

June 17, 2009

In response to NAS request for input on geoengineering concepts:

**Geoengineering via Chemical Enhancement of Ocean CO₂ Uptake and Storage
or
Ignore Ocean Chemistry at our Peril**

Scheme type: Non-biological greenhouse gas reduction systems

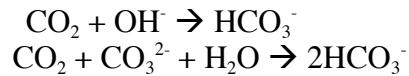
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Summary:

- Excess atmospheric CO₂ is the core cause of anthropogenic climate change AND ocean acidification (the latter, also a NAS concern?). Stabilization if not reduction of atmospheric CO₂, not just climate modification, must therefore be the first priority if we are going to effectively manage earth habitability.
- The ocean: i) is the largest CO₂ absorber on the planet (gross absorption equals about 92 GT C/y = 337 GT CO₂/y), ii) plays the central role in the natural mitigation of excess atmospheric CO₂ (1/3 to 1/2 of cumulative anthropogenic emissions already absorbed by the ocean), and iii) is by far the largest potential reservoir of excess carbon on the earth's surface.
- Therefore, ways of safely enhancing atmospheric C uptake and storage by the ocean must not be ignored, especially since it is not obvious that currently favored land- and atmosphere-base mitigation methods by themselves will be safe, effective, and timely.
- It is well known that the absorption of atmospheric CO₂ can be chemically enhanced by increasing ocean alkalinity and that such reactions convert the CO₂ to relatively stable and benign if not beneficial dissolved mineral bicarbonates and carbonates. This contrasts with adding carbon to the ocean in potentially less stable, environmentally safe forms, e.g. as molecular CO₂, or as organic carbon (marine or land biomass).
- Furthermore, ocean alkalinity modification as reviewed in the following section can also directly moderate ocean acidity (currently being increased by the invasion of excess air CO₂) and directly help preserve or enhance ocean biogeochemistry (e.g., bio calcification). Such benefits are not offered by geoengineering schemes employing albedo manipulation or land-based air CO₂ capture (bio or non-bio).
- The uncertainties in capacity, efficacy, impacts, and/or cost inherent in non-ocean approaches demands that the vast mitigation potential of the ocean be included in our attempts to preserve earth habitability. Further work is clearly needed, however, to accurately determine the effectiveness, safety, cost-benefit, and possible scale of marine chemical approaches in stabilizing or even reducing atmospheric CO₂ concentration.
- Finally, I am underwhelmed by NAS's apparent lack of open and aggressive solicitation for input to the meeting and the panels, given the magnitude and urgency of the problem addressed. I learned about ACC and the meeting on June 16. History is replete with outside-the-box solutions to big problems that were initially missed or actively ignored by insular science establishments. Let's hope that NAS's influential if not important effort here is not another example.

Background

The ocean currently absorbs about 92 GT of C as CO₂ per year and emits about 90 GT C/yr, for a net gain of about 2 GT C/yr, the largest CO₂ sink on earth. This net absorption is driven by an average difference in CO₂ concentration between the atmosphere and the ocean, currently maintained by anthropogenic CO₂ emissions into the atmosphere. However, once in the ocean, little of the absorbed CO₂ remains in molecular form; rather it reacts with the OH⁻ and CO₃²⁻ ions naturally present in seawater to form primarily dissolved bicarbonates:



It is therefore understood that any increase in concentration of OH⁻ and CO₃²⁻ in the ocean (loosely - "alkalinity") increases the ability of seawater to absorb and store CO₂. Thus, Kheshgi (1995) proposed to exploit this feature by purposely adding OH⁻ to the ocean in the form of highly soluble Ca(OH)₂ in order to chemically enhance absorption of atmospheric CO₂. Even considering the carbon intensive nature of Ca(OH)₂ production via limestone calcination, Kheshgi showed that the net effect would still be to produce a net ocean CO₂ sink.

More recently House et al, (2007) proposed using the electrochemical chlor-alkali process to produce NaOH which when added to the ocean would enhance ocean CO₂ absorption, The Cl₂ and H₂ co-generated by the process would be reacted in a fuel cell to produce electricity and the strong acid, HCl. They proposed that this HCl be consumed and neutralized by reacting it with globally abundant silicate minerals to form more environmentally benign chlorides. Use of electricity from abundant, stranded renewable energy sources would create a strong net-CO₂-absorptive process.

Also employing electrochemistry, Rau (2008) demonstrated that seawater pH and OH⁻ could be significantly increased when the anode of a seawater electrolysis cell was encased in porous calcium carbonate. The excess OH⁻ resulting from the dissolution of the carbonate at the acidic anode with the excess calcium ions combining with the hydroxyl ions from the cathode to form Ca(OH)₂. It was proposed that various known methods be employed to promote oxygen over chlorine evolution at the anode, thus allowing the hydrogen produced to further mitigate CO₂ by substituting for fossil transportation fuels or for chemical feed stock. Use of electricity from renewable rather than from fossil energy sources ensures that the process would be very significantly carbon-negative (CO₂ consumed per H₂ produced = 22/1 by mass; CO₂ avoided/H₂ produced = 31/1 by mass; Rau, 2008)

The input of additional C to the ocean is more problematic since the most abundant, naturally occurring carbonate forms are virtually insoluble in surface seawater (CaCO₃, MgCO₃). Nevertheless, such carbonates will dissolve and absorb CO₂ when exposed to water acidified with excess carbon dioxide:



This reaction was proposed as a means of absorbing and mitigating terrestrial point CO₂ sources, using the ocean both as a source of water and as a reservoir for the resulting Ca(HCO₃)₂ produced (Rau and Caldeira, 1999; Rau et al., 2007). Recently, Harvey (2008) suggested that calcium carbonate particles be "rained" into the mildly acidic, carbonate-undersaturated environment of the subsurface ocean to generate excess alkalinity for CO₂ absorption. Both methods essentially are a way of accelerating natural

marine or continental carbonate weathering that will otherwise absorb most excess atmospheric CO₂, but over geologic time scales (Archer et al. 1997).

Ocean Chemistry Modification as Large-Scale Geoengineering

With an objective of absorbing 1 GT C (3.7 GT CO₂) per year, what are the prospects for any of the preceding methods? The following is a preliminary outline of the issues:

Reactants - With seawater, carbonate or silicate minerals, and/or NaCl as starting compounds, the global abundance of these are orders of magnitude greater than needed to mitigate all fossil-derived CO₂, i.e., the capacity of the schemes is not limited by global availability of reactants. Rather, the local availability of these commodities to mitigation process sites can be limiting, but unlike point source CO₂ mitigation, ocean-based air capture schemes have the luxury of being sited anywhere that seawater and reactant availability, energy supplies, and infrastructure are optimized (Keith et al., 2006; House et al. 2007). In the case of water demand, it was estimated that 6000 m³ of seawater per sec would need to be pumped to mitigate 1 GT C/yr via electrolytic NaOH formation, a volume equivalent to that pumped by about 100 sewage treatment plants (House et al. 2007). Rau suggested seawater pumping could be avoided by conducting the electrolysis directly in seawater from stationary or mobile platforms. Assuming >2 tonnes of mineral is required per tonne CO₂ mitigated (House et al., 2007; Harvey, 2008; Rau, 2008), then >7GT/yr of mineral would be needed to consume 1 GT C/yr as CO₂. This is >5X the annual crushed stone production of the US (global statistics not available), indicating a significant increase in global mineral extraction would be needed by such CO₂ mitigation approaches.

Energy - For electrochemical schemes, House et al. (2007) and Rau (2008) reported required energy expenditures ranging from 0.8 to 2.3 MWh of renewable electricity required per tonne of CO₂ mitigated, meaning a global expenditure of 3 - 9 x10³ TWh_e per 1 GT C mitigated/yr. For comparison, global annual electricity production is about 19x10³ TWh_e, but the use of grid electricity for these electrochemistry schemes is not suggested. Rather, stranded renewable energy could be exploited, with the potential ocean energy alone (wind, wave, thermal, solar etc.) amounting to >2 10⁶TWh/yr (Rogner, 2000). Considerably less energy would be required for limestone mining, crushing, transport, and ocean application (Harvey, 2008).

Environmental impacts/benefits - Based on the widespread practice of adding mineral hydroxide or bicarbonate to seawater aquaria to preserve or enhance pet marine biota (e.g., Holmes-Farley, 2002), adding such compounds to the ocean should in principle be similarly safe and beneficial. However, the concentration of these additives would need to be kept below impactful levels, and there could be soluble contaminants in the minerals used that could have negative downstream effects. Also, increased environmental impacts will accompany increased mineral extraction, crushing, transport, etc. Disposal of residual solids could also pose a problem. Increased exploitation of renewable energy for such systems would also likely have environmental consequences. An accurate estimate of impacts versus benefits is obviously needed before any ocean chemical schemes or other alternatives are employed at large scales.

Economics - Most ocean chemistry modification schemes decline to mention economics, no doubt due to the preliminary, conceptual state of this technology. Using a host of assumptions, Rau (2008) calculated a net mitigation cost of \$74/net tonne CO₂ mitigated using the electrochemical limestone splitting approach. Costs in excess of \$100/tonne CO₂ have been calculated for various land-based chemical air CO₂ capture approaches (Keith et al, 2006; Zeman, 2007). Passive addition of limestone to the subsurface ocean (Harvey, 2008) would be much less expensive, but also less immediately effective in influencing atmospheric CO₂ due the time lag in subsurface ocean chemistry influencing atmospheric CO₂. If a mean cost of \$50/tonne CO₂ mitigated is assumed for all ocean chemistry approaches, then mitigation of 3.7 GT of CO₂ per year would require an expenditure of about \$190B or about 0.3% of current global annual GDP.

Needs and next steps - Lab to pilot scale testing is needed to fully evaluate effectiveness, capacity, costs, environmental impacts, and safety. At this early stage, ocean chemistry modification needs to be part of a larger geoengineering roadmap, and its potential cost, impacts, and benefits need to be fairly evaluated and weighed with those of other approaches in the process of allocating available R&D resources.

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