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 CO_2-in-Water (C/W) emulsions stabilized by fine particles. In previous semi-annual reports we described the formation of stable C/W emulsions using pulverized limestone ($CaCO_3$), flyash, beach sand, shale and lizardite, a rock rich in magnesium silicate. For the creation of these emulsions we used a High-Pressure Batch Reactor (HPBR) equipped with view windows for illumination and video camera recording.

For deep ocean sequestration, a C/W emulsion using pulverized limestone may be the most suitable. (a) Limestone (mainly $CaCO_3$) is cheap and plentiful; (b) limestone is innocuous for marine organisms (in fact, it is the natural ingredient of shells and corals; (c) it buffers the carbonic acid that forms when CO_2 dissolves in water. For large-scale sequestration of a $CO_2/H_2O/CaCO_3$ emulsion a device is needed that mixes the ingredients, liquid carbon dioxide, seawater, and a slurry of pulverized limestone in seawater continuously, rather than incrementally as in a batch reactor. A practical mixing device is a Kenics-type static mixer. The static mixer has no moving parts, and the shear force for mixing is provided by the hydrostatic pressure of liquid CO_2 and $CaCO_3$ slurry in the delivery pipes from the shore to the disposal depth.

This semi-annual progress report is dedicated to the description of the static mixer and the results that have been obtained using a bench-scale static mixer for the continuous formation of a $CO_2/H_2O/CaCO_3$ emulsion.

The static mixer has an ID of 0.63 cm, length 23.5 cm, number of baffles 27. Under pressure, a slurry of $CaCO_3$ in artificial seawater (3.5% by weight NaCl) and liquid CO_2 are co-injected into the mixer. From the mixer, the resulting emulsion flows into a Jerguson cell with two oblong windows on opposite sides, then it is vented. A fully ported ball valve inserted after the Jerguson cell allows the emulsion to be stopped in the cell. In such a manner the emulsion can be photographed while it is flowing through the cell, or after it has stagnated in the cell. A slurry of 10 g/L $CaCO_3$ (Sigma Chemicals C-4830 reagent grade) in artificial seawater, co-injected into the static mixer at a rate of 1.5 L/min with liquid CO_2 at a rate of 150 mL/min, at temperature 5-10˚C, pressure 10 MPa, produced an emulsion with mean globule diameter in the 70 – 100 μm range. In a HPBR, using the same materials, proportions, temperature and pressure, mixed with a magnetic stir bar at 1300 rpm, the mean globule diameter is in the 200 – 300 μm range. Evidently, the static mixer produces an emulsion with smaller globule diameters and narrower distribution of globule diameters than a batch reactor.

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EXPERIMENTAL

(a) Materials

Carbon Dioxide. Industrial grade liquid carbon dioxide was supplied from 50 lb syphon cylinders (Northeast Airgas).

Water. For make-up of a $CaCO_3$ slurry**,** we used either de-ionized and filtered water from a laboratory still (Millipore Milli-RO), or artificial seawater (3.5% by weight reagent grade NaCl) in de-ionized water.

$CaCO_3$. Sigma Chemicals C-4830 reagent grade $CaCO_3$ 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.

(b) Apparatus

The laboratory set-up with the static mixer is depicted in Figure 2. The heart of the apparatus is a Kenics-type static mixer (Koflow ¼-27), 0.63 cm internal diameter, 23.5 cm length, 27 baffles. A $CaCO_3$/water slurry is prepared in a reservoir. Calcium carbonate particle sedimentation in the slurry is prevented by using constant recirculation with a pump. The slurry is pumped (Wanner Engineering D04-S) to 10 MPa through a double pipe heat exchanger, where it is cooled to 5-10 °C, into a mixing tee upstream of the static mixer. Compressed liquid CO_2 from a syringe pump (Isco 500D) at 10 MPa is co-injected into the static mixer. The two fluids are thoroughly mixed in the static mixer, and then flow into the view cell (Jerguson T32-11) in a downward flow. A quarter turn ball valve downstream of the cell may be closed to stagnate the emulsion for observation. The outlet of the cell is throttled through a back-pressure regulator (Tescom 54-2162) and the gas is vented. A 35 W halogen lamp with a parabolic reflector is used for illumination through one of the cell windows. A mat reflector is used on the opposite window for reflecting the illumination. Photographs are taken through the same cell window where the illuminating lamp is mounted. A fast frame video camera is used (Olympus C-730UZ) either mounted directly on the window of the cell, or looking through a 40x stereomicroscope (Leitz).

RESULTS

(a) Dispersion of liquid CO_2 in water

The static mixer was used to disperse liquid CO_2 in deionized water without any addition of $CaCO_3$. Depending on relative flow rates of water and CO_2, different CO_2 droplet size dispersed in water can be obtained. In the left frame of Figure 3, the flow rates were 1 L/min water and 0.17 L/min liquid CO_2, both at 10 MPa, with temperature in the static mixer 15 ˚C. The resulting CO_2 droplet diameters are in the 300 – 700 μm range. In the right frame of Figure 3, the flow rates were 2 L/min water and 0.17 L/min liquid CO_2. With the higher flow rate of water, the resulting CO_2 droplet diameters are smaller than with the lower flow rate. Most globules are less than 100 μm in diameter. Similar results have been obtained by Tajima et al. (2005), also using a static mixer for dispersing liquid CO_2 in water.

The static mixer can also be used to produce CO_2 hydrates. The static mixer was cooled to 5 – 10 ˚C, and the liquids injected at 10 MPa. Figure 4 shows the result. The dispersed liquid CO_2 droplets appear to be coated with a thin film of hydrate, because they are less transparent than the droplets obtained at higher temperature (Figure 3). However, more runs need to be performed with different flow rates and illumination in order to confirm the existence of a hydrate film. Hydrate formation was observed when a co-flow injector was used in deep ocean releases of liquid CO_2 in Monterey Bay, CA (Tsouris et al., 2004).

(b) Emulsion during flow conditions

The slurry contained 10 g/L Sigma Chemicals C-4830 $CaCO_3$ in "seawater."(3.5 wt% NaCl) The flow rates were 1.5 L/min slurry and 0.15 L/min liquid CO_2, both at 10 MPa, temperature in the static mixer 5-10 ˚C. A fast frame video picture taken whilst the emulsion is flowing through the Jerguson cell is shown in Figure 5. Because the white background of excess $CaCO_3$ particles and low resolution, no distinct globules are visible. However, no phase separation of liquid CO_2 is noticeable, indicating that a stable emulsion was formed.

(c) Emulsion at stagnating conditions

The slurry contained 10 g/L Sigma Chemicals C-4830 $CaCO_3$ in "seawater." The flow rates were 1.5 L/min slurry and 0.15 L/min liquid CO_2, both at 10 MPa, temperature in the static mixer 5-10 ˚C. The fully ported ball valve (see Figure 2) was closed, bringing the emulsion to rest in the Jerguson cell. A video picture of the emulsion is shown in Figure 6. The $CaCO_3$ particle-sheathed globules are clearly visible. The diameter of the globules is in the 70 – 100 μm range, which is much smaller than obtained in a High Pressure Batch Reactor, where the globule diameter was in the 200 – 300 μm range, using the same ingredients under similar pressure and temperature conditions, but with the ingredients stirred with a magnetic stir bar at 1300 rpm (Golomb et al., 2005).

DISCUSSION

In this reporting period a major milestone was reached, that of constructing, testing and evaluating a Kenics-type static mixer for the formation of an emulsion of liquid carbon dioxide-in-water using fine particulate calcium carbonate as an emulsion stabilizer. While the static mixer is a relatively simple device for mixing two (or more) miscible or immiscible fluids, the mixing of liquid CO_2 and a heterogeneous slurry of $CaCO_3$ in water posed formidable challenges. First of all, liquid CO_2 must be kept under high pressure ($\geq$ 10 MPa). Second, the slurry must also be injected into the static mixer at the same pressure as liquid CO_2, otherwise there would be a backflow. Third, the slurry must be kept free of sedimentation before injection. Fourth, the inflows and the static mixer must be kept at a constant temperature for characterizing the emulsion at a specific temperature. The temperature may be adjusted for characterizing the emulsion at sub- and super-critical conditions of CO_2. Also, it is desirable to maintain a temperature regime ($\leq$ 10˚C) in order to investigate the possibility of pure CO_2 hydrate or mixed hydrate/$CaCO_3$ particle formation.

Another great challenge that had to be overcome is the characterization of the outflow emulsion by optical measurements. The outflow from the static mixer passes a Jerguson cell with two oblong windows on opposite sides for illumination and observation by the naked eye, or by video camera. However, because of the rapid movement of the emulsion in the cell, and because of the white background of excess $CaCO_3$ particles in the emulsion, photography often resulted in blurred pictures without seeing distinct features of particle-sheathed globules (Figure 5). Therefore, we had to install at the exit of the Jerguson cell a fully ported ball valve, which stalled the emulsion flow in the cell for several seconds, and allowed picture taking of the stagnated emulsion (Figure 6).

Using these procedures, we determined the following important parameters:

- The static mixer can produce a dispersion of tiny liquid CO_2 droplets in water with a narrow distribution of droplet diameters in the 70 − 100 μm range.
- The static mixer may produce CO_2 hydrate when operated at temperatures below 10 ˚C and pressures above 10 MPa.
- Using a volume flow ratio of $CaCO_3$ slurry to liquid CO_2 of 10 : 1 with Sigma Chemicals reagent grade $CaCO_3$ particles (mean diameter 5-10 μm) at a concentration of 10 g/L, particle-sheathed globules are formed in the 70 – 100 μm range. These globules are smaller than those formed in a high pressure batch reactor with a magnetic stir bar rotating at 1300 rpm with similar proportions of the ingredients, viz. 200 – 300 μm.

CONCLUSIONS

A Kenics-type static mixer has been constructed, tested and evaluated in the laboratory. The static mixer can be used for the dispersion of tiny liquid CO_2 droplets in water, for hydrate particle formation, and for formation of an emulsion of liquid (or supercritical) CO_2-in-water stabilized by fine particles of $CaCO_3$. Such an emulsion is heavier than seawater, hence when released at depth, 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 CO_2 and a slurry of $CaCO_3$ in water.

REFERENCES

D. Golomb, E. Barry, D. Ryan, P. Swett, H. Duan, "Macro-Emulsions of Liquid and Supercritical CO_2-in-Water and Water-in-Liquid CO_2 Stabilized by Fine Particles," Submitted to *Industrial and Engineering Chemical Research*, September 2005.

Tajima, H., Yamasaki, A., Kiyono, F., Process design of a new injection method of liquid CO_2 at the intermediate depths in the ocean using a static mixer, *Fuel Processing Technology*, **86**, 1667 – 1678, 2005.

Tsouris, C., Riestenberg, D., Brewer, P. Peltzer, E., Waltz, P., Chow, A., Adams, E., Warzinski, R., Field studies of CO_2/water coflow injection for ocean carbon sequestration, Paper presented at the 3rd Annual Conference on Carbon Capture and Sequestration, Alexandria, VA, 2004.

ILLUSTRATIONS

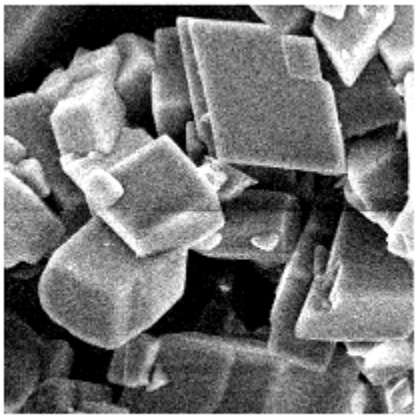

Figure 1. Scanning Electron Micrograph of Sigma Chemicals C-4830 reagent grade $CaCO_3$.

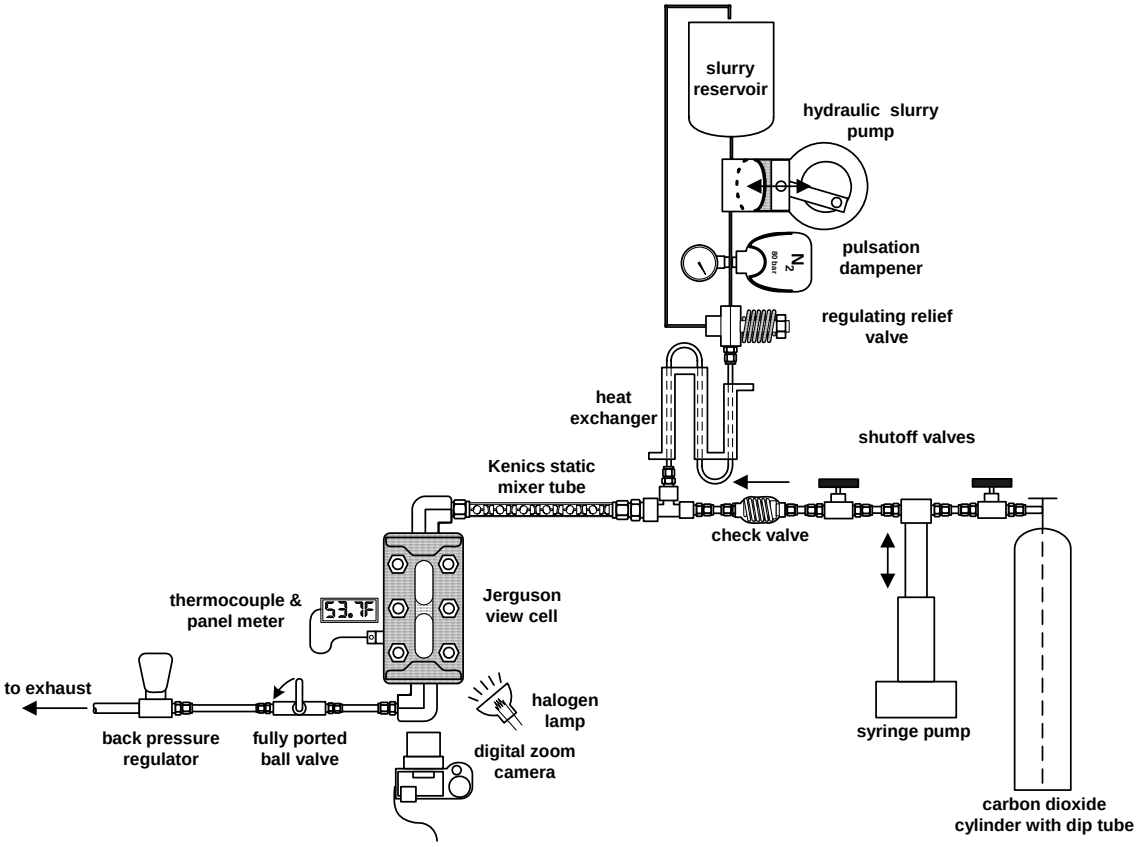

Figure 2. Laboratory apparatus with Kenics-type static mixer.

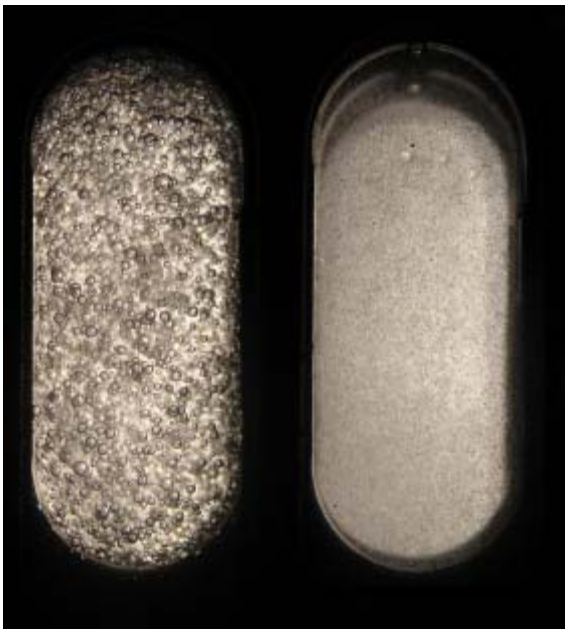

Figure 3. Digital image of liquid CO_2 droplets dispersed in water using the static mixer (no $CaCO_3$ addition). Left frame H_2O : CO_2 flow rate ratio 1 : 0.17; right frame 2 : 0.17.

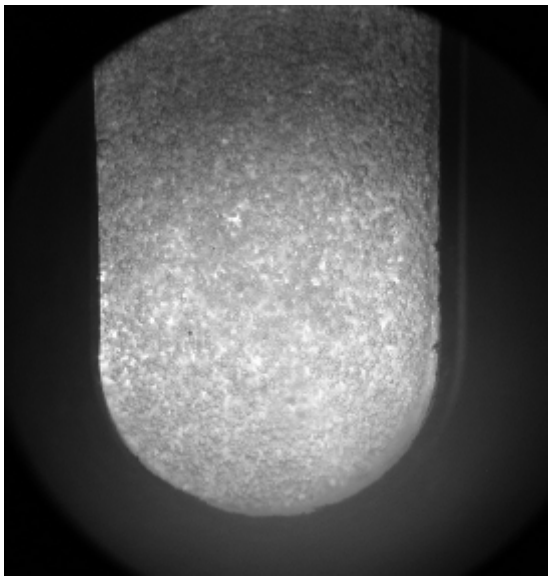

Figure 4. Digital image of CO_2 hydrates formed at H_2O : CO_2 flow ratio 1 : 0.17, temperature in static mixer 5 – 10 ˚C, pressure 10 MPa.

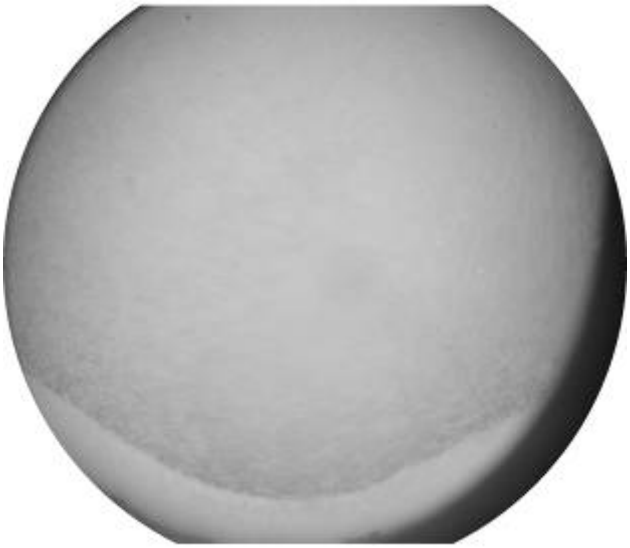

Figure 5. Digital image of CO_2-in-Water emulsion stabilized by $CaCO_3$ particles during flow conditions. Some excess $CaCO_3$ particle and globule accumulation is visible in the bottom recesses of the Jerguson cell.

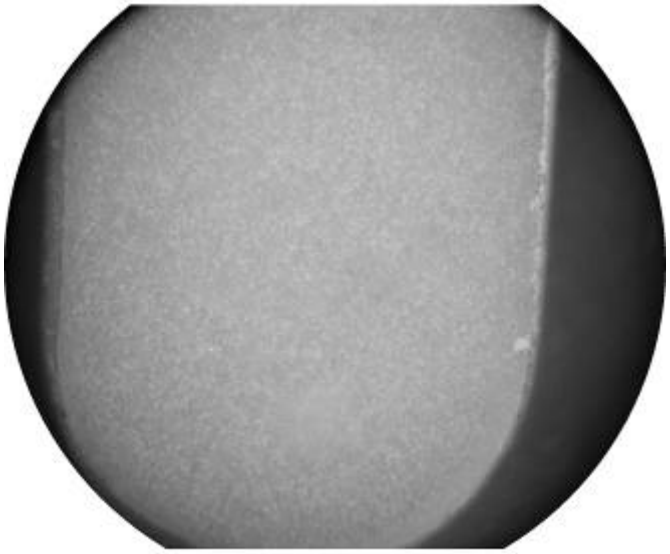

Figure 6. Digital image of CO_2-in-Water emulsion stabilized by $CaCO_3$ particles at stagnating conditions. Globule diameter in the 70 – 100 μm range.

PUBLICATIONS

D. Golomb, E. Barry, D. Ryan, C. Lawton, P. Swett, R. Warzinski and R. Lynn "CO_2-in-Water Emulsion Stabilized by Pulverized Limestone for Benign Ocean Storage," Paper presented at the IVth Annual Conference on Carbon Capture and Sequestration, May 2-5, 2005, Alexandria, VA.

PLANS FOR THE NEXT SEMI-ANNUAL PERIOD

- Testing and evaluation of the static mixer in NETL Water Tunnel Facility.
- Testing and evaluation of a microfluidizer for the production of micro-emulsions of CO_2-in-water and water-in-CO_2 using very fine particles as stabilizers.
- Formation of acid gas (H_2S/CO_2)-in-water emulsions using fine particles as stabilizers for geologic sequestration.