Limestone-Particle-Stabilized Macroemulsion of Liquid and Supercritical Carbon Dioxide in Water for Ocean Sequestration

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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 macroemulsion is formed consisting of droplets of CO_2 coated with a sheath of $CaCO_3$ particles dispersed in water. The coated droplets are called *globules.* 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 $CaCO_3$ particles are lodged at the CO_2/H_2O interface, preventing the coalescence of the CO_2 droplets, and thus stabilizing the CO_2-in-water emulsion. We describe the expected behavior of a CO_2/H_2O/$CaCO_3$ emulsion plume released in the deep ocean for sequestration of CO_2 in the ocean to ameliorate global warming. Depending on the amount of CO_2 injected, the dense plume will descend a few hundred meters while entraining ambient seawater until it acquires neutral buoyancy in the stratified ocean. After equilibration, the globules will rain out from the plume toward the ocean bottom. This mode of CO_2 release will prevent acidification of the seawater around the release point, which is a major environmental drawback of ocean sequestration of liquid, unemulsified CO_2.

Introduction

In the quest of finding a benign way of sequestering CO_2 in the deep ocean (*1*) we mixed liquid CO_2 with an aqueous slurry of pulverized limestone ($CaCO_3$) in a high-pressure reactor. We found that, with certain particle sizes, mixing shear, mass ratio, and physical conditions, a macroemulsion is formed consisting of tiny CO_2 droplets coated with a sheath of $CaCO_3$ particles dispersed in water. Particle-coated oil drops in water have been named by Ramsden *emulsified globules* (*2*). Research on particle-stabilized oil-in-water (O/W) and water-in-oil (W/O) macroemulsions has been recently reviewed by Binks and co-workers (*3, 4*). Emulsion formation between water and carbon dioxide with the aid of various surfactants has been investigated by Johnston and co-workers (*5, 6*). However, to the best of our knowledge, particle-stabilized emulsions of carbon dioxide in water have not been investigated. Particle-stabilized liquid or supercritical CO_2-in-water macroemulsions may find applications in ocean and geologic sequestration of CO_2, in acid gas (CO_2/H_2S)

subterranean disposal, in enhanced oil recovery, in supercritical CO_2 extraction processes, and in liquid or supercritical CO_2 reaction schemes. Here we emphasize the application of $CaCO_3$-particle-stabilized CO_2-in-water macroemulsions for ocean sequestration of CO_2 to ameliorate global warming.

Materials and Methods

The exploration of the formation and properties of a calcite-particle-stabilized liquid carbon dioxide in water macro-emulsion is performed in a high-pressure batch reactor with view windows. The reactor, the auxiliary equipment for introducing the reactants into the reactor, and the monitoring instruments are depicted in Figure 1. The reactor consists of a 110 mL volume high-pressure stainless steel cell equipped with tempered glass windows (PresSure Products F03XC06B). The windows are placed at right angles, one illuminated with a 20 W 12 V compact halogen bulb, the other allowing recording on a video camera. The view window diameter is 24 mm. The window diameter is used as a scale for determining droplet and globule diameter sizes. The reactor is equipped with a pressure relief valve (Swagelok R3-A), thermocouple (Omega KMQSS-125G-6), pressure gauge (Swagelok PGI-63B), bleed valve (Swagelok SS-BVM2), and 3.2 mm port for admitting CO_2. A cylindrical magnetic stir bar with a cross shape on top (VWR Spinplus) is utilized for internal mixing. The reactor temperature is adjusted by application of hot air from a heat gun, or solid dry ice chips.

Finely ground $CaCO_3$ was used for the experiments. For most runs "as-mined" pulverized limestone was used, obtained from Huber Engineered Materials, Quincy, IL. The samples are labeled Hubercarb Q1, Q3, Q4, Q6, and Q325. The cumulative particle size distribution for samples Q1–Q325 is given in Figure 2. The designation of Q325 refers to U.S. mesh size 325. For some runs reagent grade $CaCO_3$ was used, obtained from Sigma Corp. The average size of Sigma particles is in the 10–20 μm range. Scanning electron microscopy (SEM) photographs revealed that the majority of Sigma particles are rhombohedral calcite crystals (Figure 3a). An SEM photograph of Hubercarb Q6 is shown in Figure 3b. It is seen that the structure of these particles is more irregular than that of the Sigma particles. Most likely, the Sigma particles are calcite precipitate from calcium hydroxide reacted with carbonic acid, whereas the Hubercarb particles are finely ground, as-mined, limestone ores, some crystalline, some amorphous.

Pulverized $CaCO_3$ is slurried in deionized water or artificial seawater (3.5 wt % NaCl). With one of the windows removed, the slurry is introduced into the reactor, and the window is reinserted. Liquid carbon dioxide is drawn from a supply cylinder and injected with a manual piston screw pump (High-Pressure Equipment Co., Erie, PA) until the reactor is filled completely. After the $CaCO_3$ slurry and liquid CO_2 are introduced into the reactor, the ingredients are thoroughly mixed with the magnetic stir bar rotating at 1500 rpm. The time evolution of the mixture inside the reactor is observed with the video camera. Sizing of the formed globules inside the reactor is performed by comparison to the window diameter.

A density vs pressure diagram of liquid and supercritical CO_2 is given in Figure 4 based on the National Institute of Standards and Technology database (*7*). The figure also shows the density vs pressure variation of water at 4 °C. Over the range of 1–20 MPa the density of water changes very little.

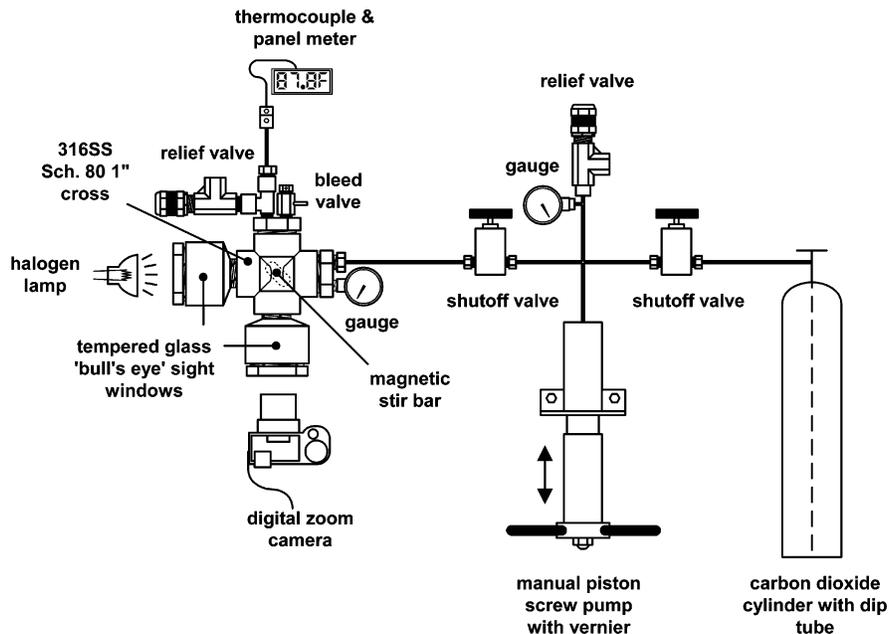* Corresponding author phone: (978) 934-2274; fax: (978) 934-3069; e-mail: dan_golomb@uml.edu.

FIGURE 1. Schematic of high-pressure batch reactor with view windows and auxiliary equipment.
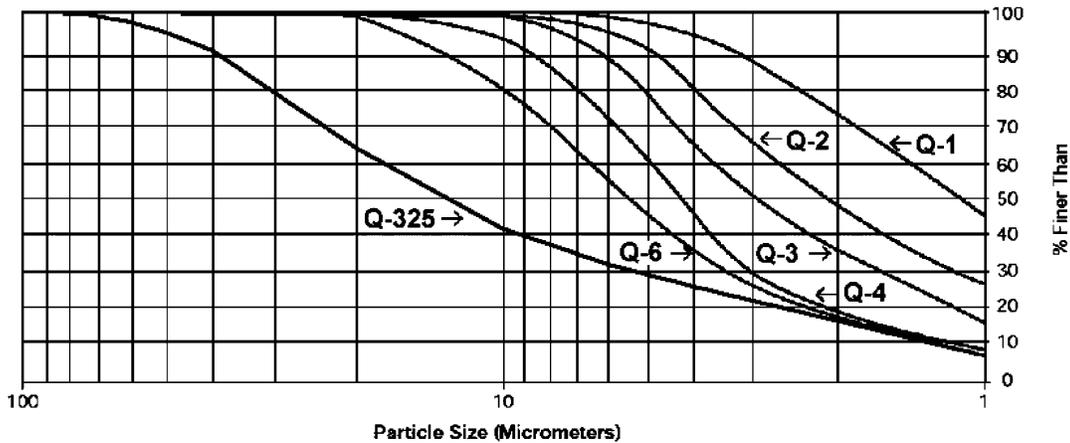

FIGURE 2. Cumulative size distribution of Hubercarb pulverized limestone samples Q1–Q325 (*23*).
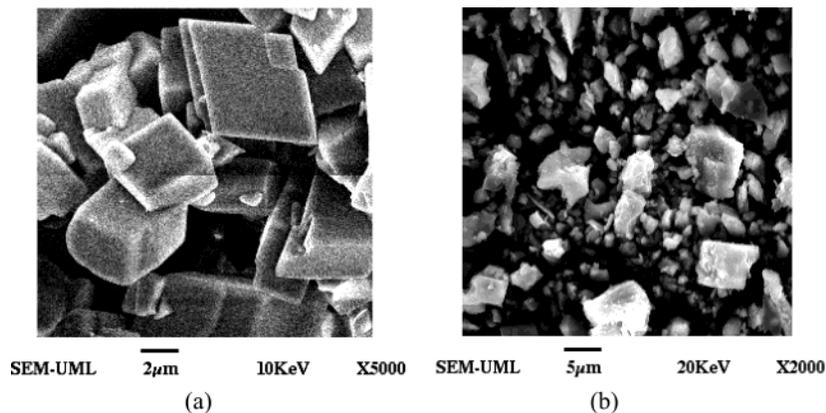

FIGURE 3. SEM micrograph of (a) Sigma reagent grade pulverized $CaCO_3$ and (b) Hubercarb pulverized limestone sample Q6.

Most experiments were performed at a temperature of 12–15 °C and pressure of 17 MPa, at which the density of liquid CO_2 is about 930 kg m^{-3}. At a temperature lower than 10 °C and pressure greater than 4.5 MPa, carbon dioxide and water form a solid, icelike hydrate (clathrate) in which a CO_2 molecule is surrounded with a cage of 5–6 H_2O molecules (*8–10*). Liquid CO_2 and water are poorly miscible. Under the high pressures of these experiments, and in the deep ocean, the solubility of CO_2 in water is in the range of 5–7 wt % (*11, 12*).
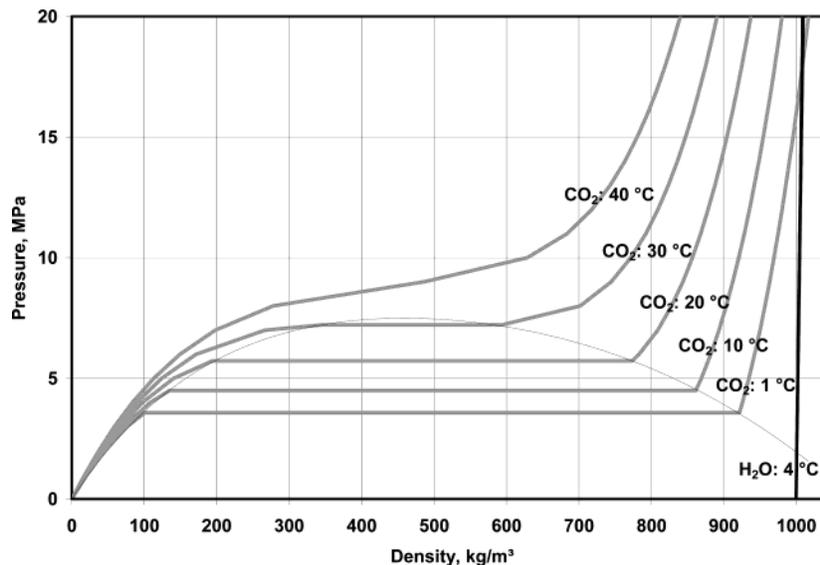
FIGURE 4. Density—pressure—temperature nomogram of liquid and supercritical CO_2 and H_2O. Adapted from ref 7.

Results

The results of the various runs, the experimental conditions, and the video camera photos of the resulting mixtures are given in Figure 5. In run M, liquid CO_2 was mixed with deionized water without the presence of $CaCO_3$ particles. Within a few minutes of the magnetic stir bar being brought to rest, the CO_2 droplets coalesced and buoyed upward. A sharp meniscus is evident separating the two liquids. The lighter CO_2 is on top; the heavier water is at the bottom. In run H, deionized water and liquid CO_2 were mixed at a temperature of $5-10\,°C$ and pressure of 17 MPa in the absence of $CaCO_3$ particles. A mixture was formed resembling ice slush, most likely consisting of CO_2 hydrates embedded in water (10).

When liquid or supercritical CO_2 is added to a slurry of pulverized $CaCO_3$, after thorough stirring a stable macro-emulsion is formed consisting of $CaCO_3$-particle-coated CO_2 droplets dispersed in water. The particle-coated droplets are called globules (2). Stable globules were produced with both Hubercarb and Sigma particles. Except where noted the globule diameter is in the $100-200\ \mu m$ range. In run Q1, Hubercarb particles with a median size of $1.2\ \mu m$ were used. Because of the thin sheath of particles, most globules have a specific gravity that is less than that of water, so they float in water. In run Q6, Hubercarb particles with a median size of $6\ \mu m$ were used. Here most globules have a specific gravity that is greater than that of water, so they sink in water, although the fine ($1-2\ \mu m$) particles produced floating globules. In run Q325, Hubercarb particles with a median size of $13\ \mu m$ were used. The video picture was taken while the globules were slowly settling at the bottom of the cell. In run Q6-SC, the temperature was $40-45\ °C$ and pressure 17 MPa, conditions at which CO_2 is in the supercritical phase ($T_c = 31\ °C$, $p_c = 7.3$ MPa). Supercritical CO_2 produced smaller neutrally buoyant globules than liquid CO_2, in the $50-100$ μm range. We also mixed liquid CO_2 with a slurry of Q6 particles in simulated seawater (3.5 wt % NaCl solution in deionized water). The results were similar to those of run Q6. Apparently, the increased ionic strength of the saline solution has no major effect on globule formation.

Preliminary results with color indicators showed an alkaline medium in the cell containing the $CO_2/H_2O/CaCO_3$ emulsion. This is not surprising because of the excess $CaCO_3$ that is present in the cell, which gives an alkaline reaction.

Discussion

Water (polar) and carbon dioxide (nonpolar) are poorly miscible as liquids, and when mixed together form two separate phases with a meniscus between them. However, when the two liquids are mixed in the presence of solid particles, a stable emulsion is formed much the same way as surfactants stabilize CO_2/H_2O emulsions (5). The particles are firmly lodged at the CO_2/H_2O interface, preventing the coalescence of CO_2 into larger droplets, and ultimately into a bulk liquid layer. A similar effect has been reported for other particle-stabilized oil-in-water emulsions (3, 13). Evidently, the process is spontaneous, with a free energy decrease, because no work is necessary for the formation of the globules other than mixing up the ingredients. For hydrophilic particles, as is the case for $CaCO_3$, the particle layer will curve such that the larger area of the particle surface remains in the external, water side, giving rise to an O/W-type emulsion, as shown on the left side of Figure 6. The angle θ is the contact angle that the particle makes with the interface of the two fluids. For hydrophilic particles, the angle $\theta < 90°$. For hydrophobic particles, the angle $\theta > 90°$, and a larger surface area of the particles would reside in the CO_2 phase, giving rise to a W/O-type emulsion, as shown on the right side of Figure 6 (3).

An optimal $CaCO_3$ particle size is required to form stable globules. The energy required to dislodge particles from the interface of two liquids varies directly with the square of the particle diameter (13). Very small particles (submicrometer diameter) can be dislodged easily from the interface, and do not form stable globules. Large particles (tens of micrometers) cannot fit onto the dispersed droplets because of the packing density. In our experiments, we found that stable globules are formed with the CO_2 droplet diameter in the $100-200$ μm range and $CaCO_3$ particle size in the $1-20\ \mu m$ range. Depending on the CO_2 droplet diameter and $CaCO_3$ sheath thickness, the globules either float or sink in the water column.

Particle-stabilized emulsion formation is not unique to CO_2. In Figure 7 globules are shown that were formed when octadecylsebacate (Octoil), water, and Sigma $CaCO_3$ particles were mixed under ambient pressure and temperature. The stir bar rotated at a modest speed. The globule diameter is in the $200-300\ \mu m$ range. Octoil has a specific gravity of 0.97, which together with the sheath of $CaCO_3$ particles makes the globules sink in water.
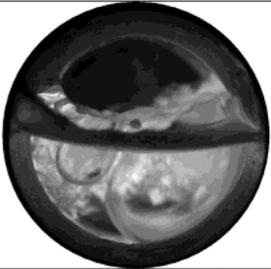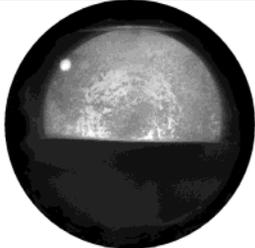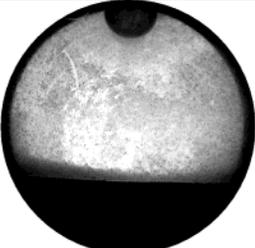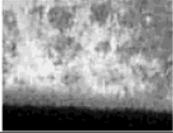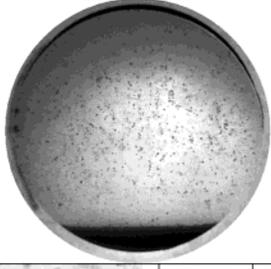
M			H		
No calcite	17 MPa 12-15°C	55 mL H_2O, 55 mL CO_2	No calcite	17 MPa 5-10 °C	55 mL H_2O, 55 mL CO_2
Q1			**Q6**		
	17 MPa 12-15°C	10g $CaCO_3$, 95 mL H_2O, 15-18 mL CO_2, 1500 RPM		17 MPa 5-10 °C	10g $CaCO_3$, 95 mL H_2O, 15-18 mL CO_2, 1500 RPM
Q-325			**Q6-SC**		
	17 MPa 12-15°C	10g $CaCO_3$, 65 mL H_2O, 23-25 mL CO_2, 700 RPM		17 MPa 40-45 °C	10g $CaCO_3$, 95 mL H_2O, 12-15 mL CO_2, 1500 RPM
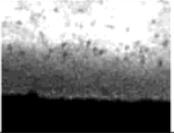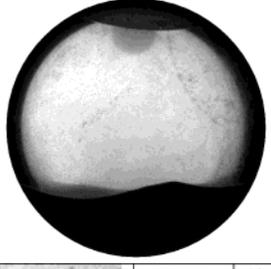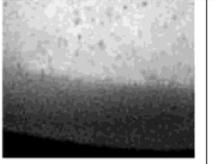
FIGURE 5. Experimental conditions and video frames of CO_2/H_2O/$CaCO_3$ experiments. Run M: CO_2 and H_2O only, no $CaCO_3$. The white object in the bottom of the cell is the magnetic stir bar. Run H: CO_2 and H_2O only, hydrate formation regime. Run Q1: CO_2, H_2O, and Q1 particles. In the lower left corner the video camera zooms in on the floating globules. Run Q6: CO_2, H_2O, and Q6 particles. In the lower left corner the camera zooms in on the settling globules. Run Q325: CO_2, H_2O, and Q325 particles. Run Q6-SC: supercritical CO_2, H_2O, and Q6 particles.
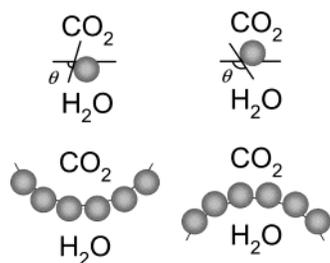

FIGURE 6. Schematic of particle-stabilized CO_2/H_2O emulsions. Modified from ref *3*.

FIGURE 7. Octoil-in-water globules stabilized with Sigma $CaCO_3$ particles.

Implication for Ocean Sequestration. The ocean presents the largest potential sink for anthropogenic CO_2. Disposing of significant quantities of anthropogenic CO_2 would greatly ameliorate the CO_2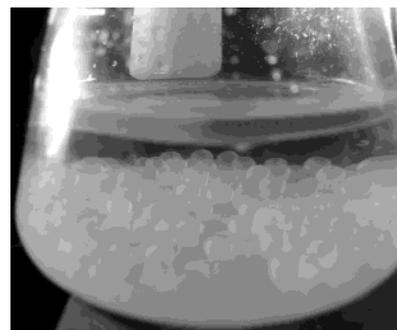-caused global warming (*14*). However, ocean sequestration raises serious environmental, technical, and economic problems. Injection into the deep ocean of a

$CO_2/H_2O/CaCO_3$ emulsion may alleviate some of these problems for the following reasons.

(a) A massive point injection of pure liquid CO_2 at depth would create a plume of carbonic acid with a pH lower than 7 in a volume of hundreds of km³ (*15*). Acidified seawater is thought to be harmful to aquatic organisms (*16*). On the other hand, the $CaCO_3$-encapsulated CO_2 globules may not acidify the seawater at all. Although the globules may disintegrate eventually due to wave and sediment action, the presence of $CaCO_3$ will buffer at least partially the dissolving CO_2 in seawater. Because calcium carbonate and bicarbonate are natural ingredients of seawater, and indeed nutrients for most aquatic organisms, there is no expected harm due to the additive $CaCO_3$.

(b) Models show that the injection of pure liquid CO_2 must occur at several hundred meters below 500 m, so that the positively buoyant CO_2 droplets will dissolve in seawater before they flash into vapor at 500 m. The optimal depth is thought to be 1000−1500 m (*17*). However, such depths are not accessible by pipeline within a reasonable distance (say 100−200 km) from most coastal sites on industrialized continents. Other sites may have to use tanker transport to a floating platform in midocean with a vertical pipe attached to it. Because tanker transport is much more expensive than pipeline transport, this would add significantly to the cost of ocean sequestration (*18*). On the other hand, a $CO_2/H_2O/CaCO_3$ emulsion plume could be discharged at much shallower depth, just below the flash depth of 500 m. Such depths are found at relatively short distances from shore on the continental shelf or precipice, for example, along river mouths or fjord canyons. They are accessible by pipeline to many more coastal sites on industrialized continents. Even inland seas, such as the Mediterranean and Black Seas, could be considered for sequestration of a $CO_2/H_2O/CaCO_3$ emulsion.

It is noted that at a depth of 500 m or below the ambient temperature and pressure may be conducive to hydrate formation (*10*). In a forthcoming paper we describe an in situ mixing apparatus for globule formation that uses ambient seawater. The seawater can be pumped from a depth where the temperature is above 10 °C to prevent hydrate formation.

(c) The formation of a $CO_2/H_2O/CaCO_3$ emulsion needs much less than a stoichiometric amount of $CaCO_3$ that would be required for complete neutralization of pure liquid CO_2 (see below). This will greatly reduce the cost of the additive and the expense of its handling and transport.

Emulsion Plume Behavior in the Ocean. When released along a canyon, the dense emulsion plume will roll further along the slope while entraining seawater to a depth where the plume reaches a neutral buoyancy with the ambient seawater (*19*). When released in the open sea, the dense emulsion plume will descend to greater depth while entraining seawater. Using the MIT droplet/particle plume model, Wannamaker and Adams (*20*) estimate that a plume with a mass flux of 100 kg s⁻¹ of CO_2 (corresponding to a 500 MW coal-fired power plant) will descend about 100−200 m before becoming trapped by ambient stratification (Figure 8). Because of entrainment of large quantities of ambient seawater, the plume, after reaching a neutral buoyancy, will spread outward a distance of several hundred meters. Insofar as the $CaCO_3$-coated globules are stable, they will "rain out" of the laterally dispersed plume toward the ocean bottom. The settling velocity of globules in a viscous medium is given by the Stokes equation $v_s = [gd_g^2(\rho_g - \rho_{sw})]/[18\mu_{sw}]$, where v_s is the settling velocity, g is the gravitational constant (9.81 m s⁻²), d_g is the globule diameter (assumed to be spherical), ρ_g is the globule density, ρ_{sw} is the ambient seawater density, and μ_{sw} is the dynamic viscosity of seawater.

The following input parameters were used: coated globule diameter $d_g = 2.16 \times 10^{-4}$ m; CO_2 density at a depth of 700
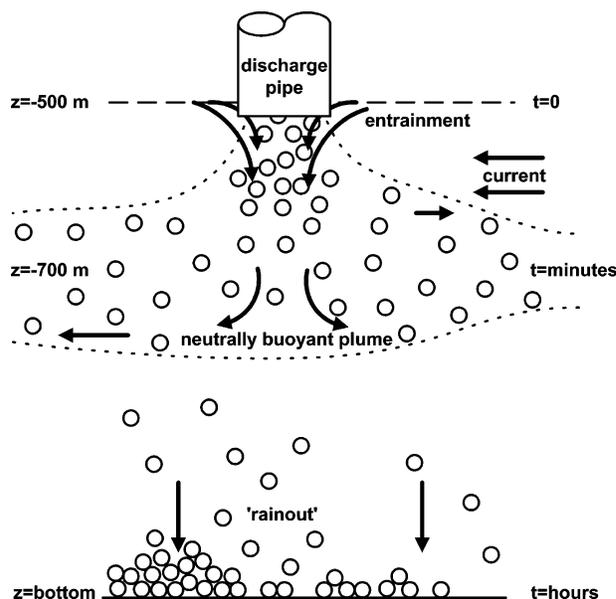

FIGURE 8. Schematic of $CO_2/H_2O/CaCO_3$ emulsion plume behavior when released below about 500 m depth in the open ocean.

m (hydrostatic pressure about 7 MPa, temperature about 4 °C) 930 kg m⁻³; $CaCO_3$ density 2700 kg m⁻³. With a monolayer of 6 μm $CaCO_3$ particles, the estimated globule density is $\rho_g = 1210$ kg m⁻³. The seawater density at 700 m is $\rho_a = 1029$ kg m⁻³ (*21*); the dynamic viscosity of water at 4 °C is $\mu_{sw} = 1.567 \times 10^{-3}$ kg s⁻¹ m⁻¹ (*22*). From the Stokes equation, the settling velocity of the coated globules in seawater is obtained, $v_s \approx 2.2 \times 10^{-3}$ m s⁻¹. This means that the globules will rain out from the neutrally buoyant plume at a rate of about 200 m/day.

Mass Ratio of CO_2 to $CaCO_3$. Using the above parameters for CO_2 and $CaCO_3$ densities, globule diameter, and $CaCO_3$ sheath thickness, the mass ratio of CO_2 to $CaCO_3$ is 1:0.56; that is, we need 0.56 t of pulverized limestone/t of liquid carbon dioxide for emulsification. This mass ratio is confirmed in our experiments. In most runs, 10 g of $CaCO_3$ was mixed with 18 mL of liquid CO_2 (~15 g). No phase separation was evident, and almost all the CO_2 was emulsified. This indicates a mass ratio of 1:0.66. To be on the safe side, some excess limestone may be necessary, perhaps 0.75 t of limestone/t of carbon dioxide. This compares with 2.3 t of limestone/t of carbon dioxide that would be necessary for complete neutralization of carbonic acid.

In conclusion, while adding pulverized limestone to liquid CO_2 and the necessary mixing apparatus will increase the cost of ocean sequestration of CO_2, the added cost may be more than compensated by savings realized for not needing to transport the CO_2 to great depth. Furthermore, this method of CO_2 sequestration is not expected to acidify the ocean to the same extent as disposal of pure liquid CO_2 would.

Acknowledgments

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