

A BENIGN FORM OF CO₂ SEQUESTRATION IN THE OCEAN

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ABSTRACT

It is proposed that liquid CO₂ is mixed with pulverized limestone (CaCO₃) and seawater in a pressure vessel. An emulsion is created which is piped to intermediate depth in the ocean, where the emulsion is released through a diffuser. The emulsion plume has a bulk density of 1.4 kg m⁻³, thus it will sink as a gravity current to greater depth from the release point. Several kinetic processes occur simultaneously: (a) the entrainment of seawater by the emulsion plume, (b) the dissolution of CaCO₃, (c) the dissolution of CO₂, and (d) the reaction of dissolved CO₂ with CaCO₃ to form bicarbonate. In the presence of CaCO₃, the plume around the release point has a pH 5 instead of 3 around the release point of liquid CO₂. Subsequent entrainment of seawater brings rapidly the pH to near ambient values. The resulting calcium and bicarbonate ions are available nutrients for marine organisms. The bicarbonate solution will stay in the ocean indefinitely as contrasted with carbonic acid which eventually would resurface and equilibrate with the atmosphere. Most importantly, the emulsion can be released slightly below 500 m, as the emulsified CO₂ will not phase-separate and ascend to a depth where it would flash into vapor. This makes the release depth accessible to many more coastal power plants than the previously thought minimum depth of 1000 m for the release of pure liquid CO₂.

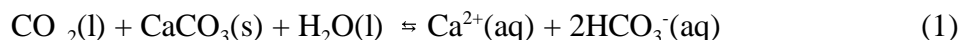
INTRODUCTION

Discharging liquid CO₂ at depths 1000 m or deeper has been shown to be technically feasible and not prohibitively expensive (Herzog et al., 1991, Ormerod et al., 1994, Herzog, 1999). Depending on the amount of discharged CO₂, a significant volume of seawater around the discharge point will have a depressed pH, jeopardizing marine organisms (Caulfield et al., 1997). Furthermore, a part of the discharged CO₂ droplet plume may ascend by buoyancy to a shallower depth where the liquid CO₂ will flash into vapor and re-emerge into the atmosphere. Wadsley (1995) suggested that calcium carbonate (CaCO₃) could be slurried with high density fluid CO₂ to raise the pH around the release point. Golomb (1997) proposed that CaCO₃ be used to eliminate the hazard from accumulated CO₂ at the bottom of Lake Nyos in the Cameroons. Caldeira and Rau (1999) proposed that flue gas CO₂ be mixed with seawater and CaCO₃ and released into the surface layer of the ocean. A part of the CO₂ and CaCO₃ would form a bicarbonate solution with a pH of about 5.7. However, since their scheme would employ flue gas CO₂ at a partial pressure of about 0.15 atm, vast amounts of water and limestone would need to be mixed with gaseous CO₂ in order to facilitate dissolution and bicarbonate formation, making such a proposition prohibitively costly. In this paper we propose that liquid CO₂ be mixed with pulverized limestone and water, and that the resulting emulsion be released

at a depth of slightly below 500 m. After entrainment of seawater into the emulsion plume, a solution of bicarbonate will ensue with a higher pH than pure carbonic acid. The bicarbonate solution will have an indefinite sequestration time.

CHEMICAL EQUILIBRIUM

When liquid CO₂ is mixed with CaCO₃ and water, the following equilibrium is established:



The species concentrations can be calculated from the known equilibrium constants

$$K_{\text{H}} = [\text{H}_2\text{CO}_3^*]/p_{\text{CO}_2} = 10^{-1.5}$$

$$K_{\text{a},1} = [\text{H}^+][\text{HCO}_3^{-}]/[\text{H}_2\text{CO}_3^*] = 10^{-6.3}$$

$$K_{\text{a},2} = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^{-}] = 10^{-10.3}$$

$$K_{\text{SO}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 10^{-8.3}$$

where [H₂CO₃^{*}] is hydrated CO₂, p_{CO₂} is the pressure of CO₂ in atm, K_{SO} is the solubility constant of CaCO₃. Equilibrium calculations show that with CO₂ at a pressure of 100 atm, the resulting solution/suspension contains 0.032 M Ca²⁺, 0.064 M HCO₃⁻, and a pH = 4.65. Without the presence of CaCO₃, the pH would be slightly less than 3, i.e. about 100 times more acidic. The pH as a function of p_{CO₂} in the presence and absence of CaCO₃ is given in Fig. 1. At all CO₂ pressures the effect of CaCO₃ is to raise the pH by about 2 units, i.e. the solution is about 100 times less acidic than in the absence of CaCO₃. After complete dissolution of the ingredients of the emulsion, the resulting seawater solution will contain the above concentrations of calcium and bicarbonate ions plus the appropriate concentrations of hydrogen, hydroxyl and carbonate ions, as well as the concentrations of normal ingredients of seawater. The pH will be close to ambient values.

EMULSION

Liquid CO₂ and water are not perfectly miscible. At a pressure of 100 atm and a temperature of 12 °C, 1.8 x 10⁻³ g of CO₂ is soluble per g of water (Wiebe and Gaddy, 1940). A solution of one mole of liquid CO₂ at 100 atm pressure (44 g) with a stoichiometric amount of water (1 mole, 18 g) will separate into two phases, just as in the case of an oil/water mixture. Disposal of liquid CO₂ at ocean depths less than 1000 meters will yield CO₂ droplets which will ascend due to buoyancy to a depth where liquid CO₂ will vaporize and re-emerge into the atmosphere. Suspension of CaCO₃ particles in a stable CO₂/water emulsion prior to ocean disposal will not only mitigate the environmental (pH) impact of CO₂ ocean disposal, but will also possess an average specific gravity of 1.4, and permit CO₂ disposal at ocean depths well above 1000 meters.

Stabilization of oil/water emulsions by a film of highly dispersed solid particles is well known, particularly in the production of crude oil. Particles in the form of clays, resins, asphaltenes and wax have been identified as potential stabilizers of crude oil-brine emulsions. For example, CaCO₃ particles having a diameter of 2 μm have been shown capable of stabilizing an emulsion of n-decane in brine (Tambe and Sharma, 1993). In laboratory experiments, we have demonstrated that ~10 μm CaCO₃ particles (Fisher) will readily stabilize an emulsion of vacuum pump oil (Octoil) in distilled water without the addition of surfactant. A photograph of the emulsion is shown in Fig. 2, where the

translucent droplets of oil were found to be stable in excess of 24 hours. The oil droplets are heavier than water because of the CaCO_3 coating, hence they sink to the bottom of the vial. To our knowledge, stabilization of CO_2 -water emulsions by highly dispersed particles has never been previously attempted. Whether the results of previous studies on the use of highly dispersed particles as emulsifying agents for hydrocarbon-water mixtures may be extended to CO_2 -water mixtures is uncertain, due to the weak van der Waals forces of liquid CO_2 in comparison to hydrocarbon solvents. Calcium carbonate particles are very hydrophilic, yet also possess carbonyl groups which are known to interact specifically with CO_2 (Kazarian, et al., 1996). Such dual functionality has the potential to form a stable film of highly dispersed CaCO_3 particles at the CO_2 -water interface. Water will wet the CaCO_3 particles to a greater extent than CO_2 due to the presence of polar interactions and hydrogen bonding, and form the outer, continuous emulsion phase, whereas CO_2 will be present in the form of droplets due to the weaker van der Waals interactions. Thus, we envisage an inner core of a CO_2 droplet, surrounded by a film of CaCO_3 particles, which in turn is surrounded by water. Such an emulsion will be similar to the experimental oil-in-water emulsion shown in Fig. 2 and will have a cross section as depicted by the schematic in Fig. 3 (a). Surfactants which are known to stabilize CO_2 -water emulsions may also be incorporated into the CO_2 /water/ CaCO_3 mixture (Johnston et al., 1996; Sarbu et al., 2000). The surfactants may either adsorb onto the surface of the particles and improve the stability of the interfacial particle film or stabilize water-in- CO_2 emulsions with CaCO_3 particles dispersed within the inner aqueous phase. A cross-sectional schematic of such an emulsion with CO_2 as the hydrophobic membrane is shown in Fig. 3 (b).

FLUID DYNAMICS

The density of liquid CO_2 is approximately 0.9 kg m^{-3} , the bulk density of pulverized limestone (CaCO_3) is about 2 kg m^{-3} , that of water 1 kg m^{-3} . Mixing 1:1:1 mole of these species, the bulk density of the emulsion is about 1.4 kg m^{-3} . This is much denser than seawater at the depth of release, amounting to about 1.027 kg m^{-3} at 500 m (Adams et al., 1997). The emulsion plume will sink to greater depth while entraining seawater. The fluid dynamics of a density current in the ocean has been modeled by Liro et al. (1992), Drange and Haugan (1992), Adams et al. (1997) and Alendal (1997). Depending on the initial density of the release mix, the stratigraphy of the ocean, and whether the release occurs in the free ocean, along the continental slope, or in a trench, a density current will sink hundreds to thousands of meters until the density difference between the sinking plume and ambient seawater vanishes. In the free ocean, prevailing ocean currents and the Coriolis force will bend the sinking gravity current. When released along the continental slope or a trench, drag will slow down the creeping plume, and entrainment of seawater occurs only over the top side of the plume. Most likely, the plume will creep toward the ocean bottom, where it will continue to spread laterally. After sufficient entrainment of seawater, all the CaCO_3 will dissolve and form calcium bicarbonate in the reaction with CO_2 . Regardless of whether the final dissolution occurs at some intermediate depth or at the ocean bottom, the final plume will not contain any residual CO_2 . When CO_2 and solid CaCO_3 are not yet completely dissolved, the plume pH will be about 5. After complete dissolution, the pH will be close to ambient seawater values. Most importantly, the bicarbonate solution will remain sequestered indefinitely.

RELEASE SCHEME

A 1000 MW_e coal fired power plant emits about 260 kg s⁻¹ of CO₂. The CO₂ is separated from the flue gas and compressed to 100 atm. At this pressure, CO₂ is liquid below 31°C, and supercritical above that temperature. The liquid CO₂ is mixed with 591 kg s⁻¹ pulverized CaCO₃ (limestone) suspended in seawater in a pressure vessel. The emulsified mix contains 1:1 mole of CO₂ and CaCO₃. This molar ratio is only necessary for complete reaction of CO₂ with CaCO₃. If less CaCO₃ is added, a homogenous high density emulsion may still be formed, albeit the excess CO₂ will remain unreacted. The emulsion is pumped through a pipe laying on the continental slope or precipice to a depth somewhat below 500 m. At a shallower depth, liquid CO₂ from the emulsion would immediately flash into vapor without completing the bicarbonate formation. The emulsion is released into the ocean through a diffuser with orifice sizes of about 1 cm diameter, so as to prevent clogging of the orifices by the emulsion. At 500 m, the hydrostatic pressure of seawater is about 50 atm. Thus, the emulsion exits the orifices with an overpressure of about a factor of 2. This will ensure a jetted release plume and turbulent entrainment of seawater as was shown in tank experiments by Masutani et al. (1993). The complete release scheme is depicted in Fig. 4, including the power plant with CO₂ capture, compressor, pressurized mixing vessel, pump, transport pipe, diffuser, and the emulsion plume ejected from the diffuser.

SEQUESTRATION SITES

Golomb (1994) surveyed potential coastal sites where liquid CO₂ could be discharged via pipe to a depth of 1000 m, such that the pipe length does not exceed 200-300 km. It turned out that most industrial continents have limited access to potential sequestration sites. For example, along the eastern coast of North America, the only available sites are at the Hudson, Delaware and Hatteras Canyons. Europe has only a few sites: at the outflow of Gibraltar, along the coast of Portugal, the Bay of Biscay, the abyss beyond the Hebridian Shelf west of the British Isles, and some fjords along the coast of Norway. China has access to the deep South China Sea between the islands of Hainan and Taiwan. The proposed scheme of releasing a CO₂/H₂O/CaCO₃ emulsion opens many more potential sequestration sites. Along the eastern coast of North America, a depth of 500 m can be reached within 200-300 km distance from Long Island to Florida. In Europe, North Africa and Asia Minor, potential sequestration sites open all along the Mediterranean Sea and Black Sea. These seas would have a sufficient depth even for a pure liquid CO₂ release, but being enclosed by continents, acidification of these seas would pose an environmental problem. The release of a CO₂/H₂O/CaCO₃ emulsion would alleviate that problem; in fact, it may prove beneficial for the marine ecology of these seas.

ECONOMICS

The proposed method will increase the cost of sequestering CO₂ in the ocean. The cost of ocean disposal of liquid CO₂ has been estimated at about \$15 per tonne of avoided CO₂ (Ormerod et al., 1994). Due to admixing pulverized limestone, the major increase of the cost is the price of limestone. A survey of limestone suppliers resulted in a median price of \$7.50 per tonne of crushed (but not pulverized) limestone, FOB. Railroad or barge transport to the power plant site and milling may rise the price of in situ pulverized limestone to about \$10 per tonne. Since 2.3 tonnes of CaCO₃ are required per tonne of CO₂, the added cost is about \$23 per tonne of CO₂. As mentioned above, if a part of the CO₂ can be left unreacted, less CaCO₃ is required. A cost/benefit analysis should show the

optimal quantity of CaCO_3 to be used. Depending on the amount of limestone used, this method may add up to 150% to the cost of ocean disposal. The added cost is partially offset by requiring shorter pipelines. Assuming that the 500 m depth can be reached in 100 km distance instead of 200 km distance to 1000 m, this saves 100 km of deep pipe laying costs. At a cost of \$2 M per kilometer of deep pipe (Golomb, 1994), this represents a saving of \$200 M of pipe laying investment. Amortizing the pipe over 15 years, and considering that the pipeline carries 8.2 million tonnes per year of CO_2 from a 1000 MW coal fired power plant, \$1.6 is saved per tonne of avoided CO_2 by not needing to pipe it to a 1000 m depth. However, the biggest benefit will be realized in the intangible savings of not hurting the environment.

CONCLUSION

An alternative method is proposed to sequestering CO_2 in the ocean, that is, to release an emulsion of liquid carbon dioxide, water and pulverized limestone instead of liquid CO_2 alone. This scheme has several advantages: (a) The release can occur at a relatively shallow depth of slightly below 500 m, which is accessible to more coastal power plants than the previously thought minimum depth of 1000m. (b) CO_2 will react with CaCO_3 and water to form a bicarbonate solution. After complete reaction, the pH will be close to ambient values. (c) Bicarbonate solution is a beneficial nutrient to marine organisms. (d) Bicarbonate solution may remain in the ocean indefinitely. (e) Intracontinental seas, such as the Mediterranean Sea and Black Sea may be used as a sequestration medium. The disadvantage of this method is the increased cost. Admixing pulverized limestone may add 150% to the sequestration cost of CO_2 in the ocean.

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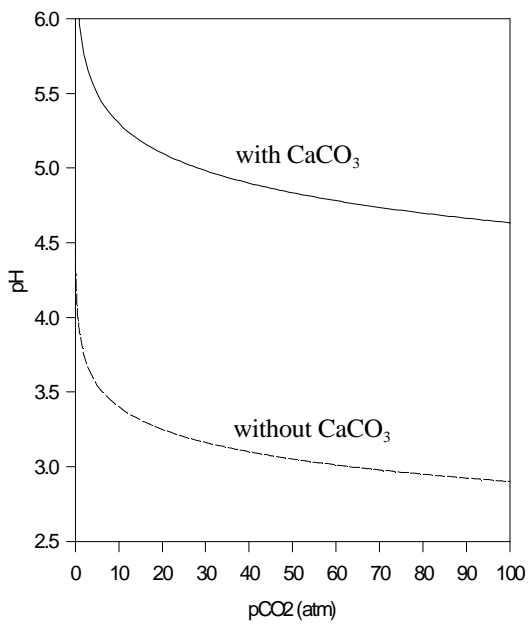


Figure 1: Ideal equilibrium pH of CO₂/H₂O in the presence of CaCO₃ as a function of CO₂ pressure.



Figure 2: Octoil in water emulsion stabilized with ~10 μm CaCO₃ particles.

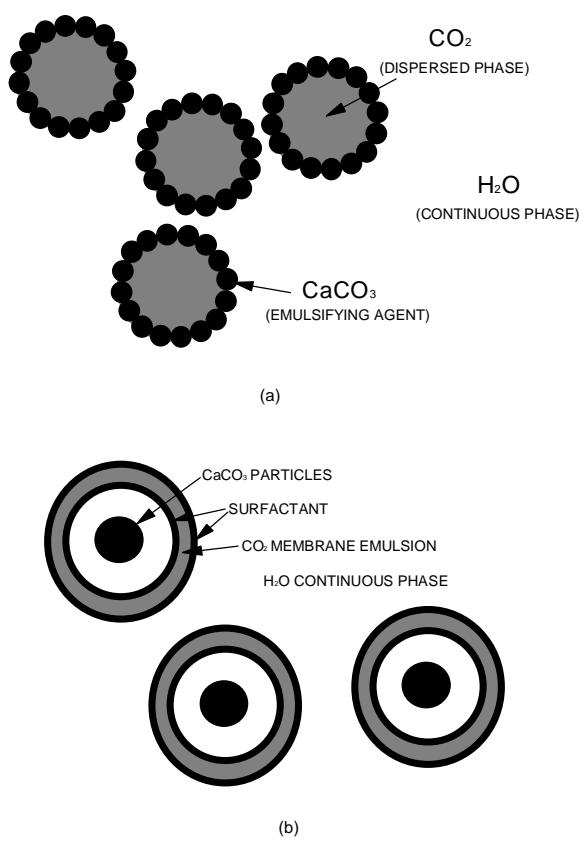


Figure 3: (a) Cross-section of a CO₂-in-water emulsion with a stabilizing CaCO₃ film, and (b) a membrane emulsion with CaCO₃ particles in the inner aqueous phase.

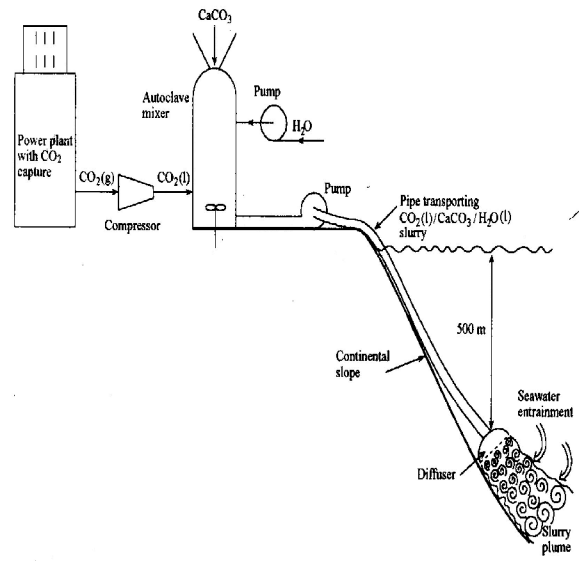


Figure 4: Schematic of CO₂/H₂O/CaCO₃ release method.