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 (CaCO₃) 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).

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).

Carbon Footprint and Energy Balance

Fig 3 considers the carbon footprint and energy requirements of the process for a tonne of CaCO₃. 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.
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 (MgCO$_3$) or dolomite (CaMg(CO$_3$)$_2$) 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.

**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 km$^3$ 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 10,000 km$^3$ 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 CO$_2$) and the externalities of carbon dioxide as calculated in the Stern Review (~$85 per tonne CO$_2$).

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