INTRODUCTION

Eight hundred tonnes of carbon dioxide (CO₂) are dumped into the atmosphere every second. There has been a progressive rise in the CO₂ content of the atmosphere, from 270 ppm in the pre-industrial era to more than 380 ppm now, rising by 15 ppm/decade. The overwhelming scientific consensus is that this is having a large effect on climate, and that as a result the Earth’s temperature will rise by about 2°C by 2100 [1]. Agriculture, forestry, fisheries, the biosphere and human health will all be affected. The level of the sea will rise by between 0.5 and 1 m, and there is a possibility of a much greater and catastrophic rise if warming should lead to a collapse of the Greenland or Antarctic ice sheets.

Adaptation to the changes and mitigation of the consequences will play a part in human response. Reducing the use of fossil fuels through energy conservation can also contribute, but the scale of the problem is so huge, and fossil fuel use is so extensive, that conservation alone will not eliminate the problem, particularly as fossil fuel use is rapidly increasing in many developing countries, above all in China and India. It is estimated that current emissions of 7 GtC/y (gigatonnes of carbon per year) will rise to 14 GtC/y by 2050 under a business-as-usual scenario, and that climate change will accelerate, as may indeed be happening already.

Another option to deal with CO₂ is carbon capture and storage (CCS), which has been the subject of a recent IPCC (Intergovernmental Panel on Climate Change) report [2]. CO₂ is most easily captured at large sources, such as power stations, cement plants, and steelworks. The technology to extract CO₂ from combustion products exists, but is expensive. Capture from small sources such as cars, buses, domestic heating furnaces, and cooking fires is likely to be very expensive indeed, and has scarcely been considered.

The next question is where to put the captured CO₂. The option that has been studied most is to inject it into the ground, into a porous formation such as an aquifer or a depleted petroleum reservoir. This is being done in the Statoil Sleipner project, which has been in operation in the Norwegian sector of the North Sea since autumn 1996. Sleipner gas contains 9 per cent of carbon dioxide. Norway has a 315 NOK/tonne (about
55$tonne) carbon tax. The project extracts carbon dioxide from the gas on the production platform, and injects it into the Utsira formation, at a depth of 800 m below the seabed. The sandstone aquifer formation is 250 m thick, and is thought to have a capacity of 600 Gt carbon dioxide. The cap is an 80 m layer of shale, several hundred km long, and 150 km wide. Statoil has stated that “The entire carbon dioxide emissions from all the power stations in Europe could be deposited in this structure for 600 years”: this presumably refers to contemporary emissions rates, and does not allow for exhaustion of fossil fuels.

Another option is to put CO$_2$ into the ocean. In fact some 30 per cent of CO$_2$ dumped into the air ends up in the ocean. Its presence tends to reduce the pH of water, and that has adverse effects on marine organisms. A better option is to put the CO$_2$ into very deep water. Liquid CO$_2$ injected at depths above 2750 m is lighter than the surrounding seawater, and tends to rise towards the surface and release to the atmosphere. However, liquid CO$_2$ is more compressible than seawater, and at pressures corresponding to depths greater than 2750 m liquid CO$_2$ is denser than seawater and therefore sinks towards the bottom. Marchetti [3] suggested the possibility of exploiting this to create lakes of liquid CO$_2$ in depressions on the ocean floor. Palmer and Ormerod [4] is a brief introduction, and Caldeira et al. [5] examine in detail the scientific aspects of the proposal. A CO$_2$ lake would become covered with a layer of hydrate. It would tend to retard CO$_2$ exchange with the atmosphere, but some CO$_2$ would diffuse to higher levels, and ultimately a proportion of it would continue into the atmosphere. There is thought to be no danger of a catastrophic overturning like the 1986 Lake Nyos event in Cameroun, which suddenly released 2 Mt of natural CO$_2$ and caused the deaths of some 2000 people [6,7].

An appropriate site for a CO$_2$ lake would be a large depression in the ocean floor, in a location free of seismic activity, significant bottom currents, indications of previous turbidity currents, and potentially unstable slopes that might create flow slides. The potential capacity is very large: a seabed depression 20 km across, 200 m deep and parabolic in cross-section holds $3.1 \times 10^{10}$ m$^3$, 33 Gt. The additional load on the seabed corresponds to the depth of liquid CO$_2$ multiplied by the density difference, and for a 10 kg/m$^3$ difference and 200 m depth is 20 kPa. Taking a bearing capacity factor of 5, this means that the seabed can withstand the additional load if its shear strength is greater than 4 kPa, which corresponds to soft clay.

Attempts have been made to carry out small-scale trials, but they have failed to secure permission from regulatory agencies. In the words of an article announcing the abandonment of planned trials off the coast of Hawaii:

“Environmentalists are suspicious of the experiment because they see carbon sequestration as a ‘red herring’ introduced into the Kyoto negotiations to divert attention from the need to reduce greenhouse gas emissions.” [8]

The present paper is concerned with the engineering aspects. It first briefly summarises the relevant physical properties of CO$_2$ and experience with CO$_2$ pipelines. It considers in turn a pipeline from a shore-based capture plant and a riser from a ship. There is some opposition to the notion of an ‘open’ lake, and the paper goes on to examine alternatives.
RELEVANT PHYSICAL PROPERTIES OF CO₂

Carbon dioxide has a 31°C critical temperature and a 7.4 MPa critical pressure. At an ocean temperature of 5°C, the saturation pressure is 4 MPa (corresponding to a 400 m depth). Remembering that a useful CCS scheme has to deal with very large quantities, it is disadvantageous to operate in the single-phase gas region below 4 MPa, because the density is very low and the gas volumes correspondingly large, so that the facilities have to be large. Operation in the two-phase regime is possible but potentially troublesome during shutdown and start-up. There is every advantage in working in the dense-phase region, where many natural gas pipelines operate. The viscosity of liquid CO₂ is 140×10⁻⁶ Pa s at 5°C and 30 MPa [2]

Corrosion is an important issue. Dry CO₂ does not corrode the carbon-manganese steels generally used for pipelines, as long as the relative humidity is less than 60 per cent; this conclusion continues to apply in the presence of O₂, N₂, NOₓ and SOₓ contaminants, which would probably be components of any CO₂ produced by a CCS process. CO₂ that contains CO as a contaminant can induce corrosion. Seiersten [9] wrote:

“The corrosion rate of carbon steel in dry supercritical CO₂ is low. For AISI 1080 values around 0.01 mm/y have been measured at 90-120 bar [9-12 MPa] and 160-180°C during 200 days. Short-term tests confirm this. In a test conducted at 3 and 22°C at 140 bar CO₂, 800 to 1000 ppm H₂S, the corrosion rate for X-60 carbon steel was measured to less than 0.5 μm/y [0.0005 mm/y]. Field experience also indicates very few problems with transportation of high-pressure dry CO₂ in carbon steel pipelines. During 12 years, the corrosion rate in an operating pipeline amounts to 0.25-2.5 μm/y [0.00025 to 0.0025 mm/y]”

The water solubility limit in high-pressure CO₂ (50 MPa) is 2000 ppm at 30°C [9]. Methane lowers the solubility limit, and H₂S O₂ and N₂ may have the same effect.

Corrosion is much faster if free water is present. Seiersten measured a 0.7 mm/y corrosion rate in 150 to 300 hours exposure at 40°C in water equilibrated with CO₂ at 95 bars, and higher rates at lower pressures, and she found little difference between carbon-manganese steel (API grade X65) and 0.5 chromium corrosion-resistant alloy.

It follows that a CCS scheme ought to dry the CO₂ as far upstream as possible, with no liquid and a vapour phase water content below 4.8×10⁻⁴ kg/m³, the level allowed in a current specification for pipeline quality CO₂ [2].

CO₂ PIPELINES

CO₂ is routinely transported over long distances as part of enhanced oil recovery schemes in North America, and there are thousands of km of CO₂ pipeline, mostly in the Permian
Basin [2]. West [10] describes the design of the SACROC (Scurry Area Canyon Reef Operators Committee) CO₂ pipeline that carries 6.2×10⁶ m³/d over a distance of 350 km to the Kelly Snyder oilfield in north Texas. The transportation options examined were a low-pressure CO₂ gas pipeline, a high-pressure CO₂ gas pipeline, a refrigerated liquid CO₂ pipeline, road tank trucks and rail tankers. He found a high-pressure pipeline to be 20 per cent cheaper than a low-pressure pipeline, and the other options much more expensive.

A PIPELINE FROM SHORE TO DEEP WATER

Figure 1 is a schematic. To fix ideas, consider a 100 km pipeline from a group of large sources onshore out to an outlet at an ocean depth of 3000 m. A 3000 m depth is reached within this distance along most of the continental margins of the Americas, Australia and East Asia. Similar depths are attained in the North Atlantic and in parts of the Mediterranean, but further from shore.

![Figure 1. Alternative schemes for ocean storage](image)

Consider first how large the pipe needs to be. Suppose the pipe to carry 2 tonnes/s of liquid CO₂ density 1050 kg/m³, which corresponds to the CO₂ from new NGCC (natural gas combined cycle) power stations generating 20 GW[2]. Applying the conventional (and somewhat conservative) empirical formula to determine the maximum velocity below which internal pipe erosion will not occur, the mean velocity is 3.7 m/s and the pipe internal diameter is 809.6 mm. This is close to one of the standard API sizes for pipelines, 914.4 m (36 inches) outside diameter, a diameter used for many marine pipelines.

Re is 2.2×10⁷ and the Fanning friction factor [11] is 0.005, taking the dimensionless internal roughness as 0.001. Assuming negligible pressure drop in valves and a diffuser at
the downstream end 2 at a depth of 3000 m, and taking the upstream end 1 as 15 m above sea level, the absolute pressure at the upstream end is 17.1 MPa, which is within the customary pressure range for marine pipelines.

The combination of depth and diameter is within the capacity of existing marine pipelaying technology. Figure 2 plots maximum water depth and diameter for a number of completed projects. The maximum depth for this project is not much more than the maximum depth of the pipeline crossing of the Black Sea and several projects in the Gulf of Mexico. The diameter is rather larger, but within the reach of existing S-lay and J-lay pipeline laybarges, with some modifications to the stingers and perhaps also to the tensioners and the firing line.

![Figure 2 Deepwater pipelaying state of the art](image)

If the pipeline is conventionally laid, filled with air at atmospheric pressure, the pipe has to carry the external hydrostatic pressure. Taking the outside diameter at 914.4 mm, following the DnV 2000 [12] standard and calculation method, taking the steel specified minimum yield stress as 485 MPa (X70), the specification as consistent with supplementary requirement U in those rules, out-of-roundness as 0.005 and safety class low (because pipelaying is a temporary condition) the required collapse pressure for the deepest section of the pipe is 39.7 MPa and the minimum wall thickness is 45.0 mm. With an anti-corrosion coating of 3 mm of polypropylene and no weight coating, the pipe submerged weight air-filled is 2.85 kN/m (290 kg/m), which is heavy, but not impossibly so. Laid by the J-lay method in 3000 m, it would correspond to a surface applied tension of about 10 MN, well within the tension capacity of the pipe.

A better option might be to adopt a different strategy and to lay the pipeline liquid-filled rather than air-filled. That option is known to have many advantages in deep water [13]. The wall thickness can then be much reduced, because in operation the pressure
difference between the inside and the outside is much smaller. The conditions that govern the design are then that

1. during construction the pipe be able to withstand the pressure difference corresponding to the density difference between the seawater and the fluid inside the pipe;
2. in operation the pipe be able to withstand the operation pressure, and
3. that the pipe be sufficiently robust to withstand laying.

Condition 1 is most critical at the greatest depth, and condition 2 at the surface.

The submerged weight of the liquid-filled thinner pipe during laying turns out to be only slightly larger than the much thicker air-filled pipe. If the pipe is laid filled with gasoline (petrol), density 737 kg/m³, the factored maximum pressure difference is 11.15 MPa, condition 1 governs, and the required minimum wall thickness is 27.2 mm. The submerged weight during laying when the pipe is gasoline-filled is 3.42 kN/m (350 kg/m). This design can obviously be refined, but it is clear that laying liquid-filled is an economical and practicable option. When the line is complete, the gasoline can be displaced to shore with liquid CO₂, pumped in at the lower end and separated by one or more pigs.

If the overall length is much shorter than 100 km, the pipeline could alternatively be constructed by bottom pull [11]. The greatest length so far constructed by this method is 30 km.

At the upstream end on shore, the pressure would need to be maintained during any shutdown in order to prevent vaporisation

A FALL PIPE FROM A SHIP

An alternative also sketched in Figure 1 is to transport liquid CO₂ from shore by shuttle tanker, and to transfer it to a ship that would carry a long vertical fallpipe that terminates below 2750 m. The tankers are similar to large LPG tankers, because the physical properties of LPG and CO₂ are not markedly different: propane has a 97°C critical temperature and a 4.2 MPa critical pressure and carbon dioxide a 31°C critical temperature and a 7.4 MPa critical pressure. Small tankers of this type are already use to transport CO₂.

DIFFICULTIES WITH UNCONTAINED SEABED CO₂ LAKES

Surveys have been carried out to explore the public acceptability of CCS, but they are of limited value, because the public at large has little information about what is proposed and do not think that wide-ranging CO₂ is imminent: that remark applies equally to politicians and to many technologists. Most people prefer underground storage to ocean
At the conclusion of a conference on macro-engineering responses to climate change [14], held in Cambridge in January 2005, the participants were asked in a straw poll which of the many options – not only CCS – they preferred. They were by definition people engaged with the issue, and more informed than the public generally, but again a majority preferred underground storage. Ocean storage came second, but some way behind.

The objection is in part psychological, but is nonetheless serious and real. The ocean represents an extremely important part of that the environmental community calls the “commons”. There are complex legal issues related to the London convention against ocean dumping an emerging international law [2]. People like to think that the CO₂ is ‘contained’, just as if they had some rat poison in their apartments they would not like it to be in an open bowl, and would rather that it was in a stoppered bottle, or better still a sealed bottle in a safe, or best of all a sealed bottle in a bank vault in the next state. Moreover, physical containment suppresses CO₂ interchange with the ocean and progressive acidification.

That suggests that it would be better to enclose the liquid CO₂ in some kind of flexible envelope.

CONTAINMENT

Figure 3 is a schematic. A pipeline leads at a depth of 3000 m to a large inflatable membrane bag (‘sausage’) deployed down a gentle slope.

Figure 3 Containment scheme

The sausage’s length is large by comparison with its diameter. It inflates from the lower end. The shape it takes up depends on the interaction between the applied pressure, the circumferential tension in the membrane, and the unit weight differential between the
ocean water outside and the liquid CO$_2$ inside. Finding the cross-section is the 2-dimensional analog of the 3-dimensional problem of finding the shape taken up by a liquid droplet on a non-wetting plane surface, under the influence of its weight and surface tension. In that case, if the surface tension is high, the droplet is almost spherical. If the surface tension is low, the droplet spreads out into a puddle, with an almost flat top.

Figure 4 is across-section of an infinitely-flexible weightless cylindrical membrane that encloses a fluid of density $\rho_1$ in a less dense liquid of density $\rho_2$. $S$ is distance measured around the perimeter. $Y$ is height, positive downward, and $X$ is horizontal distance. $S$, $X$ and $Y$ are measured from the highest point O. The inclination of the membrane to the horizontal is $\psi$, the membrane tension per unit length in the direction perpendicular to the plane of the diagram is $T$, and the differential pressure at O is $p$. The governing equations are simply

$$\frac{d\psi}{dS} = \frac{p + (\rho_1 - \rho_2)gY}{T}$$  \hspace{1cm} (1)

$$\frac{dY}{dS} = \sin \psi$$  \hspace{1cm} (2)

Nondimensionalising $S$ and $Y$ with respect to a characteristic length

$$\ell = \frac{T}{(\rho_1 - \rho_2)g}$$  \hspace{1cm} (3)

so that
the governing equations become
\[
\frac{dy}{ds} = \frac{p \ell}{T} + y \\
\frac{d\psi}{ds} = \sin \psi
\]  
and so the shape depends on the dimensionless group \( p \ell / T \). At O, \( s = x = y = 0 \) and \( \psi = 0 \).

At the contact point where the membrane reaches the horizontal seabed, \( \psi = \pi \), since otherwise there would have to be an outward-directed point force. The cross-section is readily calculated by Runge-Kutta integration.

If \( p \ell / T \) is large compared to \( y \), so that \( p > (\rho_1 - \rho_2)Y \), the cross-section is almost circular, with a narrow flattened region in contact with the seabed. That form maximizes the ratio between contained volume and membrane area, but implies a high tension in the membrane and a higher load on the seabed. If on the other hand \( p \) is small, the cross-section spreads out to a thin puddle, and the contained volume is small. Figure 4 illustrates the cross-section form taken up at a compromise \( p \ell / T \) of 0.2. The height is then \( 1.77 \ell \), the breadth \( 4.48 \ell \), the perimeter \( 10.49 \ell \) and the cross-sectional area \( 6.72 \ell^2 \).

If the membrane perimeter is 500 m, so that it flattens into a bag 250 m wide, the cross-sectional area is \( 1.53 \times 10^4 \text{ m}^2 \). Each km length of the sausage holds \( 1.53 \times 10^7 \text{ m}^3 \) of liquid CO\(_2\), about 16 million tonnes. A sausage 10 km long holds 0.16 Gt CO\(_2\), about 2.2 days of current global emissions. If 20 per cent of the forecast increase of emissions from 7 to 14 GtC/y were stored in this way, one 10 km sausage would need to be installed every 11 days. They are plainly very large, and it might be preferable to have a larger number of smaller sausages.

Because the density difference is small, the mechanical demands on the membrane are modest. Continuing with the 500 m perimeter membrane and \( p \ell / T = 0.2 \), \( T/(\rho_1 - \rho_2)g \) is 47.7, and if the density difference \( \rho_1 - \rho_2 \) is 10 kg/m\(^3\) \( T \) is 4.7 kN/m (480 kg/m). This should easily be achievable by a polymer reinforced with carbon fiber. The membrane would have to be able to resist liquid CO\(_2\) and seawater for a long time, ideally for thousands of years. Polymers such as polypropylene and nylon 6 appear to have good resistance to CO\(_2\) [15,16]. Fluoropolymers are less suitable, because CO\(_2\) dissolves in them and they have a much higher permeability [17].

INSTALLATION

The membrane described in the previous section could most easily be installed by rolling it onto a large floating drum linked to a tow vessel by a yoke, and with a control mechanism to prevent free rotation. This is analogous to the installation of the PLUTO pipeline from towed floating drums, but in that instance the drums were free to rotate. Another analogy is the reel used to install seabed mattresses in the Oosterschelde project in the Netherlands.
COST

Continuing the example of the 500 m perimeter membrane discussed earlier, if the membrane costs 100 $/m², the membrane cost per tonne of CO₂ stored is 3.1$, which is a small fraction of the capture cost [2]. There are additional costs for end fittings and connections. A smaller membrane is easier to install, but the membrane cost per tonne is larger, and connection costs are larger. If the installation and connection spread costs $500,000 /day, and one 10 km sausage is installed every 11 days (allowing 4 days for laying and connection, 1 day for loading, and 6 days for sailing, positioning and weather downtime), the installation cost per tonne of CO₂ stored is $0.035, which is unexpectedly small.

It goes without saying that these are very rough numbers, but they suggest that the key to economic practicability is the design of the membrane.

CONCLUSION

The scale of the engineering required to tackle CCS by ocean storage may appear frighteningly large, but that is an inescapable consequence of the vast quantities of carbon dioxide that humankind currently dumps. The schemes are technically practicable. The political will to carry them out is another matter.

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