

Enhanced Carbonate Dissolution as a Means of Capturing and Sequestering Carbon Dioxide

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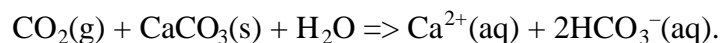
Introduction

Various methods have been proposed for mitigating anthropogenic CO₂ release to the atmosphere, including storage via enhanced biological uptake on land or in the ocean and via subterranean or –marine injection of captured CO₂. DOE alone is currently investing >20M\$/yr on research of such sequestration technologies. We propose an alternate, geochemistry-based capture and sequestration method which hydrates the CO₂ contained in power plant flue gas with water to produce a carbonic acid solution. This in turn is reacted on-site with carbonate mineral (e.g., limestone) to convert the original CO₂ gas to bicarbonate in solution (Rau and Caldeira, 1999; Caldeira and Rau, 2000). This dissolved bicarbonate is then released and diluted in the ocean where it would add minimally to the large, benign pool of these ions already present in seawater.

Such a process is geochemically equivalent to carbonate weathering which will otherwise naturally consume anthropogenic CO₂, but over many millennia (Archer et al., 1997; Murray and Wilson, 1997). As we will show, under certain conditions enhanced carbonate dissolution appears to have important economic and environmental advantages that merit further investigation.

Approach

We envision allowing CO₂-rich effluent gas streams to flow over or through a porous bed of limestone particles which are wetted by a continuous spray or flow of water (Rau and Caldeira, 1999; Fig. 1). High-CO₂ waste gas (pCO₂ >0.1atm) is passed through the reactor so as to contact the water and wetted surfaces, forming carbonic acid which would in turn react with the carbonate solids (e.g., calcium carbonate) to produce HCO₃⁻ in solution, the net reaction being:



However, due to equilibria within the dissolved inorganic carbon system, the solution formed would still contain substantial quantities of molecular CO₂ which if contacted with air would lead to CO₂ loss to the atmosphere and precipitation of carbonate. This can be avoided by subsurface ocean release and mixing of the solution, or with partial CO₂ degassing and recapture prior to re-

lease in the ocean (Caldeira and Rau, 2000).

It would take 2.3 tonnes of calcium carbonate and 0.3 tonnes of water to react 1 tonne of CO_2 to form 2.8 tonnes of HCO_3^- in solution. The required carbonate volume for such a reaction to occur on a daily basis would scale directly with particle diameter, e.g. 0.45 m^3 for 10-mm-diameter particles. If such a bed is continuously bathed in a 3/4-saturated bicarbonate solution (5.0×10^{-3} Molar at $\text{pCO}_2 = 0.15 \text{ atm}$), it would require a water flow and discharge of 10^4 tonnes H_2O per tonne CO_2 sequestered. Based on bicarbonate formation rates and depending on reactor configuration, this form of CO_2 “fixation” per area is at least several orders of magnitude greater than biological CO_2 fixation rates in highly-managed land or aquatic plant cultures.

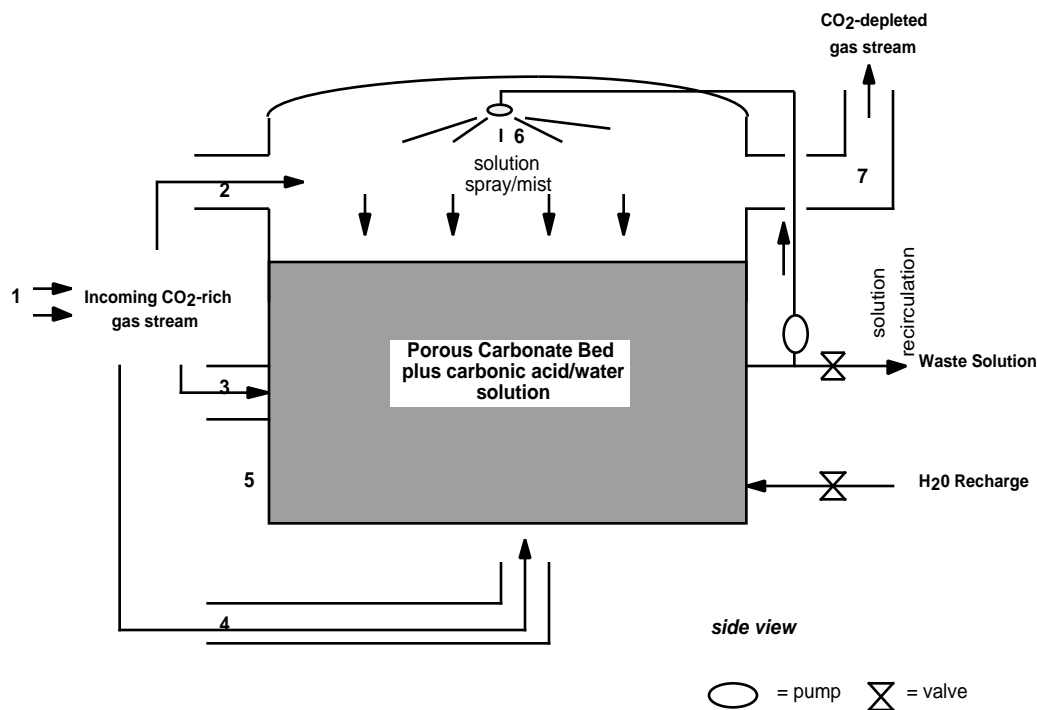


Figure 1. An example of a possible carbonate dissolution reactor design. A CO_2 -rich gas stream (1) enters the reactor vessel (5) by one or more entryways (e.g., 2, 3, and/or 4). The gas stream then passes over or through a wetted, porous bed of limestone particles within the reactor. This carbonate mass is sprayed (6) and wetted with and partially submerged in a water/carbonic acid solution which is unsaturated with respect to bicarbonate ion. This arrangement exposes the incoming gas to a large surface area of water/solution in the form of droplets and wetted carbonate particle surfaces in (5), facilitating hydration of the entering CO_2 to form a carbonic acid solution within the reactor. CO_2 -depleted gas then exits the reactor (7). The carbonic acid solution formed reacts with the carbonate to form calcium ions and bicarbonate in solution which is either recirculated or bled from the reactor and replaced with unreacted water within the reactor at a rate which maximizes benefit/cost.

Costs

Assuming free access to water (e.g., seawater), preliminary cost per tonne CO₂ sequestered using carbonate dissolution varies from about \$6 to >\$40, which is principally dependent on the distances required for limestone and seawater transport. This includes the cost of crushing (\$1.45) and transporting 2.3 tonnes of limestone (@ \$0.04 tonne⁻¹ km⁻¹) as well the cost of vertically pumping the required seawater (@ \$2.38 m⁻¹). We point out that significant pumping of seawater for single pass cooling is already conducted by many coastal power plants (10⁴ tonnes H₂O/GWh), and this water could be reused for the carbonate dissolution process. The total energy penalty of such a CO₂ capture and sequestration system could be <5% of the energy produced, again depending on plant siting and configuration. By comparison, costs and energy penalties for CO₂ capture technologies alone (without disposal or sequestration) are >\$30 and >27%, respectively (Herzog et al., 1997). Cost estimates of CO₂ capture, transport, and open-ocean injection range from \$90 to \$180/tonne CO₂ (Fujioka et al., 1997). It would appear that carbonate dissolution is economically competitive with other CO₂ capture and sequestration technologies, at least in regions where seawater and limestone are in close proximity to waste CO₂ generation. However, the relatively low cost of CO₂ pipeline transport (<\$0.06 tonne⁻¹ km⁻¹; DOE, 1999) would allow coastal processing of CO₂ produced some distance from the coastline and hence could expand this type of sequestration to inland CO₂ sources. Use of freshwater and disposal of effluent in large lakes or rivers may also be an option for inland sites.

Effectiveness and Capacity

Carbonate dissolution would greatly expand the capacity of the ocean to store anthropogenic carbon while minimizing degassing back to the atmosphere. The ocean already contains carbon as dissolved bicarbonate that is about 10 times that contained in all recoverable oil and coal reserves and about 60 times that of the atmospheric CO₂ reservoir (Morse and Mackenzie, 1990). The only solid reactant needed for the sequestration process, carbonate mineral, is roughly 4,000 times more abundant globally than the carbon contained in oil and coal deposits (Morse and Mackenzie, 1990). Hence, the global reserves of carbonate and liquid water (>10¹⁵ tonnes) are more than sufficient to sequester anthropogenic CO₂ by this method.

Using a box model of ocean chemistry and transport we found (Caldeira and Rau, 2000) that the release of the bicarbonate-charged effluent from carbonate dissolution would more effectively sequester CO₂ over the long term relative to direct CO₂ injection at equivalent ocean depths (Figs. 2 and 3). This has been subsequently confirmed for releases at several different ocean locations and depths in a 3-D ocean general circulation model. Injection of pure CO₂ at depth in the ocean effectively stores most of the injected carbon for hundreds of years or more (Fig. 2). Therefore, the additional slowing of CO₂ leakage that would be gained by releasing carbonate dissolution effluent at the same depth may not be economically significant. Nevertheless, we note that carbonate dissolution can make a major contribution for shallow water releases and greatly improves effectiveness of long-term ocean carbon sequestration regardless of the depth at which the effluent is released.

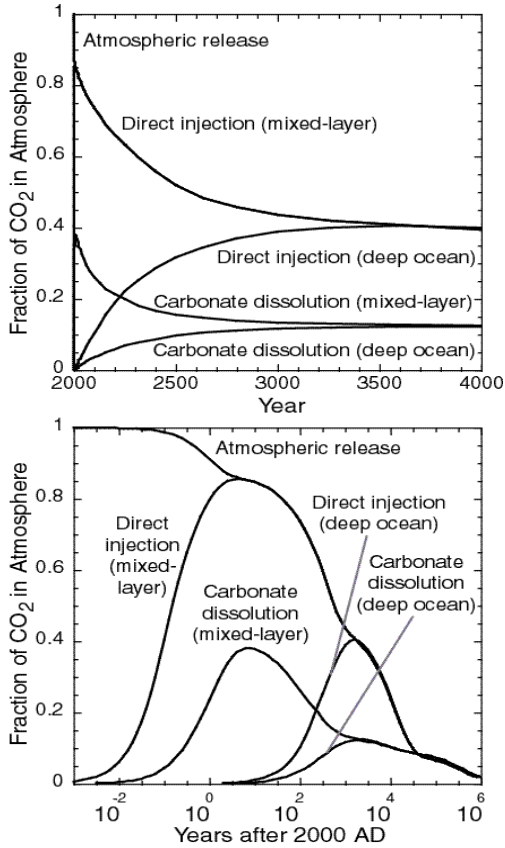
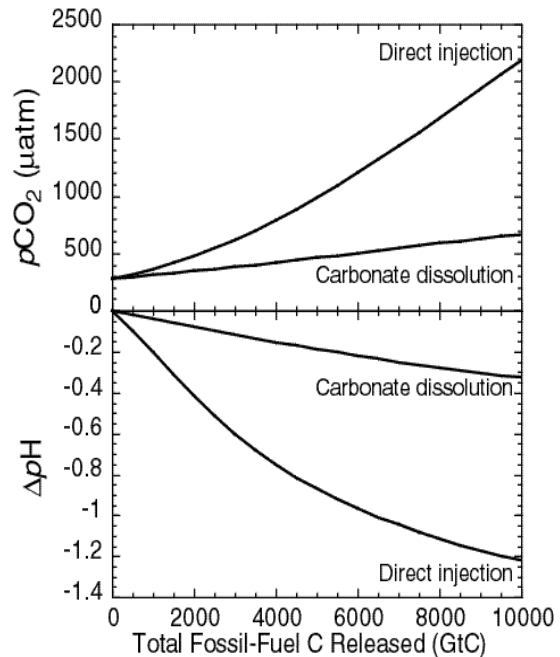


Figure 2. A comparison of the fraction of fossil-fuel CO₂ released that is in the atmosphere as a function of time under five different release scenarios. These scenarios are: atmospheric release, direct injection into the mixed-layer (mean depth: 100m), release of carbonate dissolution effluent into the mixed-layer (100m), direct injection into the deep ocean (1950m), and release of carbonate dissolution effluent into the deep-ocean (1950m), assuming background CO₂ concentrations stabilizing at 750 μatm as specified by the IPCC S750 scenario (Enting et al., 1994). The model was first run in inverse mode to compute the CO₂ emissions to the atmosphere that would yield the S750 atmospheric CO₂ concentrations. Supplementing these atmospheric emissions, all scenarios involve an additional release of fossil-fuel CO₂ equivalent to that present in the pre-industrial atmospheric content. Top panel has a linear horizontal axis; bottom panel is on a log scale.

Figure 3. Comparison of the effects of direct CO₂ injection and the carbonate dissolution technique, both released into the deep-ocean (mean depth: 1950m), on atmospheric CO₂ content (top panel) and deep-ocean pH (bottom panel) 1000 years after injection. If the ocean's anthropogenic carbon capacity were determined by the amount of CO₂ that would shift ocean pH by 0.3 units, then the carbonate dissolution technique would increase the ocean's capacity by roughly a factor of six. With the direct-injection method, for large amounts of anthropogenic CO₂ released, over 45 % of the injected CO₂ is in the atmosphere after 1000 yr. With the carbonate dissolution method, less than 15 % of the initially released CO₂ degasses to the atmosphere.



Environmental Benefits

An increase in ocean acidity (reduction in pH) would be substantially lessened when carbon is added to the ocean in the form of bicarbonate rather than as CO₂ (Fig. 3). This would significantly reduce the harmful effects to marine biota of direct ocean CO₂ additions (Caulfield et al., 1997; Takeuchi et al., 1997; Tamburri et al., 2000). Furthermore, the addition of bicarbonate-rich effluent to the ocean would be environmentally beneficial in that it would counteract the ongoing reduction of ocean pH, alkalinity, and hence biological calcification rates caused by the passive air-to-sea uptake of anthropogenic CO₂ (Kleypas, 1999; Riebesell et al., 2000). We also point out that enhanced carbonate dissolution captures and sequesters CO₂ without the use of any Man-made or exotic chemicals, unlike many current and proposed CO₂ capture schemes (DOE, 1999).

Limitations

While globally very abundant, we view the local availability and transport of the reactants, limestone and water, as the principle limitation of this CO₂ sequestration strategy. The quantities of water required and the need for dilution of the effluent may limit the use of freshwater, although the use of such water and effluent disposal in large lakes or rivers may be an option at inland sites. Favored locations for carbonate dissolution reactors would probably be coastal settings in proximity to limestone sources and seawater. Based on an evaluation of flue-gas CO₂ scrubbing with seawater (without limestone dissolution; IEA, 2000), it is very conservatively estimated that at least 89 power plants with a generating capacity of >35GW are appropriately sited world-wide. However, the relative low cost of CO₂ pipeline transport (see above) would allow coastal processing of CO₂ produced some distance from the coastline, expanding the CO₂ sequestration potential.

Future Activities and Objectives

With modest internal funding from the Energy and Environment Directorate of LLNL and with additional funding pending from NETL/DOE, the following four research activities are being pursued:

Laboratory experiments (bench-top scale) - We plan to demonstrate the carbonate dissolution technique for sequestration of CO₂ in the ocean at the bench-top scale, and to validate/refine existing computers models. We plan to run a relatively concentrated CO₂ gas stream and water (fresh and seawater) into inert chemical reactors of either mixed or plug flow design containing crushed carbonate of known surface area/volume. We will monitor gas and liquid effluent chemistry (including pCO₂, pH, conductivity, alkalinity, and metal-ion concentration) to determine dissolution rates and reactor performance under a range of conditions. Questions to be addressed include: a) impact of flow rate, reactor residence time, bubble size, mixing rate, etc., on the rate of carbonic acid formation (the rate limiting step being CO₂(aq) + H₂O → H₂CO₃), b) impact of particle size and presence/addition of inhibitors/catalysts on the rate of calcite dissolution, c) impact of acidification, degassing and dilution steps on other seawater solutes, d) maximum degree of supersaturation achievable during partial degassing step prior to carbonate precipitation.

Computer modeling of the carbonate dissolution reactor - Based on the preceding experimental results and other relevant information, we will refine our computer model of reactor chemistry and performance. We will explore issues involved in how rate constants and other factors affect model results and fidelity with observations. Once we can confidently simulate the behavior of our reactor vessel, we will then use this model to evaluate and optimize this approach for large-scale applications.

More sophisticated cost estimates - We will use the preceding results to evaluate reactor economics and costs under various scenarios. These will be critically compared to other CO₂ sequestration options.

Three-dimensional global-scale computer modeling - To study the long-term effectiveness of the carbonate dissolution technique for ocean carbon sequestration, we need to understand the fate of the waste water generated by the process after it is released in the ocean as a function of (1) the chemistry of the effluent, and (2) location and depth of release. Both of these factors will affect the effectiveness of carbonate dissolution as a carbon sequestration strategy. We have performed some preliminary schematic model calculations that will test the effectiveness of this technique using sophisticated ocean circulation and chemistry models available at LLNL. We are conducting three-dimensional ocean carbon-cycle/general-circulation model simulations comparing carbon-cycle consequences of atmospheric CO₂ release, direct CO₂ injection, and the carbonate dissolution method.

Based on the outcome of the preceding activities further resources for evaluation and demonstration will be sought to determine feasibility, economics, and potential markets of the process on an industrial and global scale.

Conclusions

In certain settings, the cheap and abundant reactants used by the process, its low technology and energy requirements, and the benign nature of the waste products produced make carbonate dissolution an attractive alternative to other CO₂ capture and sequestration approaches. More research is needed, however, before an accurate assessment of this and other CO₂ sequestration options can be made.

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