

Increasing the Alkalinity of the Ocean to Enhance its Capacity to Act as a Carbon Sink and to Counteract the Effect of Ocean Acidification

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Summary

The addition of calcium hydroxide to seawater as a way of sequestering carbon dioxide from the atmosphere was first put forward by Haroon Kheshgi in a paper in *Energy* in 1995. Recently this approach has been re-examined and current indications are that it may be a feasible 'carbon negative' technology and one which can simultaneously tackle ocean acidification.

Positive aspects of the process include:

- The process is an adaptation of a naturally occurring process, which utilises the oceans' capacity to buffer atmospheric carbon dioxide levels
- The process counteracts ocean acidification, so it might actually have a beneficial effect on marine ecosystems
- If done on a large enough scale this process could return atmospheric levels of carbon dioxide back to what they were before the Industrial Revolution

Potential weaknesses of the process include:

- The impact on marine ecosystems of the process is currently unknown
- The alkalinity needs to be mixed across a large part of the ocean
- The process is energy intensive

Work to determine the economics of the process is being finalized and will be presented at the conference.

Introduction

A number of schemes involving altering ocean alkalinity as means to counteract the effects of anthropogenic carbon dioxide emissions have been proposed. (KHESHGI (1995), RAU and CALDERA (1999), RAU et al (2007), HOUSE et al (2007) and HARVEY (2008))

This submission focuses on a method first proposed by Kheshgi. In his paper in *Energy* in 1995 he outlined an approach which involved the calcination of limestone and subsequent addition of hydrated lime (Ca(OH)_2) to seawater. In his conclusion he stated "Increasing ocean alkalinity is a means by which CO_2 might be sequestered from the atmosphere, but not without significant consumption of energy resources and significant cost. Nevertheless, this approach appears to be limited only by the availability of energy."

In the past year, this approach has been re-examined and current indications are that it may be a feasible 'carbon negative' technology and one which can simultaneously tackle ocean acidification. Two reports on this process – one from the Department of Earth Sciences at the University of Oxford (HENDERSON et al, 2008) and the other from Plymouth Marine Laboratory (ALLEN et al, 2008) consider the potential impact on the biology and chemistry of the ocean. The Oxford report concludes "Overall, there appears to be no serious flaw in the oceanic aspect" of the process, but calls for more research.

The Process

The first step of the process involves the calcination of limestone (CaCO_3) into lime (CaO) and carbon dioxide. This first step is counter-intuitive – it generates carbon dioxide and consumes a large amount of energy. However, it is possible to produce lime from limestone in such a way that the carbon dioxide that is generated is pure and thus easy to sequester.

In the second step, the lime is hydrated to form calcium hydroxide. This calcium hydroxide is then added to seawater. This increases ocean alkalinity by two moles of alkalinity per mole of calcium hydroxide added. In turn this shifts the series of equilibria which govern the relative concentration of species of dissolved inorganic carbon in the ocean over to the right (see Fig 1)

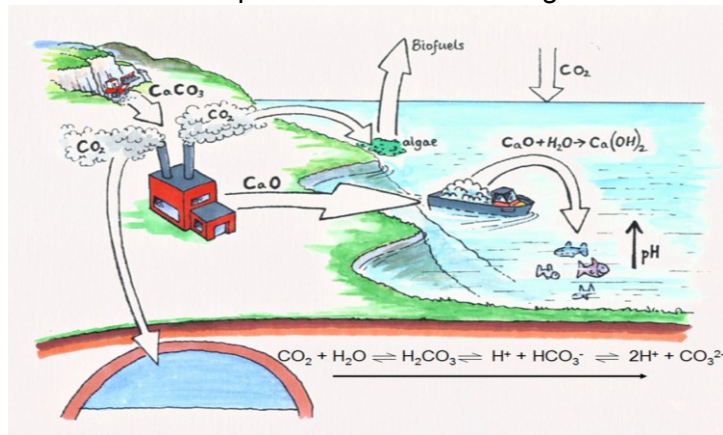


Fig 1: A simplified schematic of the process

This results in a decrease in the amount of carbon dioxide dissolved in the seawater as it is converted into bicarbonate and carbonate ions. Each mol of calcium hydroxide will reduce the amount of carbon dioxide dissolved in the seawater by between 1.6 and 1.8 moles, dependent primarily on the temperature of the seawater (see Fig 2)

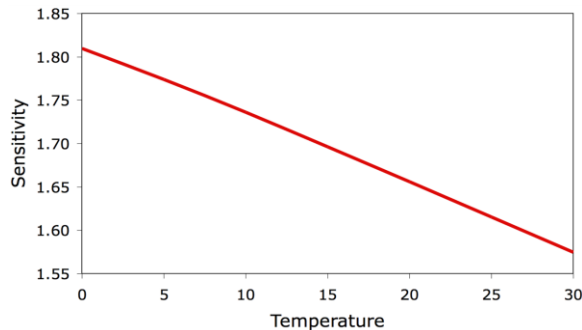


Fig .2: Sensitivity (=mole of atmospheric carbon uptake per mole of added $\text{Ca}(\text{OH})_2$) versus temperature at an atmospheric pCO_2 of 390 ppmV. Calculated using the equilibrium coefficients of DICKSON and MILLERO 1987 and the CO_2Sys programme of LEWIS and WALLACE (1998). (From HENDERSON et al, 2008)

Carbon Footprint and Energy Balance

Fig 3 considers the carbon footprint and energy requirements of the process for a tonne of CaCO_3 . The amounts of carbon dioxide generated in the quarrying and transport of the materials are small in comparison with the energy required for calcination. Each tonne of lime requires 45kg of methane to provide the energy for calcining the lime. In addition a further 15kg of methane is required to generate oxygen sufficient to oxy-combust both amounts of methane for the calcinations and the power generation (this is necessary so that the carbon dioxide generated both from the calcinations and the power generation is pure and thus easy to sequester). Overall the processing of each tonne of limestone is sufficient to sequester between 633 and 724kg of carbon dioxide – or to put it another way, in order to sequester a tonne of carbon dioxide approximately 1.5 tonnes of limestone are required. The energy requirement is approximately 5GJ per tonne of carbon dioxide sequestered.

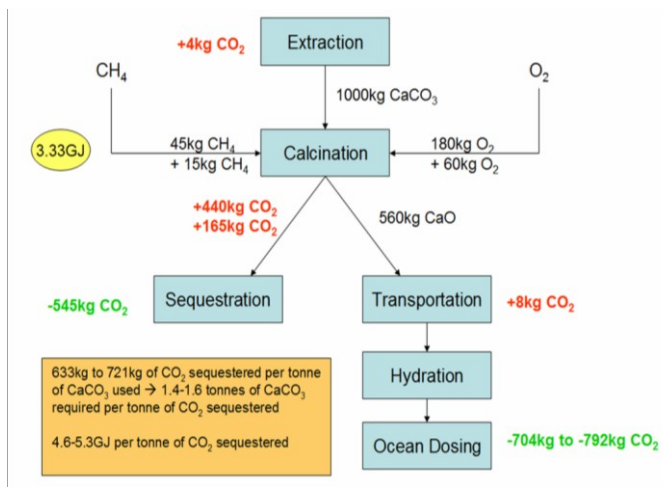


Fig 3: The carbon footprint and energy requirements for a tonne of CaCO₃ used in the process (from KRUGER and HENDERSON, 2008)

There are several things to note about this carbon and energy balance: firstly, it is very high-level and work is currently underway to refine the numbers; secondly, the calculations have been performed using calcium carbonate as the source of alkalinity – if magnesite (MgCO₃) or dolomite (CaMg(CO₃)₂) are used instead the quantity of material and energy required is slightly reduced; and thirdly, the energy requirement is high.

Energy and Location

As noted by Kheshgi, the availability of energy is likely to be the limiting factor for this approach. The cost of energy is extremely location dependent. As shown in Fig 4 the cost of natural gas varies dramatically depending on its location. The wholesale price of natural gas delivered to markets in Europe and North America is typically in the range of USD5-10 per MMBtu – yet in many locations around the world the cost of extracting the gas from the ground can be as little as USD0.05-0.10 per MMBtu. The reason that this very cheap gas is not extracted is that the cost of transporting the gas from these locations to a market exceeds the price that can be achieved in that market – the gas is ‘stranded’ – it has no economic value. If this stranded energy can be utilised in this process then carbon dioxide can be removed from the atmosphere at a relatively low cost.

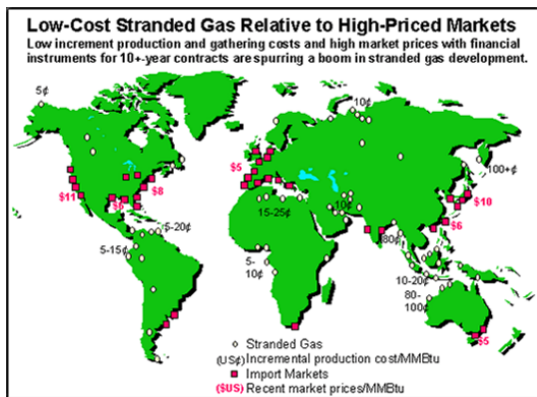


Fig 4: Map showing stranded gas deposits (ZEUS DEVELOPMENT CORP., 2003)

Scale and Availability of Limestone

To sequester 15 billion tonnes of carbon dioxide (equivalent to the approximately 2ppmv of carbon dioxide, by which atmospheric levels of the gas are increasing each year) would require the processing of some 10 km³ of limestone per year. This is equivalent to over twenty times the scale of annual US extraction of limestone, which, whilst large, is not outside the bounds of current quarrying and calcining technology. There are ample quantities of limestone available in

the world – the Nullarbor Plain in Australia contains some 10,000km³ of limestone - and that is just one of many large deposits of limestone available around the world.

Conclusions

The process has the potential to return atmospheric levels of carbon dioxide back to what they were before the Industrial Revolution. Further work needs to be undertaken to ensure that the process does not produce countervailing environmental effects, but the theoretical analysis of these risks is broadly positive.

As previously indicated the economics of the process are being finalized, but indications are that the cost of this carbon negative process will lie somewhere between the current price of credits from the EU ETS (~€15 per tonne CO₂) and the externalities of carbon dioxide as calculated in the Stern Review (~\$85 per tonne CO₂).

Acknowledgements

The author would like to thank Shell for their generous support in providing funding for the research through their GameChanger programme.

The author would also like to thank faculty members and students at the Department of Earth Sciences, the Department of Engineering and at the Smith School of Enterprise and the Environment, all at the University of Oxford for their help and support in conducting the research, especially Prof Gideon Henderson, Prof Sir David King, Dr Adam Candy, Dr Dave Frame, Dr Alex Lubansky, Araz Taeihagh and Michi Tannenberger.

References

- Allen, I., Richardson, K., Robins, D., Nightingale, P., Whitfield, M., Turley, C., Blackford, J., Hattam, C., Lowe, D., Wheeler, G. and Gilbert, J., 2008. An assessment of Questions Posed to Plymouth Marine Laboratory (PML) by Cquestrate Regarding a Concept Process for the Oceanic Sequestration of Carbon Dioxide and the Mitigation of Ocean Acidification. PML Applications Ltd (not published)
- Dickson, A. and Millero F., 1987 A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Res.* **34**, 1733-1743. (Corrigenda. *Deep-Sea Res.* **36**, 983).
- Harvey, L. D. D., 2008. Mitigating the atmospheric CO₂ increase and ocean acidification by adding limestone powder to upwelling regions. *Journal of Geophysical Research-Oceans* **113**.
- Henderson, G., Rickaby, R. and Bouman, H., 2008. Decreasing atmospheric CO₂ by increasing ocean alkalinity. The ocean dimension: would the concept work and what would be the environmental consequences, University of Oxford, Department of Earth Sciences and The James Martin 21st Century Ocean Institute (not published)
- House, K. Z., House, C. H., Schrag, D. P., and Aziz, M. J., 2007. Electrochemical acceleration of chemical weathering as an energetically feasible approach to mitigating anthropogenic climate change. *Environmental Science & Technology* **41**, 8464-8470.
- Kheshgi, H. S., 1995. Sequestering atmospheric carbon dioxide by increasing ocean alkalinity. *Energy* **20**, 915-922.
- Kruger, T. and Henderson, G., 2008. Sequestering carbon dioxide from the atmosphere by enhancing the capacity of the oceans to act as a carbon sink. Presentation to Shell GameChanger (not published)
- Lewis, E. and Wallace, D. W. R., 1998. Program developed for CO₂ system calculations. <http://cdiac.ornl.gov/oceans/co2rprt.html>.
- Rau, G. H. and Caldeira, K., 1999. Enhanced carbonate dissolution: a means of sequestering waste CO₂ as ocean bicarbonate. *Energy Conversion and Management* **40**, 1803-1813.
- Rau, G. H., Knauss, K. G., Langer, W. H., and Caldeira, K., 2007. Reducing energy-related CO₂ emissions using accelerated weathering of limestone. *Energy* **32**, 1471-1477.
- Stern, N., S. Peters, V. Bakhshi, A. Bowen, C. Cameron, S. Catovsky, D. Crane, S. Cruickshank, S. Dietz, N. Edmonson, S.-L. Garbett, L. Hamid, G. Hoffman, D. Ingram, B. Jones, N. Patmore, H. Radcliffe, R. Sathiyarajah, M. Stock, C. Taylor, T. Vernon, H. Wanjie, and D. Zenghelis (2006), *Stern Review: The Economics of Climate Change*, HM Treasury, London.
- Zeus Development Corp., 2003. Stranded Gas Locations and Statistics. World LNG/GTL Review.