**CO₂ capture by pumping surface acidity to the deep ocean†**

Michael D. Tyka,∗a Christopher Van Arsdale,a and John C. Platt

This paper is a non-peer reviewed preprint submitted to EarthArXiv. It has been submitted to Energy & Environmental Science.

The majority of IPCC scenarios call for active CO₂ removal (CDR) to remain below 2ºC of warming. On geological timescales, ocean uptake regulates atmospheric CO₂ concentration, with two homeostats driving CO₂ uptake: dissolution of deep ocean calcite deposits and terrestrial weathering of silicate rocks, acting on 1ka to 100ka timescales, respectively. Many current ocean-based CDR proposals effectively act to accelerate the latter. Here we present a method which relies purely on the redistribution and dilution of acidity from a thin layer of the surface ocean to a thicker layer of deep ocean, with the aim of reducing surface acidification and accelerating the former carbonate homeostasis. This downward transport could be seen analogous to the action of the natural biological carbon pump. The method offers advantages over other ocean CDR methods and direct air capture approaches (DAC): the conveyance of mass is minimized (acidity is pumped in situ to depth), and expensive mining, grinding and distribution of alkaline material is eliminated. No dilute substance needs to be concentrated, avoiding the Sherwood’s Rule costs typically encountered in DAC. Finally, no terrestrial material is added to the ocean, avoiding significant alteration of seawater ion concentrations or issues with heavy metal toxicity encountered in mineral-based alkalinity schemes. The artificial transport of acidity accelerates the natural deep ocean compensation by calcium carbonate. It has been estimated that the total compensation capacity of the ocean is on the order of 1500GtC. We show through simulation that pumping of ocean acidity could remove up to 150GtC from the atmosphere by 2100 without excessive increase of local ocean pH. For an acidity release below 2000m, the relaxation half-life of CO₂ return to the atmosphere was found to be ~2500 years (~1000yr without accounting for carbonate dissolution), with ~85% retained for at least 300 years. The uptake efficiency and residence time were found to vary with the location of acidity pumping, and optimal areas were determined. Requiring only local resources (ocean water and energy), this method could be uniquely suited to utilize otherwise-unusable open ocean energy sources at scale. We examine technological pathways that could be used to implement it and present a brief techno-economic estimate of 130-250$/tCO₂ at current prices and as low as 93$/tCO₂ under modest learning-curve assumptions.

1 Introduction

Stabilizing the earth’s climate into the next centuries will require a near total decarbonization of the world energy supply, i.e. reducing emissions from their current peak levels. However, some industrial processes, such as industrial heat and concrete manufacturing as well as emissions from land use changes, air travel, or livestock are very difficult to decarbonize. Further, even if future emissions were curbed, enough historical CO₂ has already accumulated in the atmosphere to cause problematic warming and could trigger tipping points. Thus, the vast majority of IPCC
RCP2.6 scenarios which remain under 2°C of warming require negative emissions on the order of 150GtC before 2100 in addition to rapid decarbonization. On geological timescales several mechanisms act to regulate the atmospheric CO₂ concentration: Over periods of hundreds of years the oceans will absorb the majority of the excess CO₂ leading to very significant surface acidification. Subsequent downward transport of the CO₂ brings the acidity in contact with CaCO₃ deposits, dissolving them and releasing alkalinity, and thus stabilizing the pH. This has been termed the CaCO₃ pH-stat. On even longer timescales (100ka), weathering of terrestrial silicate rocks releases additional alkalinity which brings new alkalinity to the oceans and allows the previously dissolved CaCO₃ to be redeposited while the lysoclines return to their original depths. This is termed the CO₂ weathering stat. The consecutive transfer of the excess CO₂ along these three sinks acts to keep the temperature of the earth within relatively stable bounds over long periods of time. Unfortunately, the response time of even the first of these two buffers is too slow to keep up with the rate of human emissions, leading to a temporary but extremely dangerous spike in atmospheric CO₂ concentrations, warming and surface ocean acidification, potentially triggering mass extinction.

The primary limiting step is the net transport of CO₂ into the deep ocean due to the action of the biological pumps. Anthropogenic CO₂ has not yet penetrated deeply into the ocean, because most of the remineralization of sinking organic matter occurs in the first 500m beyond the euphotic zone, with peak acidification at about 250m depth. Anthropogenic CO₂ has acidified mostly surface waters, impacting carbonate shell-forming organisms, while staying out of reach of inorganic CaCO₃ deposits located well below the euphotic zone. Positive feedbacks are also present in this system, where CO₂-saturated surface waters oppose further CO₂ uptake, reduce the ocean buffering ability and accelerate future pH changes due to the nonlinearity of the carbonate system; these issues are further compounded under increasing stratification and a decreased biological pump predicted for a warming ocean.

While methods have been proposed to accelerate the terrestrial CO₂-weathering stat, by mechanical or electrochemical means, acceleration of the CaCO₃ pH-stat has not yet been explored. Here, we examine the feasibility of artificially accelerating the transport of acidity to the deep ocean, in order to dilute the surface acidification and enable the action of the natural carbonate compensation on accelerated timescales. Such an action cannot be a replacement for total decarbonization of the economy, but could contribute to blunt the ecological impact of past emissions by dilution in spatial and temporal dimensions. The inventory of erodible CaCO₃ on the ocean floor is estimated to be ~1600 GtC, theoretically more than sufficient to compensate for the ~640GtC that humanity has released since pre-industrial times.

1.1 Accelerating deep water equilibration

We envision an artificial method to increase the downward transport of acidity from the surface ocean to the deep ocean that first involves electrochemically splitting seawater into acid and base. The weakly alkaline effluent would be released at the surface, while the weakly acidic water would be pumped into the deep ocean (see Figure 1). In the surface water the alkalinity would thus be raised and the pH stabilized. This maintains an increased flux of CO₂ into the ocean and reduces atmospheric CO₂, helping to alleviate immediate radiative forcing. The increased pH (decreased acidity) would also help stabilize the health of coral reefs and Coccolithophores and help preserve these ecosystems past the anthropogenic CO₂ spike. Synthesis and subsequent sinking of coccoliths plays a vital role in ballast formation in the biological pump and indirectly aids the downward transport of organic carbon in the ocean. These surface-ocean effects would be the same as those of ocean liming proposals, i.e. surface dissolved inorganic carbon (DIC) would increase together with an equally increased alkalinity and the carbonate equilibrium would remain stable. A common approximation for the concentration of carbonate ions is $[CO_3^{2-}] \approx Alk - DIC$, which makes this immediately apparent.

Meanwhile the acidic, low-pH effluent could be diluted across a large section of the deep water column using perforated, flexible, deep vertical pipes. As the deep water column contains much more water than the thin surface water layer that the acidity originated in, such redistribution of surface-ocean acidity dilutes the surface acidity and its ecological effects. Isopycnal deep water circulation would then spread and dilute this acidity horizontally, bringing it in contact with calcite sediments. The precise impact of such a redistribution on pH and calcite saturation is complex and will be explored through ocean simulation in this paper.

![Fig. 1 Schematic showing how pumping of acidity from surface water would accelerate the natural pH stat of the ocean, help stabilize atmospheric CO₂ and accelerate deep water carbonate compensation. Any unreacted acidity would eventually return with ocean circulation. Alternatively, for shallow ocean areas, acidity could be pumped into underground basalt formations or depleted oil reservoirs, leading to permanent CO₂ drawdown into the ocean.](image)

1.1.0.1 Comparison with mineral alkalinization A great variety of methods have been proposed to increase ocean capacity for CO₂, without raising ocean acidity, by dissolving terrestrial minerals. These proposals aim to accelerate the terrestrial weathering CO₂-stat by about 5-6 orders of magnitude. In practice, the mining, grinding, transport and distribution of gigatones of rock per year poses significant challenges. If the mate-
rial is ground to $\sim 100\mu m$, the dissolution of these minerals is on
the order of many decades $^{14,15}$ and particles would sink out of
the mixed layer long before dissolution $^{21}$, limiting applicability
to shallow coastal areas $^{22}$. Grinding down to $1\mu m$ would en-
able open ocean distribution, but significantly increase grinding
energy costs $^{23}$. Iron, abundant in most olivine minerals, would
inadvertently fertilize the ocean leading to significant ecological
disruption $^{2,14}$. Silicates would shift the phytoplankton species
composition towards diatoms $^{24}$ and heavy metals (Nickel, Cad-
mium, etc) would exhibit acute toxicity and potentially bioaccu-
mulate. Thus these co-dissolving contaminants likely limit de-
ployment at the scale needed ($\sim 150$GtC before 2100). To solve
these problems a number of methods have been put forward
which extract alkalinity from rocks without adding bulk rock to
the oceans. Typically, ocean-derived brine is split into acid and
base electrochemically $^{16,17,24}$. The base can be added to the sur-
face ocean, while the excess acid can be neutralized using rocks
on land. This also circumvents the need for expensive fine grind-
ing, but the negative impacts of mining itself remain.

This proposal shares many properties with the above ocean al-
kalinity enhancement proposals, with some advantages. Firstly
there is no need for large mass transport of alkaline rocks to the
ocean $^{13}$ or transport of products away from electrolysers $^{24}$. The
only matter transport needed is the pumping of a small amount
of water a few kilometers downwards. This locality makes the
method uniquely suitable for open ocean deployment and pro-
vides a way to use otherwise unusable renewable energy re-
sources. Open waters offer greater scalability at reduced eco-
logical impact as dilution over large areas is trivial and marine
ecosystems are much sparser. The proposed method also avoids
the severe impacts of creating a gigatonne-scale mining operation
on terrestrial ecosystems. The net cation composition of the ocean
is not changed, avoiding introduction of iron, silicate or toxic
trace metals into ocean ecosystems, a major concern with most
mineral-based alkalization approaches $^{2}$. The redistribution
of alkalinity dilutes the already occurring anthropogenic acidifica-
tion of the surface ocean into the deeper ocean. Due to these ad-
vantageous ecological properties, the proposed method may find
it easier to gain support and acceptance from the public, as it aims
to mitigate human impact by spatial and temporal dilution.

We note also that widely discussed biological ocean CDRs $^{25}$
which propose increasing primary biological productivity and
sinking of biogenous matter, such as ocean fertilization, could be
seen as equivalent to the acidity pumping proposed here. This
is because the vast majority of sunk soft tissue is remineralized
in the water column or on the ocean floor, thus acidifying deep
waters $^{26}$. Only 0.4% of the originally fixed carbon is buried in
sediments and permanently removed from circulation $^{10}$. Thus
efforts increasing primary biological production likewise rely on
the dissolution of deep CaCO$_3$ deposits to prevent the transported
carbon from being re-emitted to the atmosphere on the timescales
of ocean circulation. Thus, these methods also aim to accelerate
the carbonate pH-stat, albeit indirectly. The same can be said for
efforts to directly inject CO$_2$ into the deep sea, as the resulting
CO$_2$ lakes or hydrates gradually dissolve $^{27}$.

In this paper we present ocean circulation simulations to exam-
ine the effects and limitations of large-scale acidity pumping as
well as techno-economic arguments which suggest that the cost
per tonne of CO$_2$ could potentially be competitive with terrestrial
direct air capture (DAC) and other negative emissions technolo-
gies while avoiding the ecological impacts of accelerated mineral
weathering $^{2}$.

2 Methods

2.1 Global Circulation Model of acid-base pumping

To simulate the effect of acid-base pumping on surface and deep
water pH, as well as net ocean CO$_2$ uptake, and evaluate the re-
turn time of acidity, we used a full ocean circulation model in
a $128\times 64$ worldwide spherical polar grid using MITgcm $^{28}$. The
simulation had cell sizes of $2.8\times 2.8^\circ$ divided into 20 exponen-
tially spaced depth levels, from 10m thick at the surface to 690m
thick at depth. The simulation was initialized and forced as de-
tailed in Dutkiewicz et al. 2005 $^{29}$. The MITgcm GEOM and
DIC modules were used to simulate the soft tissue and carbonate
pumps, as well as ocean-atmosphere gas exchange. A number of
studies $^{30,31}$ have simulated addition of alkalinity to the ocean in
the context of realistic emission scenarios with increasing atmo-
spheric pCO$_2$. Here we chose to focus instead on the efficiency
of CO$_2$ uptake and the circulation aspects of acidity return, and thus
the atmospheric concentration of CO$_2$ was simply held constant
at 415ppm similar to work by Kähler et al. $^{21}$.

2.1.1 Perturbation.

Custom code was added to simulate the transport of alkalinity
from a parameterizable slab of deep water to the top 10m of sur-
face water corresponding to the pumping of acidity in the op-
posite direction, keeping the total ocean alkalinity constant. To
investigate the fate of alkalinity and acidity separately, some sim-
ulations were modified to only alkalize, in which case the total
alkalinity change was not conservative. These simulations repres-
ent an idealized addition of pure alkalinity to the surface ocean.
In all experiments the pumped alkalinity was released into the top
10m slab, but the acid-injection slab position and thickness, as
well as the distribution of pumping, were varied from experiment
to experiment, as detailed in the results section. The movement
of volume was not explicitly modelled, as the involved quanti-
ties are tiny ($\sim 5 \times 10^{-3}$ Sv/GtC) compared to the natural ocean
overturning.

2.1.2 Carbonate compensation.

The return of the acidity with the overturning circulation is the
timeframe in which the transported acidity can be neutral-
ized by dissolving carbonate sediments. Both the dissolution
of existing CaCO$_3$ deposit inventories (estimated $^{6}$ at a total of
1600GtC), and reduction of new carbonate deposition (estimated
at 0.27GtC/yr to 0.1GtC/yr $^{32,33}$) increase net alkalinity in the
ocean and would act to neutralize any pumped acidity. Due to the
relatively short amount of time that sinking particles spend in the
water column, most of the dissolution below the carbonate satu-
ration horizon (CSD) occurs on the ocean floors. Despite the re-
latively uncertain current carbonate dissolution rates (0.3GtC/yr
\[ r = k^* ([CO_3^{2-}]_{\text{sat}} - [CO_3^{2-}]) \]  

(1)

The effective rate constant, \( k^* \), is limited by sediment-side mass transport \( (K_s) \) or water-side diffusion \( (\beta) \) through a boundary layer, whichever is slower:\n
\[ k^* = K_s \beta / (K_s + \beta) \]  

(2)

Most locations of significant (>20%) carbonate content are limited by water-side diffusion, as bottom water speeds are relatively slow. Thus the resulting kinetics are linear with respect to the carbonate ion concentration and relatively independent of sediment CaCO_3 content. To simulate the dissolution of CaCO_3 deposits during our simulations, a gridded map of dissolution rate constant, \( k^* \) and sedimentary CaCO_3 content was obtained from work by Sulpizio et al.\(^{11}\). The bottom dissolution rate was then calculated by equation 1 for all grid tiles where the CaCO_3 fraction > 10%. For grid tiles containing less than 10% the dissolution rate was set to 0. At the same time, any biological carbonate flux reaching the ocean floor was modelled to have settled onto the seafloor. At steady state the rate of sedimentation and dissolution was found to be relatively balanced, i.e. the total ocean alkalinity was not changing rapidly. Riverine alkalinity input was not modelled. An initial simulation allowed the ocean system to equilibrate for 2500 years and was used as the starting point for all subsequent pumping simulations. All the simulation setups, code modifications and parameters are available.\(^7\)

3 Results

3.1 Uniform pumping

In our initial simulations alkalinity was pumped uniformly over the entire ocean, wherever the respective depth was available to pump acidity to. The amount of alkalinity pumped was 0.25Pmol/yr the equivalent to a maximum uptake of 3GtCeq/yr, roughly the same amount as was used by\(^{21}\). Note that throughout this paper we will use units of 1GtCeq=0.833Tmol to provide a better intuitive sense for the quantities involved (relative to human emissions of \(~10GtC/yr\)). Pumping proceeded for 50 years which would yield roughly the required amount of negative emissions called for by most RCP2.6 pathways. We also investigated lower and higher pumping rates up to 10GtCeq/yr to examine the effect on pH and carbonate saturation and establish a way to estimate a reasonable level of alkalization without excessively affecting marine ecology. Previous work\(^{31}\) examined alkalinity addition as high as \(~22 GtCeq/yr\) although such a high rate is unlikely to be practical or ecologically safe. After the 50 year pumping period was over the simulation was allowed to continue up to the 5000-year mark to investigate carbonate compensation and the longevity of the stored carbon. To identify the role of carbonate compensation a control run was performed with sediment compensation turned off. A positive control run was also performed to compare to the case where alkalinity is added at the surface but no compensating acid is deposited at depth, effectively simulating the addition of a fast dissolving alkaline material.

Figure 2a shows that alkalinity pumping results in rapid uptake of CO_3, virtually indistinguishable from simple net alkalinity addition to the surface for the first 50 years. In the subsequent period, the depth of acid release strongly determines the return time and the eventual re-emission of any previously captured CO_2. Injection of acidity in too shallow waters causes reemission within 100-200 years, an insufficient amount of time for any significant amount of carbonate compensation to occur. However, for acid depths greater than 3000m the CO_2 absorbed doesn’t begin to be re-emitted for at least 300 years, retaining 85-95% of the absorbed CO_2. For an acidity release below 2000m, the relaxation half-life of CO_2 return to the atmosphere is found to be \(~2500\) years. This time provides sufficient contact time for deep carbonate dissolution to occur as shown in Figure 2b, with the global calcite dissolution rate increasing by as much as 0.25 GtCeq/yr.

We note that the system relaxation time is significantly increased due to this dissolution, as the half-life for CO_2 return in the reference simulations without carbonate dissolution was much shorter (\(~1000\) years), depending solely on ocean circulation. We note that because the ocean pH stat is a bidirectional homeostat, the proportion of CO_2 which will be permanently removed depends on the future emissions scenarios and the eventual equilibrium point of the ocean. The method proposed here simply allows the thermostat to respond much more quickly than it would have otherwise done.

Figure 3 tracks median and 95%ile changes in surface and ocean floor pH. See Figure S1 for the corresponding change in calcite saturation. The median surface \( \Delta pH \) rises rapidly for the first 1-2 years (0.03/yr) but slows within 10 years to a steady rate of \( 2 \times 10^{-4}/yr \), reaching a maximum median \( \Delta pH \) of 0.022 after 50 yrs. The increased rate of CO_2 dissolution is mostly able to buffer the increase in surface alkalinity. The seafloor pH however continues to decrease throughout the pumping period due to the considerably slower calcite dissolution rate. Despite this, the perturbation is at most -0.15 pH units at its most extreme point. Varying the global pumping rate between 0.3 and 10GtCeq/yr we found a roughly linear dependence of pH and Omega perturbation and pumping rate (Figure 4). The sensitivity of benthic ecosystems to pH perturbation is poorly understood and requires further research. However, seasonal changes in open-ocean pH can be up to 0.2 pH units\(^{36}\) while diurnal changes in coastal areas can reach as much as a full pH unit\(^{37}\). Using this as a guide we suggest that alkalinity pumping at global rates of 1-3GtCeq/yr is likely feasible without excessive stress on marine systems, though this is a critical area in need of further research.

3.2 Location dependence

Uniform pumping is neither practical nor efficient. From a practical perspective, the location of pumping will depend strongly on the mode of deployment (see discussion section). From an oceanographic perspective, both the efficiency of alkalinity compensation at the surface and the timescales of return of acidity from deep waters vary substantially depending on the location in
the ocean. The former varies due to differences in the uptake efficiency factor and surface currents, while the latter depends on how soon deep waters are returned to the surface with the global overturning circulation.

The carbonate equilibrium in seawater responds to an increase in alkalinity by shifting towards the carbonate ion. The concomitant reduction in the partial pressure of pCO₂ causes an uptake of CO₂ from the atmosphere until equilibrium is restored. The number of moles of CO₂ absorbed for every mole of alkalinity added, the uptake efficiency ηCO₂, can be expressed as the ratio of the partial pressure sensitivities of pCO₂ with respect to total alkalinity (Alk) and total inorganic carbon (DIC)\(^{13,32}\). This compensation ratio presents a fundamental inefficiency that needs to be taken into account when calculating potential CO₂ uptake of any ocean alkalination method in addition to any process inefficiencies. The commonly used approximations \(\text{DIC} \approx [\text{HCO}_3^-] + [\text{CO}_3^{2-}]\) and \(\text{Alk} \approx [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]\) at typical ocean pH yield a good approximation for the uptake factor: (derivation in supplementary materials).

\[
\eta_{\text{CO}_2} = 1 \left(1 + \frac{1}{2}\right) = 0.8
\]

which evaluates to \(\sim 0.8\) at average surface ocean concentrations of DIC=2000µM and Alk=2300µM. The intuition why \(\eta_{\text{CO}_2}\) is smaller than 1 is that while each mole of additionally absorbed CO₂ will be neutralized by one mole of OH- to bicarbonate, some fraction will consume a mole of OH- to become a carbonate ion. A full carbonate model\(^{19,20}\) was used to calculate the plot in supplementary figure S1, showing that this uptake factor varies substantially depending on the latitude and is one factor to inform optimal alkalinity release locations. Alkalinity addition to areas with high efficiency factor will cause a greater uptake of CO₂ in the near term, however ocean surface currents will tend to move the uptake towards an average efficiency over time, so longer term efficiency can only be predicted with explicit circulation simulation\(^{30,31}\). Furthermore, in our case, the return time of the acidity is dependent on the direction and speed of bottom currents and the proximity to upwelling areas.

We thus performed a grid scan of the ocean, where in each simulation an amount of 100Tmol/yr of alkalinity (0.12 GtCeq/yr) was pumped at any one grid point only. Altogether \(\sim 1000\) independent simulations were conducted, one for every gridpoint with sufficient depth to inject acidity. In each case the entire ocean biogeochemistry was monitored compared to a reference simulation with no pumping.

Figure 5 and supplementary figure S3 show the normalized total uptake of CO₂, such that a value of 1.0 represents an ocean uptake equimolar to the amount of alkalinity pumped. Previous work that examined alkalinity addition in different coarse latitude bands\(^{21}\) found not all areas are equally efficient at CO₂ uptake or retention. We extend this work with a finegrained map and find...
that on short timescales the efficiency is dominated by the surface efficiency, and the local atmospheric pCO$_2$. However, after some time surface currents spread the excess surface alkalinity and the effect becomes less pronounced. For the case of alkalinity addition (rather than pumping) most of the locations eventually reach close to the full average efficiency of 0.85 except areas of significant downwelling in the polar regions (see Supplementary Figure S2). The alkalinity is pulled downwards and removed from the surface as is evident in depth plots of calcite saturation (Supplementary Figure S3). In the case of acidity pumping the behaviour is very similar, but on longer timescales, uptake efficiency becomes dominated by the rate of acid return. Since deep return currents generally move southwards, injection of acidity in the northern hemisphere appears to be significantly more efficient in the long run, with some small areas as notable exceptions. Two large areas in the southern ocean appear to return acidity faster than others and are inefficient locations for alkalinity pumping (Figure 5). Figure S2 gives detailed plots of the total excess absorbed CO$_2$ due to pumping at a selected number of locations.

3.3 Impact on surface and deep water pH

Understanding the pH sensitivity of different locations allows optimization of the alkalinization strategy to minimize ecological effects and costs while maximizing CO$_2$ uptake.

At the surface, the pH increase will be highest right at the injection site, decreasing exponentially with distance. The alkalinity will be compensated by CO$_2$ uptake, but depending on the currents and eddy diffusivities which transport and distribute the alkalinity, as well as wind speeds, surface agitation and local atmospheric CO$_2$ concentration, we can expect different sensitivities at different injection sites. It is important to avoid too large a pH change both for ecological reasons as well as needing to avoid triggering inorganic precipitation$^{38}$ of CaCO$_3$. At depth, the injection of acidity must also be considered against an ecological safety margin. We propose that the acidity is injected no closer than 500m to the seafloor and at least 2000m from the surface. This area of the ocean is the least populated by marine species and thus gives ample time for the acidity to dilute horizontally away from the diffuser pipes. Figure 6 shows the sensitivity of surface and deep water pH on the pumping location from $\sim$2000 individual simulations of single-point alkalinity pumping. The sensitivity (m$^2$mol$^{-1}$) was calculated by dividing the maximal ΔpH observed for any given simulation by the pumping rate density (molm$^{-2}$s$^{-1}$). As expected, areas with stronger surface currents spread surface alkalinity most efficiently, reducing the pH impact at the release location. This effect would be less pronounced if the release stations were free floating with these bulk water movements; however, the horizontal eddy diffusivity is considerably larger in these currents, which would make them preferential release sites nevertheless. Another factor reducing surface pH impact are wind speeds, which reduce the ocean-atmosphere CO$_2$ equilibration time. The circumpolar wind band likely accounts for the low surface sensitivities observed in the southern ocean (Figure 6, S4).
Fig. 5 Efficiency of alkalinity pumping ($\eta_{\text{CO}_2}$) as a function of latitude and longitude. Here ($\eta_{\text{CO}_2}$) is the number of moles of excess CO$_2$ absorbed by the ocean normalized by the number of moles of alkalinity pumped. Each point on the grid represents an entire ocean simulation in which 1Tmol/yr were pumped at that point only (a total of $\sim$2000 simulations). Mapped is the relative increase in total oceanic dissolved inorganic carbon (relative to the reference), normalized by the amount of acidity pumped. Three different timepoints are shown: a) Uptake of CO$_2$ at the end of the 50year pumping period. Significant differences in the effective ($\eta_{\text{CO}_2}$) are observed, depending on where the alkalinity was pumped, varying from 0.5 to 0.85. The differences during this period are driven primarily by the efficiency of CO$_2$ uptake, as the distribution closely matches that of simple alkalinity addition. In particular the northern Atlantic exhibits poor CO$_2$ uptake. b) CO$_2$ uptake 100 years after the end of pumping. Alkalinity Pumping in most northern hemisphere areas has caught up to an uptake efficiency of 0.85 with equatorial regions exhibiting the best retention. c) 200 years after the end of pumping. The apparent CO$_2$ uptake is fully dominated by the acid return kinetics (cf Fig. S5, where alkalinity was added instead of pumped). It is apparent that acidity pumping in the southern hemisphere is less efficient, likely due to the fact that ventilation of deep water occurs in the Southern Ocean and thus acidity returns to the surface more rapidly. Conversely the North Pacific retains pumped acidity the best.

Fig. 6 Local surface pH sensitivity in s$\text{km}^2\text{mol}^{-1}$ obtained by injection at each grid point only (each grid point represents an entire independent simulation). The sensitivity was calculated by dividing the globally maximal $\Delta \text{pH}$ in either direction observed for any given simulation by the pumping rate density($\text{mol km}^{-2}\text{s}^{-1}$). Panel a) reflects pH changes in the alkaline direction (typically found at the surface release site). The surface sensitivity represents the efficiency with which a stationary addition of alkalinity at any given location with some constant rate is distributed and neutralized by CO$_2$ invasion. Larger values indicate slower spreading from the release site and/or slower neutralization by CO$_2$ invasion. Areas with stronger surface currents can spread surface alkalinity most efficiently and are least sensitive to surface pH changes. Panel b) reflects pH changes in the acidic direction (found in deep water where acid is pumped too). The crosses mark the location of the individual plots in Figure S4.
4 Discussion

4.1 Deployment possibilities

The proposed method is only reliant on local resources (seawater) and power and could be implemented in a variety of locations with varying power sources, as shown in Figure 1. Specifically, it would be uniquely matched for untethered power generators, obviating the otherwise arising problem of energy storage or transmission and material transport encountered in other offshore methods, providing a productive use of open-ocean power sources in situ. Open-ocean stations could operate on wave, wind or ocean thermal (OTEC) power and could be scaled with a large number of untethered, identical units. Open-ocean photovoltaics have been investigated and trial projects are underway. All of these technologies are still in early development and have not yet benefited from commercial efficiencies of scale and are thus currently relatively expensive. Part of the reason for the lack of wide scale adoption is the need for energy transmission in one form or another. Ocean acidity pumping could thus be a perfect match for these technologies. The lack of need for power transmission or transport can further reduce costs compared to current estimates. Since open ocean is ecologically sparse, alkalinity release in open waters could be less impactful to marine biology than coastal release and could be deployed at larger scale. An alternative approach could involve near-coast operation; larger sized plants could tap into cheap terrestrial energy, especially daytime excess solar. Acid/Base generators could potentially be located just-off-coast with a grid connection to land - transportation of electricity being considerably cheaper than transport of matter, i.e. the pumping of seawater onto land and back should be avoided. Decommissioned oil rigs may offer an ideal platform for such deployment. Coastal locations where the continental slope is close to the coast and strong surface current occur would be ideal, because it shortens the distance acid and base need to be transported, and currents are able to distribute the excess surface alkalinity effectively. A potential intermediate deployment would consist of near-shore wind farms. Where possible, especially in areas where deep waters are not accessible, the acid stream could also be injected underground, into flood basalt formations or depleted oil wells where it would react with silicate rocks and be neutralized. Such a deployment could be ideal for example for the North Sea although such areas may be limited to smaller amounts of alkalinity that can be safely released while keeping pH changes below ecological thresholds. However, this could present a feasible method to stabilize ocean pH in localized areas to counteract ecological damage from acidification.

4.2 Techno-economic estimation

Although a full techno-economic analysis is beyond the scope of this paper, we conduct a rough estimation of potential costs of electrodialysis, using published data from other methods which create pH gradients. Acid/base production could be implemented using either electrolysis or bipolar membrane electrodialysis. Electrolysis was among the first methods suggested for negative emissions technology, though the generation of gases is energetically inefficient and has to be either recouped using a fuel cell, adding complexity and cost, or recouped by selling the products, which necessitates mass transport of the products. The use of electrolysis on seawater at gigatonne scale may also produce significant quantities of volatile halogenated organics which are ozone depleting, such as bromo- and chloromethane. Here we choose to focus on electrodialysis methods, which have been proposed and tested for seawater CO₂ extraction. However, even if colocated with desalination plants, costs are high (373-604$/tCO₂, 540$/tCO₂ Digdaya 2020) in part due to very large quantities of seawater needing to be processed (about 11,000m³/tCO₂). In contrast, releasing the alkalinity to the ocean for passive CO₂ absorption and storage is conceptually and technologically simpler, consisting only of the acid/base generator. The quantity of seawater needing to be processed is greatly reduced (~250m³/tCO₂ depending on the exact concentration of effluent acid and base). There is no CO₂ extraction, thus saving capital and operational costs of membrane contactors. Indeed Digdaya found membrane contactors and vacuum pumps accounted for 90% of the equipment cost. Instead, leveraging the ocean as a sorbent surface obviates the need for air contactors as well as additional storage, as the CO₂ is stored as relatively benign carbonate ions. From a capital and operational cost perspective, alkalinity pumping is a strict subset of electrodialysis-driven CO₂ extraction and should thus always be cheaper, whether the acidity is moved to deep ocean or underground. The three largest contributors to overall levelized cost would be the cost of electricity to drive the electrodialysis stack, the cost of pre-treating seawater to prevent fouling of the membrane stack and the cost and lifetime of the membranes themselves. Minor contribution costs are the pumping of acidified water to depth. In the open ocean scenario we assume that the cost of the structure are implicit in the assumed levelized costs for open-ocean electricity, and that the electrodialysis apparatus is generally much smaller than the structure. In the following we discuss the likely current ranges of these costs and likely learning curve improvements into the future. However it should be noted that in order to further narrow these estimates, construction of medium-size prototypes is essential.

4.2.1 Energy costs.

In bipolar membrane electrodialysis (BPME), the thermodynamic minimum energy to create effluent streams at a given pH can be calculated from the Nernst equation as

\[ \Delta G = 2.303RT \Delta pH \]  

where \( \Delta pH \) is the pH difference between the acid and base effluents. For a base effluent concentration of 1M NaOH, the minimum energy is \( \sim 80kJ/mol \) \( (E^0 \approx 0.83V) \) at ambient conditions. A real BPME stack of course will require considerably more energy due to ohmic losses in the membranes and the thin solution layers, electrolytic losses at the electrodes, and back-leakage of protons or hydroxide ions. Electrodialysis is, in principle, more efficient than electrolysis for creating a pH gradient, since no additional energy is expended to generate...
gaseous O$_2$ or H$_2$ (E$_{0}$=1.23V) which has to be recouped economically\textsuperscript{39} or via fuel cell\textsuperscript{16}. The specific energy consumption ($E_{sp}$, kJ mol$^{-1}$) varies substantially in the literature ranging from 160 to over 350kJ/mol (162kJ/mol\textsuperscript{57}, 155kJ/mol\textsuperscript{55}, 242kJ/mol\textsuperscript{52}, 236kJ/mol\textsuperscript{56}, 255kJ/mol\textsuperscript{58}, 259kJ/mol\textsuperscript{59}, 328kJ/mol\textsuperscript{60}, 341kJ/mol\textsuperscript{61}). This represents process efficiencies of only 20-45\%, suggesting that there is potential for learning curves and technological improvements. Many of the above studies aim to valorize reject brines and are optimized to produce both concentrated (>1M) and pure acids and bases for industrial use and thus require deionized water to feed acid and base tanks in feed-and-bled flow schemes. For purposes of acidity pumping the effluent can be more impure and dilute than in the above studies, affording potentially lower costs. The levized cost of electricity for free floating power generation is highly variable, and likely suboptimal due to the lack of current economies. Wind power has been estimated at $30-$80/MWh\textsuperscript{43}. OTEC is estimated to provide energy at a cost of $150-$200/MWh\textsuperscript{39,42}. Wave power generators levized costs are highly uncertain and maybe in the range of $120-$470/MWh\textsuperscript{62}. Even though transmission costs can be saved in our case, the present-day costs are likely too high for economical carbon capture, but have considerable potential for reduction with economies of scale. As an alternative, land-base power could be used in near-coast applications where strong currents allow for nearby alkalinity distribution. Examples include the Agulhas, the Kuroshio, the Gulfstream and the North Brazilian current. However deep-water acid disposal becomes more limited as bottom currents are much slower and it may be better to instead pump the acidified stream underground if suitable basalt formations are available. Utility scale solar is likely the cheapest land-based energy source with unsubsidized levized costs as cheap as $32-$44/MWh and wind at $28-$54/MWh\textsuperscript{63}. It is thought that there will be a considerable excess of this power during daytime hours, for which finding a carbon negative use would be desirable to help with load leveling.

Assuming an efficiency range of 160-250kJ/mol, energy prices of 30-80$/MWh and an ocean uptake efficiency $\eta_{CO_2}$ of 0.8 we obtain a range for the energy costs of 38$-$158$/tCO_2$. It is interesting to compare these energy requirements to other CDR approaches. Electrolytic approaches require about $\sim$300kJ/mol\textsuperscript{24}. Direct air capture (DAC) has been estimated at 200-1000kJ/mol\textsuperscript{64} and more recently at 370-550kJ/mol\textsuperscript{65}. Energy requirements for methods involving mafic or ultramafic rocks to the ocean, likely needing to be ground to 1\,$\mu$m for open ocean application\textsuperscript{21}, vary substantially from\textsuperscript{15,38} 175-315 kWh/t to\textsuperscript{23} 500-1000 kWh/t. Depending on the rock type, with a net uptake efficiency of 0.3-0.8 tCO$_2$ per tonne of rock, one obtains an energy requirement of 35-528kJ per mol of CO$_2$ absorbed.

4.2.2 Water pretreatment costs.

As ion-exchange membranes are prone to scaling and fouling\textsuperscript{66}, methods that electrodiLyse seawater typically use nano-filtration (nF) and reverse osmosis (RO) pretreatment to remove divalent ions\textsuperscript{51,39}, concentrate the input brine and provide deionized water, especially for the base compartment where scaling would be most pronounced. The associated costs are not negligible and tradeoffs need to be considered. Higher flow rates increase pretreatment costs but reduce concentration gradients in the BPMED stack leading to higher faradaic efficiency. There is a tradeoff point, typically around 0.50-1.0M effluent acid/base, corresponding to a pretreated water need of 56-114m$^3$/tCO$_2$ (accounting for an uptake factor of 0.8). We estimate the cost of water pretreatment\textsuperscript{67} at $0.5$/m$^3$, leading to a cost range of 28-57$/tCO_2$. Development of BPMED processes which are more resistant to fouling, may mitigate this pretreatment cost.

4.2.3 Bipolar membrane capital costs.

Current densities in BPM stacks vary typically between 450-700 A m$^{-1}$ REFS and cell resistivities of 0.003 $\Omega$m$^2$, giving a power density of $P_D$=1.5-0.6kW/m$^2$. We can thus calculate the levized cost contribution of the membranes as $C_M\eta E_{sp}/P_D$, where $C_M$ ($$/m^2$) is the levized discounted cost of the membranes and $\eta$ = 0.8 is the CO$_2$ uptake efficiency. Lower current densities improve the energy efficiency due to lower resistive losses but increase membrane capital costs\textsuperscript{60}, leading to cost tradeoffs. Reduction of membrane costs by 5x-10x through economies of scale and technological advances thus have the opportunity to drastically reduce energy costs. Commercial bipolar membrane stacks (consisting of one bipolar membrane and two monopolar membranes) are currently produced at relatively small quantities, but at scale, with an assumed active lifetime of about 3 years we could reasonably expect a levized cost\textsuperscript{32,55} of $C_M$ = 200$/s^{-1}$m$^{-2}$. Thus we estimate the membrane capital cost contribution between $20-75$/tCO$_2$.

4.2.4 Dispersion.

Depending on the deployment mode, the alkalinity and acidity need to be separated and transported. In the case of open ocean deployment, the alkalinity is simply released on site, while the acidity is pumped to depth. We can assume that the capital costs of the floating structure are implicitly included in the levized cost of the chosen off-shore energy system, as the electrodialysis unit would be quite small compared to the energy structure. We can estimate the additional requirements for pumping as follows. Assuming an acid concentration of 0.5-1.0M, the quantity of water to be pumped is 28-56m$^3$/tCO$_2$. As no net work is done against gravity, the energy for pumping is that of overcoming the friction in the pipe. We can estimate the head loss (in meters of water) using the empirical Hazen–Williams equation (in SI units):

$$h_f = 10.67 \left( \frac{Q}{C} \right)^{1.852} d^{-4.804} L$$

(5)

where Q is the flow rate (m$^3$/s), d and L are the diameter and length of the pipe (m), respectively, and C is an empirical pipe roughness coefficient, about 140 for a typical smooth pipe. For example a 3000m long pipe, 5cm wide, and a flow rate of 5L/s would require a head pressure of $\sim$40bar. This is quite similar to injection of CO$_2$ into basalt formations requiring $\sim$27m$^3$/tCO$_2$ of water and pressures of 25bar\textsuperscript{47}. The power needed to pump water at a rate of Q through the pipe is given by:
\[ P_{\text{pump}} = h_f \gamma_w Q \]  

(6)

where \( \gamma_w \) is the specific weight of water, \( 9.8 \text{ kN/m}^3 \). The power required to generate the acid and base is given by

\[ P_{ED} = c_H E_{sp} Q \]  

(7)

Where \( E_{sp} \) is the specific energy requirement of the BPMED stack (kJ/mol) and \( c_H \) is the concentration of acid produced (\( c_H = 10^{-pH} \)). Assuming for example \( c_H \approx 0.75M \) and \( E_{sp} \approx 180kW/mol \) we obtain \( P_{ED} \approx 675kW \) and \( P_{\text{pump}} \approx 20kW, \) just 3% of the dialysis energy requirements. However, the engineering requirements for a deep-ocean pipe system are non-negligible, resembling in many ways that of deep ocean lift cables for deep ocean ROV systems in terms of size, design and required resistance to ocean stress. The amortized costs, for a production at scale, are highly dependent on the particular ocean location and mode of deployment and thus difficult to estimate. As an orientation, if we assume conservatively a 5 year lifespan and a cost of \( 60$/m \) for a 2500m pipe we obtain a levelized cost of about \( 7.2/tCO_2 \). However the challenges of open-sea engineering are formidable and pilot studies would be necessary to narrow the cost estimates.

If alkalinity is generated near shore at scale it will need to be dispersed away far from the shore to avoid local pH spikes. However, because the alkalinity is relatively dilute \((0.1-1mol/kg)\) compared to dry solid alkaline materials \((~25mol/kg)\) bulk transportation is considerably less efficient. For example, at \( \eta = 0.8, 28.4 \) tonnes of 1mol/kg hydroxide solution are required for every tonne of \( CO_2 \) absorbed. Large-scale shipping costs are around \( \$0.0016-$0.004/t.km \) and produce about \( 7gCO_2/t.km \). Assuming alkalinity to be dispersed in a 300km strip around the coast, i.e. within the exclusive economic zone of any bordering country, and typical tanker speeds of 14knots \((7.2m/s)\), a 300km roundtrip \((150km\) zone\) could be completed in 12 hours, with a daily turnaround. Assuming a factor of 2 inefficiency compared to ordinary shipping, due to the very frequent loading, we obtain a cost of \( 13-33$/tCO_2 \). Furthermore, as tankers are hard to decarbonize, \(~57kgCO_2\) are emitted for every tonne of \( CO_2 \) absorbed, about a 5% reduction in efficiency. The additional costs and the additional \( CO_2 \) impact of transport limit alkalinity release to coastal areas and thus limit the total scaling of landbased alkalinity production.

Overall we obtain a minimum cost per tonne of \( CO_2 \) captured of \(~93-297$/tCO_2 \). This estimate is quite close to estimations obtained by a recent study\(^{46,52}\) \((110-325$/tCO_2)\) for the BPMED portion of their process, which conducted a much more detailed techno economic analysis for \( CO_2 \) extraction. As expected the costs are much lower than estimates for \( CO_2 \) extraction \((373-604$/tCO_2 \), \( 540$/tCO_2 \)).

At the lower end, the total cost estimate has similar-sized cost contributions from energy cost, membrane cost and water treatment cost. Thus to drive down overall costs development and cost reduction is needed in all three areas. Furthermore, as with all ocean CDRs, working with ocean water and in marine environments in general poses significant challenges in terms of corrosion and longevity of the equipment which will need to be addressed for a practical, scalable application.

5 Conclusions

We have explored the feasibility of accelerating the natural compensation of ocean acidification by CaCO3 deposits by artificially pumping excess acidity towards the abyssal CaCO3 sediments. The subsequent alkalization of the surface would counteract anthropogenic acidification and increase the uptake of significant quantities of atmospheric CO2. Thus alkalinity pumping could meaningfully contribute to a portfolio of negative emissions technologies. Based on our simulation we estimate 1-3GtC/yr could be removed over a 50yr period, without raising deep water pH excessively. For acid injection depth>3000m we show that carbonate compensation is significantly engaged, permanently removing up to 40% of the absorbed \( CO_2 \). Reemission of the remainder occurs ionly after 300 years and slowly over several millenia of gradual outgassing, effectively flattening the curve of the anthropogenic \( CO_2 \) shock to the atmosphere. In total up to 150GtC could be removed this way before the end of the century, satisfying requirements for negative emissions laid out by RCP2.6 pathways. What might a scaled up deployment look like? Modern offshore 10MW wind turbines can generate on the order of 50 GWh of energy per year, which could be used to sequester up to 50ktC per year. Thus for a total scale of 1GtC/yr about 20000 of such units would be necessary (i.e. about 200GW of total capacity). Current global offshore wind capacity is expected to reach about 500GW by 2050, thus a goal of 1GtC negative emissions could be feasible.

The pumping of ocean acidity presented in this paper avoids many of the environmental issues with mineral-adding alkalinity methods both in terms of impurity dissolution in the ocean and mining impacts on land. It is conceptually simple and requires only locally available resources (seawater and energy), and is thus uniquely suited to openwater deployment. While in the short term, on-shore electrochemical alkalinization is likely more economical due to the inherent engineering challenges of marine engineering, it is also inherently limited in scale. We have shown that transport of dilute acid or base is not economical beyond 150km away from the production site. Disposal of dilute acid into deep basalt aquifers provides a partial solution but its scaling limits are not well understood. Therefore open-water production of acid and base could supplement terrestrial powered CDR and is an interesting avenue of research despite the usual challenges of marine engineering. Open-water CD also provides a route to make use of otherwise unusable renewable energy, an area of CDR research that has been underexplored. In general, manipulation of acidity/alkalinity as a proxy for \( CO_2 \) may be technologically simpler and/or more efficient than manipulation of \( CO_2 \) directly, whether the acidity is moved into deep ocean or underground. We also presented the first fine-grained analysis of location dependence of surface alkalinization and show that in the short term there is substantial variation in \( CO_2 \) uptake efficiency which will need to be considered in any ocean alkalinization plan, mineral-based or not. As with all ocean-based CDR methods, simulations have inherent limits and the ecological parameters and
limitations require substantial further research and experimentation in meso-scale pilot programs.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
We thank Matt Eisaman, Ben Saenz, Rob Dunbar, Joel Atwater, Will Regan, Daniel Rosenfeld and Kevin McCloskey for many helpful discussions and comments on the manuscript.

Notes and references
25 IPCC special report on carbon dioxide capture and storage, ed. B. Metz and Intergovernmental Panel on Climate Change, Cambridge University Press, for the Intergovernmental Panel on Climate Change, Cambridge, 2005.
37 C. E. Cornwall, C. D. Hepburn, C. M. McGraw, K. I. Currie,
1 A simple approximation to CO$_2$ uptake efficiency

Addition of alkalinity to the ocean lowers pCO$_2$, the partial pressure of CO$_2$, and thus subsequently more CO$_2$ is taken up from the atmosphere until pCO$_2$ = pCO$_2$$_{atm}$ again. Dissolved inorganic carbon (DIC) exists in the ocean in an equilibrium between the three carbonate species, which can be written:

$$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{CO}_3^{2-} + 2\text{H}^+$$

Introduction of alkalinity consumes H$^+$ ions and moves the above equilibrium to the right. Under normal ocean pH the vast majority of DIC is in the bicarbonate (HCO$_3^-$) form, thus addition of alkalinity allows for an approximately equimolar quantity of CO$_2$ to enter from the atmosphere. However the actual amount is slightly smaller than 1: the intuition here is that for every mol of CO$_2$ entering the ocean we need $\sim$ 1mol of alkalinity to convert all the CO$_2$ to bicarbonate, plus additional alkalinity to further convert some fraction to carbonate ions and pull the equilibrium over such that the concentration of CO$_2$ (and thus pCO$_2$) returns to it’s starting value. The unitless uptake efficiency $\eta_{CO_2}$ can be calculated from the partial derivatives of pCO$_2$ with respect to alkalinity and DIC and represents the slope of the pCO$_2$ isolines in an Alk vs DIC plot (see Figure S1).

$$\eta_{CO_2} = -\frac{\partial pCO_2}{\partial \text{Alk}} / \frac{\partial pCO_2}{\partial \text{DIC}}$$

(1)

The carbonate system with equilibrium constants, K0, K1 and K2 is defined as:

$$[\text{H}_2\text{CO}_3^*] = K_0 p\text{CO}_2$$

(2)

$$K_1[\text{H}_2\text{CO}_3^*] = [\text{HCO}_3^-][\text{H}^+]$$

(3)

$$K_2[\text{HCO}_3^-] = [\text{CO}_3^{2-}][\text{H}^+]$$

(4)

where [H$_2$CO$_3^*$] = [CO$_2$] + [H$_2$CO$_3$]

A full carbonate system yields a complex expression for pCO$_2$ as a function of Alk and DIC, but we can easily estimate $\eta_{CO_2}$ from a common approximation of Alk and DIC, which assumes that in the ocean [H$_2$CO$_3^*$] is not a major contributor to the total inorganic carbon and that several minor species don’t significantly contribute to alkalinity:

$$DIC = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \approx [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

(5)

$$\text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + ... \approx [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

(6)

Combining all 5 equations, an expression is obtained for pCO$_2$, where we’ve contracted all the constants into one constant $K$.

$$p\text{CO}_2 = \frac{K_2[\text{HCO}_3^-]^2}{K_0 K_1 [\text{CO}_3^{2-}]} = K \frac{(2\text{DIC} - \text{Alk})^2}{\text{Alk} - \text{DIC}}$$

(7)

Differentiating with respect to Alk and DIC, respectively, yields:

$$\frac{\partial p\text{CO}_2}{\partial \text{Alk}} = K \frac{(\text{Alk} - \text{DIC})^2 - \text{DIC}^2}{(\text{Alk} - \text{DIC})^2}$$

(8)
\[
\frac{\partial p_{CO_2}}{\partial DIC} = K \frac{Alk^2 - 4(Alk - DIC)^2}{(Alk - DIC)^2}
\]  

(9)

Inserting these into the expression for \( \eta_{CO_2} \) and simplifying yields

\[
\eta_{CO_2} = -\frac{\partial p_{CO_2}}{\partial Alk} \left/ \frac{\partial p_{CO_2}}{\partial DIC} \right. \approx -\frac{(Alk - DIC)^2 - DIC^2}{Alk^2 - 4(Alk - DIC)^2} = \frac{1}{3 - 2DIC/Alk} = \frac{1}{1 + 2[CO_3^2-]/Alk}
\]  

(10)

This yields \( \approx 0.8 \) for stereotypical ocean values of DIC=2000µM and Alk=2300µM

Thus for every mol of alkalinity added, only \(~0.8\) mols of CO\(_2\) are absorbed until the partial pressure equilibrium with the atmosphere is restored. This limitation is inherent for all ocean alkalinity methods. A numerical calculation with a full carbonate system yields \( \eta_{CO_2} \approx 0.81 \) in close agreement the above approximate calculation.
Figure S1 a) Plot of the partial pressure as a function of dissolved inorganic carbon (DIC) and total alkalinity (Alk). Addition of any given quantity of alkalinity $\Delta$Alk to the surface will draw in additional $\Delta$DIC $= \eta$ $\text{CO}_2$ $\Delta$Alk until the partial pressure re-equilibrates. b) Graph of CO$_2$ compensation efficiency $\eta$ $\text{CO}_2$ as a function of latitude, calculated from GLODAPv2 data using pyCO2SYS. The worldwide average is $\eta$ $\text{CO}_2$ = 0.81. Areas of higher efficiency at the poles will take up more CO$_2$ per mol of alkalinity added to the surface ocean and would a priori be preferred for alkalinization, however the practical amounts also depend strongly on currents, up/downwellings and the atmospheric CO$_2$ concentrations, thus the true uptake efficiency must be calculated using simulation (e.g. see Figure 5 in main text).
Figure S2 Median and 95% ile changes in calcite saturation (Ω) at the surface (a&b) (increased saturation) and at the seafloor (c&d) (decreased saturation) for the same runs. Analogous to Figure 3 in the main text.
Figure S3 Time-resolved details for individual locations indicated in Figure 5, showing CO$_2$ uptake relative to the amount of acidity pumped (indicated by the dotted line). The black line shows the behaviour if acidity is pumped to depth and blue if the acidity is removed entirely (simple alkalinity addition). As expected the molar uptake ratio $\eta$$_{CO_2}$ is 80-85% and then decreases slowly as acidity returns to the surface. However some locations, such as the northern atlantic have markedly lower initial uptake ratios and are unadvisable for acidity pumping or alkalinity addition. Likewise the timescale of acidity return differs significantly depending on location.
Figure S4 Depth plots of changes in calcite saturation (Ω) at the end of the pumping period (50yrs) for globally uniform acid pumping to 2-3km depth. In some locations, like the Gulf stream and Denmark Straight, sinking surface waters pull surface alkalinity into deeper waters where it can’t be neutralized by atmospheric CO₂ (e.g.) and explain the significantly reduced uptake efficiency in these areas (Figure 5, main text). Surface-omega changes are also lower in the southern ocean, perhaps due to the consistent high circum polar winds which reduce the ocean-atmosphere equilibration time for CO₂.
Figure S5 Time-resolved pH changes for individual locations indicated in Figure 5, showing $\Delta$H extrema at the surface (dashed) and at depth (solid) for the pumping time and 50 years beyond. In each simulation acidity was pumped at just one grid point, with a pumping density of 0.54mol/km2/s (approximately equivalent to 200tC/km2/yr). Note that because in each simulation acidity pumping was only performed at one location, the perturbation can diffuse and dilute horizontally leading to a faster return to baseline than shown in Figure C, where pumping was done uniformly across the entire ocean and at a much larger total rate.
Figure S6 Uptake efficiency upon addition rather than pumping. Analogous to Figure 5 in main text. There exists significant variation in uptake efficiency which any practical ocean alkalinization scheme will need to take into account to maximize early rapid uptake of CO2 and balance against costs of alkalinity transport.