Capturing Carbon Dioxide from The Atmosphere: Kinetics, Energetics, and Scaling

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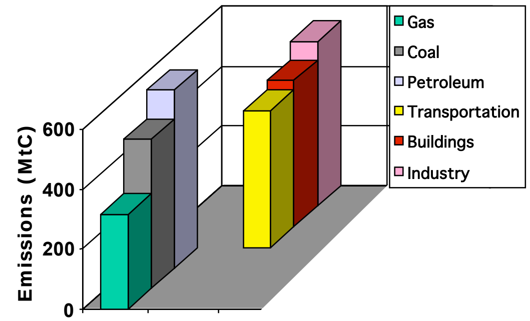
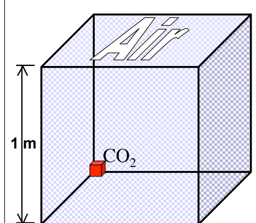
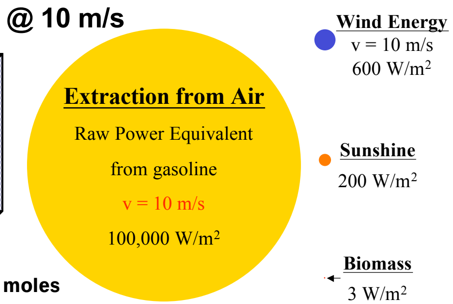
The 21st Century Grand Challenge: Enabling Energy and Environmental Security By Solving the Carbon Problem

> Half of CO_2 emissions are from *small dispersed sources* (transportation, home, small industries)



"Power" from 1m² of area @ 10 m/s





CO_2 in 1 m³ of Air: 0.015 moles

In 1 year, at 370 ppm & 3 m/sec, the air moving through a 1 m² opening carries several times the 20 tons/capita for the US.

0.66 g CO_2/m³
(× 3 m/s × 3.15 × 10⁷ s/yr)

Fossil Energy Density is VERY High

At 370 ppm & 10 m/sec, the CO_2 in air moving through a 1 m² opening allows the generation of several hundred times the energy extracted by a 1 m² windmill.

Order of Magnitude Cost Estimate ~ $25 ton of CO_2

CO_2 Collection Cost by Analogy to Wind Mills: ~ $8/ton of CO_2

- Windmills cost ~$700/m² of swept area.
- 1 m² sweep area, 3 m/s velocity, 50% efficiency, 3.5 kg CO_2 / hour
- Annual loan, operation & maintenance costs ~ 30% of capital cost

CO_2 Calcination Costs by Analogy to Cement: ~ $14/ ton of CO_2

Another estimate of Calcination Costs

- At 100% efficiency 0.14 ton of coal needed per ton of CO_2.
- At a price of $20/t, 70% eff., coal costs are $4 per ton of CO_2
- Annualized cost of the coal power plant ~4 × fuel cost: $16

Issues to Address

1) Energy expenditure for pressurizing CO_2
- 20 kJ/mole minimum to P = 1 atm

2) Sorbent Issues
- Recycling penalty
- Selectivity
- Handling

3) Minimization of active extraction area
- Optimal unit size
- Air remixing
- Downwind low CO_2 concentrations

4) Predictable/efficient air flow
- Wind vs. forced air flow
  - Energy requirements
  - Fraction of air/CO_2 intercepted
- Minimizing system size
- Maximizing CO_2 removal
- Overall optimization

5) Makeup supplies
- Water
- Sorbent

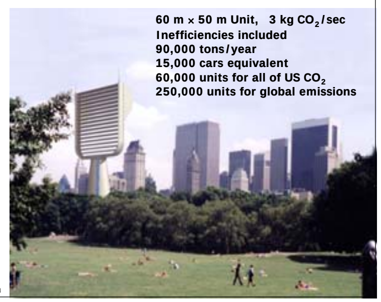


Image courtesy of Stonehaven CCS Canada

Experimental Work

Measurements of CO_2 Uptake from ambient Los Alamos Air

ACTIVE

Air passed thru adsorbent @ 750 ml/min

CO_2 measured continuously before & after by non-dispersive IR absorption (LICOR),

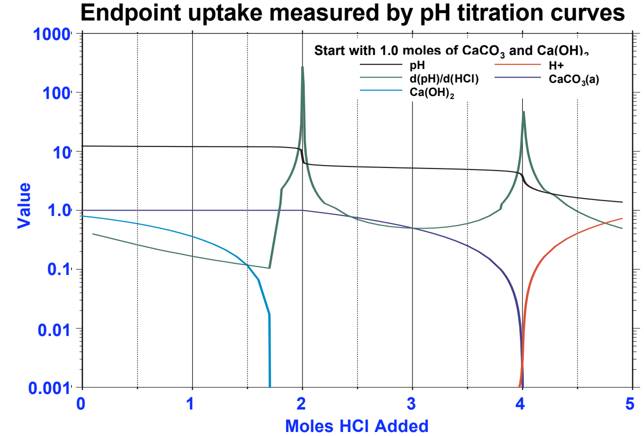
And at the end point by pH titration

PASSIVE

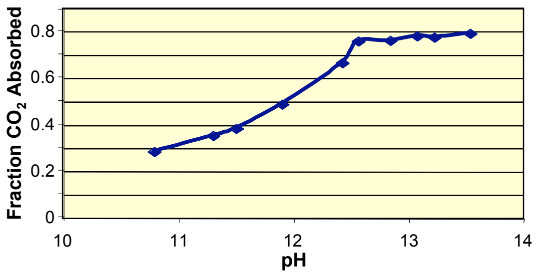
Room air drawn into fume hood interacts with alkaline solution.

pH titration of small aliquots yield CO_2 uptake as a function of time.

Endpoint uptake measured by pH titration curves



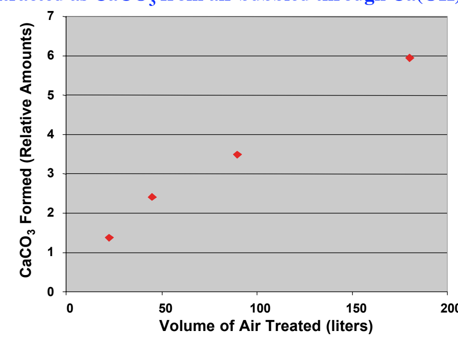
pH dependence for CO_2 uptake from air bubbled through NaOH Solutions



Need pH > 10 or a catalyst at low pH.

Active Uptake Exps.: LICOR CO_2 & pH titration

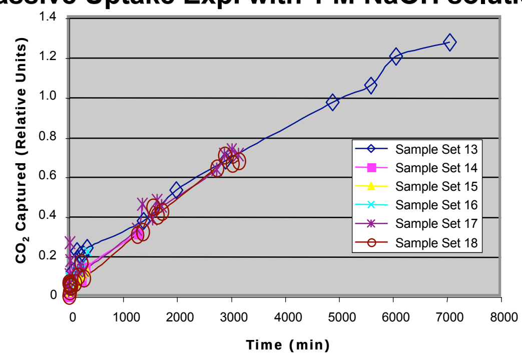
CO_2 extracted as $CaCO_3$ from air bubbled through $Ca(OH)_2$ solution



LICOR CO_2 & pH titration agree; Collection increases ~ linearly with time

Collection eff. = 53±5%(non-fritted impinger); > 70%(fritted impinger)

Passive Uptake Exp. with 1 M NaOH solution



Observed Uptake ~ Ton C / m^2·yr. Slow flow, air mixing in the fume hood.

Mixing of liquid maintains alkalinity at surface.

Design ideal CO_2 adsorbent for air capture

- **Fast kinetics but weak binding**
- **High selectivity for CO_2 over H_2O**
- **Nonvolatile and environmentally benign**
- **Aqueous, porous/coated solids, active 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**

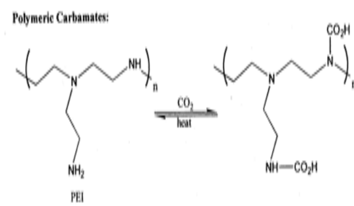
Competitive adsorbents to save energy for CO_2 recovery after capture

CO_2 Adsorbents	ΔH (CO_2) kJ/mole	ΔH(H_2O) kJ/mole	T(CO_2) Recovery	Energy Penalty (Coal) Dry!
$Ca(OH)_2$	179	-	~900	36%
Prim. Amine	84	47	~300	17%
Sec. Amine	72	47	~250	14%
Ter. Amine	48	47	~200	10%
Polyamine	94	47	350	19%
Ionic Liquids	Low	?	80-100	<10%

Entropic limit for CO_2: 370 ppm to 1 bar is 20 kJ/mole-°C
[RT ln (P/P_0); RT ~ 2.5 kJ/mole]

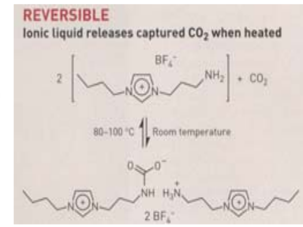
High technology CO_2 adsorbents for open air: Recent Breakthroughs

Polyethyleneimine



Used to stabilize CO_2 in space shuttle using pressure swing adsorption-desorption.

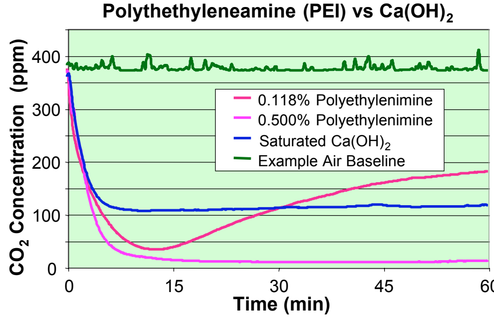
Ionic Liquid Imidazolium Salt



Rapid uptake & weak binding (~80 °C) reversal temperature

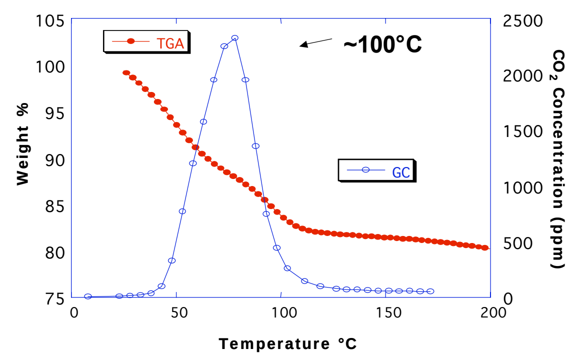
Viscous with low vapor pressure

CO_2 uptake by Solutions in a Fritted Impinger: Polythethyleneamine (PEI) vs $Ca(OH)_2$

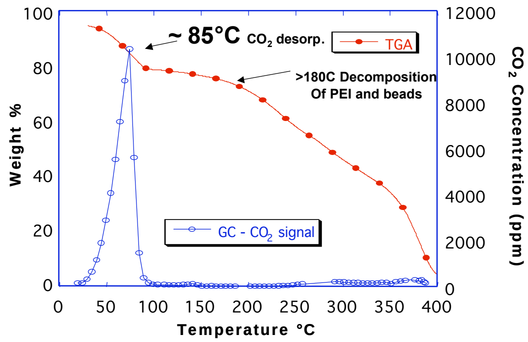


PEI has good uptake kinetics & thermodynamics for CO_2 recovery, low vapor pressure and can be coated on high surface area solids, BUT solid polyamines will take up water as well!

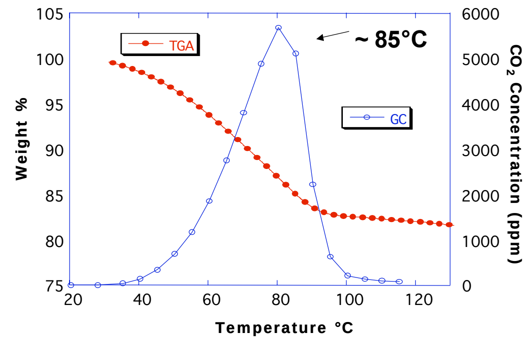
TGA and CO_2 desorption (XPEI)

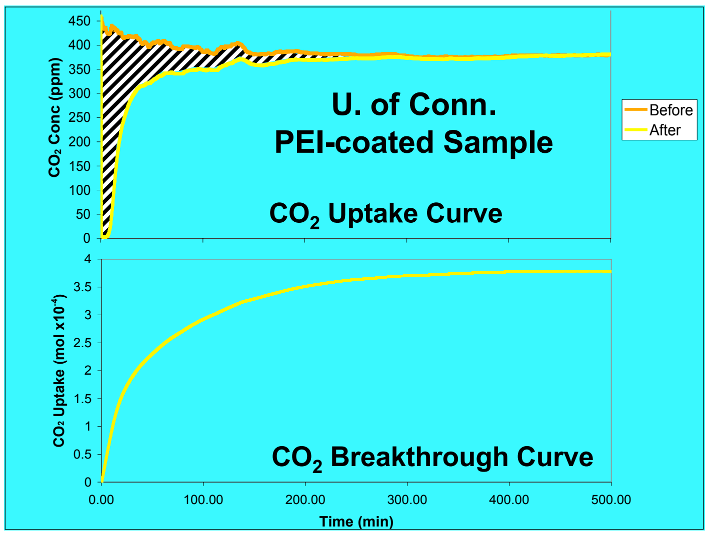


TGA and CO_2 desorption (PEI-100)



TGA and CO_2 desorption (PEI-275)





Solid Polyethylinimine (PEI) Results

- **PEI coated beads (UConn) Sorbent**
  - Modified for T-swing adsorption process
  - Capacity: 0.08-0.15 g CO_2/g-sorbent
  - Scales with surface area: 0.06g CO_2/g-sorbent
  - Water uptake 0.1-0.5 g H_2O/g-sorbent
  - Regeneration temperature: 85°C
- **Cross-linked polyethylenimine (XPEI)**
  - Lower hydrophilicity (insoluble)
  - Capacity: 0.1-0.5 g CO_2/g XPEI
  - Water uptake 0.1-0.3 g H_2O/g-sorbent
  - Regeneration temperature: 100°C

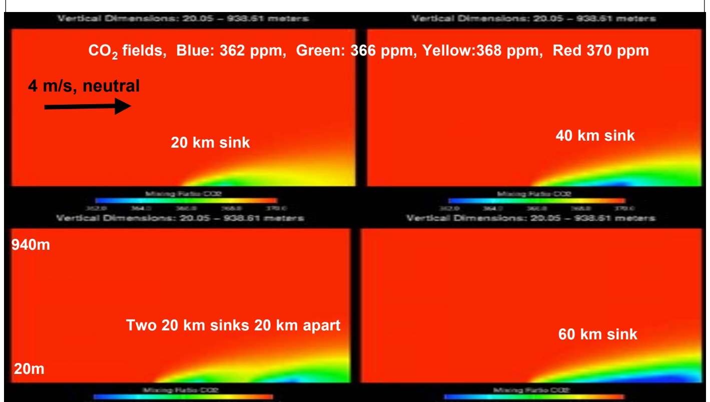
Ongoing and Future Work

- Examine more ***solid amines*** for CO_2 capture in dry air.
- Construct/operate 1 m^2 unit.
- Continue study of collector unit design.
- High resolution dispersion modeling to optimize the geometry, configuration, and nature of collection units.
- Examine participation in possible pilot project by Kelly Wright & Assoc., Tucson, AZ.

Design Topics

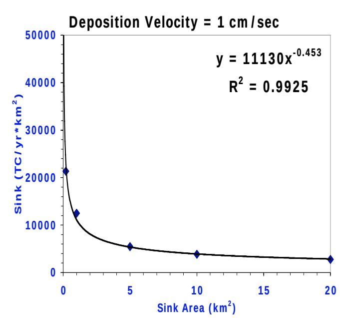
High resolution CFD modeling of CO_2 sink: Size dependence

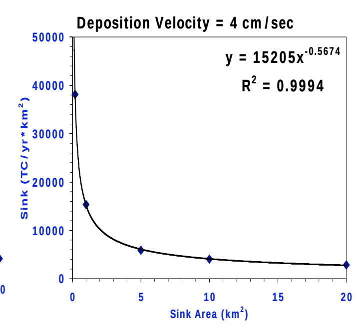
Shadow effects & vertical mixing to re-supply CO_2 to the surface



CO_2 uptake flux as a function of sink size

Due to shadow effects, flux is higher for smaller sinks
Models numerically validates anticipated $L^{1/2}$ scaling.





Extraction: Natural Air Flow (~25%)

- CO_2 removal equivalent to momentum removal
- For 50% CO_2 removal, drop air velocity in 1/2
- 1/2 the surrounding velocity * 1/2 the CO_2 in air

- Gives 1/4 of CO_2 in surrounding external air flow

Energy for Moving Air: (Insignificant)

- CO_2 370 ppm = 0.015 moles CO^2/m^3 air
- Air: 66.67 m^3 = 1 mole CO_2, ρ_{air} = 1.225 kg/m^3 air
- 1 mole CO_2 = 82 kg air

- CO_2 removal equivalent to momentum removal
- For 100% CO_2 removal effectively stop air
- Accelerate air from stop to v, stop it, reaccelerate it
- Total energy added = 2 * 1/2 mv^2 = mv^2
- v = 3 m/sec: Energy to move air for 1 mole CO_2 = 735 J
- Gasoline ~ 650,000 J/mole C

Absorber: Wet vs. Dry

WET	DRY
+ Liquids easy to move	+ Likely lower calcination energy
+ Precipitates easy to collect	– Solids handling / Calcination
– Lots of dead mass	– Diffusion into solids
– Evaporation (Loss of water)	– Active solid mass handling
– Deposits / Scaling	– Water Absorption into sorbent

Scales: Capturing the CO_2

- Molecular diff. coef. of CO_2 in air: $D = 1.39 \times 10^{-5}\ m^2/s$
- Mass flux to absorbing surface: $N = D \text{ grad } \rho \cong D\, \rho_{CO_2} / d$
- d is the transport distance (normal distance to wall)
- ρ_{CO_2} = 370 ppm * 1.225 kg/m^3 * (44/29) (perfect absorber)
- Have box: height: h; length: $L = vt$; 1/2 width: d (center-wall)
- v = air speed, t = time to remove all CO_2 from box
- CO_2 mass in box = $Vol^*\rho_{CO_2} = hL2d\rho_{CO_2} = hvt2d\rho_{CO_2}$
- Mass flow to 2 walls = $hL2N = hvt2N = hvt2D\, \rho_{CO_2}/d$
- By box end the 2 are equal: $d^2 = Dt$ or $L = vd^2/D$

- For v = 3 m/s, d = 2 mm (4 mm absorber spacing); L = 86 cm
- For v = 3 m/s, d = 1 mm (2 mm absorber spacing); L = 21 cm

System can be quite short