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Reducing energy-related CO₂ emissions using accelerated weathering of limestone

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Abstract

The use and impacts of accelerated weathering of limestone (AWL; reaction: $\text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + 2(\text{HCO}_3^-)$) is explored as a CO₂ capture and sequestration method. It is shown that significant limestone resources are relatively close to a majority of CO₂-emitting power plants along the coastal US, a favored siting location for AWL. Waste fines, representing more than 20% of current US crushed limestone production (> 10⁹ tonnes/yr), could provide an inexpensive or free source of AWL carbonate. With limestone transportation then as the dominant cost variable, CO₂ mitigation costs of \$3–\$4/tonne appear to be possible in certain locations. Perhaps 10–20% of US point-source CO₂ emissions could be mitigated in this fashion. It is experimentally shown that CO₂ sequestration rates of 10⁻⁶ to 10⁻⁵ moles/sec per m² of limestone surface area are achievable, with reaction densities on the order of 10⁻² tonnes CO₂ m⁻³day⁻¹, highly dependent on limestone particle size, solution turbulence and flow, and CO₂ concentration. Modeling shows that AWL would allow carbon storage in the ocean with significantly reduced impacts to seawater pH relative to direct CO₂ disposal into the atmosphere or sea. The addition of AWL-derived alkalinity to the ocean may itself be beneficial for marine biota.

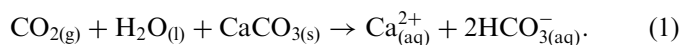
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Keywords: CO₂; Power plant; Mitigation; Capture; Sequestration; Storage; Limestone; Ocean

1. Introduction

The climate and environmental impacts of our current, carbon-intensive energy usage demand that effective and practical energy alternatives and CO₂ mitigation strategies be found (e.g. [1,2]). As part of this effort, various means of capturing and storing CO₂ 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 CO₂ with water to produce a carbonic acid solution. This in turn is reacted and neutralized with limestone, thus converting the original CO₂ gas to calcium

bicarbonate in solution, the overall reaction being:



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 CO₂, but over many millennia (e.g. [7–9]). We identify the enhanced form of this process as accelerated weathering of limestone (AWL). Previously, it has been shown that AWL can effectively convert a significant fraction of US CO₂ 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 CO₂ into the ocean [6,10]. Being analogous to the

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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 CO₂ 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 CO₂ mitigation.

2. 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 CO₂ could theoretically be mitigated by reaction 1. Indeed, over geologic time scales significant, natural increases in atmospheric CO₂ have been moderated and consumed via carbonate weathering, and the same process will eventually consume the majority of anthropogenic CO₂ 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 CO₂ (and lower oceanic pH) 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 CO₂ emissions is then not in principle reactant-limited, what are the practical limitations to AWL as a CO₂ capture and sequestration tool?

Based on the stoichiometry of reaction 1, it would take 2.3 tonnes of calcium carbonate and 0.3 tonnes of water to react with 1 tonne of CO₂ to form 2.8 tonnes of HCO₃⁻ in solution. While pure CaCO₃ (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% CaCO₃) would be used. US production of this mineral is presently 10⁹ tonnes/yr [13], about 76% of which is used in construction, about 19% for chemical and metallurgical applications, and the remaining for miscellaneous uses. 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 CO₂ 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 at least in certain locations 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 CO₂ and to carry and dilute the resulting bicarbonate (>10⁴ tonnes H₂O/tonne CO₂ [5]), AWL reactors in close proximity to seawater would be at a distinct cost advantage. Even with this geographic limitation, about 12% of CO₂ 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 seaboard, which also have the highest density of coastal US power plants and coastal electricity-related CO₂ production. For example there is more than 20 GW of fossil-fueled power generation (≈10⁸ tonnes CO₂ 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 limestone (e.g., waste fines) was free and nearby (negligible transportation expense), the CO₂ mitigation cost offered by AWL could be as low as \$3–\$4/tonne CO₂ 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 CO₂ 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 CO₂ mitigated [4]. However, the number of ideal sites and hence the volume of CO₂ 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 CO₂ mitigated, and with carbonate supplied via 2.5 tonnes of low-grade limestone (92% CaCO₃)/tonne CO₂, a limestone transport distance of 200 km yields an AWL CO₂ mitigation cost of about \$6, \$9, \$21, or \$48/tonne CO₂ 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/tonne CO₂ using the preceding transportation modes. In addition, if fresh seawater rather than recycled cooling water must be used and pumped 2 vertical meters the cost increases to \$23 to \$66/tonne CO₂ (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 CO₂ capture and sequestration, and is often below the cost of

Table 1
Cost of accelerated limestone weathering under various water, limestone, and transport cost assumptions

| | Limestone transportation mode | | | |
|--|-------------------------------|---------|---------|---------|
| | Freighter | Barge | Train | Truck |
| <i>Base capital, operating, and maintenance cost (\$/tonne CO₂)</i> | \$4.00 | \$4.00 | \$4.00 | \$4.00 |
| Limestone transport cost rate (\$/tonne/km) | \$0.003 | \$0.010 | \$0.034 | \$0.089 |
| Limestone transport cost (rate × 2.5 tonnes × 200 km) | \$1.71 | \$4.77 | \$17.05 | \$44.33 |
| <i>Total cost including limestone transportation costs (\$/tonne CO₂)</i> | \$5.71 | \$8.77 | \$21.05 | \$48.33 |
| Limestone cost (2.5 tonnes × \$5/tonne) | \$12.50 | \$12.50 | \$12.50 | \$12.50 |
| <i>Total cost including cost of limestone and its transportation (\$/tonne CO₂)</i> | \$18.21 | \$21.27 | \$33.55 | \$60.83 |
| Pumped water cost (\$2.38 m ⁻¹ per 10 ⁴ tonnes × 2 m) | \$4.76 | \$4.76 | \$4.76 | \$4.76 |
| <i>Total cost including limestone, its transportation, and water pumping (\$/tonne CO₂)</i> | \$22.97 | \$26.03 | \$38.31 | \$65.59 |

Base COM (capital, operating, and maintenance) cost (\$/tonne CO₂ 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 [38], assuming that 2.5 tonnes limestone is required/tonne CO₂ mitigated (see text). Water tonnage and pumping cost rate from Rau and Caldeira [5].

amine CO₂ capture alone (generally > \$30/tonne CO₂ [18]). AWL will clearly be more economical under circumstances where limestone and water are low-cost and close at hand.

3. Alternative reactor sitings

The preceding assumes an AWL reactor sited at the source of waste CO₂ (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 CO₂ produced inland and transported to coastal AWL reactors sited at or near limestone quarries. Transport of CO₂ can be inexpensive (\$0.06 tonne/km [19]) relative to the cost of transporting the AWL equivalent (2.5 tonnes) of limestone (Table 1). However, such CO₂ transport requires initial CO₂ separation, capture, and liquefaction, with associated technology and energy costs that are presently significant, as mentioned above. Still, if inexpensive CO₂ capture/separation is developed, piping CO₂ to coastal AWL reactors could prove cost-competitive with other forms of CO₂ sequestration such as underground storage, especially in regions where the underlying geology does not allow CO₂ retention.

Another alternative would place AWL reactors on or in seagoing barges or ships that would bring both the limestone and the AWL process to coastal CO₂ 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 (anticipated to be mostly SiO₂) at sea, subject to ocean dumping regulations. The preceding would obviously only be amendable to power plants (or coastal CO₂ sources supplied by pipeline) that are dock-accessible. It also assumes that a limestone-supplying port is within a reasonable shipping distance to the CO₂ 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.

4. 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 CO₂ to HCO₃⁻. In turn, specifying a carbonate particle surface area per packed reactor volume (A/V) of the carbonate particles determines the basic size of the reactor required for a given CO₂ 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 H₂O or

seawater equilibrated with various %CO₂/air streams, and with various water flushing rates, and internal stirring rates (see Fig. 1 legend). The results of these experiments yielded dissolution rates ranging from roughly 10⁻⁷–10⁻⁵ mol/m² limestone surface area/s with positive sensitivity to flow rate, stir rate, and CO₂ 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% CO₂, low-stir-rate and low-flow rate treatments would be characteristic of a large-scale reactor, a reaction rate of about 10⁻⁶ mol/m² limestone surface area/s is implied (Fig. 1). A limestone particle diameter of 1 mm (within the range typical of waste limestone fines discussed above) yields an *A/V* of 4.4 × 10³ m²/m³ or higher depending on the deviation of true particle shape from that of a sphere. Therefore, in this hypothetical case a maximum of about 60 m³ of internal reactor volume packed with such limestone particles would be needed to react 1 tonne of CO₂/day. For a cubic reactor volume (roughly 4 m × 4 m × 4 m), this equates to an areal reaction rate of about 4 tonnes CO₂/m² of internal reactor footprint per day, or more than 5 orders of magnitude greater than optimum areal CO₂ uptake and sequestration rates in managed forests or algal ponds [19]. The experiments show that this density of CO₂ conversion to HCO₃⁻ 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, by actively recirculating the partially-reacted solution, or by other means, but all with added energy and cost penalties.

Based on the above rates, reaction densities on the order of 10⁻² tonnes CO₂/m³ of internal reactor volume/day might be attainable. This means a 20% reduction of the CO₂ emissions from a typical 500 MW coal-fired power plant (10⁴ tonnes CO₂/day × 0.2 = 2 × 10³ tonnes CO₂/day) would require an AWL reactor volume of 2 × 10⁵ m³, roughly equivalent to a 60 m cube. However, we stress that optimum reactor size and configuration required for a given CO₂ mitigation application will be highly dependent on factors such as limestone particle size, shape and purity, water/gas/solids contacting efficiency (esp. boundary layer issues), the reactor's liquid/solids ratio, water flow and chemistry, and CO₂ concentration. For example, 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 to optimize AWL reactor designs for the best cost/benefit.

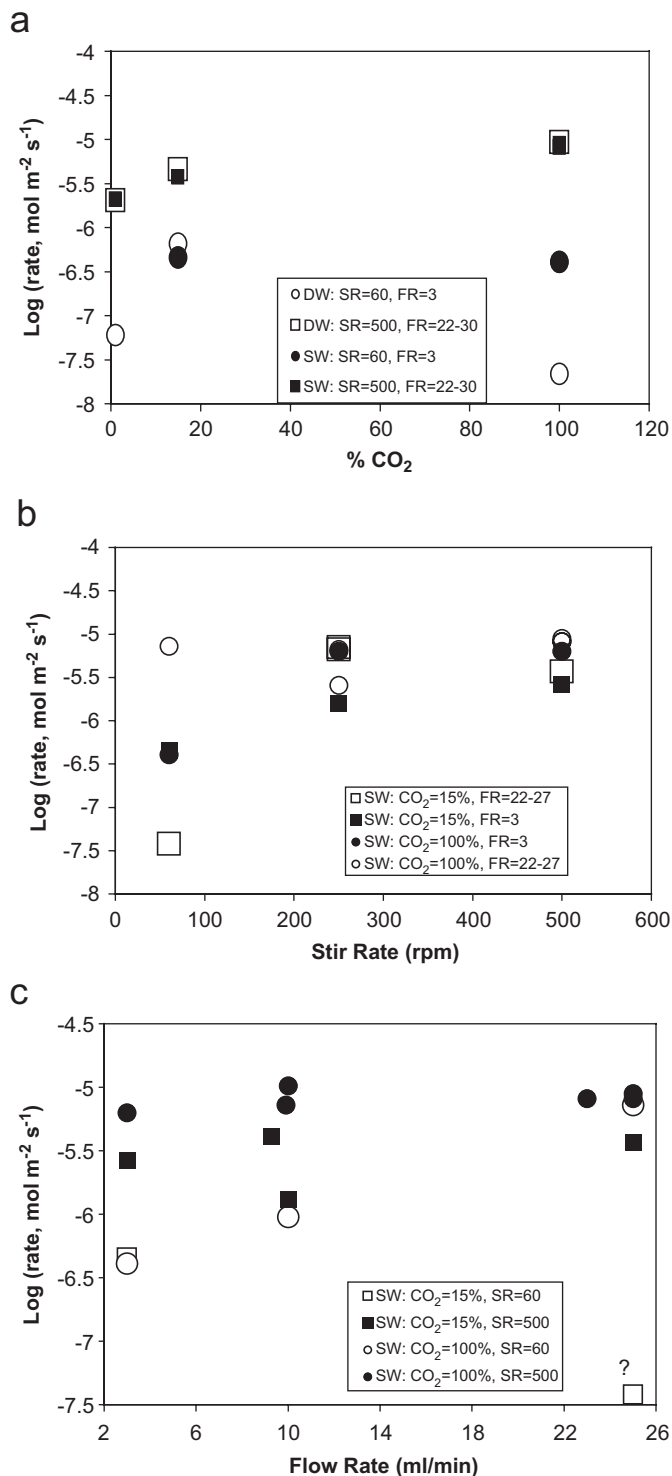


Fig. 1. Conversion rate of CO₂ to HCO₃⁻ in an experimental carbonate dissolution reactor flushed with distilled water (DW) or seawater (SW) equilibrated with the % CO₂ shown, and at the various reactor solution flow rates (FR) and internal stir rates (SR) indicated. Stir rates are in revolutions per minute. Conversion rate = ([Ca]_{out} - [Ca]_{in}) × FR/area, where [Ca] refers to the concentration of Ca²⁺ in the solutions entering or leaving a 370 ml reactor containing 5 g of limestone particles (size range 425–850 microns) under the respective solution %CO₂, 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 determined by mean particle geometry [36]. The mean particle surface area-to-volume ratio was 0.489 cm⁻¹, and the solid-to-solution weight ratio was 0.0136. [Ca] was determined by ICP-ES of discrete solution samples.

5. 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 (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, additional slowing of CO_2 leakage would be gained by releasing carbonate dissolution effluent at the same depth. We also note that carbonate dissolution can make a major contribution to CO_2 storage with 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).

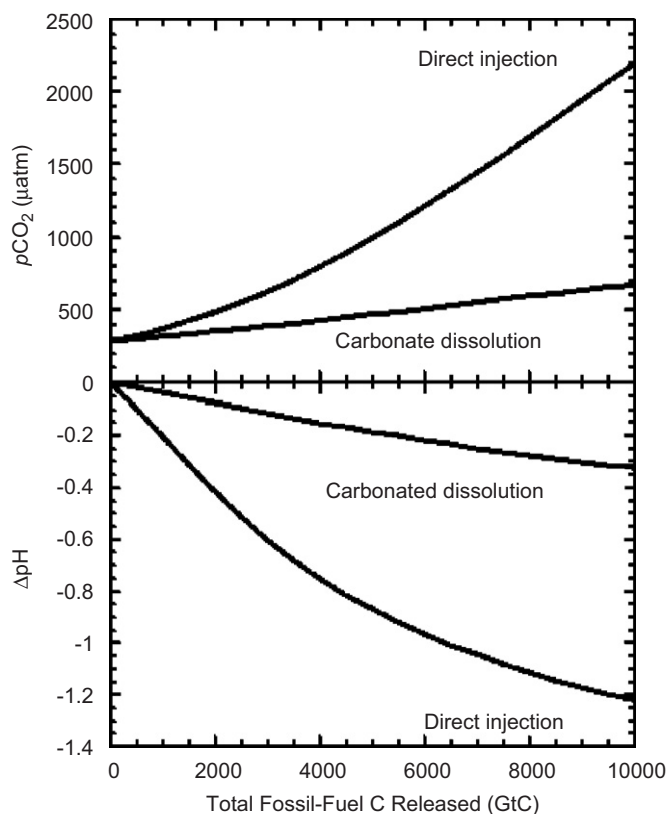


Fig. 2. Comparison of the effects on atmospheric CO_2 content (top panel) and on deep-ocean pH (bottom panel) 1000 years after the injection of the specified quantities of either molecular CO_2 or carbonate dissolution effluent into the deep-ocean (mean depth: 1950m). If the ocean's anthropogenic carbon capacity were determined by the amount of CO_2 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_2 released, over 45% of the injected CO_2 is in the atmosphere after 1000yr. With the carbonate dissolution method, less than 15% of the initially released CO_2 degasses to the atmosphere (from [6]).

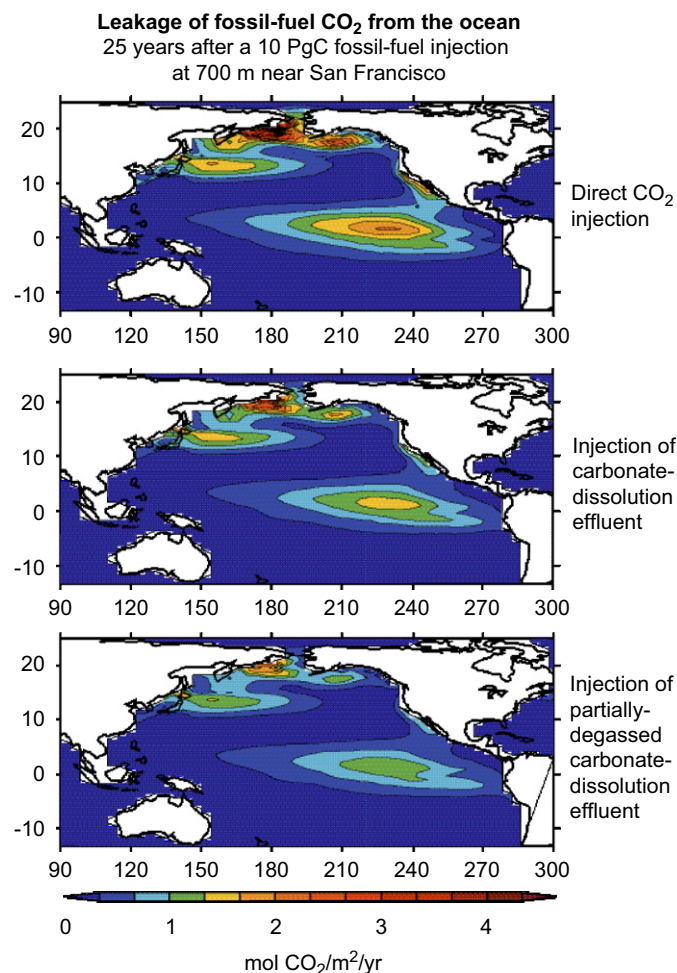


Fig. 3. Ocean general circulation model results showing the greater effectiveness (less CO_2 leakage to atmosphere) inherent in the injection of carbonate dissolution effluent (with and without pre-injection CO_2 adjustment) as compared to injection of molecular CO_2 at equivalent depths. The model is a modified version of the Geophysical Fluid Dynamics Laboratory Modular Ocean Model [37].

6. 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 tonne of carbon added to the ocean (Fig. 2), while reducing harmful effects to marine biota of direct ocean CO_2 additions [20–22]. 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, carbonate ions, 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., [25–27]). We also point out that AWL captures and sequesters CO₂ without the use of any exotic or toxic chemicals, unlike CO₂ capture methods using for example amines [4] or ammonia [28].

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% O₂. 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. However, we note that limestone/CO₂/seawater reactors using chemistry identical to AWL are employed by saltwater aquarists to generate aquarium alkalinity in order to safely maintain or promote the health of captive marine organisms [29,30]. As well, the ocean naturally receives and accommodates about 2 × 10⁹ tonnes of dissolved calcium bicarbonate/yr produced from continental carbonate weathering as delivered by rivers [12]. The threat of calcium carbonate precipitation (reversal of reaction 1) from AWL effluent after release into the ocean appears to be small because CaCO₃ ion concentrations in excess of 18X saturation are required to abiotically precipitate carbonate from seawater [31]. Further research is needed, however, to fully determine the benefits and impacts of AWL effluent on the ocean.

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. The 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 [32].

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. For example by our calculation using AWL to reduce CO₂ emissions from a coal-fired powered plant by 20% would more than double the material transport requirement to the plant [33]. Additionally, because some fraction of the limestone will not be reacted or be reactible, perhaps 5–10% of the original limestone mass transported to AWL reactors (principally SiO₂) 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 transport mode would 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. Certainly, the energy and carbon penalties associated with both the mining and transportation of limestone would need to be included in calculating AWL's net CO₂ mitigation potential.

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 [34] and acid mine waste neutralization [35] 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.

7. Conclusions

In the appropriate settings, AWL is an attractive option for CO₂ mitigation because: (1) the required reactants are relatively inexpensive, abundant, and environmentally benign; (2) the technology is relatively simple, low-cost, and applicable 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 CO₂ mitigation mechanism, carbonate weathering. However, as we have reviewed, these advantages must be weighed against more detailed engineering, economic, and environmental assessments of this method for reducing the carbon intensity of global power generation.

Acknowledgements

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