LABORATORY EXPERIMENTS TO SIMULATE CO$_2$ OCEAN DISPOSAL

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Abstract

This paper provides an overview of the motivation, objectives, and methods of a 36 month laboratory study which has been initiated to simulate deep ocean disposal of anthropogenic CO$_2$. Data obtained in these tests will be applied to the development and validation of predictive models which can estimate the term of CO$_2$ sequestration from the atmosphere, perform (ocean) environmental hazard assessments, and be employed to devise injection methods and to identify candidate nozzle designs that ensure rapid dissolution. The investigation focuses on two key aspects of the disposal process: (1) near-field phenomena related to the break up of jets of liquid CO$_2$ in seawater and the dispersion and coalescence/agglomeration of the resultant droplets; and (2) far-field dissolution of CO$_2$ droplets encased in a thin hydrate shell rising through the water column. Experiments will be performed in a facility that can reproduce conditions in the ocean at depths down to 600 m.

Introduction

Greenhouse gas emissions and their potential impact on global climate have been the focus of intensifying interest and debate. Carbon dioxide (CO$_2$) currently is the most important of these gas species due to the preponderant quantities being released into the atmosphere by anthropogenic sources–largely through the combustion of fossil fuels. During the 1992 UNCED conference in Rio de Janeiro, an agreement was reached which called for industrialized countries to stabilize their greenhouse gas emissions by the year 2000 at 1990 levels. Although the extent of implementation of related policies and technical activities has varied greatly among the signatory nations, the most recent negotiations held in Berlin in 1995 suggest a renewed commitment to the goals of the 1992 agreement. It appears, therefore, that a shift in energy policy and redirection of resources to accelerate development of technologies that limit greenhouse gas emissions may be forthcoming.

Since combustion of coal in the U.S. releases about 1,450 million tonnes of CO$_2$ annually into the environment (about 30% of the total annual U.S. carbon emissions), the implications of the inter-national greenhouse gas agreement related to this important energy resource are significant. If the stabilization of CO$_2$ emissions is adopted as a policy goal in the U.S., then advanced control tech-nologies for coal combustors need to be developed to supplement or to provide alternatives to options such as efficiency improvements, energy conservation, or fuel switching. To this end, a number of studies have been initiated to evaluate the feasibility of techniques to recover, reuse, and/or dispose of CO$_2$ generated through the combustion of coal and other fossil fuels. One technique that has emerged as a primary candidate for the control of CO$_2$ emissions involves extraction of CO$_2$ from flue gases or via fuel reforming, followed by liquefaction and sequestration in the deep ocean (Steinberg *et al.* 1984; Golomb *et al.* 1989; Mori *et al.* 1993).

Removal and liquefaction of CO$_2$ from the effluent streams of industrial fossil fuel combustors can be accomplished utilizing existing technologies, albeit at substantial cost. The technical viability of the concept as a means to stabilize emissions therefore depends on whether long term (i.e., of the order of

centuries) sequestration of the captured CO_2 from the atmosphere can be achieved. Given the limited range of reuse options, large quantities of CO_2 will need to be disposed of in an environmentally safe, and cost effective manner. Disposal in the ocean and in subterranean sites such as spent gas wells, aquifers, salt domes, and rock caverns has been considered. Several factors recommend marine disposal, the foremost being the very large capacity of the oceans to absorb and to retain CO_2. According to recent IPCC (Intergovernmental Panel on Climate Change) estimates, the deep ocean, which is unsaturated with CO_2, currently contains approximately 38,000 Gt (Gigatonne = 10^9 tonnes) of dissolved inorganic carbon (DIC). For a maximum DIC concentration of about 1.6% carbon by weight, saturation of the deep ocean would require dissolution of more than 10^7 Gt CO_2 (Ormerod *et al.* 1993). Existing recoverable fossil fuel reserves are believed to hold between 4,000 and 7,000 Gt of carbon which, if completely oxidized, would yield no more than 2.5 x 10^4 Gt CO_2. In comparison, Koide *et al.* (1992) have suggested that the CO_2 storage capacity of all the world's depleted natural gas reservoirs is only about 180 Gt, while useless (i.e., saline) aquifers can absorb an additional 320 Gt.

In order to realize long term confinement, CO_2 must be transported below the ocean's thermocline to depths in excess of about 500 m. Deep discharge ensures that advective and diffusive transport of CO_2 back to the surface proceeds slowly. The very strong effect that depth of dissolution exercises on the long term fate of disposed CO_2 effluent has been demonstrated in a number of modeling studies (Bacastow and Stegen 1991; Nihous *et al.* 1994). Figure 1, reproduced from Nihous *et al.* (1994), shows the impact of dissolving different percentages of global anthropogenic CO_2 production at 500 m (starting at year 2000) on average atmospheric concentrations of this species. Figure 2 (also from Nihous *et al.*) demonstrates the dependence of the year 2100 concentration of CO_2 on depth of dissolution and vertical diffusion coefficient.

Figure 1 Atmospheric carbon concentration predictions with 'fast' consumption input, CO_2 removal levels of 0, 15, 30, 50, and 100% (from top to bottom) and discharge at 500 m depth.

Figure 2 Atmospheric concentration predictions in Year 2100, for 50% CO_2 removal and 'fast' consumption input, as a function of discharge depth (K is the ocean vertical diffusion coefficient).

Pure liquid CO_2 effluent released in the ocean is buoyant at depths above about 3,000 m. Moreover, the effluent is hydrodynamically unstable and will break up into a dispersed droplet phase that rises as it slowly dissolves. As a consequence, the CO_2 may be distributed over a considerable distance above the point of release with an associated reduction in the term of sequestration. This situation is further exacerbated by the fact that a thin (of the order of 10 µm), solid hydrate film, which greatly inhibits mass transfer, can form rapidly at the CO_2-water interface when local pressures exceed 44.5 bar and temperatures are less than 283 K (Teng *et al.* 1995). These pressures and temperatures prevail below 450 m depth in the ocean. The effect of a hydrate film on the dissolution of a buoyant 3 mm diameter droplet of CO_2 released at 1,000 m is shown in Figure 3. These model predictions suggest that the hydrate film will increase the distance over which a buoyant droplet rises before complete dissolution by more than an order of magnitude.

Figure 3 Effect of a hydrate film on the dissolution of a 3 mm CO_2 droplet released at 1,000 m.

Although release below 3,000 m has been proposed (Baes *et al.* 1980; Shindo *et al.* 1993) to avoid problems associated with CO_2 buoyancy, accessing such depths with a submerged pipeline may not be feasible in the near term. Moreover, this strategy would restrict the pool of candidate disposal sites. Recognizing that existing pipeline technology limits discharge depth to less than 1,500 m, and in consideration of the direct relationship between increasing system costs and submerged pipeline length, Herzog *et al.* (1993) have recommended that research focus on the development of disposal techniques that can achieve long term sequestration of CO_2 effluent released at moderate depths, i.e., between 300 m and 1,500 m. Their survey identified two techniques which appear to hold promise: (1) discharge of liquid CO_2 through atomization nozzles to produce small droplets (≤ 2 mm diameter) which models predict will dissolve completely over a vertical rise of <100 m, even with a hydrate shell; and (2) discharge of liquid CO_2 into a submerged, confinement structure where dissolution proceeds to completion, producing a sinking plume of CO_2-enriched seawater (Drange and Haugen 1992).

Development of viable techniques to dispose and to sequester CO_2 at moderate depths in the ocean requires experimental data not currently available in the technical literature. Specifically, additional information is needed on liquid CO_2 jet break up and atomization, droplet agglomeration and coalescence, and droplet dissolution under deep ocean conditions. These data also are essential in evaluating potential environmental hazards, such as local acidification of seawater (Herzog *et al.* 1996), associated with the ocean disposal concept.

Experimental Objectives
The overall objective of the investigation is to obtain fundamental data that can be employed in the development of predictive models to assess technical feasibility, effectiveness, and environmental impacts of the oceanic CO_2 disposal process. Recognizing that *in situ* (i.e., at-sea) tests will eventually need to be pursued, results of the laboratory experiments will be applied to plan such tests. Finally, since the generation of fine droplets of CO_2, which ensures rapid dissolution, appears to be essential for successful implementation of disposal at moderate depths in the ocean, experiments will be conducted to characterize the performance of candidate discharge nozzles. These data are expected to be useful in future system design activities.

Two general categories of experiments will be performed to investigate the phenomena of: (1) CO_2 jet break up and the formation of a dispersed droplet phase; and (2) dissolution of single droplets of liquid

CO_2. The break up tests will attempt to elucidate the dependence of initial droplet size distribution, coalescence/agglomeration, and lateral dispersion on: simulated discharge depth; jet velocity; nozzle orifice size and geometry; and the formation of a hydrate phase.

Since the rate at which the dispersed CO_2 phase dissolves will profoundly impact both the effectiveness of the oceanic sequestration concept and the magnitude and extent of potential hazards posed to the marine environment, experiments will be conducted which examine the dissolution of single droplets–with and without a hydrate film–of buoyant, liquid CO_2 stabilized by a downward flow of water. Droplet size will be monitored to obtain quantitative data on mass transfer rates. Stabilizing droplets in a downward current of water more closely simulates convective effects experienced by a rising, buoyant droplet than previous studies that have employed mechanical restraints (Hirai *et al.* 1996).

Methods and Approach
The two categories of experiments described above will be conducted in a pressure vessel that can simulate conditions in the ocean at depths down to approximately 600 m. This unique facility, which is described in the following section, was specifically designed to investigate CO_2 jet break up phenomena; it is sufficiently large to minimize wall and surface effects on jet development and can sustain a continuous discharge of liquid CO_2 for periods of the order of minutes.

In the jet break up experiments, spatially- and temporally-resolved measurements of droplet size and number density, and continuous and dispersed phase velocities will be performed throughout the near-field (up to about 70 cm downstream of the discharge orifice) of laminar and turbulent jets of liquid CO_2. Test parameters which will be varied include: (1) jet velocity; (2) simulated depth of discharge; and (3) nozzle orifice size and geometry. These quantitative data will be supplemented by qualitative flow visualization images.

In the dissolution tests, seawater will be circulated downward through a clear vertical diffuser sus-pended on the axis of the pressure vessel to stabilize single buoyant droplets of liquid CO_2. The size of these droplets will monitored continuously to obtain time records of the dissolution process. Multiple droplets will be introduced into the diffuser to study agglomeration phenomena.

Since the effect of hydrates on jet break up and droplet dispersion, interactions, and dissolution is a major topic of interest, the experiments will be performed at combinations of water pressure and temperature that both foster and preclude formation of this solid phase.

Facility and Instrumentation
A detailed description of the pressure vessel may be found in Masutani *et al.* (1993). A photograph of the facility is presented in Figure 4. The facility comprises an insulated steel pressure vessel, liquid CO_2 and seawater supply systems, and various probe and optical diagnostics.

The pressure vessel is constructed in three parts, is 2.46 m tall and has an inside diameter of 55 cm. Numerous viewports provide optical access to the interior of the vessel. During experiments, the vessel is partially filled with fresh or seawater chilled to a temperature representative of the depth being simulated. The interior of the vessel is pressurized by charging the space above the water with N_2 or another gas. Pressures up to 6.3 MPa and temperatures as low as 0^0C can be attained in this facility.

Figure 4 Photograph of the experimental facility.

Liquid CO_2 is drawn from a 2,800 kg capacity refrigerated storage tank and discharged vertically into the water through a removable injector at the base of the tank. The injector presently is being modified to permit translation in two dimensions relative to fixed instrumentation optics. The CO_2 can be introduced as single droplets (for dissolution experiments) using a screw hand pump, or, employing a high-pressure motor-driven pump, as a continuous jet. Maximum injection rate is 16 kg/min at 7 MPa delivery pressure. An electronic valve and controller vents the pressurizing gas to maintain constant system pressure as liquid CO_2 accumulates in the fixed volume vessel.

A flow device to stabilize buoyant droplets of liquid CO_2 for observation during the dissolution tests currently is being fabricated and tested. A downward flow of water through a clear diffuser submerged within the vessel above the CO_2 injector will provide the drag force necessary to balance droplet buoyancy. As dissolution proceeds, this balance will be altered and the droplet will migrate to a new vertical location in the diffuser with a different water velocity. This arrangement closely simulates the hydrodynamics and convective mass transfer effects experienced in the moving frame of reference of a rising droplet.

Access provided by the multiple viewports and clear diffuser section permits the use of non-intrusive optical measurement techniques. The principal diagnostic for the jet break up experiments will be a phase Doppler particle analyzer (PDPA) that has the capability of performing simultaneous, spatially- and temporally-resolved measurements of spherical droplet size and velocity. The PDPA can also monitor droplet number density and seawater velocity. With the selected optics, droplets with diameters ranging from about 10 µm to 5,000 µm can be accurately detected. Qualitative flow visualization studies employing both conventional and laser sheet illumination also will be performed to supplement the quantitative PDPA data.

Single droplet dissolution will be monitored using close-up video and digital image analysis techniques. The luminance output of a Hi-8 mm video camcorder will be digitized with a Scion PC-based frame grabber board. The digital images will be analyzed using special software to obtain estimates of droplet volume as a function of time. The imaging system can resolve changes in droplet diameter of approximately 20 µm. Since dissolution times are expected to be of the order of minutes or longer, frame rate is not an important consideration. Water velocities around the droplets in the diffuser will be monitored with the PDPA.

Summary

Stabilization of CO_2 emissions in accordance with the 1992 UNCED agreement requires development of advanced control technologies for coal and other fossil fuel combustors. One technique that has emerged as a primary candidate for CO_2 emissions control involves extraction of CO_2 from flue gases, followed by liquefaction and sequestration in the deep ocean. Accurate assessment of the viability of this control technique has been hampered by insufficient information on the ocean disposal component of the process. To this end, a 36 month laboratory study has been initiated that will simulate many of the salient features of deep ocean disposal of CO_2. This investigation will attempt to address key technical deficiencies identified by previous studies and provide input for the planning of future *in situ*

tests.

Experiments will be performed in a unique facility that can reproduce conditions in the ocean down to 600 m. Fundamental data will be obtained to develop and to calibrate predictive models which can be employed to identify effective sequestration strategies and to evaluate impacts on the local marine environment. Two general categories of experiments will be performed which will investigate: (1) the phenomena of CO_2 jet break up and the formation of a dispersed droplet phase; and (2) dissolution of droplets of liquid CO_2 rising through the water column.

Efforts currently focus on modifying the facility and developing new instrumentation. Experiments are anticipated to begin before the end of 1996.

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