

## Capturing and Sequestering Flue-Gas CO<sub>2</sub> Using a Wet Limestone Scrubber

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### Introduction

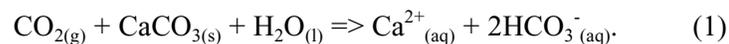
Various methods have been proposed for mitigating anthropogenic CO<sub>2</sub> release to the atmosphere, including storage via enhanced biological uptake on land or in the ocean and via sub-terranean or -marine injection of captured CO<sub>2</sub>. DOE alone is currently investing >\$30M/yr in research on such technologies. We have previously proposed (Rau and Caldeira, 1999; Caldeira and Rau, 2000) an alternate, geochemistry-based capture and sequestration method, which hydrates waste CO<sub>2</sub> with water to produce a carbonic acid solution. This in turn is reacted and neutralized on-site with limestone, thus converting the original CO<sub>2</sub> gas to calcium bicarbonate in solution. 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 CO<sub>2</sub>, but over many millennia (Archer et al., 1997; Murray and Wilson, 1997). The approach is also analogous to the well-established use of wet limestone to desulfurize flue gas, a mature technology that could guide the design and construction of CO<sub>2</sub> capture and sequestration reactors of the type described here. This is a low-tech strategy requiring no separate, costly CO<sub>2</sub> capture and pressurization, and is suitable for retrofitting on existing power plants.

As we will show, in certain settings enhanced carbonate dissolution appears to have important economic and environmental advantages that merit further investigation. We have demonstrated this sequestration method at bench-top scale, and it is now ready for larger scale testing leading to a demonstration pilot plant. This technology should be part of the active research portfolio of carbon management options.

### Approach

We envision allowing CO<sub>2</sub>-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-CO<sub>2</sub> waste gas (CO<sub>2</sub> >10%) is passed through the reactor so as to contact the water and wetted surfaces, forming carbonic acid, which would in turn react with limestone (principally calcium carbonate) to produce HCO<sub>3</sub><sup>-</sup> 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 CO<sub>2</sub> which if contacted with air would lead to CO<sub>2</sub> loss to the atmosphere and precipitation of carbonate. This can be avoided by subsurface ocean release and mixing of the solution, or with partial CO<sub>2</sub> degassing and recapture prior to release in the ocean (Caldeira and Rau, 2000).

Based on reaction 1, it would take 2.3 tonnes of calcium carbonate and 0.3 tonnes of water to react 1 tonne of CO<sub>2</sub> to form 2.8 tonnes of HCO<sub>3</sub><sup>-</sup> in solution. The required volume of a carbonate particle bed or pile for such a reaction will scale directly with particle diameter (see below). If such a bed is continuously bathed in a 3/4-saturated bicarbonate solution (5 x 10<sup>-3</sup> Molar at pCO<sub>2</sub> = 0.15 atm), it would require a water flow and discharge of 10<sup>4</sup> tonnes H<sub>2</sub>O per tonne CO<sub>2</sub> sequestered.

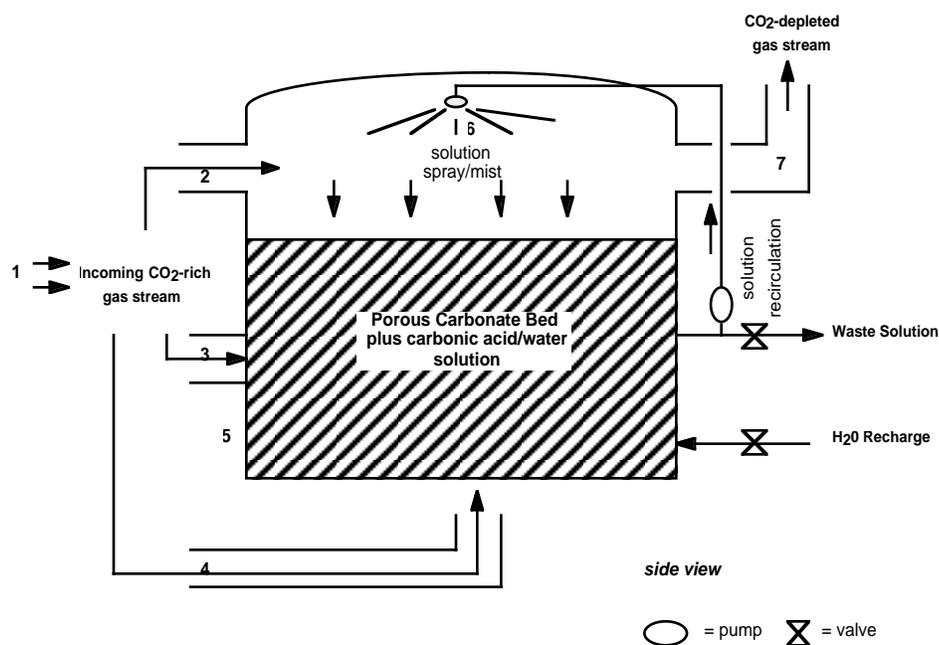


Figure 1. An example of a possible carbonate dissolution reactor design. A CO<sub>2</sub>-rich gas stream (1) enters the reactor vessel (5) by one or more entry-ways (e.g., 2, 3, and/or 4). The gas stream then passes over or through a wetted, porous bed of limestone particles within the reactor. This 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<sub>2</sub> to form a carbonic acid solution within the reactor. CO<sub>2</sub>-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.

The rate at which reaction 1 occurs (on a per unit carbonate surface area per unit time basis) determines the amount of carbonate surface area and time needed to transform a given quantity of CO<sub>2</sub> to HCO<sub>3</sub><sup>-</sup>. In turn, specifying a surface area/volume (A/V) of the carbonate particles determines the volume of the reactor required for a given quantity of CO<sub>2</sub> conversion. While previous estimates of these parameters have been made (Rau and Caldeira, 1999), the reaction rates used were based for the most part on idealized dissolution experiments using pure calcite mineral under conditions where the diffusional boundary layer around the mineral surfaces were greatly diminished (via stirring). To provide a more realistic assessment of reaction rates, an experimental, 370 ml (internal volume) bench-scale reactor was used to measure the dissolution rate of limestone in either distilled- or sea-water that was equilibrated with various %CO<sub>2</sub> gas streams, and various water flushing rates and internal stirring rates. The results of these experiments yielded dissolution rates ranging from roughly 10<sup>-11</sup> to 10<sup>-9</sup> mols cm<sup>-2</sup> s<sup>-1</sup> with significant, positive sensitivity to flow rate, stir rate, and CO<sub>2</sub> concentration (Fig. 2). Dissolution rates were generally higher in seawater than in distilled water treatments under otherwise identical conditions (Fig. 2).

Assuming the conditions and results of the 15% CO<sub>2</sub>, low-stir-rate and low-flow rate treatments are characteristic of a large scale reactor, a reaction rate of about 10<sup>-10</sup> mols cm<sup>-2</sup> s<sup>-1</sup> is implied (Fig. 2). With a limestone particle diameter of 1mm yielding an A/V of about 4.4 x10<sup>3</sup> m<sup>2</sup>/m<sup>3</sup>, roughly 60 m<sup>3</sup> of such limestone particles would be needed to react 1 tonne of CO<sub>2</sub> per day. For an equilateral (cubic) reactor, this equates to an areal reaction rate of about 15 tonnes CO<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup>, or about one million times the CO<sub>2</sub> sequestration rate in managed forests or algal ponds. The experiments show that this density of CO<sub>2</sub> conversion to HCO<sub>3</sub><sup>-</sup> could be increased by as much as an order of magnitude by increasing stirring and flushing rate, perhaps achieved in a full-scale reactor by vigorous bubbling of flue gas within the reactor or by actively recirculating the partially-reacted solution.

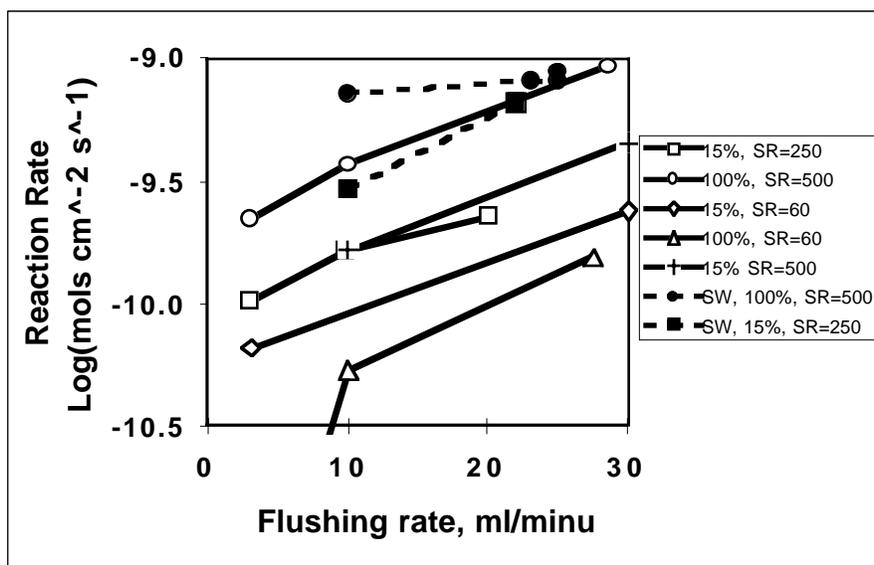


Figure 2. Conversion rate of CO<sub>2</sub> to HCO<sub>3</sub><sup>-</sup> in an experimental carbonate dissolution reactor flushed by distilled water or seawater (SW) equilibrated with the % CO<sub>2</sub> shown, and at the various reactor flushing rates and internal stir rates (SR) indicated. Stir rates are in revolutions per minute.

### Costs

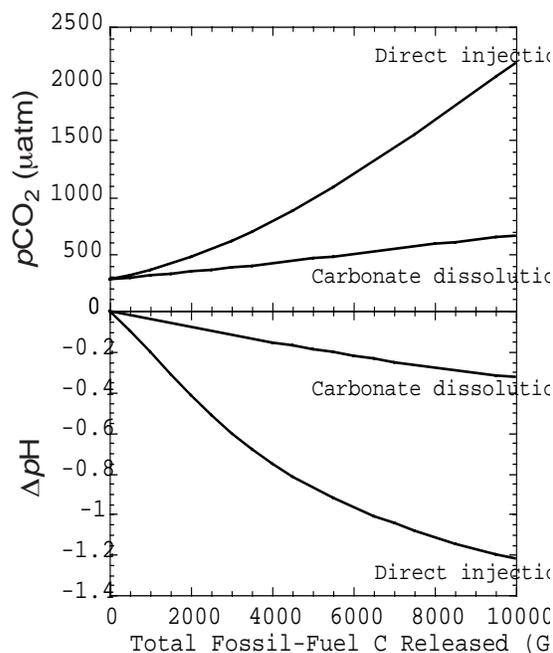
Assuming free access to water (e.g., recycled cooling water or seawater), preliminary cost per tonne CO<sub>2</sub> sequestered using carbonate dissolution could be as low as \$12, the cost for a given location being principally determined by the distances required for limestone and seawater transport. Earlier calculations showed that a significant fraction of US waste CO<sub>2</sub> could be captured and sequestered for around \$20/tonne CO<sub>2</sub> (Rau and Caldeira, 1999; Sarv and Downs, 2002). Such estimates include the cost of 2.3 tonnes of crushed limestone (~\$11), its transportation (@ ~\$0.04 tonne<sup>-1</sup> km<sup>-1</sup>) as well as the cost of vertically pumping the required seawater (@\$2.38 m<sup>-1</sup>). The total energy penalty of such a CO<sub>2</sub> capture and sequestration system could be <5% of the energy produced, again depending on plant siting and configuration (Sarv and Downs, 2002). By comparison, costs and energy penalties for CO<sub>2</sub> capture technologies alone (without disposal or sequestration) are >\$30/tonne CO<sub>2</sub> and >27%, respectively (Herzog et al., 1997). Cost estimates of CO<sub>2</sub> capture, transport, and open-ocean injection range from \$90 to \$180/tonne CO<sub>2</sub> (Fujioka et al., 1997). At least in regions where seawater and limestone are in close proximity to waste CO<sub>2</sub> generation, it would appear that carbonate dissolution is much more economical than CO<sub>2</sub> capture and direct injection technologies. The relative low cost of CO<sub>2</sub> pipeline transport (<\$0.06 tonne<sup>-1</sup> km<sup>-1</sup>; DOE, 1999) could allow coastal processing of CO<sub>2</sub> produced and captured some distance from the coastline and hence could expand the capacity of this type of sequestration to inland CO<sub>2</sub> 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 CO<sub>2</sub> 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 (>10<sup>15</sup> tonnes) are more than sufficient to sequester anthropogenic CO<sub>2</sub> 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 CO<sub>2</sub> over the long term relative to direct CO<sub>2</sub> injection at equivalent ocean depths (Fig. 3). This has been subsequently confirmed for releases at several different ocean locations and depths in a 3-D ocean general circulation model (e.g., Fig. 4). Injection of pure CO<sub>2</sub> at great depth in the ocean effectively stores most of the injected carbon for hundreds of years or more (Caldeira and Rau, 2000). Therefore, the additional slowing of CO<sub>2</sub> 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 less costly shallow water releases and greatly improves effectiveness of long-term ocean carbon sequestration regardless of the depth at which the effluent is released (Fig. 4).

Figure 3. Comparison of the effects of direct CO<sub>2</sub> injection and the carbonate dissolution technique, both released into the deep-ocean (mean depth: 1950m), on atmospheric CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> released, over 45% of the injected CO<sub>2</sub> is in the atmosphere after 1000 yr. With the carbonate dissolution method, less than 15% of the initially released CO<sub>2</sub> degasses to the atmosphere. (From Caldeira and Rau, 2000)



Leakage of fossil-fuel CO<sub>2</sub> from the ocean  
25 years after a 10 PgC fossil-fuel injection at 700 m near San Francisco

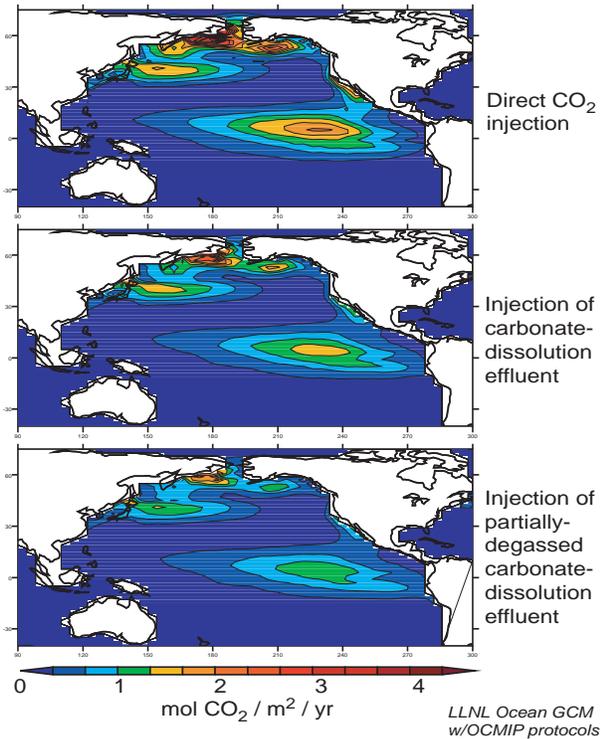


Figure 4. Ocean general circulation model results showing the greater effectiveness (less CO<sub>2</sub> leakage to atmosphere) inherent in the injection of carbonate dissolution effluent as compared to direct injection of molecular CO<sub>2</sub> at equivalent depth.

### Environmental Impacts/Benefits

An increase in ocean acidity (reduction in pH) is a serious environmental issue caused either by the diffusive uptake of anthropogenic CO<sub>2</sub> from the atmosphere or the proposed purposeful injection of CO<sub>2</sub> into the ocean. Storing waste CO<sub>2</sub> in the form of calcium bicarbonate ion rather than as dissolved CO<sub>2</sub> (i.e., carbonic acid) substantially lessened the increase in acidity per tone of carbon added to the ocean (Fig. 3), reducing harmful effects to marine biota of direct ocean CO<sub>2</sub> additions (Caulfield et al., 1997; Takeuchi et al., 1997; Tamburri et al., 2000). In fact, the addition of calcium 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 and productivity (Kleypas, 1999; Riebesell et al., 2000). For example, such an approach could protect coral reefs from the corrosive effects of ocean CO<sub>2</sub> elevated due to anthropogenic CO<sub>2</sub> invasion (Kleypas et al., 1999). The carbonate-dissolution effluent could be adjusted to produce high- or relatively low-carbonate-ion concentrations, depending on local environmental considerations and costs. We also point out that enhanced carbonate dissolution captures and sequesters CO<sub>2</sub> without the use of any exotic and potentially harmful chemicals, unlike some current and proposed CO<sub>2</sub> capture schemes (DOE, 2003).

Nevertheless, negative environmental impacts could result downstream from the release of the reactor effluent solution whose oxygen concentration would be reduced through partial equilibration with flue-gas streams that typically contain 2-4% O<sub>2</sub>. There may also be impurities released into the effluent solution from the limestone or the flue gas streams that could be environmentally impactful. To our knowledge no previous studies have been conducted on the effects of effluent streams of this type, thus direct experimentation will be required to quantify such impacts. Also, the expanded demand for limestone would increase surface mining of this mineral with likely negative environmental consequences.

## Limitations

While globally very abundant, we view the local availability and transport of the reactants, limestone and water, as the principle limitation of this CO<sub>2</sub> sequestration strategy. The quantities of water required and the need for dilution of the effluent may limit the use of freshwater, and siting of reactors at inland sites. Favored locations for carbonate dissolution would probably be coastal settings in close proximity to limestone sources and seawater. Even with this limitation it is estimated that about 2.2 billion tonnes CO<sub>2</sub>/yr (12% of the US emissions from electricity production) could be captured and sequestered by carbonate dissolution at a cost of \$21/tonne CO<sub>2</sub> (Sarv and Downs, 2002). However, the relative low cost of CO<sub>2</sub> pipeline transport (see above) would allow coastal processing of CO<sub>2</sub> produced some distance from the coastline, expanding the CO<sub>2</sub> sequestration potential. Limitations posed by possible environmental impacts of carbonate dissolution require further study.

## Future Activities and Objectives

With modest internal funding from LLNL we have conducted preliminary bench-top scale experiments on reactor kinetics and have modeled the fate and impacts of the waste effluent in the ocean at various scales. We now seek funding to expand this research to more realistic, prototype experimental reactors with which to more accurately predict the behavior, efficacy, and costs in scaled-up industrial applications. The upstream and downstream environmental impacts associated with such reactors also need to be studied. Such research will provide a more accurate assessment of this low-tech CO<sub>2</sub> capture/sequestration approach, allowing for better comparisons to other CO<sub>2</sub> mitigation technologies.

## Conclusions

In certain settings, the cheap and abundant reactants used by carbonate dissolution, its low technology and energy requirements, and the relatively benign nature of the waste products produced make carbonate dissolution an attractive alternative to other CO<sub>2</sub> capture and sequestration methodologies. Thus, enhanced carbonate dissolution deserves to be included in the portfolio of CO<sub>2</sub> mitigation options the DOE and others are researching.

## References

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