

Formation and Spectroscopy of a CO₂ Hydrate Composite for Ocean Carbon Sequestration

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Abstract

Recent investigations into the formation of a negatively-buoyant, paste-like material consisting of liquid CO₂, water, and CO₂ (hydrate composite) is discussed in this presentation. Hydrate composite particles are formed using a co-flow injector/reactor in a 70-L pressurized vessel that simulates ocean depths up to 2.5 km. The density of the composite particles depends on the conversion rate of liquid CO₂ into hydrate, which is approximately 10% denser than the surrounding water. Based on the hypothesis that mass transfer at the water-liquid CO₂ interface in the reaction zone of the injector is the key promoting factor for hydrate formation, we have undertaken a study of jet breakup regimes and droplet size distributions of CO₂ in water and vice versa, as affected by fluid velocity and orifice size. Under high pressure and low temperature, the jet breakup pattern follows three distinct modes: Rayleigh, transitional, and spray modes. Droplet size distributions were determined at these modes, with the spray mode producing the smallest droplet sizes and the most uniform size distribution. *In-situ* Raman spectroscopic analysis of a hydrate composite was carried out, under hydrate formation conditions for direct determination of mixture composition. Shifts in frequency (wavenumbers, cm⁻¹) were observed indicating the various phases of CO₂, both in the hydrate composite and the surrounding water. The injector/reactor has also been tested at intermediate ocean depths at Monterey Bay, California, in collaboration with Peter Brewer and Ed Peltzer of the Monterey Bay Aquarium Research Institute (MBARI). Field experiments reproduced laboratory experimental results on the formation of hydrate composite particles.

Introduction

A form of CO₂ that sinks in seawater is attractive for an ocean carbon sequestration strategy because it has the least potential for CO₂ to re-enter the atmosphere. A coflow injection system has been developed at Oak Ridge National Laboratory (ORNL) in which water is sprayed at high velocity through a capillary tube into a stream of liquid CO₂ at high pressures (10-13 MPa) and low temperatures (4-6°C) equivalent to those of the ocean at a depth of 1000-1500 m (West et al., 2003; Lee et al., 2003; Tsouris et al, 2004). Under these conditions, a dense, solid-like composite consisting of liquid CO₂, water, and CO₂ hydrate forms. CO₂ hydrate is a solid clathrate compound in which water molecules form hydrogen bonded cages that trap CO₂ gas. It has been determined that if 20-30% of the injected CO₂ is converted into hydrate, the composite will sink in seawater at intermediate ocean depths (1000–1500 m). Formation

of hydrate is beneficial because it will increase the density of the particles and lower their dissolution rate, potentially decreasing the environmental impact of dissolved CO₂ near the injection point. Sinking composite has been studied extensively in the laboratory at ORNL, however, in field experiments with MBARI in 2002, composite formed in the ocean was found to be neutrally buoyant (Tsouris et al., 2004).

Recently, investigations have been conducted on the behavior of water jets in CO₂ and CO₂ jets in water to better optimize the injector design for scaling-up. *In situ* Raman spectroscopic studies have been conducted on the hydrate composite in the laboratory to help determine the chemical nature of the composite. Furthermore, ocean injections were recently conducted in Monterey Bay, Ca, with the focus on Raman spectroscopy and scaling up of the injector.

Equipment

Jet breakup experiments were conducted in the ORNL Seafloor Process Simulator (SPS), a 70-L pressure vessel that has been described previously in detail (Phelps et al., 2001). Briefly, the SPS is a pressure vessel capable of pressures of up to 20 MPa, kept in a coldroom under temperatures of -10 to 20 °C. The SPS has several 5 cm sapphire windows for viewing hydrate formation, jet destabilization, and other phenomena. Syringe pumps (ISCO, model 100 DM) were used for CO₂ and water injections with maximum flow rates of 25 mL/min.

Raman studies were conducted in a 450-mL pressure vessel (Parr Instrument Company) with two 1-cm quartz windows for laser light entry and collection. The spectroscopy setup consisted of the Raman probe, spectrometer, the laser monochromatic light source and charge-couple detection device, and the data acquisition device. Raman spectra were collected using the macro-stage of a Dilor XY 800 Raman microprobe (Jobin Yvon, Inc., Edison, NJ) with the 5145 Å excitation from an Innova 308 C Ar⁺ ion laser (Coherent, Inc., Santa Clara, CA) operating at 100mW output power. Power delivery at the sample was ~10mW and the spot size was ~100µm. Light was directed into the pressure vessel using a long working distance lens, and 180° backscattered light was collected and dispersed with the spectrometer. Raman spectra were detected with an Integrated Charge Couple Detector (ICCD) device and data acquired at the computer terminal.

Field injections were performed with the Monterey Bay Aquarium Research Institute. The injection system was installed on an arm of the remotely operated vehicle (ROV) *Ventana* on the research vessel *Point Lobos*. Injections were performed at 900-1600 m depth. A larger injector design was used for the ocean injections because pumps available on *Ventana* allowed for flow rates of up to 150 mL/min.

Jet Breakup Studies

Liquid-in-liquid jet instability has been recognized as an important process in CO₂ sequestration in the deep ocean (Teng et al. 1995; Tang et al. 2002; Lee et al. 2003). As a result of interface instability in direct injections of liquid CO₂ into seawater, CO₂ droplets form following jet breakup (Teng et al. 1995). The breakup pattern and the size distribution of the CO₂ droplets are important for assessing impacts on the marine environment because CO₂ dissolution, dispersion, and its subsequent acidification of

seawater are closely related to droplet sizes (Tang et al. 2002). Because smaller droplets have a higher surface-to-volume ratio, mass transfer and reaction rates can be significantly increased as droplet size decreases (Teng and Zhao 1999). This phenomenon has also been suggested as a means of increasing conversion of CO₂ to CO₂ hydrate in experiments in which water droplets were sprayed into a stream of liquid CO₂ in order to produce sinking hydrate-containing particles for direct ocean injection (Lee et al. 2003; West et al. 2003; Tsouris et al. 2004). Through experimental investigation, this portion of the study aimed at understanding the behavior of liquid-in-liquid jet breakup with systems of CO₂ in water and water in CO₂ under high-pressure and low-temperature conditions. Jet breakup regimes and droplet size distributions were determined under different flow conditions with varying orifice diameters.

Liquid-liquid jet breakup experiments showed distinct breakup regimes, Rayleigh, transitional, and spray, at increasing Reynolds number ($Re = \rho U d_0 / \mu_d$, where U is the velocity of the dispersed fluid, ρ is its density, μ_d is its viscosity, and d_0 is the orifice diameter) (Figure 1). The regimes are defined by boundaries in a plot of Ohnesorge number ($Z = \mu_d / (\rho \sigma d_0)^{0.5}$, where d is the average diameter of droplets and σ is the interfacial surface tension) versus the Reynolds number for the water and liquid CO₂ systems under high-pressure conditions. The systems appear to progress from Rayleigh mode to transitional mode at approximately $Z \approx 5.5 Re^{-1}$ and from transitional mode to spray mode at $Z \approx 18 Re^{-1}$ (Tang et al., 2002). The observed droplet sizes are consistently smaller in the transitional and spray modes than in the Rayleigh regime. The confined space in the coflow injector used for ORNL experiments (West et al. 2003; Lee et al. 2003; Tsouris et al., 2004), however, may promote droplet coalescence, yielding higher average size than that observed under spray mode. In comparing the two systems studied, the spray mode provided the smallest average droplet size, with the water-in-CO₂ drops being approximately 47% smaller than the CO₂-in-water spray droplets (Table 1). This result makes injection of water into liquid CO₂ an attractive option to increase hydrate formation. With knowledge of the dynamics of jet breakup of water in CO₂, an injector design strategy can be developed. For example, we can estimate the drop size for Rayleigh mode to select an injector size and then use the relationship $Z \approx 18 Re^{-1}$ to select the minimum flow rate necessary for the spray mode.

When all the different capillaries are compared, it appears to be more effective to perform the injections using the capillaries with smaller internal diameters because the spray breakup mode can be achieved at relatively low flow rates (Table 1). However, under spray mode, the drop size increase is small as capillary size doubled in the water-in-CO₂ experiments. This effect suggests that there may be advantages in using a larger-diameter injector, without a dramatic increase in droplet size, provided that the water is injected in the spray mode.

Additional knowledge of the dynamics of the CO₂-in-water system may also be beneficial to the development of injectors where CO₂ is injected directly into bulk ocean water (Holder et al., 1995; Brewer et al., 2002). In these injection schemes, minimizing the droplet size lowers the chances of CO₂ re-entering the atmosphere. The relationship $Z \approx 18 Re^{-1}$ for the transition to spray mode appears to be valid for this system as well over a wide range of injector diameters (Tang et al., 2002). Therefore, this relationship could be used to determine the minimum injection flow rate to achieve spray mode at any

injector diameter in direct ocean CO₂ injection as well. This further understanding of the hydrodynamics of CO₂-in-water and water-in-CO₂ may result in the development of a wide range of phase contact applications, particularly in the conversion of CO₂ to hydrate as a strategy for carbon sequestration in the ocean.

Raman Spectroscopic Studies of the Hydrate

In Situ Raman spectroscopic studies were conducted on the CO₂ hydrate composite to determine the phases of the CO₂ and water molecules in the composite. The Raman spectra for the composite as well as that of the surrounding water media are shown in Figures 2 and 3. Raman activity of CO₂ is due to the polarity and vibrational motions of its atoms and is characterized by the C—O-bend at ~1281 cm⁻¹ and C—O-stretch at ~1384 cm⁻¹. The surrounding water also gave two prominent peaks in the spectrum; the O—H-bend and O—H-stretch at ~1645 cm⁻¹ and ~3426 cm⁻¹ respectively. We also performed Raman spectroscopy on CO₂-saturated distilled water at the same temperature and pressure used for CO₂ hydrate formation to study the phase difference between CO₂ in solution and in hydrate. Carbon dioxide was detected at relatively the same frequency (wavenumbers) shifts as in hydrate but at much smaller relative intensities.

Field Experiments

Field experiments conducted in March 2004 on the research vessel *Point Lobos* in Monterey Bay, Ca, were focussed on laser Raman spectroscopy of the composite, on scaling up the coflow injector, and producing a rapidly sinking composite. Injections were conducted at intermediate depths using the remotely operated vehicle (ROV) *Ventana*. For the Raman experiments, the Deep-Ocean Raman *In Situ* Spectrometer (DORISS) system was employed. The DORISS system allows for rapid determination of the composition and CO₂ phase of the composite directly after formation at depth. Composite was produced at 900–1600 meters using the coflow injector and collected in a basket where it was excited by the Raman laser. On the ship, the scans were collected and are currently being analyzed at MBARI.

Scale-up sinking composite experiments were conducted using a larger injector than the one used in the laboratory. It was expected that the larger injector would allow for higher flow rates of the two fluids, which would result in better mixing and more hydrate formation. The resulting particles would sink rapidly, due to more hydrate, and be larger in diameter to slow the CO₂ dissolution. The larger coflow injector was placed in a plexiglass box that was open at the top and bottom. After injection, the box allowed the particles to float or sink freely in the water column, and the ROV moved vertically to follow the particles. A 50% larger water capillary was used and flow rates of CO₂ and water were roughly six times higher than in the laboratory injections. The resulting composite produced sank at a rate of about 3 meters per minute, suggesting 30-40% of the CO₂ was converted to hydrate. One particle was followed by the ROV for over 40 meters as it sank.

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Table 1. Measured average droplet size (d) under different jet breakup regimes, compared with the theoretically calculated droplet size using Rayleigh’s maximum stability theory (Teng et al. 1995)

Capillary d_0 (μm)	average measured d (μm)		
	Spray	Transitional	Rayleigh
	CO₂-in-water injections		
127	268	352	395
178	276	298	483
254	443	612	775
381	NA	617	1201
508	NA	NA	1781
	Water-in-CO₂ injections		
127	127	327	344
254	162	365	578
508	NA	NA	1035
127 (Lee et al. 2003)	267*		

*injection was performed at 4 °C, resulting in higher viscosities and a lower interfacial tension. All other injections were performed at 10–12 °C.

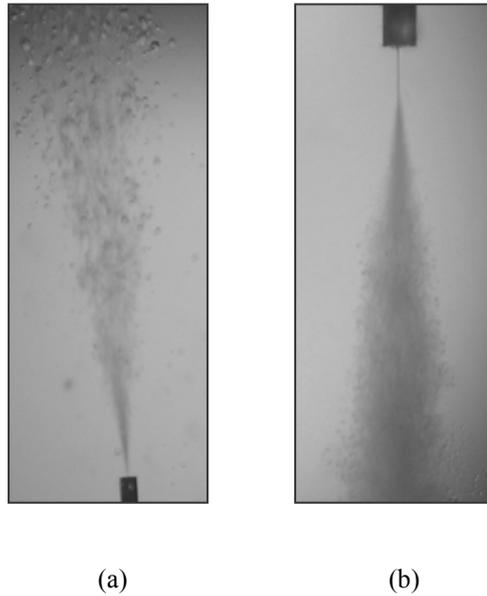


FIGURE 1. (a) Visualization of “spray” jet breakup regime in CO₂ injection experiments. Internal diameter of capillary = 178 μm , external diameter of capillary = 794 μm , system temperature = 11.0 °C, system pressure = 845 psi. **(b)** Visualization of “spray jet breakup regimes in H₂O injection experiments. Internal diameter of capillary = 127 μm , external diameter of capillary = 1587 μm , system temperature = 11.5 °C, system pressure = 847 psi.

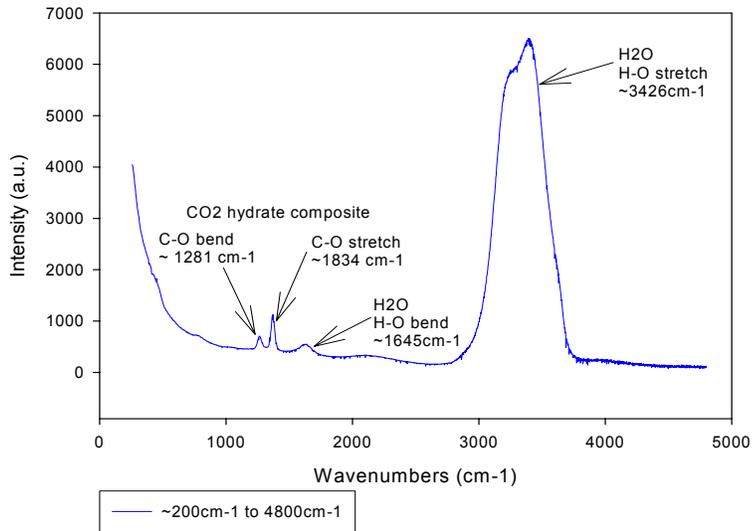


FIGURE 2 Whole Raman spectrum showing all the CO₂ hydrate and surrounding water peaks.

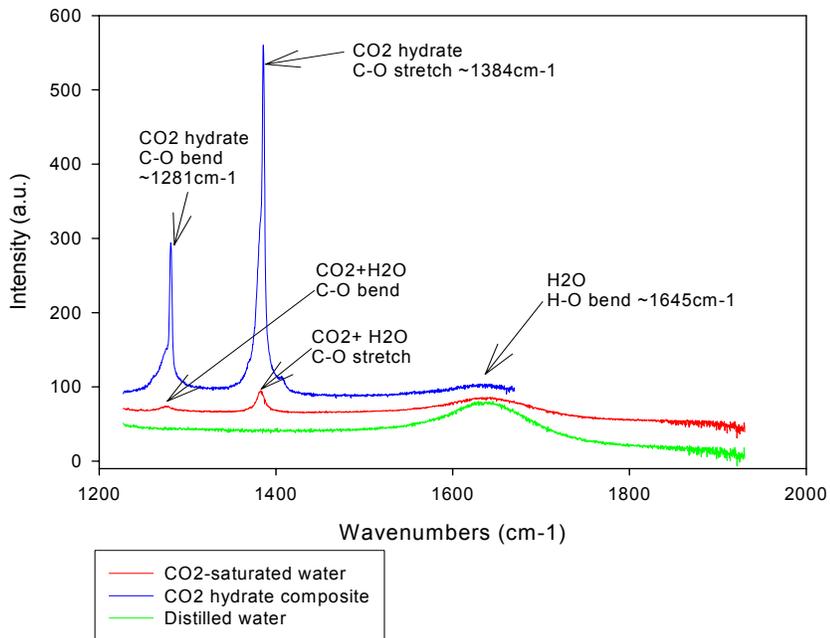


FIGURE 3 Raman spectrum of CO₂ hydrate, CO₂-saturated distilled water and ordinary distilled water.