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Ocean Carbon Sequestration by Direct Injection

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1. Introduction

The ocean is the largest sink of atmospheric CO₂ (about 7 petagrams (Pg) per year) (1 Pg = 1 gigaton = 10¹⁵ g). Dissolved CO₂ (passively entering the ocean via diffusion from the atmosphere) has already acidified the surface ocean, the most productive region of the ocean. Ocean carbon sequestration (OCS) is a method to distribute CO₂ more evenly throughout ocean depth and minimize surface ocean impacts. There are two major methods of OCS – direct injection and ocean fertilization (promoting photosynthetic fixation of CO₂ by ocean organisms). This chapter focuses only on the direct injection as a method of OCS. This chapter will first describe the physical mechanism by which CO₂ can be stored in the ocean water column at depth. It will summarize past ocean direct injection studies, and outline the effects of increased dissolved CO₂ and locally increased CO₂ partial pressure on marine organisms. It will also include a discussion of the engineering challenges of delivering CO₂ to the water column, including the selection of injection sites to minimize CO₂ outgassing to the atmosphere as well as minimizing marine life impacts. Finally, this chapter will address the legal, policy and public outreach issues that have ultimately precluded implementation of OCS using direct injection.

1.1. Motivation of Ocean Carbon Sequestration (OCS)

The ocean is presently the largest sink of atmospheric CO₂ (about 7 Pg per year) [1]. The Earth's oceans cover over 70% of the Earth's surface, and have an average depth of 3,800 m. However, dissolved CO₂ is already causing surface ocean acidification (most productive region of ocean) as it equilibrates with the atmospheric CO₂ [2]. By 1994, the total atmospheric release of anthropogenic (i.e., man-made) carbon was about 244 Pg of carbon (PgC) from fossil fuel combustion, and about 140 PgC from land use change (e.g., deforestation) [3]. The oceans have absorbed about one-third of anthropogenic CO₂ (the atmosphere retained about 43%, while the oceans absorbed about 30%), leading to a decrease of surface-ocean total pH by about 0.1 units from about 8.2 to 8.1. If CO₂ emissions continue unabated the subsurface ocean total could

decline by 0.7 units by 2300. To place in a geological perspective, the surface ocean pH (on a total scale) has not been below 8.1 during the past 2.1 million years. The total addition of carbon into the atmosphere is expected to be about 5000 PgC – the estimated fossil fuel reserves excluding hydrates -- in the next 500 years. This is a higher rate of carbon addition than ever experienced by the earth over a short geological time scale [3].

At the same time the ocean pH in the deep ocean has been decreasing at a relatively slower rate compared with the surface ocean [1, 4]. Rising concentrations of greenhouse gases in the atmosphere are implicated in adverse climate changes and two-thirds of the change is attributed to CO₂ [1]. Ocean carbon sequestration was conceived as a method to distribute CO₂ more evenly throughout the ocean column, especially into deep ocean waters, and minimize surface ocean impacts while the ocean CO₂ levels equilibrate with the atmosphere.

There are two major methods of OCS – direct injection and ocean fertilization (promoting photosynthetic fixation of CO₂ by ocean organisms). This chapter focuses only on the direct injection of CO₂.

2. Physical description of direct injection

2.1. Physical properties of ocean/CO₂ system

The conditions under which CO₂ can exist in a gas, liquid, solid or hydrate, and aqueous phases are depicted in the phase diagram (see Figure 1) [5]. At typical ocean temperatures and pressures, CO₂ exists as a gas above 500 m depth, and a liquid below this depth. Between 500 and 2700 m depth, liquid CO₂ is less dense than seawater and would float, while below 2700 m CO₂ is denser than seawater and would sink. A solid CO₂ hydrate phase is thermodynamically stable in the ocean at low temperatures; CO₂ hydrates are discussed in Section 2.3.

2.1.1. Solubility of CO₂ in the ocean

CO₂ dissolves in ambient seawater that is not saturated with CO₂. Once dissolved, aqueous CO₂ exists in various charged forms in water according to these main reactions, known as the carbonate system [6]:



The total dissolved inorganic carbon (C_T) is defined as:

$$C_T = [\text{H}_2\text{CO}_3(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (4)$$

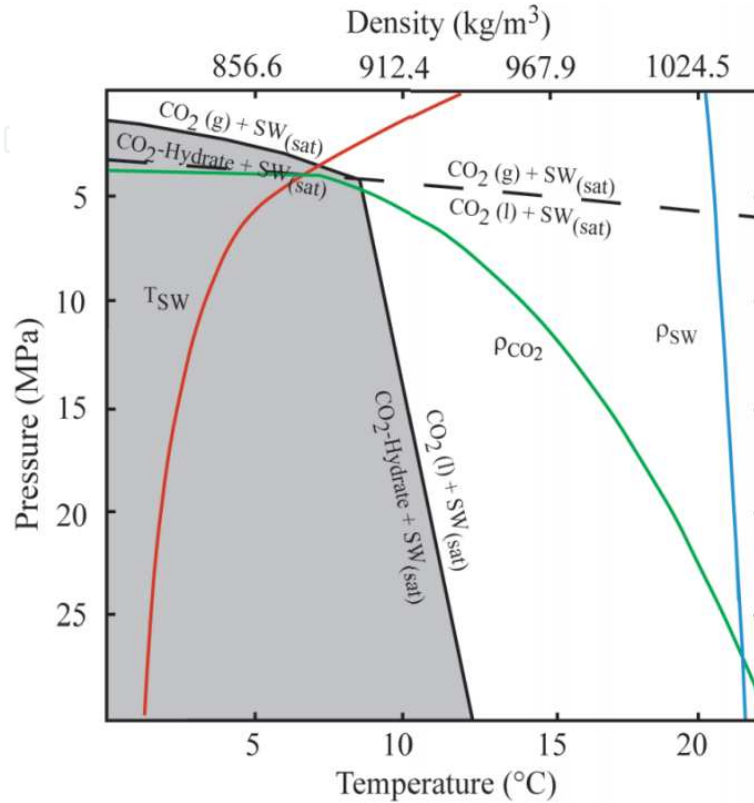


Figure 1. Phase Diagram for CO_2 in the ocean [5]. Gray area: region of stability for CO_2 hydrates; dashed line – gas/liquid phase transition for pure CO_2 ; red line – depth - temperature profile of the Pacific Ocean at 152°W , 40°N ; green line – CO_2 density; blue line – seawater density (35.0 PSU).

The result of this is that increasing dissolved CO_2 will shift the equilibria (1) and (2) above to the right, and lower the local pH of the ambient seawater. [7]. At a typical surface seawater pH of 8.2, the equilibrium (3) is shifted to the left with the addition of CO_2 . The net result of an increase in dissolved CO_2 is the decrease of pH, an increase in HCO_3^- and a decrease of CO_3^{2-} (Figure 2).

In turn, the dissolved CO_2 causes an increase of the density of the seawater via the solute density effect [9] that has implications for the physical design of a direct injection of CO_2 into the ocean.

2.1.2. CO_2 partial pressure ($p\text{CO}_2$)

The partial pressure of CO_2 of a sample of water, denoted by $p\text{CO}_2$, is the pressure of gaseous CO_2 which, if allowed to equilibrate with water, will result in the same amount of dissolved CO_2 as observed in the sample. It is related to the solubility of CO_2 , C_s , and the concentration of $\text{H}_2\text{CO}_3(\text{aq})$ by the following:

$$pCO_2 = \frac{[H_2CO_3(aq)]}{C_s(T,S)} \quad (5)$$

where $C_s(T,S)$ (usually expressed in μatm) is dependent on the local temperature T and salinity S . [10] provide empirical relations to obtain C_s .

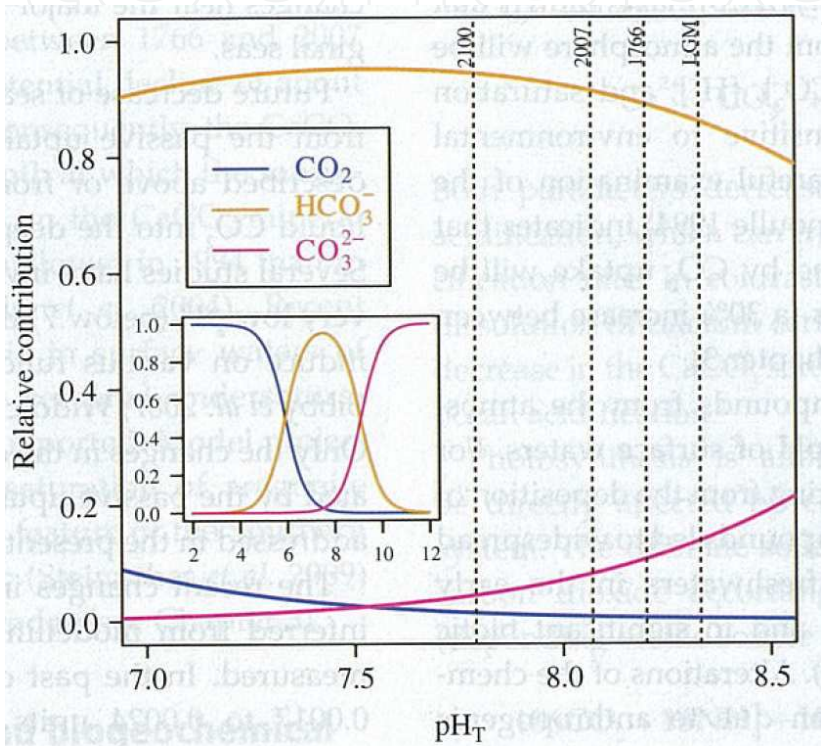


Figure 2. Bjerrum (pH_T (total scale pH) – relative speciation) plot showing the relative contributions of CO_2 , HCO_3^- and CO_3^{2-} to the dissolved inorganic carbon as a function of pH, at 15 deg C and a salinity of 35 PSU. The dashed vertical lines indicate the average open ocean surface pH_T during the Last Glacial Maximum (LGM), 1766, 2007 and 2100 (projected) [8].

As the atmospheric CO_2 concentration increases, pCO_2 levels increase in the surface ocean as it equilibrates with the atmosphere. The ratio of the relative change in pCO_2 to the relative change in C_T is known as the Revelle factor, and is inversely proportional to $[CO_3^{2-}]$. The inverse of the Revelle factor is also often termed as the buffering capacity of the ocean. According to this relation, a doubling in atmospheric CO_2 would only increase the total dissolved CO_2 by about 10%. [11]

While sea-air equilibria for most gases like oxygen occur over a time scale of days, it can take ~8 months for CO_2 to reach equilibrium at the surface, because the dissolved CO_2 in the carbonate system does not remain a dissolved gas but instead causes an increase in HCO_3^- . [4].

2.1.3. Calcium carbonate saturation state of seawater

The CaCO_3 saturation state of seawater is defined as Ω :

$$\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{sp}} \quad (6)$$

where $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ are the seawater concentrations of Ca^{2+} and CO_3^{2-} , and K_{sp} is the solubility product of either calcite or aragonite (the two major forms of CaCO_3). If Ω for aragonite (Ω_a) for instance is greater than 1, then aragonite is supersaturated and solid aragonite would begin to precipitate; if Ω_a drops to below 1 then aragonite is undersaturated with respect to the ambient ocean and solid aragonite would begin to dissolve. Because K_{sp} increases with pressure, for both aragonite and calcite there is a transition of the saturation state from $\Omega > 1$ to $\Omega < 1$ sediments with depth [3]. The depth at which $\Omega = 1$ for a mineral is known as its saturation horizon.

2.2. Methods of direct injection

CO_2 sequestration first involves capture from their sources, of which one major type of the coal-fired power plant. The CO_2 emissions are relatively pure from coal-fired power plants and could be isolated and injected into the ocean. A typical 500 MW power plant produces about 130 kg/s of CO_2 . [12]. After CO_2 capture, the CO_2 would be transported to the ocean via a pipe or ship to the ocean for direct injection. Technologies for CO_2 direct injection include: Liquid CO_2 droplets [13]; CO_2 laden seawater [9,14,15]; Solid CO_2 (dry ice) [16,17]; and CO_2 lake formation (See Figure 3)

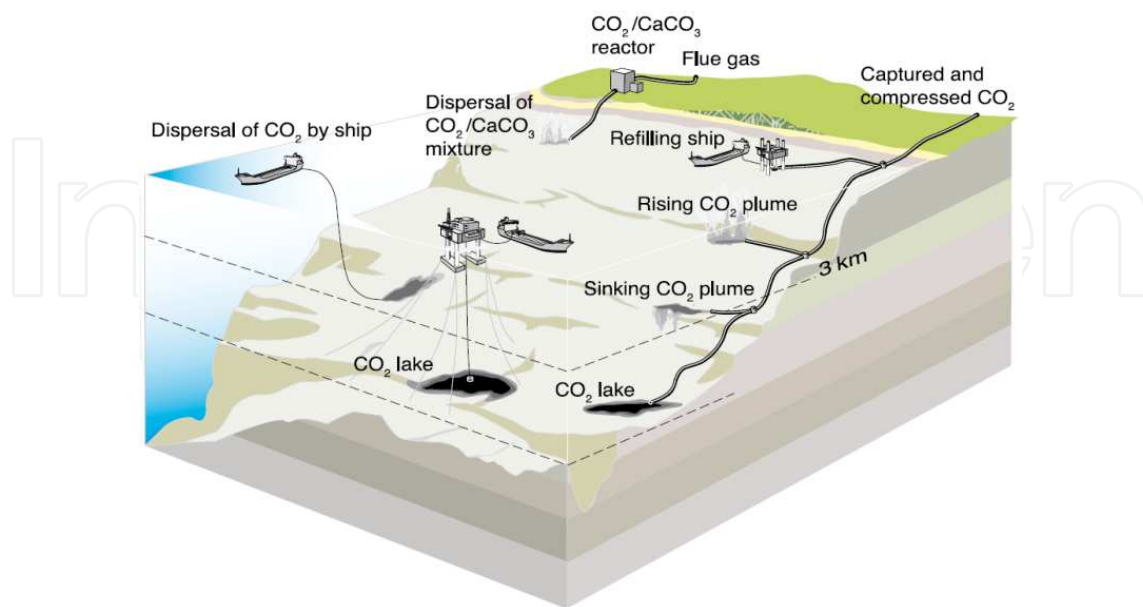


Figure 3. Ocean storage strategies (From Goddard, in [1]).

2.3. CO₂ hydrates

As shown in Figure 1, at lower temperatures (below about 5 - 10 degrees C) and at high pressure (corresponding to an ocean depth of about 400 m or greater) solid CO₂ hydrates are thermodynamically stable. CO₂ hydrates consist of molecules of CO₂ inside a cage-like structure of hydrogen-bonded water molecules [18]. They are of interest as a possible vehicle for deeper ocean carbon sequestration, because they are denser than seawater, and will sink unaided while dissolving to promote dispersion in the ocean. Pure hydrate particles are difficult to produce, but the Oak Ridge National Laboratory (ORNL) has designed a continuous CO₂-seawater co-flowing injector to create cylindrical composite particles comprised of CO₂ hydrate (negatively buoyant), liquid CO₂ (slightly positively buoyant at 1000-1500 m depths) and seawater [19].

Although CO₂ hydrates are thermodynamically stable, they will dissolve in ambient seawater upon release, because CO₂ is under-saturated in the ambient water. Field and laboratory observations confirmed that both pure hydrates and partially reacted cylindrical composite particles dissolved in the ambient seawater [20,21,23].

2.4. CO₂ droplet and hydrate studies

Numerical efforts to simulate the behaviour of CO₂ droplet plumes have included solving the full three dimensional Navier-Stokes equations in quiescent ambient sea conditions [7,22,24]. Bubble plume models calibrated using laboratory observations have also been applied to CO₂ droplet releases [25-27].

Field tests were conducted using CO₂ hydrate composite injectors [23,28]. The latest survey, with a hydrate reactor located at an ocean depth of ~1500 m, produced curved negatively buoyant cylindrical particles with diameters ~2.2 cm and lengths up to ~1 m. Applying a drag coefficient model to observed initial settling velocities and dissolution rates during the most recent survey [29,30], the hydrate conversion efficiency (percentage of liquid CO₂ converted to hydrate) in the field was ~ 15-20% resulting in particles with specific gravity 1-2% greater than seawater, which lead them to sink to a depth below discharge of roughly 100 m. Greater sinking could be achieved using larger particles. Discharging particles with a range of sizes and densities (reflecting different conversion rates) would cause differential settling resulting in spreading in the down-current and vertical directions. Furthermore, towing the source from a moving ship would contribute additional dispersion [29].

An alternative approach to enhancing mixing and vertical descent is to release a continuous stream of particles, forming a dense plume which would sink both due to the density of the particles as well as the increased density of seawater containing dissolved CO₂. An integral double plume model [25,29,31] was used to simulate the behavior of continuous streams of composite particles released to a quiescent ocean, with typical ambient stratification, at CO₂ loadings of 0.01 to 1000 kg/s. Results showed that, for a CO₂ release of 100 kg/s (roughly the emission from a 500 MW coal-fired power plant), a plume composed of 2.2 cm diameter composite particles with 16% reaction efficiency would sink about 1000 m, approximately 10 times the individual particle sinking depth. A plume composed of similar particles, but with

a diameter of 5 cm, would sink about 2000 m (~5 times the individual particle depth), while plumes composed of larger particles, or particles exhibiting higher reaction efficiency, would reach the seafloor (as would the individual particles).

Two ambient effects reduce the performance of a plume: stratification and ocean currents. Plume sinking is hampered by strong ambient stratification which causes trapping of entrained seawater at intermediate depths below release. Density stratification weakens at depths below 1500 m [32], so from the perspective of reduction of plume trapping, regions of the ocean deeper than 1500 m are potentially favourable for depositing CO₂ [33].

3. Environmental impacts/challenges

Some of the concepts relevant to the impacts of OCS by direct injection (e.g. ocean acidification) are presented in this section. The reader is directed to [1,11] for a more detailed and comprehensive summary of the causes and effects of ocean acidification.

3.1. Long term stability of dissolved CO₂ in the ocean

Investigations and estimation of the long term stability is described in greater detail in [1]. Numerical ocean models indicate that placing CO₂ in the deep ocean would isolate most of the CO₂ from the atmosphere for several centuries, but over longer times the ocean and atmosphere would equilibrate.

Relative to direct atmospheric release, direct injection of CO₂ into the ocean could reduce the rise and peak of atmospheric CO₂ levels over the next several centuries. After several centuries, the CO₂ released in the ocean would be transported back to the ocean surface and interact with the atmosphere again. However, in the new equilibrium, most (66% to 85%) of the injected CO₂ would still remain in the ocean despite contacting the atmosphere [1].

Generally, carbon injected in the deep ocean would equilibrate with the atmosphere over a time scale of 300 to 1000 years, based on radiocarbon and other tracer dating to estimate the age of the deep seawater. The estimated age of the North Pacific deep water is 700 – 1000 years, while the North Atlantic deep water is estimated to be only about 300 years old. A large number of numerical three dimensional ocean general circulation models were used to study CO₂ retention. The models generally predict a higher retention time with a deeper injection depth (isolation of CO₂ from the atmosphere is nearly complete for 100 years with an injection depth of 3000 m). Consistent with the radioactive tracer dating, many of the models suggest that the Pacific Ocean would retain a larger fraction than the Atlantic Ocean. However, the models vary greatly in their predictions on the actual time taken for CO₂ injected at a particular site to once again make contact with the atmosphere [1, 34].

Additionally, other geochemical factors may affect these predictions. For example, a higher ocean temperature, as well as a higher dissolved inorganic carbon concentration may lead to a lower efficiency for the ocean to absorb additional CO₂. (See [11]).

3.2. Potential pH and carbonate system changes from added CO₂

As described in Section 2.1, ocean acidification has been occurring since the Industrial Revolution. This section describes the effect of continued ocean acidification on the ocean's carbon cycle and marine ecosystems. Between 1991 and 2006, North Pacific ocean pHT showed a decrease of 0.06 units over the upper 500 m of ocean. In the Iceland Sea, the trend of pHT decrease between 1985 and 2008 in the surface ocean was 0.0024 units per year, with a corresponding decrease in Ω_a of 0.0117 units per year. The decline in pHT below 1,500 m in the Iceland Sea was one-quarter of that on the surface, with a corresponding decrease in Ω_a at 0.0009 units per year [4].

Another consequence of the increased dissolved CO₂ in the ocean, as described in Section 2.1.1, is the increase of HCO₃⁻ and a decrease of CO₃²⁻ in the ocean. The decreased CO₃²⁻ in turn leads to the decrease of the local value of Ω in the ocean. As there is a transition from saturation to undersaturation from $\Omega = 1$, this means that the saturation horizons for both aragonite and calcite would both become less deep with time [3]. The decrease in Ω_a caused the aragonite saturation horizon (ASH), the interface between supersaturated waters above and undersaturated waters below, to rise (shoal) at a rate of 4 m per year. The decrease in Ω , and therefore the shoaling rate for the ASH, is predicted to be more pronounced near the poles, and more severe in the Arctic Ocean than the Southern Ocean, partly because the polar oceans have lower initial concentrations of CO₃²⁻ [4].

It was proposed [3] that the addition of CO₂ followed by global increase in surface temperature can be compared to that which occurred during the Paleocene-Eocene Thermal Maximum (PETM, ~55 million years ago). During PETM, about 3000 PgC was added to the over an estimated 6000 years. However, the current estimate for expected total anthropogenic carbon addition is a larger rate of carbon input over a shorter period of time, about 5000 PgC over about ~500 years. The next highest global carbon addition was experienced by the earth during the Paleocene-Eocene Thermal Maximum, (~55 million years ago) where about 3000 PgC was added over ~6000 years. During the PETM, the effects of ocean acidification on surface calcifying organisms was limited, but the conditions of the PETM were not identical to the predicted future scenario, notably in that the carbon input rate was still much slower than the modern anthropogenic carbon addition. Nevertheless, studies of the PETM may inform future predictions of the behavior of ocean marine life with a large increase of atmospheric CO₂. [3,4].

3.3. Effect of pCO₂ increase on organisms

Effects of elevated CO₂ levels and acidified seawater on marine organisms are explained in more detail in [1,11,35,36].

At acute levels CO₂ has a narcotic effect on animals and causes respiratory distress and death. The work of [37 – 41] that model the lowered pH on passive marine organisms such as zooplankton that spend varying times in and out of a CO₂ plume, and found that minimizing the local dissolved CO₂ and pH drops will reduce the mortality rate.

Non-lethal effects have also been observed due to hypercapnia (elevated CO₂ exposure) [42-44]. Tamburri et al. [42] have observed the narcotic effects of increased CO₂ levels on mobile

deep sea animals in the field; they also observe that while many tend to avoid CO₂ plumes, some may risk the narcotic effects to obtain food. They note [42] that increased partial pressure of carbon dioxide will also have a detrimental effect on marine organisms, such as causing slow respiratory distress and inducing a narcotic effect on fish. Passive marine animals may experience depressed ion exchange capability and metabolism when exposed to lower, chronic levels CO₂. Some studies also show slowed growth in mussels and corals, as well as developmental effects on some marine larvae and eggs (brittle stars and bivalves) [35].

The primary effect of acidified seawater exposure by organisms is acidosis, the decrease of pH in body fluids. Intracellular and extracellular processes have been shown to be disrupted when seawater pH drops to a range of about 6.0 – 7.8. Many marine animals counter acidosis by increasing bicarbonate ion production (e.g. in the gills) [35]. Barry et al. report that organisms that have weaker control of their internal fluid chemistry, and that rely on passive molecular diffusion for gas exchange such as sponges, echinoderms, may have greater sensitivity to ocean acidification [45].

Some organisms may adapt to hypercapnia (elevated CO₂) better than others [46]. For example, tropical fishes, as they live closer to the edge of oxygen limitation than temperate fishes, may make them more sensitive to the combined effects of ocean temperature and ocean acidification than their temperate counterparts. For example, studies on acutely exposed tropical cardinal fishes to 1 week of pCO₂ of 1000 µatm resulted in decreases of aerobic scope and critical swimming speeds by about 40 – 50%, but a similar study conducted for Atlantic cod after 12 months of exposure to both 3000 and 6000 µatm did not result in any significant change in swimming capacity.

High CO₂ levels (up to a pCO₂ of 16,000 ppm [47] have also been observed in ocean bottom waters and marine sediments where there are high rates organic matter oxidation and low rates of mixing with the overlying seawater. Under these conditions, high CO₂ concentrations are often accompanied by low O₂ concentrations. Near the surface at night, respiratory fluxes in some relatively confined rock pools of the intertidal zone can produce high CO₂ levels. [1]. Portner et al. [46] report that high pCO₂ is found in oxygen minimum layers. They report that elevated pCO₂ is linked to acid-base regulation and respiration in fish. However, they also report that coastal and mid-water animals (both pelagic and benthic) regularly experience a large range of pCO₂ values (500 to 9400 µatm) in estuaries [46]. “These patterns suggest that in some environments, organisms have evolved to tolerate relatively wide pH oscillations and/or low pH values.” [1]

Organisms such as the Humboldt squid, although thought not to be able to adapt physiologically to future changes to the oceans oxygen balance, have been observed to thrive in oxygen minimum layers which tend to have low pH and are undersaturated with respect to calcium carbonates [46].

Deep sea ecosystems depend on sinking particles of organic carbon, made by photosynthesis near the ocean, settling down through the water. Most species living in the deep sea display very low metabolic rates [48, 49], especially in oxygen minimum layers [51]. Organisms living in the deep seawaters have adapted to the energy limited environment by conserving energy

stores and minimizing energy turnover. Turley et al. also suggest the depletion of oxygen as a contributing factor to the increased prevalence of harmful algal blooms, though the link between anthropogenic CO₂ and algal blooms remains controversial [36].

Finally, as many marine organisms synthesize and depend on calcium carbonate structures (e.g. shells), the implication of a lowered CO₃²⁻ and Ω in the ocean is the potential for reduction of their habitats.

As a guide, [1] uses a pH drop of 0.1 units as the threshold pH drop for insignificant marine life impact; it is also within the observed natural variability in the ocean. The US Environmental Protection Agency proposed that the threshold for open waters at depths greater than the euphotic zone, the pH value should not drop more than 0.2 pH units outside the range of natural variation [11]. [39] shows that some theoretically modeled scenarios of carbon dioxide releases (for example, releasing sinking CO₂ hydrates from a fixed or moving source at 1,500 m, injecting 10 to 1000 kg/s) would result in local pH drops within this guideline threshold in the vicinity of the release point. Others (e.g. Rockstrom et al.) have introduced the concept of planetary boundaries, and for CO₂ they have proposed a threshold carbonate ion concentration. As a first estimate, they proposed that the oceanic aragonite saturation state Ω_a be maintained at 80% or higher of the average global pre-industrial surface seawater level of 3.44 [50]. As with [1], these planetary boundaries are guides for a sustainable global environment, and (with the exception of the US Environmental Protection Agency for pH) have not been implemented as a regulatory threshold.

3.3.1. Comparison with naturally occurring ocean CO₂ vents

In the ocean, hydrothermal vents are submarine volcanic structures that act as natural sources of CO₂ in the ocean. These have been observed as potential natural analogues of OCS direct injection points. Field observations of hydrothermal vents have shown large fluctuations of pCO₂ (up to 80,000 ppm), over 100 times that observed in typical deep seawater). Over time, the vents have sustained organisms that are specially adapted to living in elevated pCO₂ conditions [52].

Observations near hydrothermal vents have shown that ocean acidification reduced biodiversity below a mean pH_T of 7.8 [53]. While Echinoderms are notably absent from habitats with naturally high CO₂ levels such as hydrothermal vents and shallow CO₂ vents off the coast of Italy [53], sponges appeared to tolerate these same sites.

As observed in [45], “[h]owever, while commonly the literature contains results of short term studies of organism physiology and survival, they may not be indicative of eventual long term consequences of ocean acidification.”

4. Engineering feasibility/challenges

4.1. Site selection for injection

As described in [1,54], to date there are no publications dedicated to site selection for direct ocean injection. Although numerical models have predicted CO₂ retention time as a function of the injection location, they have not consistently agreed on any individual location for direct injection. The only agreement appeared to be that a larger depth of injection would result in a longer isolation of CO₂ from the atmosphere [34]. In contrast, [55] presented a study of site selection for deep sea geological storage, highlighting the potential of storage in basalt aquifers along particular seismic and aseismic oceanic ridges. This section therefore discusses factors that should be considered site selection criteria based on to be considered when selecting a site for OCS. Environmental goals of site selection include reducing the likelihood of outgassing, and minimizing acute impacts to ocean organisms, as described in Section 3. Additional considerations include the costs of OCS, applicable international policies (such as regulations regarding disposal and cross border transport) – these factors are presented in Sections 4.2 and 4.3.

4.2. Cost of OCS

Costs were estimated for ship transport of liquid CO₂ to an injection platform, with CO₂ injection from a vertical pipe, or a ship trailing an injection pipe, to water at 3000m [1]. The cost estimate of ocean storage is the sum of three major components: tank storage of CO₂ onshore awaiting shipping; the shipping of CO₂; and direct injection of CO₂ into the ocean (either via an ocean platform, a moving ship, or a pipeline). The estimated sum of the three components (including an assumption of 3% CO₂ emissions from boil off and fuel consumption) is 11.9 and 13.2 US\$/ton CO₂ net stored from shipping to 100 km and 500 km offshore, respectively [56]. Cost estimates presented do not include transport of CO₂ onshore.

The cost for transporting CO₂ from a power plant located at the shore through a pipeline running on the sea floor to an injection nozzle was also estimated in [56]. CO₂ captured from a pulverized coal fired power plant with a net generation capacity of 600 MWe is transported either 100 or 500 km by a CO₂ pipeline for injection at a depth of 3000 m at a cost of 6.2 US\$/ton CO₂ net stored (100 km case) to 31.1 US\$/ton CO₂ net stored (500 km case). Other technical challenges that may not be accounted for include: residual chemicals, metals, minerals and oils that may be released during drilling activities; and the fact that liquefied CO₂ is highly corrosive, requiring that piping for CO₂ delivery would require anti-corrosion coatings, which themselves may pose contamination issues [35].

There are no published cost estimates specific to the production of a CO₂ lake on the sea floor; however, given the dominance of pipeline costs, it is reasonable to assume it to be similar to deep water injection. [1,56].

5. Policy issues/challenges

Since offshore OCS is likely to take place in international waters, several international environmental agreements may apply, mainly those that aim to minimize potential risks to the marine environment. The main international treaties are the Law of the Sea, the London Convention, London Protocol, and the OSPAR Convention. A succinct background of these treaties is taken directly from [57]:

“International marine environment protection was established in 1972 with the London Convention to regulate the dumping of wastes and other matter at sea. In 1982, this field was extended through the adoption of the United Nations Convention on the Law of the Seas (UNCLOS). Being an overarching construction, UNCLOS does not contain detailed operative provisions on most maritime issues; rather, it provides a framework for all areas, including marine protection, and allows other, more targeted treaties to fill in the gaps...With regard to marine pollution, global standards are set by the Convention on the Prevention of Marine Pollution by Dumping of Wastes and other Matter, signed in London in 1972 (London Convention). Beneath the London Convention exist several regional agreements that cover specific areas of the ocean [Also listed in [57]]. The most widely known of these is OSPAR, the Convention for the Protection of the Marine Environment of the North-East Atlantic. OSPAR is also notable as its regulations on marine pollution are markedly stricter than those of the London Convention, and its decisions are legally as opposed to politically binding on its Contracting Parties.”

5.1. 1996 London protocol

UN Convention on Climate Change encouraged the use of the oceans as a reservoir for CO₂, but the UNCLOS (in force since 1994) did not give clear guidance on OCS [1]. With respect to CO₂ storage, the original London Convention (with 80 contracting parties, and in force since 1975) only applied to storage by aircraft and vessels and platforms in the water column. As a result, the London Convention did not apply to storage of CO₂ in the seabed or the water column itself [57].

In November 1996, the London Protocol was established that prohibited the disposal of “industrial waste” into international waters. The list of prohibited substances that were categorized as “industrial waste” were contained in Annex I of the London Protocol. However, in 1996 the London Protocol did not give an opinion whether CO₂ was categorized as a “waste material generated by manufacturing or processing operations” [1]. The London Protocol entered into force March 2006 [57].

5.2. OSPAR convention

In 1992, the OSPAR Commission for the Protection of the Marine Environment of the North-East Atlantic, was formed which unified the 1972 Oslo and 1974 Paris Conventions. It brought together the governments of Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, Luxembourg, the Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom, together with the European Community (EC). It is considered the most compre-

hensive and strict legal framework governing the marine environment. As mentioned above, the contracting parties are legally bound to OSPAR's decisions [57,58].

5.3. 2007 OSPAR amendments for CO₂ storage and implications to OCS

In June 2007, the OSPAR issued two amendments to the OSPAR Convention: the first, a decision to prohibit the storage of CO₂ streams in the water column or on the sea bed in the Northeast Atlantic; and the second, a decision to allow the storage of CO₂ in subsea sediments. [59,60]

In the first amendment, OSPAR stated that CO₂ storage in the water column or on the sea bed "is not a sustainable storage option, is likely to result in harm to living resources and marine ecosystems and is thus neither a viable solution with regard to mitigating climate change nor compatible with the aims of the [OSPAR] Convention." However, in the first amendment, OSPAR indicated that ocean storage of CO₂ in the water column or on the seabed is nevertheless still under consideration in international forums. [59]

The OSPAR amendments provided a framework for its contracting national governments to develop permitting programs for CO₂ storage. For example, a list of the minimum items required in an offshore CO₂ storage permit included: a description of the project, including injection rates; types, amounts and sources of CO₂; the location of the facility; characteristics of the geological formation; methods of transport; and a risk management plan, with monitoring and verification measures, mitigation steps and a site closure plan [60].

In July 2011 the contracting parties of the OSPAR Convention ratified the 2007 Amendments to allow for CO₂ storage in subsea geological formations [58].

5.4. 2007 Amendment to the London Protocol

In 2007, an amendment to the London Protocol (Annex 1) allowed for storage of CO₂, if the disposal is into a sub-seabed geological formation, if CO₂ streams are "overwhelmingly" carbon dioxide, and as long as no wastes are added. This amendment provided that CO₂ streams may only be considered if [60,61]:

1. disposal is into a sub-seabed geological formation;
2. they consist overwhelmingly of CO₂. They may contain incidental associated substances-derived from the source material and the capture and sequestration processes used; and
3. no wastes or other matter are added for the purpose of disposing of those wastes or other matter.

The amendments to Annex 1 entered into force on 10 February 2007. In contrast to the OSPAR Convention Amendment that only covered the Northeast Atlantic, the 2007 London Protocol Amendment specifically prohibited direct injection of CO₂ for OCS for all London Protocol contracting parties.

5.5. 2009 London Protocol amendment for transboundary transport of CO₂

Article 6 of the London Protocol (on the export of wastes or other material) was largely interpreted by the contracting parties as prohibiting the export of CO₂ from a contracting party for injection into sub-seabed geological formations. In 2009 Article 6 was amended to allow for cross-border transportation of CO₂. [61]

As of 2011, there were 40 contracting parties to the London Protocol. Of these parties, 27 must also accept the 2009 amendment to Article 6 for it to enter into force. However, not all of the parties have been interested in offshore CO₂ storage or cross-border movement of CO₂, and have placed the ratification of Article 6 as a low priority. Cross-government cooperation will probably be required for ratification to occur. In some countries, the ratification may also be pending other laws and regulations that need to be changed for carbon storage and sequestration in general [61].

Therefore, although geological carbon sequestration in the ocean has been approved in principle the OSPAR Convention and even the London Protocol, the Article 6 amendment may continue to pose a policy barrier to OCS deployment in the foreseeable future.

5.6. Public outreach: Lessons from Hawaii

It is noteworthy that no field studies demonstrating OCS at a significant scale have been conducted so far prior to its prohibition through the 2007 London Protocol and OSPAR Convention amendments. The largest scale attempt at demonstrating OCS was the Hawaii CO₂ direct injection experiment. This section outlines the failure of the Hawaii experiment mainly fuelled by a lack of early public outreach, and outlines some lessons learnt from the Hawaii project. [62,63]

In 1997 the US Department of Energy, the New Energy and Industrial Technology Development Organization of Japan (NEDO) and the Norwegian Research Council (NRC) signed an agreement to conduct experiments to evaluate the behaviour of liquid CO₂ releases in to the ocean. While the project was announced in Kyoto in 1997, with a high profile to demonstrate the sponsors' commitment to CO₂ mitigation, few resources were subsequently invested in public outreach.

The project scientists and sponsors selected an area off the coast of the Big Island of Hawaii to conduct the pilot CO₂ study, based on technical feasibility and existing research infrastructure. However, they did not gauge the public perception prior to site selection. The local population only learnt of the injection project planned in their waters when it was first published in a newspaper article. In an area where the ocean is viewed as a major natural resource, the public perceived of the "dumping" of CO₂ as a violation, and strongly opposed its continuation.

Eventually the pilot injection project was abandoned in Hawaii. In order to salvage the project, scientists attempted to instead conduct an injection study in Norway. However, here the actions of Greenpeace stopped any further testing, thus precluding completely any chance of field scale testing of direct-injection OCS.

Although the introduction of OCS was initially high profile the sponsors' commitment to CO₂ mitigation, few resources were subsequently invested in public outreach. Moreover, the sponsors largely did not include the public in their decision to site the pilot injection experiment in Hawaii, nor did they factor public perception of potentially conducting a CO₂ injection experiment in an area where the ocean is viewed as a major environmental resource.

Reiner (2008) cited the US National Institute of Standards and Technology (NIST) 2002 workshop for "Best Practices for Communication of Science and Technology to the Public" as a resource that offered key recommendations for public outreach, including:

- Illustrating both the scientific process and unresolved scientific questions, rather than showing a result based on a black box model
- Using scientists in a public education role for a range of audiences (children and adult)
- Incorporating a wide source of knowledge from others so as to avoid parochialism
- Presenting the issues from the audiences' point of view
- Using face-to-face communications whenever possible to foster trust
- Reaching out beyond the science-attentive public, e.g. presenting at shopping malls, to disadvantaged youth
- Using multimedia and illustrations
- Providing press releases in forms easily usable to time-strapped journalists
- Avoiding perceptions of environmental injustice, bias or conspiracy
- Including the public from the start to avoid charges of "sneaking up on us" or less than full disclosure
- Avoiding letting the project become a "political football" by creating vocal supporters within the community

In addition, Reiner suggested that early outreach to the public via the internet during developmental stages of a project is important before the project becomes newsworthy and receives attention from mainstream media outlets. [63].

The lack of outreach is reflected in the low level of understanding that has remained among the public, as well as relatively low public acceptance of carbon capture and sequestration (both geologic and ocean). Reiner summarized the European Commission's survey of the public from 25 countries of the European Union (the Eurobarometer) that showed that, in 2007 (at the same time as the OSPAR convention and London Protocol amendments), only 21% of those surveyed have heard of carbon capture and storage (geologic or ocean), compared with 53% for hydrogen energy and cars, 41% for fuel cells, and 44% for geothermal energy [63]. In the US in 2004, only 2.5% of 1200 respondents in a web-based survey had previously heard of carbon sequestration. In 2007, Palmgren et al. surveyed 126 community respondents, who ranked OCS less favourable than geological carbon sequestration. Both carbon sequestration options were less favourable to the respondents than nuclear power [64].

6. Conclusions

Whether CO₂ is introduced intentionally, or passively diffusing from the atmosphere to the ocean, the ocean is and will remain the largest sink of anthropogenic CO₂. In addition to climate change implications of elevated atmospheric CO₂, a further impact is the acidification of the ocean. Effects of increased acidity and pCO₂ in organisms include respiratory distress (but some deep sea organisms take advantage of the CO₂/O₂ balance). There is also a risk of a reduced habitat as calcium carbonate stability zones decrease. However, further study is required to determine the variability of responses among marine species.

This chapter presented several methods by which direct injection of CO₂ into the ocean could be introduced. Some injection technologies were developed that would theoretically, combined with proper siting of injection points, cause a relatively minor impact to marine ecosystems. Some pilot scale field studies began that would have provided more information about environmental impacts, but they were nixed due to public opposition stemming from a lack of extensive and continuous public outreach from the onset. Since 2007, international policies began to prohibit direct discharge of CO₂ into the ocean, while favouring deep sea geological sequestration. CO₂ leaks (e.g. in the form of droplets [65]) from geological structures to the ocean water column are however still possible [35], so continued research and studies about the mechanisms of CO₂ leakage and the effects of increased dissolved carbon in the ocean continues to be an important topic of study for carbon sequestration.

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