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Electrochemical Acceleration of Chemical Weathering as an Energetically Feasible Approach to Mitigating Anthropogenic Climate Change

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We describe an approach to CO_2 capture and storage from the atmosphere that involves enhancing the solubility of CO_2 in the ocean by a process equivalent to the natural silicate weathering reaction. HCl is electrochemically removed from the ocean and neutralized through reaction with silicate rocks. The increase in ocean alkalinity resulting from the removal of HCl causes atmospheric CO_2 to dissolve into the ocean where it will be stored primarily as HCO_3^- without further acidifying the ocean. On timescales of hundreds of years or longer, some of the additional alkalinity will likely lead to precipitation or enhanced preservation of $CaCO_3$, resulting in the permanent storage of the associated carbon, and the return of an equal amount of carbon to the atmosphere. Whereas the natural silicate weathering process is effected primarily by carbonic acid, the engineered process accelerates the weathering kinetics to industrial rates by replacing this weak acid with HCl. In the thermodynamic limit—and with the appropriate silicate rocks—the overall reaction is spontaneous. A range of efficiency scenarios indicates that the process should require 100–400 kJ of work per mol of CO_2 captured and stored for relevant timescales. The process can be powered from stranded energy sources too remote to be useful for the direct needs of population centers. It may also be useful on a regional scale for protection of coral reefs from further ocean acidification. Application of this technology may involve neutralizing the alkaline solution that is coproduced with HCl with CO_2 from a point source or from the atmosphere prior to being returned to the ocean.

Introduction

Concern about anthropogenic climate change has stimulated research and investment into technologies that limit CO_2 emissions from the combustion of fossil fuels (*1*) and into technologies that remove CO_2 directly from the atmosphere (*2*). In these proposals, near pure streams of CO_2 are produced from point sources or from the atmosphere by retrofitting power plants to separate CO_2 from flue gas using various solvents (*3*), separating nitrogen from air prior to combustion to enable pure oxygen combustion (*3*), employing the water-gas-shift reaction in a gasification plant to enable hydrogen–oxygen combustion in a hydrogen gas turbine (*3*), or capturing CO_2 directly from the atmosphere using solvents with a chemical process designed to regenerate the solvents (*4*).

Once a highly concentrated stream of CO_2 is produced, the CO_2 must be stored in a near-permanent reservoir. Several technologies are being investigated for the long-term storage of captured anthropogenic CO_2. These technologies include storing CO_2 in various geologic formations (e.g., oil and gas fields (*5*), coal beds (*6*), and saline aquifers (*7*)); injecting CO_2 into the deep ocean (*8, 9*); chemically transforming CO_2 into thermodynamically stable minerals (*10, 11*) or bicarbonate brines (*12, 13*); and storing CO_2 as hydrates and in a dense liquid phase beneath deep ocean sediments (*14*).

All of the technologies to capture and store CO_2 from large CO_2 point sources can be applied to point sources that combust or gasify biomass. In such applications, capturing and storing the CO_2 that is produced during the oxidation of biomass results in the net removal of CO_2 from the atmosphere (*15*). Additionally, some quite different approaches to mitigating climate change have been proposed such as fertilizing the ocean with dissolved iron to increase biological uptake of atmospheric CO_2 or injecting sulfate into the troposphere to increase to the Earth's albedo (*16*).

Here we discuss an integrated CO_2 capture and storage process that involves increasing the solubility of CO_2 in the ocean by increasing the ocean's alkalinity—either through electrolytically removing hydrochloric acid (HCl) from the ocean and neutralizing it through reactions with silicate minerals, or by adding NaOH that was produced via electrolysis of an artificial brine to the ocean. The net result of the process is to increase the ocean's alkalinity and enhance the ocean's ability to take up atmospheric CO_2. The process is equivalent to the electrochemical acceleration of the Earth's natural chemical weathering process, which is mediated by carbonic acid. Related engineering processes have been proposed for the storage of CO_2—notably, forming carbonic acid from a stream of CO_2 and reacting it with silicates to form carbonates (*10*). The kinetics of silicate rock dissolution by carbonic acid are, however, very slow (*17*). In contrast, the process discussed in this paper involves the dissolution of silicate rocks by concentrated HCl—which is known to proceed much more rapidly (*18*) and does not require a concentrated stream of CO_2.

Theoretical Background

The amount of dissolved inorganic carbon (DIC) in the surface ocean is controlled by seawater alkalinity, and by the partial pressure of CO_2 in the atmosphere. Alkalinity is defined as the concentration difference between conservative cations and conservative anions (i.e., ions whose concentrations are independent of moderate changes in temperature). If one neglects minor nonconservative anions such as borate, then seawater alkalinity is approximately equal to the charge contribution of bicarbonate and carbonate ions (*19*):

$$\mathrm{Alk} \approx 2[Ca^{2+}] + [K^+] + 2[Mg^{2+}] + [Na^+] - [Cl^-] - 2[SO_4^{2-}] \approx [HCO_3^-] + 2[CO_3^{2-}]$$

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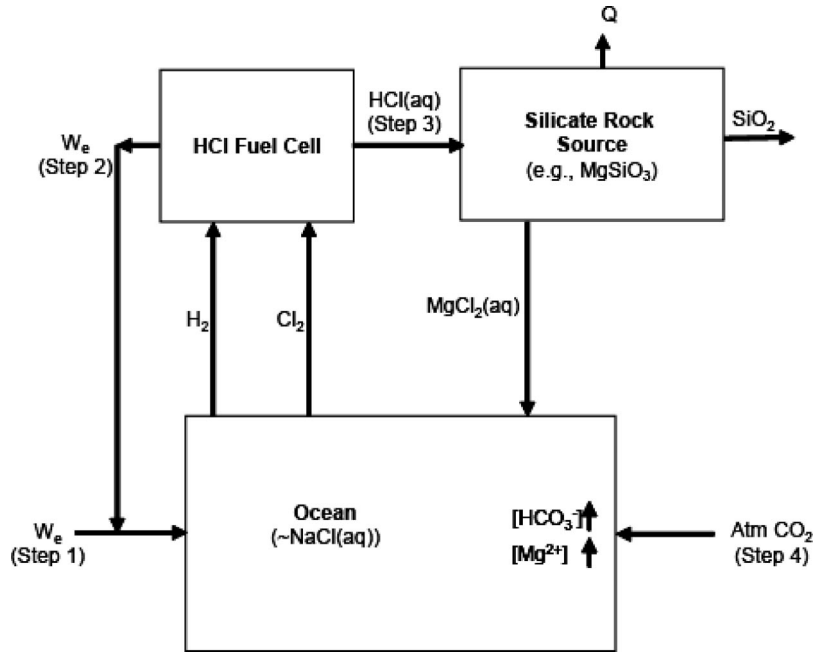

FIGURE 1. Diagram showing carbon dioxide sequestration via the removal and neutralization of hydrochloric acid from the ocean. Magnesium has been used to represent any metal found in silicate rocks. W_e represents electrical work and Q represents heat.

Increasing the ocean's alkalinity causes a shift in the partitioning of carbon between the ocean and atmosphere to balance the increase in positive conservative charge. The net result of increasing seawater alkalinity is an increase in DIC and a decrease in atmospheric CO_2. Over geologic times, silicate weathering reactions produce alkalinity, which is delivered by rivers to seawater and ultimately removed by precipitation of calcium carbonate.

In the process described here, the removal of HCl liberates sodium hydroxide and thereby increases the alkalinity of seawater. The process enhances oceanic uptake of CO_2, effectively employing the entire surface ocean as a giant carbon dioxide collector. The current uptake of anthropogenic CO_2 by the ocean is causing the surface ocean's pH to drop. Removing HCl from the ocean will cause a local rise in pH, which will be mostly offset by additional CO_2 uptake. By selectively removing HCl from the ocean, the described process will moderate the current rate at which the ocean's pH is dropping.

Alternatively, NaOH and HCl can be produced via electrolysis of an artificial brine made from mined halite mineral. After neutralizing the HCl via the dissolution of silicate rocks, the dissolution products and the NaOH are added to the ocean to increase its alkalinity. The net result of employing a high-purity artificial brine is chemically equivalent to the removal and neutralization of HCl from the ocean, and at present, it is more technologically feasible because electrochemical separation of high-purity artificial NaCl solution is well established (*20, 21*).

In both cases, the HCl can be neutralized via the dissolution of silicate rocks, and the dissolution products—primarily aqueous $MgCl_2$ and $CaCl_2$ salts—can be returned to the ocean. The neutralization of the hydrochloric acid is critical: any chloride ion that returns to the ocean with a proton rather than a corresponding conservative cation will decrease the ocean's alkalinity and cause CO_2(aq) to degas into the atmosphere—reversing the CO_2 removal effort.

Process Description

The thermodynamics of the process that employs seawater are essentially the same as the process that employs an artificial NaCl solution. (The free energy required to purify Mg^{2+} and Ca^{2+} from their values in seawater, 50 and 10 mmol/L, respectively, to the ppm levels required in diaphragm Chloralkali cells, is 1.8 and 0.3 kJ/(mol Na+), respectively). High-purity brine (i.e., less than 1 ppm impurities) can be produced by descaling seawater (*22*) or by mining and purifying halite minerals (*23*). We describe the process of electrolyzing an artificial NaCl solution, which can be largely implemented with technology currently used in the chlorine industry. Although the technical application of this case is straightforward, modifications to current technology may enable the direct extraction of HCl from seawater resulting in significantly reduced costs. Those modifications are discussed in the next section.

Step 1. The first step of the process involves the removal of chloride ions from a high-purity artificial salt solution. The Chloralkali process is a standard electrochemical process for producing chlorine gas and hydrogen gas from NaCl(aq) (*24*).

$$\mathrm{NaCl(aq) + H_2O(l) \rightarrow NaOH(aq) + \frac{1}{2}Cl_2(g) + \frac{1}{2}H_2(g)}$$

$$\Delta G_1 = +212 \frac{\mathrm{kJ}}{\mathrm{molNaOH}} \quad (1)$$

With modification (*20, 22, 25–28*), a similar process can be employed to produce Cl_2(g) and H_2(g) from seawater. Step 1's minimum electrical input requirement is given by the change in free energy of the reaction (*29*). For the purposes of this paper, all thermodynamic calculations have been performed with intermediate states at standard state conditions, and all initial and final states at in situ conditions of seawater (e.g., CO_2(g) starts at 400 μAtm, $[Na^+]$ and $[Cl^-]$ start at ~500 mmol/L, $[Mg^{2+}]$ ends at ~50 mmol/L, $[Ca^{2+}]$ ends at ~10 mmol/L, and $[HCO_3^-]$ ends at ~1.8 mmol/L). In application, it will likely be beneficial to engineer the system's initial state (e.g., increasing the concentration of NaCl) and final state (The free energy saved by starting with 6 mol/L saturated NaCl solution instead of at the concentration of sea water is 7 kJ/(mol Na+)).

Step 2. HCl is formed from the Cl_2(g) and H_2(g) that was produced in step 1. This step represents the first of several steps in which some energy input required for step 1 can be recovered. In step 2, the Cl_2(g) and H_2(g) are combined in a

fuel cell (Step 2, Figure 1) to produce either HCl(aq) or HCl(g) and electricity.

$$\frac{1}{2}Cl_2(g) + \frac{1}{2}H_2(g) \rightarrow HCl(aq) \quad \Delta G_2 = -131\frac{kJ}{molNaOH} \quad (2)$$

These cells have been investigated for large-scale peak power shaving and load leveling applications (*30, 31*), and early work suggests that HCl fuel cells can be highly efficient (*32*). The HCl that is produced in step 2 is neutralized via the dissolution of silicate rocks either in a reaction vessel or in situ. An alternative to processes 1 and 2 is the direct conversion of salt water to acid and base by a method such as bipolar membrane electrodialysis (*33*). In principle, single-step methods have the potential for increased efficiency, but at this time it is not clear whether such single-step methods can actually achieve scalable efficiency improvements over the Chloralkali process.

Step 3. HCl is neutralized by various silicate rocks. Here, the mineral enstatite ($MgSiO_3$) is used for illustration. For many plentiful silicate rocks and minerals the dissolution reaction is exothermic and spontaneous:

$$HCl(aq) + \frac{1}{2}MgSiO_3(s) \rightarrow \frac{1}{2}MgCl_2(aq) + \frac{1}{2}SiO_2(s) + \frac{1}{2}H_2O(l)$$

$$\Delta H_3 = -58\frac{kJ}{molNaOH} \quad (3)$$

For every mole of NaOH produced in Step 1, the dissolution of enstatite will generate ~58 kJ of heat. The kinetics of rock dissolution are an important consideration for this process, and the kinetics of silicate rock dissolution are highly dependent on pH and temperature (*18*).

If the dissolution reaction occurs in a near-adiabatic reaction vessel, then the heat generated in the reactor vessel will accelerate the reaction kinetics because the dissolution process is thermally activated. Additionally, some of the heat generated in the reaction vessel might be harnessed to run other aspects of the process. One obvious use for the heat generated during the rock dissolution is to increase the temperature of the incoming salt water for the purpose of performing high-temperature electrolysis (*34*). Initial heating of the salt water has the potential to decrease the overall electrical input required by 10–20 kJ/mol.

Step 4. The final step of the process involves the capturing and storing of $CO_2(g)$.

$$CO_2(g) + NaOH(aq) \rightarrow NaHCO_3(aq) \quad \Delta H_4 = -70\frac{kJ}{molNaOH} \quad (4)$$

After the electrolysis in step 1, the NaOH(aq) can be added to the surface ocean to increase its alkalinity, it can be used on land to react with atmospheric $CO_2(g)$ (e.g., from the atmosphere in a spray tower or other mass transfer device (*35*)), or it can be used at an industrial point source to react directly with a highly concentrated stream of $CO_2(g)$.

Net Reaction. Only the first step of the overall process requires energy input. The three subsequent steps are spontaneous and exothermic. Combining equations 1, 2, 3, and 4 gives the net chemical reaction of the overall process:

$$\frac{1}{2}H_2O(l) + \frac{1}{2}MgSiO_3(s) + CO_2(g) \rightarrow$$

$$\frac{1}{2}Mg^{2+} + \frac{1}{2}SiO_2(s) + HCO_3^- \quad \Delta G_{net} = -4\frac{kJ}{mol}$$

The net reaction—which includes *both* the capture and permanent storage of CO_2—is spontaneous. For each mole of enhanced CO_2 uptake by the ocean, the process illustrated here requires ~81 kJ of electrical energy in steps 1 and 2 and generates ~128 kJ of heat and ~85 kJ of availability, or work potential, in steps 3 and 4. The net reaction is identical whether we begin the process with seawater or with high-purity artificial brine. It is not surprising that the net reaction is spontaneous because it is the natural silicate weathering reaction. The pathway described via steps 1–4 uses electrical input to switch the acid from weak carbonic acid to strong HCl. That acid switch will enable the net weathering reaction to be accelerated to industrial rates. In the thermodynamic limit, the pathway described still provides ~4 kJ of availability per mole. Obviously, efficiency losses will severely impact the actual balance.

Discussion

Impact on Atmospheric CO_2 Concentration. Each mole of HCl removed from the ocean and neutralized increases ocean alkalinity by 1 mol, and on short time scales (~100 y), each additional mole of alkalinity causes ~1 mol of atmospheric $CO_2(g)$ to dissolve into the ocean (*19*). Mixing processes will distribute the additional alkalinity into deeper water over hundreds to thousands of years, enhancing the current ocean uptake, which is approximately 7.5 gigatonnes of CO_2 (2 Gt C) per year (*36*). The higher alkalinity will also increase the supersaturation of calcite or aragonite, leading to enhanced precipitation. The magnitude of enhanced precipitation depends on the degree to which the ocean's saturation state can change. In the most conservative scenario, the saturation state of the surface ocean is fixed at its current value and—at equilibrium—every mole of alkalinity added to the ocean ultimately results in the precipitation of 0.5 moles of $CaCO_3$ (*19*). That enhanced precipitation results in the permanent storage of 0.5 moles of DIC while returning another 0.5 moles of DIC to the atmosphere as CO_2. We define the process effectiveness to be the molar ratio of CO_2 stored to HCl removed and neutralized. Therefore, in the most conservative scenario of a fixed $CaCO_3$ saturation state, the ultimate process effectiveness equals 0.5. The same arguments lead us to conclude that the ultimate process effectiveness of other proposals that involve dissolving mined Na_2CO_3 or $MgCO_3$ directly into the ocean (*10*) is about zero.

In the present ocean, the $CaCO_3$ saturation state is maintained primarily by biologic activity and $CaCO_3$ precipitation. In principle, the saturation state can vary with time. A rising saturation state would enable more DIC to remain in the ocean. That implies that if increasing the alkalinity of the surface ocean by removing and neutralizing HCl resulted in a permanently higher $CaCO_3$ saturation state, then the ultimate process effectiveness will be between 0.5 and 1. Moreover, the time scale for maintaining the saturation state of the surface ocean, although shorter than the carbonate compensation for the whole ocean, is at least hundreds of years, which indicates that at the very least the process effectiveness will remain close to 1 for several generations (*37*). (Flash precipitation of calcite is probably acceptable because ocean mixing will provide for re-dissolution. Also, adding alkalinity to ocean regions under-saturated in calcite could help avoid transient precipitation). Ultimately, it is likely that biomineralization and $CaCO_3$ precipitation will return the saturation state to near its initial value resulting in a long-term decline of the process effectiveness from 1 toward 0.5. It is plausible that the saturation state will settle at a value higher than its initial value resulting in an ultimate process effectiveness greater than 0.5. It is unlikely, however, that the ultimate $CaCO_3$ saturation state will rise in direct proportion to the added alkalinity as evidence indicates that ocean pH has remained relatively stable over time (*38*).

The increasing partial pressure of CO_2 (pCO_2) due to fossil fuel combustion is causing the ocean to acidify, $CaCO_3$ to

TABLE 1. Thermodynamics (kJ/(mol of CO_2 Sequestered)) for a Variety of Rock/Mineral [a] (*55–56*): the Summation Indices Indicate for What Subset of Steps the Calculations Were Performed[b]

rock	$\sum_1^4 \Delta G_i$	$\sum_1^2 \Delta G_i$	$\Delta\varphi_3$	$\sum_1^3 \Delta\varphi_i = \sum_1^3 (\Delta H_i - T_0\Delta S_i)$	rock/CO_2 mass ratio
$MgSiO_3$	−4	+81	−51	+30	∼2
ultramafic	−3	+81	−54	+27	∼1
basalt	+0	+81	−58	+22	∼3
granite	+13	+81	−34	+47	∼6

[a] The dissolution was assumed to remove the most weakly bonded cation only. The thermodynamics for rock dissolution were estimated by treating rocks as being composed of a set of end-member minerals for which good thermodynamic data are available and chosen to match each rock's bulk geochemical composition. Ultramafic (based on Harzburgite from the Sumail Mastif, Oman) was modeled using geochemical data as 70.5% fosterite, 20% enstatite, 4% magnetite, 3% fayalite, 2% wollansonite, and 0.5 ferrosilite. Basalt (based on Icelandic basalt; USGS reference material BIR) was modeled as 29% enstatite, 23% anorthite, 17% wollastonite, 14% albite, 13.9% ferrosilite, and 3.1% magnetite. Granite (based on USGC reference material G-2 36) was modeled as 38.8% quartz, 34% orthoclase, 20.5% albite, 3.5% anorthite, 1.1% enstatite, 1.1% ferrosilite, and 1% magnetite. [b] The first column indicates the Gibbs free energy change of the overall net reaction. The second column provides the lower bound on the energy input required for the electrochemical steps (i.e., steps 1 and 2). In the fourth column $\Delta\varphi$ is the *availability* (or exergy, or work potential) of the rock dissolution reaction. The fifth column is the *availability* of all the steps except for the CO_2-capture step as it is unlikely that any work could be recovered from the CO_2-capture step. Finally, the last column indicates the rock to CO_2 mass ratio required to fully neutralize the HCl.

dissolve, and the $CaCO_3$ saturation state to decrease (*39*). If we artificially add alkalinity to the ocean, then the rate of $CaCO_3$ dissolution will slow—which is equivalent to $CaCO_3$ precipitation. The additional alkalinity will not necessarily cause additional $CaCO_3$ precipitation, but it will cause enhanced preservation because the $CaCO_3$ saturation state will be higher with the addition of artificial alkalinity than it would have been without the addition of artificial alkalinity. Thus, one can view the process as inhibiting the dissolution of $CaCO_3$ that would have occurred absent the addition of artificial alkalinity. The enhanced $CaCO_3$ preservation serves to decrease the process effectiveness in the same manner that $CaCO_3$ precipitation does so in the fixed saturation state case. So even with monotonically increasing pCO_2, the ultimate process effectiveness will be between 0.5 and 1 depending on how the $CaCO_3$ saturation state changes in the future. At the very least, the method for enhanced ocean uptake described here will have full effect (i.e., one mole of carbon storage for each mole of alkalinity added) over the next century, when anthropogenic inputs are likely to be highest.

Application. The practical application of the process discussed in this paper may differ in several ways from the description provided above.

Although the process discussed here works using mined salt or purified seawater in a standard Chloralkali plant, it is envisaged that the relaxed requirement for NaOH concentration and purity may permit the utilization of a modified, lower-cost seawater electrolysis process for the purposes described in this paper. Chloralkali plants do not use seawater because at high pH precipitates such as $CaCO_3$, $CaSO_4$, and $Mg(OH)_2$ clog the membranes, diaphragms, and electrodes (*40*). Chloralkali plants make brine from purified salt or employ technologies for removing the multivalent cations (*20*). Research into engineering electrochemical cells to operate at seawater impurity levels (*25, 28*) has had some success. For example, sodium hypochlorite and hypochlorous acid are currently being produced by the electrolysis of seawater (*41*), and seawater electrolysis is being tested for coral reef restoration (*42*). Currently coral reefs and their rich biological communities are being damaged by warming, pollution, and acidification. Regional protection from further pH drop with the careful, dispersed, monitored, and regulated application of the process described here may be beneficial.

The second possible difference between the theoretical description and the practical application is that pure minerals—such as enstatite—are not readily available. Instead, silicate rocks will likely be used to neutralize the HCl. Table 1 shows the thermodynamics and the mass of rock required for the process using three major rock types. Due to its relatively low aluminum content, ultramafic rock is more favorable thermodynamically because it releases more alkalinity per unit mass than basalt and granite. In the presence of strong acids, rocks with high aluminum content tend to produce aluminum silicates rather than silica (*43*). In our thermodynamic calculations, we have conservatively assumed the production of aluminum silicates. In addition, granite can contain >40% nonreactive silica. The silica will decrease the final temperature of the dissolution products and limit both the dissolution kinetics and the useful work that might be harnessed from the rock dissolution process. Table 1 indicates the mass of rock required to neutralize the HCl. Because pure silica and aluminum silicates are treated as nonreactive constituents of the rock, the rock to CO_2 mass ratio increases sharply in the presence of alumina and silica. The large silica content of granite indicates that approximately twice as much granite as basalt is required to neutralize the HCl.

The third possible difference involves the method of HCl neutralization. As an alternative to neutralizing the acid in a reactor vessel, the HCl could be injected into or sprayed onto a basaltic or ultramafic rock formation. In such a configuration, the HCl would be neutralized as it flowed naturally through the porous matrix of the rock formation. The seepage flow could be engineered such that the time scale of HCl flow through the fabric would be slow relative to the time scale of the rock dissolution. If the timescales are appropriately engineered, then by the time the dissolution products reached the ocean, the HCl would be largely neutralized.

The fourth possible difference between the theoretical description and the application involves the CO_2 capture point. Using the ocean as our CO_2 collector is the simplest process to implement. Increasing seawater alkalinity, however, will cause a rise in pH near the operation, which may damage local marine biota. To avoid such damage, it is plausible that the NaOH could be neutralized to $NaHCO_3$ or Na_2CO_3, e.g., at an industrial point source or with atmospheric CO_2 in spray towers (*2, 4*), prior to ocean disposal. The neutralized solution, as well as the rock dissolution product, could be disposed of in the surface ocean, the deep ocean, or terrestrial reservoirs. Either of the latter two options would ensure that the ultimate process effectiveness remains close to 1 mole of CO_2 per mole of HCl removed and neutralized. The marginal energy input required to employ the deep ocean will be minor because the solution is denser than seawater.

The final significant difference between the theoretical description and the anticipated application of the overall

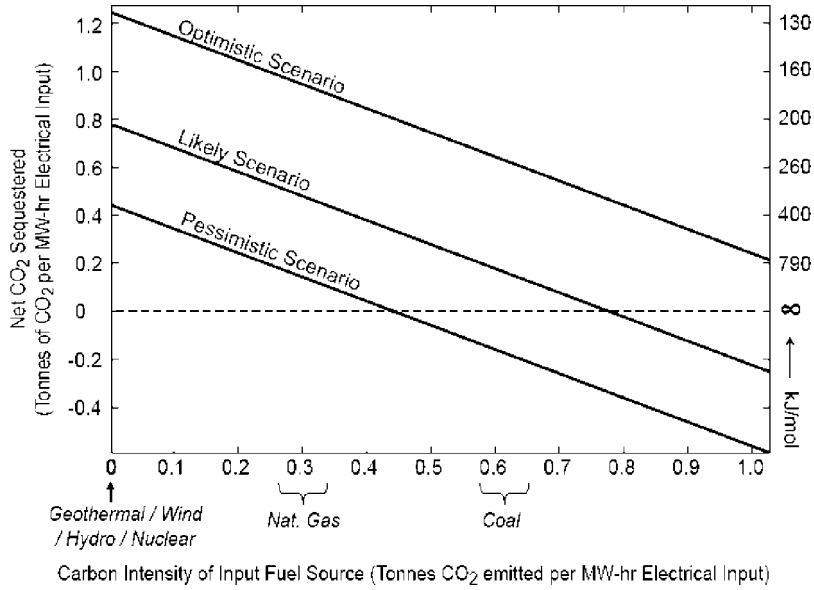

FIGURE 2. Net CO_2 sequestered (t) as a function of the carbon intensity of input fuel source for the process depicted in Figure 1 using standard Icelandic basalt (BIR-1) to neutralize the HCl. The three lines correspond to different efficiency scenarios. The optimistic scenario assumes 10 molar NaCl solution with a 1-step electrochemical process at 60% efficiency for steps 1 and 2 and 15% productive heat recovery from step 3. The likely scenario assumes 10 molar NaCl solution, a 70% efficient electrolysis (*44*), a 70% efficient HCl fuel cell (*45*), and zero heat recovery from step 3. Finally, the pessimistic scenario assumes 0.6 molar NaCl, 50% efficiency for the electrolysis, 50% efficiency for the HCl fuel cell, and zero heat recovery. Also, this figure assumes the time scale of anthropogenic climate change is similar to the time scale for the surface ocean to remove excess alkalinity. The right-hand vertical axis is required work per net mole of CO_2 sequestered.

process is the efficiency of each step. Step 1 of Figure 1 is an electrolysis step that we expect to achieve an efficiency of 60%–80% (*44*). Step 2 is a fuel cell that we expect to achieve an efficiency of 65%–75% (*45*). Step 3 may involve waste heat recovery from the rock reactor—although it is difficult to say whether such waste heat could be productively employed. The maximum useful work that can be generated from the heat recovered is given in Table 1 as the availability of the dissolution reaction.

The most important physical metric for any carbon dioxide capture and storage technology is the net quantity of CO_2 sequestered (i.e., CO_2 avoided) per unit of energy used to capture and store the CO_2. Figure 2 illustrates the net CO_2 sequestered by the overall process under three efficiency scenarios. The net CO_2 sequestered is a function of both the required energy input and the carbon intensity of the fuel source used to generate that energy input. If the fuel source has zero carbon intensity (i.e., it emits zero units of CO_2 per unit of energy produced), then the net CO_2 sequestered equals the quantity of CO_2 stored. The vertical intercept of Figure 2 is the reciprocal of the work required per unit (tonne) of CO_2 captured and stored under various efficiency scenarios for a carbon-free energy source (e.g., nuclear/geothermal/hydro/wind). Under the optimistic efficiency scenario, the net CO_2 sequestered when carbon-free energy is used to run the overall process is greater than ~1.2 t per MW-hr of electrical input. Producing one MW-hr of electricity from a new coal fired power plant produces ~0.60–0.80 t of CO_2 (*46, 47*). Thus, if a carbon-free plant were built to provide the electrical work required by the process, then—under the optimistic efficiency scenario—that plant could offset nearly twice as much emitted CO_2 as would have been eliminated by substituting a coal-fired power plant with the carbon-free power plant. Under the pessimistic efficiency scenario, however, the net CO_2 captured and stored is less than can be avoided by replacing the coal-fired power plant with a carbon-free power plant.

Benefits of Enhancing Ocean Uptake of CO_2. China, India, and other developing countries are investing substantial capital in carbon-intensive infrastructure (*48*). Given these investments and the uncertainty of future climate damages, it may—at some point—become necessary to remove CO_2 directly from the atmosphere. The process discussed here can be run anywhere in the world and works equally well for all sources of CO_2—including the ~67% of anthropogenic CO_2 emissions that do not emanate from power plants (*1*). The work input required for the overall process is expected to be between ~1.5 and ~3.5 times higher per unit of CO_2 than the work required for postcombustion capture and geologic storage of CO_2 from a modern coal-fired power plant (*1*). It is likely, however, that limiting the CO_2 emissions from the transportation sector, building heating, and various industrial processes will be more expensive than limiting that from power plants.

An additional benefit of electrolyzing seawater to enhance ocean CO_2 uptake is that it can be performed in geographic regions with an abundance of zero and low carbon power sources. For example, stranded geothermal energy from active volcanic regions is a relatively inexpensive and carbon-free power source. Therefore, volcanic islands with large geothermal resources and large basalt deposits might be ideal locations. Wind turbines—whose general deployment is partially limited by intermittency of supply—are another interesting carbon-free power option because the process can be designed to operate only when an excess of wind power exists. Alternatively, the process could be powered by gas-turbines in oil-producing regions where natural gas is flared because the infrastructure required for long-distance transport is not available.

Research into actively capturing CO_2 from the air by solvent regeneration cycles is ongoing (*35*). Enhancing ocean uptake of CO_2 via seawater electrolysis has some benefits over the solvent regeneration proposals. The goal of the solvent regeneration processes is to separate CO_2(g) from air and produce a near pure stream of CO_2(g) for compression to ~200 atm, transportation to a storage site, and injection into a geologic reservoir. In contrast, the CO_2 in the process we discuss is chemically altered to a more stable state and

permanently stored in the ocean. Hence it would not be necessary to locate and fully characterize a multitude of suitable geologic storage depositories for the captured CO_2.

Engineering Difficulties and Scale Limitations. The process must overcome several technical hurdles before it can offset an appreciable quantity of CO_2 emissions. The magnitude of the CO_2 problem is daunting, and offsetting even ~15% of global emissions by electrolysis of seawater would be a serious task. To offset ~15% of annual carbon emissions (~3.7 Gt CO_2 or 1 Gt of carbon), $\sim 10^{14}$ moles of HCl would have to be removed from the ocean and neutralized per year. Seawater would have to be separated into acid and base at a global volumetric flow rate of ~6000 m^3/s. Large sewage treatment facilities have a capacity of ~60 m^3/s (*49*). Thus, capturing and storing 3.7 Gt of CO_2 annually by the process we discuss would require ~100 plants with a volumetric flow capacity similar to that of large sewage treatment facilities.

If the process were to be employed with artificial brine from mined halite deposits, then the volumetric flow rate requirements would be reduced by an order of magnitude. The chloralkali industry would have to grow for 50 years by 3.75% per year over and above the normal consumption growth from a base of 43 million t of Cl_2 production in 2003. Chemical weathering would increase from 0.4 to 1.4 Gt of C per year over this same period. With $\sim 10^{20}$ moles of mineral NaCl in continental basins, there is a sufficient resource of mineral NaCl to offset many centuries of anthropogenic CO_2 emissions using the standard Chloralkali process coupled with an HCl fuel cell and silicate rock dissolution.

Economical electrolysis of seawater is another technological challenge. The current cost of removing multivalent cations before running the Chloralkali process is high. Additionally, ohmic losses in seawater would need to be reduced, e.g., by concentrating through evaporation, boiling, or dissolution of mineral halite.

One potential undesirable consequence of employing this process directly with seawater would be the production of halogenated organics as a byproduct of the electrochemical reactions on seawater. During the electrolysis, some dissolved organic carbon (DOC) can be expected to be halogenated and some of this could be in the form of volatile stratospheric ozone-destroying compounds such as CH_3Br_3 and CH_3Cl_3. Even when the process employs artificial brine, there is evidence for generation of chlorinated organics from chloralkali plants (*50, 51*) due to leakage. Present estimates do not list the chloralkali process as a major contributor to the atmospheric chloroform flux (*52*). Seawater electrolysis could significantly add to this contribution. The use of more concentrated NaCl solutions for electrolysis would reduce these emissions by limiting the availability of DOC. In any case, it will be important to quantify this unintended flux of bromine and chlorine to the atmosphere before any large scale implementation of this process proceeds.

Technologies currently exist that can offset or eliminate CO_2 emissions from large point sources more cost-effectively than the process described here (*1*). In time, however, the most cost-effective CO_2 mitigation schemes are likely to be fully utilized (*53*). If anthropogenic climate change is expected to remain a serious threat despite the fullest practical deployment of those schemes, then the process we discuss could provide the additional CO_2 mitigation necessary to avoid further damage from climate change. If a technology based on this process is to be ready when and if needed, substantial laboratory and field research is needed to better understand the process's effect on biogeochemical cycles and other unintended consequences; to develop efficient and robust large-scale hydrogen–chlorine fuel cells; and to develop processes to more efficiently separate seawater into acid and base with large throughput.

Our current estimates indicate that running the process described here at scales sufficiently large to impact the earth's climate is unlikely to be commercially viable in the near future. It is plausible, however, that the marginal cost for CO_2 reduction will become high enough to make the process discussed here economically competitive. It is also worth considering the possibility that abrupt climate change (*54*) will require a sudden and large-scale effort at CO_2 mitigation. Under such a scenario, wide-scale deployment could be considered along with other geoengineering options to help avoid catastrophic climate change.

A variety of technologies will be used in this century to mitigate anthropogenic climate change. The process described here enhances the solubility of CO_2 in the ocean by, in essence, electrochemically accelerating the natural chemical weathering reaction. The three key benefits of the process we describe are the permanency guaranteed by the storage of CO_2 in the ocean without acidification, the process' capability to offset the CO_2 emissions from any source including mobile point sources, and its capability to be performed in remote regions using stranded energy. Deployment of the process will be limited by any damage to local marine biota caused by local pH changes and rock dissolution products.

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Literature Cited

(1) Rubin, E.; Meyer, L.; de Coninck, H. *IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change*; Intergovernmental Panel on Climate Change: Cambridge, United Kingdom, September, 2005.

(2) Keith, D.; Ha-Duong, M.; Stolaroff, J. Climate strategy with CO_2 capture from the air. *Climate Change* **2005**, 74.

(3) Thambimuthu, K.; Soltanieh, M.; Abanades, J. C. *Capture of CO_2*; Intergovernmental Panel on Climate Change: Cambridge, United Kingdom, 2005.

(4) Zeman, F.; Lackner, K. Capturing Carbon Dioxide Directly from the Atmosphere. *World Resour. Rev.* **2004**, *16* (2), 157–171.

(5) Stevens, S.; Vello, K.; Gale, J.; Beecy, D. CO_2 Injection and Sequestration in Depleted Oil and Gas Fields and Deep Coal Seams: Worldwide Potential and Costs. *Environ. Geosci.* **2001**, *8* (3), 200–209.

(6) Gale, J.; Freund, P. Coal-Bed Methane Enhancement with CO_2 Sequestration Worldwide Potential. *Environ. Geosci.* **2001**, *8* (3), 210–217.

(7) Nordbotten, J.; Celia, M.; Bachu, S. Injection and Storage of CO_2 in Deep Saline Aquifers: Analytical Solution for CO_2 Plume Evolution During Injection. *Transp. Porous Media* **2005**, *58* (3), 339–360.

(8) Drange, H.; Alendal, G.; Johannessen, O. M. Ocean release of fossil fuel CO_2: A case study. *Geophys. Res. Lett.* **2001**, *28* (12), 2637–2640.

(9) Herzog, H. What Future for Carbon Sequestration? *Environ. Sci. Technol.* **2001**, *35* (7), 148A–153A.

(10) Lackner, K. Carbonate Chemistry for Sequestering Fossil Carbon. *Ann. Rev. Energy Environ.* **2002**, *27* (1), 193–232.

(11) O'Conner, W. K. O.; Dahlin, D. C.; Turner, P. C.; Walters, R. *Carbon Dioxide Sequestration by Ex-Situ Mineral Carbonation*; Albany Research Center, Office of Fossil Energy, U.S. DOE: Albany, OR, 1999.

(12) Rau, G.; Caldeira, K. Enhanced Carbonate Dissolution: a means of sequestering waste CO_2 as ocean bicarbonate. *Energy Convers. Manage.* **1999**, *40*, 1803–1813.
(13) Rau, G.; Caldeira, K. Accelerating carbonate dissolution to sequester carbon dioxide in the ocean: Geochemical implications. *Geophys. Res. Lett.* **2000**, *27* (2), 225–228.
(14) House, K. Z.; Schrag, D.; Harvey, C.; Lackner, K. Permanent carbon dioxide storage in deep sea sediments. *Proc. Natl. Acad. Sci.* **2006**, *103* (33), 1291–1295.
(15) Azar, C.; Lindgren, K.; Larson, E.; Mollersten, K. Carbon Capture and Storage From Fossil Fuels and Biomass–Costs and Potential Role in Stabilizing the Atmosphere. *Climate Change* **2006**, *74* (1–3), 47–79.
(16) Hoffert, M. Advanced Technology Paths to Global Climate Stability: Energy for a Greenhouse Planet. *Science* **2002**, *298* (5595), 981–987.
(17) Huijgen, W. J. J.; Comans, R. N. J. *Carbon Dioxide Sequestration by Mineral Carbonation*;ECN-C-03-016; Energy Research Centre of the Netherlands: Petten, 2004; pp 1–37.
(18) Chen, Y.; Brantley, S. Dissolution of Forsteritic Olvine at 65 °C and 2 < pH <5. *Chem. Geol.* **2000**, *165*, 267–281.
(19) Zeebe, R. E.; Wolk-Gladrow, D. *CO_2 in Seawater: Equilibrium, Kinetics, Isotopes*; Elsevier: Amsterdam, 2001.
(20) Bommaraju, T. V.; Orosz, P. J. Brine Electrolysis. In *Electrochemistry Encyclopedia*; Ernest B. Yeager Center for Electrochemical Sciences: Grand Island, NY, 2001.
(21) Pletcher, D.; Walsh, F. C. *Industrial Electrochemistry*; Kluwer: Norwell, MA, 1990.
(22) Dunseth, M. G.; Salutsky, M. Removal of Scale-Forming Elements from Sewater. *Ind. Eng. Chem.* **1964**, *56* (6), 56.
(23) Kaufmann, D. W. *Sodium Chloride: The Production and Properties of Salt and Brine*; Reinhold: New York, 1960.
(24) Mazrou, S.; Kerdjoudj, A.; Cherif, A. T. Sodium hydroxide and hydrochloric acid generation from sodium chloride and rock salt by electro-electrodialysis. *J. Appl. Electrochem.* **1997**, (27), 558–567.
(25) Salutsky, M. Process of Descaling Sea Water. U.S. Patent 3163599, 1964.
(26) Nakamatsu, S.; Harada, H.; Shinomiya, Y.; Omizu, T. Electrolytic cell for electrolysis of sea water. U.S. Patent 4173525, 1978.
(27) Spaziante, P. M. Process for electrolysis of sea water. U.S. Patent 4510026, 1983,
(28) Shimamune, T.; Nakajima, Y.; Kawaguchi, Y. Seawater electrolysis apparatus. U.S. Patent 6113773, 1998.
(29) Carrette, L.; Friedrich, A. K.; Stimming, U. Fuel Cell: Principles, Types, Fuels, and Applications. *ChemPhysChem* **2000**, *1*, 162–173.
(30) Thomassen, M.; Borresen, B.; Hagen, G.; Tunold, R. H_2/Cl_2 fuel cell for co-generation of electricity and HCl. *J. Appl. Electrochem.* **2002**, *33*, 9–13.
(31) Yeo, R. S.; McBreen, J.; Tseung, A. C. C.; Srinivasan, S.; McElroy, J. An electrochemically regenerative hydrogen-chlorine energy storage system: electrode kinetics and cell performance. *J. Appl. Electrochem.* **1980**, *10* (3), 393–404.
(32) Anderson, E.; Taylor, E. J.; Wilemski, G.; Gelb, A. A high performance hydrogen/chlorine fuel cell for space power applications. *J. Power Sources* **1994**, *1994* (47), 321–328.
(33) Tongwen, X. Electrodialysis process with bipolar membranes (EDBM) in environmental protection - a review. *Resour., Conserv., Recycl.* **2002**, *37* (1), 1–22.
(34) Iwahara, H.; Uchida, H.; Maeda, N. High Temperature Fuel and Steam Electrolysis Cells Using Proton Conductive Solid Electrolytes. *J. Power Sources* **1982**, *7*, 293–301.
(35) Zeman, F. S.; Lackner, K. Capturing carbon dioxide directly from the atmosphere. *Environ. Eng.* **2004**, *16* (2), 157–172.
(36) McNeil, B.; Matear, R.; Key, R.; Bullister, J.; Sarmiento, J. Anthropogenic CO_2 Uptake by the Ocean Based on the Global Chlorofluorocarbon Data Set. *Science* **2003**, *299*, 235–239, January 10, 2003.
(37) Archer, D. The Fate of fossil fuel CO_2 in Geologic Time. *J. Geophys. Res.* **2005**, *110*, 1–6.
(38) Caldeira, K.; Wickett, M. E. Anthropogenic carbon and ocean pH. *Nature* **2003**, 425, 365.
(39) Feely, R. A.; Sabine, C.; Lee, K.; Berelson, W.; Joanie, K.; Fabry, V. J.; Millero, F. J. Impact of Anthropogenic CO_2 on the $CaCO_3$ System in the Oceans. *Science* **2004**, *305*, 362–366.
(40) Bergner, D. Membrane cells for chor-alkali electrolysis. *J. Appl. Electrochem.* **1982**, *12* (6), 631–644.
(41) Belmont, C.; Ferrigno, R.; Leclerc, O.; Girault, H. Coplanar interdigitated band electrodes for electrosynthesis. Part 4: Application to sea water electrolysis. *Electrochim. Acta* **1998**, *44* (4), 597.
(42) Goreau, T. J.; Hilbertz, W. In *Reef Restoration Using Seawater Electrolysis in Jamaica*, 8th International Coral Reef Symposium, Panama, 1996.
(43) Sherlock, E. J.; Lawrence, R. W.; Poulin, R. On the neutralization of acid rock drainage by carbonate and silicate minerals. *Environ. Geol.* **1995**, *25* (1), 43–54.
(44) Fauvarque, J. The chlorine industry. *Pure Appl. Chem.* **1996**, *68* (9), 1713–1720.
(45) McElroy, J. F.; Kelly, J. H. Development of a regenerative solid polymer electrolyte hydrogen halogen fuel cell for high efficiency energy storage. Department of Energy: Washington, DC, 1978.
(46) Halmann, M. M.; Steinberg, M. *Greenhouse Gas Carbon Dioxide Mitigation: Science and Technology*; CRC: Boca Raton, FL, 1998.
(47) Deutch, J. M.; Moniz, E. J. *The Future of Coal*; MA Institute of Technology: Cambridge, MA, 2007.
(48) Kroeze, C.; Vlasblom, J.; Gupta, J.; Boudri, C.; Blok, K. The power sector in China and India: greenhouse gas emissions reduction potential and scenarios for 1990–2020. *Energy Policy* **2004**, *32* (1), 55–76.
(49) http://www.mwrd.org/plants/default.htm#Stickney%20WRP.
(50) Kurunthachalam Kannan, M. K.; Kashima, Y.; Matsui, M.; Giesy, J. P. Extractable Organohalogens (EOX) in Sediment and Biota Collected at an Estuarine Marsh near a Former Chloralkali Facility. *Environ. Sci. Technol.* **1999**, *33* (7), 1004–1008.
(51) Järnberg, U. A. L.; de Wit, C.; Egebäck, A.-L.; Wideqvist, U.; Jakobsson, E. Distribution of Polychlorinated Naphthalene Congeners in Environmental and Source-Related Samples. *Arch. Environ. Contam. Toxicol.* **1997**, *32*, 232–245.
(52) Aucott, M. L. A. M.; Graedel, T. E.; Kleiman, G.; Midgley, P. Anthropogenic emissions of trichloromethane (chloroform, $CHCl_3$) and chlorodifluoromethane (HCFC-22): Reactive Chlorine Emissions Inventory. *J. Geophys. Res.* **1999**, *104* (D7), 8405–8415.
(53) Socolow, R.; Pacala, S. Stabilization Wedges: Solving the Climate Problem for the next 50 Years with Current Technologies. *Science* **2004**, *305* (5686), 968–972.
(54) NAS. *Abrupt Climate Change: Inevitable Surprises*; National Academy of Sciences: Washington, DC, 2002.
(55) Flanagan, F. J. Three USGS mafic rock reference samples, W-2, DNC-1, and BIR-1. *U.S. Geological Survey Bulletin* **1984**, *1623*, 54.
(56) Godard, M.; Jousselin, D.; Bodinier, J. Relationships between geochemistry and structure beneath a paleo-spreading centre: a study of the mantle section in the Oman ophiolite. *Earth Planet. Sci. Lett.* **2000**, *180*, 133–148.

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