Negatively Buoyant CO_2-Hydrate Composite for Ocean Carbon Sequestration

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Direct ocean CO_2 injection, currently being evaluated to counteract anthropogenic increases in atmospheric CO_2, takes advantage of the large carbon storage capacity offered by the world oceans (Audus, 1997). A proposed method for direct ocean injection is to release CO_2 as a rising plume of droplets at depths between 800 and 1,500 m (Liro et al., 1992), where CO_2 is positively buoyant. The injection point must be sufficiently deep to allow complete dissolution of the liquid CO_2 into the surrounding seawater before the droplets reach depths $< \sim 500$ m, where CO_2 will gasify and repartition faster into the atmosphere. Another approach is to inject CO_2 at depths greater than 3,000 m, where CO_2 is denser than seawater (Brewer et al., 1999) and will form a CO_2 "lake" on the seafloor. This approach will result in increased residence time and improved carbon sequestration efficiency, but these benefits are offset by infrastructure and implementation costs that increase significantly with injection depth. In addition, because of the localized high concentration of CO_2, local biological effects are expected to be greater than with other injection methods.

CO_2 hydrate, a nonstoichiometric CO_2-water solid phase, is thermodynamically stable at ocean depths >500 m (Sloan, 1998) and approximately 10% denser than seawater (Holder et al., 1995). In this article, we propose a concept for an injector system that produces a negatively buoyant CO_2 material by promoting the conversion of CO_2 to CO_2 hydrate. Starting with a mole of liquid CO_2, if x_h is the mole fraction converted to CO_2 hydrate (with a hydration number of n) and assuming that the CO_2 hydrate and unconverted liquid CO_2 form a cohesive material, the total mass of the composite is $(44+18nx_h)$ with a bulk volume of $[44(1-x_h)/\rho_c+(44+18n)x_h/\rho_h]$, where ρ_h and ρ_c are the hydrate and liquid CO_2 densities, respectively. Thus, the bulk density of the composite is (Holder et al., 1995)

$$\rho_{\text{com}} = \frac{1+n(18/44)x_h}{(1-x_h)/\rho_c+[1+n(18/44)]x_h/\rho_h}$$

Hydration numbers reported in the literature for CO_2 hydrate range from 6 to 8 (Holder et al., 1995). Using $n=7$ and a corresponding density of $\rho_h = 1{,}100$ kg/m^3 (Aya et al., 1997), a composite mass of liquid CO_2 and CO_2 hydrate will be negatively buoyant at 1,500, 1,300, and 1,100 m if the mole fraction of CO_2 converted to hydrate were at least 0.19, 0.22, and 0.24, respectively (Figure 1). Thus, only moderate amounts of CO_2 hydrate are needed to produce a sinking composite at intermediate ocean depths (1,000–1,500 m). In the proposed injector design, hydrate conversion is achieved by entraining seawater in a stream of liquid CO_2 shortly before being discharged from a pipeline into the ocean. Vigorous mixing of the two phases forms a liquid emulsion with a high interfacial area for hydrate formation. By converting a sufficient amount of CO_2 into hydrate, a negatively buoyant material can be discharged from the injector at depths significantly shallower than 3,000 m where liquid CO_2 becomes denser than seawater at 4°C (Figure 1).

To demonstrate the concept of promoting hydrate formation by entraining water into a stream of CO_2, a co-flow injector was designed and tested using a 0.070-m^3 (0.3175-m ID, 0.914-m internal height) temperature-controlled, high-pressure vessel that simulates conditions at ocean depths up to 2,000 m (Phelps et al., 2001). The injector (Figure 2) consists of an outer tube (9.5×10^{-3}-m OD and 6.4×10^{-3}-m ID) and a concentrically located inner capillary tube (1.6×10^{-3}-m OD and 0.125×10^{-3}-m ID) for liquid CO_2 and water, respectively. The stainless steel capillary tube terminates approximately 0.14 m from the end of the outer tube, creating a zone in which the liquid CO_2 and water can mix before being discharged into the water-filled pressure vessel (Figure 2).

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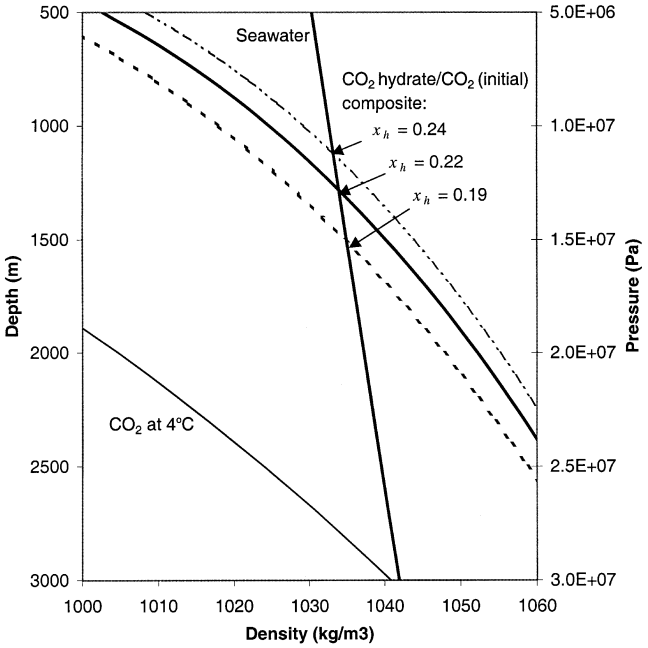

Figure 1. Density as a function of pressure and ocean depth for liquid CO_2 (NIST, 2001), seawater (Brewer et al., 1999), and a liquid CO_2-CO_2 hydrate composite with varying mole fractions (x_h) of CO_2 hydrate.

The outer tube consists primarily of stainless steel with a 0.125 m section of Teflon at the end; this prevents wetting of the wall by the water phase in the mixing zone and keeps water dispersed in CO_2. In a typical experiment, the vessel was filled with water, pressurized to near experimental levels (10×10^6 to 13×10^6 Pa), and then cooled in a temperature-controlled (cold) room to the experimental temperature (4–5°C). Liquid CO_2 and water, pre-equilibrated at the experimental temperature, were delivered using syringe pumps through the injector into the vessel at predetermined flow rates of 15–25

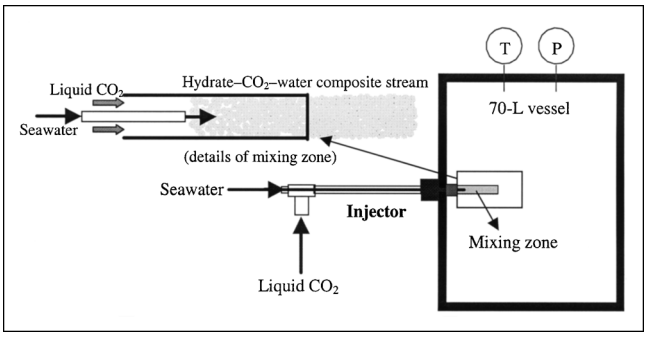

Figure 2. Experimental arrangement designed for a coflow injector producing a high interfacial area between liquid CO_2 and water in a mixing zone before injecting the mixture into the surrounding seawater.

Upon exiting the injector, the composite contains CO_2 hydrate and liquid CO_2.

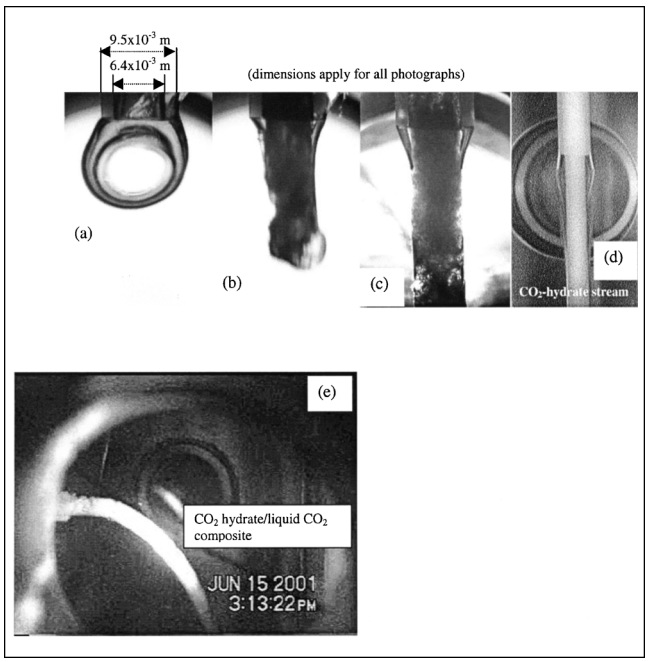

Figure 3. Experimental observations using the coflow injector under conditions simulating intermediate ocean depth.

$T = 5$°C, $P = 13\times10^6$ Pa, equivalent to 1,300 m depth of water. (a) Drop of liquid CO_2 released in water with no premixing; (b) transition from drops to a composite stream when liquid CO_2 is mixed with water; (c) steady flow of the negatively buoyant composite stream; (d) the injector under continuous operation; (e) horizontally mounted injection system producing a negatively buoyant composite stream. Water-to-CO_2 volumetric ratio = 3; residence time of the mixture in the mixing zone = 8 s; Reynolds number at the tip of the capillary tube = 2,000.

and 2–10 mL/min, respectively. During an injection experiment, the vessel pressure typically increased slightly (less than 0.5×10^6 Pa) or was kept constant using a backpressure regulator. The material ensuing from the injector was observed and recorded by a video camera through one of the 0.050 m diameter sapphire windows of the pressure vessel.

Injections of liquid CO_2 alone at temperature and pressure conditions simulating intermediate ocean depths (that is, temperature = 4–5°C, pressure = 10.3×10^6–13.1×10^6 Pa) produced rising droplets of liquid CO_2, which were eventually covered with a thin translucent shell of CO_2 hydrate (Figure 3a). This observation is consistent with previous experimental results (Teng et al., 1995). By introducing water into CO_2 using the co-flow injector, a solid-like material was extruded from the injector, as shown in Figure 3b. Depending on the water and CO_2 flow rates, the extruded material either bends upward due to positive buoyancy or sinks when released from the injector. Figures 3c and 3d show steady production of a negatively buoyant material at 13.1×10^6 Pa, corresponding to 1,300 m depth. To further verify negative buoyancy, we placed the injector horizontally in the pressurized vessel. The resulting material bends downward, demonstrating its higher density relative to that of the surrounding water (Figure 3e). Further experiments showed that with a higher flow-rate ratio for water to CO_2, a negatively buoyant material can be produced at pressures as low as 10.3×10^6

Pa, which corresponds to an ocean depth of 1,100 m. Experiments using distilled water and saline solution (3.5% NaCl) showed similar results.

The cohesive nature and ice-like appearance of the extruded material is likely caused by hydrate formation that occurs within the mixing zone of the injector (Figure 2). The residence time of the CO_2-water mixture in the injector, which ranged from 8 to 12 s, was clearly sufficient for CO_2 hydrate to form. In some experiments, extruded material that was initially positively buoyant would eventually sink—either when the vessel pressure was increased or several minutes after the material was released from the injector. The latter phenomenon is probably caused by continued hydrate formation, while the former likely results from the composite nature of the extruded material, which still contains compressible liquid CO_2. At the end of some experiments where extruded material remained attached to the injector and within view, we did not see any leakage of CO_2 as the composite dissolved into the surrounding seawater at constant temperature and pressure. Thus, it appears that liquid CO_2 is contained by the hydrate phase of the composite even during dissolution. More detailed dissolution experiments are currently underway.

We observed that, for a given CO_2 flow rate and vessel pressure, the buoyancy of the composite extruded from the injector changed from positive to negative with increasing water flow rates, implying increased hydrate conversion. At the flow rates used in the experiments, water ejected from the 0.125×10^{-3} m capillary tube forms droplets on the order of 0.25×10^{-3} m in diameter. Such small water droplets dispersed in CO_2 within the mixing zone of the injector produced a high interfacial area for hydrate formation (Sloan, 1998). The influence of water flow rate on the composite buoyancy is likely from an interfacial area that increases with an increasing volumetric ratio between the water and CO_2 phases. We also observed that, for a given CO_2 flow rate, the minimum water flow rate needed to make a sinking composite increases with decreasing pressure. For example, at 13.1×10^6 MPa and a flow rate of 4 mL/min of CO_2, the resultant material was denser than the surrounding saline water when at least 21 mL/min of saline water was co-flowed through the injector with the CO_2. On the other hand, at 10.3×10^6 Pa, this same combination of CO_2 and saline water flow rates resulted in a positively buoyant composite; the saline water flow rate had to be increased to 23 mL/min for the produced material to sink. This is consistent with our hypothesis regarding interfacial area for hydrate formation increasing with the water:CO_2 volumetric ratio, and the higher hydrate mole fraction needed for negative buoyancy at lower pressure (0.24 at 10.3×10^6 Pa vs. 0.22 at 13.1×10^6 Pa, Figure 1).

Using the concept of premixing seawater into a CO_2 stream, we produced a negatively buoyant composite material containing CO_2 hydrate and liquid CO_2 at conditions simulating intermediate ocean depths ($\sim$1,000–1,300 m). Such a development is significant because injecting CO_2 in a form that will sink through the water column will prolong its residence time in the ocean. This approach allows efficient CO_2 injections without a significant increase in operating cost when compared with releasing dense liquid CO_2 at depths greater than 3,000 m. Additionally, scaling up the proposed injector design can potentially produce large masses of CO_2/CO_2 hydrate composite with low surface-to-volume ratio, resulting in increased settling velocities and slower dissolution when compared to small hydrate particles such as those made in stirred tank reactors (Yamasaki et al., 2000). Increased settling velocity and potentially reduced dissolution rates will increase the dispersion of CO_2 in the ocean, improve sequestration efficiency, and reduce negative impacts on the marine environment.

Acknowledgments

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