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A case for deep-ocean CO_2 sequestration

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Abstract

Carbon sequestration (CO_2 disposal) may be only a temporary measure for bridging from the current situation in which carbon emissions to the atmosphere are unacceptably high and increasing, to a carbon-free economy, but it is a practical and immediate process that can be undertaken. Sequestration methods vary in effectiveness and cost, and each may have different opportunities, benefits, and drawbacks and periods of time over which the CO_2 is retarded from emitting into the atmosphere. Sequestration methods need to be tested on an appropriate scale as quickly as possible because carbon sequestration may help reverse the trend of increasing carbon emissions and remediate the atmosphere for a significant period of time.

Among proposed carbon sequestration technologies, temporary storage of CO_2 in the deep ocean may be the most practicable for many locations, and possibly the most energy efficient and cost-effective. In addition, an important added value benefit may be derived from deep ocean sequestration. A CO_2 hydrate industrial crystallization desalination/disposal process is particularly applicable to oceanic islands and coastal areas adjacent to narrow continental shelves where abyssal depths can be reached by the dense, dissolved CO_2-rich water gravity mass flows composed of processed water rejected from the desalination process.

1. Introduction

Slowing and then reversing the flood of anthropogenic CO_2 into the atmosphere is a defining challenge that may be near to the limit of humanity's ability for timely response. It has been recognized that urgent action is required to decrease CO_2 emissions [1] because the economic and environmental cost of reducing CO_2 emissions now may be much less than the cost of dealing with the impact of climate change in the future [2, 3].

Although it would be preferable to attain international consensus before undertaking any major geo-engineering options, this may not be practically achievable. Continued inactivity will only result in increasing emission of CO_2 to the atmosphere. An emerging option is for practical action that can be taken as soon as possible to reduce the volume of CO_2 emissions to the atmosphere. Near-term industrial-scale pilot sequestration (CO_2 disposal) demonstration projects will generate data, delineate options, and provide precise information regarding environmental effects [4] that will allow cost and benefit tradeoff decisions to be made for initiation of large-scale CO_2 disposal projects.

Carbon Capture and Storage (CCS), that is the capture and storage of carbon emissions, has long been suggested to mitigate climate change [5]. A variety of storage media, technologies, and value-chain components have been

proposed. Major disposal initiatives can be grouped into 4 major modes: 1) Biological Sequestration, 2) Oceanic Sequestration, 3) Chemical Sequestration, and 4) Geological Sequestration. The overall cost of CCS requires considerable analysis [6]. In addition, each sequestration mode has a characteristic effectiveness, benefits and risks.

As part of a process for rapid evaluation of different sequestration options, pilot projects promise to be most useful. Although trading carbon credits may have a beneficial effect in lowering carbon emissions to the atmosphere, it can also be characterized as a temporary expedient that allows the worst polluters to avoid making necessary large-scale emissions-reductions. Disposal of industrially relevant quantities of CO_2 under carefully controlled and monitored conditions is likely to identify acceptable sequestration methodologies more rapidly than a conventional research and development plan in which broad understanding is the primary objective. The goal of this piloting strategy is to simultaneously provide economic and environmental impact data for use in decision-making. These pilot projects are intended to be of relatively small industrial scale and to provoke a limited risk to the environment.

1.1. Major Sequestration Mechanisms

1.1.1. *Biological Sequestration*:

Biological sequestration involves sequestering carbon in biomass either alive or dead. This can be accomplished on land, as in the case of forestry and soil carbon enhancement [7] or in the ocean, in the case of Ocean Iron Fertilization [8,9,]. The basic premise of this type of project is that carbon bound up in the bodies of organisms, whether living or dead, is effectively sequestered from the atmosphere. Agricultural and forestry management projects reduce emissions effects by removing carbon directly from the atmosphere via photosynthesis and sequestering it in the form of organic-rich soils, which can then be used to grow more biomass [10].

Ocean iron fertilization (OIF) increases photosynthesis in the surface ocean. A certain amount of the resultant biomass will sink, sequestering the CO_2 in deep ocean water and sediments (where it is a type of geological sequestration). The concept is currently controversial as the long-term impacts of large-scale iron fertilization are not well understood [11, 12]. Riebesell et al., [13] note that in a high CO_2 ocean, the rate of carbon uptake by the ecosystem naturally increases even though nutrient levels, including dissolved iron concentrations, may remain the same. Thus, there is some question as to whether artificial iron fertilization is necessary or desirable. The possibility of irreversible impact as a result of ocean iron fertilization is also not understood. Despite these objections, at least one company, Climos, has signaled their intent to carry on with plans for a commercial OIF demonstration project [14].

1.1.2. *Chemical/Mineral Sequestration:*

The reactive nature of CO_2 forms the basis of research into mineral and chemical sequestration technologies. Processes can be based on sorption (either absorption or adsorption) or chemical reactions. Coal-bed sorption may enhance the rate of coal-bed methane production while simultaneously sequestering CO_2. One of the attractive features of this technology is that the CO_2 can be injected as flue gas instead of pure CO_2 [15], which considerably reduces CCS costs. While this method has received considerable attention, the addition of CO_2 and other gases can cause the coal and carbonaceous sediment to swell, which could reduce porosity and permeability [16]. Other processes take advantage of the chemical reactivity of CO_2 to sequester it as a different material, for example, the reaction of CO_2 with steel slag/wollastonite ($CaSiO_3$, calcium silicate) to produce calcium carbonate ($CaCO_3$, limestone) and silica (SiO_2, glass or sand) [17, 18]. Unlike other sequestration methods, the routes to readmission of CO_2 from chemical sequestration are few. The materials do not burn, do not spontaneously decompose, and do not need to be contained in a "sealed" environment or trap.

1.1.3. *Geological Sequestration:*

Geological sequestration options involve pumping CO_2, as either a liquid or a critical fluid, into subsurface reservoirs including aquifers, oil and gas reservoirs where suitable porosity and permeability exist. Geological sequestration has also been applied to rocks and sediments in marine continental shelf and slopes areas. Unlithified marine sediments, which may extend to considerable depths are generally characterized by gas and fluid expulsion that takes place as a factor of their compaction, and these are not promising hosts for long-term geological

sequestration. The permanence and long-term safety of geological storage options are not yet well defined and will almost certainly vary for each geological and geographic site because of differences in reservoir characteristics and storage potential as well as site stability. The success of any geological storage plan must be examined on a reservoir-by-reservoir basis [19]. Saline aquifers may represent the greatest amount of long-term geological storage capacity but shorter-term hydrocarbon reservoir-related sequestration is possible because of suitable knowledge base.

CO_2 injected into saline aquifers can be less dense than resident brines, this density difference, combined with the chemical potential of CO_2, may drive complex, gravity-driven dispersion [20] and dissolution systems.   It is also not clear how the dissolved CO_2, or the CO_2-saturated brines, will react with different reservoir rock, and how this might affect a reservoir's long-term CO_2 storage potential [21]. Modeling undertaken to determine changes in equilibrium conditions in reservoirs due to CO_2 sequestration in saline aquifers generally do not include a complete geochemical analysis [22].

A benefit of CO_2 injection into petroleum reservoirs may be enhanced recovery of liquid petroleum (EOR) through reduction of petroleum viscosity and simply increasing pressure to drive flow rate. A negative aspect of enhanced oil recovery is that considerable CO_2 may be brought back to the surface with petroleum. CO_2 has the potential to increase porosity and permeability by dissolving or chemically reacting with host rock, but host rock dissolution or overpressure of fault systems could also lead to mechanical breaching of the reservoir.

1.1.4. Oceanic Sequestration:

Ocean-atmosphere gas exchange naturally removes large amounts of carbon from the atmosphere at shallow depths in the photic zone. This stresses carbonate and other organisms because dissolved CO_2 increases seawater acidity [23]. Increasing the CO_2 levels in the deep ocean by purposefully sequestering captured carbon emissions is less well understood, but potentially should not have such an immediate impact in the photic zone.

Purposeful disposal of carbon in the ocean has been studied for over 30 years. Sarv [24] concluded that large-scale CO_2 transport and deep ocean disposal below 3000 m is technologically feasible, although injection of CO_2 at shallower depths and its plunging to the seafloor as a density plume [25] has been suggested. Riestenberg et al. [26] model direct injection of liquid CO_2 at mid-water depths to achieve a downward plunging plume driven by dense CO_2 hydrate. A feature of injection at shallower than abyssal depths is that the saturation levels of the descending CO_2-rich water will decrease in saturation as it descends.

Although immobile biota in deep ocean regions in which the CO_2-enriched seawater will concentrate will be most affected, mobile deep-sea animals may also be affected [27]. The method of CO_2 release to the deep seafloor will be important in determining the extent of the degree of biological impact: the more concentrated the discharge of CO_2, the greater the potential immediate impact. Herzog & Adams [28] show that direct injection of liquid CO_2 yields complex dispersion halos for both deep and shallow injection owing to oceanic density and temperature gradients. Once CO_2 is injected into the ocean, it may take one of several forms, depending on injection methodology and oceanographic characteristics of the injection site.   If the injection location pressure and temperature are suitable (below 300m and 8 °C), CO_2 hydrate will form. Alternatively, CO_2 will dissolve directly into the surrounding seawater, or pool into CO_2 puddles, whose size might depend on the bottom morphology, bathymetric slope, and CO_2 injection rate. The biological and chemical impacts of a plume of pre-dissolved, dense, CO_2- enriched water in the abyssal ocean, however, may not be significantly different from the impacts of naturally occurring CO_2 lakes and seeps found in the deep ocean [29].

The London Convention on Marine Pollution of 1972 allows for the disposal of wastes or other matter directly arising from, or related to the exploration, exploitation, and associated offshore processing of seabed mineral resources. The disposal of CO_2 that is generated by the production of oil and or natural gas at sea is thus permitted under the Convention, so long as the corresponding processing operations are carried out at sea [30]. CO_2 produced by manufacturing or processing operations on land cannot, under these rules, be dumped at sea. A similar legal position exists under the Marine Pollution protocol of 1996, which will replace the 1972 convention when it is ratified. The 1996 Convention identifies a number of waste products, created on land, that may be dumped at sea, but CO_2 is not presently included among these exceptions. The use of the deep sea for CO_2 sequestration as part of CCS, however, has not been a significant part of the considerations for either the 1972 or the 1996 Marine Pollution documents. This is understandable because the topic of CO_2 sequestration as an industrial process is new. The legal status of intentional carbon storage in the ocean has not yet been adjudicated [31].

2. Comparison of sequestration modes

In order to assess the best sequestration methods, depending on different geographic, geo-political, environmental and economic situations, we have directly compared the major types of sequestration, discussed above, according to some basic parameters (Table 1).

Table 1. A comparison of major sequestration types and estimates of their parameters

Sequestration Type	Permanence	Volatility	Reversible?	Capacity	Time Scale	Cost
Oceanic	Medium	Medium	No	Large	30-500 yrs	Low
Afforestation	Low	High	Yes	Requires land	5-85 yrs	Low
Soil Carbon	Low	High	Yes	Requires land	5-25 yrs	Medium
Geologic	Variable	Low	Yes	Uncertain	Unknown	High
Ocean Iron Fertilization	Low	Low	No	Uncertain	Unknown	Uncertain
Chemical	High	Very low	No	Large	Infinite	High

Permanence: From the point of view of controlling anthropogenic climate change, effectiveness of sequestration depends on the common denominator of storage longevity. Considering longevity as a function of cost provides a means for judging economic effectiveness. Even though the degree of permanence of different methods is subject to debate, general attributes can be identified.

Volatility: The likelihood of the sequestered CO_2 to react chemically and mechanically with its surroundings will determine its stability in each mode. Hydrocarbon-related reservoirs, and especially saline aquifers should be carefully characterized in terms of reactivity with CO_2 before geological storage proceeds. The volatility of components within the storage media may also be important. The volatility of oceanic storage depends in part on the CO_2 saturation and salinity of different component water masses.

Reversibility: Some sequestration mechanisms are fully reversible, while others are not. For example, storage of carbon in biological reservoirs, such as soil and forests has a known and high reversibility. The processes by which carbon is held in these are well understood, and the ways of reversing carbon storage is easy to accomplish. Storage of carbon as a result of ocean iron fertilization, in contrast, is less well understood, and may therefore initially appear to be more robust than it might prove in practice. Deep ocean sequestration within dense water masses also requires modeling to test the proposition that it will be more stable at depth than natural water masses.

Capacity: The capacity of different sequestration mechanisms to hold carbon plays a large role in determining its applicability. The storage capacity of geologic sequestration, for example, is unknown. Additionally, geological sequestration is not an option where there are no suitable reservoirs within a transport distance within a range of allowable cost. Biological sequestration mechanisms, both on land and at sea require large, dedicated areas in order to sequester any significant volume of carbon, and these may or may not be available over very large areas. Of the mechanisms with a known, large capacity, only deep ocean sequestration is economically feasible in the short term.

Time Scales: The timescale on which each type of sequestration is effective is controlled by very different factors. For many sequestration mechanisms, a lack of knowledge of exact timescales remains. For instance, in some cases, carbon leakage may take place suddenly and for a large percentage of sequestered carbon; in other cases leakage could be dominated by an irregular leakage profile. In the case of ocean sequestration, there is a degree of uncertainty in the sequestration timescale, which is mainly due to local oceanographic conditions. Ocean currents, tides, and upwelling cycles may allow for only short-term sequestration in some locations, but much more long-term sequestration of carbon in others; there is a good deal of site specificity but identification of these parameters are not costly.

Cost: Under Kyoto, the financing of research, development of engineering of carbon sequestration projects falls to private industry, government and non-governmental organization, but with no governing internal framework. One result of this structural hurdle is that the main thrust of sequestration research being carried out is for applied

industrial projects, primarily enhanced oil recovery. Large-scale research and development partnerships for geological sequestration are in various stages of development. Other sequestration methods, while possibly of equal or greater value, in terms of capacity, time-scales, volatility and other criteria, have faced difficulties in gathering sufficient funding as well as governmental approvals in order to plan and carry out critical large-scale pilot projects.

4. Adding value to CO_2 sequestration: Desalination as part of the process

Adding value to any sequestration process is a way of mitigating the disposal cost while providing some useful product (Table 3). A wide variety of products have been suggested, most of them related to chemical processing of CO_2 to produce such items as plastics and cement. Others propose using CO_2 in the same ways as it is currently used (for example, in EOR), but at a much larger scale than is currently practiced. MDS Research proposes that the industrial deep-ocean sequestration process presents a unique opportunity to produce desalinated water at a low-energy cost [32]. MDS research applies a patented and patent-pending chemical engineering approach using distinct technologies to produce a dense water mass that acts as a host for CO_2 to be sequestered. The MDS process, which we call Dilute Deep Ocean Sequestration (or DDOS), increases seawater salinity so that it provides an energy-efficient host for dissolved CO_2 that will plunge to deep or abyssal ocean depths.

Two modes of crystallization can be used to extract water and increase salinity of the residual to the level required to provide a gravity-driven CO_2 sequestration media; CO_2 hydrate and ice. Gas hydrate is a solid crystalline material that forms spontaneously under suitable conditions of pressure and temperature when water (in this case seawater) is supersaturated with hydrate-forming material. Water molecules in the hydrate structure form a network of cages that are usually occupied by individual gas molecules; weak electrostatic force between the guests and water cage hosts stabilizes the structure. Crystallization of ice involves a phase change of water. Both require refrigeration as their respective crystallization processes produce heat, in the case of hydrate, or require heat energy to be removed to cause the phase change, in the case of ice. The latent energy in the liquid CO_2 itself is used to power the greater part of the process, which is localized refrigeration that causes hydrate or ice to form. Rejection of small, dissolved and suspended solids, and chemicals is a characteristic of both hydrate and ice. Although both hydrate and ice can be formed in bulk seawater, it is more likely that a static film crystallization process will be used for this process.

The ocean is stratified with respect to density, which is a function of temperature and salinity (Table 2). Ocean surface temperatures vary seasonally, and can be in excess of 20 to 30 °C in the summer, where as open ocean seafloor temperature hover around 1.5 °C or less year round, even in tropical regions. The most dramatic increase in seawater density occurs at a water temperature of about 4 °C, at which water is at its densest. The addition of CO_2 to seawater alone is not sufficient to insure that the density of the seawater host will be sufficient to plunge to abyssal depths as a gravity-driven mass flow. Where the concern is to produce a dense enough plume that will sink to full ocean depths, density must be raised to a point significantly greater than the highest density seawater liable to be encountered in the descent in order that frictional and fluid displacement resistance factors are overcome. Table 3 demonstrates the salinity that can be reached using the CO_2 hydrate or ice enhancement processes.

Table 2. Calculated temperature dependence of density in the ocean, as compared to the effect on density of CO_2 saturation

Water Depth	Water Temperature (°C)	Density (kg/m^3)	Density at CO_2 Saturation
0 m	20	1028.4	1028.4
350 m	15	1029.6	1029.6
1 Km	4	1031.6	1031.7
3.5 Km	1	1031.8	1031.8

Table 3. Density as a function of salinity at assumed temperature of 4°C as compared to the effect of CO_2 saturation on density.

Salinity (ppt)	Density (kg/m^3)	Density at CO_2 Saturation
38	1034.8	1034.8
42	1938.4	1038.4
48	1043.0	1043.0
56	1049.1	1049.1
66	1057.4	1057.4
73	1062.9	1062.9

In the DDOS process, either hydrate or ice is grown in raw seawater, with no expensive pre-treatment such as is required by other desalination methods. The only consumable in the process is liquid CO_2, which is eventually sequestered. No membrane separation processes are used and no chemicals other than the CO_2 are added to the source seawater. The ambient temperatures and the natural pressure found at approximately 300 m depth in the ocean lower energy requirements for DDOS using either hydrate or ice. Although it is possible to produce the saline CO_2 host at pressures as low as atmospheric using ice, the CO_2 injection should be made at least at the best pressure-depth for CO_2 hydrate formation so that more CO_2 can be sequestered per volume of host water formed at lower pressures. Whether the salinity-enhancement is accomplished on land or in a marine installation, final dissolving of CO_2 in the saline host should be carried near the lowest point of a discharge system to increase the degree of sequestration for a fixed volume of water.

The process is intended to operate in geographic areas where full ocean depths are immediately accessible by gravity mass flow of the saline host water from the desalination installation. The crystallizer can be placed in either a fixed or mobile ocean installation or in a land-based installation. A marine installation can discharge directly into the sea. If the apparatus were operated on land, pipes would be required to bring the CO_2-enriched residual water to appropriate ocean depths. The saline host-CO_2-enriched water will naturally flow to abyssal depths, as it is negatively buoyant. The bathymetric configuration that would be most conducive to this form of sequestration can be found on narrow continental shelves, such as off the SW and SE coasts of the United States, Mediterranean countries, the South-eastern Australian coast, South Africa, and on oceanic islands virtually everywhere.

5. Discussion

In principle, hydrate desalination can be regarded as only a different means for dissolving large volumes of CO_2 in deep seawater than has already been envisaged [33]. Delivering pre-dissolved CO_2 to the seafloor as part of the sequestration process, however, will result in a potentially less deleterious environmental impact than direct injection of CO_2 at depth. As the CO_2-saturated water sinks to depth, the pressure on it rises, decreasing the saturation state of the dissolved CO_2. The result is an introduced water mass that is considerably less acidic than would be found in the vicinity of direct CO_2 injection at depth. Additionally, as the water mass descends, the increased pressure, and decreased temperature ensures that CO_2 hosted in this way is highly unlikely to form a gas phase, reducing the likelihood that the dissolved CO_2 might be able to return to the atmosphere. Furthermore, as some mixing with normal seawater will occur during mass flow saline water descent to abyssal regions, the saturation level of dissolved CO_2 will be further decreased.

Although sequestration of CO_2 in the deep ocean will increase acidity, implementing a system of DDOS will not alter deep ocean conditions as much as direct injection of CO_2. It is not immediately obvious that DDOS will involve a significant negative biological impact that would preclude its practice. Natural examples of high concentrations of CO_2 on the seafloor have been observed [29]. Liquid CO_2 has been observed venting through the seafloor in the presence of abundant marine life, *in-situ* experiments have confirmed that the halo surrounding liquid CO_2 on the seafloor is relatively narrow, and CO_2-consuming biota has been observed in abundance in the presence of liquid CO_2 and fully saturated seawater [29]. Whereas some biological impact assessment has been made for

ocean sequestration [34], no such impact assessment has yet been made for geological sequestration, which cannot be assumed to be without environmental impact.

There are areas of the world's oceans where deep saline host sequestration may be more effective than others. Injection into areas where upwelling and mixing are at a minimum, and where deep waters are therefore characteristically older, will significantly lengthen the time span by which this sequestered CO_2 can be kept from the atmosphere. In some areas of the ocean, this may extend beyond the time span of power generation from combustible materials. Some ocean areas or seas are also better because of their restricted nature. For instance, the Mediterranean Sea is a large enclosed basin with warm, poorly ventilated, high-salinity deep water with little propensity for upwelling that is near anoxic near the seafloor. The Mediterranean Sea is thus an excellent candidate for deep sequestration of CO_2-rich saline water. Since virtually all countries bordering the Mediterranean are very water stressed, a new supply of inexpensive desalinated water that could be produced as a by-product of CO_2 sequestration would thus be a welcome additional benefit.

6. Conclusions

Ideally, disposal should take place as close to where large volumes of CO_2 are generated so that transport costs can be minimized. The disposal cost of CCS is probably considerably less expensive for deep ocean sequestration than for geologic sequestration owing to differences in pumping costs required for each process. Both geologic and oceanic sequestration, however, may have their place, and other forms of CCS may also be practiced. There does not appear to us to be a single solution. Different sequestration methods may be preferable in different situations. The sequestration methodology that makes the best economic and environmental sense should be made on a case-by-case basis.

If the need to abate the flood of anthropogenic CO_2 into the atmosphere to mediate the greenhouse requires immediate action, then pilot projects for both geologic and ocean sequestration, as well as other opportunities, should be undertaken at once. The political imperative is becoming strong enough so that it may become necessary to skip the years of research and impact assessment that normally would precede such projects. This means that a new paradigm of environmental monitoring and iterative chemical and physical modeling must accompany pilot sequestration projects so that industrial scale data sets can be established quickly that will guide decision-making for large-scale CCS sequestration. Among the sequestration methodologies considered in this paper, the only immediately available, technologically feasible, temporary solution having an inherently low cost is oceanic sequestration.

7. Acknowledgements

8. References

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