

Limestone Emulsion to Allay Concerns about Deep Ocean Storage of CO₂

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ABSTRACT

Liquid or supercritical carbon dioxide when mixed with water and finely pulverized limestone creates a stable emulsion of CaCO₃-coated CO₂ globules dispersed in water. A pressure cell with windows was constructed in which various proportions of CO₂, water and pulverized CaCO₃ can be mixed. Stable globules form when about equal volumes of liquid CO₂ and pure or saline water are mixed with pulverized (1-20 μm) CaCO₃.

Assuming that a monolayer of particles forms around the CO₂ droplets, the pulverized CaCO₃ constitutes only a fraction of the weight of CO₂. Depending on particle size, the average mass of a coated globule can be lighter, equal or heavier than pure or saline water, thus floating, suspending or sinking in the water. Upon release in the ocean, the heavier globules may sink all the way to the ocean bottom without dissolution, and without acidifying the seawater around the injection point.

INTRODUCTION

The problems of ocean storage of CO₂ are manifold: (1) If released above about 500 m depth, liquid CO₂ would flash immediately into vapor. The vapor bubbles would ascend to the surface, and re-emerge into the atmosphere. (2) Below 500 m depth liquid CO₂ is lighter than seawater and will buoy upward. Therefore, liquid CO₂ would have to be injected at sufficient depth, estimated to be between 1000-1500 m, so that the buoyant droplets will dissolve completely before reaching the flashpoint depth at 500 m (Herzog et al., 1991, Liro et al., 1992). This limits severely the coastal areas from whence pipelines can be laid economically to such depths (Golomb, 1997). (3) Dissolution of CO₂ in seawater forms carbonic acid, depressing the ambient pH, which may be harmful to aquatic organisms (Caulfield et al., 1997).

We presented previously the idea of releasing in the deep ocean liquid CO₂ mixed with a *slurry* of pulverized limestone in water (Golomb and Angelopoulos, 2001).

Equimolar proportions of CO₂ and CaCO₃ would have to be mixed in water, so that all the CO₂ and CaCO₃ react to form calcium and bicarbonate ions. After complete reaction, the surrounding seawater would have a pH that is approximately two units higher than if pure CO₂ were dissolved in seawater. The problem with that idea is that for every ton of CO₂, 2.3 tons of CaCO₃ would be required. If one considers a coal-fired power plant, roughly 8 tons of limestone would be needed for every ton of coal burned. While limestone is relatively cheap (\$5-10/ton FOB), the transport and milling of large quantities of limestone and the piping to the appropriate depth of all the material would increase the cost of CO₂ storage significantly.

In laboratory scale experiments we found that admixing finely ground CaCO₃ with liquid CO₂ and water, an *emulsion* is formed of droplets of liquid CO₂ coated with CaCO₃ particles. We call the particle coated droplets *globules*. For the formation of the emulsion only a fraction of the weight of liquid carbon dioxide in the form of pulverized limestone is necessary. The globules appear to be stable, and depending on the CaCO₃ particle size and droplet diameter, their mass can be lighter, equal or heavier than pure or seawater.

LABORATORY EMULSION EXPERIMENTS

A 100 mL volume high pressure stainless steel cell equipped with tempered glass windows was assembled. The windows are placed at right angles, one illuminated with a 20W 12V compact halogen bulb, the other allowing recording on a video camera. The cell 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 a 32 mm port for admitting CO₂. A magnetic stir bar in the shape of a cross (VWR Spinplus) is utilized for internal mixing. Cell temperature is adjusted by application of hot air from a heat gun, or solid dry ice chips.

Finely ground, as-mined, CaCO₃ was obtained from Huber Engineered Materials, Quincy, IL. The median particle sizes as specified on the labels are 1, 2, 3, 4, 6, 13 and 20 μm . Typically, 10 g CaCO₃ is slurried in deionized water or artificial seawater (3.5% by weight NaCl). With one of the windows removed, about 60 mL of the slurry is introduced into the cell, 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 Company, Erie, PA). After filling the cell completely, about 50 mL of CO₂ is present in the cell. Depending on temperature and pressure, the CO₂ is in the liquid or supercritical phase ($T_c = 31^\circ\text{C}$, $p_c = 7.3 \text{ MPa}$). When pure water is used, without CaCO₃ particles, after thorough mixing and rest, the two liquids separate with a sharp meniscus delineating them (Figure 2a). The lighter CO₂ is on top, and the heavier water is in the bottom. When a slurry of CaCO₃ particles is used, after thorough mixing and rest, no meniscus is apparent, and CaCO₃ particle-coated CO₂ globules are evident. Depending primarily on particle size, but also on the intensity of mixing (which breaks the bulk CO₂ into droplets), and on pressure and temperature (which affects the CO₂ density), the globules float on top or are suspended in water (Figure 2b), or sink to the bottom (Figure 2c). Using a 3.5% NaCl solution, simulating seawater, does not prevent globule formation. At temperatures below 10°C and pressures above 10 MPa, hydrate formation is evident, which interferes with globule formation.

THEORY OF EMULSION FORMATION

Water (polar) and carbon dioxide (non-polar) are immiscible as liquids and when mixed together form two separate phases with a meniscus in between them. However, when the two liquids are mixed in presence of pulverized calcite (CaCO₃), which acts as an emulsifying agent, the mixture forms a stable emulsion with water as the continuous phase and carbon dioxide as the dispersed phase.

Since the contact angle of calcite with water is 40° (Tambe and Sharma, 1993), and that of calcite with carbon dioxide is greater than 90°, calcite is preferentially water-wet and stays in the aqueous phase of the interface (Figure 3). Presence of calcite in the water phase reduces the interfacial tension (i.e. the interface free energy per unit interfacial area) by increasing the interfacial area, and provides the hindrance for coalescence of the carbon dioxide phase.

An optimal calcite particle size is required to form a stable emulsion. The energy required to dislodge particles from the interface of two liquids varies directly with the square of particle diameter (Binks and Lumsdon, 2001). Very small particles (submicron diameter) can be dislodged easily from the interface, and do not form a stable emulsion. Large particles (tens of μm) cannot fit onto the dispersed droplets because of packing density. In our experiments, we found that for 200 – 300 μm CO₂ droplets, the optimal

calcite particle size is in the few to ten μm range. However, the 1-2 μm particles do not increase the average globule density sufficiently for it to sink to the bottom of the water column. To achieve sinking, we found the optimal particle diameter to be in the 4-6 μm range.

Unlike oil-in-water stabilized emulsions, which form spontaneously at ambient conditions, calcite stabilized carbon dioxide-in-water emulsion is temperature and pressure sensitive. This is because as the pressure increases, the density of the CO_2 phase increases, and its free energy density becomes closer to that of water. Thus, the interfacial tension between water and CO_2 decreases. As the temperature decreases, the CO_2 density increases and the interfacial tension decreases further. Thus, we found that optimal conditions for stable emulsion formation are $p > 5 \text{ MPa}$ and $T < 15^\circ\text{C}$.

EMULSION PLUME BEHAVIOR IN THE OCEAN

If discharged through a pipe, the plume containing CaCO_3 -coated CO_2 globules will sink from the discharge point to greater depths while entraining ambient seawater. Using the MIT droplet/particle plume model, Wannamaker and Adams (2002) 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) would descend about 200 m before becoming trapped at a level of neutral buoyancy within the ambient seawater. Because of entrainment of large quantities of ambient seawater, the plume, after reaching a neutral buoyancy, would spread outward a distance of several hundred meters.

Based on our observations, the CaCO_3 -coated globules are stable. Thus, they will “rain” out of the laterally dispersed plume toward the ocean bottom. The settling velocity

of the globules in seawater can be estimated by the Stokes’ equation $v_s = \frac{g d_g^2 (\rho_g - \rho_{sw})}{18 \mu_{sw}}$

where v_s is the settling velocity, g is the gravitational constant, d_g is the globule diameter (assumed to be spherical), ρ_g the globule density, ρ_{sw} the ambient seawater density, and μ_{sw} is the dynamic viscosity of seawater.

Using a coated globule diameter $d_g = 200 \mu\text{m}$ (observed), liquid CO_2 bulk density 850 kg m^{-3} , CaCO_3 particle bulk density 2710 kg m^{-3} , a $6 \mu\text{m}$ monolayer of particles coating the liquid CO_2 droplets, the average mass of the coated globules is estimated at $5.725 \times 10^{-9} \text{ kg}$, and the density of the globules $\rho_g = 1.15 \times 10^3 \text{ kg m}^{-3}$. This compares with the density of seawater at 500 m $\rho_{sw} = 1029 \text{ kg m}^{-3}$ (Teng et al., 1996). The dynamic viscosity of seawater is taken as $\mu_{sw} = 1.567 \times 10^{-3} \text{ kg s}^{-1} \text{ m}^{-1}$ (Stommel and Yoshida, 1972). Thus, the coated globules will sink in seawater. The settling velocity of the coated globules in seawater is obtained $v_s = 1.7 \times 10^{-3} \text{ m s}^{-1}$, or about 6 m/hr.

For a $6 \mu\text{m}$ sheath of CaCO_3 particles on a $200 \mu\text{m}$ CO_2 droplet, the mass ratio of $\text{CaCO}_3:\text{CO}_2 = 0.6:1$, that is, we need 0.6 tons of limestone per ton of liquid carbon dioxide for emulsification. To be on the safe side, some excess limestone may be necessary, perhaps 0.75 tons limestone per ton of carbon dioxide. This compares with 2.3 tons of limestone per ton of carbon dioxide that would be necessary for complete neutralization of carbonic acid.

CONCLUSIONS

The injection into the deep ocean of an emulsion of liquid CO₂ in water stabilized with pulverized limestone (CaCO₃) may alleviate some of the problems associated with ocean storage of CO₂. (1) The mass of the individual globules is heavier than seawater, so they will sink toward the ocean bottom, rather than buoy upward as lighter-than-seawater liquid CO₂ droplets would. Thus, the emulsion may be released just slightly below 500 m depth, which is the flashpoint of liquid CO₂ into vapor. The depths of 500+ m are reachable within 100-200 km from the shoreline at many more sites around industrial continents than the 1000+ m depths that were thought previously to be the minimum depths for ocean storage of liquid CO₂. (2) The coated globules appear to be stable over time. Thus, the surrounding seawater is not in direct contact with the coated globules, and the pH of seawater may not be affected. In fact, some excess CaCO₃ may buffer any carbonic acid that escaped emulsification. (3) Since the coated globules appear to be stable, they may fall to the ocean bottom, prolonging the storage time period. (4) The formation of the coated globules requires only modest quantities of pulverized limestone, about 0.75 tons per ton of CO₂. This reduces greatly the cost of the additive and its handling and transport.

The long-term stability of the CaCO₃-coated CO₂ globules and their environmental impact on the ocean floor should be further assessed.

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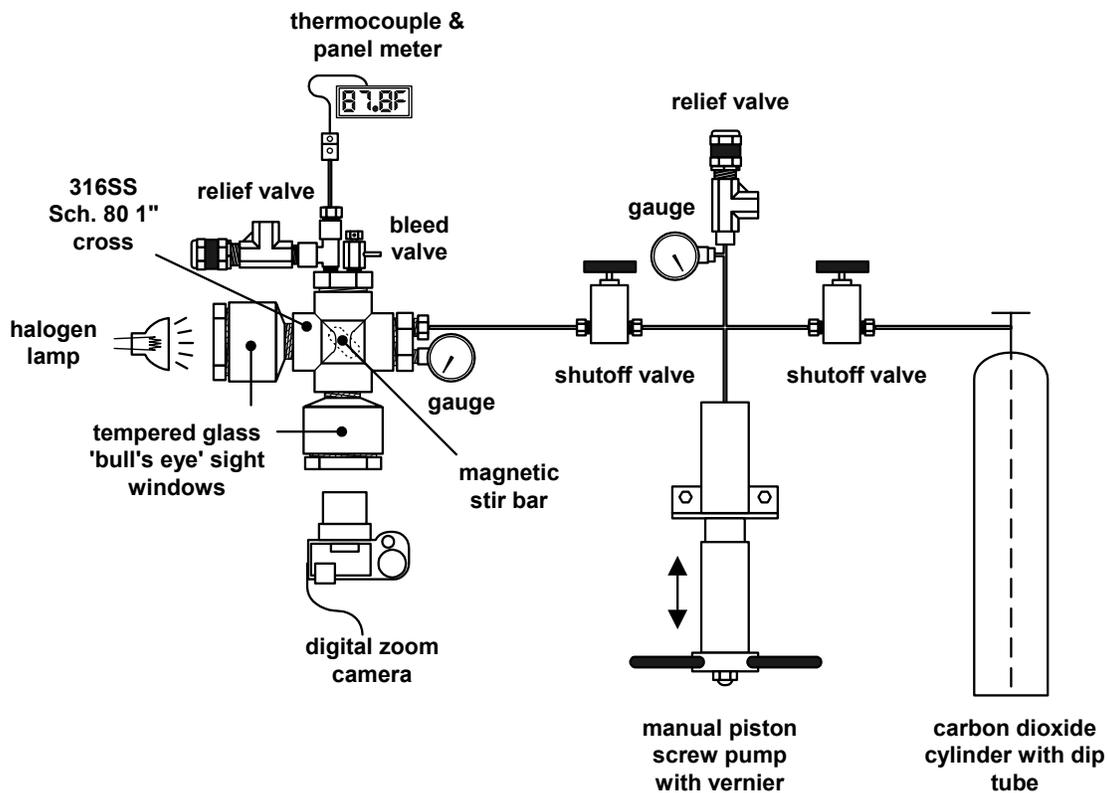


Figure 1: Laboratory apparatus for emulsion formation

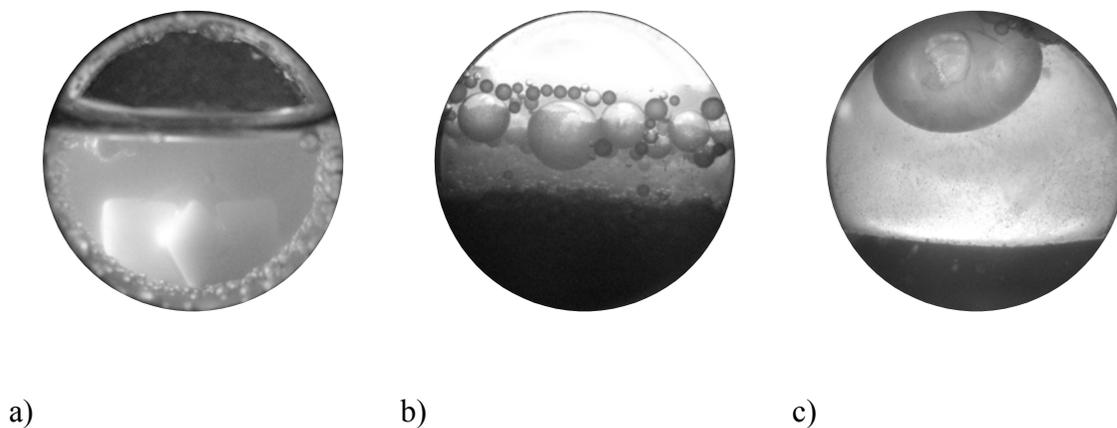


Figure 2: Emulsions as observed through sight window of cell
 a) No calcite present. Liquid CO₂ on top of water. Magnetic stir bar visible at bottom.
 b) Emulsion with various size calcite particles. Lighter globules float; heavier ones sink.
 c) Emulsion with 6 μm average diameter calcite particles. Average globule size is 200 μm. Bubble on top is unmixed CO₂.

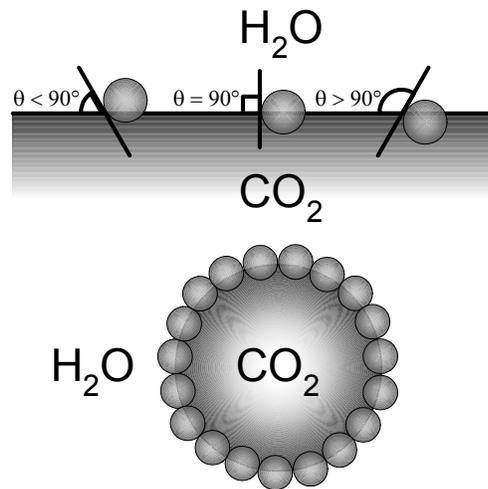


Figure 3: Contact angles and globule formation

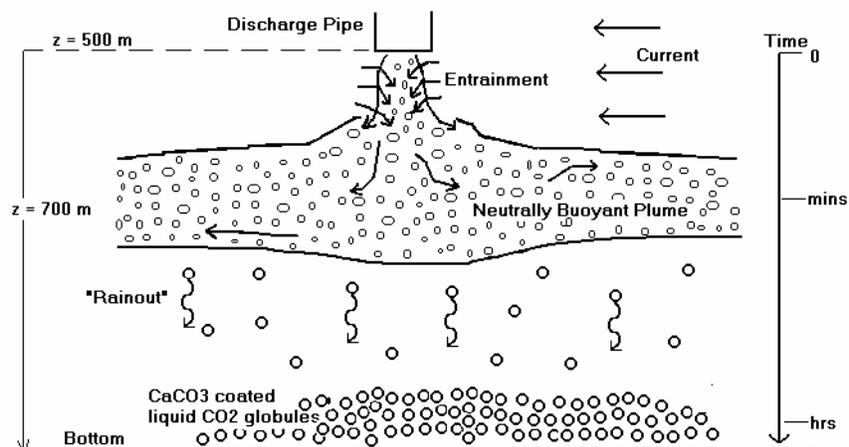


Figure 4: Emulsion upon release below 500 m. Plume sinks while entraining seawater. Ambient current distorts plume. Globules rain out after plume reaches neutral buoyancy.