9. CO$_2$-Removal – “Direct Air Capture”
Lecture Program of „Climate Engineering“

Part 1: Introduction to the Climate System (4 sessions)
1. Introduction and scope of the lecture
2. The Climate System – Radiation Balance
3. Elements of the Climate System - Greenhouse Gases, Clouds, Aerosol
4. Dynamics of the Climate System - Sensitivity, Predictions

Part 2: Climate Engineering Methods - Solar Radiation Management, SRM
1. SRM – Reflectors in space
2. SRM – Aerosol in the Stratosphere
3. SRM – Cloud Whitening
4. SRM – Anything else

Part 3: Climate Engineering Methods – Carbon Dioxide Removal, CDR
1. Direct CO$_2$ removal (CDR) from air
2. Alkalinity to the ocean (enhanced weathering)
3. Ocean fertilization
4. Removal of other greenhouse gases

Part 4: CE – Effectiveness, Side Effects (3 sessions)
1. Comparison of Techniques, characterisation of side effects
2. Other parameters than temperature
3. Summary
Literature

Socolow, R. et al. (2011), Direct Air Capture of CO2 with Chemicals, A Technology Assessment for the APS Panel on Public Affairs, June 1, 2011.
Contents of Today's Lecture

- Taxonomy of CDR Methods
- The basic physics of removing CO$_2$ from air
- The basic chemistry of removing CO$_2$ from air
- Where to store the removed CO$_2$?
- Some „practical“ suggestions
- Summary
Direct Air Capture (DAC) usually refers to industrial direct capture of CO$_2$ to make a CO$_2$ product. (another taxonomy from Stephens and Keith, 2008)

Almost every carbon dioxide removal method by definition directly captures CO$_2$ from the atmosphere, and thus they may all be thought of as some form of direct capture of CO$_2$ from the air.

DAC is sometimes used to refer only to centralized chemical-industrial facilities that remove CO$_2$ form the atmosphere (rather than to nearly all carbon dioxide removal (CDR) approaches).

Important dimensions to consider are:
1. Biological (plants) vs. chemical approaches
2. Centralized vs. distributed approaches
3. Is the carbon stored as oxidized (molecular CO$_2$, HCO$_3^-$, etc) or re-used (organic carbon, black carbon)?

These 3 choices define 8 categories, examples:
- Centralized industrialized direct air capture is investigating (1) chemical approaches that are (2) centralized and (3) store the carbon as molecular CO$_2$ [oxidized].
- Ocean fertilization is (1) biological approach that is (2) distributed and (3) ultimately stores C as HCO$_3^-$ [oxidized] carbon in the deep sea.
- Biochar is a (1) biological approach to capture that is (2) distributed and (3) stores C as reduced carbon.
- Liming the ocean is a (1) chemical approach that is (2) distributed over a wide area and (3) stores C as oxidized carbon (HCO$_3^-$).
- Afforestation is a (1) biological approach that is (2) distributed over a wide area and (3) stores the carbon as reduced [organic] carbon.

Which of these 8 basic categories are populated? Do we have clear unambiguous terms to refer to each of the populated categories? There appear to be no feasible centralized biological approaches because photosynthesis by its very nature involves large areas to capture enough sunlight to be quantitatively important.
CO$_2$ – Removal from the Atmosphere

“Synthetic Tree”

Art: Stonehaven CCS, Montreal, from Klaus Lackner, Columbia University
Net Zero Carbon Economy

CO₂ extraction from air

CO₂ from concentrated sources

Permanent & safe disposal

From: Klaus Lackner

LENFEST CENTER FOR SUSTAINABLE ENERGY
Initially Air Capture is Tied to CO₂ - Storage

**CARBON DIOXIDE CAPTURE AND STORAGE**

Summary for Policymakers and Technical Summary

Intergovernmental Panel on Climate Change

\[
\text{Mg}_3\text{Si}_2\text{O}_5\text{(OH)}_4 + 3\text{CO}_2(g) \rightarrow 3\text{MgCO}_3 + 2\text{SiO}_2 + 2\text{H}_2\text{O(l)} + 63\text{kJ/mol CO}_2
\]
Air Capture

• Takes CO₂ from the atmosphere to offset CO₂ emissions
• Can compensate for all CO₂ emissions
• Particularly interesting to offset emission from distributed, small and mobile sources (e.g. cars, aircraft)
• Hydrocarbon fuels could still be used
Natural Air Extraction

• **Ocean Uptake**
  
  30% of anthropogenic CO$_2$ emission

• **Trees**

  Biomass absorbs 100 GtC annually
  
  Capture cost ~ $27/ton of CO$_2$
  
  Land demand too large

  Leaves are underutilized for CO$_2$ extraction

From: Klaus Lackner
Chemical Capture

From Appell 2013
Air Capture: Collection & Regeneration

“Synthetic Tree”

From: Klaus Lackner

Courtesy GRT
„Energy Contents“ of Air

Combustion, e.g.:
\[
\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \quad \Delta H^\circ = -890.5 \text{ kJ/mol}
\]

(This corresponds to 20.2 kJ/g of CO\(_2\))

1 m\(^3\) air at 293K (=41.6 moles) contains (at 400 ppm)
\[
n=0.0166 \text{ moles of CO}_2
\]

\[
E = \Delta H^\circ \cdot n \approx 14.8 \text{ kJ} \quad \text{(a bit less, if gasoline or coal was burned)}
\]

→ If we remove all CO\(_2\) from a m\(^3\) of air, we offset the energy release from combustion of fossil fuels of about 10-15 kJ (approx. 3-4 Wh)

→ Energy consumption should for scrubbing 1 m\(^3\) should be << 10 kJ!
Challenge: CO$_2$ in Air is Dilute

- Energetics limits options
  - Work done on air must be small!
    - compared to heat content of carbon
    - 10 kJ/m$^3$ of air (equiv. to cooling 1 m$^3$ of air ($\approx$41.6 mol) by $\approx$8K)
- No heating, no compression, no cooling
- Low velocity 10 m/s (60 J/m$^3$)

Solution: Sorbents remove CO$_2$ from air flow

From: Klaus Lackner
Minimum Energy Needed to Extract CO$_2$ from Air

Entropy relative to a component with mixing ratio x for one mole of mixture:

$$\Delta S = -R \cdot \left[ x \ln x + (1-x) \cdot \ln (1-x) \right] = \frac{\Delta W}{T} \quad x = \text{(molar) mixing ratio of species to be removed from mixture}$$

$$\approx -R \cdot x \ln x$$

$$R \approx 8.31 \text{ Jmol}^{-1}\text{K}^{-1} = \text{gas constant}$$

Atm. CO$_2$: $x \approx 4 \cdot 10^{-4}$ (400ppm) $\Rightarrow \Delta S \approx 0.026 \text{ Jmol}^{-1}\text{K}^{-1}$ for 1 mole of air

Entropy relative to a component for one mole of component:

$$\Delta S_x = -\frac{R}{x} \cdot \left[ x \ln x + (1-x) \cdot \ln (1-x) \right] = \frac{\Delta W_x}{T} \approx -R \cdot \ln x$$

Minimum energy required to separate 1 mole of CO$_2$ at $x_{CO2} = 4 \cdot 10^{-4}$:

$$\Delta W_x = \Delta S_x \cdot T = -\frac{RT}{x} \cdot \left[ x \ln x + (1-x) \cdot \ln (1-x) \right] \approx -RT \cdot \ln x$$

for $x \approx 4 \cdot 10^{-4}$ (400ppm) and 300K $\Rightarrow \ln(4 \cdot 10^{-4}) \approx -7.824$

$\Rightarrow \Delta W_{CO2} \approx 19.5 \text{ kJ/mol of CO}_2$ extracted (or 320J for all CO$_2$ of 1 m$^3$ air)

$\Rightarrow \approx 443 \text{ kJ/kg of CO}_2$ extracted ($M_{CO2} = 0.044 \text{ Kg/mole}$)

For comparison: $\Delta H(\text{coal}) \approx 11 \text{ MJ/(kg CO}_2$), $\Delta H(\text{CH}_4) \approx 20 \text{ MJ/(kg CO}_2$),
CO\textsubscript{2} Capture from Air

1 m\textsuperscript{3} of Air

\[ \approx 40 \text{ moles of gas, } 1.16 \text{ kg wind speed } 6 \text{ m/s:} \]

\[ E_{\text{kin}} = \frac{mv^2}{2} \approx 20 \text{ J} \]

0.0166 moles of CO\textsubscript{2} (0.73 g) produced by \( \approx 11 \text{ kJ} \) of gasoline

Minimum energy to remove: 320 J

From: Klaus Lackner
How much Wind?

Area that carries 0.73g of CO$_2$ per second (22 tons/year)  

(6m/sec)

0.2 m$^2$ for CO$_2$

Area that carries 0.73g of CO$_2$ per second (22 tons/year)

80 m$^2$  

for Wind Energy

50 cents/ton of CO$_2$ for contacting

From: Klaus Lackner
Ca(OH)$_2$ as an absorbent

Air Flow

CO$_2$ diffusion

Ca(OH)$_2$ solution

CaCO$_3$ precipitate

CO$_2$ mass transfer is limited by diffusion in air boundary layer

From: Klaus Lackner

LENFEST CENTER FOR SUSTAINABLE ENERGY
A First Attempt

Ion exchanger:
\[ \text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightarrow 2\text{Na(OH)} + \text{CaCO}_3 \]

Calciner:
\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]

Air contactor:
\[ 2\text{Na(OH)} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 \]

From: Klaus Lackner
(1) \( 2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \) \( \Delta \text{H}^0 = -171.8 \text{ kJ/mol} \)

(2) \( \text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightarrow 2\text{NaOH} + \text{CaCO}_3 \) \( \Delta \text{H}^0 = 57.1 \text{ kJ/mol} \)

(3) \( \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \) \( \Delta \text{H}^0 \) \( \text{kJ/mol} \)

(4) \( \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \) \( \Delta \text{H}^0 = -64.5 \text{ kJ/mol} \)

(5) \( \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \) \( \Delta \text{H}^0 = -890.5 \text{ kJ/mol} \)

(6) \( \text{H}_2\text{O} (l) \rightarrow \text{H}_2\text{O} (g) \) \( \Delta \text{H}^0 = 41.0 \text{ kJ/mol} \)

Source: Frank Zeman
Optimum Binding Energy?

Strong CO$_2$ - sorbent bond:
- Can remove all CO$_2$ (low residual concentration)
- Much energy needed to extract CO$_2$ from sorbent
  (= regeneration of sorbent)

Weak CO$_2$ - sorbent bond:
- Can only remove part of CO$_2$ (high residual concentration)
- Little energy needed to extract CO$_2$ from sorbent
  (easy regeneration of sorbent)

→ Search for Optimum
From: Klaus Lackner

Remember: Minimum energy required (at 400ppm, 300K)

$$\Delta W_{CO_2} \approx 19.5 \text{ kJ/mol of CO}_2$$
Cost of Contacting the Air

Cost of CO\textsubscript{2} from Air
Cost of CO$_2$ from Air
(rescaled)

Unit Cost

Fixed Cost

$1/\rho$

From: Klaus Lackner
Sketching out a design

Compare to windmills in 1960

Cost goal:

$30/ton of CO$_2$

Motivated by cost of fuel, oxygen, electricity, raw materials

From: Klaus Lackner
Convection Tower for CO₂-Removal

15 km³/day of air

Lackner et al. 2011

9,500t of CO₂ pass through the tower daily.

Half of it could be collected

450 MWₑ

NGCC plant

As electricity producer the tower generates 3-4 MWₑ

15 km³/day of air

Cross section 10,000 m²

Air fall velocity ~15m/s

Water sprayed into the air at the top of the tower cools the air and generates a downdraft.
Air Extraction can compensate for CO₂ emissions anywhere

2NaOH + CO₂ → Na₂CO₃

Art Courtesy Stonehaven CCS, Montreal
Small factory produced units can be packed into a standard 40 foot shipping container.

From: Klaus Lackner
From: Klaus Lackner
Collection

- Natural wind carries CO\textsubscript{2} to collector
- CO\textsubscript{2} binds to surface on ion exchange sorbent materials

Regeneration

- CO\textsubscript{2} is recovered with:
  - liquid water wash
  - or carbonate solution wash
  - or low-temperature water vapor
  - plus optional low grade heat
- Regenerated sorbent is reused many times over

From: Klaus Lackner

Courtesy GRT
Options for Regeneration

• Pressure Swing
• Thermal Swing
• Water Swing
  Liquid water – wet water swing
  Water vapor – humidity swing
• Carbonate wash is a water swing
  With CO$_2$ transfer
  Salt splitter for CO$_2$ recovery

From: Klaus Lackner
Cost per ton CO$_2$ captured from the atmosphere: 94 - 232 $.

Keith et al. (2018), A Process for Capturing CO$_2$ from the Atmosphere, Joule, https://doi.org/10.1016/j.joule.2018.05.006
David Keith and his carbon-capture machine.
Schematic representations of a facility for capturing 1 MtCO$_2$/yr. It consists of five structures, each 10 meters high and 1 km long, and could collect 1 MtCO$_2$/yr if air passed through at 2 m/s and 50% of the CO$_2$ were collected. The structures are spaced 250 meters apart, and the footprint of the system is roughly 1.5 km$^2$. Approximately six of these systems would be required to compensate for the emissions of a 1 GW coal plant. Buildings not to scale.
Removing CO$_2$ from the Ocean


In principle not much difference in the effect of removing CO$_2$ from air (DAC) and removing CO$_2$ from ocean water, as long as CO$_2$ is extracted from surface ocean water. Advantage of removing CO$_2$ from ocean water: Higher volumetric density of CO$_2$ (DIC) in ocean water. Volume specific CO$_2$ concentration in sea water ≈120 times that of air.

→ 120-times less volume has to be processed.

However: water is much denser than air (which requires more power for pumping it), Mass specific CO$_2$ conc. is only about 20% of that of air (at sea level pressure).

Neither pump air nor water to remove CO$_2$.

Rather rely on natural flow of the media (i.e. wind or ocean currents, respectively).

→ Compare the product of CO$_2$ volume specific concentration and typical velocities in air/water. Typical velocities in the ocean are 1-2 orders of magnitude slower than in the atmosphere,

→ This largely offsets the higher volume specific CO$_2$ density in ocean water.

Another problem is the energy consumption:

Eisaman et al. 2012 requires 242 kJ/mol to remove one mole of CO$_2$ from the ocean

→ 27% (or more) of the energy gained by burning fossil fuel.

Summary: The scheme does not appear to be a very bad idea, however advantages are no entirely obvious (although they may be there). Also, it may be possible to improve the technique.
Where to Store the Captured CO$_2$??

- Ocean
- Somewhere Underground
- Old oil/gas fields
Air Capture Supports Underground Injection

• **Safety Valve**
  Unpredicted changes in the underground reservoir should trigger a safe release of CO₂
  Compensated for by air capture

• **Carbon Accounting**
  Losses can be made up by air capture
  Air capture can introduce C-14 tracking

From: Klaus Lackner
A CO$_2$-Injection Experiment

1600 t of CO$_2$ injected at 1540 m depth in southeast Texas

Seismic Tomography Image

Change in CO$_2$-conc. after injection

From: DePaolo and Orr 2008
The diagram illustrates the relationship between fuel types and their combustion products. On the diagram:

- **Oxidizer** is represented at the top, indicating increasing oxidation state.
- **Combustion products** are shown on the horizontal axis, with **CO₂** and **H₂O** at the ends.
- **Fuels** are depicted along the bottom axis, ranging from **Carbon** (coal) to **Hydrogen**.
- The **Increasing Hydrogen Content** axis runs from left to right, with **Methane** to **Ethanol** to **Biomass** to **Petroleum** to **Natural Gas** to **Town Gas**.

The diagram also highlights the **Increasing Oxidation State** from **Free O₂** at the bottom to **Free C-H** at the top.
The OCH – Diagram - 2

- **Oxidizer**
- **Combustion products**
- **Fuels**

- Increasing Oxidation State
- Free O₂
- Free C-H

- CO₂
- H₂O

- Carbon
- Benzene
- Gasoline
- Methane
- Hydrogen
- Coal
- Biomass
- Petroleum
- Methanol
- Fischer Tropsch Synthesis Gas

- Increasing Hydrogen Content
The OCH – Diagram - 3

- Oxidizer
- Combustion products
- Fuels

Increasing Hydrogen Content

- Increasing Oxidation State

- Free C-H

- Free O₂

Fuels:
- Coal
- Town Gas
- Natural Gas
- Methane
- Methanol
- Fischer-Tropsch Synthesis Gas

Combustion products:
- CO₂
- H₂O

Oxidizer:
- CO

Elements:
- Carbon
- Benzene
- Gasoline
- Hydrogen

Diagram showing the relationship between oxidizer, combustion products, and fuels, with arrows indicating the increasing hydrogen content and oxidation state.
Cost of Air-Capture CDR Measures

1) Minimum Energy required: 443 kJ/kg of CO$_2$ extracted, corresponds to 0.12 KWh
   → at 0.25 €/KWh: 0.03 €/kg or 30 €/t of CO$_2$
   (note that electricity becomes cheaper if you consume more, also there is cheaper energy than electricity.)

2) Estimate by Socolow et al. 2011: 62$ (50€) per t of CO$_2$

3) Estimate by Stolarow 2006: 80-250$ per t of CO$_2$

For comparison: 1 barrel of oil produces about 0.5 t of CO$_2$
   → at 100$ (75€)/barrel it „costs“ 200$ (150€) to produce a ton of CO$_2$
How much air do we need to treat annually?

1) Annual emission of C to the atmosphere: 10 Gt (does not all stay in the atmosphere, but this does not matter because of equilibrium)

2) Which is about 2.5% of the 800GtC that are already there.

3) Assuming that we remove all CO$_2$ in the treated air we need to blow 2.5% of the atmospheric volume through the plant annually.

4) Atmospheric volume: $V_{Atm} = A_{Earth} \cdot h_{Scale} \approx 5 \cdot 10^8 \text{ km}^2 \cdot 8 \text{ km} \approx 4 \cdot 10^9 \text{ km}^3/\text{a}$

5) At a wind (blower) speed of $v=10\text{m/s}$ ($3.14 \cdot 10^5 \text{ km/a}$) this corresponds to an Exchanger area of:

$$A_E = \frac{V_{Atm}}{v} \approx \frac{4 \cdot 10^9 \text{ km}^3/\text{a}}{(3.14 \cdot 10^5 \text{ km/a})} \approx 10^4 \text{ km}^2$$
Klaus Lackner has imagined huge ‘farms’ featuring thousands of air-scrubbing devices that could soak up billions of tonnes of carbon from the atmosphere.

From: Jones 2009
CDR-3: Bioenergy + Carbon Capture & Storage (BECCS)

The Idea: Burn biomass (containing carbon removed from the atmosphere by Photosynthesis), burn it and store the CO$_2$ underground:

Advantages:
- Possibly cheap

Disadvantages:
- Availability of Biomass?
- Water demand
- Proximity of suitable storage sites
- Total annual capacity?
- Competition to food production

Edström E. & Öberg C. (2013), Review of Bioenergy with Carbon Capture and Storage (BECCS) and Possibilities of Introducing a Small-Scale Unit, Master's Thesis KTH School of Industrial Engineering and Management Energy Technology EGI-2013-048MSC EKV950, Stockholm.
Summary

• Direct removal of CO$_2$ from air by technical means is possible

• Minimum energy required for CO$_2$ removal is 2-5% of energy gained by combustion of fossil fuel

• Cost needs to be determined, present estimates of the order of present cost of fossil fuel.

• Higher cost of CO$_2$ removal could be justified by emission from mobile sources

• There is the „Double Integral“ Problem

• Big problem: Where to put the CO$_2$?