



U.S. DEPARTMENT OF ENERGY
OFFICE OF FOSSIL ENERGY
NATIONAL ENERGY TECHNOLOGY LABORATORY



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NEUTRALIZING CARBONIC ACID IN DEEP CARBONATE STRATA BELOW THE NORTH ATLANTIC OCEAN

Background

The eastern seaboard of the United States is the most densely populated region in the country and generates a large fraction of all U.S. anthropogenic carbon dioxide (CO₂) emissions. Disposal options for this large volume of CO₂ are limited, and land transport and disposal are difficult due to high population density. From geographical considerations, offshore disposal might seem a reasonable approach. However, a number of technical uncertainties and environmental concerns make this option difficult to implement at this time.

The Atlantic Ocean is the site of most of the world's deep sea carbonate deposition, with a wide range of sediment compositions ranging from almost pure limestone to marly shales and claystones occurring at a wide range of water depths. A number of potential disposal sites are within 200 miles of the U.S. coastline. Thus, it is essential to the Department of Energy's Carbon Sequestration Program to evaluate the suitability of CO_2 storage in deep-sea carbonate sediments as part of an overall strategy of carbon storage and management.

The major advantage of CO_2 injection into carbonate sediments beneath the sea floor is the natural chemical buffer created by the reaction between calcium carbonate and carbonic acid, producing high-alkalinity pore fluid. Unfortunately, the reaction kinetics of CO_2 /water mixtures with natural carbonate sediments is not well understood at the pressures and temperatures of interest.

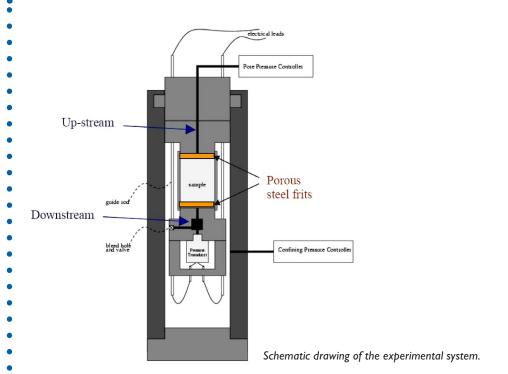
The technical issues of injection are relatively straightforward, although some questions do exist. Drilling into carbonate sediments is relatively easy. At shallow depths below the ocean floor, these deposits have high porosity but very little structural integrity. At greater depths, deposits have lower porosity and would allow little flow. However, oil extraction from such fields shows that hydrofracturing is a viable option. Also, after a relatively short period of injection, dissolution of carbonate material could provide greatly increased permeability. The calcium carbonate present will be consumed in neutralizing carbonic acid and leave behind an increased pore volume filled with calcium bicarbonate solution.

PARTNERS

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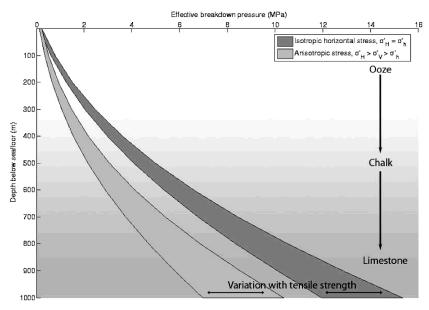
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Disposal by injection into carbonate sediments below the sea floor could provide a very large sink for CO_2 , and the CO_2 would be neutralized in a chemical reaction that turns solid calcium carbonate into dissolved bicarbonate. The physical characteristics of the reservoir could provide a series of barriers to the escape of the CO_2 . If the bicarbonate-rich pore fluid did mix with seawater, the ocean would provide an additional safeguard by buffering pH changes. Effects on the atmosphere, even on the time scale of millennia, would be extremely small, and the process should qualify as a near-permanent sequestration method.

Description

This project investigated several technical issues associated with carbon dioxide sequestration in calcium carbonate sediments below the sea floor through laboratory experiments and chemical transport modeling. The 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. Researchers studied the flow of liquid carbon dioxide and carbon dioxide-water mixtures through calcium carbonate sediments to better understand the geo-mechanical and structural stability of the sediments during and after injection. The research included investigations of the kinetics of calcium carbonate dissolution in the presence of CO₂-water fluids (a critical feature of the system as it allows for increased permeability during injection) and the possibility of carbon dioxide hydrate formation in the pore fluid. Hydrate formation may 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, the investigators performed an economic analysis to estimate costs of drilling and gas injection, and site monitoring, as well as the availability of potential disposal sites with particular emphasis on those sites within the 200-mile Exclusive Economic Zone of the United States.



Graph showing the effective breakdown pressure as a function of burial depth.

Primary Project Goal

The primary goal was to investigate the feasibility of carbon dioxide disposal by injection and neutralization in calcium carbonate sediments below the ocean floor.

Objectives

The research objectives for this project were to:

- Understand the mechanical and chemical behavior of CO₂ and CO₂/water mixtures injected into carbonate sediments of various compositions under a range of pressures and temperatures.
- Investigate the kinetics of calcium carbonate dissolution in the presence of CO₂/water.
- Investigate the possibility of CO₂ hydrate formation in the pore fluid.
- Conduct an economic analysis to estimate costs of drilling, gas injection, and site monitoring

Benefits

Modeling and experimental results suggest that injection of carbon dioxide in deep sea sediments below 3000 meters (m) of water depth, and then 300 to 400 m deep within the underlying sediment should provide for permanent storage of carbon dioxide. Data and conclusions developed by this research provide key background information necessary to further evaluate this CO₂ mitigation option.

PERFORMANCE PERIOD

1/12/2004 to 1/14/2008

COST

Total Project Value \$801,374

DOE/Non-DOE Share \$801,374/\$0

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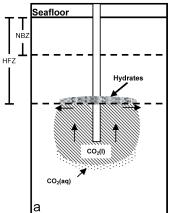
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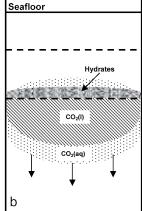
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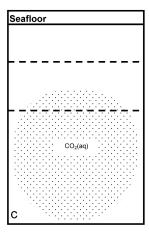
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Accomplishments

Through a variety of modeling and laboratory efforts, researchers examined the feasibility of CO, injection into deep-sea sediments for permanent storage. Calculations show that once injected, the higher density of 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, make this approach essentially a leak-proof method for CO₂ storage. Thermal modeling shows that 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 will require further study. Analysis of the porosity and permeability of deep-sea sediments shows that some places have high enough permeability for direct injection, but finding such sediments represents one of the challenges associated with this strategy of ocean sequestration of CO₂. Hydrofracturing of the sediments is probably not a viable strategy as this may propagate upwards and allow some CO₂ to escape. Instead, an approach that involves injection through a network of horizontal wells that increases the effective surface area during injection would be preferable, allowing adequate flow rates even in lower permeability sediments. 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 injected CO₂.







The expected long-term evolution of injected CO₂: (a) I year; (b) 100 years, and (c) 10,000 years.

Planned Activities

This research project has recently ended and a final report will be completed in the near future. This report will include the results of the economic and site analysis.