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

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ABSTRACT

In the first half of the second contractual year the High Pressure Flow Reactor (HPFR) was fully designed. Most components have been ordered, and assembly of the flow reactor has been started. Also, the High Pressure Batch Reactor (HPBR) was redesigned for more efficient operation and observation of the emulsion of liquid or supercritical CO₂ dispersed in water stabilized by pulverized limestone and other particles.

In this period we firmly established that when about equal volumes of liquid CO₂ and a slurry of pulverized limestone (CaCO₃) in de-ionized or artificial seawater (3.5% NaCl solution in de-ionized water) are thoroughly mixed, a macro-emulsion ensues consisting of liquid CO₂ droplets coated with a sheath of CaCO₃ particles dispersed in water. We call the coated CO₂ droplets *globules*, and the macro-emulsion a *globulsion*. Depending on the degree of mixing (rotational speed of the magnetic stir bar) and the size of the CaCO₃ particles, the globules float on top of the water column, are suspended in it, or sink to the bottom of the water column. With CO₂ droplet diameter in the 100 - 200 µm range, and CaCO₃ particles in the 6 - 20 µm range, most of the globules sink to the bottom. The formation of sinking globules is desirable for ocean sequestration of CO₂. The properties and stability of the globules will be further investigated in the HPFR in the second contractual year.

It has also been demonstrated that flyash can be substituted for pulverized limestone to obtain a stable globulsion of CO₂-in-water.

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EXPERIMENTAL

(a) High Pressure Flow Reactor

In the reporting period, the design of the High Pressure Flow Reactor (HPFR) was completed, and components thereof are already assembled. The schematic of the HPFR is presented in Figure 1 at the end of the report. The HPFR mixes a stream of liquid carbon dioxide with a slurry of pulverized limestone (CaCO_3) in water or seawater at pressures up to 2,500 psi.

The heart of the HPFR is a Kenics-type static mixer, which is depicted in greater detail in Figure 2. This is a tubular mixer 11 inch long with $\frac{1}{4}$ inch OD, with a series of 27 alternating helical baffles inside the mixer. Two fluids are forced into the mixer, one is liquid or supercritical CO_2 , the other is a slurry of pulverized limestone (CaCO_3). The high velocity in the narrow tube and the shearing and streamline cleaving action of the helical baffles efficiently mix the immiscible liquids, so that at the end of the tube a homogenized emulsion will ensue. The emulsion consists of liquid or supercritical CO_2 droplets coated with a sheath of CaCO_3 particles dispersed in water. We call this emulsion a *globulsion*. The globulsion will flow into the observation cell equipped with windows. The size distribution of the globules will be measured with a fast-frame video camera using the window dimensions as a scale reference. Furthermore, the fast-frame video camera will allow the measurement of the settling velocity of the globules. Using Stokes' Law, the measured globule diameter, and the viscosity of the medium (pure or saline water), the specific gravity of the falling globules can be measured.

Experiments presented by Tajima et al. at the 2nd Annual Conference on Carbon Sequestration demonstrated that monodisperse droplets of CO_2 -in-water can be obtained in this type of mixer. Our aim is to obtain uniform globules of liquid or supercritical CO_2 coated with a sheath of pulverized CaCO_3 that are heavier than seawater. From our batch-type experiments we established that if the size of the CO_2 droplets is in the 100 – 200 μm range, and the CaCO_3 particle size is in the 6 – 20 μm range, globules are formed with a specific gravity that is greater than that of seawater. Hence, if released in the deep ocean, such globules would sink toward the ocean bottom.

We expect the HPFR to be operational by the end of April 2004.

(b) New High Pressure Batch Reactor

In the reporting period a new and improved High Pressure Batch Reactor (HPBR) was constructed. The modified design of the HPBR is shown in Figure 3. Several limitations of the original batch reactor were addressed. As before, the cell comprises the intersection of two cylinders. However, some of the dead volume of the cylinders has been reduced in order to avoid stagnation of the globules outside of the field of view of the windows. Also, a curved bottom of the reactor will allow for higher rotational speeds of the stir bar and better mixing. More ports have been added for the insertion of a high pressure pH electrode assembly and other probes. The window material is tempered borosilicate glass (Pyrex), which permits operation up to 5000 psi (34.5 MPa) and temperature up to 50°C. A convective air bath allows more precise cell temperature regulation.

RESULTS AND DISCUSSION

Flyash Experiments

In the new High-Pressure Batch Reactor we conducted further experiments with the aim of determining whether other pulverized materials than limestone can produce a stable globulsion. So far, we experimented with flyash. A sample of flyash was obtained from the Salem Harbor Station, Massachusetts, operated by the Pacific Gas and Electric Company. This is a 750 MW power plant with three pulverized coal-fired boilers, and one oil-fired boiler. The flyash sample was obtained from one of the coal-fired boilers. The flyash was collected by an Electrostatic Precipitator (ESP). The coal is a low-sulfur type of Venezuelan origin. The exact composition has not been established, but reputedly it has a fairly high Loss-on-Ignition (LOI) in the 12 – 18% range. Indeed, the color of the flyash is grey-black, indicating a high carbon content. The consistency of the flyash is that of talcum powder.

We mixed 18 mL liquid CO₂, 10 g flyash, and 3 g NaCl dispersed in 95 mL water at 15°C, 20 MPa, using the cylindrical magnetic mixing bar with a cross-shape on top of the cylinder. Rotational speed was 1500 rpm. Stable globules were formed, some of them heavier than water, hence they sank to the bottom of the view cell (Figure 4). This experiment demonstrates that flyash can produce a stable globulsion of CO₂ droplets coated with flyash dispersed in water. Further experiments are planned using various types of flyash with known composition and size distribution. Flyash samples will be purchased from the National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) program.

PLANS FOR THE NEXT PERIOD

In the next period we expect the High Pressure Flow Reactor (HPFR) to be fully operational. We shall commence establishing the operating conditions for the HPFR such that the CaCO₃ coated CO₂ globules sink to the bottom of the observation cell. The variables include relative flow rates of the two fluids (CO₂ and CaCO₃ slurry), temperature, phase of CO₂ (sub- or super-critical), injection pressure into Kenics mixer, and particle size of CaCO₃. Refinement of the variables and measurement of the settling velocity of the globules will continue.

Also, in the next period we expect the new High Pressure Batch Reactor (HPBR) will be utilized to form particle stabilized globulsions of sub- and super-critical CO₂ using the following particles: flyash, silica (SiO₂ in the form of pure sand), alumina (Al₂O₃), iron filings, olivine, serpentine and carbon black. A wide range of particle sizes will be covered.

CONCLUSION

In the first 18 months of the contractual period it has been amply demonstrated that a stable emulsion can be formed when liquid or supercritical carbon dioxide is mixed with a slurry of pulverized limestone (CaCO_3) in water. The emulsion consists of droplets of liquid or supercritical CO_2 coated with a sheath of CaCO_3 particles dispersed in water. We call the coated droplets *globules*, and the resulting macro-emulsion a *globulsion*. Depending on the globule diameter and the CaCO_3 sheath thickness, the globules sink to the bottom of the water column, are neutrally buoyant, or float on top of the water. The presence of particles reduces the interfacial tension by decreasing the interfacial area, and hinders coalescence of the CO_2 droplets. Both a slurry of CaCO_3 in de-ionized water and in artificial seawater (3.5% NaCl solution in de-ionized water) forms the globulsion. The CaCO_3 stabilized globulsion could be used for ocean sequestration of CO_2 . The globulsion, being denser than seawater would sink to greater depth from the injection point, and the CaCO_3 -coated CO_2 droplets would not acidify the seawater, thereby not harming aquatic organisms.

We also demonstrated that flyash particles can be used instead of limestone particles to form a stable globulsion of CO_2 in water.

PUBLICATIONS

1. We submitted to *Environmental Sciences and Technology* a manuscript entitled **“Limestone Particle Stabilized Macro-Emulsion of Liquid and Supercritical Carbon Dioxide in Water for Ocean Sequestration”**

The manuscript is presently undergoing peer review. Following is the Abstract.

When liquid or supercritical CO_2 is mixed with an aqueous slurry of finely pulverized (1 – 20 μm) limestone (CaCO_3) in a high-pressure reactor, a macro-emulsion is formed consisting of droplets of CO_2 coated with a sheath of CaCO_3 particles dispersed in water. We call the coated droplets *globules*, and the resulting macro-emulsion a *globulsion*. Depending on the globule diameter and the CaCO_3 sheath thickness, the globules sink to the bottom of the water column, are neutrally buoyant, or float on top of the water. The presence of particles reduces the interfacial tension by decreasing the interfacial area, and hinders coalescence of the CO_2 droplets. Apparently, a larger fraction of the surface of the hydrophilic CaCO_3 particles resides in water than in carbon dioxide, resulting in an oil-in-water (O/W) type emulsion. We describe the expected behavior of a globulsion plume released at depth for ocean sequestration of CO_2 in order to ameliorate global warming.

2. We submitted to the *7th International Conference on Greenhouse Gas Control Technologies (GHGT-7)*, to be held 5-9 Sep 2004 in Vancouver, BC, Canada the following Abstract. The Abstract has been accepted for poster presentation at the Conference.

Liquid Carbon Dioxide/Pulverized Limestone Emulsion Delivery System for Deep Ocean Storage

We demonstrated previously (1) that when liquid or supercritical CO₂ is mixed with a slurry of pure or saline water containing finely pulverized (1 – 20 µm) limestone (CaCO₃), a macro-emulsion is formed consisting of CO₂ droplets coated with a sheath of CaCO₃ particles dispersed in water. The sheathed droplets are called globules, and the dispersion of globules in water is called a globulsion. Depending on the globule diameter and the CaCO₃ sheath thickness, the globules sink to the bottom of the water column, are neutrally buoyant, or float on top of the water column. Using a Kenics-type static mixer and pulverized limestone with particle size in the 5 – 10 µm range, monodisperse globules of about 200 µm diameter can be produced. Assuming a monolayer of pulverized limestone around the globules, the specific gravity of each globule is greater than that of seawater. For complete encapsulation of liquid CO₂ about 0.6 t of limestone is needed per ton of CO₂. The globulsion has a slightly alkaline pH.

A practical delivery system for the underwater creation of the globulsion is described. Liquid CO₂ is piped to about 500 m depth along the continental shelf or precipice. This depth is below the flash point of liquid CO₂ into vapor. A dense slurry of pulverized limestone in seawater is separately piped along the CO₂ pipe. A Kenics-type static mixer is mounted on the bottom slope. Three fluids are entering the static mixer: (a) liquid CO₂, (b) the dense slurry of pulverized limestone, and (c) ambient seawater pumped into the mixer by a turbine. The quantities of each fluid are metered so that complete encapsulation of CO₂ is obtained, and the resulting globulsion is denser than ambient seawater. The globulsion plume will sink several hundred meters along the slope while entraining ambient seawater until the plume reaches neutral buoyancy. Then the globules will roll- out from the plume further along the slope to greater depth. In the open ocean, liquid CO₂ and pulverized limestone are barged to an anchored platform. A static mixer and a seawater turbine are attached to the anchors at a depth of about 500 m. The three fluids are mixed as above in the static mixer. The dense globulsion plume will sink several hundred meters while entraining seawater until a neutral buoyancy is reached. Then the CaCO₃ encapsulated CO₂ globules will rain-out from the plume toward the ocean bottom. With this method of discharging CO₂, the ocean will not be acidified.

(1) Golomb, D. Carbon Dioxide/Limestone/Water Emulsion for Ocean and Geologic Sequestration of CO₂, GHGT-6, J. Gale and Y. Kaya (Eds.), Elsevier Science Ltd., Vol. I, pp. 683-688, 2003.

GRAPHICS

Figure 1: High Pressure Flow Reactor

Figure 2: Kenics-type Static Mixer Detail

Figure 3: Modified High Pressure Batch Reactor

Figure 4: Flyash Globulsion in Simulated Seawater

Figure 1: High Pressure Flow Reactor

Figure 2: Kenics-type Static Mixer Detail

Figure 3: High Pressure Batch Reactor

Figure 4: Flyash Globulsion in Simulated Seawater