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Reducing Energy-Related CO_2 Emissions Using Accelerated Limestone Weathering

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Abstract.

Following earlier descriptions, the use and impacts of accelerated weathering of limestone (AWL; reaction: $CO_2 + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2(HCO_3^-)$) as a CO_2 capture and sequestration method is further explored. Since ready access to the ocean is likely an essential requirement for AWL, it is shown that significant limestone resources are relatively close to a majority of CO_2-emitting power plants along the coastal US. Furthermore, waste fines, representing more than 20% of current US crushed limestone production ($>10^9$ tonnes/yr), could be used in many instances as an inexpensive or free source of AWL carbonate. With limestone transportation to coastal sites then as the dominant cost variable, CO_2 sequestration (plus capture) costs of \$3-\$4/tonne are achievable in certain locations. While there is vastly more limestone and water on earth than that required for AWL to capture and sequester all fossil fuel CO_2 production, the transportation cost of bringing limestone, seawater, and waste CO_2 into contact likely limits the method's applicability to perhaps 10-20% of US point-source emissions. Using a bench-scale laboratory reactor, it is shown that CO_2 sequestration rates of 10^{-6} to 10^{-5} moles/sec per m^2 of limestone surface area are readily achievable using seawater. This translates into reaction densities as high as $2x10^{-2}$ tonnes CO_2 $m^{-3}day^{-1}$, highly dependent on limestone particle size, solution turbulence and flow, and CO_2 concentration. Modeling of AWL end-solution disposal in the ocean shows significantly reduced effects on ocean pH and carbonate chemistry relative to those caused by direct CO_2 disposal into the atmosphere or ocean. In fact the increase in ocean Ca^{2+} and bicarbonate offered by AWL should significantly enhance the growth of corals and other marine calcifiers whose health is currently being threatened by anthropogenic CO_2 invasion and pH reduction in the ocean.

Introduction

As reviewed in this issue of *Energy* and elsewhere (e.g. [1,2]), the climate and environmental impacts of our current, carbon-intensive energy usage demands that effective and practical energy alternatives and CO_2 mitigation strategies be found. As part of this effort, various means of capturing and storing CO_2 generated from fossil-fuel-based energy production are being investigated (e.g. [3,4]). One of the proposed methods involves a geochemistry-based capture and sequestration process [5,6] that hydrates point-source, waste CO_2 with water to produce a carbonic acid solution. This in turn is reacted and neutralized with limestone, thus converting the original CO_2 gas to calcium bicarbonate in solution, the overall reaction being:

$$CO_{2(g)} + H_2O_{(l)} + CaCO_{3(s)} \rightarrow Ca^{2+}{}_{(aq)} + 2HCO_3^-{}_{(aq)}. \quad (1)$$

The dissolved calcium bicarbonate produced 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 continental and marine carbonate weathering which will otherwise naturally consume anthropogenic CO_2, but over many millennia (e.g. [7,8,9]). We identify the enhanced form of this process as Accelerated Weathering of Limestone or AWL. Previously, it has been shown that AWL can effectively convert a significant fraction of US CO_2 emissions to long-term storage as bicarbonate in the ocean, while avoiding or possibly reversing environmental impacts associated with either the ongoing passive or the proposed active injection of CO_2 into the ocean [6,10]. Being analogous to the wide-spread use of wet limestone to desulfurize flue gas, AWL reactors could be retrofitted to many existing coastal power plants at a typical cost estimated to be \$20-\$30/tonne CO_2 mitigated [5,11]. This paper further explores limestone availability, cost, transportation, and reaction kinetics as well as ocean and environmental impacts, and the overall economics and practicality of AWL CO_2 mitigation.

Limestone and Seawater Availability

Because the global abundance of water (i.e., seawater) and carbonate is orders of magnitude larger than the entire global reservoir of fossil fuels [12], all anthropogenic emissions of CO_2 could theoretically be mitigated by reaction 1. Indeed, over geologic time scales significant, natural increases in atmospheric CO_2 have been moderated and consumed via carbonate weathering, and the same process will eventually consume the majority of anthropogenic CO_2 as well [7,8]. But if we wait for nature to perform this task, the earth in the meantime would be subjected to much higher atmospheric CO_2 than at present, and for many thousands of years. Thus it is worth considering proactively speeding up the carbonate weathering process. If the employment of reaction 1 to reduce CO_2 emissions is then not in principle reactant-limited, what are the practical limitations to AWL as a CO_2 capture and sequestration tool?

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_2 to form 2.8 tonnes of HCO_3^- in solution. While pure $CaCO_3$ (calcite and aragonite) is mined and commercially available, its relatively low abundance in this form and its high cost prohibit its use on the scale considered here. Rather it is envisioned that much more abundant and inexpensive limestone (containing 92-98% $CaCO_3$) would be used. US production of this mineral is presently 10^9 tonnes/yr [13], and while there are no figures available on the size of the US limestone reserve, it is reasonable to assume that it is sufficient to satisfy current US demand for many decades if not centuries. Channeling the entire yearly US limestone production to AWL could consume roughly 18% of the annual CO_2 generated by electricity production in the US. This implies that a substantial increase in the US limestone mining rate or foreign importation would be required to accommodate the US demands of both extensive AWL and conventional limestone uses.

There is an important caveat to the preceding conclusion in that currently more than 20% of US limestone production and processing results in waste limestone fines (<10 mm) that have little or no market value and are accumulating at limestone mining and processing sites [14,15]. This suggests that a sizeable, free or low-cost source of limestone could be available for AWL whose use could also help alleviate the significant limestone waste problem.

But even if a free source of limestone was available, it has been recognized that the cost of transporting such limestone to AWL reactors is a critical factor in the overall economics of the process [5,11]. Also, because of the significant quantities of water required to react the CO_2 and to carry and dilute the resulting bicarbonate ($>10^4$ tonnes H_2O/tonne CO_2 [5]), AWL reactors in close proximity to seawater would be at a distinct cost advantage. Even with this geographic limitation, about 12% of CO_2 emissions from US electricity production occurs at plants within 10 km of the US coastline [11]. Fortuitously, the majority of this coastline is also within 400 km of known limestone reserves [16]. This is especially true of the southern and eastern seaboards, which also have the highest density of coastal US power plants and coastal electricity-related CO_2 production. For example there is more than 20 GW of fossil-fueled power generation ($\approx$ 100 billion tonnes CO_2 emitted/yr) by coastal power plants in Florida [11], a state that essentially is entirely underlain by carbonate deposits [17]. In such ideal settings, if both limestone and its transportation costs were negligible, the CO_2 mitigation cost offered by AWL would be \$3 - \$4/tonne CO_2 based on previous cost analyses [5,11]. This would especially pertain if the hundreds of millions of gallons of seawater already pumped and used for cooling by these plants each day were subsequently used as a "free" AWL water source.

The preceding baseline CO_2 capture and sequestration cost would significantly out-compete most other current or proposed abiotic technologies and is near DOE's target of \$2.73/tonne CO_2 mitigated [4]. However, the number of ideal sites and hence the volume of CO_2 that could be treated at this very attractive cost would be small. What cost might be attainable in the more numerous but less favorable settings?

Again assuming free access to seawater and free limestone, the transportation cost of limestone using various modes is listed in Table 1. Assuming a base capital, operating, and maintenance (COM) cost of \$4/tonne CO_2 mitigated, and with carbonate supplied via 2.5 tonnes of low-grade limestone (92% $CaCO_3$), a limestone transport distance of 200 km yields an AWL CO_2 mitigation cost of about \$6, \$9, \$21, or \$48 per tonne CO_2 using freighter, barge, train, or truck transportation, respectively (Table 1). If limestone must first be purchased at a typical market price of \$5/tonne, this adds \$12.50 to each of the preceding calculations , with the resulting mitigation cost ranging from \$18 to \$61 per tonne CO_2 using the preceding transportation modes. In turn, if fresh seawater rather than recycled cooling water must be used and pumped 2 vertical meters the cost increases to \$23 to \$66/tonne CO_2 (Table 1). By these calculations it is seen that in all but the least ideal cases AWL can be cost-competitive with other forms of CO_2 capture and sequestration, and is often below the cost of amine CO_2 capture alone (generally

>\$30/tonne CO_2 [18]). AWL will clearly be more economical under circumstances where limestone and water are low-cost and close at hand.

Alternative Reactor Sitings

The preceding assumes an AWL reactor sited at the source of waste CO_2 (i.e. a power plant) and to which limestone and seawater are transported. While close reactor proximity to the ocean would seem required both to supply water and to dispose of the waste solution, this would not preclude the treatment of waste CO_2 produced inland and transported to coastal AWL reactors sited at or near limestone quarries. Transport of CO_2 is inexpensive (\$0.06 $tonne^{-1}$ km^{-1} [19]) relative to the cost of transporting the AWL equivalent (2.5 tonnes) of limestone (Table 1). However, such CO_2 transport requires initial CO_2 separation, capture, and liquefaction, with the associated technology and energy costs that are presently significant, as mentioned above. Still, if inexpensive CO_2 capture/separation is developed, piping CO_2 to coastal AWL reactors could prove cost-competitive with other forms of CO_2 sequestration such as underground storage, especially in regions where the underlying geology is not amenable to CO_2 retention.

Another alternative places AWL reactors on or in seagoing barges or ships that would bring both the limestone and the AWL process to coastal CO_2 point sources accessible by seagoing vessel. In this way the capital expenditure of an AWL reactor and limestone transport are merged, avoiding potentially costly land-siting of the reactor, and with the ocean readily accessible as a water source and for effluent disposal. This configuration would require that flue gas be piped to and reacted within the docked vessel. Once the ship's supply of limestone had been exhausted by AWL, the ship would be replaced by another loaded vessel/reactor. On its way back to port for limestone reloading, the vessel could dispose of the small amount of unreacted limestone spoils at sea, subject to ocean dumping regulations. The preceding would obviously only be amendable to power plants (or coastal CO_2 sources supplied by pipeline) that are dock-accessible. It also assumes that a limestone-supplying port is within a reasonable shipping distance to the CO_2 source to be mitigated. Rather than the construction and use of new AWL-capable ships, the retrofitting and upgrading of retired or underutilized vessels should be considered as a means of both reducing costs and extending ship utility. Because of their existing hold configuration, freighters and especially tankers would be particularly attractive for such retrofits.

Reaction Rates and Densities

The rate at which reaction 1 occurs (on a per unit limestone surface area per unit time basis) determines the amount of carbonate surface area and time needed to transform a given quantity of CO_2 to HCO_3^-. In turn, specifying a surface area per volume (A/V) of the carbonate particles determines the basic size of the reactor required for a given CO_2 conversion rate. While previous estimates of these parameters have been made [5], the reaction rates used were based for the most part on idealized dissolution experiments using pure calcite mineral in distilled water under conditions where the diffusional boundary layer around the mineral surfaces were greatly diminished (via stirring). To provide a more realistic assessment of the reaction rate of impure limestone, an experimental, 370 ml (internal volume) bench-scale reactor was used to measure the dissolution rate of limestone in either distilled H_2O or seawater equilibrated with various $\%CO_2$ air streams, and with various water flushing rates, and internal stirring rates (see Figure 1 legend). The results of these experiments yielded dissolution rates ranging from roughly 10^{-7} to 10^{-5} mols m^{-2} s^{-1} with positive sensitivity to flow rate, stir rate, and CO_2 concentration (Fig. 1). Dissolution rates in seawater were equal to or higher than those in distilled water under otherwise identical conditions (Fig. 1), i.e., the impurities in seawater do not significantly diminish the AWL reaction rate.

Assuming the conditions and results of the 15% CO_2, low-stir-rate and low-flow rate treatments would be characteristic of a large-scale reactor, a reaction rate of about 10^{-6} mols m^{-2} s^{-1} is implied (Fig. 1). A limestone particle diameter of 1mm (within the range typical of waste limestone fines discussed above) yields an A/V of 4.4 x10^3 m^2/m^3 or higher depending on the deviation of true particle shape from that of a sphere. Therefore a maximum of 60 m^3 of such limestone particles would be needed to react 1 tonne of CO_2 per day. For a cubic reactor volume (roughly 4m x 4m x 4m), this equates to an areal reaction rate of at least15 tonnes CO_2 m^{-2} day^{-1}, or about one million times greater than optimum CO_2 uptake and sequestration rates in managed forests or algal ponds [19]. The experiments show that this density of CO_2 conversion to HCO_3^- could be enhanced by increasing reactor solution stirring and flushing rate. This could be achieved in a full-scale reactor by vigorous bubbling of flue gas within the reactor or by actively recirculating the partially-reacted solution, but with added energy and cost penalties.

Base on the above rates, reaction densities on the order of 10^{-2} tonnes CO_2 m^{-3} day^{-1} appear attainable. This means a 20% reduction of the CO_2 emissions from a typical 500MW coal-fired power plant (10^4 tonnes CO_2/day x 0.2 = $2x10^3$ tonnes CO_2/day) would require an AWL reactor volume of $2x10^5$ m^3, roughly equivalent to a 60m cube. The reactor size required for a given CO_2 mitigation will be highly dependent on limestone particle size, water/gas/solids contacting efficiency, and CO_2 concentration, as well as the purity of the limestone. However, while particle size reduction will theoretically increase limestone surface area and hence reaction density within a reactor, water space between particles and hence flow resistance and contacting efficiency will be reduced. Further research and experimentation is needed in order to determine how to optimize AWL reactor designs for the best cost/benefit.

Effectiveness

Using a box model of ocean chemistry and transport Caldeira and Rau [6] showed that the release of the bicarbonate-charged effluent from carbonate dissolution would more effectively sequester CO_2 over the long term relative to direct CO_2 injection at equivalent ocean depths (Fig. 2). 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. 3). Injection of pure CO_2 at great depth in the ocean effectively stores most of the injected carbon for hundreds of years or more [6]. Therefore, the additional slowing of CO_2 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. 3).

Environmental Impacts/Benefits

An increase in ocean acidity (reduction in pH) is a serious environmental issue caused either by the ongoing diffusive uptake of anthropogenic CO_2 from the atmosphere or the proposed purposeful injection of CO_2 into the ocean (e.g., [10]). Storing waste CO_2 in the form of bicarbonate balanced by calcium ions rather than as dissolved CO_2 (i.e., carbonic acid; bicarbonate balanced by H^+) substantially lessens the increase in acidity per tone of carbon added to the ocean (Fig. 2), while reducing harmful effects to marine biota of direct ocean CO_2 additions [20,21,22]. In fact 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 and productivity [23,24]. Indeed, addition of calcium and/or bicarbonate ions to seawater has been shown to significantly enhance the calcification and growth rate of marine corals (e.g., [25,26,27]). We also point out that AWL captures and sequesters CO_2 without the use of any exotic or toxic chemicals, unlike CO_2 capture methods using amines [4].

Nevertheless, negative marine environmental impacts could result downstream from the release of the reactor effluent solution. For example, oxygen concentration would be reduced in the effluent through partial equilibration with flue-gas streams, typically containing only 2-4% O_2. There may also be impurities released into the effluent solution from the limestone or the flue gas that could be biotically impactful. This could be especially relevant in AWL processing of flue gas from coal-fired power plants, where SO_x, NO_x, trace element, and heavy metal contamination are characteristic. Processing relatively clean flue gas from natural-gas-fired plants or from integrated gasification combine cycle generators would be advantageous in this regard. To our knowledge no previous studies have investigated the marine impacts of effluent streams like those that would emanate from AWL. New, direct experimentation will be required to quantify such effects. We point out, however, that the ocean naturally receives and accommodates about 2 $\times 10^9$ tonnes of dissolved calcium bicarbonate per year produced from continental carbonate weathering as delivered by rivers [12].

With regard to environmental effects of AWL on land, the current production of crushed stone creates environmental impacts, and these need to be considered for AWL. These impacts include dust and noise generated in mining and processing, but these are relatively benign and confined to the area at or very near the quarries. Most impacts can be controlled or kept within permissible limits through careful quarry planning and by employing best management practices. However, poorly designed or careless operated quarries, especially in areas of active karst (which occurs in some carbonate rock terrains), have the potential to create far-reaching, serious environmental impacts including lowering of the water table, changing surface- and ground-water flow, pollution of ground water, and sinkhole collapse [28].

The increased transportation of limestone required for AWL would also generate dust and noise en route and during off-loading, and depending on the magnitude of AWL deployment, could significantly tax the existing transportation infrastructure. Additionally, because some fraction of the limestone will not be reacted or reactible, perhaps 5-10% of the original limestone mass transported to AWL reactors would ultimately need to be removed and transported to appropriate waste sites. In addition to ocean disposal of the solid waste (mentioned above), disposal might be performed by loading this waste onto the otherwise empty, overland transports that return to the limestone source, wherein the waste could be used to fill in the original limestone mining excavations. This would make efficient use of the transportation stream and would help reclaim unsightly mining impacts while avoiding the need for new waste sites.

In summary, some environmental effects would result from limestone mining and transportation, but we point out that large-scale mineral extraction and transport is currently an integral part of energy production (e.g., coal, natural gas). We also note that limestone is already used on a large scale for environmental benefit, flue gas desulfurization [29] and acid mine waste neutralization [30] being prime examples. While the benefits of AWL would appear to outweigh whatever environmental and societal impacts might accrue, further assessment of this technology's terrestrial, marine, and human effects is required.

Conclusions

In the appropriate settings AWL is an attractive option for CO_2 mitigation because: 1) the required reactants are relatively inexpensive, abundant, and environmentally benign, 2) the technology is relatively simple, low-cost, and amenable to power plant retrofitting, even in developing countries, 3) the storage is effective and long-term, and 4) the waste products are stable and may have net positive environmental effects for marine life. All of these features derive from the fact that AWL merely enhances Nature's own CO_2 mitigation mechanism, carbonate weathering. More research is needed, however, to more accurately assess the costs, benefits, and impacts of this means of reducing the carbon intensity of global power generation.

Acknowledgements

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Table 1. Cost of accelerated limestone weathering under various water, limestone and transport cost assumptions. Base COM (capital, operating, and maintenance) cost (\$/tonne CO_2 captured and sequestered) under the assumption that waste (free) limestone and cooling water are immediately available with no transportation required (estimation derived from Sarv and Downs [11]). The increase to COM with the addition of limestone, transport, and water costs are listed for the respective transportation options, and for the cost rate, weight, and distances denoted. Limestone cost and transport cost rates from Everist and Burhans [31], assuming that 2.5 tonnes limestone is required per tonne CO_2 mitigated (see text). Water tonnage and pumping cost rate from Rau and Caldeira [5].

Limestone Transportation Mode-->:	truck	train	barge	freighter
Base COM (\$/tonne CO2)	**\$4.00**	**\$4.00**	**\$4.00**	**\$4.00**
Limestone transport cost rate (\$ $tonne^{-1}km^{-1}$)	\$0.089	\$0.034	\$0.010	\$0.003
Limestone transport cost (rate x 2.5 tonnes x 200 km)	\$44.33	\$17.05	\$4.77	\$1.71
COM with costed limestone transport (\$/tonne CO2)	**\$48.33**	**\$21.05**	**\$8.77**	**\$5.71**
Limestone cost (2.5 tonnes x \$5/tonne)	\$12.50	\$12.50	\$12.50	\$12.50
COM with costed limestone and transport (\$/tonne CO2)	**\$60.83**	**\$33.55**	**\$21.27**	**\$18.21**
Pumped water cost (\$2.38 m^{-1} per 10^4 tonnes x 2 m)	\$4.76	\$4.76	\$4.76	\$4.76
COM with costed limestone, transport, and water (\$/tonne CO2)	**\$65.59**	**\$38.31**	**\$26.03**	**\$22.97**

Figure 1. Conversion rate of CO_2 to HCO_3^- in an experimental carbonate dissolution reactor flushed with distilled water (DW) or seawater (SW) equilibrated with the % CO_2 shown, and at the various reactor solution flow rates (FR) and internal stir rates (SR) indicated. Stir rates are in revolutions per minute. Conversion rate = $([Ca]_{out} - [Ca]_{in})$ x FR / area, where [Ca] refers to the concentration of Ca^{2+} in the solutions entering or leaving a 370ml reactor containing 5 g of limestone particles (size range 425-850 microns) under the respective solution %CO_2, FR, and SR conditions at steady state and at room temperature and pressure, and where area refers to the total surface area of the limestone particles as determine by mean particle geometry. [Ca] was determined by ICP-ES of discrete solution samples.

Figure 2. Comparison of the effects of direct CO_2 injection and the carbonate dissolution technique, both released into the deep-ocean (mean depth: 1950m), on atmospheric CO_2 content (top panel) and deep-ocean *p*H (bottom panel) 1000 years after injection. If the ocean's anthropogenic carbon capacity were determined by the amount of CO_2 that would shift ocean *p*H 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_2 released, over 45 % of the injected CO_2 is in the atmosphere after 1000 yr. With the carbonate dissolution method, less than 15 % of the initially released CO_2 degasses to the atmosphere. (from Caldeira and Rau, [6]).

Figure 3. Ocean general circulation model results showing the greater effectiveness (less CO_2 leakage to atmosphere) inherent in the injection of carbonate dissolution effluent as compared to molecular CO_2 at equivalent depths.

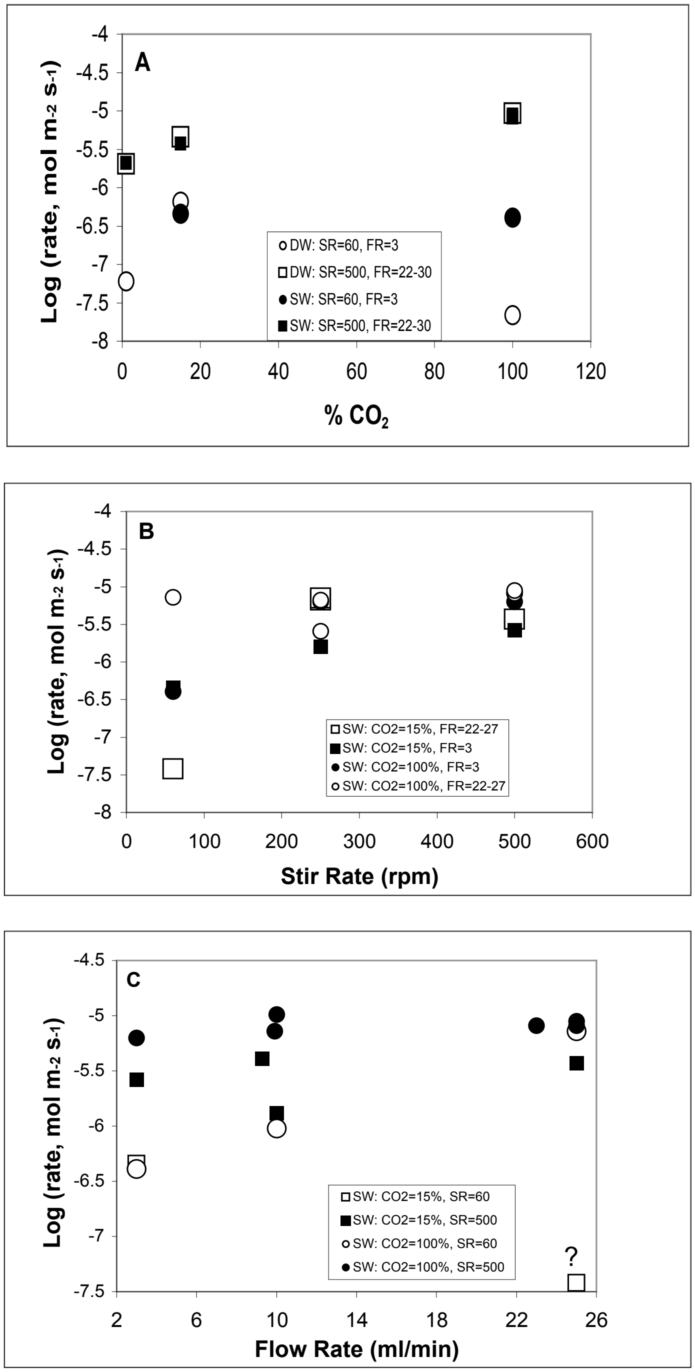
A
Log (rate, mol m-2 s-1)
-4
-4.5
-5
-5.5
-6
-6.5
-7
-7.5
-8
0
20
40
60
80
100
120
% CO2
DW: SR=60, FR=3
DW: SR=500, FR=22-30
SW: SR=60, FR=3
SW: SR=500, FR=22-30
B
Log (rate, mol m-2 s-1)
-4
-4.5
-5
-5.5
-6
-6.5
-7
-7.5
-8
0
100
200
300
400
500
600
Stir Rate (rpm)
SW: CO2=15%, FR=22-27
SW: CO2=15%, FR=3
SW: CO2=100%, FR=3
SW: CO2=100%, FR=22-27
C
Log (rate, mol m-2 s-1)
-4.5
-5
-5.5
-6
-6.5
-7
-7.5
2
6
10
14
18
22
26
Flow Rate (ml/min)
SW: CO2=15%, SR=60
SW: CO2=15%, SR=500
SW: CO2=100%, SR=60
SW: CO2=100%, SR=500
?

Figure 1

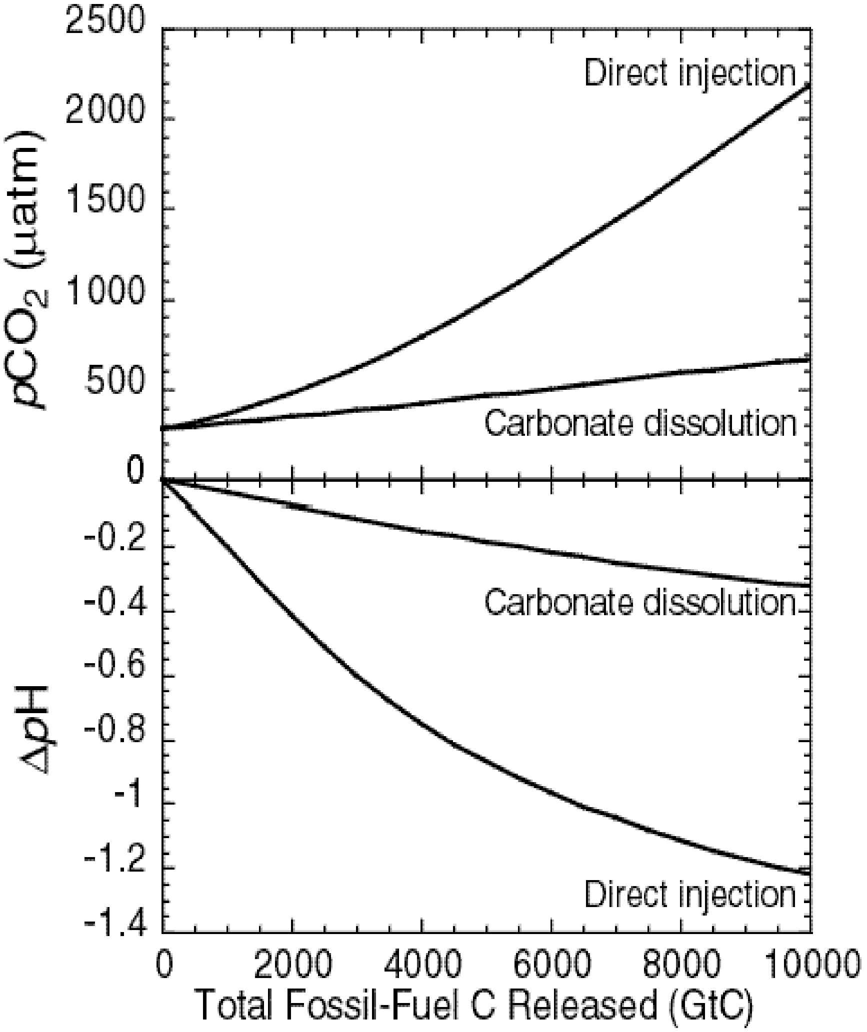
2500
2000
1500
1000
500
0
pCO_2 (µatm)
Direct injection
Carbonate dissolution
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
ΔpH
Carbonate dissolution
Direct injection
0
2000
4000
6000
8000
10000
Total Fossil-Fuel C Released (GtC)

Figure 2

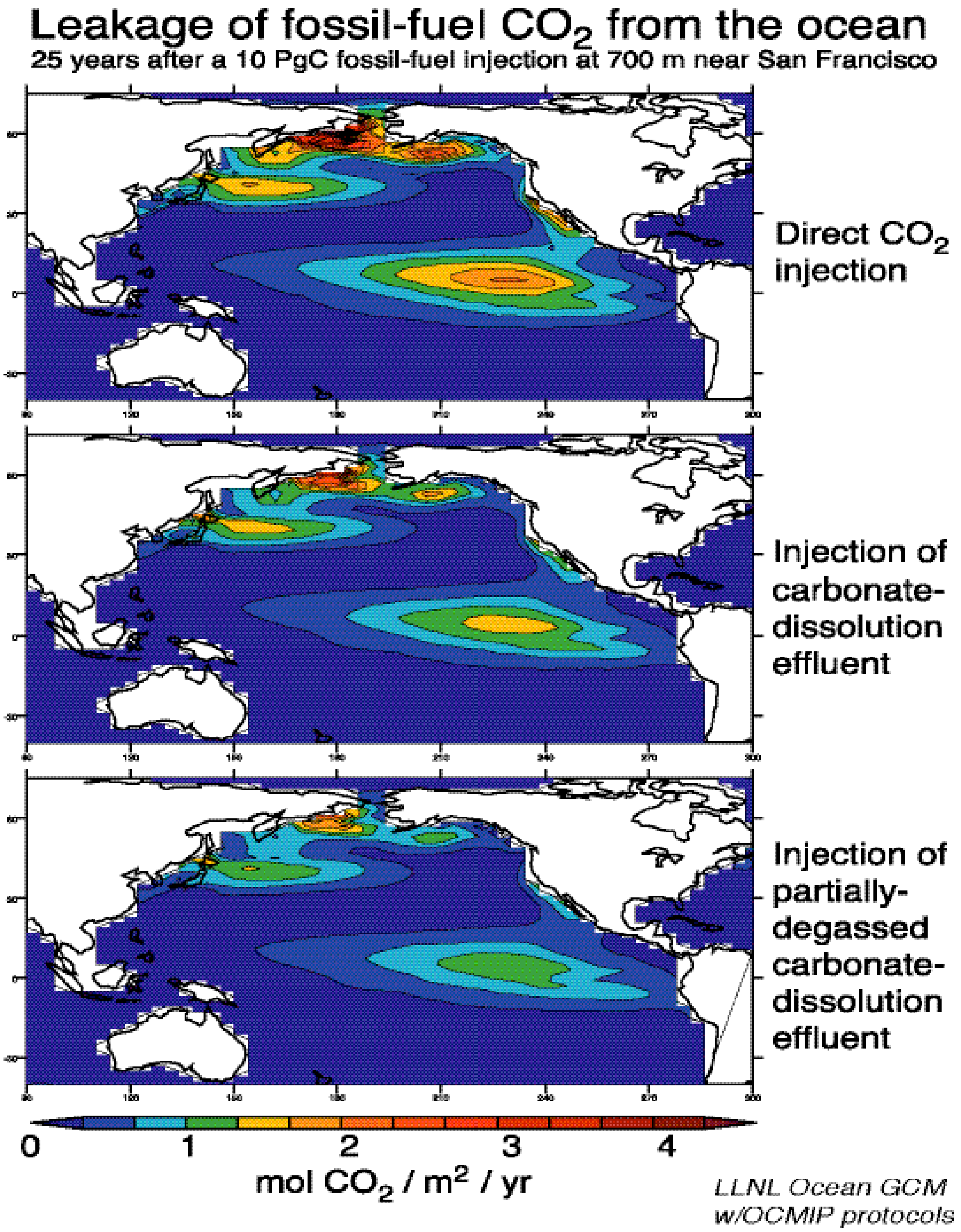
Leakage of fossil-fuel CO2 from the ocean
25 years after a 10 PgC fossil-fuel injection at 700 m near San Francisco
Direct CO2 injection
Injection of carbonate-dissolution effluent
Injection of partially-degassed carbonate-dissolution effluent
0
1
2
3
4
mol CO2 / m2 / yr
LLNL Ocean GCM w/OCMIP protocols

Figure 3