

Final Technical Report
for Project Titled

“Neutralizing Carbonic Acid in Deep Carbonate Strata below the North Atlantic”

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ABSTRACT:

Carbon dioxide injection into deep sea sediments below 2700 m water depth and a few hundred meters to fifteen hundred meters deep in the sediment column may provide permanent geologic storage by gravitational trapping. At high pressures and low temperatures common in deep sea sediments a few hundred meters below sea floor, CO₂ will be in its liquid phase and will be denser than the overlying pore fluid. The lower density of the pore fluid provides a cap to the denser CO₂ and ensures gravitational trapping in the short term. The overall storage capacity for CO₂ in such deep sea formations below the ocean floor is primarily determined by the permeability, and will vary with seafloor depth, geothermal gradient, porosity, and pore water salinity. Furthermore, the dissemination of the injected CO₂ in the sediments and potential chemical reactions between CO₂, pore fluid and sediments will define its fate in the storage reservoir.

The main objectives of our research was to evaluate the potential for sub-seabed CO₂ storage in deep sea sediments using a range of approaches including experiments, permeability analysis, and modeling. Over the course of the three-year award, our results support an important role for sub-seabed storage in a diverse portfolio of carbons sequestration options. Our analysis has shown the feasibility of this type of storage, and also emphasizes that escape or leakage from such sites would be negligible. The most difficult challenge is to overcome the low permeability of typical deep-sea sediments, and a variety of approaches are suggested for future research.

TABLE OF CONTENTS:

| Section: | Page |
|-----------------------------|-------------|
| Introduction | 5 |
| Executive Summary | 6 |
| Experimental methods | 8 |
| Results and Discussion: | 11 |
| Conclusion | 19 |
| References and Bibliography | 20 |

INTRODUCTION:

Our research was aimed at investigating several technical issues associated with carbon dioxide sequestration in calcium carbonate sediments below the sea floor through laboratory experiments and chemical transport modeling. Our goal was to evaluate the basic feasibility of this approach, including an assessment of optimal depths, sediment types, and other issues related to site selection. Through laboratory and modeling efforts, we were studying the flow of liquid carbon dioxide and carbon dioxide-water mixtures through calcium carbonate sediments to better understand the geomechanical and structural stability of the sediments during and after injection. In addition, we were investigating the kinetics of calcium carbonate dissolution in the presence of CO₂ -water fluids, which is a critical feature of the system as it allows for increased permeability during injection. We were also investigating the possibility of carbon dioxide hydrate formation in the pore fluid, which might complicate the injection procedure by reducing sediment permeability but might also provide an upper seal in the sediment-pore fluid system, preventing release of CO₂ into the deep ocean, particularly if depth and temperature at the injection point rule out immediate hydrate formation. Finally, we performed an economic analysis to estimate costs of drilling and gas injection, site monitoring as well as the availability of potential disposal sites with particular emphasis on those sites that are within the 200-mile economic zone of the United States.

This project was a collaboration between Dan Schrag and his group at Harvard University and Klaus Lackner and his group at Columbia University. In addition, there were several other collaborators brought in during the course of the award, including Charles Harvey, Professor of Hydrology at MIT, who played a critical role in the project, and Bruce Watson from RPI who worked with the group on some high pressure experiments.

For the purposes of this technical report, our project can be divided into three parts: modeling of fluid flow and chemical reactions during injection of CO₂; experimental measurements of kinetics of chemical reactions and permeabilities and dynamics of liquid CO₂ injection into sediments; and economic analysis of deep sea injection and comparison with other approaches in a geographic context.

EXECUTIVE SUMMARY:

Due to the high compressibility of $\text{CO}_2(\text{l})$ relative to water, $\text{CO}_2(\text{l})$ becomes denser than water at high pressures and low temperatures. These temperature-pressure regimes do not exist in terrestrial settings; they are, however, common in the deep ocean. When $\text{CO}_2(\text{l})$ is injected into the ocean at a depth of 3000 m, it sinks, forming a lake of $\text{CO}_2(\text{l})$ on the seafloor. Ocean currents, however, can mix the injected $\text{CO}_2(\text{l})$ causing a large fraction to eventually be released into the atmosphere (1). To ensure that deep ocean currents will not mix the CO_2 into shallower regions, CO_2 can be injected below the seafloor. Furthermore, if the seafloor depth of injection is greater than ~3000 m, then the injected CO_2 will be denser than the ambient pore-fluid.

We refer to the sub-seafloor region with low enough temperatures and high enough pressures to compress CO_2 to greater density than seawater as the Negative Buoyancy Zone (NBZ). When CO_2 is injected beneath the NBZ, the lower density pore-fluid acts as a buoyancy-cap on the system and ensures gravitational stability. The gravitational stability of the system in deep-sea sediments is in contrast with terrestrial geologic storage where the high pressures and *high* temperatures cause the injected supercritical CO_2 to be gravitationally unstable. The buoyancy-cap, provided by the pore water, serves the same purpose in deep-sea sediments as a cap rock serves in terrestrial geologic formations. The buoyancy-cap, however, is superior to a cap rock because conduits in a cap rock enable buoyant CO_2 to escape. In contrast, the gravitational stability provided by the buoyancy-cap guarantees that fractures in the sediment column cannot serve as conduits for the CO_2 , and even large geomechanical perturbations—such as earthquakes—cannot cause the $\text{CO}_2(\text{l})$ to be released.

The high pressures and low temperatures necessary to compress $\text{CO}_2(\text{l})$ to greater density than the pore-fluid are similar to the conditions necessary for CO_2 -hydrates to form. We refer to the sub-seafloor region with low enough temperatures and high enough pressures for hydrate formation as the *hydrate formation zone* (HFZ). The HFZ extends from the seafloor downward into the sediment until the temperature rises above the boundary of the hydrate stability field. A comparison that we have performed of the stability conditions for CO_2 -hydrates with the $\text{CO}_2(\text{l})$ buoyancy-depth relationship reveals that the HFZ overlaps to a great extent with the NBZ. Although the HFZ exists in submarine sediment at seafloor depths of ~400 m, $\text{CO}_2(\text{l})$ does not become denser than seawater until a seafloor depth of ~2900 m. Below ~2900 m of ocean, however, the thickness of the NBZ grows more rapidly than the thickness of the HFZ, and at seafloor depths below 4000 m, the NBZ is thicker than the HFZ. The HFZ acts as a second cap on the system as CO_2 below the HFZ will be unable to migrate through the HFZ without forming hydrates, which we believe will severely impede the upward flow of CO_2 .

We have investigated several technical issues associated with carbon dioxide sequestration in deep sea sediments below the sea floor through laboratory experiments and chemical transport modeling. First, we examined the feasibility of this approach by making a systematic survey of permeabilities of deep sea sediments at depths and locations compatible with carbon storage. Through laboratory and modeling efforts, we were studying the flow of liquid carbon dioxide and carbon dioxide-water mixtures through calcium carbonate sediments to better

understand the geomechanical and structural stability of the sediments during and after injection. In addition, we were investigating the kinetics of calcium carbonate dissolution in the presence of CO₂ -water fluids, which is a critical feature of the system as it allows for increased permeability during injection. We were also investigating the possibility of carbon dioxide hydrate formation in the pore fluid, which might complicate the injection procedure by reducing sediment permeability but might also provide an upper seal in the sediment-pore fluid system, preventing release of CO₂ into the deep ocean, particularly if depth and temperature at the injection point rule out immediate hydrate formation. Finally, we performed an economic analysis to estimate costs of drilling and gas injection, site monitoring as well as the availability of potential disposal sites with particular emphasis on those sites that are within the 200-mile economic zone of the United States.

EXPERIMENTAL:

Porosity and Permeability Analysis:

Permeabilities were measured using an AutoLab 1000 test system developed by New England Research, Inc., and capable of automated hydraulic control of confining and pore pressures (Figure 1). Samples were saturated with NaCl brines (35,000 ppm) at room temperature for these tests.

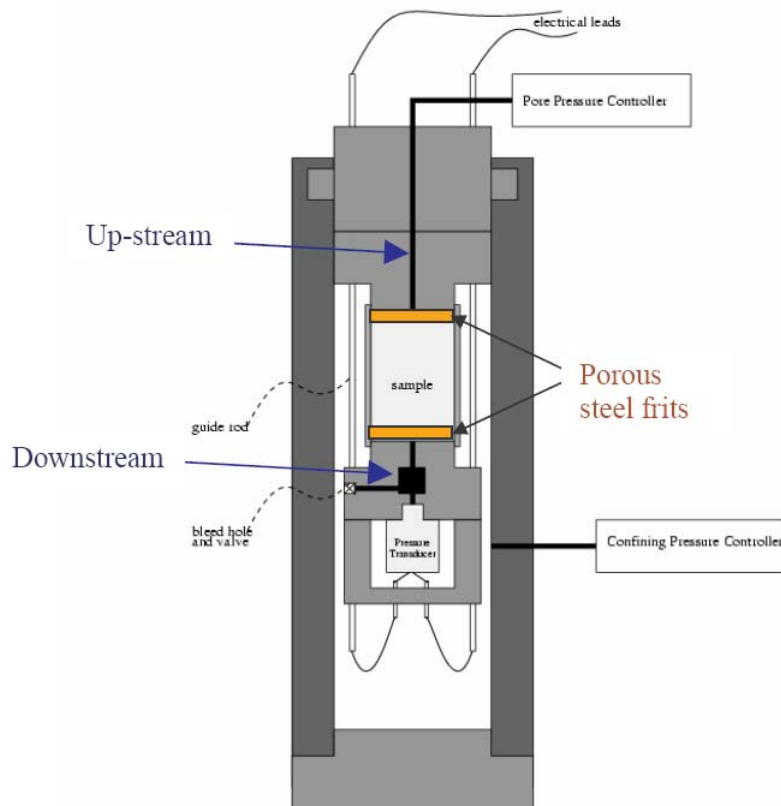


Figure 1: Schematic drawing of the New England Research, Inc. test apparatus (core holder assembly); <http://newenglandresearch.com/site/>.

The samples were placed in a low dead volume permeability core holder with a 1.3 cc downstream volume monitored by a miniature pressure transducer. Porous steel frits were used to distribute flow to the sample ends without the need for fluid distribution grooves. The samples were loaded to the desired effective stresses by simultaneously ramping the confining and pore pressures to the target conditions. A complex transient method, using the equipment and technique described in Boitnott (1997) was used to measure permeability. The frequency and shape to the transient was tuned to optimize signal to noise for each sample. Data processing was modified to incorporate the effective of storativity on permeability estimation. Once the test was completed, the samples were unloaded slowly to avoid overpressuring the samples. Post-test dimensions and weights were recorded and samples were dried. Dry weights were then recorded and the difference between the computed dry and saturated post-test densities were used to estimate the grain density and porosity.

Flow-Through Experimental Apparatus

To better understand the effects of CO₂-hydrate formation on the flow of liquid CO₂ in deep marine sediments, we built an experimental flow-through apparatus that is capable of injecting liquid CO₂ at a constant flow rate of 0.1 to 24 ml/min into seawater saturated capillary tubes or porous media at back pressures of up to 4000 psi [see figure 1]. The apparatus consists of a *Chromtech* constant flow rate duel piston pump that can inject liquid CO₂ from a dip tank at variable pressures of up to 10,000 psi and an Omega differential pressure transducer capable of measuring differential pressures from 0.1 psi to 300 pis.

The experiment is performed by initially injecting liquid-CO₂ into the seawater saturated and pressurized flow chamber at a temperature above that for hydrate stability. During this control experiment, the differential pressure across the flow chamber is recorded with a linear 4 to 24 mAmp data-logger. The differential pressure is a measure of the total effective permeability (i.e., the product of the intrinsic permeability and the relative permeability over the viscosity) of the seawater saturated flow chamber to liquid CO₂. The characteristic curve generated for the initial injection indicates that the total effective permeability tends to increase over time as the CO₂ dries out the flow vessel via evaporation causing the relative permeability of the liquid CO₂ to approach unity.

After the baseline curve of total effective permeability for a particular flow vessel (e.g., a bundle of capillary tubes, glass beads, sediment, etc) is established, then the experiment is repeated with the flow vessel temperature held constant below the theoretical temperature of CO₂ stability. Again, since the mass flow rate is constant, then the differential pressure across the flow vessel is proportional to its total effective permeability. As CO₂ dissolves into the pore-water, then CO₂-hydrates begin to form in the pore spaces. The formation of these hydrates changes the total effective permeability and results in a different curve of differential pressure against time than in the initial control experiment. From the differences between the two differential pressure curves we can calculate the relative permeability of liquid CO₂ to seawater AND CO₂-hydrate formation. The ultimate goal of these experiments is to understand how effectively CO₂-hydrate formation will impede the upward flow of liquid CO₂ injected below the hydrate stability zone. Initial results suggest that the ability of CO₂-hydrates to impede the flow of liquid CO₂ is dependent on pore composition and structure.

High-Pressure Apparatus (RPI)

The role of RPI researchers in this project was to investigate the physical and chemical properties of liquid CO₂, CO₂ hydrates and sediment-CO₂ mixtures through experiments at conditions corresponding to those in the sea-floor sedimentary pile where CO₂ sequestration has been proposed. However, they became involved in the project after the first year had already passed, so their efforts have mostly gone into development apparatus. Those experimental systems are described here. The necessary first phase of this effort has been to construct a relatively large volume, high-pressure system in which to conduct the experiments. This system must be capable of operating at sustained conditions up to 600 bars pressure and temperatures down to ~0°C. It must further be provisioned with 'flow-through' capability and optical ports for spectroscopic characterization of materials at sea-floor conditions (hydrates decompose rapidly at room temperature and pressure, so the apparatus must have optical windows through which we can observe reaction progress and characterize phases *in situ* using Raman spectroscopy). The design of the new high-pressure system was

carried out before any funds arrived at RPI, so immediately following the receipt of DOE funds (in the second year of the project) we ordered the necessary components for the new system, including: 1) a specially designed pressure vessel (Leco Corp.); an air-driven, high throughput pump (Haskel International, Inc.); a screw pump for fine pressure control and adjustment; a chiller; a 488-nm sapphire laser for use with our existing micro-Raman spectrometer; and assorted valves and tubing for fabrication of the pressure lines (see schematic below).

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are needed to see this picture.

At the end of the third year, we completed construction of this system except for the machining of an aluminum cooling jacket for the pressure vessel, which is now underway in the RPI machine shop. We attempted a pressure test earlier this month only to discover that the CO₂ pump had a manufacturing defect; this was shipped back to Haskel for repairs. We hope to be fully operational by January, 2008, when we will initiate the experimental phase of the project by synthesis of CO₂ hydrates and calibration of the laser-Raman imaging system. We will then proceed, as planned, to examination of the microstructural (textural) aspects of hydrate-sediment mixtures and the wetting characteristics of hydrate with respect to liquid CO₂ and CO₂-saturated seawater.

RESULTS AND DISCUSSION:

Porosity and Permeability Analysis

Deep sea sediments must have sufficient permeability to allow for the injection of large volumes of liquid CO₂ at reasonable injection pressures. First we accomplished an analysis of available core and borehole data from the DSDP and ODP databases. The data search was geographically limited to the U.S. Atlantic, Pacific and Gulf coasts. A database was developed and all available borehole logs and key geochemical data from existing DSDP and ODP sites were included. Based on this data survey we identified 16 sites, and approximately 30 geological units at these sites that may be used as potential CO₂ storage reservoirs. Because formation permeability data were missing at all sites, we collected 45 small (1-inch diameter) core plugs for porosity and permeability measurements. The sampling was performed at the Lamont-Doherty Earth Observatory core repository as well as at the ODP repositories at Texas A&M University and University of Bremen (Germany). Ten plug samples from three different sites in the western Atlantic were selected for extensive testing (Table 1). The test sites included one site on the New Jersey shelf (ODP Leg 150), one close to the Great Bahamas Bank (ODP Leg 166) and one on the Blake Ridge (DSDP Leg 11). These sites were chosen because of their lithologies, and with respect to their range of carbonate content. The samples from the New Jersey shelf contain clayey to sandy sediments, whereas the samples from the Blake Ridge contain deep sea carbonate oozes and the Great Bahamas Bank samples contain shallow carbonate oozes.

Table 1: Density, porosity and permeability measurements on selected core samples from the Atlantic.

| Leg | Site | Core | Locality | Lithology | Brine Salinity (ppm) | Bulk Saturated Density (post-test) (g/cm ³) | Oven Dry Bulk Density (g/cm ³) | Porosity | Grain Density (g/cm ³) | Permeability microD | Effective Stress MPa | Comments |
|-----|------|------|------------------------|------------------------------|----------------------|---|--|----------|------------------------------------|---------------------|----------------------|------------------|
| 11 | 0105 | 025 | lower continental rise | nannoplankton-rich limestone | 35,000 | 1.881 | 1.416 | 0.47 | 2.65 | 27.2 | 3.7 | Fractured |
| 11 | 0105 | 027 | lower continental rise | nannoplankton-rich limestone | 35,000 | 2.148 | 1.847 | 0.30 | 2.64 | 9.7 | 3.7 | |
| 11 | 0105 | 030 | lower continental rise | nannoplankton-rich limestone | 35,000 | 2.098 | 1.728 | 0.37 | 2.74 | 3.57 | 3.7 | |
| 11 | 0105 | 033 | lower continental rise | limestone with red clay | 35,000 | 2.000 | 1.610 | 0.39 | 2.64 | 0.024 | 3.7 | |
| 11 | 0105 | 038 | lower continental rise | very clay-rich limestone | 35,000 | 1.990 | 1.624 | 0.37 | 2.56 | 0.045 | 3.7 | |
| 150 | 0906 | 062 | continental slope | clayey chalk | 50,000 | 1.949 | 1.531 | 0.42 | 2.63 | 0.005 | 5.9 | Visibly deformed |
| 150 | 0906 | 065 | continental slope | clayey chalk | 50,000 | 1.989 | 1.610 | 0.38 | 2.59 | 0.007 | 5.9 | Visibly deformed |
| 166 | 1003 | 054 | platform slope | bioclastic wackestone | 50,000 | 2.242 | 1.991 | 0.25 | 2.66 | 4.83 | 11.8 | |
| 166 | 1003 | 063 | platform slope | foraminifer wackestone | 50,000 | 2.374 | 2.195 | 0.18 | 2.67 | 10.3 | 11.8 | |
| 166 | 1003 | 067 | platform slope | foraminifer wackestone | 50,000 | 2.266 | 2.021 | 0.25 | 2.68 | 6.9 | 11.8 | |

Permeability ranges from $\kappa = 0.005$ to $27.2 \mu\text{D}$, while porosity ranges between 0.18 and 0.47 (Table 1). One sample from DSDP Leg 11 (Site 105, Core 025) was visibly fractured and the fracture did not fully heal during the testing, likely causing high permeability and porosity measurements. The lowest values of $\kappa = 5\text{--}7 \text{ nD}$ are probably due to visible deformation that occurred during testing of samples from Leg 150 (Site 906, Cores 062 and 065). Other

nanodarcy permeability measurements from DSDP Leg 11 (Site 105, Cores 033 and 038) are attributed to high clay content in those samples.

In addition to the permeability measurements on core plugs, a review of existing permeability and porosity data from deep marine sediments was conducted. The results are illustrated in Figure 2.

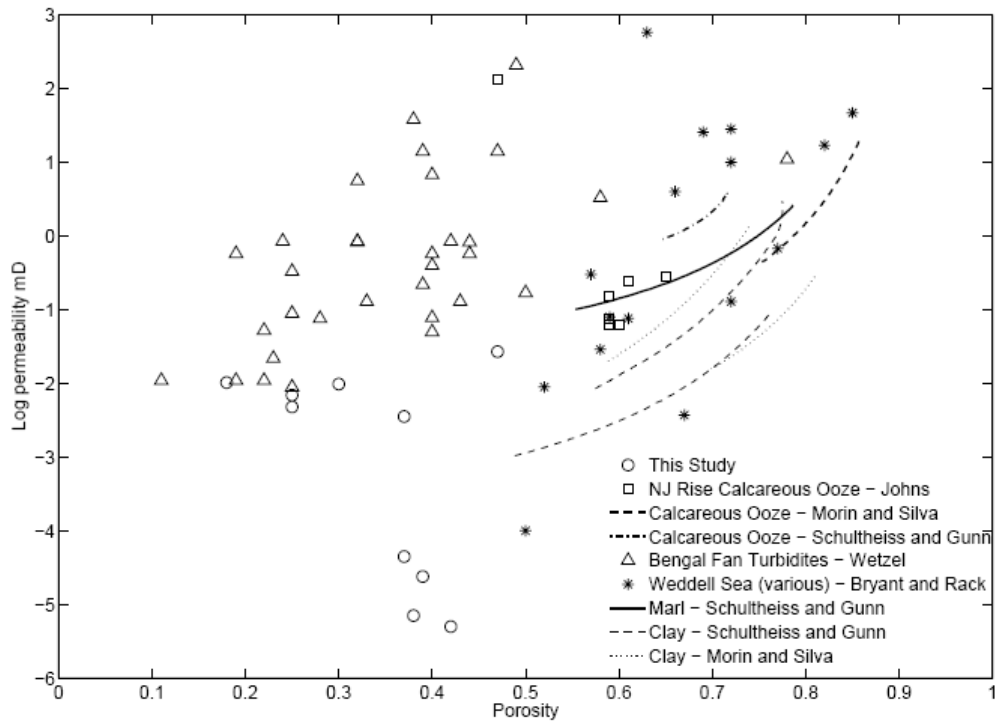


Figure 2: Compilation of permeability and porosity data for marine sediments (Levine et al. GRL, 2007, in press).

Permeabilities in calcareous ooze from shallow burial depths range from 1 mD at very high porosity and very shallow burial depth to 10 μ D at lower porosities and deeper burial depths. Platform carbonates reveal a wide range of permeabilities but are not present at the required depth of >2700 m. Our permeability measurements as well as literature data suggest that pelagic sediments may have high porosities but insufficient permeabilities to achieve reasonable CO₂ injection rates. Hydraulic fracturing will be necessary to enable reasonable high injection volumes. Alternatively, our collaboration with Royal Dutch Shell suggests that there may be some methods for injecting CO₂, such as through long, horizontal wells, that may increase the effective surface area during injection which will allow sufficient flow rates even when permeabilities are too low. We are continuing to explore these approaches. It should be noted that this challenge of putting CO₂ into low permeability sediments is analogous to getting oil out of low permeability sediments, a problem that the oil industry has worked on for many years.

Geomechanical Analysis – Hydrofracturing

Low permeabilities in pelagic sediments (10-100 μD) require hydraulic fracturing to attain sufficient injection rates and volumes. The relative thickness and lateral homogeneity of pelagic sediments may allow hydraulic fractures to be induced and create permeable pathways for the injected CO_2 . Hydraulic fracturing induces a tensile failure in the rock formation by increasing borehole pressure above the ambient pore pressure until the effective stresses around the borehole are exceeded (Hubbert and Willis, 1957). The pressure at which a hydraulic fracture occurs is defined as the breakdown pressure P_b , which is a function of the pore pressure, the minor horizontal stress, the intermediate effective stress and the tensile strength. We computed breakdown pressures (P_b) of typical pelagic sediments for two stress cases, the horizontally isotropic and anisotropic stress case. Results are summarized in Figure 3. The breakdown pressures for both cases is between 2-15 MPa above the in situ pore pressure P_{pore} and depends on the depth of fracture initiation and state of stress.

Important to note is that a fracture initiated at depth would require a breakdown pressure greater than that required at any overlying depth. Thus a hydraulic fracture at a certain depth below seafloor would encounter weaker, less consolidated sediments above it and would propagate upwards to the seafloor unless a shallower layers exists that is less susceptible to fracturing. In the absence of such a high strength caprock, a considerable risk exists that the injected CO_2 may reach the seafloor. This analysis also supports the approach of injection through a network of horizontal wells discussed above, as this would allow injection to proceed without hydrofracture, and thus no risk of propagation of fractures and release of CO_2 to the sea floor. An alternative approach, and one that is likely to be most economical, comes from the realization that the cost of drilling additional wells to depths shallower than fifteen hundred meters below the seafloor, once the pipeline and injection apparatus are on site, is relatively low cost compared with additional wells on land. This means that a very straightforward approach is simply to divide the required flow between multiple wells, directly reducing the required permeability. This approach, combined with drilling to slightly deeper depths (between 1000 and 1500 meters below the sea floor), which allows for some hydrofracturing without risk of escape to the seafloor, is likely to be effective and inexpensive.

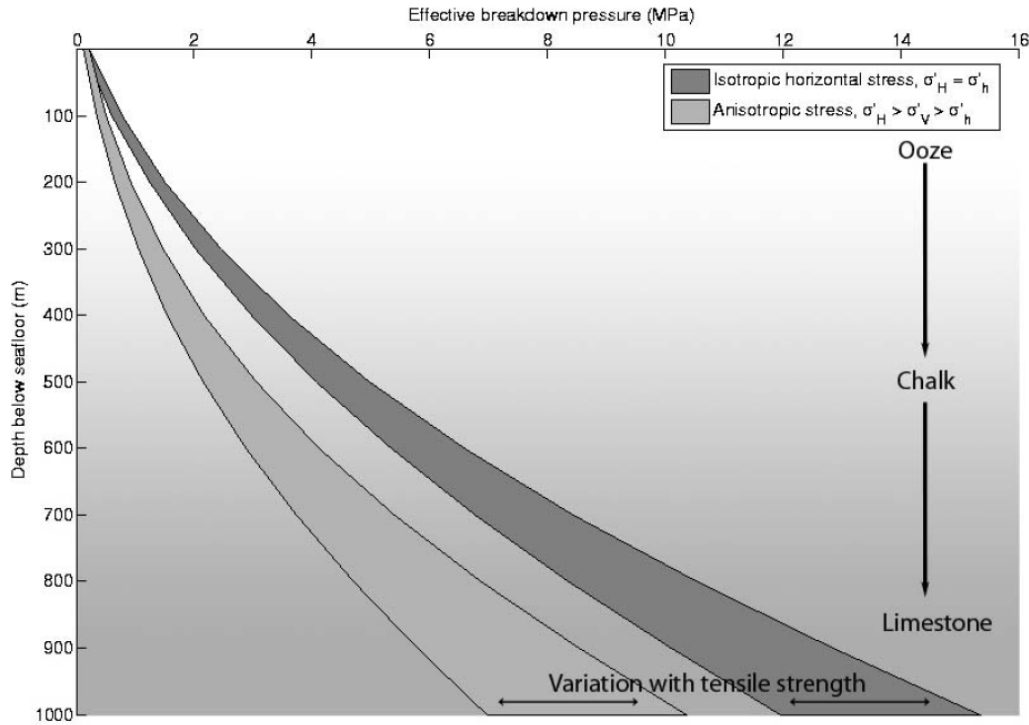


Figure 3. Effective breakdown pressure (breakdown pressure – pore pressure) as a function of burial depth in calcareous sediments. Breakdown pressure depends on the stress conditions and sediment tensile strength (Levine et al. GRL, 2007, in press).

Storage Capacity

The theoretical storage capacity of pelagic sediments is a function of permeability and porosity, and the depth of the neutral buoyancy level at which liquid CO₂ has the same density as pore fluids or seawater. The depth of the neutral buoyancy level itself depends on the temperature and salinity of the pore fluid. We analyzed the effect of temperature and salinity on the neutral buoyancy level and storage capacity for sites along the U.S. Atlantic, Gulf and Pacific coasts. Pore fluid salinities between 32 and 60 psu in the Gulf of Mexico result in high water densities which causes the neutral buoyancy level to move towards the seafloor (Figure 4). In extreme cases (salinities up to 60 psu) as in the Gulf of Mexico, the neutral buoyancy level may reach the seafloor, eliminating the possibility of gravitational trapping. A steep geothermal gradient has a similar effect. It will raise the neutral buoyancy level within the sediments and diminish the storage capacity. Geothermal gradients along the Pacific coast are about 0.1°C/m (e.g. Lyle et al., 1997) compared to 0.03°C/m along the Atlantic Coast (e.g. Mountain et al., 1994). Thus the neutral buoyancy level along the Pacific coast is closer to the seafloor and the storage capacity is smaller than along the Atlantic Coast.

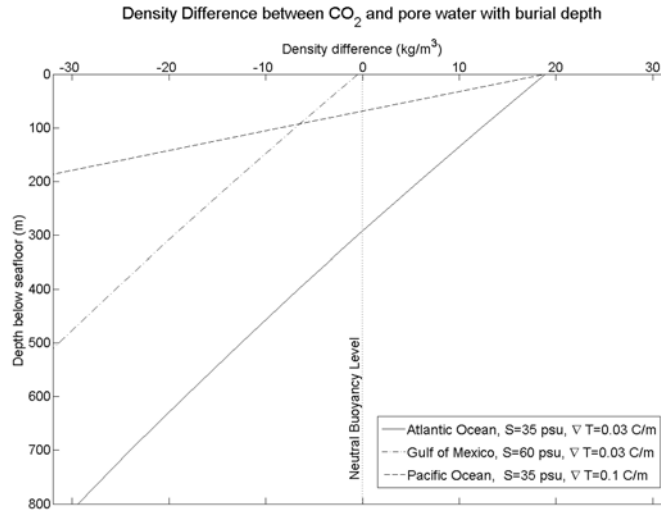


Figure 4. Density difference between CO₂ and water as a function of burial depth. Densities are based on salinities and temperature gradients from sites in the Atlantic, Gulf of Mexico, and Pacific (Levine et al. GRL, 2007, in press).

Matrix Dissolution versus “Wormholing”

Dissolution of carbonate rocks with carbonic acid occurs as matrix dissolution (isotropic) or as “wormholing” in which preferential flow paths develop. Whether a matrix or wormholing regime exists is defined by the Damkohler number which relates acid strength to fluid transport (Hoefner, 1987). The development of preferential flow paths may have important implications for the gravitational storage of CO₂ in pelagic sediments in the long term. Some of the stored CO₂ will dissolve into the pore water, forming carbonic acid, dissolving the reservoir rock and potentially creating preferential flow paths. We performed a series of flow-through dissolution experiments on Cretaceous chalk samples from the North Sea to evaluate the dissolution regime and dissolution rates. The experiments were performed with carbonic acid and maleic acid as a proxy for carbonic acid solutions with P_{CO2} greater than one atmosphere. All experiments were run at atmospheric pressure and ambient temperature conditions.

The results indicate that wormholing within the chalk samples started to take place when the Damkohler number was above 6×10^{-7} mol/cm at a given acid strength. Below that threshold value only matrix dissolution occurred. Overall, the experiments show that preferential flow paths can be created by weak acids and can be formed in homogenous, unfractured rocks. This raises a potential concern for long-term stability of the deposit with the possibility of large scale leaching that might leave behind brine filled caverns that – as their content is naturally buoyant relative to the surrounding rock – would raise questions of geomechanical stability (Nunn and Meulbroek 2002). However, our calculations using our simple models have shown that such karstification is impossible during CO₂ injection because the system is essentially water limited. As CO₂ is injected at a pressure greater than 30 MPa, approximately 5% of the CO₂ will dissolve in the pore fluid. This means that for a given volume of CO₂ injected into the pore fluid, complete dissolution requires interaction with pore fluid in 20 times the pore volume – which requires substantial time for fluid flow to occur. Even after dissolution has occurred, only 3 to 5% of the host rock would actually dissolve – which is important for permeability during injection, but is not enough to create large caverns.

This means that the benefits of carbonate dissolution (i.e., increased permeability) come without the risks of karst collapse and CO₂ escape.

Modeling of Injection of CO₂ in Deep Sea Sediments:

Our work on modeling of the fluid flow associated with CO₂ injection into sediments has proceeded as planned. This work is the major component of the Ph.D. thesis of Kurt House, graduate student at Harvard with Dan Schrag. Kurt's initial approach was to use very simple fluid flow models to explore some of the interesting fluid mechanics associated with liquid CO₂ injection. These calculations revealed that there are several different components of the flow including 1) basic buoyancy issues of the CO₂ plume relative to the pore fluid within a local geothermal gradient, 2) hydrate formation and its effect on limiting permeability and upward migration of a CO₂ plume, 3) convection within the CO₂ plume due to the high thermal expansion coefficient of liquid CO₂, and 4) downward flow of pore fluid saturated in CO₂ once it has encountered the CO₂ plume. Simple calculations show that all these processes are important on various timescales, but that the downward advection of water saturated with CO₂ will ultimately determine the fate of CO₂ sequestered in deep sea sediments, with the final state being a diffuse plume of CO₂-saturated water sitting between 300 and 500 meters below the sea floor. The next step in Kurt's thesis project is to apply more sophisticated modeling tools to this problem. This is currently underway, in collaboration with Schlumberger using their reservoir simulating software (ECLIPSE). We were encouraged to pursue this collaboration with Schlumberger during the review of this project in the first year, and we are happy to report that we have established a strong relationship and Schlumberger has shown great interest in this work. Schlumberger has recently moved one of their main research laboratories from Ridgefield, Connecticut to Cambridge, Massachusetts, which greatly facilitates our collaboration. Charles Harvey, a hydrologist from MIT, is assisting with this modeling effort. We expect we will have publishable results on the modeling effort next year.

The coupled chemical and fluid modeling has focused on answering three questions:

- 1) How will the thermal evolution effect the formation of CO₂-hydrates?
- 2) How will the formation of CO₂-hydrates effect the upward migration of CO₂?
- 3) How long will convective mixing and diffuse take to dissolve the liquid CO₂ and the CO₂ hydrates?

Our modeling has unambiguously answered the first question. The proposed CO₂ storage approach involves injecting CO₂ below the hydrate formation zone (HFZ) to avoid forming hydrates near the well head. As such, the injection will immediately cause cold pore-fluid near the seafloor to be expelled into the ocean and warm pore fluid to flow vertically toward the seafloor. The flow of warm pore fluid toward the seafloor perturbs the geothermal gradient and subsequently perturbs the hydrate formation zone and the negative buoyancy zone. The perturbation of those zones indicates that our trapping mechanisms might vanish during the injection. Our calculations indicate that even after 100 years of injecting 20 MT of CO₂ per year, the negative buoyancy zone (NBZ) is still 100 meters thick and the HFZ is still over 200 meters thick. Therefore, we are certain that hydrates will form during the injection

and that thermal perturbations will not disrupt the primary and secondary trapping mechanisms. *This result is an extremely important finding of this report, and accomplishes one of the major goals in the original proposal.* Below, we address the remaining two questions.

Pore Scale Modeling:

A key question from our initial findings is how the dynamic formation of CO₂-hydrates in porous media will affect the relative permeabilities of CO₂(l) and seawater. In order to answer that question with confidence, we have engaged in parallel tracks of experimentation and numerical modeling of multiphase pore-scale flow in the hydrate stability regimes. Large scale reservoir simulators (i.e., Eclipse or ToughReact) have *not* been built with the capability to model multiphase flow in the presence of hydrate formation. Too little is known about the effects of hydrate formation on relative permeabilities to accurately model large scale plume evolution with CO₂-hydrate formation. We believe that a dynamic pore-scale model coupled with an experiment of CO₂(l) displacing H₂O(l) in a capillary tube will produce the necessary background to build a more complete theory of dynamic hydrate formation in porous media.

At the pore-scale, three forces affect the dynamics of multiphase flow: buoyancy, friction, and capillarity. There are a few key assumptions associated with our dynamic model. In particular, the model is one-dimensional in space and assumes the shape of the meniscus—indicated in part by the wetting angle—is constant. That assumption implies the expectation of a Poiseuille flow distribution within the capillary. This assumption is likely valid as the Reynolds number is $\sim 10^{-2} - \sim 10^{-4}$. The dynamic model can be solved numerically for any pore geometry by simply applying the necessary geometric relationship $r_1 = r_1(z)$. When these equations are applied to a stochastic pore structure of many pores and many connecting tubes, then the fundamental pore dynamics will in aggregate produce large scale flow patterns. From such a pore-scale model, relative permeabilities curves for reservoir scale simulations can be produced.

We are working on several approaches to integrating hydrate forming into our pore-scale. The simplest approach is to assume that hydrates form on the pore walls, and thus reduce the pore radius as they form. Such a simple model would require r_1 to be a function of the hydrate concentration: $r_1 = r_1(z, [n\text{H}_2\text{O} \cdot \text{CO}_2])$. To calculate the concentration of CO₂-hydrate, we need a thermodynamic model of hydrate formation. There are several thermodynamic models of hydrate formation in the literature that we are using to predict when and where hydrates will form.

Thermal Evolution of the CO₂ Plume and Reservoir-Scale Modeling

In addition to the pore-scale modeling and experimentation, we engaged in reservoir-scale modeling of the post injection plume and thermal evolution. Until hydrate formation is better understood, the reservoir scale modeling is focusing on the behavior of liquid CO₂ and seawater below both the negative buoyancy zone and the hydrate formation zone. For these purposes, we have partnered with the oil services firm Schlumberger. Schlumberger has invested substantial resources into optimizing its reservoir-scale model of multi-phase porous media flow, and they have granted Harvard University an Eclipse license for these purposes.

Once the initial injection of CO₂(l) is complete, then the system will evolve by several

processes including: buoyancy-driven advection of the CO₂(l), convection within the pure CO₂(l) plume, dissolution of the CO₂(l) into the pore fluid, and dissolution of carbonate host rock,. To model these processes, the equations for multiphase flow in porous media and the chemical relationships associated with the system must be solved simultaneously for an inhomogeneous intrinsic permeability field. As previously mentioned, large investments have gone into writing reservoir models to simulate multiphase flow and chemistry at various reservoir conditions. Eclipse has been optimized for high temperature and high pressure conditions. Therefore, we are working with Schlumberger to extend the Eclipse code to handle the relevant temperature-pressure space. That work is still underway.

Schlumberger's Eclipse model solves the standard multiphase flow equations with the empirical relative permeability functions and capillary functions applied to complete the set of equations. For the system of interest, the standard multiphase flow equations must be coupled with the thermal energy balance, the dissolved species balance, and the equations of state for CO₂ and seawater at *low* temperature and *high* pressure. To date, nobody has reliably measured the relative permeability of liquid CO₂ and seawater. Until such measurements are made in reliable ways, then we are relying on relative permeability curves such as the van Gunucten curves for oil and water (3).

As revealed in our PNAS paper, the temperature of the injected CO₂(l)—without an insulated pipe—will be equivalent to the seafloor bottom temperature. That is a potential problem because we will likely need to avoid hydrate formation near the injection point. Avoiding hydrate formation near the well-head will require controlling the temperature at the point of injection. A linear stability analysis indicates that at a high enough intrinsic permeability ($\sim 10^{-13} \text{ m}^2$) the saturated CO₂ plume will be unstable. Therefore, the post-injection plume evolution may involve convective mixing of the pure CO₂ plume, which may accelerate the dissolution of the CO₂ liquid phase. Determining the timescales of dissolution through accurate modeling of the CO₂ plume and thermal evolution is an important goal of the Schlumberger-Harvard collaboration.

Experiments of Sediment Permeability and Behavior of Liquid CO₂ in Sediments:

To both validate the pore scale model of multiphase flow and to observe the effects of CO₂-hydrate formation on the relative permeabilities, we are building an experiment to observe the flow of CO₂(l) and H₂O in capillary tubes. The first goal of the capillary flow experiment is to validate the dynamic model previous discussed. We are currently validating the model with immiscible fluids that are liquid at surface conditions. Using immiscible fluids that are liquids at surface conditions is a natural step as they are easier to manipulate than fluids—such as CO₂—that must be pressurized and cooled. We are currently injecting oil—the non-wetting phase—into water and measuring the flow characteristics. Upon the completion of the oil-H₂O experiments, CO₂(l) will replace oil as the non-wetting phase being injected into an H₂O saturated capillary tube.

The final step in the pore scale experiment is to place a portion of the capillary tube in a cold bath. The liquid/hydrate/vapor triple point of CO₂ occurs at $\sim 4.5 \text{ MPa}$ ($\sim 650 \text{ psi}$) and $\sim 9 \text{ C}$. By keeping the pressure above $\sim 4.5 \text{ MPa}$ and a portion of the capillary tube below 9 C , we can guarantee hydrate stability at particular point in the capillary tube. We envision running the experiment with the temperature throughout the entire capillary tube above the hydrate

stability temperature. In the absence of hydrate formation, the position of the meniscus as a function of time should follow the solution to the above dynamic model.

The next step is to decrease the temperature over a portion of the capillary tube. After that decrease in temperature, hydrates will form in the capillary tube. It is not clear how the flow in the capillary tube will change once hydrates start to form. We will, however, have detailed pressure and flow data to indicate how the flow was disrupted by the formation of CO₂-hydrates. It is our goal in future research to combine that pressure and flow data with the above dynamic model and with existing models of the kinetics and thermodynamics of CO₂-hydrate formation to develop a robust relative permeability model for the CO₂(l)-Hydrate-H₂O system. Ultimately, we intend to upscale this model and integrate it into reservoir-scale simulators.

In addition to the pore-scale experiments, we are also continuing the experimental component of the proposal involved measurements of reaction kinetics associated with carbonate dissolution in CO₂ rich fluids. Considerable progress was made on this front over the course of the award, and some results from the Columbia group are currently being prepared for publication. However, because our calculations have shown that carbonate dissolution is likely to be important only for the permeability – and then only to a minor extent – our experimental focus has been on identifying complications associated with permeability in these systems, and also measuring rates of hydrate formation and dissolution. Our major goal was to design a high pressure experimental apparatus that would allow us to measure reaction kinetics and permeability changes at 300 bars pressure or greater. This has been accomplished, in collaboration with Schlumberger, and experiments are currently underway. These experiments are being led by Klaus Lackner and Juerg Matter from Columbia, with colleagues at Schlumberger. Kurt House is assisting with some of the experiments as well. A new focus has been the role that CO₂ hydrates may play in affecting the permeability. We expect to have results from these high pressure experiments this summer, with at least one publication prepared early in 2008.

Economic and Site Analysis:

The final component of our project can be broadly characterized as an economic assessment, although this includes a variety of other activities including site surveys. We have examined more than 25 cores from the Deep Sea Drilling Project and Ocean Drilling Program that are most relevant to injecting CO₂ into deep sea sediments. We are using the chemical and physical properties from these sites to aid the choices in our modeling and experimental efforts. The sites with most relevant data are shown on the map below. Graduate student Jeff Bielicki is currently finishing a Ph.D. dissertation in the Kennedy School of Government at Harvard that contains an economic analysis of the costs of sequestration in deep sea sediments, including estimates of where in the US this approach might be most efficient. What we have found is that deep sea sediment sequestration is likely to be most important in urban areas like the Northeast or Southern California where it may be very expensive to route pipelines that will carry CO₂ to an appropriate terrestrial sequestration site. Although offshore engineering is expensive relative to similar efforts on land, there are good analogues for deep sea sediment sequestration that exist in the oil and gas industry. We have initiated a

collaboration with Royal Dutch Shell to take advantage of the experience in deep sea engineering. Preliminary calculations suggest that total cost of injection of CO₂ from a pressurized, pure stream of liquid CO₂ is in the range of \$10 to \$20 per ton of CO₂. We hope to refine this number through out collaboration with Shell. Bielicki and Schrag have also completed a manuscript that grew out of this work on optimizing locations of new coal plants with carbon capture capability based on the trade-offs between distance to site of sequestration and distance to the consumer of electricity. Bielicki presented these results this summer in Europe at the Carbon Sequestration Conference.

CONCLUSION:

Through a variety of modeling and laboratory efforts, we have examined the feasibility of injection of CO₂ into deep-sea sediments as a permanent storage facility. Our calculations show that once injected, the higher density of the liquid CO₂ at appropriate pressures and temperatures, as well as the potential to form CO₂ hydrates that will impede the migration of CO₂ upward towards the sea floor, makes this approach essentially a leak-proof method for CO₂ storage. Our thermal modeling has shown that the continued injection of CO₂ will not perturb the local geothermal gradients to allow an escape route. The actual evolution of the CO₂ in the sub-seafloor is a complex, multiphase flow problem that we are continuing to study through a collaboration with Schlumberger. Our analysis of porosity and permeability of deep sea sediments shows that there are some places with high enough permeability for direct injection, but finding such sediments represents one of the challenges associated with this strategy. Hydrofracture of the sediments is probably not a viable strategy as this may propagate upwards and allow some CO₂ to escape, unless deeper injection to depths between 1000 and 1500 meters below sea floor is used instead of shallower injections that were originally envisioned. We have explored an approach that involves injection through a network of horizontal wells that increases the effective surface area during injection, allowing adequate flow rates to proceed even in lower permeability sediments. A simpler approach has also been explored, which involved simply drilling many additional wells as the marginal cost increase is extremely small given the ease of drilling shallow holes through the ocean floor. Additional work has also demonstrated that calcium carbonate dissolution is not an important factor in the process, and that karstification will not be an important process, nor can collapse of karst structures result in escape of CO₂.

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