Alternative Strategies for CO$_2$ Removal and Storage

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Why we need to consider alternative CO₂ mitigation strategies

Current technologies and policies are failing to solve problem:
Strategies for decarbonizing fossil energy

- Increase efficiency

- Fuel switching, e.g. coal → nat. gas, biomass

- Pre-emissions removal and sequestration of CO₂
  - CCS – Carbon Capture and Storage - the capture, concentration and underground storage of CO₂ in molecular form
  - Alternative mitigation approaches

- Air CO₂ management
  - air CO₂ removal
  - reduction in natural CO₂ emissions

Rationale: *Buy time until C-neutral energy dominates*
Point-Source CCS Realities

CCS can effectively mitigate CO$_2$ at some scale, but it’s:

- Expensive
  - $50-$150/tonne CO$_2$ avoided
- Energy intensive
  - 10% to >30% energy penalty
  - decapture from absorbant and further concentration and pressurization strongly endothermic
- Difficult to retrofit
- Risky
  - conc CO$_2$ must be contained without leakage
    - underground storage can be problematic
    - must insure against leakage, water contamination, seismic effects, etc.
  - conc CO$_2$ use is limited
16% believe that CCS will measurably affect the global climate by 2050. 
3% would choose CCS as a top priority for large private investment attempting to avoid dangerous levels of global warming.
Alternative strategies:

Examples provided by mitigation of other gaseous pollutants eg. SO$_x$, NO$_x$, NH$_3$, Hg, etc

- All non-CO$_2$ mitigated via reaction to form other compounds, or adsorption.
- No examples of capture, concentration and storage?!
- So what’s is so special about CO$_2$ mitigation?

CO$_2$ is a reactive gas, e.g.:

- CO$_2$ + Amines $\leftrightarrow$ R-CO$_2$  
- CO$_2$ + NH$_3$ + H$_2$O $\leftrightarrow$ NH$_4$HCO$_3$
- CO$_2$ + NaOH $\leftrightarrow$ NaHCO$_3$
- CO$_2$ + MgO $\rightarrow$ MgCO$_3$
- CO$_2$ + MgSiO$_3$ $\rightarrow$ MgCO$_3$ + SiO$_2$
- CO$_2$ + CaCO$_3$ + H$_2$O $\leftrightarrow$ Ca(HCO$_3$)$_2$

$\Delta G^o < 0$ for all of these capture reactions

$\Delta G^o >> 0$ if reversed to recover conc. CO$_2$ and reagent
The Skyonic process:

1) \( \text{NaCl} + \text{H}_2\text{O} + V_{\text{dc}} \rightarrow \text{NaOH} + \text{HCl} \quad \Delta G^\circ = +152 \text{ kJ/mol} \)

2) \( \text{NaOH} + \text{CO}_2 \rightarrow \text{NaHCO}_3 \quad \Delta G^\circ = -83 \text{ kJ/mol} \)

- $value of \text{NaHCO}_3 and \text{HCl} > $cost of \( V_{\text{dc}} \) + $COM
- High energy and $ gross cost, yet more than offset by value of products produced.
- BUT niche application: the demand for products limits global \text{CO}_2 mitigation capacity.
Example #2: Accelerated Weathering of Limestone

The AWL process:

\[ \text{CO}_2 + \text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca(HCO}_3\text{)}_2, \quad \Delta G^\circ = -38 \text{ kJ/mol} \]

Analogous to FGD:

\[ \text{SO}_2 + \text{CaCO}_3 + 0.5\text{O}_2 \rightarrow \text{CO}_2 + \text{CaSO}_4 \]

Using seawater and limestone, the principle costs are:

- limestone: $0 - $25/tonne CO\(_2\)
- seawater: $0 - $3/tonne CO\(_2\)
- COM: $2 - $4/tonne CO\(_2\)

Total potential cost: $2 - $32/tonne CO\(_2\) mitigated

AWL advantages:

- Avoids costly/risky conc. CO$_2$ production and storage
  \[ \text{Ca(HCO}_3\text{)}_{2aq} \text{ addition to the ocean} \]
  - Safely exploits vast ocean storage potential
    \[ \text{Ca(HCO}_3\text{)}_{2aq}, \text{ 4}^{th} \text{ most abundant seawater compound} \]
  - "unlimited market" for counteracting ocean acidification

- Builds on existing wet limestone scrubbing for SO$_x$

- Retrofitable

- Useable in developing world; this is not rocket science!

- Mimics natural global-scale CO$_2$ absorption process - carbonate mineral weathering.
AWL limitations:

- Confined to coastal power plants (but possible wastewater/saline groundwater applications).
- Sources of limestone must be nearby (they usually are).
- Natural gas mitigation preferred over coal to avoid downstream ocean impacts (but let’s explore. Once-through seawater scrubbing of coal flue gas for SO$_x$ control is routinely done in Asia).
- Further, larger scale R&D needed to determine true capacity and cost effectiveness.
Air CO₂ management
Strategy #1 - Air Capture

“...the cost of this [Direct Air Capture] system is estimated to be of the order of $600 or more per metric ton of CO₂....Thus, DAC is not currently an economically viable approach to mitigating climate change.”       Socolow et al. (APS, 2011)

“We estimate that total system costs of an air capture system will be on the order of $1,000 per tonne of CO₂, based on experience with as-built large-scale trace gas removal systems.”       House et al. (PNAS, 2011)

However, these conclusions thankfully do not apply to air capture systems that don’t make concentrated CO₂
Natural "Direct Air Capture": Globally Effective and "Free"
An equivalent of 55% of annual anthropogenic CO$_2$ emissions are removed each year!
Natural "Direct Air Capture" Processes:

Atmospheric CO₂

Photosynthesis
CO₂ + H₂O + photons
---→ R-(CH₂O) + O₂

Ocean uptake
CO₂ + H₂O + CO₃²⁻
---→ 2H⁺ + 2HCO₃⁻

Weathering Reactions

Silicate weathering: CO₂ + Mg/CaSiO₃ ---→ Mg/CaCO₃ + SiO₂

Carbonate weathering: CO₂ + H₂O + CaCO₃ ---→ Ca²⁺ + 2HCO₃⁻
Enhance/Engineer Natural Air Capture - Strategies

- Increase biological uptake e.g.:
  - Ocean/land fertilization
  - Biochar
  - Genetic engineering?

- Increased abiotic/geochemical uptake e.g.:
  - Addition of OH\textsuperscript{-} to ocean (Kheshgi, 1995)
  - Addition of base minerals to ocean (Harvey 2008, Schuiling et al. 2006-2011, Koehler et al. 2013)
  - Electrochemically assisted base mineral weathering, and CO\textsubscript{2} removal (House et al. 2007, Rau 2008, Rau et al. 2013)
  - Additional benefit - ocean alkalinity (mineral bicarbonate) increased and ocean acidification neutralized or offset
Electro-Geochemical, Carbon-Negative H\textsubscript{2} Production

\[ \text{net reaction: } \text{CO}_2 + \text{MgSiO}_3 + \text{H}_2\text{O} + V_{dc} \rightarrow \text{Mg(HCO}_3\text{)}_{2a} + \text{H}_2 + 0.5\text{O}_2 \]

Net cost: \text{\textless} $100/\text{tonne CO}_2 \text{ mitigated}

Net energy cost: \text{\textless} 200 kJ/mol vs \text{\textgreater} 400 kJ/mol for DAC

Rau, ES\&T, 2008
Rau et al., PNAS, 2013
Global C fluxes (fluxes – GT/yr):

Air CO₂ Management: Strategy #2 – Reduce Natural Emissions/Leakage

(Rau, 2014)
Strategies to Decrease Emissions/Leakage

- **On land:**
  - Decrease plant/soil resp via management practices
  - Bury plant plant production
  - Biochar
  - Biomass energy + CCS/AWL, BECCS/BEAWL
  - Genetic engineering?

- **In ocean:**
  - Enhance marine and land organic matter burial
  - Marine BECCS? BEAWL?
  - Reduce ventilation of excess ocean CO$_2$ to air
    - Increase chemical uptake
    - Increase biological uptake
  - Genetic engineering?
Ocean Air Capture vs Ocean CO₂ Removal

- Rather than capture air CO₂, consume excess CO₂ already dissolved in the surface ocean prior to its degassing to the air. (Rau et al., 2013)

Ocean Air Capture:

Surface Ocean + Ca(OH)₂, CaCO₃, MgSiO₃ → Surface Ocean

Ocean Emissions Reduction:

Surface Ocean + Ca(OH)₂, CaCO₃, MgSiO₃ → Surface Ocean

- Does not add carbon to ocean, converts existing dissolved CO₂ to bicarbonate
- Eliminates the slow kinetics and time needed to get air CO₂ into solution
- Reduces “rebound” (ocean→air) effect in inherent in using air capture alone
Conclusions

- Expensively making concentrated CO$_2$ from dilute sources and sequestering from air is not the only way to manage anthropogenic and atmospheric CO$_2$.

- Methods employing geochemistry have the proven capacity to significantly and safely contribute to the solution and need to be exploited.

- Ocean- as well as land-based methods need to be considered.

  - We don't have the luxury of ignoring 70% of the Earth's surface in solving a global problem. Nature doesn't.

- Therefore, both CO$_2$ mitigation policy and R&D must more broadly foster and support options, thus increasing the likelihood of timely, large scale, cost effective and beneficial CO$_2$ management as long as fossil sources dominate energy mix.
Additional Slides ↓
Multi-Millenial Lifetime of Fossil CO2

Archer et al. 2009
AWL example:
McDermott’s limestone CO₂ scrubber concept

CO₂ acidification effects on carbonate saturation and marine biocalcification:

Mod. from McCulloch et al. 2012 Nature Climate Change DOI 101038/NCLIMATE147
Added Benefit of Ocean Alkalinity Addition: Preservation of corals and shellfish

CO₂ + H₂O + CaCO₃s → Ca(HCO₃)₂aq (+ CaCO₃aq), \[ \Omega \propto [Ca^{2+}] \times [CO_3^{2-}] \]

### Diagram

- Low sensitivity
  - Ref. 10
  - Ref. 9
  - Ref. 31
  - Ref. 32 (25 °C)
  - Ref. 2 (+N)
  - Ref. 33
  - Ref. 34
  - Ref. 35
  - Ref. 11

- IpHRAC model (this study)
  - Range
  - Average

- High sensitivity
  - Ref. 36
  - Ref. 32 (28 °C)
  - Ref. 2 (−N)
  - Ref. 6
  - Ref. 37
  - Ref. 38
  - Ref. 35

(Mod. from McCulloch et al. 2012)
CCS alone is not delivering cost-effective CO$_2$ mitigation. Due to the intrinsic energy intensity, and real and perceived risks in transporting and storing supercritical CO$_2$, this situation is unlikely to change any time soon regardless of R&D effort.

Therefore, it's time to more broadly consider what other options might be available.

**Given the urgent need for mitigation, let’s make sure that all options in addition to CCS are considered.**