Electrochemical Splitting of Calcium Carbonate to Increase Solution Alkalinity: Implications for Mitigation of Carbon Dioxide and Ocean Acidity

G R E G   H .   R A U *

Institute of Marine Sciences, University of California, Santa Cruz, California 95064, and Carbon Management Program, Energy and Environmental Security Division, Lawrence Livermore National Laboratory, 7000 East Ave. Livermore, California 94550

Electrochemical splitting of calcium carbonate (e.g., as contained in limestone or other minerals) is explored as a means of forming dissolve hydroxides for absorbing, neutralizing, and storing carbon dioxide, and for restoring, preserving, or enhancing ocean calcification. While essentially insoluble in water, $CaCO_3$ can be dissolved in the presence of the highly acidic anolyte of a water electrolysis cell. The resulting charged constituents, Ca^{2+} and CO_3^{2-}, migrate to the cathode and anode, respectively, forming $Ca(OH)_2$ on the one hand and H_2CO_3 (or H_2O and CO_2) on the other. By maintaining a pH between 6 and 9, subsequent hydroxide reactions with CO_2 primarily produce dissolved calcium bicarbonate, $Ca(HCO_3)_{2aq}$. Thus, for each mole of $CaCO_3$ split, there can be a net capture of up to 1 mol of CO_2. $Ca(HCO_3)_{2aq}$ is thus the carbon sequestrant that can be diluted and stored in the ocean, in natural or artificial surface water reservoirs, or underground. The theoretical work requirement for the reaction is 266 kJ_e per net mole CO_2 consumed. Even with inefficiencies, a realized net energy expenditure lower than the preceding quantity appears possible considering energy recovery via oxidation of the H_2 produced. The net process cost is estimated to be <$100/tonne CO_2 mitigated. An experimental demonstration of the concept is presented, and further implementation issues are discussed.

1. Introduction

Due to the climate and environmental effects of excess CO_2 in the atmosphere, a variety of methods exist or have been proposed for pre- or post-emission capture and sequestration of CO_2 (*1*, *2*). For example, it is well-known that CO_2 will react with dissolved hydroxides such that the CO_2 concentration in a gas mixture in contact with the solution will be reduced via absorption and reaction within the solution, with such processes having industrial applications (*3*). More recently the use of solutions containing $Ca(OH)_2$ or NaOH have been proposed for large-scale chemical absorption of air CO_2 using various means of active or passive contacting of air or other gas mixture and the solution. For example, Kheshgi (*4*) suggested placing CaO or $Ca(OH)_2$ in the ocean to chemically enhance passive uptake of CO_2 from the atmosphere, largely forming $Ca(HCO_3)_2$ in solution as the CO_2 storage product. Other schemes employ engineered structures for actively contacting of air with NaOH, forming Na_2CO_3 in solution (*5*–*7*). By subsequently reacting this solution with $Ca(OH)_2$, $CaCO_3$ is formed and NaOH is regenerated. The $CaCO_3$ is then calcined at high temperature to form concentrated CO_2 as the final storage product while also forming CaO. The latter is then hydrated to regenerate $Ca(OH)_2$. In this way alkaline hydroxide solutions are recycled and conserved as opposed to the once-through production and release of alkalinity in the concept proposed by Kheshgi (*4*). However, in both cases significant quantities of thermal energy are required to either produce or regenerate the hydroxide solutions, especially the calcination of $CaCO_3$. This contributes significantly to the cost of either process, plus additional CO_2 is produced if the source of the thermal energy is derived from the combustion of fossil fuels. One way to avoid this CO_2 production in calcining is to employ nonfossil energy sources such as solar thermal energy (*8*, *9*).

Another source of hydroxide is electrochemical salt splitting wherein a dissolved salt is split into acid and hydroxide components in the presence of a charged anode and cathode, respectively. For example a solution containing dissolved NaCl can be electrolyzed to form hydrochloric acid (HCl), hypochlorite (ClO^-), chlorate (ClO_3^-), and/or chlorine gas (Cl_2) at the anode and sodium hydroxide (NaOH) at the cathode (*10*, *11*). The hydroxide solution can then be removed for subsequent use. Various electrodes and cation- and anion-permeable membranes can also be employed to facilitate the hydroxide formation and separation (*12*, *13*). Such a process can be used for the recovery and removal of salts in a solution or waste stream, thus also allowing for the purification of the original solution (*12*, *13*).

Obviously, such electrochemically produced hydroxide solutions could be used for CO_2 and other acid gas mitigation (*14*). However, producing hydroxide in quantities sufficient for large scale CO_2 removal could in the case of a metal chloride-containing electrolyte means massive coproduction of one or more chlorine-containing compounds. If these were not consumed in appropriate ways they would pose a significant environmental impact. In addressing this problem House et al. (*15*) proposed that the Cl_2 and H_2 formed during the electrochemical splitting of dissolved NaCl be reacted in a fuel cell to produce electricity and HCl. This strong acid could then be neutralized by reacting with mineral bases as contained in naturally occurring and abundant silicate minerals, thus converting the chlorine to relatively innocuous magnesium and calcium chlorides. Implementing such a scheme on a scale relevant to global CO_2 mitigation would, however, require the careful handling and management of large quantities of Cl_2 and HCl (*15*).

2. An Alternative

As a potentially safer and simpler approach, it is proposed that $CaCO_3$ rather NaCl be used as the primary compound for the electrochemical formation of mineral hydroxide. Due to its very low solubility, $CaCO_3$ is not an obvious choice for such aqueous electrochemistry. However, $CaCO_3$ is soluble in acid, which is locally produced in high concentrations in the anolyte of a water electrolysis cell (*10*). Specifically, as shown in Figure 1, the acidity (H^+) generated at the anode will react with and dissolve mineral carbonate placed immediately adjacent to the anode. The resulting Ca^{2+} and CO_3^{2-} ions then migrate toward the cathode and anode, forming $Ca(OH)_2$ and H_2CO_3 (and/or $CO_2 + H_2O$), respec-
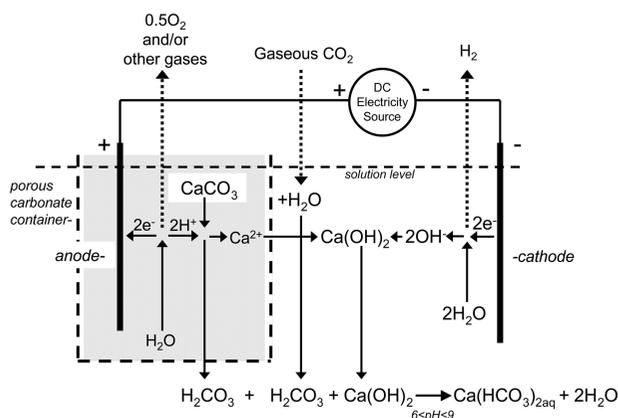
FIGURE 1. Schematic of the electrochemical splitting of calcium carbonate, CaCO₃, to form calcium hydroxide, Ca(OH)₂. The initial passage of direct electrical current through the solution by the presence of soluble salt ions is not shown. The excess Ca(OH)₂ can subsequently react with dissolved CO₂ to form predominantly Ca(HCO₃)₂aq when solution pH is between 6 and 9.

tively. This therefore allows the use of very abundant and inexpensive carbonate minerals, such as limestone and dolomite, to generate hydroxide solutions without resorting to thermal calcination of mineral carbonates or, necessarily, the electrochemical splitting of NaCl. Previously, the electrochemical splitting of highly soluble K_2CO_3 was proposed as a means of regenerating KOH for air CO_2 capture (16).

The calcium hydroxide formed will subsequently react with the CO_2 dissolved in the solution, forming dissolved calcium carbonate and bicarbonate. The formation of the bicarbonate will be favored when solution pH is kept between 6 and 9 (17). Under such conditions, because bicarbonate ions (valence = −1) require half the balancing cation equivalents as do carbonate ions (valence = −2), the carbonic acid formed at the anode is quantitatively insufficient to react with and hence neutralize all of the metal hydroxides produced in the solution. That is, at such pH even if all of the excess carbonic acid originally produced at the anode were to quantitatively react with the Ca(OH)₂ produced at the cathode, there would be insufficient acid to neutralize all of the Ca(OH)₂ generated. This excess Ca(OH)₂ would then be free to react with any additional acid contained in the solution including CO_2. As dissolved CO_2 is consumed, a difference in CO_2 partial pressure would be produced between the solution and the overlying air causing the CO_2 in the overlying air to diffuse into the solution. In this way CO_2 is removed from the overlying gas mixture or air and reacted with the excess hydroxide to form Ca(HCO₃)₂aq that then becomes the storage compound of the CO_2 consumed.

3. Net CO₂ Sequestration

In the course of forming calcium bicarbonate, some calcium carbonate will spontaneously form via well-know, pH-dependent equilibrium reactions, and if above a certain saturation concentration, will subsequently precipitate from solution, unlike Ca(HCO₃)₂. Since CaCO₃ is the starting compound that is initially electrochemically split, there can be no net CO_2 uptake and storage unless at least some of the calcium salt formed remains as Ca(HCO₃)₂ in solution. Thus CaCO₃ precipitation from the solution formed must be avoided if maximum CO_2 removal is to be achieved. Such chemical precipitation can be avoided by (i) dilution with water, (ii) pH adjustment, (iii) thermal adjustment, and (iv) the addition of carbonate precipitation inhibitors (e.g., Mg^{2+}, sulfates, phosphates, certain organic compounds). In the case of seawater, it has been observed that CaCO₃ stays in solution

and will not abiotically precipitate even in concentrations approaching 20 times saturation (18, 19) due to chemical inhibitors naturally present in ocean water (20).

However, CaCO₃ precipitation can be biologically effected. Of particular concern for CO_2 mitigation would be the enhancement of marine biological calcification by the presence of the added alkalinity in the form of mineral bicarbonates (21, 22), with the CaCO₃ precipitated being balanced by an equimolar regeneration of molecular CO_2. In the extreme this could ultimately result in the eventual biological removal of all excess carbon absorbed by the ocean via Ca(OH)₂ addition, though over geologic time scales (15, 23). On the other hand such alkalinity addition could help offset the loss of biological calcification that is presently occurring due to CO_2-induced ocean acidification (24, 25). The net long-term effectiveness and benefits to CO_2 mitigation and to biological calcification of adding calcium hydroxide and/or calcium bicarbonate to natural waters requires further study. At the very least, adding 1 mol of net CO_2 storage per mole of CaCO₃ split by the process would likely be in effect over the next century, when CO_2 emissions will be highest (15). Such issues would be moot with underground Ca(HCO₃)₂aq storage.

Another factor affecting net CO_2 mitigation by the process would be the CO_2 emissions associated with supplying and operating such an electrochemical system. Assuming the required electricity would come from rewable sources (types and quantities discussed below), additional energy requirements and hence CO_2 emissions can be anticipated in limestone/carbonate mining, crushing, and transport, in water pumping (if required), and in harvesting end products such as H₂ (if conducted). However, analyses of such emissions from related technologies (15, 26, 27) suggest that CO_2 emissions from such activities could be small relative to the CO_2 consumed and avoided in an optimized system. A full lifecycle analysis of CO_2 emissions, consumption, avoidance, and hence, net mitigation by such a system is needed.

4. Thermodynamics and Energy Cost

Assuming the net reaction,

$$CaCO_3 + 2H_2O + CO_2 + (DC\ electricity) \rightarrow \uparrow H_2 + \uparrow 0.5O_2 + Ca^{2+} + 2(HCO_3^-)\ (1)$$

the theoretical work requirement, ΔG, is 266 kJ/mol CO_2 consumed (1682 kWh/tonne CO_2 consumed). This compares with an energy expenditure of 360 kJ$_e$/mol CO_2 (2273 kWh$_e$/tonne CO_2) estimated from the typical energy used in the commercial production of H₂ in alkaline electrolysis cells (26), assuming a 1:1 molar ratio in H₂ produced:net CO_2 consumed (eq 1). Some of this energy cost could be offset or avoided via the subsequent oxidation of the H₂ in a fuel cell or by diverting the H₂ to a gas diffusion anode if used in the electrolysis cell. In the former case, about 121 kJ$_e$/mol H₂ could be recovered in a 50% efficient fuel cell, for an offset of 121 kJ$_e$/mol CO_2 yielding a net energy expenditure based on the commercial electrolyzer example of 360 − 121 = 239 kJ$_e$/mol CO_2 consumed. Use of gas diffusion electrodes would reduce energy expenditure by about $1/3$ (13), which would then yield about the same net energy expenditure. Thus, energy requirements of this magnitude might be feasible, though with added capital and operating costs. For comparison, land-based air capture schemes reportedly have a primary energy requirement (mostly thermal) of >350 kJ/mol CO_2 captured (7), but where air contacting is mechanically assisted, hydroxide is thermally regenerated, pressurized molecular CO_2 rather than Ca(HCO₃)₂aq is the end product, and gross CO_2 capture rather than net CO_2 mitigation may be calculated.
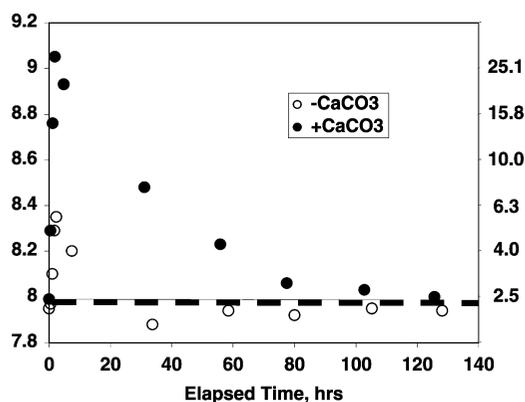
FIGURE 2. Time course of seawater pH during 1.5 h of electrolysis using an anode that either was or was not encased in seawater-saturated $CaCO_3$ powder, followed by 5 days of solution exposure to ambient air. The corresponding solution $[OH^-] = 10^{(pH-7.6)}$ at a mean experiment temperature of 16.5 °C and salinity of 35 ppt (17). Dashed line denotes pretreatment values.

Note also that in principle 22 tonnes of CO_2 can be captured per tonne H_2 generated (eq 1). Thus, depending the amount of CO_2 emitted directly or indirectly in operating such a system (see "Net Carbon Sequestration" section), the system has the potential of producing hydrogen that is significantly carbon-negative, in contrast to current commercial H_2 production methods (26).

5. Experimental Demonstration

A 9 cm × 1 mm diameter graphite rod anode was placed vertically into a hollow, porous cylindrical container (tea strainer; mean i.d. = 4 cm, height = 8 cm) the inside surface of which had been lined with a porous paper filter and then filled with reagent grade, powdered $CaCO_3$. This anode container was then submerged in a glass beaker containing 300 mL of local (Santa Cruz, CA) seawater. The anode container was positioned such that the upper surface of the $CaCO_3$ mass was just above the surface of the seawater, while the vertical anode penetrated into the mass such that about 1 cm of the anode was below the seawater level, the submerged part of the anode thus being completely encased by a seawater-saturated carbonate "paste". An equivalent, naked graphite rod (cathode) was placed vertically into the solution at a distance of about 4 cm from the anode at equivalent seawater depth outside of the anode container. The initial pH of the seawater solution was then measured using a calibrated pH probe (Oakton model 300). The anode was then connected to the positive lead and the cathode to the negative lead of a DC power source providing a measured voltage through the cell that ranged from 3.5 to 3.6 V at 6.4 to 7.0 mA. After 1.5 h of electricity application the pH of the solution rose to a value of 9.05 (Figure 2), measured while electricity was temporarily turned off and after gentle stirring of the seawater to reduce chemical heterogeneity, thus determining true bulk solution pH. The electricity was then permanently turned off, the electrodes and anode container removed from the seawater, and the solution poured into a shallow dish (11 cm i.d.). The pH of the solution was then periodically monitored and was observed to return to near its initial value over the course of 5 days (Figure 2). The experiment was repeated without the presence of $CaCO_3$ and paper filter (experimental control), with a maximum pH of 8.35 being obtained, followed by a return to pH values near that of the initial seawater (Figure 2).

It is concluded that the rise in pH observed in both treatments was the consequent of the reduction and loss from solution of hydrogen and the production of hydroxide

at the cathode. Using a seawater chemistry model (28) with starting chemistry typical of central California coastal surface water, the alkalinity addition required to effect the maximum pH deviations observed was calculated to be 1.1 and 0.3 mmol/L, respectively, for the experimental and the control treatments. In the latter treatment the OH^- produced is presumed to have been balanced by Na^+ from the splitting of seawater NaCl, whereas Ca^{2+} from the splitting of $CaCO_3$ is presumed to balance the additional OH^- generated in the carbonate treatment, in this case 0.8 mmol/L. Evidence of NaCl splitting was indicated by the odor of chlorine in both treatments, and possibly another unidentified irritant gas was also generated. Such experiments must be conducted under adequate ventilation both during and after electrolysis.

The decrease in pH following the termination of electricity input in both treatments is consistent with the excess OH^- reacting with CO_2 that slowly diffused in from the overlying air to form primarily HCO_3^- balanced by the excess Ca^{2+} and/or Na^+. According to the preceding chemistry model (28) such neutralization would have required the absorption of 1.0 and 0.2 mmol/L of CO_2 in the experimental and the control, respectively, yielding a net increase in CO_2 absorption in the carbonate treatment of 0.8 mmol/L. An absorption of 1.0 mmol/L of CO_2 occurring over approximately 120 h into 0.3 L of solution with a surface area of 95 cm² yields a mean gross CO_2 absorption rate of 0.073 μmole m^{-2} sec^{-1}. Subtracting the CO_2 generated by the splitting of $CaCO_3$, 0.4 mmol/L, then leads to an estimated net CO_2 uptake of about 0.6 mmol/L in the carbonate treatment, requiring a mean net CO_2 absorption rate of 0.044 μmole m^{-2} sec^{-1}. For comparison, an estimated net CO_2 absorption by the ocean of 7 Gt/yr (29) yields a mean net air-to-sea CO_2 absorption rate of 0.015 μmole m^{-2} sec^{-1} or about $^1/_3$ that estimated for the experiment. Conducting the experiments under more realistic ocean or surface reservoir conditions (wind, waves, mixing) would likely have greatly enhanced the CO_2 flux rate in the experiments.

The energy input for the preceding net CO_2 absorption amounted to about 34 mWh$_e$, or about 8 × 10⁶ kWh$_e$/net tonne CO_2 consumed. This energy expenditure is >10³ higher than anticipated from the commercial alkaline solution electrolysis example discussed above, indicating that the experimental cell configuration used was very far from being thermodynamically optimal.

6. Large Scale Implementation

While the electrochemical system described could have application to localized hydroxide production, CO_2 absorption, and/or hydrogen generation in various industrial or commercial settings, might such a system be applicable at a scale large enough to make an impact globally? For example, the use of hydroxide solutions in specially designed air contacting devices have been considered for large scale atmospheric CO_2 absorption (5–7, 30, 31), and such devices might provide an effective use for the calcium hydroxide produced here for CO_2 mitigation. Also, to the extent that CO_2 rather than carbonate or bicarbonate would be the desired end product in such systems, the preceding electrochemistry might prove useful for stripping (calcining) and concentrating the captured CO_2 from the carbonate or bicarbonate formed, and for reforming hydroxides. It would also be possible to add the hydroxide solution produced to large bodies of water in contact with air so as to chemically remove and store at least some atmosphereic CO_2 (4, 15). Comprising 71% of the earth's surface (3.61 × 10⁸ km², excluding surface roughness), the ocean is the ultimate air contactor for planetary scale CO_2 absorption. Indeed <5% of the ocean surface would be needed to absorb an additional 1 Gtonne of atmospheric CO_2/yr if seawater CO_2 absorption

rates could be continuously enhanced as experimentally observed above.

The electrolysis could in fact be done directly in open reservoirs or the ocean where the electrodes and carbonate would penetrate the water surface from either stationary (e.g., docks, jetties, platforms) or mobile, piloted, or autonomous vessels (barges, ships, buoys, etc.). With nonfossil-fuel electrical power generated onsite (wind, wave, tidal, ocean thermal, solar), the electrochemical splitting of the carbonate could proceed in situ, generating hydroxide alkalinity directly into the water body. Calcium carbonate would need to be supplied to the structure at the rate of at least 2.3 tones per net tonne CO_2 consumed, the exact quantity dependent upon the purity and reactivity of the mineral carbonate used. In turn the H_2 and other gases produced (if produced) would need to be harvested, used, or safely disposed.

For ease of access and transportation of reactants and products, flow-through, shore-based systems would be attractive, with the adjacent ocean providing a ready source of water and energy as well as a subsequent air-contacting surface and carbon storage reservoir. At inland sites, wastewater or groundwater could be used for the process, with above- or below-ground reservoirs providing a storage area for the solution once reacted with CO_2. In any case, unlike point-source mitigation, air CO_2 capture has the advantage of being able to be sited anywhere that energy, reagents, air contacting surface area, and societal and economic interests are optimal (5, 7, 15).

While any source of DC electricity of appropriate current and voltage could be used for the preceding electrolysis, use of low- or non-CO_2 producing renewable electrical energy sources would be particularly attractive for maximizing net CO_2 mitigation. Nonreactive electrodes such as graphite or stainless steel would be preferred, but more exotic metals, alloys, or coatings might prove beneficial and cost-effective. For example, manganese-containing, oxygen-selective anodes (10, 32) could be used to reduce or avoid the generation of chlorine and/or chlorine compounds under circumstances where a chloride salt is present in the electrolyzing solution, e.g., seawater. Chlorine generation may also be suppressed by (1) the use of very high or very low electrode current densities (10), (2) the use of ion selective membranes to exclude chloride ion from entering the anolyte (12, 13), or (3) the diversion of the H_2 produced at the cathode to a gas diffusion anode (12, 13). It might also be possible to avoid gas production altogether through the use of bipolar membranes that selectively block gas-generating cations or anions from leaving or entering the catholyte or anolyte, respectively (12, 13). Prevention of some or all gas evolution would reduce the overall electrical energy required for the carbonate splitting. In any case, the ancillary production of compounds by this process and their use, fate, impact, or avoidance requires further study.

7. Other Benefits and Issues

The H_2 produced at the cathode could be used as an energy source/carrier or as a chemical feed stock, the value of which could help offset the cost of the simultaneous hydroxide solution production. For example the oxidation of the H_2 using a fuel cell or internal combustion engine could be used to generate electrical or mechanical energy, thus recovering some of the energy used in the original electrochemical process. Electricity so generated could in fact be used to power the electrolysis during periods of renewable power intermittency, as in the case of wind, wave, solar, or tidal power usage. Alternatively, the ability to electrochemically produce CO_2-absorbing solutions and thus carbon credits could add value to systems otherwise primarily designed to levelize intermittent energy sources using electrolytic hydrogen production/energy storage, e.g., wind-hydrogen

systems (26). Using O_2 or air as the H_2 oxidant, fresh water would be the chemical end product, which may have significant added value in certain settings, for example, deserts adjacent to the ocean or other saline reservoirs.

The addition to the ocean of $Ca(OH)_2$ produced by the electrolysis would be useful at least locally in neutralizing marine acidity that is being generated by the ongoing, passive invasion of anthropogenic CO_2 into the ocean (24, 33). Furthermore, this hydroxide and/or the subsequent formation of $Ca(HCO_3)_{2aq}$ via reaction with CO_2 would be beneficial to biological marine calcification (21, 22) that is otherwise threatened by the above decrease in ocean pH. Indeed, enhanced calcification on and around negatively charged cathodes submerged in seawater have been observed and proposed as a way of stimulating reef building (34). However, unlike the process presented above where an external source of alkalinity is added to seawater via the electrochemical splitting of limestone, cathodic carbonate precipitation effected by simple electrolysis of seawater alone will occur at the expense of excess CO_2 lose from seawater at the acidic anode, resulting in a net source rather than a net sink of atmospheric CO_2. Also, if carbonate or hydroxide precipitation occurs on the cathode this could impact the performance of the electrolysis cell. Indeed, a white precipitate was observed on the experimental cathode above, but did not seem to degrade current passage through the solution over the course of the experiments, perhaps due to the relatively high voltage used. In large-scale applications, such precipitation might be managed or avoided via sufficient solution flow or adjustment of electrical current densities (10), or by the occasional reversal of electrode polarity.

8. Economics

Given the uncertainties in the optimum chemistry, design, and operation of such a system, a precise assessment of net cost is currently not possible, but the following might be illustrative. Assuming a net reaction as described by eq 1, process costs are estimated. *Energy*: Commercial electrolytic generation of H_2 requires at least 50 kWh_e/kg H_2 (26). Since 2 kg H_2 would be produced per 44 kg noncarbonate CO_2 consumed (eq 1), $50 \times 2/44 = 2.273$ kWh_e would be used per net kg CO_2 captured, or 2273 kWh_e/net tonne CO_2 consumed. Assuming \$0.06/kWh_e (e.g., unsubsidized wind (26)), then $2273 \times \$0.06 = \$136.38$/net tonne CO_2 consumed. *Capital, operation, and maintenance (O&M)*: Advanced alkaline (KOH) electrolyzer capital cost is reportedly \$600/tonne H_2 produced (35). Assuming a similar capital cost for the electrolyzer envisioned here yields a CO_2 equivalent capital cost of $600 \times 2/44 = \$27.27$/net tonne CO_2 consumed. O&M charges are assumed to be 3% of capital expenditure (26), bringing the total CO & M cost to \$28.09/net tonne CO_2 consumed. *Mineral carbonate*: If the limestone used contains 95% $CaCO_3$, 2.42 tonnes of limestone are then required per net tonne CO_2 consumed. At an assumed delivered price of \$8/tonne of crushed stone (36), mineral carbonate cost would then be \$19.36/net tonne CO_2 consumed. Substantial cost savings could be achieved, however, through the use of waste limestone fines (<9.5 mm) that comprise more than 20% of U.S. limestone production (37). Since it is currently unknown what the most cost-effective carbonate particle size for the process might be, it is uncertain if additional grinding/sieving of the crushed/waste stone would be required. Based on grinding cost estimates for a related process (27), an additional \$3/net tonne CO_2 consumed is budgeted here, bringing the estimated total carbonate cost to \$22.36/net tonne CO_2 consumed. *Water*: 0.82 tonnes of water are consumed per net tonne CO_2 consumed. Assuming in situ use of seawater, cost would be nil. Otherwise, water source and pumping costs would need to be considered. Assuming an excess net CO_2 storage potential of 0.6 mmole CO_2/L in

seawater whose pH is initially elevated to 9 (see "Experimental Demonstration" section) then some 3.8×10^4 tonnes of water are required per tonne of CO_2 stored. This water quantity further recommends that the process be done very near or within the ocean or other water body to reduce or avoid pumping costs. The total gross cost of such a system is then projected to be \$136.38 + \$28.09 + \$22.36 = \$186.83/net tonne CO_2 consumed.

Potential cost offsets include H_2: Assuming the value of the H_2 produced is \$1500/tonne H_2, then the value added to CO_2 capture is \$1500 × 2/44 = \$68.18/net tonne CO_2 consumed. *Quantity and value of CO_2 mitigated*: If 9 tonnes of CO_2 are avoided per tonne H_2 produced (via this carbon-free electrolysis versus natural gas reforming (*26*)), and if 44/2 = 22 tonnes CO_2 are consumed from air per tonne H_2 produced (eq 1), then at total of 9 + 22 = 31 tonnes CO_2 are mitigated/tonne H_2 produced, or 31 tonnes × 2/44 = 1.41 tonnes CO_2 mitigated/net tonne CO_2 consumed. Assuming a value of \$10/tonne CO_2 mitigated yields \$10 × 1.41 tonnes CO_2 mitigated/net tonne CO_2 consumed = \$14.10/net tonne CO_2 consumed. *Other potential cost offsets (not monetarily valued here)*: (a) Energy storage and recovery including load leveling and peak shaving via H_2 storage/oxidation (*26*), (b) subsequent freshwater production via H_2 oxidation, (c) the value of O_2 or other gases produced, and (d) ocean acid mitigation, e.g., local or regional preservation or enhancement of economically important marine shellfish. The total estimated cost offset is then \$68.18 + \$14.10 = \$82.28/net tonne CO_2 consumed. Subtracting this from gross cost, yields a net cost of \$186.83 − \$82.28 = \$104.55/net tonne CO_2 consumed or (÷ 1.41 tonnes CO_2 mitigated/net tonne CO_2 consumed =) \$74.15/tonne CO_2 mitigated. For comparison, this latter figure is at the high end of the cost range estimated for the capture and geologic storage of molecular CO_2 from conventional power plant waste streams (*1*). However, lacking an optimized prototype system, the true cost, effectiveness, and potential of this electrolysis-based CO_2 mitigation scheme remains to be demonstrated.

To conclude, the magnitude and urgency of the global CO_2 problem requires that all mitigation alternatives be carefully considered and evaluated under the assumption that multiple technologies will be required (*38*). Because fossil fuels will remain our primary energy source for the foreseeable future (*39*), and because most of the associated CO_2 emissions cannot be feasibly controlled by point-source methods (e.g., automobiles, ships, planes, noncompliant point-source emitters), options for post-emission absorption of CO_2 from the air are needed. The passive absorption of air CO_2 by the ocean has already saved us from the climate impacts of about half of the anthropogenic CO_2 released thus far (*29*), and will ultimately absorb most of the human-induced atmospheric CO_2 transient whatever its ultimate size and duration (*40*). Yet we cannot rely on this natural ocean process to avoid severe climate and environmental impacts because it would take many tens of thousand of years to return to near preindustrial CO_2 levels under such a scenario (*40*), and in the meantime it would result in significant acidification of the ocean (*33*). Ways of using chemical reactions with globally abundant minerals to (i) mitigate point source CO_2 (*23, 41−44*) or (ii) to proactively modify ocean chemistry to enhance air CO_2 uptake (*4, 15, 23, 27*) have been proposed including the method described here. Most of the latter approaches will require significant energy input, yet the ocean itself has abundant and virtually untapped solar, wind, thermal, tidal, and kinetic energy (>2 × 10^6 TWh/yr (*45*)). Some small fraction of this energy could conceivably be converted to electricity and used to help electrochemically stabilize or reduce atmospheric CO_2 and/or to neutralize ocean acidity and to add alkalinity to preserve marine calcifying organisms such as corals and shellfish.

However, the actual cost, impact, safety, benefit, and practical scale of such a mitigation method remain to be demonstrated.

Literature Cited

(1) Metz, B.; Davidson, O.; de Conick, H.; Loos, M.; Meyer, L. *IPCC Special Report on Carbon Dioxide Capture and Storage*; Cambridge: New York, 2005.

(2) *U.S. Climate Change Technology Program Strategic Plan. Climate Change Technology Program*; National Energy Technology Laboratory, DOE: Washington, DC, 2006; Available at http://www.climatetechnology.gov/stratplan/ final/ index.htm.

(3) Danckwerts, P. V. *Gas-Liquid Reactions*; McGraw-Hill: New York, 1970.

(4) Kheshgi, H. S. Sequestering atmospheric carbon dioxide by increasing ocean alkalinity. *Energy* 1995, *20*, 915–922.

(5) Keith, D. W.; Ha-Duong, M.; Stolaroff, J. K. Climate strategy with CO_2 capture from the air. *Climatic Change* 2006, *74*, 17–45.

(6) Baciocchi, R.; Storti, G.; Mazzotti, M. Process design and energy requirements for the capture of carbon dioxide from air. *Chem. Eng. Process.* 2006, *45*, 1047–1058.

(7) Zeman, F. Energy and material balance of CO_2 capture from ambient air. *Environ. Sci. Technol.* 2007, *41*, 7558–7563.

(8) Meier, A.; Bonaldi, E.; Cella, G. M.; Lipinski, W.; Wuillemin, D. Solar chemical reactor technology for industrial production of lime. *Solar Energy* 2006, *80*, 1355–1362.

(9) Nikulshina, V.; Hirsch, D.; Mazzotti, M.; Steinfeld, A. CO_2 capture from air and co-production of H_2 via the Ca(OH) $_2$-$CaCO_3$ cycle using concentrated solar power - Thermodynamic analysis. *Energy* 2006, *31*, 1715–1725.

(10) Bennett, J. E. Electrodes for generation of hydrogen and oxygen from seawater. *Int. J. Hydrogen* 1980, *5*, 401–408.

(11) Abdel-Aal, H. K.; Sultan, S. M.; Hussein, I. A. Parametric study for saline water electrolysis 2. Chlorine evolution, selectivity and determination. *Int. J. Hydrogen Energy* 1993, *18*, 545–551.

(12) Rajeshwar, K.; Ibanez, J. *Environmental Electrochemistry*; Academic Press: San Diego, 1997.

(13) Genders, J. D. Electrochemical salt splitting *Watts New* 1995, 1 Available at http://www.electrosynthesis.com/news/mwatts.html.

(14) An, S.; Nishida, O. New application of seawater and electrolyzed seawater in air pollution control of marine diesel engine. *JSME Int. J. Series B* 2003, *46*, 206–213.

(15) House, K. Z.; House, C. H.; Schrag, D. P.; Aziz, M. J. Electrochemical acceleration of chemical weathering as an energetically feasible approach to mitigating anthropogenic climate change. *Environ. Sci. Technol.* 2007, *41*, 8464–8470.

(16) Stucki, S.; Schuler, A.; Constantinescu, M. Coupled CO_2 recovery from the atmosphere and water electrolysis: Feasibility of a new process for hydrogen storage. *Int. J. Hydrogen Energy* 1995, *20*, 653–663.

(17) Zeebe, R. E.; Wolf-Gladrow, D. A. *CO_2 in Seawater: Equilibrium, Kinetics, Isotopes;* Elsevier Science: Amsterdam, 2001.

(18) Morse, J. W.; He, S. Influences of T, S and PCO_2: on the pseudo-homogeneous precipitation of $CaCO_3$ from seawater: Implications for whiting formation. *Mar. Chem.* 1993, *41*, 291–297.

(19) Morse, J. W.; Gledhill, D. K.; Millero, F. J. $CaCO_3$ precipitation kinetics in waters from the Great Bahama Bank: implications for the relationship between Bank hydrochemistry and whitings. *Geochim. Cosmochim. Acta* 2003, *67*, 2819–2826.

(20) Morse, J. W.; Mackenzie, F. T. *Geochemistry of Sedimentary Carbonates*; Elsevier: Amsterdam, 1990.

(21) Marubini, F.; Thake, B. Bicarbonate addition promotes coral growth. *Limnol. Oceanog.* 1999, *44*, 716–720.

(22) Langdon, C.; Takahashi, T.; Sweeney, C.; Chipman, D.; Goddard, J.; Marubini, F.; Aceves, H.; Barnett, H.; Atkinson, M. J. Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef. *Glob. Biogeochem. Cycles* 2000, *14*, 639–654.

(23) Lackner, K. S. Carbonate chemistry for sequestering fossil carbon. *Ann. Rev. Energy Environ.* **2002**, *27*, 193–232.

(24) Feely, R. A.; Sabine, C. L.; Lee, K.; Berelson, W.; Kleypas, J.; Fabry, V. J.; Millero, F. J. Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. *Science* **2004**, *305*, 362–366.

(25) Hoegh-Guldberg, O.; Mumby, P.; Hooten, A. J.; Steneck, R. S.; Greenfield, P.; Gomez, E.; Harvell, C. D.; Sale, P. F.; Edwards, A. J.; Caldeira, K.; Knowlton, N.; Eakin, C. M.; Iglesias-Prieto, R.; Muthiga, N.; Bradbury, R. H.; Dubi, A.; Hatziolos, M. E. Coral reefs under rapid climate change and ocean acidification. *Science* **2007**, *318*, 1737–1742.

(26) Committee on Alternatives and Strategies for Future Hydrogen Production and Use, National Research Council and National Academy of Engineering. *The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs*; National Academies Press: Washington DC, 2004.

(27) Harvey, L. D. D. Mitigating the atmospheric CO_2 increase and ocean acidification by adding limestone powder to upwelling regions *J. Geophys. Res., [Oceans]* **2008**, 113 doi: 10.1029/2007JC004373.

(28) Lewis, E.; Wallace, D. W. R. Program Developed for CO_2 System Calculations, ORNL/CDIAC-105; Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy: Oak Ridge, TN, 1998; Available at http://cdiac.ornl.gov/oceans/co2rprt.html#single.

(29) Sabine, C. L.; Feely, R. A.; Gruber, N.; Key, R. M.; Lee, K.; Bullister, J. L.; Wanninkhof, R.; Wong, C. S.; Wallace, D. W. R.; Tilbrook, B.; Millero, F. J.; Peng, T. H.; Kozyr, A.; Ono, T.; Rios, A. F. The oceanic sink for anthropogenic CO_2. *Science* **2004**, *305*, 367–371.

(30) Elliott, S.; Lackner, K. S.; Ziock, H. J.; Dubey, M. K.; Hanson, H. P.; Barr, S.; Ciszkowski, N. A.; Blake, D. R. Compensation of atmospheric CO_2 buildup through engineered chemical sinkage. *Geophys. Res. Lett.* **2001**, *28*, 1235–1238.

(31) Johnson, N. A. C.; Blake, D. R.; Rowland, F. S.; Elliot, S.; Lackner, K. S.; Ziock, H. J.; Dubey, M. K.; Hanson, H. P.; Barr, S. Chemical transport modeling of potential atmospheric CO_2 sinks. *Energy Convers. Manag.* **2003**, *44*, 681–689.

(32) Fujimura, K.; Matsui, T.; Izumiya, K.; Kumagai, N.; Habazaki, H.; Kawashima, A.; Asami, K.; Hashimoto, K. Oxygen evolution on manganese-molybdenum oxide anodes in seawater electrolysis. *Mater. Sci. Eng., A* **1999**, *267*, 254–259.

(33) Caldeira, K.; Wickett, M. E. Anthropogenic carbon and ocean pH. *Nature* **2003**, *425*, 365–365.

(34) Hilbertz, W. Solar-generated building material from seawater as a sink for carbon. *Ambio* **1992**, *21*, 126–129.

(35) Bourgeois, R. *Alkaline Electrolysis Final Technical Report, DOE Award DE-FC36−04GO14223*; General Electric Global Research Center: Niskayuna, NY, 2006; Available at http://www.osti.gov/bridge/servlets/purl/886689-RWJlW5/886689.PDF.

(36) Willett, J. C. Stone, Crushed. In *2006 Minerals Yearbook*; USGS: Reston, VA, 2007.

(37) Hudson, W. R.; Little, D.; Razmi, A. M.; Anderson, V.; Weissmann, A. An Investigation of the Status of by-Product Fines in the United States, Report ICAR-101-1; International Center for Aggregates Research: Austin, TX, 1997.

(38) Pacala, S.; Sokolow, R. Stabilization wedges: Solving the climate problem for the next 50 years with current technologies. *Science* **2004**, *305*, 968–972.

(39) *World Energy Outlook*; International Energy Agency: Paris, 2006.

(40) Archer, D.; Kheshgi, H.; Maier-Reimer, E. Multiple timescales for neutralization of fossil fuel CO_2. *Geophys. Res. Lett.* **1997**, *24*, 405–408.

(41) Rau, G. H.; Caldeira, K. Enhanced carbonate dissolution: A means of sequestering waste CO_2 as ocean bicarbonate. *Energy Convers. Manag.* **1999**, *40*, 1803–1813.

(42) Caldeira, K.; Rau, G. H. Accelerating carbonate dissolution to sequester carbon dioxide in the ocean: Geochemical implications. *Geophys. Res. Lett.* **2000**, *27*, 225–228.

(43) Rau, G. H.; Knauss, K. G.; Langer, W. H.; Caldeira, K. Reducing energy-related CO_2 emissions using accelerated weathering of limestone. *Energy* **2007**, *32*, 1471–1477.

(44) Golomb, D.; Pennell, S.; Ryan, D.; Barry, E.; Swett, P. Ocean sequestration of carbon dioxide: Modeling the deep ocean release of a dense emulsion of liquid CO_2 in water stabilized by pulverized limestone particles. *Environ. Sci. Technol.* **2007**, *41*, 4698–4704.

(45) Rogner, H.-H. Energy resources. In *World Energy Assessment: Energy and the Challenge of Sustainability*; United Nations Development Program: New York, 2000.

ES800366Q