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Electrochemical acceleration of chemical weathering for carbon capture and sequestration

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Abstract

We describe an approach to CO₂ capture and storage from the atmosphere that involves enhancing the solubility of CO₂ in the ocean by an engineered process equivalent to the natural silicate weathering process. HCl is electrochemically removed from the ocean and neutralized through reaction with silicate rocks. The alkaline solution resulting from the removal of HCl is neutralized by capturing atmospheric CO₂ and is dissolved into the ocean where the carbon will be stored primarily as HCO₃⁻ without further acidifying the ocean. On time scales of hundreds of years or longer, some of the additional alkalinity is expected to lead to precipitation or enhanced preservation of CaCO₃, resulting in the permanent storage of the associated carbon, and the return of an equal amount of carbon to the atmosphere. The overall process is equivalent to the earth's natural chemical weathering process of silicate rocks. 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 CO₂ 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 populations.

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1. Introduction

A major concern about ocean sequestration of CO₂ is the acceleration of ocean acidification, which is currently occurring due to invasion of CO₂ from enhanced atmospheric concentration into the surface ocean. To circumvent this problem we have sketched out [1] an integrated CO₂ capture and storage process that involves increasing the solubility of CO₂ in the ocean by increasing the ocean's alkalinity—either by electrolytically removing hydrochloric acid (HCl) from the ocean and neutralizing it through reactions with silicate rocks; by adding to the ocean NaOH that was produced via electrolysis of an artificial brine; or by adding to the ocean the NaHCO₃ that is produced by

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reacting this NaOH with CO₂. The net result of the process is to increase the ocean's alkalinity and enhance the ocean's ability to take up CO₂. The net 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 CO₂ — notably, forming carbonic acid from a stream of CO₂ and reacting it with silicates to form carbonates [2]. The kinetics of silicate rock dissolution by carbonic acid are, however, very slow [3]. In contrast, the process we describe involves the dissolution of silicate rocks by concentrated HCl — which is known to proceed much more rapidly [4] and does not require a concentrated stream of CO₂.

2. Process Description

We discuss here a version of the process shown schematically in Fig. 1. Brine, NaCl(aq), is provided either from seawater or from mined halite. The thermodynamics of the process that employs seawater are essentially the same as of the process that employs an artificial NaCl solution. High purity brine (i.e., less than 1 ppm impurities) can be produced by de-scaling seawater [5] or by mining and purifying halite minerals [6]. We describe the process of electrolyzing an artificial NaCl solution of purified halite dissolved in fresh water, which can be implemented with technology currently used in the chlorine industry. Although the technical application of this case is the most straightforward, modifications to current technology may enable the utilization of halite dissolved in seawater or possibly the extraction of HCl directly from seawater resulting in significantly increased potential scale and reduced costs, respectively.

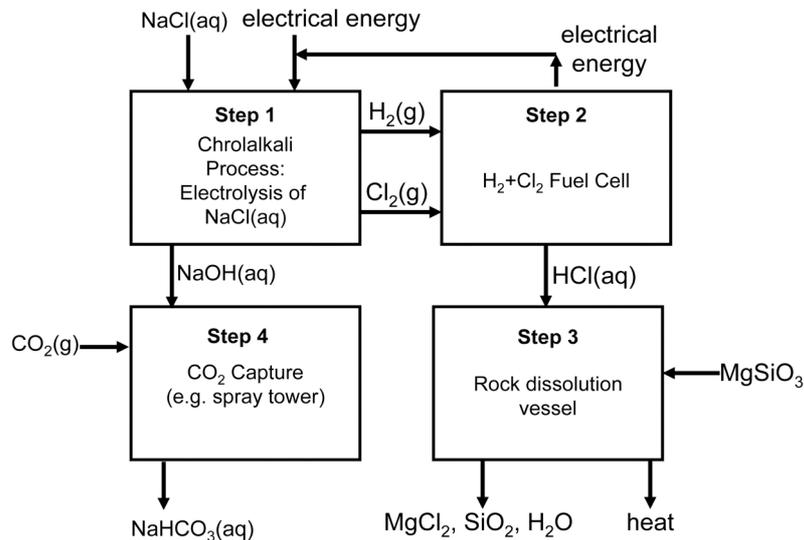
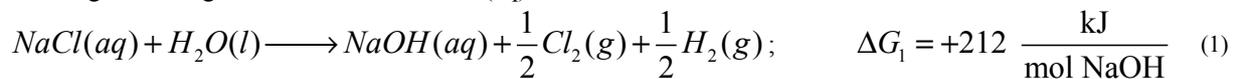


Fig. 1. Processes involved in CO₂ capture and sequestration. Magnesium has been used to represent any metal found in silicate rocks.

Step 1. The first step of the process is the Chloralkali process, the standard electrochemical process for producing chlorine gas and caustic soda NaCl(aq).



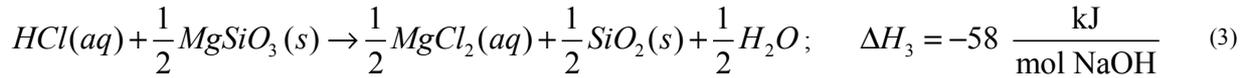
This is the only step that requires work input in the thermodynamic limit. The minimum input requirement for Step 1 is given by the change in Gibbs free energy of the reaction. In this paper all thermodynamic calculations have been performed with intermediate states at standard state conditions, and all initial and final states at in-situ conditions of seawater (e.g., CO₂(g) starts at 400 μAtm, [Na⁺] and [Cl⁻] start at ~500 mmol/liter, [Mg²⁺] ends at ~50 mmol/liter, [Ca²⁺] ends at ~10 mmol/liter, and [HCO₃⁻] ends at ~1.8 mmol/liter). In application, it will likely be beneficial to engineer the concentrations in all states.

Step 2. Hydrochloric acid is formed from the Cl₂(g) and H₂(g) that was produced in Step 1:



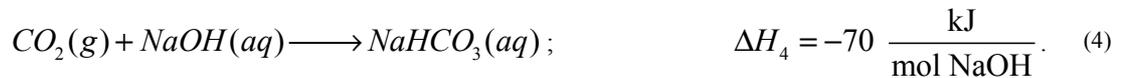
This is the first of several steps in which some energy input required for Step 1 can be recovered. The reaction is spontaneous and exothermic and the $Cl_2(g)$ and $H_2(g)$ may be combusted to drive a heat engine or combined in a fuel cell (Step 2, Figure 1) to produce either $HCl(aq)$ or $HCl(g)$ and electricity. Hydrogen-chlorine fuel cells have been investigated for large scale peak power shaving and load leveling applications [7,8], and early work suggests that these fuel cells can be highly efficient [9].

Step 3. Hydrochloric acid is neutralized by reaction with silicate rocks. For many common silicate rocks and minerals the reaction is spontaneous and exothermic. We use the abundant mineral enstatite ($MgSiO_3$) as a prototype.



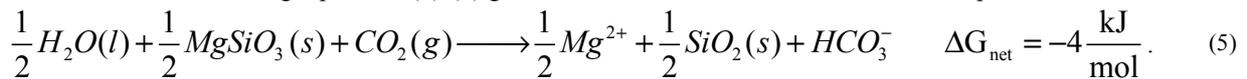
The kinetics of silicate rock dissolution are highly dependent on pH and temperature but can be very much faster for hydrochloric acid than for carbonic acid [4]. Some of the heat generated in the reaction might be harnessed, e.g. to increase the temperature of the incoming salt water for the purpose of performing high temperature electrolysis [10]. Initial heating of the salt water has the potential to decrease the overall electrical input required by 10 – 20 kJ/mol.

Step 4. Capture of $CO_2(g)$ by caustic soda to form sodium bicarbonate:



The caustic soda formed in Step 1 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 [11]) as indicated in Fig. 1; it can be added to the surface ocean to increase its alkalinity; or it can be used at an industrial point source to react directly with an exhaust stream.

Net reaction. Combining equations (1)-(4) gives the net chemical reaction of the overall process:



Only Step 1 requires work input; the three subsequent steps are spontaneous and exothermic. The net reaction—which is identical whether we begin the process with seawater or with high-purity artificial brine, and which includes *both* the capture and the permanent storage of CO_2 —is spontaneous. In the thermodynamic limit, for each mole of enhanced CO_2 uptake by the ocean, the process illustrated here requires ~81 kJ of electrical work in Steps 1 and 2 and generates ~128 kJ of heat and ~85 kJ of availability, or work potential, in Steps 3 and 4. 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 creates the potential for 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. Efficiency losses will severely impact the actual balance and a realistic industrial-scale process will consume rather than produce work.

3. Application

In our original manuscript [1] we discussed five ways in which the practical application of the process might differ from the theoretical description: (a) the potential advantages and practical difficulties of using sea water instead of fresh water feedstock; (b) the use of various rocks, especially basalt and ultramafic rock, instead of the pure mineral enstatite; (c) options for HCl neutralization by injection into a natural rock formation rather than in a reaction vessel; (d) options for CO_2 capture by NaOH either after the NaOH is released into the surface ocean or beforehand in a spray tower or other mass transfer device, and options for sequestration of the $NaHCO_3$ in terrestrial reservoirs; and (e) practical efficiency scenarios. In Fig. 2 we reproduce our estimates of the net tonnage of CO_2 sequestered — after accounting for the carbon emissions of the power source used to run the process — vs. the carbon intensity of the power source.

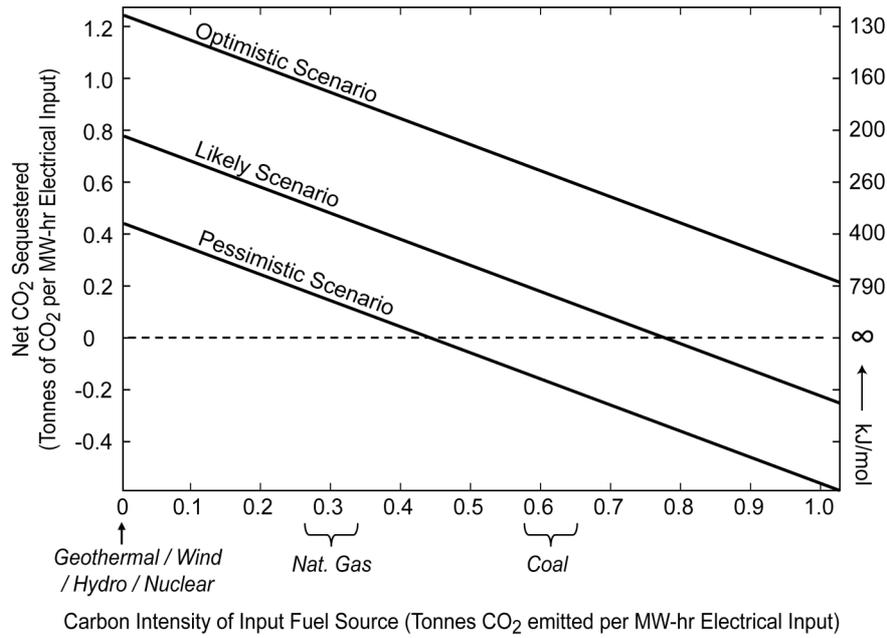


Fig. 2. Net CO₂ sequestered (tonnes) vs. the carbon intensity of the power source for the process depicted in Fig. 1 using standard Icelandic basalt (BIR-1) to neutralize the HCl. From [1]. The three lines correspond to different efficiency scenarios. The optimistic scenario assumes 10 molar NaCl solution with a 1-step electrochemical process at 60% efficiency for Steps 1 & 2 and 15% productive heat recovery from Step 3. The likely scenario assumes 10 molar NaCl solution, a 70% efficient electrolysis [12], a 70% efficient H₂+Cl₂ fuel cell [13], 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 H₂+Cl₂ fuel cell, and zero heat recovery. Also, this figure assumes the timescale of anthropogenic climate change is similar to the timescale for the surface ocean to remove excess alkalinity. The right hand vertical axis is required work per net mole of CO₂ sequestered.

4. Effect on carbon partitioning

The amount of dissolved inorganic carbon (DIC),

$$DIC \equiv [CO_2(aq)] + [HCO_3^-] + [CO_3^{2-}] \quad (6)$$

in the surface ocean is controlled by the partial pressure of CO₂ in the atmosphere and by seawater alkalinity, which is the concentration excess of conservative (i.e., ions whose concentrations are independent of moderate changes in pH) cation charge over conservative anion charge. If one neglects minor non-conservative anions such as borate, then seawater alkalinity (*Alk*) is approximately equal to the charge contribution of bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions [14]:

$$\begin{aligned} Alk &\approx 2[Ca^{2+}] + [K^+] + 2[Mg^{2+}] + [Na^+] - [Cl^-] - 2[SO_4^{2-}] \\ &\approx [HCO_3^-] + 2[CO_3^{2-}] \end{aligned} \quad (7)$$

The equilibrium concentrations of the three species of dissolved inorganic carbon are determined by the first and second dissociation reactions of carbonic acid:





Because of the presence of the proton (hydronium) concentration in the equilibrium constants, these equilibria are sensitive to pH and are coupled to



Only the neutral species of DIC interacts with atmospheric CO₂ with a local equilibrium at the surface given by



Equations (6)-(9) represent four relationships among the six unknowns [CO₃²⁻], [HCO₃⁻], [CO₂(aq)], [H⁺], DIC, and *Alk*. Treating DIC as a fixed independent variable, solutions for the dependence of the other variables on [H⁺] are presented in Fig. 3 [14].

Each mole of alkalinity added to the ocean by the net reaction (5) results in the transfer of ~1 mole of CO₂ from the atmosphere to the ocean at constant pH on short time scales (~100 y). 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 Gt CO₂ (2 Gt C) per year [15].

Because most of the surface ocean is supersaturated with respect to the precipitation of calcium carbonate in the form of aragonite, and even more supersaturated with respect to the precipitation of the calcite form, the added alkalinity will result in some enhancement in the precipitation reaction

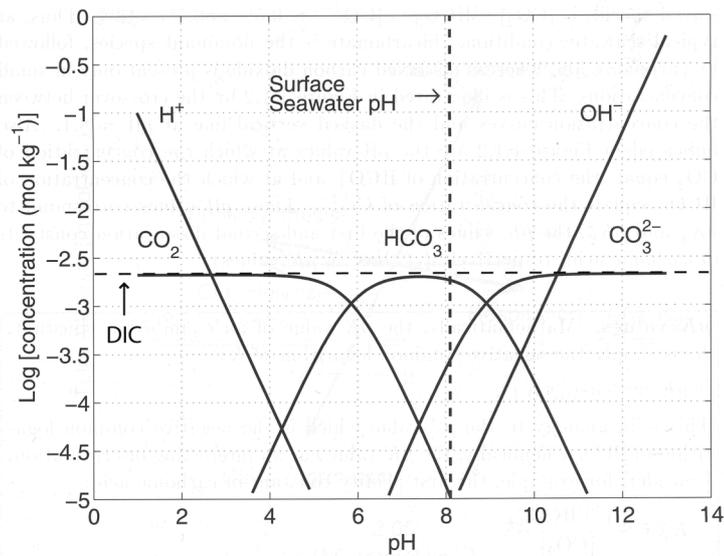
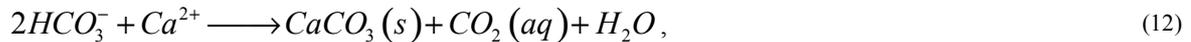


Fig. 3. Major ions involved in the carbonate system in the ocean. Adapted from Zeebe and Wolf-Gladrow [14]. Horizontal line approached asymptotically by [CO₂], [HCO₃⁻] and [CO₃²⁻] is DIC = 2.1 mmol/kg. As DIC varies, these three curves shift vertically whereas [H⁺] and [OH⁻] are invariant.



resulting in the permanent sequestration of some of the added carbon and the return of an equal amount of carbon to the atmosphere by the outgassing of CO₂(aq). Cutting the carbonate concentration at constant pH causes a drop in the bicarbonate concentration by eq. (9), and cutting the bicarbonate concentration at constant pH (eq. (8)) causes a drop in the concentration of neutral CO₂ by outgassing to the atmosphere (eq. (11)). We define the (time-dependent) process effectiveness to be the molar ratio of atmospheric CO₂ stored to alkalinity added. The magnitude of

enhanced precipitation depends on the degree to which the ocean's saturation state changes. If the saturation state remains at its current value then every mole of bicarbonate added to the ocean ultimately results in the precipitation of 0.5 moles of CaCO_3 , for an ultimate process effectiveness of 0.5.

In the shallow 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 (falling) saturation state would enable more (less) DIC to remain in the ocean, thereby raising (lowering) the long-time process effectiveness. It is unlikely 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 [16].

The increasing partial pressure of CO_2 ($p\text{CO}_2$) due to fossil fuel combustion is causing the ocean to acidify, CaCO_3 to dissolve, and CaCO_3 saturation state to decrease [17]. The artificial addition of alkalinity to the ocean will cause the rate of CaCO_3 dissolution to 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 in the fixed saturation state case.

To run the process of eq. (5) at any significant scale, adding (locally) large amounts of HCO_3^- to the ocean at constant pH will significantly raise local DIC and thereby uniformly raise all three curves representing the concentrations of the various DIC species in Fig. 3 due to the rapid kinetics of reactions (8) and (9). The increased supersaturation will result in flash precipitation of calcium carbonate according to eq. (12) and immediately drop the process effectiveness to 0.5. To maintain the process effectiveness near unity at scale, it may be necessary to add the bicarbonate directly to the deep ocean, which is undersaturated with respect to calcium carbonate precipitation. Even during injection into undersaturated ocean waters, the local DIC concentration spike will cause flash precipitation of calcium carbonate, necessitating the engineered mixing of CO_2 bubbles, particulate calcium carbonate, and undersaturated ocean water on large scales in order to preserve the ultimate process effectiveness near unity.

The engineering problem is that changing the supersaturation of a solution by adding insufficiently diluted chemicals (rather than, say, the action of a body force such as gravity on a fluid mass) is likely to cause rapid precipitation. This statement is applicable not only to electrochemical weathering but also generically to all proposals (some of which are discussed below) for adding mineral alkalinity to the ocean. The presence of supersaturation rather than equilibrium makes it insufficient to consider only the thermodynamic starting and (mixed and diluted) end states. One cannot neglect the supersaturation spike in the intermediate state at the beginning of mixing, which possesses continuous gradations of all components between their concentrations in the bulk of each of the unmixed waters. To run any such process at a massive scale without triggering the kinetic phenomenon of flash precipitation requires dilution at the outset on a massive scale.

If the NaOH produced in Step 1 is released directly into the ocean surface in order to let the ocean surface act as a giant collector of atmospheric CO_2 , as we discussed originally [1], the local spike in pH will drop $[\text{H}^+]$ significantly and thereby shift the equilibrium of reaction (9) from HCO_3^- to CO_3^{2-} . This will raise the carbonate ion concentration and result in the flash precipitation of calcium carbonate as either calcite or aragonite via



The loss of carbonate ions and protons causes outgassing of $\text{CO}_2(\text{aq})$ via eqs. (8), (9), and (11) similarly to the case discussed above.

5. Effect of adding mineral alkalinity to the ocean

Others have proposed dissolving mined Na_2CO_3 [2,18], MgCO_3 [2], or CaO or $\text{Ca}(\text{OH})_2$ [18,19] into the ocean to enhance the ocean's rate of carbon uptake from the atmosphere. Addition of Na_2CO_3 or MgCO_3 will result in the added carbonate ion predominantly shifting to bicarbonate via eq. (9) (see equilibrium $[\text{CO}_3^{2-}]/[\text{HCO}_3^-]$ ratio at vertical dashed line at surface seawater pH in Fig. 2) along with the loss of a proton according to the reaction in (9). The result will be calcium carbonate precipitation according to eq. (12), along with an increase in pH that causes $[\text{CO}_2(\text{aq})]$ to decrease by outgassing to the atmosphere. The ultimate process effectiveness is therefore near zero

(depending on whether there is any long-term change in the calcium carbonate saturation state of the ocean); if flash precipitation is not avoided then the immediate process effectiveness drops to near zero.

Adding $\text{Ca}(\text{OH})_2$ to the ocean raises the calcium carbonate supersaturation two ways. Not only does the increased pH shift the equilibrium of reaction (9) from HCO_3^- to CO_3^{2-} , as discussed at the end of the previous section, but also there is a direct supersaturation boost from the added calcium. Hence this process suffers from the difficulties described above for the process of adding NaOH to the surface ocean, but with increased severity. With flash precipitation in the absence of prior dilution and the associated outgassing, the immediate process effectiveness is near 0.5. If CaO is added to the ocean it dissolves as $\text{Ca}^{2+} + \text{O}^{2-}$, but then immediately reacts with H_2O ,



thereby yielding the same effect as the direct addition of $\text{Ca}(\text{OH})_2$. Furthermore, if CaO is manufactured from limestone (CaCO_3) then the CO_2 released in the manufacturing, if not captured and sequestered, causes -1 to be added to the process effectiveness.

6. Advantages of accelerated chemical weathering

Humanity's massive capital investments in carbon intensive infrastructure make it difficult to cut CO_2 emissions. Given these investments and the uncertainty of future climate damages, it may become necessary to remove CO_2 directly from the atmosphere. Electrochemical weathering can be run anywhere in the world and works equally well for all sources of CO_2 —including the $\sim 2/3$ of anthropogenic CO_2 emissions that do not emanate from power plants [20]. The work input required for the overall process is expected to be between ~ 1.5 and ~ 3.5 times as high per unit of CO_2 than the work required for post-combustion capture and geologic storage of CO_2 from a modern coal fired-power plant [20]. It is likely, however, that limiting the CO_2 emissions from the transportation sector, building heating, and various industrial processes will require more work than from power plants.

An additional benefit of electrochemical weathering 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 run on intermittent power. Alternatively, the process could be powered by gas turbines in oil-producing regions where natural gas is flared.

If the H_2 and Cl_2 resulting from Step 1 can be sold into healthy markets then only Steps 1 and 4 are necessary for carbon sequestration and the sale of Cl_2 , H_2 , and carbon credits could be profitable immediately. The scale cannot approach that of worldwide chlorine production by the chloralkali process (43 million tonnes of Cl_2 production in 2003) without crashing the chlorine market. Long-distance shipping of chlorine also raises safety concerns.

Research into actively capturing CO_2 from the air by solvent regeneration cycles is ongoing [11]. Enhancing ocean uptake of CO_2 via electrochemical weathering has some comparative benefits. The solvent regeneration processes aims to separate $\text{CO}_2(\text{g})$ from air and produce a near pure stream of $\text{CO}_2(\text{g})$ for compression to ~ 200 atmospheres, transportation to storage sites, and injection into geologic reservoirs, which have uncertain long-term leakage rates. In contrast, the CO_2 storage in electrochemical weathering is ensured by the thermodynamics and kinetics of marine chemistry to be stored permanently in a more stable chemical state. Hence it would not be necessary to locate and fully characterize a multitude of suitable geologic storage depositories for the captured CO_2 .

7. Engineering difficulties and scale limitations

The process must overcome several technical hurdles before it can offset an appreciable quantity of CO_2 emissions. To offset $\sim 15\%$ of annual carbon emissions (~ 3.7 gigatonnes CO_2 or 1 gigatonne 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 $\sim 6000 \text{ m}^3/\text{s}$. Large sewage treatment facilities have a capacity of $\sim 60 \text{ m}^3/\text{s}$ [21]. Thus, capturing and storing 3.7 gigatonnes of CO_2 annually by electrochemical weathering 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. Chemical weathering would increase from 0.4 to 1.4 gigatonnes of C per year over this same period. Economical electrolysis of seawater is another challenge, as the current cost of removing multivalent cations before running the Chloralkali process is high.

Technologies currently exist that can offset or eliminate CO₂ emissions from large point sources more cost-effectively than electrochemical weathering [20]. In time, however, the most cost-effective CO₂ mitigation schemes are likely to approach full utilization [22]. If anthropogenic climate change is expected to remain a serious threat despite the fullest practical deployment of those schemes, then electrochemical weathering could provide the additional CO₂ mitigation necessary to avoid further damage from climate change. It is also worth considering the possibility that abrupt climate change [23] will require a sudden and large scale effort at CO₂ mitigation. Under such a scenario, wide scale deployment could be considered along with other geoengineering options to help avoid catastrophic 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.

8. Acknowledgments

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