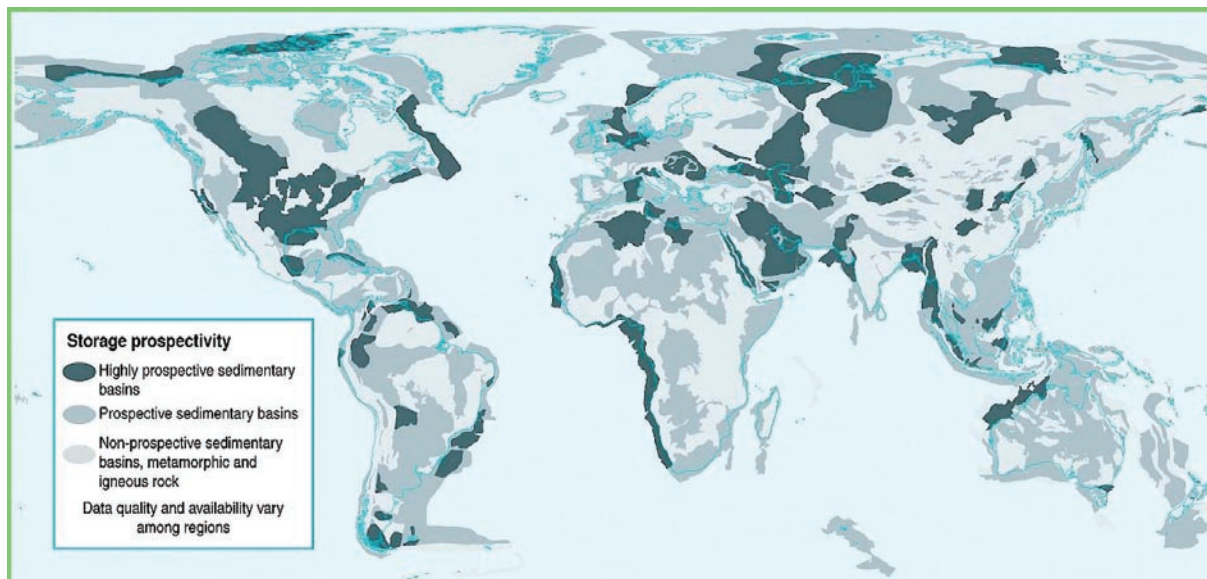


FIGURE 1 Sedimentary basins showing suitability as sequestration sites (IPCC 2005)

North American capacity, oil and gas reservoirs are estimated to be able to contain ~80 Gt C, saline aquifers between 900 and 3300 Gt C, and coal beds about 150 Gt C, for a total of about 1160 to 3500 Gt C (DOE 2007). If these estimates are correct, there is sufficient capacity to sequester several hundreds of years of emissions. Only time and experience will tell whether these estimates are correct.

In the short term, the biggest challenge is to match sequestration sites to CO₂ sources. For example, the large capacity in oil and gas reservoirs will only become available when the operator declares them depleted or implements enhanced oil recovery (EOR) (ARI 2006). A comparison of sequestration capacity and emissions indicates that some of the greatest CO₂ emitters (e.g. in the Ohio River Valley, India, and parts of China) are located in regions without large sequestration capacities. On the other hand, Texas, the US state with the highest CO₂ emissions, has extremely large sequestration capacity. CCS will likely begin in regions with large emission sources, large sequestration capacity, and opportunities for combining CO₂ sequestration and EOR. Beyond that, particularly in the case of saline aquifers and coal beds, the scientific foundations and the potential risks of large-scale injection must be established.

SCIENTIFIC FUNDAMENTALS OF GEOLOGICAL SEQUESTRATION

Physical Properties of CO₂

The physical state of CO₂ varies with temperature and pressure, as shown in FIGURE 4A (Oldenburg 2007). At ambient conditions, CO₂ is a gas, but it becomes liquid at greater depth. At high temperature, CO₂ is a supercritical fluid when pressure is high enough. The transition from one state to another depends on the geothermal gradient. In most sequestration scenarios, CO₂ is injected in liquid form (low T, modest to high P), but it transforms into a supercritical fluid as it is injected and warms to the temperature of the formation. In saline aquifers and oil reservoirs, CO₂ is less dense than the in situ fluids, so it rises to the base of the seal. Clearly, maintaining an impermeable caprock is crucial to containing the buoyant CO₂.

CO₂ Migration Behavior

When CO₂ is injected into deep geological formations, it displaces the pore fluid. Depending on the fluid's properties, CO₂ is either miscible, that is, it can mix completely to form a single liquid phase, or immiscible, so the phases

remain separate. At conditions expected for sequestration, CO₂ and water are immiscible. Oil and CO₂ may or may not be miscible, depending on the composition of the oil and the formation pressure. CO₂ and natural gas are miscible. When the fluids are miscible, the CO₂ eventually displaces nearly all of the original fluid. Injection of an immiscible fluid bypasses some fraction of the pore space, trapping some of the original fluid. With the limited exception of dry-gas reservoirs, most sequestration projects will require immiscible displacement to one degree or another. For example, although oil and CO₂ are miscible, the water that is almost always present in formations is not miscible with oil or CO₂/oil mixtures. Equilibration of CO₂ between oil and water depends on the composition of the oil.

Under conditions where the fluid phases are not miscible, the pressure needed to inject CO₂, the rate at which the leading edge of the CO₂ plume moves, and the fraction of the pore space filled with CO₂ are all governed by multiphase flow relationships (Bear 1972). For CO₂ sequestration, three particularly important consequences arise from multiphase flow behavior. First, the fraction of the pore space that can be filled with CO₂ is limited by the flow dynamics and capillary pressure resulting from interaction of two or more phases. At most, about 30% of the pore space is filled with CO₂ during initial displacement. In practice, CO₂ saturation is likely to be even less because of buoyancy and geological heterogeneity, both of which cause portions of the formation to be bypassed. After injection has stopped, CO₂ continues to move and fluid saturation approaches equilibrium, which is determined by the capillary pressure of the rock and the density difference between CO₂ and the original fluids.

The second important consequence of multiphase flow is that CO₂ mobility is limited during the post-injection period. When CO₂ saturation decreases, such as can occur after injection stops, a certain fraction—the “residual saturation”—remains immobilized in the rock, trapped by capillary forces. Water is imbibed (sucked) back into the pore space (Juanes et al. 2006; Hesse et al. 2008).

The third important consequence in a multiphase flow regime is that seals have two mechanisms for trapping CO₂ in the sequestration volume. Sealing layers are typically

Overview of Geological Storage Options

1. Depleted oil and gas reservoirs
2. Use of CO₂ in enhanced oil and gas recovery
3. Deep saline formations - (a) offshore (b) onshore
4. Use of CO₂ in enhanced coal bed methane recovery

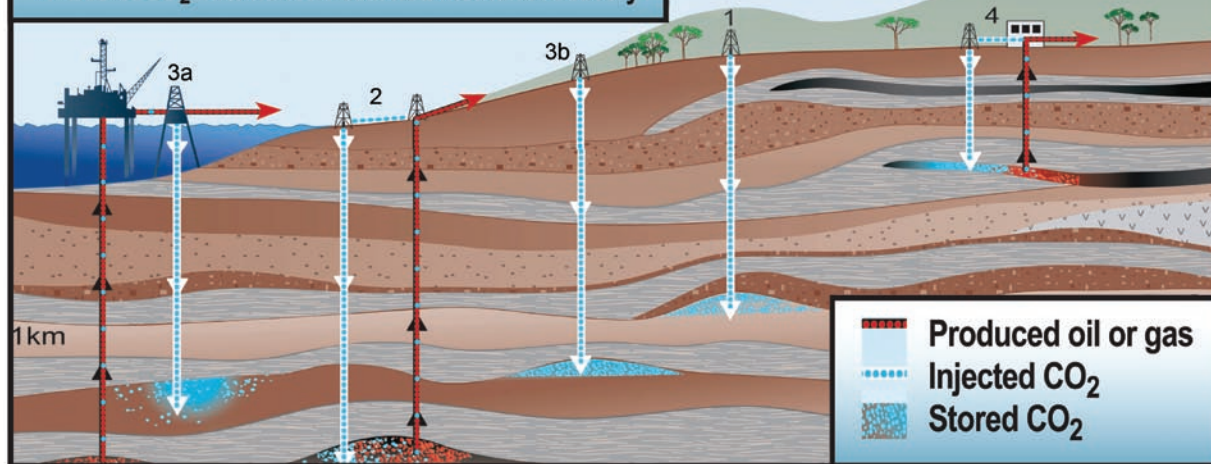


FIGURE 2 Types of geological formations and reservoirs that can be used for sequestration. MODIFIED FROM THE CARBON DIOXIDE COOPERATIVE RESEARCH CENTER (CO₂CRC), [HTTP://WWW.CO2CRC.COM.AU/ABOUT/CO2CRC](http://www.co2crc.com.au/about/co2crc)

fine-textured shales, mudstones, or carbonate rocks, which have low permeability for any fluid. Even at large pressure gradients, flow rates across a seal can be very slow. More important, the small pore spaces have very high capillary entry pressures, which causes the rock to act as a membrane that allows water to pass but blocks CO₂ unless its pressure exceeds the capillary entry pressure (Fig. 5).

Geochemical Interactions among CO₂, Brine, and Formation Rocks

Injecting CO₂ (and other power plant flue gases, such as SO_x and NO_x) promotes geochemical reactions that can alter the mineral assemblage of the host rock and shift thermodynamic equilibria from those that existed prior to injection. During injection, some CO₂ dissolves in the formation brines, decreasing pH typically from near neutral to below 4, and leading to dissolution of some primary phases and precipitation of secondary minerals. These reactions may change formation porosity and permeability (Kharaka et al. 2006a). The nature of the reactions depends on the mineralogical composition of the host rock and associated formation brine. Dissolution of some minerals, especially iron oxyhydroxides, can mobilize toxic trace metals and, where residual oil or other compounds are present, the injected CO₂ can also mobilize toxic organic compounds (e.g. toluene, benzene). Environmental impacts could be significant if these mobilized contaminants migrate into potable groundwater (Kharaka et al. 2006a, b). Furthermore, if SO₂ is coinjected, oxidation near the well bore promotes formation of sulfuric acid, leading to extremely low pH (Knauss et al. 2005).

Reactive chemical transport simulations have been used to study how these reactions evolve over time. In general, the simulations suggest that, initially, carbonate cements dissolve, potentially increasing porosity; later, reactions are dominated by the dissolution of feldspar and the precipitation of carbonate minerals and clays, thus decreasing

porosity and permeability (Gaus et al. 2005). These reactions can also impact the strength and integrity of the rock formation and can modify fluid flow paths, thereby influencing subsequent geochemical reactions. Site-specific assessments of geochemical and hydrological conditions are needed in order to minimize the potential for groundwater contamination resulting from CO₂ sequestration projects.

Trapping Mechanisms and Long-Term Fate of CO₂

Performance standards for sequestration projects have not yet been established, but there is growing agreement that very high retention rates are needed. Hepple and Benson (2005) calculated that retention between 90 and 99% over 1000 years should be the goal, if sequestration is deployed on a large scale. Four trapping mechanisms can contribute

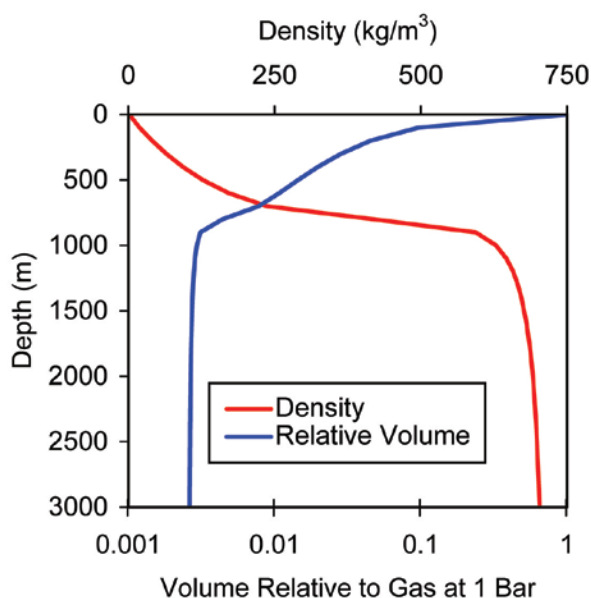


FIGURE 3 Density and change in volume of CO₂ as a function of depth below ground surface for a typical geothermal gradient

to retention over such long periods (IPCC 2005): structural trapping, solubility trapping, capillary trapping, and mineral trapping. The relative importance of these processes is expected to change over time as CO₂ migrates and reacts with the rocks and fluids, as illustrated conceptually in FIGURE 6. Reliance on the primary seal to retain CO₂ decreases as secondary immobilizing processes begin to dominate.

Structural Trapping

The single most important factor for securing CO₂ is the presence of a thick and fine-textured rock that serves as a seal above the sequestration reservoir. The seal should provide an effective permeability and capillary barrier to upward migration.

Capillary Trapping

Sometimes referred to as residual-phase trapping, this process traps CO₂ primarily after injection stops and water begins to imbibe into the CO₂ plume. The trailing edge of the CO₂ is immobilized, slowing up-dip migration. Capillary trapping is particularly important for sequestration in dipping aquifers that do not have structural closure. Studies by Hesse et al. (2008) and Ide et al. (2007) suggest that eventually all the CO₂ in a plume can be immobilized this way.

Solubility Trapping

The dissolution of CO₂ and other flue-gas contaminants into the pore water can lead to trapping by solubility. The amount of gas that can dissolve into the water depends on several factors, most notably pressure, temperature, and salinity of the brine (e.g. Spycher et al. 2003; Lagneau et al. 2005; Koschel et al. 2006; Oldenburg 2007). At the conditions expected for most geological sequestration (ambient to

Capillary Barrier Effectiveness

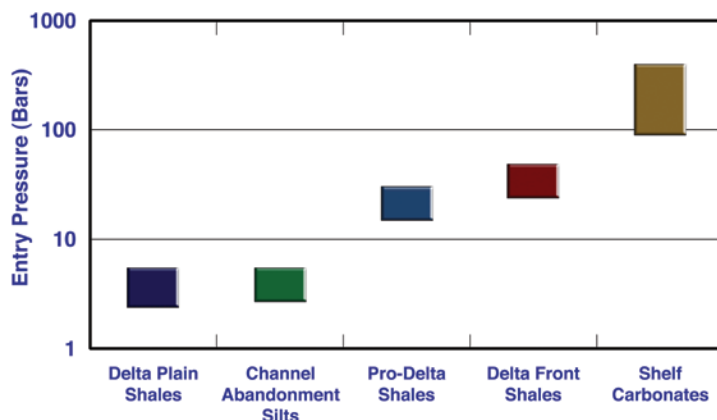


FIGURE 5 Capillary entry pressure for some typical seal rocks

~150°C and a few hundred bars total pressure), CO₂ solubility increases with increasing pressure (i.e. depth) but decreases with increasing temperature and salinity (FIG. 4B). Bench-scale experiments demonstrate that CO₂ dissolution is rapid at high pressure when the water and CO₂ share the same pore space (Czernichowski-Lauriol et al. 1996). However, in a real injection system, CO₂ dissolution may be rate-limited by the magnitude of the contact area between the CO₂ and the fluid phase. The principal benefit of solubility trapping is that once the CO₂ is dissolved, there is less CO₂ subject to the buoyant forces that drive it upwards.

Mineral Trapping

This mechanism occurs when dissolved CO₂ reacts directly or indirectly with minerals in the geologic formation, promoting precipitation of carbonate minerals (Oelkers et al. 2008). Mineral trapping is attractive because it could immobilize CO₂ for very long periods (Gunter et al. 1997). However, the process is thought to be comparatively slow because it depends on dissolution of silicate minerals, so the overall impact may not be realized for tens to hundreds of years or longer.

A COMPREHENSIVE APPROACH FOR SECURE GEOLOGICAL SEQUESTRATION

A fundamental understanding of the geologic, hydrologic, geomechanical, and geochemical processes controlling the fate and migration of CO₂ in the subsurface is necessary to provide a base for developing methods to characterize storage sites and to select sites with minimal leakage risk. However, even at a good storage site, engineering practices must be optimized to ensure reservoir integrity. Monitoring will play a key role in observing CO₂ behavior, in calibrating and validating predictive models, and in providing early warning that leakage may be imminent. In the event of threatened or actual leakage, remediation measures, such as plugging abandoned wells, would be needed. A regulatory infrastructure would be required to ensure due diligence in locating, engineering, operating, monitoring, and remediating CO₂ storage projects. Finally, private- and public-sector frameworks would be needed to ensure financial responsibility for covering short- and long-term liabilities.

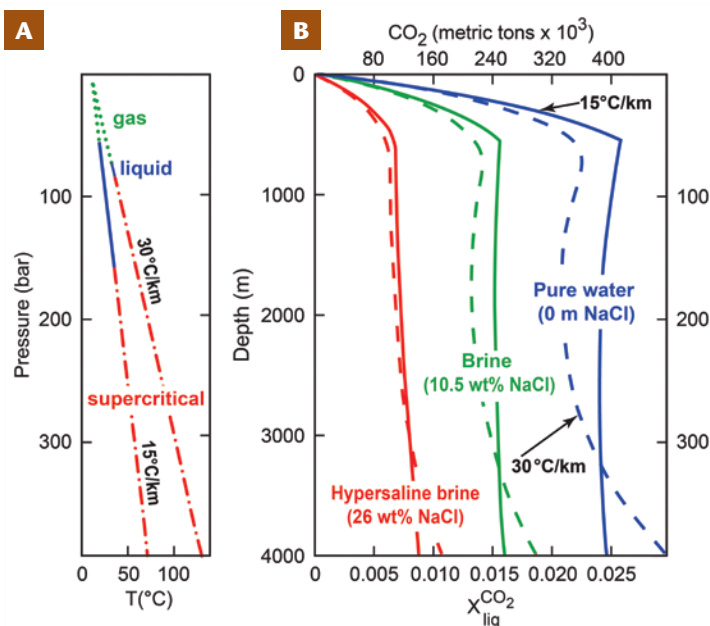


FIGURE 4 (A) Phase behavior of CO₂ as a function of temperature and pressure for two geothermal gradients. (B) Solubility (mole fraction, x) of CO₂ in a NaCl solution as a function of depth and salinity for two geothermal gradients. Model calculations (scaled by the top axis) estimate the mass of injected CO₂ trapped in a 20 m thick formation with 10% of its void space available for CO₂, in a volume extending 1 km out from the well in all directions. A pure-water system can dissolve 5 times more CO₂ than a hypersaline brine. BOTH FIGURES MODIFIED FROM OLDENBURG (2007)

MONITORING THE MIGRATION AND FATE OF INJECTED CO₂

Every sequestration project is likely to use a combination of monitoring techniques to track CO₂-plume migration and assess leakage risk. Technology for monitoring underground sites is available from a variety of other applications, including oil and gas recovery, natural gas storage, liquid and hazardous waste disposal, groundwater monitoring, food and beverage storage, fire suppression, and ecosystem monitoring. Many of these techniques have been tested at the three existing sequestration projects and at many smaller-scale pilot projects around the world (e.g. Arts et al. 2004; Hovorka et al. 2006). Specific regulatory requirements for monitoring have yet to be established. TABLE 1 provides examples of two programs that could be deployed to assure project performance and guard against safety and environmental hazards (Benson et al. 2005).

Geophysical Monitoring

Several methods can be used to observe the migration of the CO₂ plume. Seismic imaging can detect changes in compressional-wave velocity and attenuation caused by the presence of CO₂. Electromagnetic imaging can detect decreases in electrical conductivity when CO₂ is present in rock pores as a separate phase. Gravity measurements are sensitive to the decrease in bulk-rock density when CO₂ is present. To date, seismic imaging has been used most extensively and with great success.

FIGURE 7 shows a sequence of seismic cross sections collected from the Sleipner project. The first image, from 1994, was obtained before injection started. Only two major reflections are evident, correlating with the top and bottom of the Utsira Sand. By the first post-injection survey in 1999, three years after injection began, about 3 million tons of CO₂ had been injected. Several new reflections are present, which are interpreted to represent CO₂ trapped within the pores of the Utsira Sand. The plume is about 1 km wide. Subsequent images show continued plume growth as more CO₂ is injected.

Seismic imaging can also be used in other geometric configurations, such as between two or more wells (cross-well imaging) or with a combination of surface sources and borehole sensors (vertical seismic profiling). These higher-resolution methods have been applied with success at several pilot-scale CO₂ injection tests (Hovorka et al. 2006).

Geochemical Monitoring

Two approaches can be used to monitor CO₂ injection. The first uses fluid samples collected from observation wells where changes in brine composition or the presence of introduced or natural tracers are monitored. The second monitors the near-surface for CO₂ leakage.

By far the most rapid and inexpensive on-site measurement tools available to aid in tracking the injected CO₂ and its breakthrough to observation wells are pH, alkalinity, and gas composition. Of these, pH is probably the most diagnostic indicator of brine-CO₂ interaction. A marked decrease in pH correlates directly with CO₂ breakthrough. The compositions of major, minor, and trace elements can be used to assess the extent of water-CO₂-rock interactions. Enrichment of constituents such as Fe, Mn, and Sr can indicate mineral dissolution at depth during reaction of CO₂-saturated brine with rock (Emberley et al. 2005; Kharaka et al. 2006a, b).

Tracer studies are important for in situ subsurface characterization, monitoring, and validation. Naturally occurring elements, such as the stable isotopes of light elements (¹⁸O, D, ¹³C, ³⁴S, ¹⁵N), noble gases (He, Ne, Ar, Kr, Xe), and

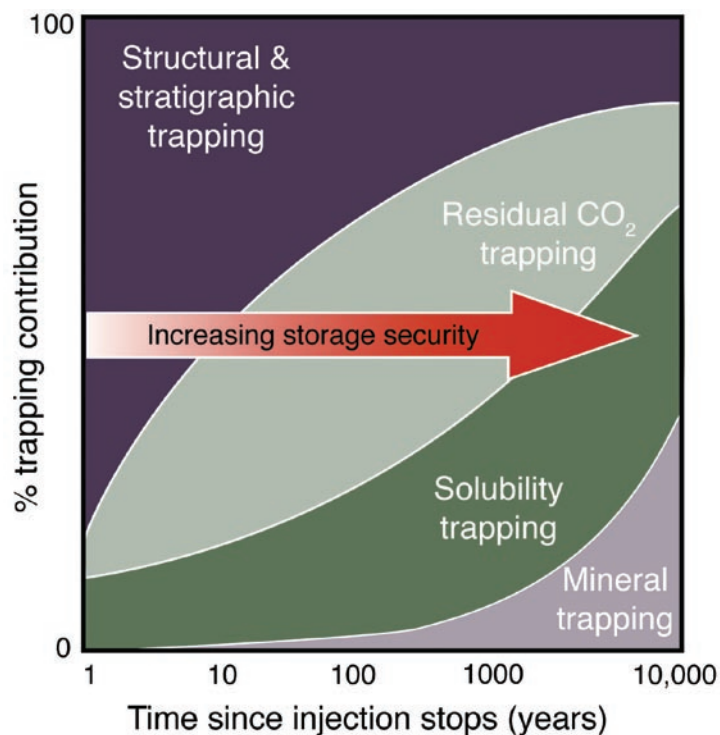


FIGURE 6 A general representation of the evolution of trapping mechanisms over time (IPCC 2005). Actual trapping mechanisms and evolution vary from site to site.

TABLE 1 MONITORING PROGRAMS THAT COULD BE USED OVER THE LIFETIME OF A SEQUESTRATION PROJECT (AFTER BENSON ET AL. 2005)

Basic monitoring program	Enhanced monitoring program
<i>Pre-operational monitoring</i>	<i>Pre-operational monitoring</i>
Well logs Wellhead pressure Formation pressure Injection- and production-rate testing Seismic survey Atmospheric-CO ₂ monitoring	Well logs Wellhead pressure Formation pressure Injection- and production-rate testing Seismic survey Gravity survey Electromagnetic survey Atmospheric-CO ₂ monitoring CO ₂ -flux monitoring Pressure and water quality above the storage formation
<i>Operational monitoring</i>	<i>Operational monitoring</i>
Wellhead pressure Injection and production rates Wellhead atmospheric-CO ₂ monitoring Microseismicity Seismic surveys	Well logs Wellhead pressure Injection and production rates Wellhead atmospheric-CO ₂ monitoring Microseismicity Seismic survey Gravity survey Electromagnetic survey Continuous CO ₂ -flux monitoring Pressure and water quality above the storage formation
<i>Closure monitoring</i>	<i>Closure monitoring</i>
Seismic survey	Seismic survey Gravity survey Electromagnetic survey CO ₂ -flux monitoring Pressure and water quality above the storage formation Wellhead pressure monitoring

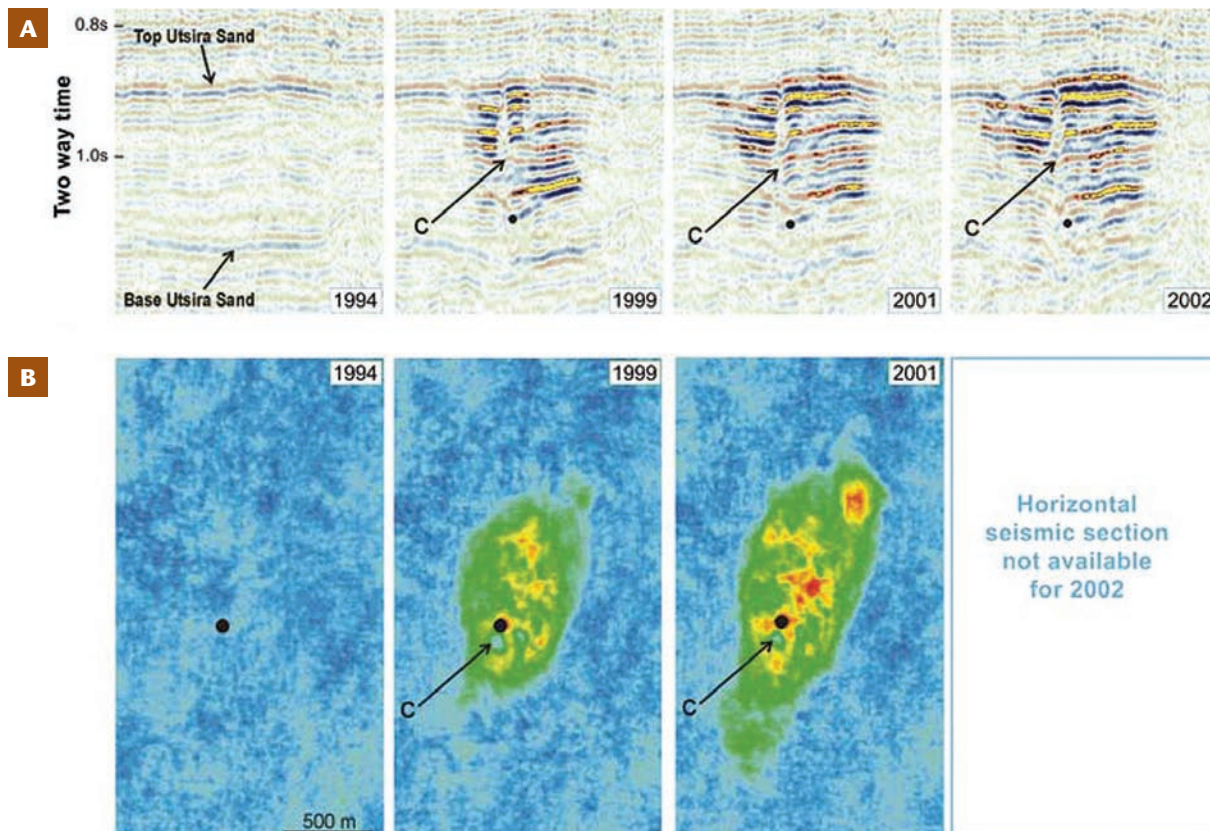


FIGURE 7 (A) Time series of vertical seismic sections through the CO₂ plume in the Utsira Sand at the Sleipner field under the North Sea. CO₂ saturation (c) is high above the injection point (black dot); the bright layers (black) correspond to high acoustic response where CO₂ is present as a separate phase in sandstone beneath thin, low-permeability horizons. (B) Horizontal sections. FROM IPCC (2005)

radioactive isotopes (e.g. tritium, ¹⁴C, ³⁶Cl, ¹²⁵I, ¹²⁹I, ¹³¹I), can be used to complement information from gas and brine composition and to determine the sources of liquid and gas and the processes controlling their migration. This information then allows assessment of the extent of fluid–rock interactions and quantification of fluid residence times in the subsurface (e.g. Kharaka et al. 2006a, b). Although naturally occurring constituents and isotopic composition have the advantage of being available, tracers can be injected for additional insight into subsurface conditions (Wells et al. 2007).

Surface-flux monitoring can directly detect and measure leakage. It may be measured directly with eddy covariance towers, flux accumulation chambers, and instruments such as a field-portable, high-resolution infrared (IR) gas analyzer (Klusman 2003; Miles et al. 2005). Year-round monitoring is needed to distinguish leakage from the highly variable natural biological CO₂ fluxes caused by microbial respiration and photosynthesis at the surface (Klusman 2003; Cortis et al. 2008).

RISKS AND PUBLIC PERCEPTION

Gaining support for CCS will require engaging the interest and building the support of a variety of stakeholders, each with different perspectives and goals. Policy makers want to understand the effects of CCS on the economy. Regulators want to know about the environmental impacts. Commercial developers need confidence in feasibility and financial security. The local community wants to be assured that the process is safe, that groundwater resources are not endangered, and that property values will increase, or at least will not be degraded by proximity to a storage reservoir—and the community perhaps also wants to be informed of other benefits. Public perception will ultimately determine whether or not CCS is implemented on a large scale.

While these perspectives bring a new dimension to large-scale deployment prospects, at the heart of them are four key questions:

- Will geological storage reservoirs leak?
- If leakage occurs, what are the health, safety, and environmental risks?
- Can leakage be predicted, detected, and quantified?
- What can be done to stop or slow a leak, should it occur, and how much would it cost?

Deploying CCS on a large scale will require developing persuasive answers—and effectively communicating them to all stakeholders. Geoscientists from many disciplines are needed to develop the base, test the various aspects, answer the questions, and continue to build a strong scientific foundation. The stakes are high and time is running out.

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