Chemical Extraction of Carbon Dioxide from Air to Sustain Fossil Energy by Avoiding Climate Change

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Fossil fuels are plentiful, practical & versatile. Their supplies will not limit their use but their environmental impact will.

**Carbon Reservoirs**

This Century Mankind will Overwhelm Nature

Carbon Reservoirs:
- Atmosphere 2000:
  - pH < 0.3
  - 39,000 Gt
- Ocean 1800:
- Plants
- Soil & Detritus
- 20th Century:
  - x4
  - x3
  - x2
  - constant
- Coal
- Oil, Gas, Tars & Shales
- Methane Hydrates

This graph shows the distribution of carbon reservoirs, highlighting the overwhelming emission of CO₂ in the 21st century. The graph indicates that the atmosphere, ocean, plants, soil & detritus, and coal reservoirs are significant contributors to carbon emissions, with the ocean and plants showing a constant increase in CO₂ levels.
The 21st Century Grand Challenge: Enabling Energy and Environmental Security

- Sustain fossil energy use by containing or reducing atmospheric CO₂
- CO₂ capture/sequestration focus is on large point sources (power plants)
- Half of CO₂ emissions from small dispersed sources (transportation, home, small industries) are currently being overlooked
The case for direct capture of CO$_2$ from air (370ppm)

• Concept from Scaling Arguments
  – Minimal land needs relative to renewables, m$^2$/capita for today’s emissions.
  – Addresses all sources including transportation and small dispersed ones.
  – Winds provide free CO$_2$ transport to remote sites advantageous for disposal.
  – Preserves existing infrastructure. Offers economies of scale advantages.
  – *Can turn back the clock:* Restore CO$_2$ to pre-industrial level in worst case.
  – Order of magnitude cost estimates justify further R & D.

• Global transport modeling: Effectiveness & Impact
• High resolution modeling: Optimize collection configurations
• Measurements of CO$_2$ uptake from ambient Los Alamos air
• Ongoing and Future Work

References.
(2) S. M. Elliott et al., Geophysical Research Letters, 2001, 28, 1235-1238
Case for extraction of CO$_2$ from air:
Harness the energy richness of fossil fuels by closing the carbon cycle.

1 m$^3$ of Air

40 moles of gas, 1.16 kg
wind speed 10 m/s

\[ \frac{mv^2}{2} = 60 \text{ J} \]

0.015 moles of CO$_2$
Same as produced by combustion of gasoline to supply 10,000 J of energy

By removing one unit of CO$_2$ from air we can put one unit of CO$_2$ back in by burning fossil fuels and generating energy.
Effective energy density gained by CO\textsubscript{2} Extraction >> Wind > Solar > Biomass

Extraction from Air
Power Equivalent

\[ v = 10\text{m/s} \]
\[ 75000\text{W/m}^2 \]

Wind Energy
\[ v = 10\text{m/s} \]
\[ 600\text{ W/m}^2 \]

Photovoltaics
\[ 200\text{ W/m}^2 \]

Biomass
\[ 3\text{ W/m}^2 \]
Calcium Hydroxide: Proof of concept adsorbent

Air Flow, 370ppm CO₂

Flux = Dr/L  CO₂ "turbulent" diffusion

Ca(OH)₂ solution

CaCO₃ precipitate

CaO + CO₂

0.14g-coal/g-

CaCO₃ + 179 kJ/M

Collect CaCO₃

Recycle CaO

Pure CO₂

Permanent Disposal: Mineral carbonation, Ocean/Geo Injection

Energy to recover captured CO₂ ~ 179 kJ/mole-C is less than half of fossil energy (500, 750, and 900 kJ/mole-C for coal, oil, and CH₄ respectively)

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Order of Magnitude Cost Estimate

~ $25 (< $100) tonne of CO₂

CO₂ Collection Cost by Analogy to Wind Mills: ~ $8/tonne of CO₂

- Windmills cost ~$700/m² of swept area.
- 1 m² sweep area, 3 m/s velocity, 50% efficiency, 3.5 kg of CO₂ per hour.
- Annual capital investment, operation & maintenance ~ 30% of machine cost

CO₂ Calcination Costs by Analogy to Cement: ~ $14/tonne of CO₂

- At 100% efficiency 0.14 tonnes of coal needed per tonne of CO₂. At a price of $20/t, 50% efficiency coal costs would be $5.60 per ton of CO₂
- Annualized cost of the calcination plant ~4 ¥ fuel cost (e.g. Power Plants)
CO₂ Capture from Air with Sequestration

CO₂ Air Capture:
- Chemical, High uptake

Transportation
- Small Dispersed Sources >50% CO₂

370 ppm CO₂

Solid Carbonate Mg

20 ton C/(m² yr)

Pure CO₂

CO₂ Gas: EOR/Saline Aquifer

Coal, Wind, Biomass, or Nuclear Energy

Ocean Systems

CO₂ liq.

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Global CO₂ Sink Model Calculations: Area 400 km x 400 km, Nevada, v(deposition) varied

Can extract ~25 Gt C/yr globally for a typical $v_{dep}$ of ~1 cm s⁻¹. The sink flux of ~Tonnes C m⁻² yr⁻¹ is two orders of magnitude greater than ecosystems.

Refn. NAC Johnston et al Energy Conversion & Management; 2003; 44, 681–689
High resolution CFD modeling of CO$_2$ sink: Size dependence
Does vertical mixing re-supply CO$_2$ to the surface?
Can we engineer surface turbulence to enhance mixing and uptake?

Resolves atmospheric mixing, boundary layer turbulence, and CO$_2$ shadow effects. Flux higher for smaller areas and the coarse global results
CO$_2$ uptake flux as a function of sink size. Due to interference effects flux is higher for smaller sinks and also the coarse global CTM results, numerically validates anticipated $L^{1/2}$ scaling.

Extrapolates to fluxes of $>$ Tonnes C m$^2$ yr$^{-1}$

On small scales relevant to extraction plant design
Measurements of CO$_2$ Uptake from ambient Los Alamos Air

**ACTIVE:** Air bubbled through adsorbent in impinger at 750 ml/mt, CO$_2$ measured continuously before and after the adsorption using non-dispersive IR absorption (LICOR), and at the end point a pH titration yield net CO$_2$ uptake.

**PASSIVE:** Room air interacts with alkaline solution and pH titration of small aliquots yield CO$_2$ uptake as a function of time.
CO$_2$ uptake from ambient air by Ca(OH)$_2$: Mixing effects
Collection increases almost linearly with time.

Closure: LICOR CO₂ & pH titration results agree
Collection efficiency = 53±5%, non-fritted impinger
> 70%, fritted impinger
Carbon dioxide taken up from ambient air bubbled through NaOH Solutions pH dependence

Need pH > 10 or a catalyst at low pH.
Gram scale CO₂ collected by Ca(OH)₂ from Los Alamos air and CaCO₃ analyzed by X-Ray Diffraction, Thermal Gravimetric Analysis and Electron Microscopy

CaCO₃ collected is almost pure (>99%) Calcite and as fine particles due to high turbulence
Passive Uptake Experiments with 1 M NaOH solutions

Observed Uptake ~ Tonnes C m$^2$ yr$^{-1}$. Mixing of liquid promotes uptake by maintaining alkalinity at surface. Atmospheric mixing was relatively slow in the fume hood.
Design ideal CO$_2$ adsorbent for air capture

- Fast kinetics but weak thermodynamics
- High selectivity for CO$_2$ over H$_2$O
- Nonvolatile and environmentally benign
- Aqueous, porous solids, coated beads, hollow membranes
- Large supplies, cost effective, and recyclable
- Target candidate scrubbers
  - Ca(OH)$_2$, Mg(OH)$_2$ with promoters
  - Solid amines and Ionic liquids
  - Zeolites, biomimics, membranes, carbon
  - Temperature, electric, pressure swing
High technology CO₂ adsorbents for open air: Recent Breakthroughs

Polyethyleneimine

Used to stabilize CO₂ in space shuttle using pressure swing adsorption-desorption.

Ionic Liquid Imidazolium Salt

Rapid uptake & weak binding (~80 C)
Viscous with low vapor pressure.
### Competitive adsorbents to save energy for CO$_2$ recovery after capture

<table>
<thead>
<tr>
<th>CO$_2$ Adsorbents</th>
<th>$\Delta H$ (CO$_2$) kJ/mole</th>
<th>$\Delta H$(H$_2$O) kJ/mole</th>
<th>T(CO$_2$) Recovery C</th>
<th>En. Penalty (Coal) Dry!</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)$_2$</td>
<td>179</td>
<td>-</td>
<td>~900</td>
<td>36%</td>
</tr>
<tr>
<td>Prim. Amine</td>
<td>84</td>
<td>47</td>
<td>~300</td>
<td>17%</td>
</tr>
<tr>
<td>Sec. Amine</td>
<td>72</td>
<td>47</td>
<td>~250</td>
<td>14%</td>
</tr>
<tr>
<td>Ter. Amine</td>
<td>48</td>
<td>47</td>
<td>~200</td>
<td>10%</td>
</tr>
<tr>
<td>Polyamine</td>
<td>94</td>
<td>47</td>
<td>350</td>
<td>19%</td>
</tr>
<tr>
<td>Ionic Liquids</td>
<td>Low</td>
<td>?</td>
<td>80-100</td>
<td>&lt;10%</td>
</tr>
</tbody>
</table>

Entropic limit to deliver CO$_2$ from 370ppm to 1 bar is 20 kJ/mole-C
Polyethyeneimine has good uptake kinetics and thermodynamics for CO₂ recovery, low vapor pressure and can be coated on high surface area solids. But solid polyamines will take up water as well!
Natural Analogues: Alkaline lakes in Oregon
CO₂ Uptake Observations with Eddy Flux Tower

pH 8 to 10⁺
LANL’s Portable Eddy Flux Tower

Diurnal Variation in CO₂ in ppm due to Photosynthesis and Respiration at Los Alamos (TA-49)

CO₂ in ppm vs Time

Day
Night

Conclusions

- Air capture of CO$_2$ has the potential to sustain fossil energy use, preserve our infrastructure, and avoid climate change.
- CO$_2$ uptake $> \text{Tonnes C m}^2 \text{ yr}^{-1}$ achievable in passive configurations. Can be increased by engineering mixing.
- Gram amounts CO$_2$ were collected by limewater from Los Alamos air and the product determined to be pure Calcite.
- Atmospheric mixing that re-supplies CO$_2$ to the surface layer and slow-overturning of the solution to maintain alkalinity at the liquid-surface essential for high uptake.
- Polyethyleneimine is an effective CO$_2$ adsorbent which may allow us to reduce the energy penalty significantly.
Ongoing and Future Work

- Investigate **solid amines** for CO$_2$ capture in dry air.
- Outdoor eddy flux CO$_2$ uptake measurements by a *synthetic alkaline pond* and *natural alkaline lake* analogues
- High resolution dispersion modeling to optimize the geometry, configuration, and nature of collection units
- Global & regional modeling to identify location for maximum collection and minimum environmental impact
- Active CO$_2$ extraction design: cooling towers
- Propose pilot project to DOE!
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