

Laboratory Investigations in Support of Carbon Dioxide-Limestone Sequestration in the Ocean

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ABSTRACT

This semi-annual progress reports includes further findings on CO₂-in-Water emulsions stabilized by fine particles of limestone (CaCO₃). Specifically, here we report on the tests performed in the DOE National Energy Technology Laboratory High Pressure Water Tunnel Facility (HPWTF) using a Kenics-type static mixer for the formation of a CO₂-H₂O emulsion stabilized by fine particles of CaCO₃.

The tested static mixer has an ID of 0.5 cm, length 23.5 cm, number of baffles 27. Under pressure, a slurry of CaCO₃ particles (mean particle size 6 μm) in reverse osmosis (RO) water and liquid CO₂ were co-injected into the mixer. From the mixer, the resulting emulsion flowed into the HPWTF, which was filled with RO water kept at 6.8 MPa pressure and 4, 8 or 12 °C. The emulsion plume was photographed by three video cameras through spy windows mounted on the wall of the HPWTF.

The mixer produced an emulsion consisting of tiny CO₂ droplets sheathed with a layer of CaCO₃ particles dispersed in water. The sheathed droplets are called globules. The globules' diameter was measured to be in the 300 – 500 μm range. The globules were sinking in the HPWTF, indicating that they are heavier than the ambient water.

The tests in the HPWTF confirmed that the Kenics-type static mixer is an efficient device for forming a CO₂-H₂O emulsion stabilized by fine particles of CaCO₃. The static mixer may prove to be a practical device for sequestering large quantities of CO₂ in the deep ocean in the form of a CO₂-H₂O-CaCO₃ emulsion. The static mixer can be mounted at the end of pipelines feeding the mixer. The static mixer has no moving parts. The pressure drop across the mixer that is necessary to sustain good mixing is created by the hydrostatic pressure of liquid CO₂ and the slurry of CaCO₃ in the pipes that feed the mixer. The tests in the HPWTF demonstrated that the emulsion plume is heavier than ambient seawater, hence the plume will sink to greater depth from the release point. Preliminary modeling indicates that an emulsion plume released at 500 m depth (the minimum depth required to prevent liquid CO₂ flashing into vapor) may sink hundreds of meters before the plume comes to rest in the density stratified ocean water. Furthermore, tests in our laboratory showed that the emulsion is slightly alkaline, not acidic, because of the excess of CaCO₃ particles present in the plume. Thus, the release of the CO₂-H₂O-CaCO₃ emulsion in the deep ocean is not likely to acidify the seawater around the release point. The possible acidification of seawater is the major environmental hazard if pure liquid CO₂ were released in the deep ocean.

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Figure 5. Hydrate structure formation on globules at 6.8 MPa, 8 °C. Ambient water containing $\sim 2 \text{ wt}\% \text{ CO}_2$. Side and upper cameras.

EXPERIMENTAL

(a) Materials

Carbon Dioxide. Coleman instrument grade 99.99% CO₂ (Airgas) was supplied from a siphon cylinder. The liquefied phase of CO₂ was co-injected into the Kenics-type static mixer.

Water. Water purified by reverse osmosis (RO) and activated carbon filtration or an artificial, 35-salinity seawater prepared following the recipe given by Millero (1996) were used. Water was co-injected into the static mixer.

CaCO₃. Sigma Chemicals C-4830 reagent grade CaCO₃ was used. A Scanning Electron Microscope (SEM) image of the particles is given in Figure 1. The particles appear to be mostly rhombohedral calcite crystals, with most particles in the 5-10 µm size range. The particles were mixed with RO water or artificial seawater in a beaker in a proportion of ~ 0.5 g/mL. The concentrated paste was co-injected together with liquid CO₂ and RO water or artificial seawater into the static mixer.

(b) Apparatus

The NETL High Pressure Water Tunnel Facility (HPWTF) was used for the experiments. The HPWTF is described by Tsouris et al. (2004). The static mixer was adapted to the HPWTF as shown in Figure 2. Total liquid volume of the HPWTF comprises approximately 16.5 L. The static mixer is a Kenics type (Koflo) of 0.5 cm ID and with 27 mixing elements. The HPWTF was evacuated, filled with reverse osmosis or artificial seawater, and brought to operating pressure (6.8 MPa) and temperature (4, 8 or 12 °C). The flow rate of water to the static mixer was controlled by varying the speed and hence dynamic pressure of the centrifugal pump and measured by an ultrasonic flow meter (Controlotron 1010FT). Flow rates are controllable between 0 and 1.9 L/min. A paste of 0.5 g/mL CaCO₃ was loaded into a high pressure syringe pump (Isco 500D) with a maximum delivery rate of 170 mL/min. Liquid CO₂ of 99.99% purity was loaded into a high pressure syringe pump (Isco 260D) with a maximum delivery rate of 100 mL/min. The observation section of the HPWTF is instrumented with 3 cameras, one digital on the upper oblong window, and two analog on the upper and lower bull's eye windows, which recorded the appearance of the emulsion plume ensuing from the static mixer tube. The static mixer device was operated in short intervals at varying proportions and flow rates. The outflow from the static mixer was stopped to observe the sinking or rising behavior of the emulsion plume in the HPWTF.

RESULTS AND DISCUSSION

Dispersion of liquid CO₂ in water

Pure liquid CO₂ was co-injected with RO water or seawater into the static mixer, but without CaCO₃ paste co-injection, followed by injection of the effluent into the HPWTF. A plume of liquid CO₂ droplets dispersed in water was observed. The CO₂ delivery rate was held constant at the maximum rate, 100 mL/min. The water delivery rate was varied from 0.5 to 1.9 L/min. The droplet size varies depending on flow conditions, but typically is in the 500 – 1000 µm range (see Figure 3).

Emulsions of liquid CO₂ stabilized by CaCO₃

CaCO₃ paste was co-injected with CO₂ and water in the static mixer, followed by injection of the effluent into the HPWTF. CO₂ was delivered at the maximum rate, 100 mL/min. Paste feed rate (~0.5 g/mL CaCO₃) was varied from 5 to 15 mL/min and the rate 10 mL/min was selected to provide acceptable yield and effluent visibility under experimental conditions. Water was delivered to the static mixer at the rate of 1 L/min for most determinations. The ambient water was at a temperature of 12 °C. An emulsion plume was observed, consisting of droplets of liquid CO₂ coated with a sheath of CaCO₃ particles dispersed in water. The coated droplets are called *globules*, and the emulsion is called a *globulsion*. Typical globule diameter is in the range 300 – 500 µm (see Figure 4). The globules are heavier than ambient water, therefore they sink toward the bottom of the HPWTF. From previous experiments conducted in 2004 in the HPWTF, we determined an average density of the globules of 1210 kg m⁻³, and a settling velocity of the globules of 2.2×10^{-3} m s⁻¹ (Golomb et al., 2004).

When the emulsion is injected into the HPWTF with ambient water saturated with 2% by weight CO₂, at a pressure of 6.8 MPa and temperature of 4 °C, the globules clumped together due to the formation of a hydrate film at the surface of the globules (Figure 5). At low levels of CO₂ saturation, no hydrate film was observed, even though the ambient temperature and pressure was in the hydrate formation regime.

CONCLUSIONS

A Kenics-type static mixer has been constructed, tested and evaluated in the NETL High Pressure Water Tunnel Facility (HPWTF). The static mixer produces an emulsion of CO₂-in-water stabilized by CaCO₃ particles. Such an emulsion is heavier than seawater, hence when released in the deep ocean, the emulsion would sink to greater depths on account of its negative buoyancy. The static mixer would be ideally suited for deep ocean releases of the emulsion because it has no moving parts, and the pressure gradient across the mixer can be maintained by the hydrostatic pressure of the inflows: liquid CO₂ and a slurry of CaCO₃ in water.

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- Tsouris, C., Riestenberg, D., Brewer, P., Peltzer, E., Waltz, P., Chow, A., Adams, E., Warzinski, R., Field studies of CO₂/water co-flow injection for ocean carbon sequestration, Paper presented at the 3rd Annual Conference on Carbon Capture and Sequestration, Alexandria, VA, 2004.

ILLUSTRATIONS

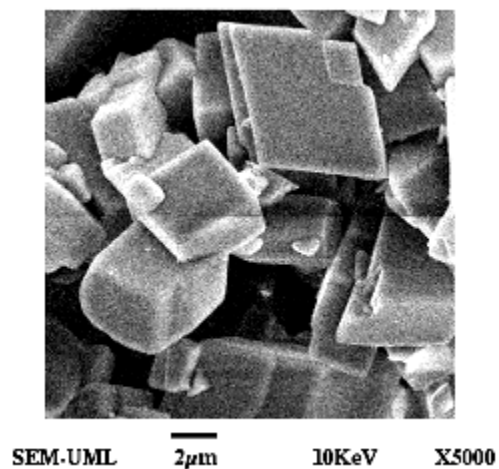


Figure 1. Scanning Electron Micrograph of Sigma Chemicals C-4830 reagent grade CaCO_3 . Mean diameter of particles $\sim 6 \mu\text{m}$.

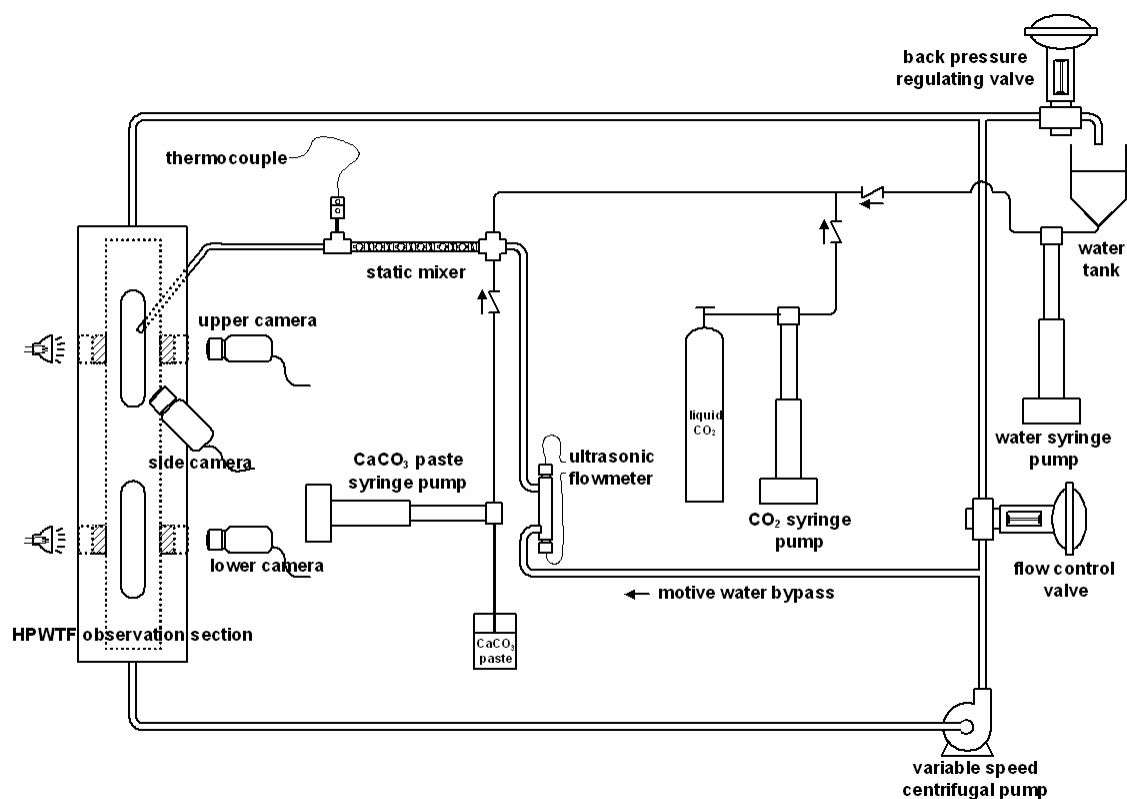


Figure 2. High Pressure Water Tunnel Facility (HPWTF) with adapted Kenics-type static mixer and auxiliary equipment .

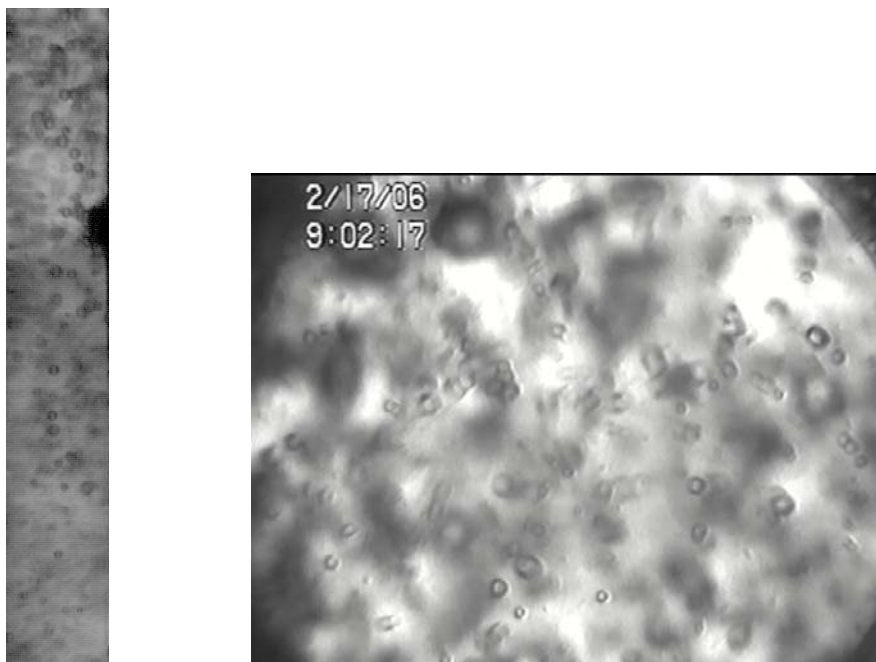


Figure 3. Liquid CO₂ droplets dispersed in water without CaCO₃ sheath. Side and upper cameras.

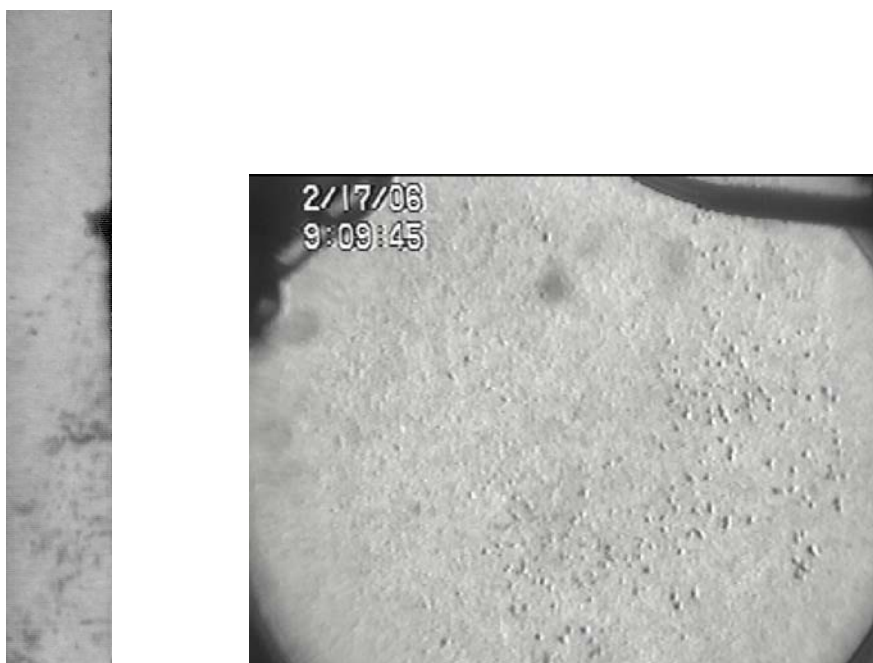


Figure 4. Globules of CaCO₃ sheathed CO₂ droplets in HPWTF. Globule diameter in the 300 – 500 μm range. Globules are heavier than ambient water, sinking downward. Side and upper cameras.

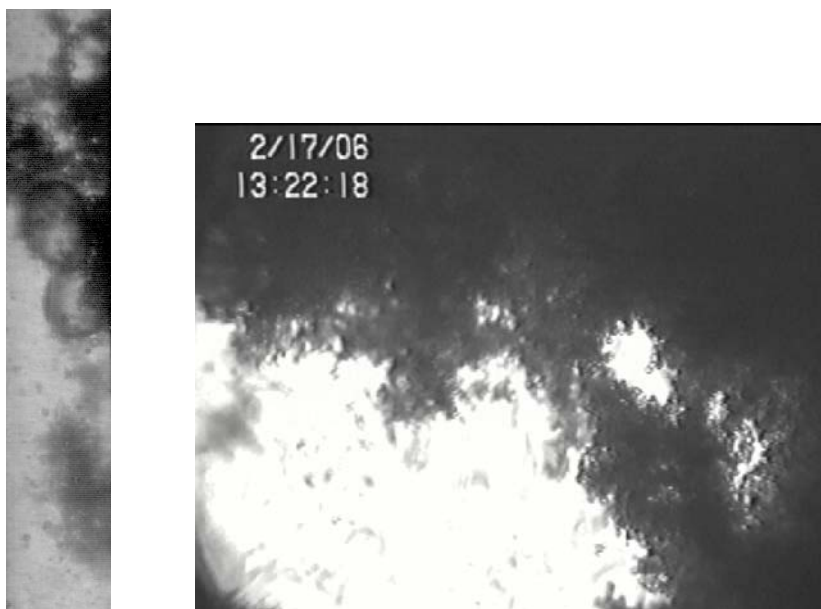


Figure 5. Hydrate structure formation on globules at 6.8 MPa and 4 °C. Ambient water containing ~2 wt% CO₂. Side and upper cameras.

PUBLICATIONS

D. Golomb, E. Barry, D. Ryan, P. Swett, and H. Duan, Macroemulsions of Liquid and Supercritical CO₂-in-Water and Water-in-Liquid CO₂ Stabilized by Fine Particles, *Ind. Eng. Chem. Res.*; 2006; 45(8), pp 2728 – 2733.

PLANS FOR THE NEXT SEMI-ANNUAL PERIOD

- Testing and evaluation of a microfluidizer for the production of micro-emulsions of CO₂-in-water and water-in-CO₂ using very fine particles as stabilizers.
- Formation of acid gas (H₂S/CO₂)-in-water emulsions using fine particles as stabilizers for geologic sequestration.