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

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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, CaCO3 can be dissolved in the presence of the highly acidic anolyte of a water electrolysis cell. The resulting charged constituents, Ca2+ and CO32−, migrate to the cathode and anode, respectively, forming Ca(OH)2 on the one hand and H2CO3 or H2O and CO2 on the other. By maintaining a pH between 6 and 9, subsequent hydroxide reactions with CO2 primarily produce dissolved calcium bicarbonate, Ca(HCO3)2aq. Thus, for each mole of CaCO3 split, there can be a net capture of up to 1 mol of CO2. Ca(HCO3)2aq is thus the carbon sequestrant that can enhance passive uptake of CO2 from the atmosphere, largely forming Ca(HCO3)2 in solution as the CO2 storage product. Other schemes employ engineered structures for actively contacting of air with NaOH, forming Na2CO3 in solution (5–7). By subsequently reacting this solution with Ca(OH)2, CaCO3 is formed and NaOH is regenerated. The CaCO3 is then calcined at high temperature to form concentrated CO2 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 CaCO3. This contributes significantly to the cost of either process, plus additional CO2 is produced if the source of the thermal energy is derived from the combustion of fossil fuels. One way to avoid this CO2 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 (ClO3−), and/or chlorine gas (Cl2) 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 CO2 and other acid gas mitigation (14). However, producing hydroxide in quantities sufficient for large scale CO2 removal could in the case of a metal chloride-containing electrolyte means massive coproduction of one or more chloride-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 Cl2 and H2 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 chloride to relatively innocuous magnesium and calcium chlorides. Implementing such a scheme on a scale relevant to global CO2 mitigation would, however, require the careful handling and management of large quantities of Cl2 and HCl (15).

2. An Alternative

As a potentially safer and simpler approach, it is proposed that CaCO3 rather NaCl be used as the primary compound for the electrochemical formation of mineral hydroxide. Due to its very low solubility, CaCO3 is not an obvious choice for such aqueous electrochemistry. However, CaCO3 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 Ca2+ and CO32− ions then migrate toward the cathode and anode, forming Ca(OH)2 and H2CO3 (and/or CO2 + H2O), 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.

The calcium hydroxide formed will subsequently react with the CO₂ 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 carbonate 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 carbonate 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 CO₂. As dissolved CO₂ is consumed, a difference in CO₂ partial pressure would be produced between the solution and the overlying air causing the CO₂ in the overlying air to diffuse into the solution. In this way CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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., Mg²⁺, 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 CO₂ 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 CO₂. 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 CO₂-induced ocean acidification (24, 25). The net long-term effectiveness and benefits to CO₂ 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 CO₂ storage per mole of CaCO₃ split by the process would likely be in effect over the next century, when CO₂ emissions will be highest (15). Such issues would be moot with underground Ca(HCO₃)₂aq storage.

Another factor affecting net CO₂ mitigation by the process would be the CO₂ emissions associated with supplying and operating such an electrochemical system. Assuming the required electricity would come from releasable sources (types and quantities discussed below), additional energy requirements and hence CO₂ 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 CO₂ emissions from such activities could be small relative to the CO₂ consumed and avoided in an optimized system. A full lifecycle analysis of CO₂ emissions, consumption, avoidance, and hence, net mitigation by such a system is needed.

4. Thermodynamics and Energy Cost

Assuming the net reaction,

\[
\text{CaCO}_3 + 2\text{H}_2\text{O} + \text{CO}_2 + (\text{DC electricity}) \rightarrow \text{H}_2 + \text{Ca(OH)}_2 + 0.5\text{O}_2 + \text{Ca}^{2+} + 2(\text{HCO}_3^-) \tag{1}
\]

the theoretical work requirement, ΔG, is 266 kJ/mol CO₂ consumed (1682 kWh/tonne CO₂ consumed). This compares with an energy expenditure of 360 kJ/mol CO₂ (2273 kWh/tonne CO₂) 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 CO₂ 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/mol H₂ could be recovered in a 50% efficient fuel cell, for an offset of 121 kJ/mol CO₂ yielding a net energy expenditure based on the commercial electrolyzer example of 360 − 121 = 239 kJ/mol CO₂ consumed. Use of gas diffusion electrodes would reduce energy expenditure by about 1/3 (15), 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 CO₂ captured (7), but where air contacting is mechanistically assisted, hydroxide is thermally regenerated, pressurized molecular CO₂ rather than Ca(HCO₃)₂aq is the end product, and gross CO₂ capture rather than net CO₂ 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 CaCO3 powder, followed by 5 days of solution exposure to ambient air. The corresponding solution [OH−] = 10−9 to 10−7 M at a mean temperature of 16.5°C and salinity of 35 ppt (17). Dashed line denotes pretreatment values.

Note also that in principle 22 tonnes of CO2 can be captured per tonne H2 produced (eq 1). Thus, depending on the amount of CO2 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 Hz 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 CaCO3. 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 CaCO3 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 CaCO3 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 consequence 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 Ca2+ from the splitting of CaCO3 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 CO2 that slowly diffused in from the overlying air to form primarily HCO3− balanced by the excess Ca2+ 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 CO2 in the experimental and the control, respectively, yielding a net increase in CO2 absorption in the carbonate treatment of 0.8 mmol/L. An absorption of 1.0 mmol/L of CO2 occurring over approximately 120 h into 0.3 L of solution with a surface area of 95 cm2 yields a mean gross CO2 absorption rate of 0.073 µmole m−2 sec−1. Subtracting the CO2 generated by the splitting of CaCO3, 0.4 mmol/L, then leads to an estimated net CO2 uptake of about 0.6 mmol/L in the carbonate treatment, requiring a mean net CO2 absorption rate of 0.044 µmole m−2 sec−1. For comparison, an estimated net CO2 absorption by the ocean of 7 Gt/yr (29) yields a mean net air-to-sea CO2 absorption rate of 0.015 µmole m−2 sec−1 or about 1/5, 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 CO2 flux rate in the experiments.

The energy input for the preceding net CO2 absorption amounted to about 34 mWh, or about 8 × 108 kWh/tonne CO2 consumed. This energy expenditure is >10 times higher than anticipated from the commercial alkaline solution electrolysis example discussed above, indicating that the experimental cell configuration used was far from being thermodynamically optimal.

6. Large Scale Implementation

While the electrochemical system described could have application to localized hydroxide production, CO2 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 CO2 absorption (5–7, 30–32), and such devices might provide an effective use for the calcium hydroxide produced here for CO2 mitigation. Also, to the extent that CO2 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 CO2 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 atmospheric CO2 (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 CO2 absorption. Indeed ≈5% of the ocean surface would be needed to absorb an additional 1 Gt/yr of atmospheric CO2 if seawater CO2 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 tonnes per net tonne CO₂ consumed, the exact quantity dependent upon the purity and reactivity of the mineral carbonate used. In turn the H₂ 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 CO₂. In any case, unlike point-source mitigation, air CO₂ 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-CO₂ producing renewable electrical energy sources would be particularly attractive for maximizing net CO₂ 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 chlorine ion from entering the anolyte (12, 13), or (3) the diversion of the H₂ 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 H₂ produced at the cathode could be used as an energy source/carrier or as a chemical feedstock, the value of which could help offset the cost of the simultaneous hydroxide solution production. For example the oxidation of the H₂ 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 CO₂-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 O₂ or air as the H₂ 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 CO₂ into the ocean (24, 33). Furthermore, this hydroxide and/or the subsequent formation of Ca(HCO₃)₂ via reaction with CO₂ 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 carbonate substrates 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 CO₂ lose from seawater at the acidic anode, resulting in a net source rather than a net sink of atmospheric CO₂. 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 H₂ requires at least 50 kWhₑ/kg H₂ (26). Since 2 kg H₂ would be produced per 44 kg noncarbonate CO₂ consumed (eq 1), 50 × 2/44 = 2.273 kWhₑ would be used per net kg CO₂ captured, or 2273 kWhₑ/tonne CO₂ consumed. Assuming $0.06/kWhₑ (e.g., unsubsidized wind (26)), then 2273 × 0.06 = $136.38/net tonne CO₂ consumed. Capital, operation, and maintenance (O&M). Advanced alkaline (KOH) electrolyzer capital cost is reportedly $600/tonne H₂ produced (35). Assuming a similar capital cost for the electrolyzer envisioned here yields a CO₂ equivalent capital cost of $600 × 2/44 = $27.27/tonne CO₂ consumed. O&M charges are assumed to be 3% of capital expenditure (26), bringing the total CO & M cost to $28.09/tonne CO₂ consumed. Mineral carbonate. If the limestone used contains 95% CaCO₃, 2.42 tonnes of limestone are then required per net tonne CO₂ consumed. At an assumed delivered price of $8/tonne of crushed stone (36), mineral carbonate cost would then be $19.36/tonne CO₂ 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/tonne CO₂ consumed is budgeted here, bringing the estimated total carbonate cost to $22.36/tonne CO₂ consumed. Water. 0.82 tonnes of water are consumed per net tonne CO₂ 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 CO₂ storage potential of 0.6 mmole CO₂/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 CO₂ 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 therefore projected to be $136.38 + $28.09 + $22.36 = $186.83/net tonne CO₂ consumed.

Potential cost offsets include HE: Assuming the value of the H₂ produced is $1500/tonne H₂, then the value added to CO₂ capture is $1500 × 2/44 = $68.18/net tonne CO₂ consumed. Quantity and value of CO₂ mitigated: If 9 tonnes of CO₂ are avoided per tonne H₂ produced (via this carbon-free electrolysis versus natural gas reforming (26)), and if 44/2 = 22 tonnes CO₂ are consumed from air per tonne H₂ produced (eq 1), then at total of 9 × 22 = 162 tonnes CO₂ are mitigated/tonne H₂ produced, or 31 tonnes × 2/44 = 1.41 tonnes CO₂ mitigated/net tonne CO₂ consumed. Assuming a value of $10/tonne CO₂ mitigated yields $10 × 1.41 tonnes CO₂ mitigated/net tonne CO₂ consumed = $14.10/net tonne CO₂ consumed. Other potential cost offsets (not monetarily valued here): (a) Energy storage and recovery including load leveling and peak shaving via H₂ storage/oxidation (26), (b) subsequent freshwater production via H₂ oxidation, (c) the value of O₂ or other gases produced, and (d) ocean acid mitigation, e.g., local or regional preservation or enhancement of economically important marine shelfish. The total estimated cost offset is then $68.18 + $14.10 = $82.28/net tonne CO₂ consumed. Subtracting this from gross cost, yields a net cost of $186.83 − $82.28 = $104.55/net tonne CO₂ consumed or ($1.41 tonnes CO₂ mitigated/net tonne CO₂ consumed) = $74.15/tonne CO₂ mitigated. For comparison, this latter figure is at the high end of the cost range estimated for the capture and geologic storage of molecular CO₂ from air. Baciocchi et al. (26) have estimated the cost of capturing CO₂ from air and co-production of H₂ via the Ca(OH)₂-CaCO₃ cycle using concentrated solar power - Thermodynamic analysis. Energy 2006, 31, 1715–1725. However, lacking an optimized prototype system, the true cost, effectiveness, and potential of this electrolysis-based CO₂ mitigation scheme remains to be demonstrated.

To conclude, the magnitude and urgency of the global CO₂ 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 CO₂ emissions cannot be feasibly controlled by point-source methods (e.g., automobiles, ships, planes, noncompliant point-source emitters), options for post-emission absorption of CO₂ from the air are needed. The passive absorption of air CO₂ by the ocean has already saved us from the climate impacts of about half of the anthropogenic CO₂ released thus far (29), and will ultimately absorb most of the human-induced atmospheric CO₂ 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 thousands of years to return to near preindustrial CO₂ 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 CO₂ (23) or (ii) to proactively modify ocean chemistry to enhance air CO₂ 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 × 10^9 TWh/yr (45)). Some small fraction of this energy could conceivably be converted to electricity and used to help electrochemically stabilize or reduce atmospheric CO₂ 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.

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