



OCEAN BICARBONATES

Understanding the positive global impact potential of adding bicarbonates to oceans to reverse acidification, promote marine flora and fauna, and sequester carbon

A climate restoration whitepaper



Authors

Charlie Dryden, Marine Environmental Consultant

Jerry Joynson, Cofounder, Herculean Climate Solutions



Herculean Climate Solutions

A thousand ways to do a million tonnes

TABLE OF CONTENTS

CLIMATE WARMING AND OCEAN ACIDIFICATION2

IMPACTS OF OCEAN ACIDIFICATION.....3

ADDITION OF ALKALISING AGENT AS A CURE3

THERE IS ANOTHER WAY.....4

THERE IS MORE THAN ENOUGH LIMESTONE4

THE OCEAN CAN ACCEPT THE BICARBONATE4

BICARBONATE - A CARBON SOURCE FOR AQUATIC FLORA5

CONCLUSIONS5

ABOUT THE AUTHORS.....6

REFERENCES.....6

Climate warming and ocean acidification

Anthropogenic emissions of carbon dioxide (CO₂) are causing an unprecedented change to the earth’s natural systems. Approximately one third of the CO₂ emitted since the industrial revolution has been absorbed by the oceans resulting in changes in ocean conditions, one of which is ocean acidificationⁱ. Ocean acidification is an inevitable consequence of rising atmospheric CO₂ levels. This describes the dissolution of CO₂ in seawater which reacts to form carbonic acid.

Since pre-industrial times there has been a drop in ocean pH of approximately 0.1 – this looks like a small change.

However, the pH scale is logarithmic, and therefore this change represents a 30% increase in the concentration of hydrogen ions which represents considerable acidification of the oceansⁱⁱ. This rate of change is unprecedented in the last 300 million yearsⁱⁱⁱ and eventually is likely to be beyond the ability of many marine species to adapt.

The atmospheric concentration of CO₂ reached 415 ppm in 2019 and continues to rise (1H2020). This equates to approximately 800 Gt of carbon or 3,000 Gt of CO₂. If we were to reduce this all the way back to the estimated pre-industrial level of 280 ppm then we would require a total reduction of about 260 Gt leaving a pre-industrial 540 Gt of carbon in the atmosphere.

Most countries are still not making enough progress towards achieving their Paris Climate Change Agreement targets^{iv}. This means that we have done little to diverge from “business as usual” which the IPCC terms the ‘Representative Concentration Pathway 8.5’ or RCP 8.5’.

Figure 1 below shows the impact of rising atmospheric CO₂ concentrations on the ocean acidity. Rapid removal of CO₂ from the atmosphere is clearly necessary to minimise the well documented damage that is occurring due to excess CO₂ in the atmosphere.

Interestingly, without human intervention, the world is slowly removing CO₂ from the atmosphere through a number of natural carbon sequestration processes, including by mineralisation and the creation of new plant mass. On a geological timescale these processes will gradually return the naturally CO₂ balance to the world. Unfortunately, that is too slow for mankind.

This paper addresses the current understanding of the potential for ocean alkalisation to sequester multi-billion tonnes of carbon as calcium bicarbonate, and at the same time both restore the ocean alkalinity and support photosynthesizing marine flora.

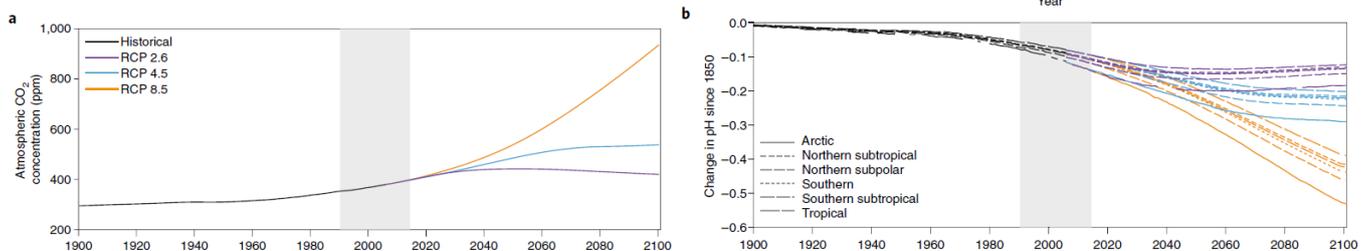


Figure 1. Projections of a) atmospheric CO₂ and b) oceanic pH, for RCPs 2.6, 4.5 and 8.5. RCP 2.6 most closely estimates the emissions required to meet the Paris Climate Change Agreement targets^{vi}



Herculean Climate Solutions

A thousand ways to do a million tonnes

Impacts of ocean acidification

The impacts of ocean acidification are far-reaching. The effects have been observed in the physical and chemical conditions of the oceans and in organisms spanning all levels of the ocean food web. Calcium carbonate minerals are the building blocks for the skeletons and shells of many marine organisms.

In areas where most marine species live in the ocean the seawater is supersaturated with respect to calcium carbonate minerals. This means there are abundant building blocks for calcifying organisms to create their skeletons and shells. However, continued ocean acidification is causing many parts of the ocean to become undersaturated with these minerals, which is affecting the ability of some organisms to produce and maintain their shells. Amongst the many calcifying species are economically and environmental important species, including oysters, clams, sea urchins, shallow water corals, deep sea corals, and calcareous plankton.

Example 1: Fisheries

Fisheries and marine aquaculture activities are sensitive to changing ocean conditions. Shellfish fisheries and aquaculture are likely to be the most at risk. There have been multiple failures and low yield cohorts of shellfish larvae that have been linked to low pH episodes caused by natural coastal upwellings. Some natural coastal upwellings are known to cause low pH in localised areas, and multiple failures and low yields of shellfish larvae have been observed in these low pH environments. These events powerfully demonstrate the impacts of a low pH future on this valuable industry. This strongly suggests that global production of this sector is likely to decrease^{vii}

Example 2: Coral reefs

Reef-building corals have been shown to have a significantly reduced ability to produce their skeletons as ocean acidification increases^{viii}. For example, it has been observed that ocean acidification compromises the successful fertilization, larval settlement and survivorship of Elkhorn coral, an endangered species^{ix}. These results point to potential catastrophe for many coral reefs as ocean acidification continues to rise, compromising the long-term viability of these ecosystems and impacting the millions of species and people that depend on these habitats.

¹ It is estimated that around 50 million Gigatonnes (Gt) of carbon are contained within limestones and other minerals in the Earth's crust. A further 50,000 Gt of carbon is estimated to be contained in several mobile stores including within the atmosphere as CO₂

Addition of alkalis agent as a cure

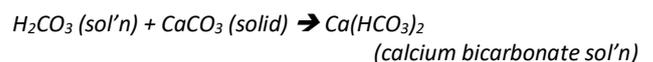
The future of our oceans does not have to be so bleak. A cure may be at hand.

In the long term, the threat of ocean acidification can only be abated through the reduction of CO₂ in the atmosphere. However, recent studies suggest that even if we could achieve significant cuts in CO₂ emissions today, this is unlikely to be enough to prevent the severe impacts of ocean acidification forecast for the next few decades^x. Therefore, rapid removal of CO₂ from the oceans by other means is likely to be necessary to minimise the damage.

The world does this naturally by adding alkalis agents, calcium bicarbonate, and to a lesser extent magnesium bicarbonate, to the oceans.

These bicarbonates create a natural buffer solution which ensures that the pH of the oceans stays near a constant value when (relatively) small amounts of an acid are added, such as when carbon dioxide dissolves in the ocean. Bicarbonates are already present in the oceans in exceptionally large quantities⁽¹⁾ and buffer the ocean acidity at a pH of around 8 ensuring an environment in which marine life can thrive.

In this natural process small amounts of atmospheric CO₂ dissolve in raindrops in the atmosphere forming a very weak carbonic acid solution. Where the acidic rain falls on limestone rocks it reacts to form calcium bicarbonate solution, as follows:



On a geological timescale this process will naturally return the CO₂ balance to the world. Unfortunately, the process is too slow for mankind.

Scientific studies have attempted to model how effective the addition of artificial alkalis agents to the ocean, a process termed artificial ocean alkalisation (AOA), may be in both reducing atmospheric CO₂ and maintaining the pre-industrial level of pH in the oceans. These studies have found AOA can reduce both the rate and magnitude of global warming, whilst simultaneously addressing ocean acidification^{xi}.

Simulations examining the addition of alkaline materials, such as olivine^{xii} and calcium hydroxide^{xiii} have

and methane; in the oceans as carbonates, bicarbonates, and dissolved CO₂; on land within soils and plants; and within fossil fuels below the ground. Of this 50,000 Gt of mobile carbon around 75% of it is present as bicarbonates in the oceans.



Herculean Climate Solutions

A thousand ways to do a million tonnes

demonstrated that the addition of such materials to the oceans can be used to achieve these goals. However, there are several adverse factors associated with the addition of these particular minerals such as high costs, additional CO₂ emissions associated with mining and the impacts of oversaturation of the environment.

There is another way

Another approach is to use the natural absorption pathway of CO₂ through limestone weathering. Instead of adding minerals to seawater to remove CO₂ from the atmosphere it is possible to bring CO₂ waste streams (e.g. from power or cement plants, and even shipping emissions²) directly into contact with seawater and limestone to facilitate the dissolution of the mineral and then conversion by reaction with CO₂ to form a calcium bicarbonate solution. This approach has the benefit of directly removing CO₂ at source, with the beneficial side effects of adding an alkalisng agent to seawater helping to both reduce the impacts of ocean acidification and facilitate the natural cycle of removal of atmospheric CO₂ by seawater^{xiv}.

In the case of shipping, their CO₂ emissions could be treated in this way, converting it to calcium bicarbonate solution on board. These emissions would be regulated by MARPOL. Annex VI of the MARPOL regulations sets limits on sulphur oxides (SO_x) and nitrogen oxides (NO_x) emissions from ship exhausts. It covers mandatory technical and operational energy efficiency measures aimed at reducing greenhouse gas emissions from ships. We anticipate that the use of calcium bicarbonate to reduce or eliminate gaseous CO₂ emissions will be regulated under this Annex VI.



Figure 2 - Limestone cliffs, Dover, UK

² This would require ships to carry substantial quantities of limestone on board to react with the CO₂.

Open-loop scrubbers used to remove SO_x form sulphuric acid that lowers the pH of the water. MARPOL regulations mandate that the return flow must have a pH of no less than 6.5. A system that uses limestone to capture the CO₂ emissions would raise the discharge water pH to 8, matching the naturally occurring pH of the oceans, and thereby removing the hazard caused by SO_x scrubber discharges.

There is more than enough limestone

It is estimated that there is between 50 and 500 million Gt of limestone in the earth's crust. The cement industry mines around 5 to 10 Gt annually, of which about 20% is unsuitable for producing cement.



Figure 3 - Limestone mining waste

For example, the shipping industry emits 800 million tonnes/year of CO₂. If it were possible to convert that on board to bicarbonates this consume 1.8 Gt/y of limestone. Much of that quantity could be sourced from the cement industry's discarded limestone.

The ocean can accept the bicarbonate

The oceans contain approximately 37,000 Gt of carbon in the form of bicarbonates today (refer to Figure 4). If all of the shipping industry's 800 million tonnes/year of CO₂ emissions, equivalent to 218 million t/y of carbon, were to be converted to calcium bicarbonate, then the increase in ocean bicarbonates would be a mere 6 ppm/year³.

Bicarbonates are ideally suited for CO₂ sequestration because they form a very long-term, stable liquid store for

³ This refers to the absolute increase in bicarbonate calculated as the new bicarbonate mass added/existing bicarbonate mass in the ocean.



Herculean Climate Solutions

A thousand ways to do a million tonnes

carbon which can reduce greenhouse gas emissions and reduce ocean acidification.

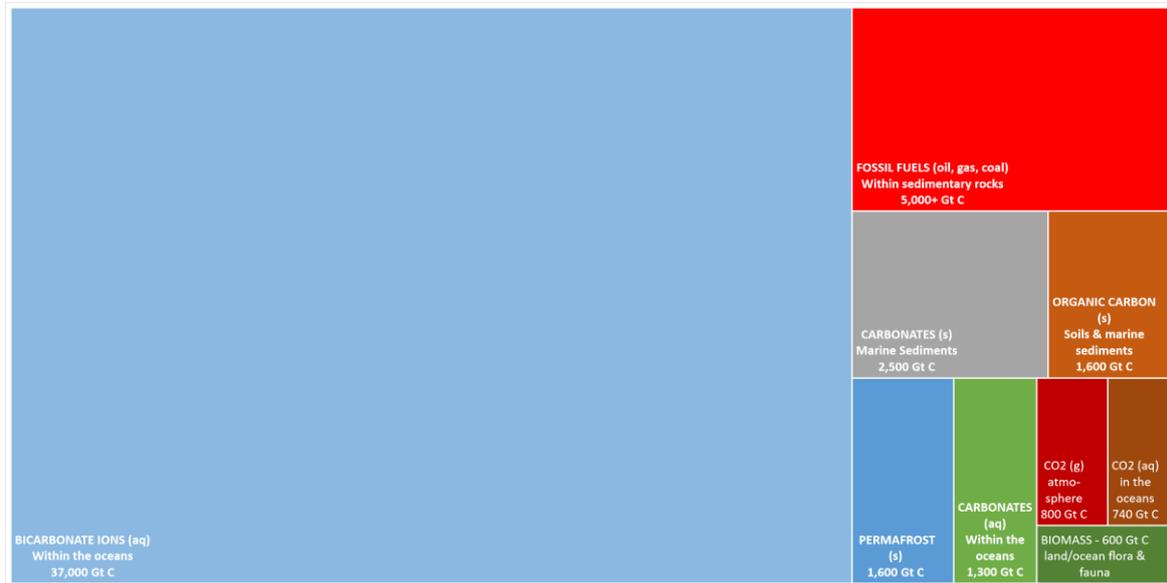


Figure 4 – Carbon locations in the Earth's system. Areas represent the relative amounts of carbon in each store (Gt C).

Bicarbonate - a carbon source for aquatic flora

Bicarbonate (HCO_3^-) comprises about 96% of the dissolved, or mobile, carbon in the oceans, with $\text{CO}_2(\text{aq})$ and soluble carbonate ions (CO_3^{2-}) making up the remaining 4%.

Given the relative abundance of the bicarbonate ion it is no surprise that many aquatic plant species use bicarbonate as the source of their carbon to grow during photosynthesis. One study determined that bicarbonate was the dominant source of carbon even under extreme pH variations^{xv}.

*"C[arbon] acquisition mechanisms are extensively studied and well-known in microalgae (Giordano et al. 2005, Spalding 2008). For example, regardless of the carbon form (CO_2 or HCO_3^-) taken up by the microalga *Chlamydomonas Reinhardtii*, HCO_3^- is the primary form accumulated into the cell"*

Conclusions

The current rate of greenhouse emissions released from anthropogenic sources is driving the global ecosystem towards massive changes at an unprecedented rate. Increased amounts of CO_2 in the atmosphere has resulted in several well-documented impacts on the global climate, together with significant acidification of the oceans.

CO_2 in the atmosphere dissolves in the ocean where it forms carbonic acid which has led to a significant lowering of ocean pH. The impact of ocean acidification on marine organisms and ecosystems continues to raise serious

scientific concern, especially given the current rate of increase. Two particularly vulnerable groups are shellfish and corals. Both use calcium carbonate in the water to create hard structures necessary for their survival. The loss of these groups would be devastating ecologically, socially, and economically.

Mitigation strategies aimed at reducing the amount of CO_2 emitted into the atmosphere are not yet showing any significant signs of success. Even in a best-case scenario where nations were implementing increasingly rapid changes to reduce emissions, this alone will not be enough to prevent the atmospheric and oceanic CO_2 concentrations from reaching catastrophic levels.

A variety of significant and scalable CO_2 removal techniques will be necessary to reduce the amount of CO_2 already in the atmosphere as quickly as possible. Ocean alkalisation is one approach that speeds up the natural rate of atmospheric CO_2 reduction by the addition of an alkalisng agent to the ocean. The use of calcium bicarbonate to do this is very promising, and it has been shown through modelling studies to have the potential to significantly reduce the impacts of both atmospheric CO_2 and ocean acidification.

It is possible to bring CO_2 waste streams (e.g. from power or cement plants) directly into contact with seawater and limestone which would remove CO_2 at source, and create calcium bicarbonate solution. This mildly alkalisng and buffering bicarbonate solution can be released into the



Herculean Climate Solutions

A thousand ways to do a million tonnes

oceans. Release of these man-made streams of this already naturally occurring bicarbonate, already prevalent in the oceans, would help reduce the impacts of ocean acidification and facilitate the natural cycle of removal of atmospheric CO₂ by natural rainwater weathering of limestone.

If all the cement kiln emissions were to be converted to bicarbonate using this method this would sequester the equivalent of around 5 Gt/y of CO₂ (~1.4 Gt C).

This alone would not solve the entire problem of excess atmospheric CO₂ emissions, but it would make a very significant difference.

The case for action now is compelling.

About the Authors

Jerry Joynson is a former oil industry chemical engineer and co-founder of Herculean Climate Solutions.

Jerry, together with HCS co-founder Steve Willis, is seeking to help implement effective, massively scalable solutions to rapidly reduce the level of atmospheric CO₂.

[linkedin.com/in/jerry-joynson/](https://www.linkedin.com/in/jerry-joynson/)

Charlie Dryden is an environmental consultant with a PhD in marine ecology. Charlie's areas of expertise are sustainability, conservation, wildlife, science, environmental impact assessment, and environmental policy.

[linkedin.com/in/charlie-dryden/](https://www.linkedin.com/in/charlie-dryden/)

References

- ⁱ IPCC. *Climate Change 2014 Synthesis Report*. (2014)
- ⁱⁱ Raven, J. *et al.* Ocean acidification due to increasing atmospheric carbon dioxide. *Coral Reefs* 12/05, 68 (2005)
- ⁱⁱⁱ Hönisch, B. *et al.* The geological record of ocean acidification. *Science* (80-.). 335, 1058–1063 (2012)
- ^{iv} Climate Action Tracker, (CAT). *Climate Action Tracker: Warming Projections Global Update 2019*. (2019)
- ^v Riahi, K. *et al.* RCP 8.5—A scenario of comparatively high greenhouse gas emissions. *Climate Change* 109, 33 (2011)
- ^{vi} Hurd, C. L., Lenton, A., Tilbrook, B. & Boyd, P. W. Current understanding and challenges for oceans in a higher-CO₂ world. *Nat. Clim. Chang.* 8, 686–694 (2018).
- ^{vii} Cooley, S. R., Kite-Powell, H. L. & Doney, S. C. Ocean acidification's potential to alter global marine ecosystem services. *Oceanography* 22, 172–181 (2009).
- ^{viii} Guinotte, J. M. & Fabry, V. J. Ocean acidification and its potential effects on marine ecosystems. *Ann. N. Y. Acad. Sci.* 1134, 320–342 (2008).
- ^{ix} Albright, R., Mason, B., Miller, M. & Langdon, C. Ocean acidification compromises recruitment success of the threatened Caribbean coral <Acropora palmata>; *Proc. Natl. Acad. Sci.* 107, 20400 LP – 20404 (2010).
- ^x Gasser, T., Guivarch, C., Tachiiri, K., Jones, C. D. & Ciais, P. Negative emissions physically needed to keep global warming below 2 C. *Nat. Commun.* 6, 1–7 (2015).
- ^{xi} Lenton, A., Matear, R. J., Keller, D. P., Scott, V. & Vaughan, N. E. Assessing carbon dioxide removal through global and regional ocean alkalization under high and low emission pathways. *Earth Syst. Dyn.* 9, 339–357 (2018).
- ^{xii} Köhler, P., Abrams, J. F., Völker, C., Hauck, J. & Wolf-Gladrow, D. A. Geoengineering impact of open ocean dissolution of olivine on atmospheric CO₂, surface ocean pH and marine biology. *Environ. Res. Lett.* 8, 14009 (2013).
- ^{xiii} Henderson, G., Rickaby, R. & Bouman, H. Decreasing atmospheric CO₂ by increasing ocean alkalinity. The ocean dimension: would the concept work and what would be the environmental consequences. *Univ. Oxford, Dep. Earth Sci. James Martin 21st Century Ocean Inst. (not Publ.* 1–20 (2008).
- ^{xiv} Keller, D. P., Feng, E. Y. & Oschlies, A. Potential climate engineering effectiveness and side effects during a high carbon dioxide-emission scenario. *Nat. Commun.* 5, (2014).
- ^{xv} Pamela A. Fernandez, Catriona L. Hurd, Michael Y. Roleda, Bicarbonate uptake via an anion exchange protein is the main mechanism of inorganic carbon acquisition by the giant kelp macrocystis pyrifera (laminariales, phaeophyceae) under variable pH, *Journal of Phycology*, DOI: 10.1111/jpy.12247, (2014).