CONFERENCE PROCEEDINGS

Formation and Dissolution of CO_2 Hydrate Composite Particles in a High-Pressure Water Tunnel Facility

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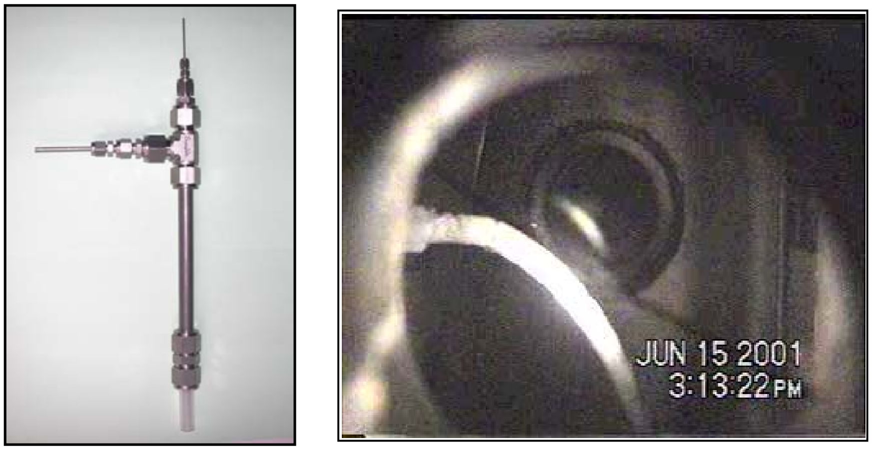
Abstract

Sinking CO_2 hydrate composite particles were produced by a coflow injector with CO_2 and artificial seawater in the NETL high-pressure water tunnel facility (HWTF). Injections were performed at pressures equivalent to 1200-1800 m depth and temperatures of approximately 3-5 °C. Immediately after injection, the cylindrical particles were observed to break off of the injector tip and aggregate into sinking clumps. The water flow in the tunnel was then adjusted to suspend the particles, and the images of the particles were continuously recorded for later analysis. After several minutes, the clumps were observed to break up into discrete particles, and selected particles were studied until they became too unstable to follow. In general, particles sank more rapidly just after injection and then sank more slowly as they shrank in size. For example, one particle produced at 1500 m and 5.1°C was filmed for over 6 minutes and was observed to sink initially at a rate of 42.6 mm/sec but reduced to 8.9 mm/sec at the end of the experiment. This particle was also observed to dissolve irregularly along its long axis.



A **B**

Figure 1. ORNL coflow hydrate reactor; **A.** Prototype of the reactor for laboratory Tests, **B.** Sinking CO_2 hydrate composite produced by the reactor in the ORNL Seafloor Process Simulator pressure vessel.

Introduction

Production of a sinking form of CO_2 in the ocean is attractive for carbon sequestration because the potential for the CO_2 to re-enter the atmosphere decreases with depth and the costs may be less if shallower injection depths can be used. CO_2 hydrate injection experiments were conducted by carbon sequestration researchers from ORNL and NETL on the formation of a sinking CO_2 hydrate composite. The CO_2 injection system has been developed at ORNL over the last several years and has been demonstrated to produce a sinking CO_2 hydrate composite both in the laboratory (West et al., 2003; Lee et al., 2003) and in ocean injections (Tsouris et al., 2004) (Figure 1). The composite is created by a coflow injection system where a jet of water is sprayed through a capillary tube into a stream of liquid CO_2 at high velocities at intermediate ocean pressures (1000-2000 m depth) and temperatures. Under these conditions, a dense, solid-like composite consisting of liquid CO_2, seawater, and CO_2 hydrate forms. CO_2 hydrate is a solid clathrate compound in which water molecules hydrogen bond to form cages that trap individual CO_2 molecules. It has been determined that if 20-30% of the injected CO_2 is converted to hydrate, the composite will sink in seawater at intermediate ocean depths. Formation of a hydrate is beneficial because it will increase the density of the particles and lower their dissolution rate, thus potentially decreasing the environmental impact of dissolved CO_2 near the injection point.

The injection system has been studied extensively in static (non-flowing) high-pressure vessels at ORNL. One of the challenges of laboratory pressure vessel experiments is the need to measure the sinking and dissolution rates of particles after injection. The High-Pressure Water Tunnel Facility (HWTF) at NETL (Figure 2) provides a system where sinking composite particles can be injected at high pressure and their fate may be tracked over time using a controlled countercurrent flow of seawater to keep them stationary in a windowed viewing section (Warzinski et al., 2000; Haljasmaa et al., 2005).

Figure 2. NETL High-Pressure Water Tunnel Facility

Methods

The hydrate reactor used in the experiments reported here had a water capillary i.d. of 254 µm and an outer tube i.d. of 6 mm. The experimental were performed using CO_2 (99.5% purity) and a 35 salinity artificial seawater that was prepared following the recipe given by Millero (1996). A series of 55 injections were conducted at various flow rates in the HWTF at pressures equivalent to ocean depths of 1200, 1500, and 1800 meters at temperatures of approximately 3-5 °C. At each depth, sinking particles of varying densities were produced by varying the CO_2 and water injection flow rates. Immediately after injection, the cylindrical particles were observed to break off of the injector tip and aggregate into sinking clumps. The seawater flow in the tunnel was then adjusted to suspend the particles, and images of the particles were continuously recorded for analysis. Particle diameters were measured at 3-4 points along their length when particles were oriented parallel to the HWFT window over time to determine a particle dissolution rate (in µm/sec).

Results

Sinking particles were successfully produced at 1200-1800 meters depth at a variety of CO_2 and seawater flow rates. Table 1 contains the results of injections where particle dissolution rates could be calculated from video images of the particles. The numbers in the first column are also used to designate the particles. In all of the experiments in Table 1, sinking particles were produced that were stabilized in the HWTF viewing window by a countercurrent flow of seawater. Figure 3 depicts several video images that represent the dissolution of Particle 1500a. This particle was originally part of a larger cluster of particles (first image in Figure 3) that broke apart. Cluster formation was common during injection of the particles. Some of the clusters broke apart as the seawater flow was adjusted for stabilization. However, some clusters were observed to remain intact for several minutes while stabilized. For example, Particle 1200c (Table 1) was observed to remain attached to a cluster of 5-6 particles throughout the 357 sec of the experiment.

Nearly all of the particles were observed to sink more slowly as the experiment progressed. For example, Particle 1500a was stabilized by a countercurrent flow of 42.6 mm/sec at the start of the experiment, but slowed to 8.9 mm/sec when the last particle measurement was taken. Figure 4 shows the countercurrent flow velocity and diameter for this particle for the duration of time that the single particle was filmed. The particle was observed to shrink irregularly in diameter as it sank (Figure 3). However, the average particle dissolution rate appeared to be linear throughout the experiment.

Table 1. Velocity and Dissolution Rates for Particles Stabilized by Counter Flow

Pressure (depth, m)	Avg. Temp (°C)	CO_2 flow (mL/mn)	H_2O flow (mL/min)	Dissoln. Rate (µm/sec)	Elapsed time (min:sec)	Init.Velocity (mm/sec)	Final Velocity (mm/sec)	Avg. Velocity (mm/sec)
1800a	4.2	10	40	10	2:43	20	4.4	12.7
1800b	4.2	10	40	5	4:04	19.2	7.5	13.9
1500a	5.1	10	40	10	5:43	42.6	8.9	29.9
1500b	3.8	20	40	5	12:57	49.3	31.6	38.3
1200a	2.7	15	40	10	7:46	23.7	6.9	19.1
1200b	3.1	15	40	8	3:39	27.3	12.8	14.3
1200c	3.1	10	40	8	5:57	45.5	55.4	56.8*
1200d	3.0	10	25	10	1:43	38	6	15.8
1200e	3.0	10	25	8	4:04	35.5	11.2	20.6
1200f	3.0	10	25	5	6:45	49.1	5.3	26.3

* This particle was part of a large 5-6 particle cluster

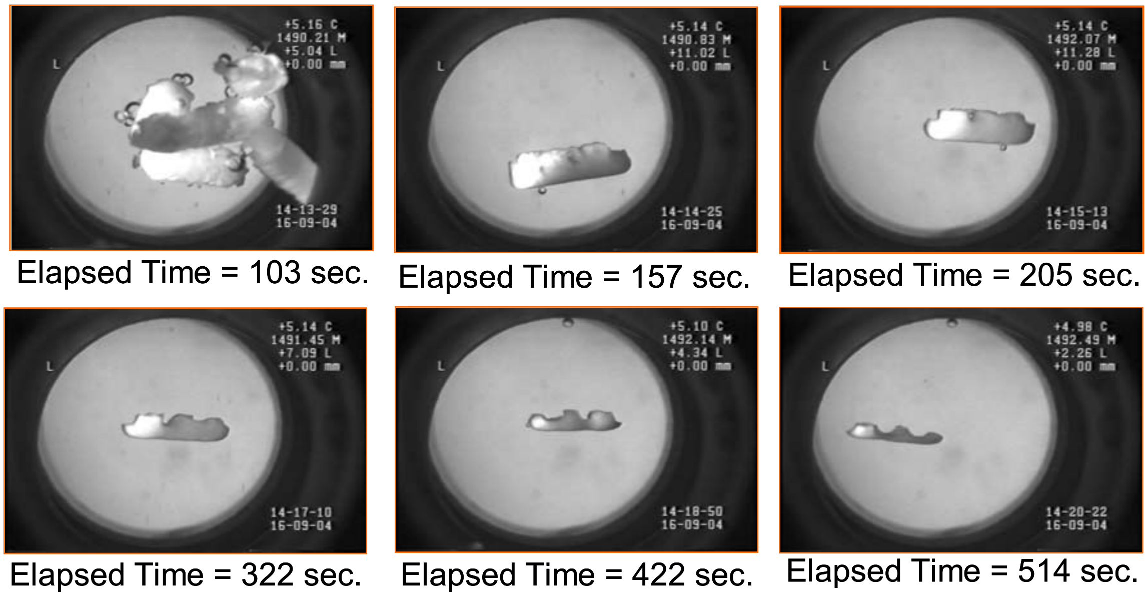


Figure 3. A time-series of images of a sinking CO_2 hydrate composite particle (1500a in Table 1) suspended by countercurrent flow of seawater in the HWTF.

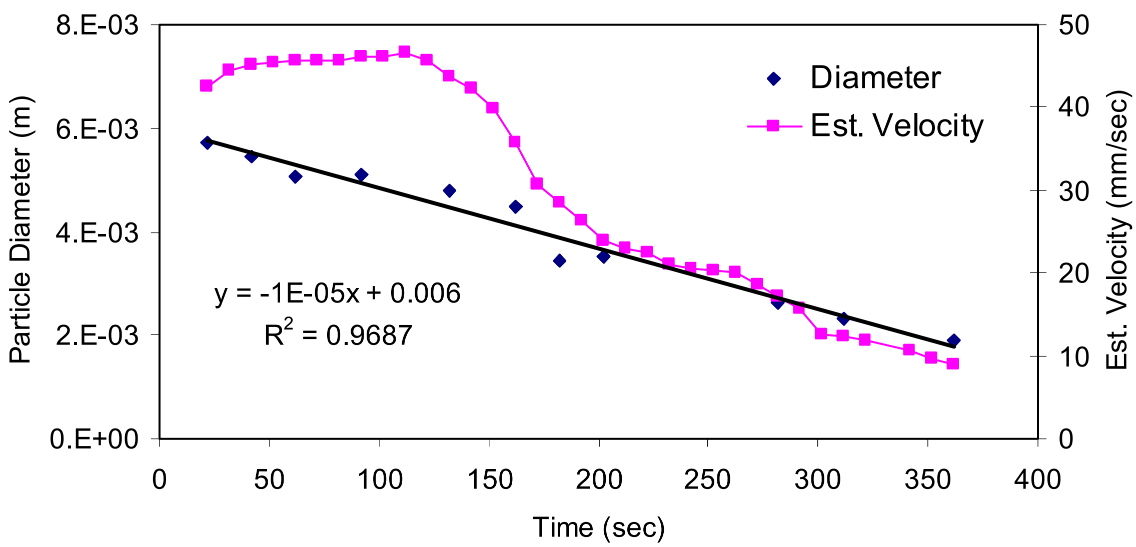


Figure 4. Diameter and velocity after injection of hydrate composite particle 1500a in the HWTF.

Discussion

Sinking CO_2 hydrate composite particles were successfully produced at depths of 1200-1800m in the NETL High-Pressure Water Tunnel Facility. Size measurement analysis of selected particles that were stabilized in the tunnel window was performed to determine their dissolution rates. Particles were observed to shrink at rates of 5-10 μm/sec in the HWTF injections. These rates compare well to those observed in ocean injections with the hydrate reactor in Monterey Bay, Ca where rates of 4.3-10.3 µm/sec were observed (Tsouris et al., 2004; Riestenberg et al., *submitted*). However, the sinking velocities of 20-49.3 mm/sec observed for the particles produced in the HWTF experiments were lower than those observed in the recent ocean injections of 50-52 mm/sec (Riestenberg et al., *submitted*). Possible explanations for this are that a larger injector was used in the ocean injections (i.d. = 9 mm) than the one used in the HWTF tests (i.d. = 6mm). In addition, higher water and overall flow rates of 140 ml/min and 165 ml/min were used in the ocean compared to those used in the HWTF (water flow = 25-40 ml/min, overall flow rate = 35-60 ml/min). Higher flow rates may result in greater mixing of the two fluids, and the increased diameter of the injector may have decreased the wall effects on the water jet breakup, both increasing the conversion of CO_2 to hydrate. Future tests of the hydrate reactor in the HWTF will focus on scale-up of the injector to one capable of more realistic injection flow rates. Individual particles were observed to slow dramatically as they sank and dissolved (Figure 1). This result suggests that the dissolution of CO_2 hydrate in the composite particles is occurring at a higher rate than hydrate formation.

Conclusion

CO_2 hydrate particle injections in the NETL High Pressure Water Tunnel using the ORNL coflow hydrate reactor demonstrated that solid, sinking CO_2 particles can be produced at a variety of ocean depths and flow rates. Particles were observed to dissolve at 5-10 µm/sec, which compares well with field injection experiments in Monterey Bay, Ca.

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