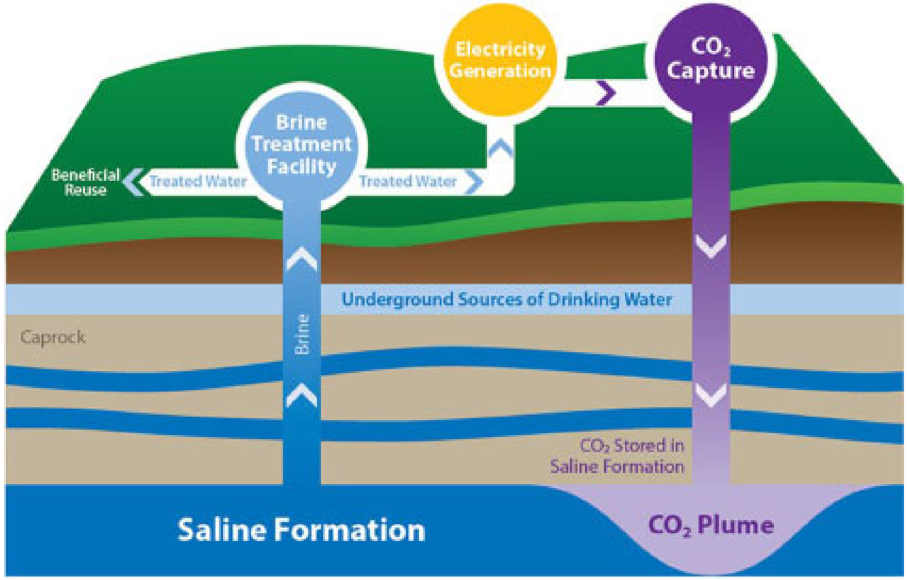
CO_2 capture and storage

From Science



From Link

Learning objectives

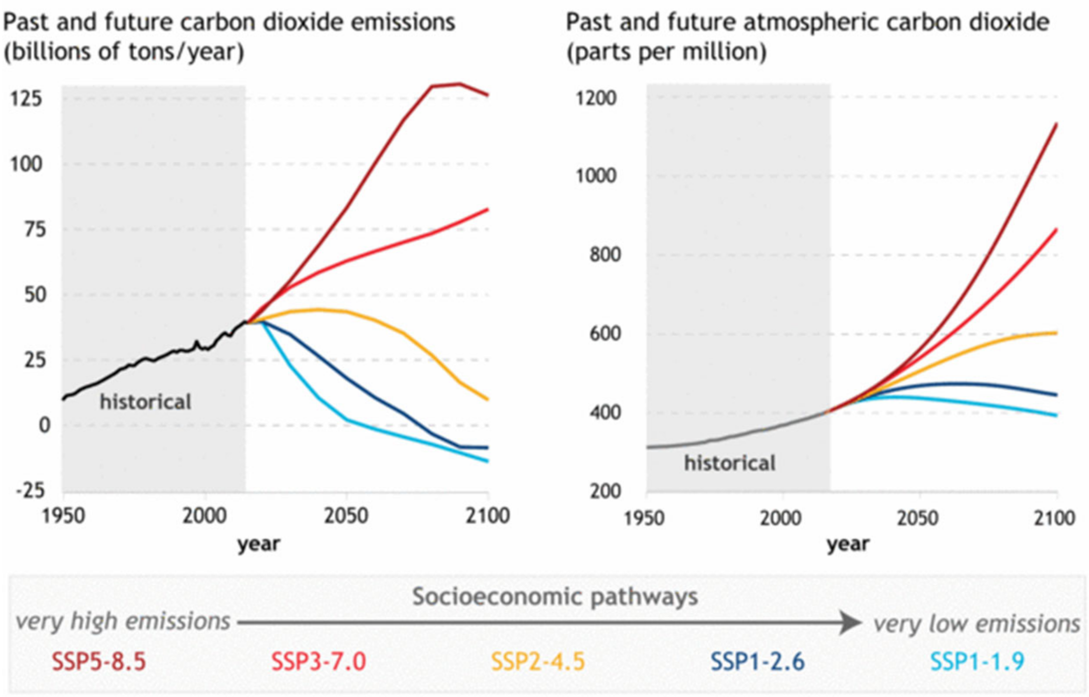
- How plants capture CO_2
- How industry captures CO_2 currently
- How direct air capture works
- How pH swing CO_2 capture works
- Physics behind CO_2 storage

CO_2 capture – overall numbers

- According to IPCC to maintain 1.5 C, we should sequester 10 billion ton/yr and be at 125 billion Gton by 2100.

- We expect this to be neccessary as of 2050.

- If we do this too early though, people will think burning fossil fuels is OK



NOAA Climate.gov, adapted from IPCC AR6 Technical Summary, Figure TS.4

Thermodynamics of CO_2 capture from air

- Currently we have ~400 ppm in the air.
- We need to upconcentrate this to ~100% CO_2 to either store it or use it
- Concentration entails an entropic loss. How big is this loss in KJ/mol CO_2 at 298K? *(For perspective, methane has 890 KJ/mol)*

Entropy of mixing

$$\Delta S = -R \sum X_{i,final} \, Ln\left(\frac{X_{i,initial}}{X_{i,final}}\right)$$

Physist to chemist conversion

$$R = k_B N_A$$

k_B = Boltzmann's constant
R= Ideal gas constant
N_A = Avogadro's number

R = 8.31 J/K/mol
MW of CO_2= 44 g/mol

Thermodynamics of CO_2 capture

$$\Delta S = R\left[\overbrace{100\% * Ln\left(\frac{4\times10^{-6}}{100\%}\right)}^{\substack{CO_2 \\ \text{concentration}}} \overbrace{+100\% * Ln\left(\frac{0{,}9996}{100\%}\right)}^{\substack{\text{Air} \\ \text{concentration}}}\right]$$

$$\Delta S = 65\ \text{J/mol/K}$$

$$T\Delta S = 65\ \text{J/mol/K} * 298\text{K} = 19.4\ \text{kJ/mol}\ CO_2$$

$$= 5\ \text{kWh/ton}\ CO_2$$

- *Or equivalently 2% the energy density of a mol of methane*

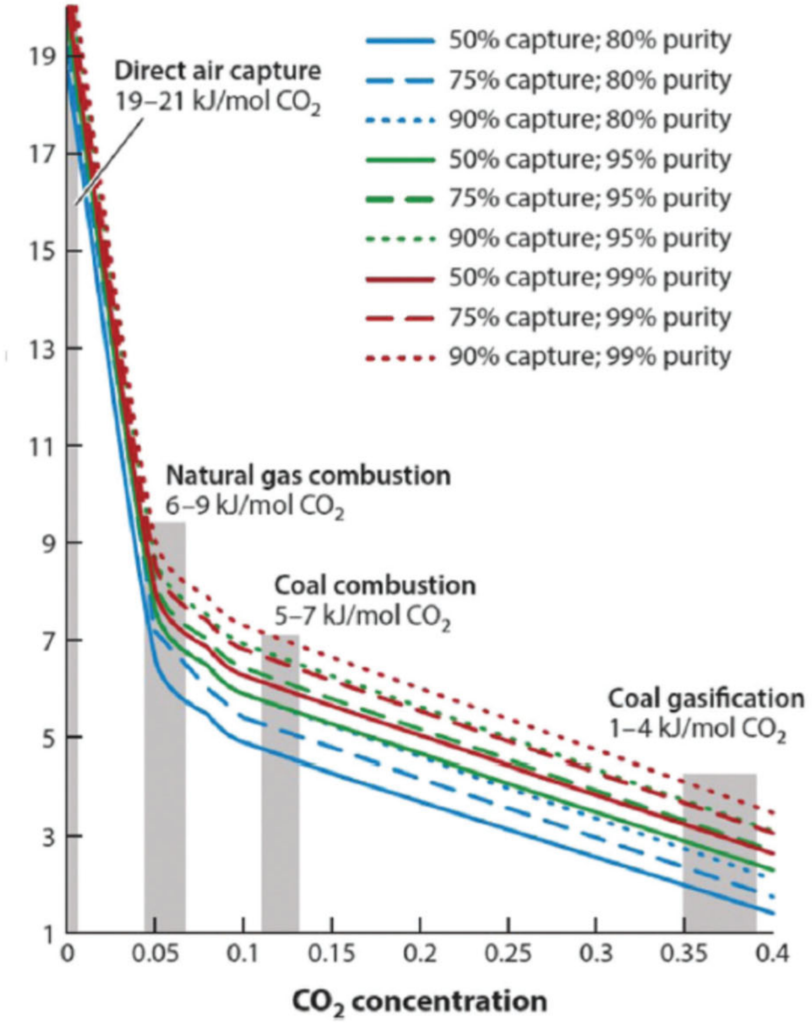


Fig. 27 Minimum work required for CO_2 capture based upon initial CO_2 concentration, capture rate, and final CO_2 purity.[308]

Broader analysis

- More concentrated CO_2 means easier capture.
- For direct air capture, 10-15x the thermodynamic minimum is where we are currently.

CO_2 capture- flue gas

- CO_2 capture from post-combustion gas is much more concentrated.

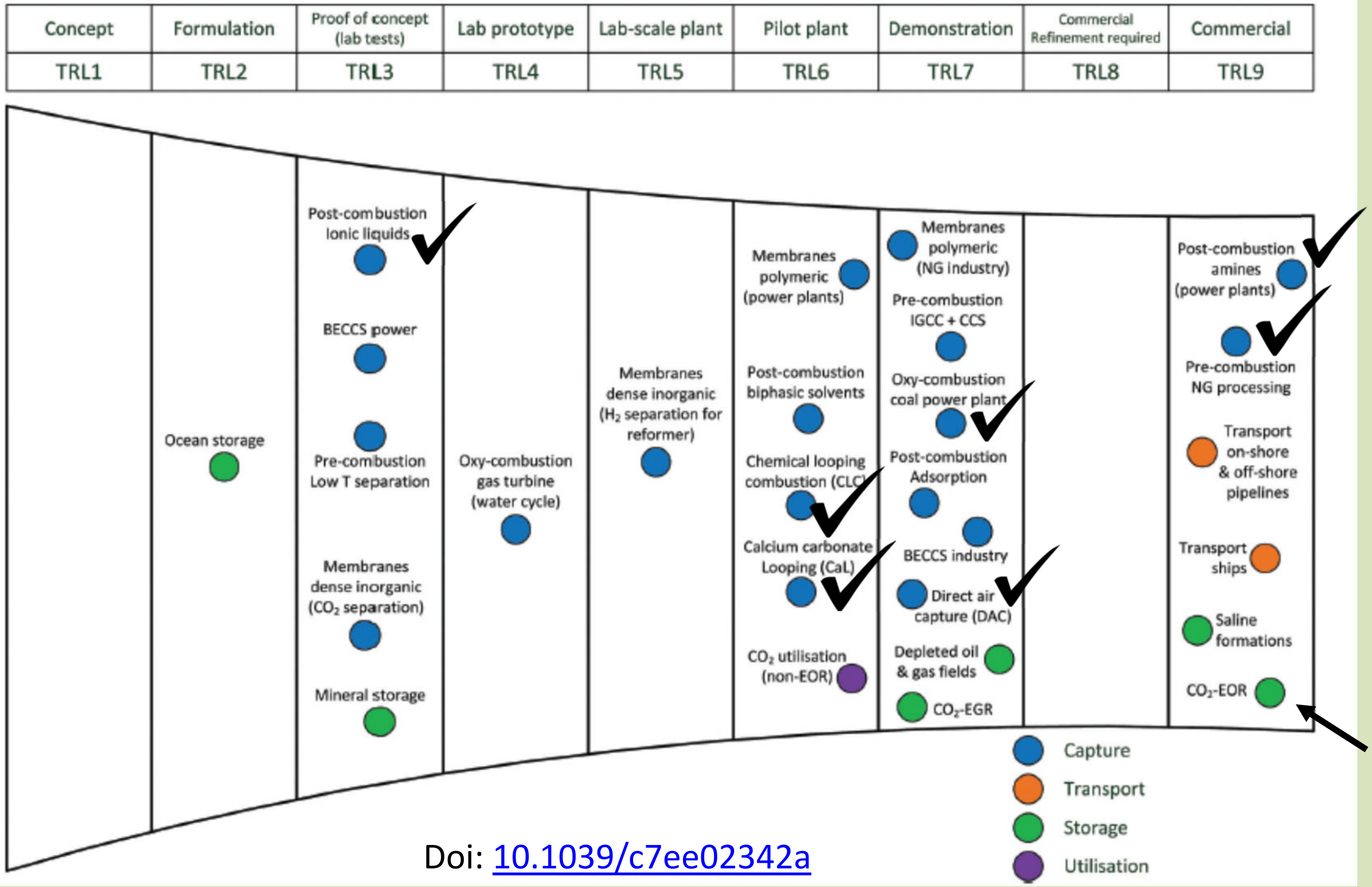
- Power plants bring in NO_x, SO_x, and ash (e.g. $CaCO_3$) which can contaminate things

- Low temperature of biomass, increase CO production

- Fossil power plants have heavy metals like Pb, Hg, etc.

	Gas	Oil	Coal	Biomass
CO_2	9 %	12%	14%	13%
H_2O	19 %	11%	9%	12%
O_2	2 %	3%	3%	4%
N_2	70 %	74%	74%	71%
NO_x (mg/MJ)	46	600-1000	99	48-200
SO_x (mg/MJ)	4		11	1-100
CO (mg/MJ)	6			70-900
Volume (m^3/ GJ fuel)	295	303	323	

CO_2 capture overview

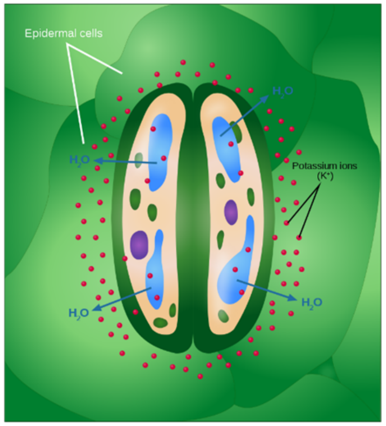


Doi: 10.1039/c7ee02342a

Pump CO_2 in oil wells to help produce more oil

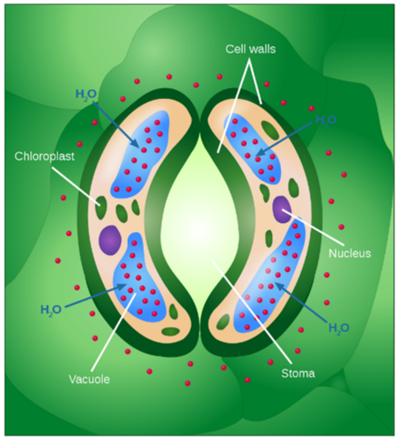
How plants capture CO_2

- When guard cells are hydrated, they open up
- This allows air (O_2, CO_2, etc) to enter
- We roughly lose 400 waters per CO_2 molecule
- Stomatal density on leaves decreases when CO_2 concentrations increase. This is 5-67% depending upon leaf and conditions.
- The opening mechanism is thought to related to salt (K^+, Ca^+) concentration effecting the pressure in the guard cells, allowing them to open/close.



Guard cells (shrunken)

Stoma closing



Guard cells (swollen)

Stoma opening

Enzyme kinetics

- Michaelis–Menten kinetics is basically mass-transfer incorporated reaction kinetics for enzymes.
- Michaelis constant gives an effective inverted activity constant for a given enzyme.
- The K_m for Rubisco ≈ 20 μM
- With CO_2 in atmosphere = 400 ppm, and the Henry's Law constant for CO_2 in water, this means we have 10 μM dissolved CO_2.

Michaelis–Menten kinetics

$$\nu = \frac{dp}{dt} = \frac{V_{max} A}{K_m + A}$$

$$\Downarrow$$

$$\frac{\nu}{V_{max}} = \frac{A}{K_m + A}$$

K_m = Michaelis constant
(Concentration at 50% V_{max})
ν = reaction rate
V_{max} = Maximum rate
A = substrate concentration (related to, but not same as CO_2 concentration)

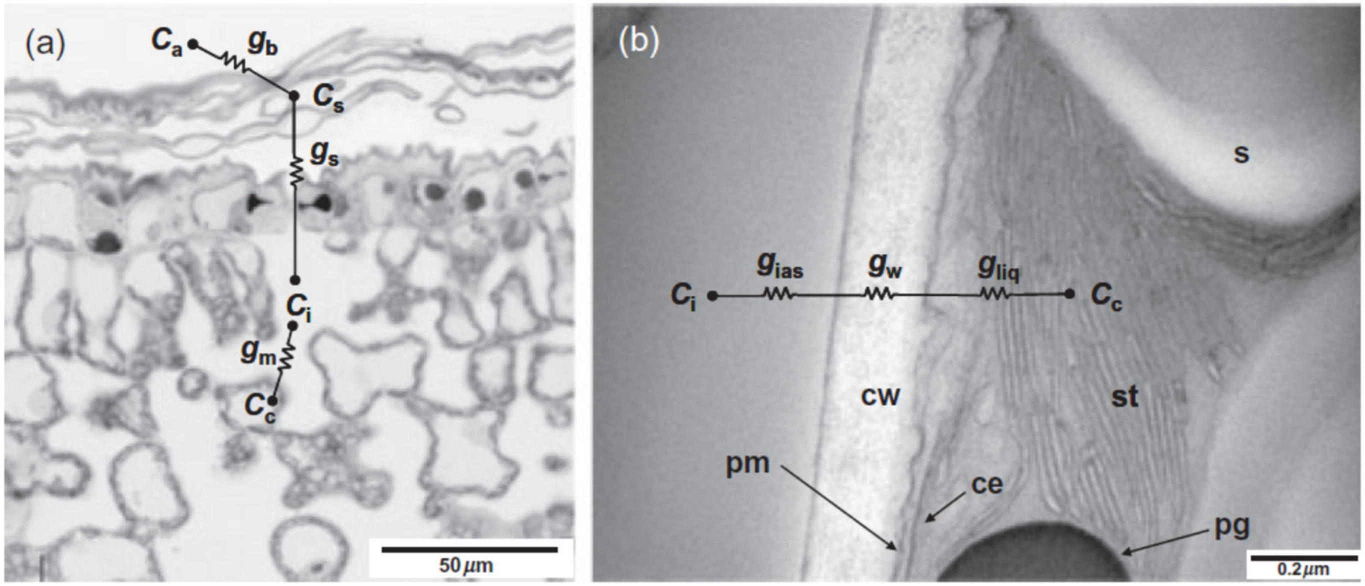
$$\frac{\nu}{V_{max}} = \frac{A}{K_m + A} = \frac{10}{20 + 10} = 30\% \longleftarrow$$

Rubisco is only operating at 30% maximum capacity

CO_2 – From atmosphere to Rubisco enzyme

- We can effectively model the path of CO_2 as going through various ‘resistors’ or ‘conductance’ or ‘diffusion coefficients’, from the atmosphere to Rubisco.
- The conductance of g_b and g_m are on the same order of magnitude.

C_a =CO_2 in atmosphere
C_s =CO_2 in leaf surface
C_i =CO_2 in intercellular air space
C_c =CO_2 in chloroplast
g_b = Boundary layer conductance
(localized mass transfer issues in air)
g_s = Stomatal conductance
g_m = Mesophyll conductance



Doi: 10.1111/j.1365-3040.2007.01757.x

Stomatal conductance

- The simplest and most used is the Ball-Berry model

$$g_s = m * A_n \frac{H_s}{C_s} + g_o$$

A_n = net CO_2 consumption rate
C_s = CO_2 in leaf surface
H_s = relative humidity
m = slope
g_o = y-intercept

Very empirical

- H_s relates to openness of stoma
- *m* is typically between 4-10 depending upon the plant

- To the right are more complex models to determine g_s.

Doi: 10.1111/j.1365-3040.2010.02181.x

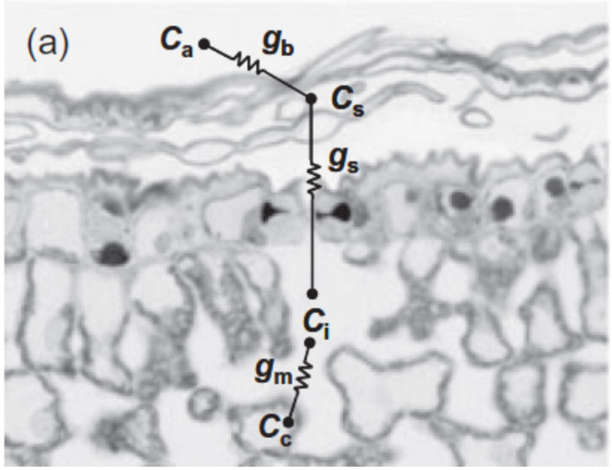
Table 2. Equations relative to the models of g_s

1.	Jarvis 1976	$g_s = f_1(Q) \cdot f_2(T_l) \cdot f_3(VPD) \cdot f_4(C_a) \cdot f_5(\Psi_l)$
2.	White *et al.* 1999	$g_s = g_{smax} \cdot f(Q) \cdot f(T_l) \cdot f(VPD)$
3.	Noe & Giersch 2004	$g_{s,w} = g_{smax} \cdot \min[f(Q), f(VPD)]$
4.	Lohammer *et al.* 1980	$g_s = \frac{1}{\left(1 + \frac{VPD}{D_0}\right)}$
5.	Monteith 1995	$g_s = g_{smax} - a \cdot VPD$
6.	Monteith 1995	$g_s = a(1 - b \cdot E)$
7.	Delwiche & Cooke 1977	$A_{st} = \pi \cdot L_a \cdot L_b \qquad L_b = f(P_g, P_{sub})$ +a set of diffential equations integrated P_g et P_{sub}, water potentials, osmotic potentials, water vapour resistances and water fluxes
8.	Dewar 1995	$g_s = \chi(P_g - P_e) \qquad g_s = \chi(\Delta\pi - \Delta\Psi)$ $\Delta\Psi = \frac{E}{k} \qquad \Delta\pi = f(A_{net}, C_i, g_s)$
9.	Ball *et al.* 1987	$g_s = g_0 + a \cdot A_{net} \frac{H_r}{C_s} \qquad g_s = g_0 + g_{1wb} \frac{A_{net} \cdot H_r}{C_s}$
10.	Aphalo & Jarvis 1993	$g_s = \frac{A_{net}}{C_s}[k_0 + k_1 \cdot VPD + k_2 \cdot T_l + k_3 \cdot T_l \cdot VPD]$
11.	Leuning 1990	$g_s = g_0 + a \cdot A_{net} \frac{H_r}{C_s - \Gamma}$
12a	Leuning 1995	$g_s = g_0 + a \frac{A_{net}}{\left(1 + \frac{VPD}{D_0}\right) \cdot (C_s - \Gamma)} \qquad g_s = g_0 + g_{1L} \frac{A_{net}}{\left(1 + \frac{VPD}{D_0}\right)(C_s - \Gamma)}$
12b 12c	Supply function and biochemical model of A_{net}	$g_s = 1.6 \frac{A_{net}}{C_s\left(1 - \frac{C_i}{C_s}\right)} \qquad A_{net} = f(J_{max}, V_{cmax}, R_d, Q, C_a, H_r, T_l)$
13.	Farquhar & Wong 1984	$g_s = 10^3 p \cdot T \qquad T = f(A_{net}, E, J_{max}, V_{cmax}, Q, T_l, R_d, \mathrm{RuBP}_{pot}, \ldots)$
14.	Jarvis & Davies 1998	$g_s = G^*(A_{max} - A_{net}) \qquad G^* = G - s \cdot E$
15.	Stewart 1988	$g_s = g_{smax} \cdot f(Q) \cdot f(T_l) \cdot f(VPD) \cdot f(\delta\theta) \qquad f(\delta\theta) = 1 - \exp[k_6(\delta\theta - \delta\theta_m)]$
16.	Misson *et al.* 2004	$g_s = f(Q) \cdot f(T_l) \cdot f(VPD) \cdot f(\Psi_{pd}) \qquad f(\Psi_{pd}) = g_{smax} - a(\Psi_{min} - \Psi_{pd})$
17.	MacFarlane *et al.* 2004	$g_s = g_{smax} \cdot f(Q) \cdot f(T_l) \cdot f(VPD) \cdot f(\Psi_{pd})$ $f(\Psi_{pd}) = 1.09 \exp^{-1.275S(\Psi)} \qquad S(\Psi) = \frac{1}{n}\sum(-\Psi_{pd} - 0.2)$
18.	Ogle & Reynolds 2002	$g_s = \begin{cases} 0 & \text{if } VPD > \exp(-b_0/m) \\ g_{smax} & \text{if } VPD > \exp(-(b_0 - \tau)/m) \\ g_{smax} \frac{m \cdot \ln(VPD) + b_0}{\eta} & \text{else} \end{cases}$ $g_{smax} = \tau \cdot \exp\left(\frac{\rho \cdot \Psi_{pd}}{T_{gro}}\right) \cdot \frac{4(T_{max} - T_{gro})(T_{gro} - T_{min})}{(T_{max} - T_{min})^2}$
19.	Tenhunen *et al.* 1990	$g_{twb} = GFAC$
20.	Baldocchi 1997	$g_{twb} = a \frac{\sum P}{\sum ETP}$
21.	Sala & Tenhunen 1996	$g_{twb} = b + a \cdot \Psi_{pd} \qquad \text{if } \Psi_{pd} < -1 \text{ MPa}$
22.	Misson *et al.* 2004	$g_{twb} = \frac{m}{1 + \left(\frac{\Psi_{pd}}{\Psi_0}\right)^n}$
23.	Wang & Leuning 1998	$g_{1L} = a \cdot \min\left(1; 10 \frac{\theta_s - \theta_f}{3(\theta_{cr} - \theta_f)}\right)$
24.	Van Wijk *et al.* 2000	$g_{twb}, g_{1L} = a\left[1 - k_4 \exp\left(k_5 \frac{\theta_{cr} - \theta_s}{\theta_{cr} - \theta_f}\right)\right]$
25.	Uddling *et al.* 2005	$g_{1L} = a \cdot f_{season} \quad f_{season} = \min(1; k_7 + k_8 \cdot \mathrm{DOY})$
26.	Tardieu & Davies 1993	$g_s = g_0 + \alpha \cdot \exp[[ABA] \cdot \beta \cdot \exp(\delta\Psi_l)] \qquad [ABA] = \frac{J_{ABA}}{J_w + b} = \frac{a \cdot \Psi_r}{J_w + b}$ $J_w = \frac{\Psi_l - \Psi_r}{R_p} \text{ et } \qquad J_w = \frac{\Psi_r - \Psi_s}{R_{sp}}$
27.	Gutschick & Simonneau 2002	$g_s = \exp(-\beta[ABA]) \cdot m \frac{A_{net} \cdot H_r}{C_s} + b$

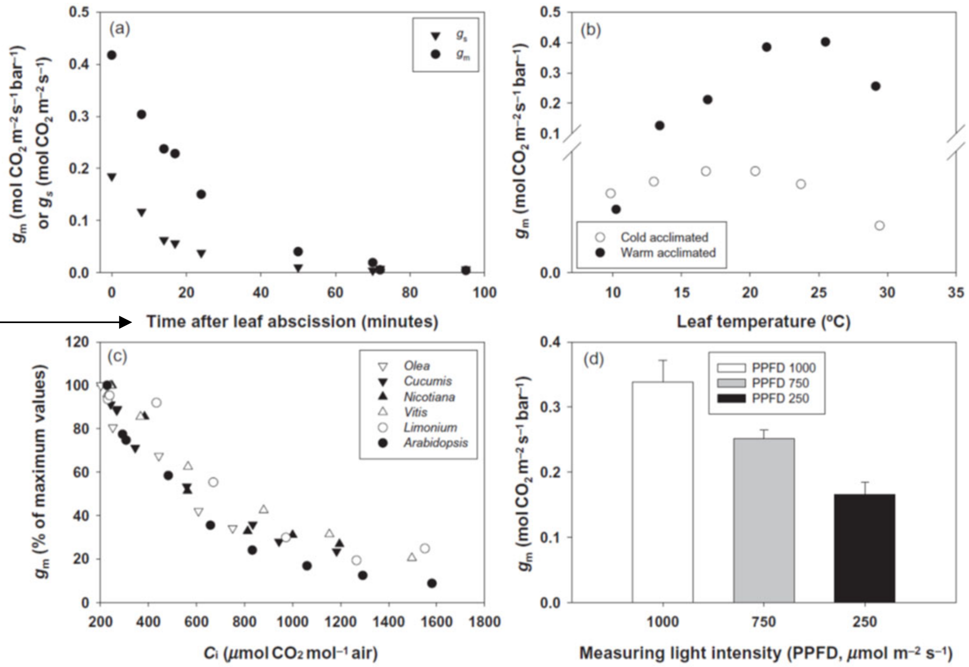
Mesophyll conductance

- g_m values can vary from 0.1-1.0 mol CO_2 m^{-2} s^{-1} bar^{-1}, with no simple trend why.

- Environmental effects can also effect the value significantly.



Abscission =
leaf fall off tree →



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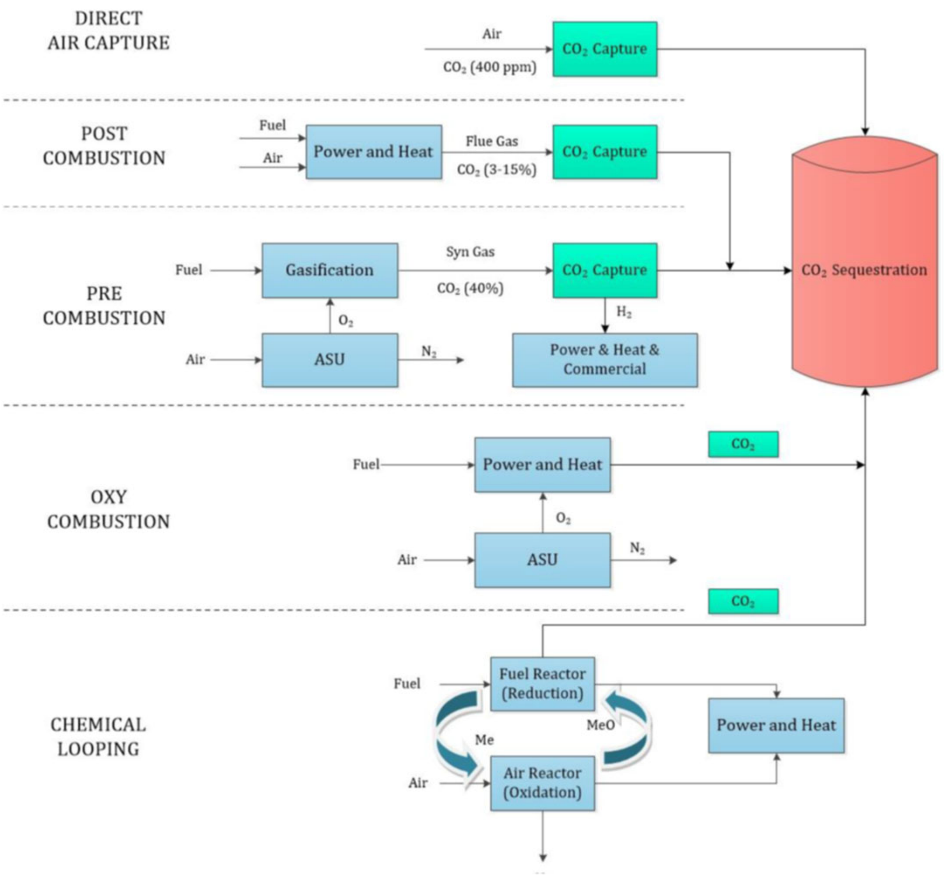
Industrial CO_2 capture

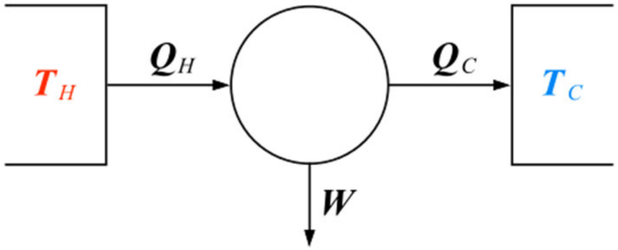
- Combustion involves hydrocarbons + air
- When to separate the O_2, N_2 and HC/CO_2 is the big debate.
- Many approaches are situation dependent.



Dubey, et al. 2022, J. Cleaner Prod.

Carnot efficiency

- In a heat engine, you are simply going from a hot temperature source (T_H) to a cold temperature source (T_C).



$$Q_H = W + Q_C$$

$$\eta_{Carnot} = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

- The Carnot Efficiency is the maximum efficiency you will ever get from a heat engine.

Heat engine - limitations

- In theory we are limited by the flame temperature of our energy source.
- In reality we are limited by the materials used for our heat engine.
- Currently boilers operate around 800 K.
- ASME SA516- steel is typically used for boilers.

Fuel	Flame Temperature (K)	Carnot Efficiency	Carnot Efficiency with Irreversibility
Coal	2446	87,8%	65,1%
Natural Gas	2327	87,2%	64,2%
Fuel Oil	2302	87,1%	64,0%
Wood	2143	86,1%	62,7%
Hydrogen	2573	88,4%	66,0%

Wikipedia

Material	Max Operating Temperature(K)
Carbon Steel	1023
Ni-Cr Steel	1700
Copper	480
Aluminum	423-523
Titanium	813
Plastics	323-473
Alumina	1700-2000

← Random sources

Heat engine - limitations

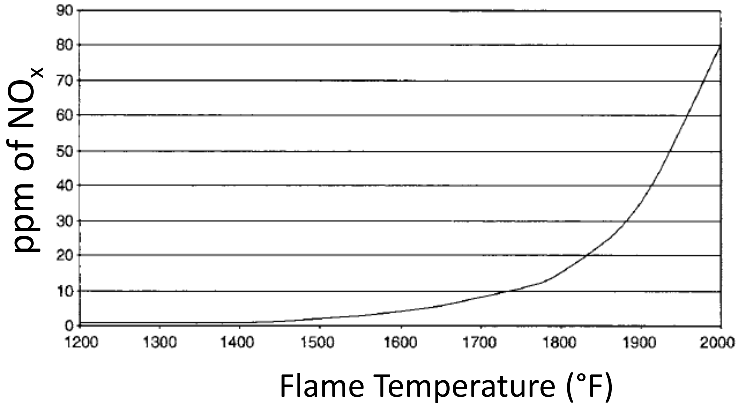
- NO_x is a pollutant that forms increasingly at high temperatures.
- The mechanism is based off an oxygen radical interacting with N_2.

1st step: $O^* + N_2 \rightarrow NO + N^*$

2nd step: $N^* + O_2 \rightarrow NO + O^*$

Overall Reaction: $O_2 + N_2 \rightarrow 2NO$

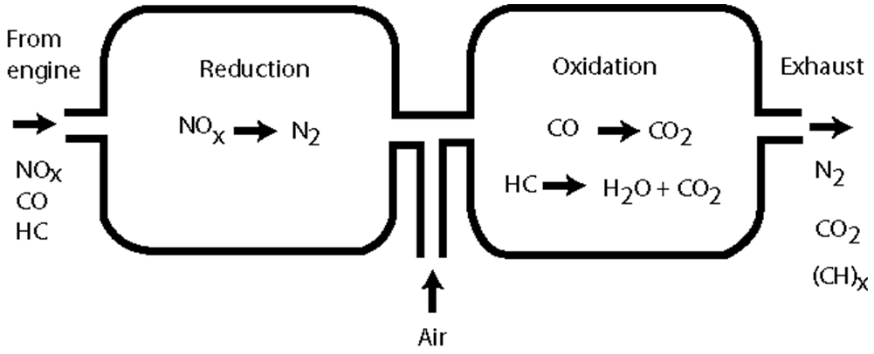
- Since air is 80% N_2 20% O_2, we are kind of stuck with this reaction.
- See here for more details.



Boyce, P. M, 2002, “Gas turbine engineering handbook, pg. 414”

Catalytic converters

- Can we catalyze our way out of the NO_x issue? –Yes !
- 3-way catalytic converters allow us to do this.



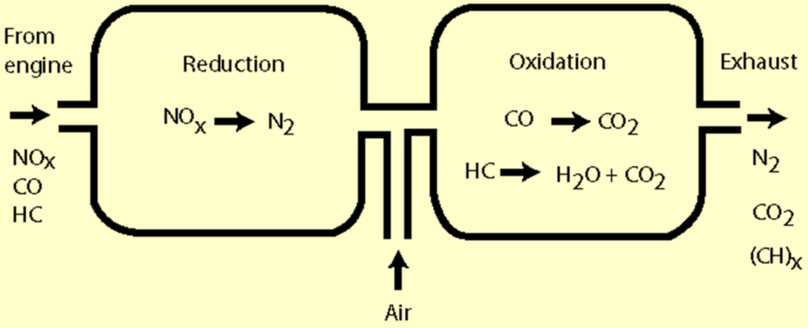
- Unburnt hydrocarbons (H_xC_y) react with the water (created during combustion) to form H_2 gas.

1st step: $H_xC_y + H_2O \rightarrow H_2 + CO_2$

- The H_2 gas then reduces the NO_x.

2nd step: $2H_2 + NO \rightarrow N_2 + 2H_2O$

Catalytic converters



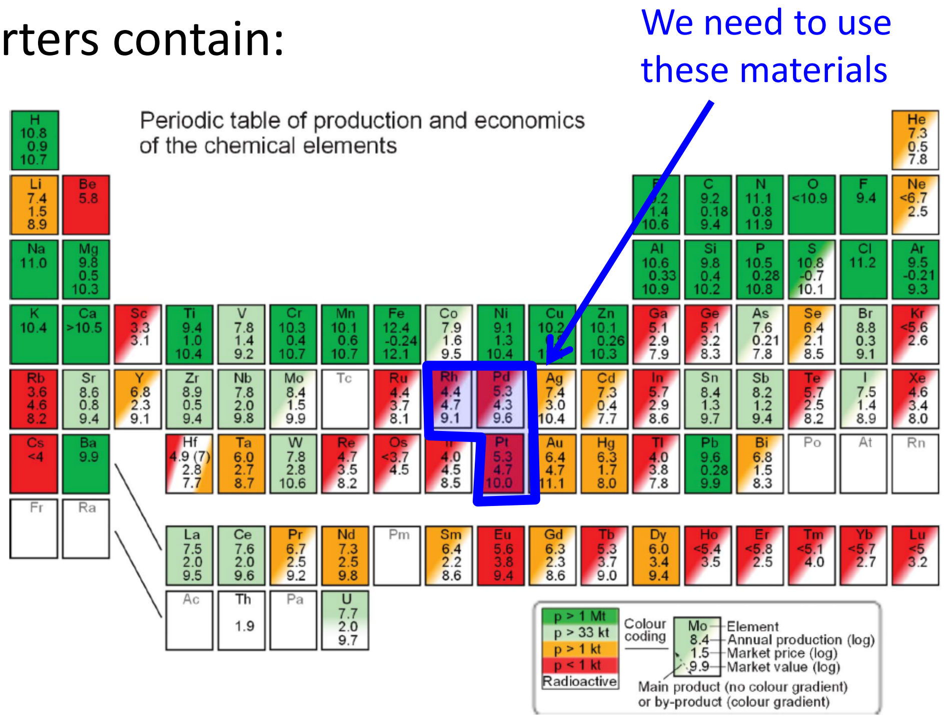
- Further down the line, CO and any remaining hydrocarbons get oxidized from additional air (i.e. O_2).

$$3^{rd}\text{ step: } \begin{cases} H_xC_y + O_2 \rightarrow \frac{x}{2}H_2O + yCO_2 \\ 2CO + O_2 \rightarrow 2CO_2 \end{cases}$$

- Why can’t we add air in from the beginning?
- While these reactions are quite efficient, the catalysts are quite expensive.

Catalytic converters

- Per car in the EU, catalytic converters contain:
  - 3 g platinum
  - 2.5 g palladium
  - 0.5 g rhodium



We need to use these materials

Periodic table of production and economics of the chemical elements

H 10.8 0.9 10.7																	He 7.3 0.5 7.8
Li 7.4 1.5 8.9	Be 5.8											[illegible] [illegible] 1.4 10.6	C 9.2 0.18 9.4	N 11.1 0.8 11.9	O <10.9	F 9.4	Ne <6.7 2.5
Na 11.0	Mg 9.8 0.5 10.3											Al 10.6 0.33 10.9	Si 9.8 0.4 10.2	P 10.5 0.28 10.8	S 10.8 -0.7 10.1	Cl 11.2	Ar 9.5 -0.21 9.3
K 10.4	Ca >10.5	Sc 3.3 3.1	Ti 9.4 1.0 10.4	V 7.8 1.4 9.2	Cr 10.3 0.4 10.7	Mn 10.1 0.6 10.7	Fe 12.4 -0.24 12.1	Co 7.9 1.6 9.5	Ni 9.1 1.3 10.4	Cu 10.2 [illegible] [illegible]	Zn 10.1 0.26 10.3	Ga 5.1 2.9 7.9	Ge 5.1 3.2 8.3	As 7.6 0.21 7.8	Se 6.4 2.1 8.5	Br 8.8 0.3 9.1	Kr <5.6 2.6
Rb 3.6 4.6 8.2	Sr 8.6 0.8 9.4	Y 6.8 2.3 9.1	Zr 8.9 0.5 9.4	Nb 7.8 2.0 9.8	Mo 8.4 1.5 9.9	Tc	Ru 4.4 3.7 8.1	Rh 4.4 4.7 9.1	Pd 5.3 4.3 9.6	Ag 7.4 3.0 10.4	Cd 7.3 0.4 7.7	In 5.7 2.9 8.6	Sn 8.4 1.3 9.7	Sb 8.2 1.2 9.4	Te 5.7 2.5 8.2	I 7.5 1.4 8.9	Xe 4.6 3.4 8.0
Cs <4	Ba 9.9		Hf 4.9 (7) 2.8 7.7	Ta 6.0 2.7 8.7	W 7.8 2.8 10.6	Re 4.7 3.5 8.2	Os <3.7 4.5	Ir 4.0 4.5 8.5	Pt 5.3 4.7 10.0	Au 6.4 4.7 11.1	Hg 6.3 1.7 8.0	Tl 4.0 3.8 7.8	Pb 9.6 0.28 9.9	Bi 6.8 1.5 8.3	Po	At	Rn
Fr	Ra																
			La 7.5 2.0 9.5	Ce 7.6 2.0 9.6	Pr 6.7 2.5 9.2	Nd 7.3 2.5 9.8	Pm	Sm 6.4 2.2 8.6	Eu 5.6 3.8 9.4	Gd 6.3 2.3 8.6	Tb 5.3 3.7 9.0	Dy 6.0 3.4 9.4	Ho <5.4 3.5	Er <5.8 2.5	Tm <5.1 4.0	Yb <5.7 2.7	Lu <5 3.2
			Ac	Th 1.9	Pa	U 7.7 2.0 9.7											

Colour coding

- 🟩 p > 1 Mt
- 🟩 p > 33 kt
- 🟧 p > 1 kt
- 🟥 p < 1 kt
- ☐ Radioactive

Mo — Element
8.4 — Annual production (log)
1.5 — Market price (log)
9.9 — Market value (log)

Main product (no colour gradient) or by-product (colour gradient)

- 80% of the world's rhodium supply goes towards catalytic converters.
- Rhodium costs are a major reason why governments don't set lower NO_x emission rates.

NO_x removal in power plants

- Power plants differ from internal combustion engines via two major points
  - They are run 24 hours a day where ICE operates maybe 5-10% a day
  - The scale and stationary aspect means we can add reactants to remove NOx
- Ammonia is typically used as a reductant with a vanadium-tungsten-titanium (VWT) catalyst.

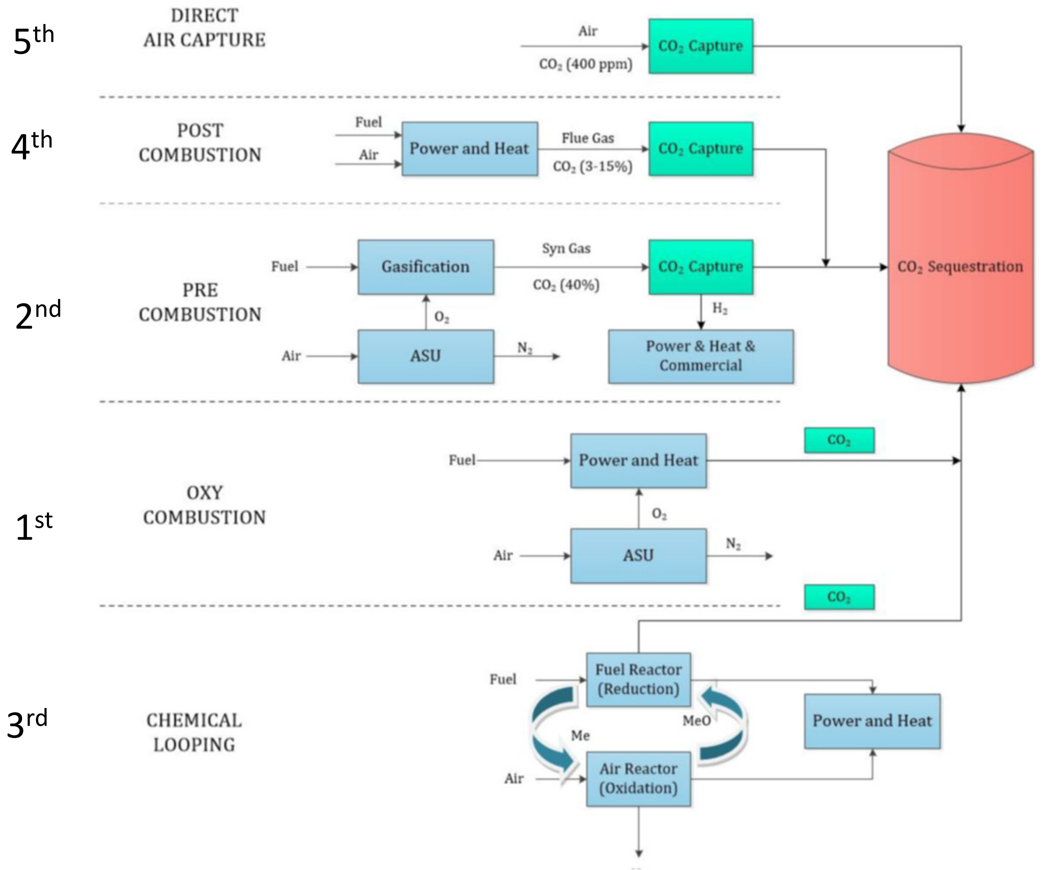
$$2NO + 2NH_3 + {}^{1}/_{2}\,O_2 \rightarrow 2H_2O$$

$$2NH_3 + {}^{3}/_{2}\,O_2 \rightarrow N_2 + 3H_2O \quad \longleftarrow \text{Unwanted reaction}$$

- Biomass combustion has lots of potassium, which poisons the catalyst.

Industrial CO_2 capture

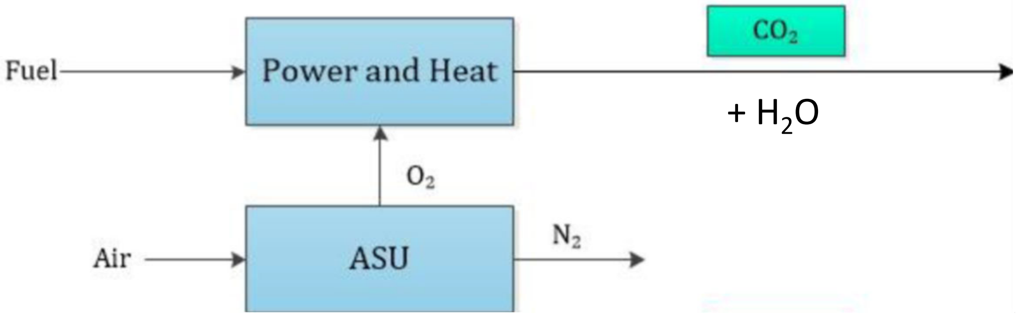
- Combustion involves hydrocarbons + air
- When to separate the O_2, N_2 and HC/CO_2 is the big debate.
- Many approaches are situation dependent.



Dubey, et al. 2022, J. Cleaner Prod.

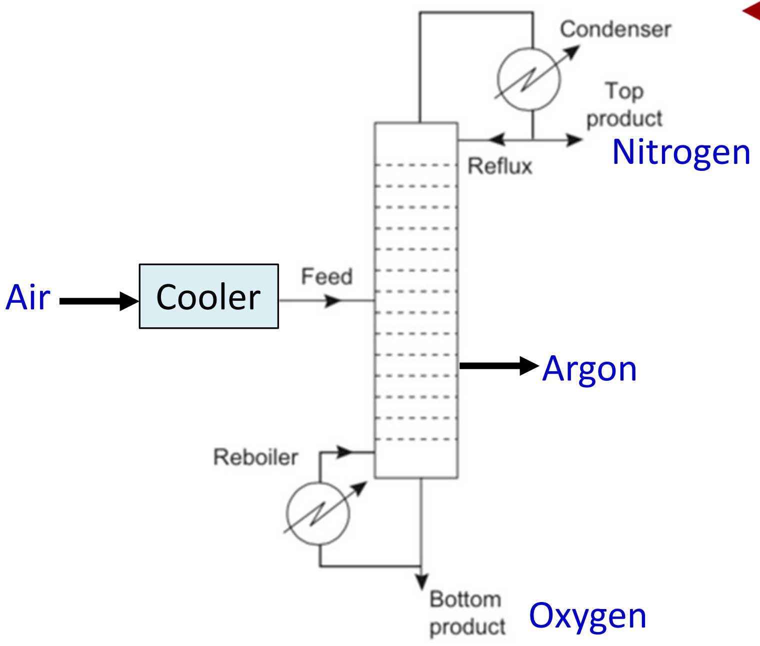
Oxy-combustion

- In this case, we separate air into O_2 and N_2.
- As air is 80% N_2, this reduces separation issues once combusted.
- Removing N_2 also resolves NO_x issues, allowing higher temperatures.
- As we want dry CO_2 to store/utilize, we can completely condense the water and gain energy from heat of condensation.



Direct air separation

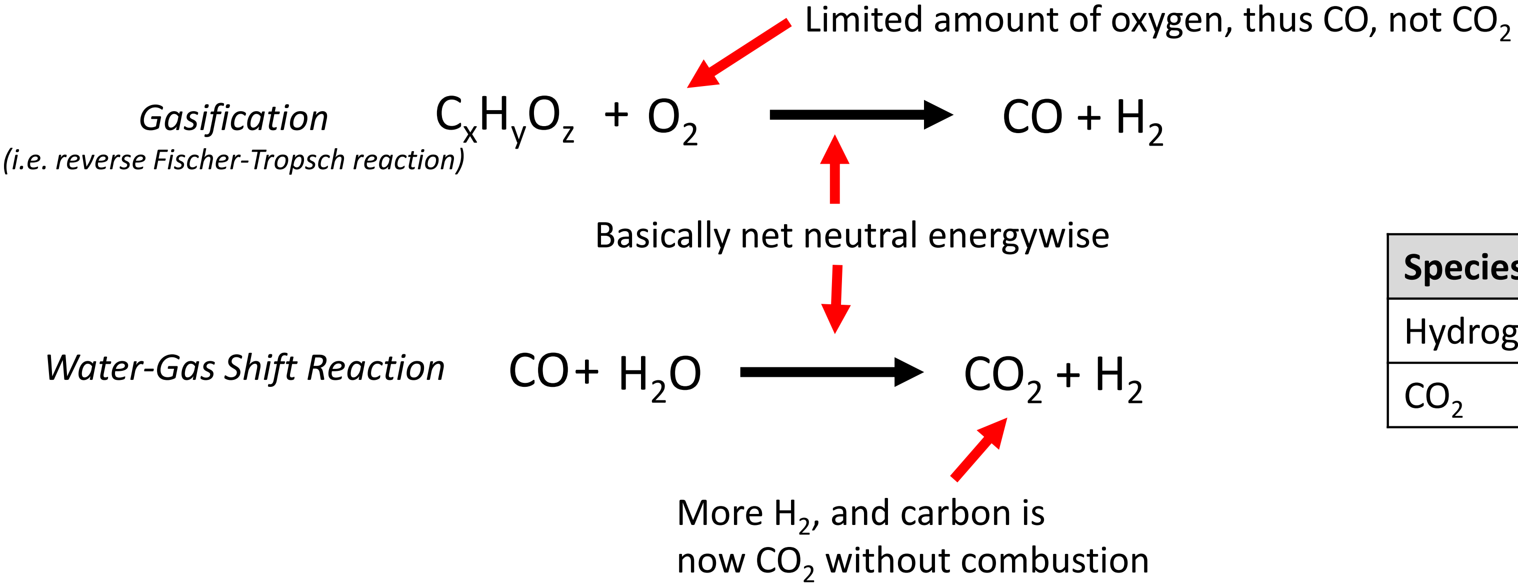
- Air is separated by cryogenic distillation.
- As the cooling unit, must go to temperatures below 77K, there is substantial energy involved in this process.
- This process was dicovered by Carlos von Linde, who created the company Linde Air /Praxair.
- Other methods such as pressure-swing absorption and molecular sieves are also have potential for air separation.



Material	Boiling point (K)
Nitrogen	77.4
Argon	87.3
Oxygen	90.2
CO_2	195

Pre-combustion

- For pre-combustion we need to first separate the carbon from the hydrogen as CO_2.
- Then we just burn the hydrogen.
- This is often used with coal and the overall process produces 6-10% in losses.



Limited amount of oxygen, thus CO, not CO_2

Gasification
(i.e. reverse Fischer-Tropsch reaction)

$$C_xH_yO_z + O_2 \longrightarrow CO + H_2$$

Basically net neutral energywise

Water-Gas Shift Reaction

$$CO + H_2O \longrightarrow CO_2 + H_2$$

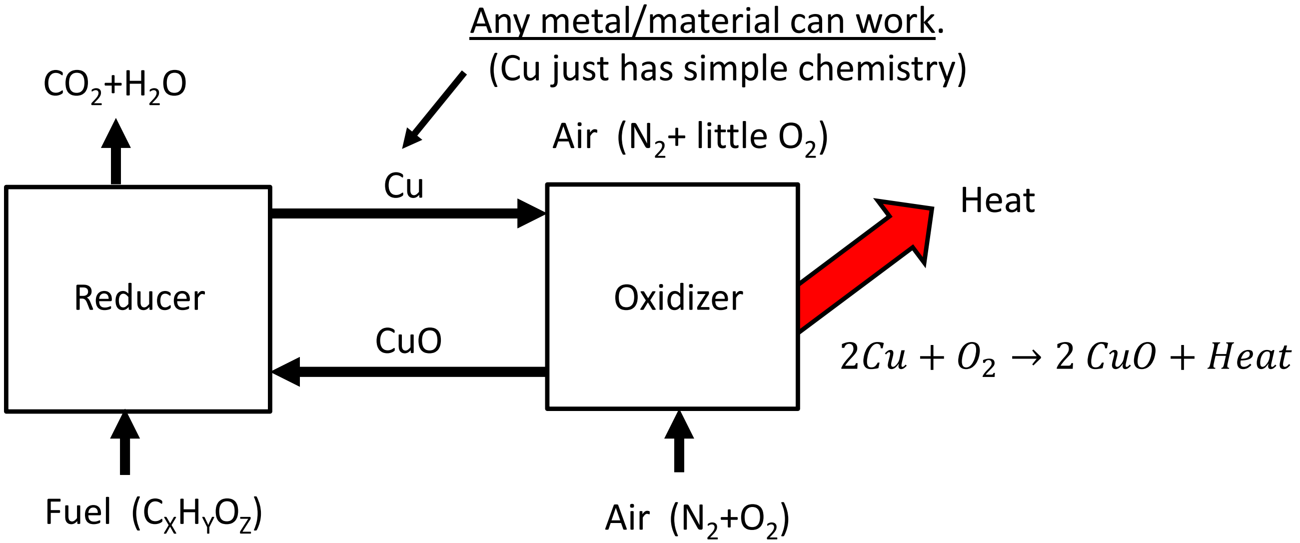
More H_2, and carbon is
now CO_2 without combustion

Species	**Boiling point (K)**
Hydrogen	20
CO_2	195

Chemical looping

- We transfer the energy emission to a recycleable source.
- The fuel works as a reducer rather than an oxidizer.

$CH_4+1.5\ O_2 \rightarrow CO_2+H_2O \quad \Delta H = -401\ KJ/mol\ O_2$



<u>Any metal/material can work</u>.

(Cu just has simple chemistry)

$2Cu + O_2 \rightarrow 2\ CuO + Heat$

$O_2+2Cu \rightarrow 2CuO\ \Delta H = -312\ KJ/mol\ O_2$

Chemical looping

- ΔG needs to be negative for the reaction to occur
- ΔG is the driving force, but ΔH is what gives us heat for a heat engine.
- Fe_2O_3, MnO or $FeTiO_3$ are used as metals due to good redox potential and being cheap

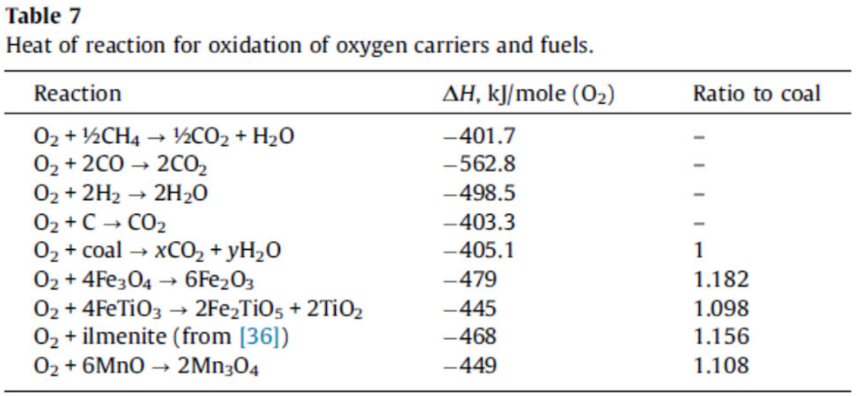


Table 7
Heat of reaction for oxidation of oxygen carriers and fuels.

Reaction	ΔH, kJ/mole (O_2)	Ratio to coal
$O_2 + ½CH_4 \rightarrow ½CO_2 + H_2O$	−401.7	–
$O_2 + 2CO \rightarrow 2CO_2$	−562.8	–
$O_2 + 2H_2 \rightarrow 2H_2O$	−498.5	–
$O_2 + C \rightarrow CO_2$	−403.3	–
$O_2 + \text{coal} \rightarrow xCO_2 + yH_2O$	−405.1	1
$O_2 + 4Fe_3O_4 \rightarrow 6Fe_2O_3$	−479	1.182
$O_2 + 4FeTiO_3 \rightarrow 2Fe_2TiO_5 + 2TiO_2$	−445	1.098
O_2 + ilmenite (from [36])	−468	1.156
$O_2 + 6MnO \rightarrow 2Mn_3O_4$	−449	1.108

doi.org/10.1016/j.apenergy.2015.04.057

- Chemical looping is estimated to add 20 €/tonne of CO_2 with an energy penalty was 4%.
- This is an early stage technology

Post combustion

- Post combustion has 9-14% CO_2
- Four major approaches
    - Amines
    - Membranes
    - Ionic Liquids
- Originally (1930-1970) lime/cement (CaO) was used to react with CO_2 to form $CaCO_3$.
- Heating $CaCO_3$ to 1200K desorbs CO_2 and regenerates CaO. *This is why cement production is a CO_2 intensive process.*

	Gas	**Oil**	**Coal**
CO_2	9 %	12%	14%
H_2O	19 %	11%	9%
O_2	2 %	3%	3%
N_2	70 %	74%	74%
Volume (m^3/ GJ fuel)	295	303	323

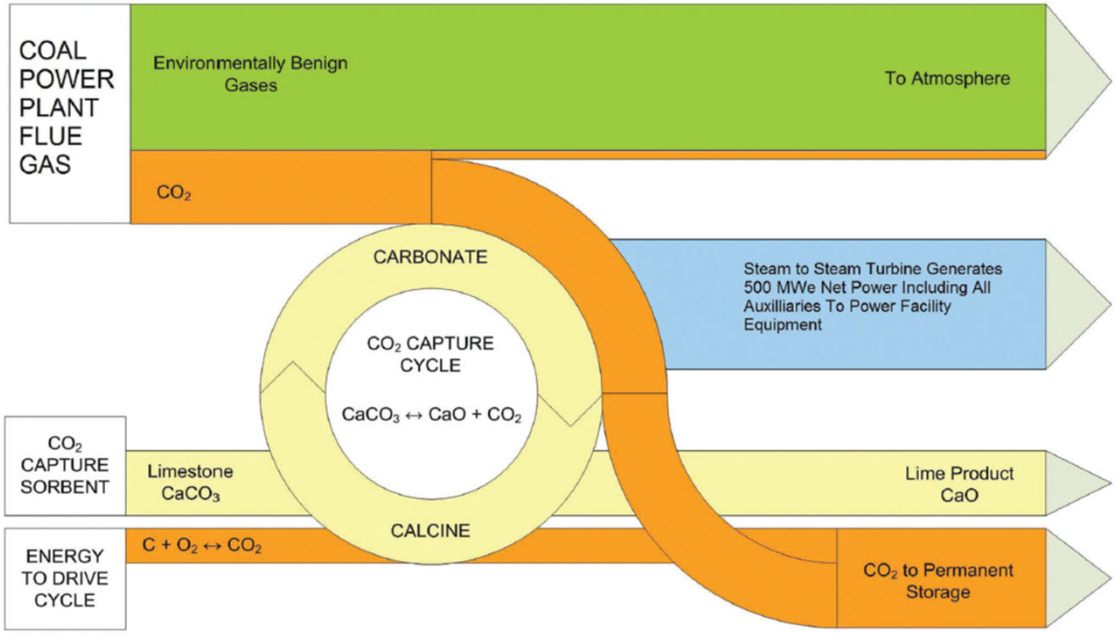
Wikipedia, thus rough estimate

Not affected by O_2

$$\begin{tikzcd} CaO + CO_2 \arrow[r] & CaCO_3 \arrow[d, "\text{Regeneration } (\Delta H = 178\ \text{kJ/mol})"] \\ CaO + CO_2 & CaCO_3 \arrow[l, "\text{1200K}"'] \end{tikzcd}$$

Calcium looping

- The calcium 'looping' process works nicely integrated with lime production
- Limestone/Lime is effectively just a catalyst. However as the catalyst deactivates (lower surface area, etc) it can still be used as lime for cement production.



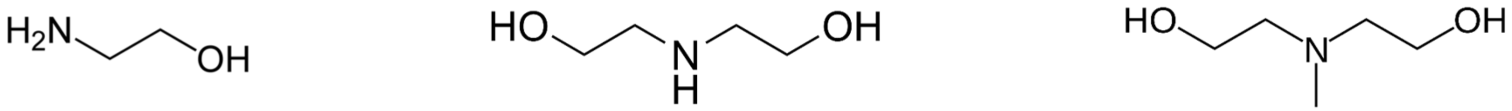
Post combustion – approaches

- CO_2 can either be captured via:
  - Absorption like O_2 in water
  - Reactions with the solvent like CO_2 converting into carbonates

- Often both approaches occur at the same time, thus complicating the CO_2 capture properties.

Post combustion – amine absorption

- Mono ethanolamine (MEA), di-ethanolamine (DEA) and N-methyldiethanolamine (MDEA)



- The N-H is the key to getting a good consumption of CO_2.

- The capacity of saturated ethylenediamine is 32 g CO_2/Kg (H_2O+EDTA) . This is ~double MEA

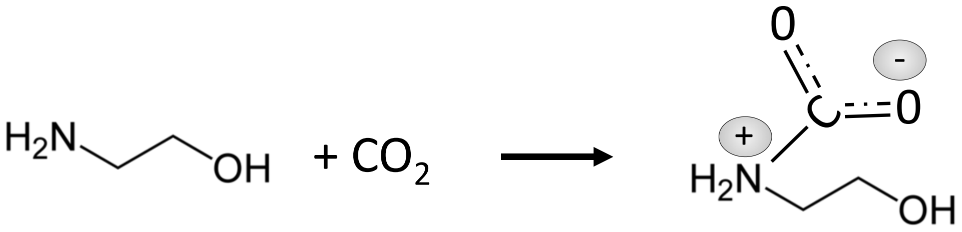
DOI: 10.1002/cssc.200900293

	MEA	DEA	MDEA
Rate constant for CO_2 adsorption (m^3/s/kmol)	7000	1200	3.5

Amine adsorption- reaction mechanism

- The chemical reaction leads to a Zwitterion (i.e one molecule with a positive and a negative charge.)

Step #1



$(C_2H_4OH)H_2N^+COO^-$

In chemical notation

Step #2

$(C_2H_4OH)H_2N^+COO^-$ + … → $(C_2H_5OH)NHCOO^-$ + …

‘Carbamate’

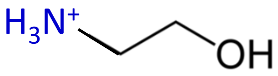
- Because we pull off a ‘H’ to get carbamate, any amine we use must have at least one hydrogen attached (i.e. tertiary amines won’t work)
- Note, we need 2 amines per 1 CO_2 captured

Carbamate vs. bicarbonate reaction

- A low stability constant and high pKa of the blue hydrogen favors a carbamate conversion to bicarbonate (The corresponding cation does not change)

‘Carbamate’ MEA ‘Bicarbonate’

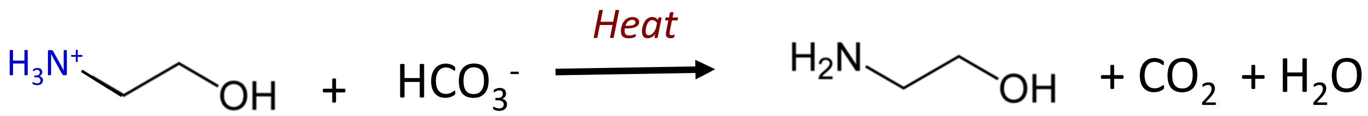
$$(C_2H_4OH)NHCOO^- + H_2O + CO_2 \longrightarrow (C_2H_4OH)NH_2 + HCO_3^-$$

- The  from the previous slide combines with the bicarbonate for a stable salt.

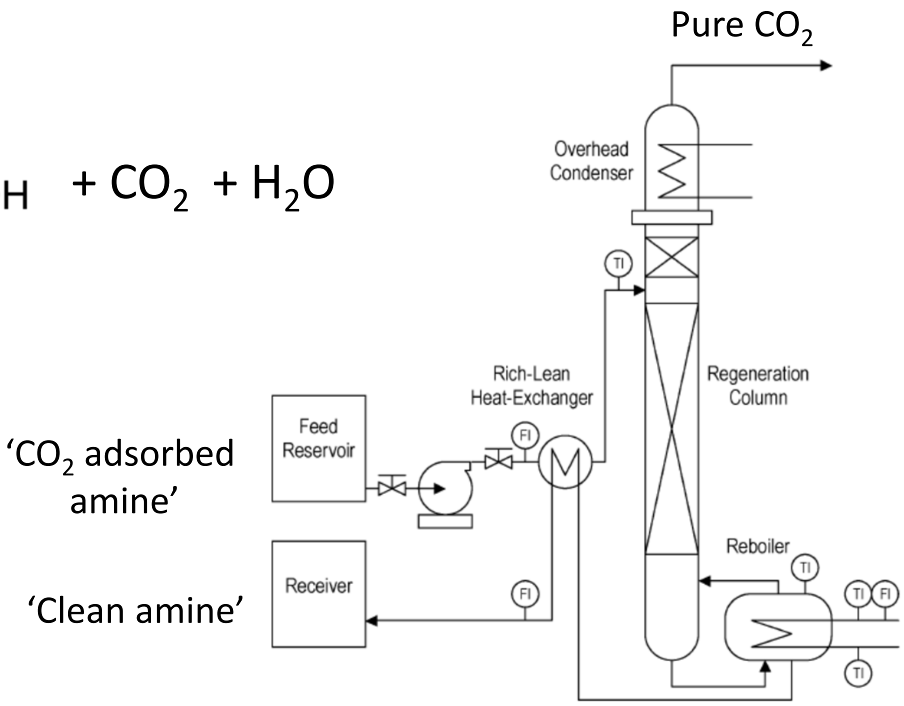
- As we regenerate one MEA forming HCO_3^-, the net result is a we have a 1:1 MEA to CO_2 absorption

Desorbing the CO_2 from the amine

- A relatively simple boiler removes the CO_2 from the amine.



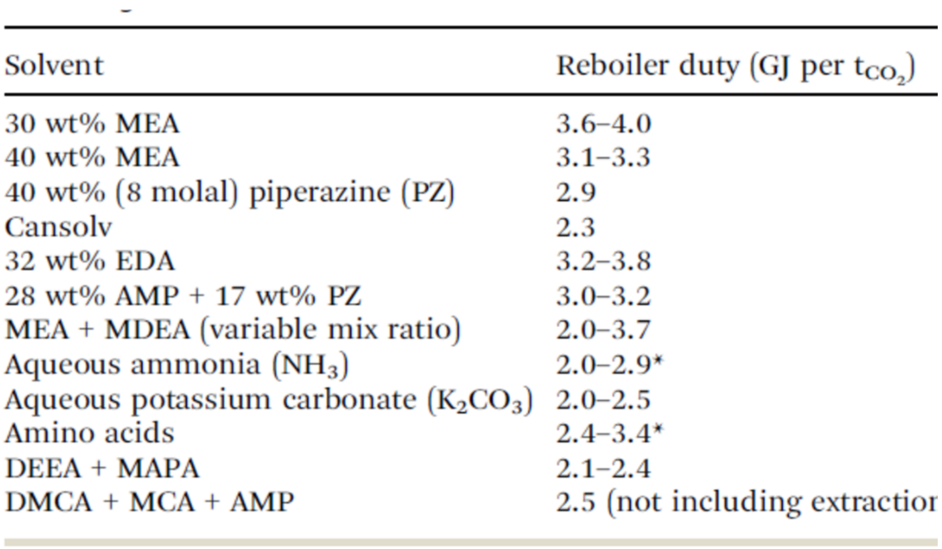
- Determining the heat needed (i.e. ΔH) is quite complex.
- The solvent contains methyl amine, carbamate, bicarbonate, water, CO_2 all at different concentrations



Ind. Eng. Chem. Res. **2005,** *44,* 4465-4473

Desorbing the CO_2 from the amine

- It is hard / pointless to desorb all the CO_2 from the MEA due to equilibrium factors
- Thus the recycled amine, tyopically has about 10% CO_2 still in it.



Solvent	Reboiler duty (GJ per t_{CO_2})
30 wt% MEA	3.6–4.0
40 wt% MEA	3.1–3.3
40 wt% (8 molal) piperazine (PZ)	2.9
Cansolv	2.3
32 wt% EDA	3.2–3.8
28 wt% AMP + 17 wt% PZ	3.0–3.2
MEA + MDEA (variable mix ratio)	2.0–3.7
Aqueous ammonia (NH_3)	2.0–2.9*
Aqueous potassium carbonate (K_2CO_3)	2.0–2.5
Amino acids	2.4–3.4*
DEEA + MAPA	2.1–2.4
DMCA + MCA + AMP	2.5 (not including extractio

Doi: 10.1039/c7ee02342a

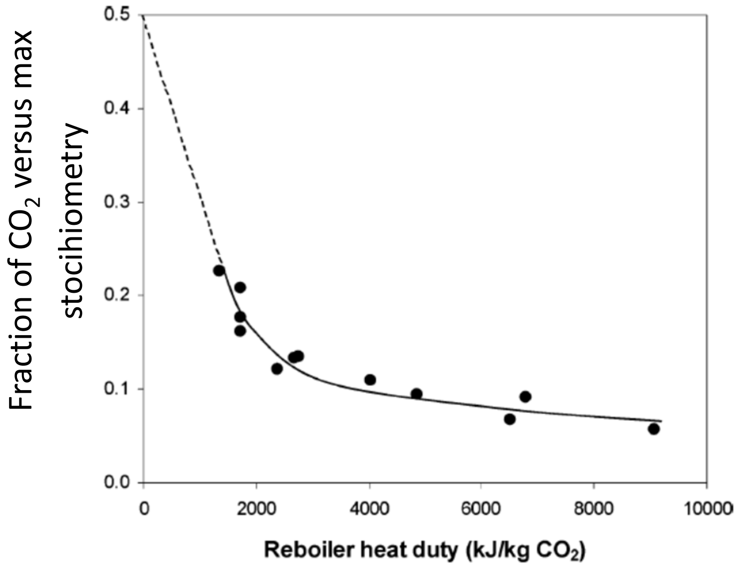


Figure 2. Reboiler heat duty of an aqueous DEA solution as a function of lean-CO_2 loading (4.0 kmol/m^3 alkanolamine concentration, 0.50 mol/mol rich loading).

Ind. Eng. Chem. Res. **2005,** *44,* 4465-4473

Paradox of CO_2 adsorption

- If we want CO_2 adsorption by a species to get much less than 400 ppm adsorption, the equilibrium constant must be really high

$$X + CO_2 \rightarrow X - CO_2$$

- If you have a high equilibirum constant going forward, that means it is going to be really hard to desorb the CO_2 to regenerate your adsobant.

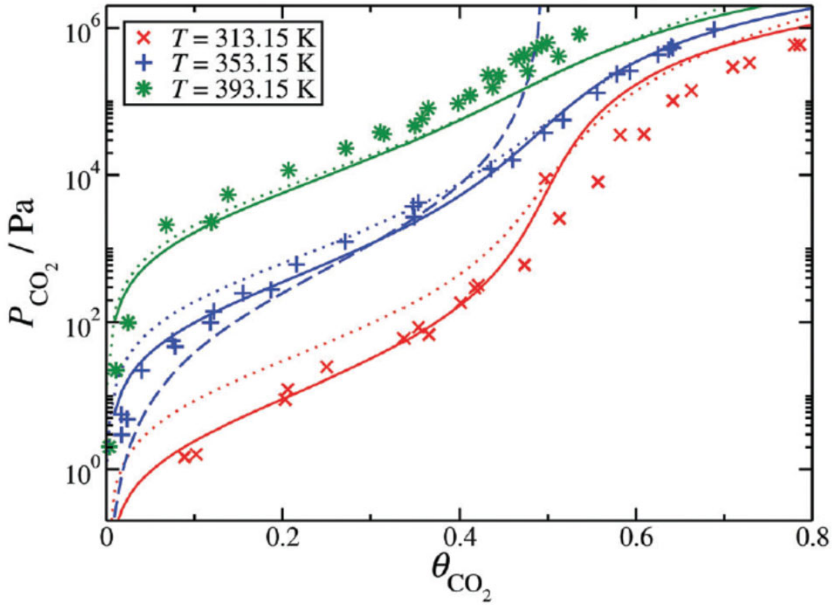
- Effectively this is an entropy effect.

CO_2 solubility vs reacting with MEA

- CO_2 uptake by MEA occurs via both solubility (physical absorption) and by the chemical reaction shown previously

- Higher temperatures means more CO_2 concentration/pressure is needed to increase uptake (i.e. θ)

- The sharp uptake in the red curve is a shift from the chemical reaction to physical absorption.



MEA solubility versus partial pressure.
(θ= moles CO_2/moles MEA)

Doi: 10.1039/c7ee02342a

MEA- thermal degradation

- There are about 20 different species of degradation so it is a big mess
- MEA degrades at 6% per week at 135 °C
- Higher temp = greater energy efficiency
- Going from 90 °C to 150 °C reduces energy costs by 30%

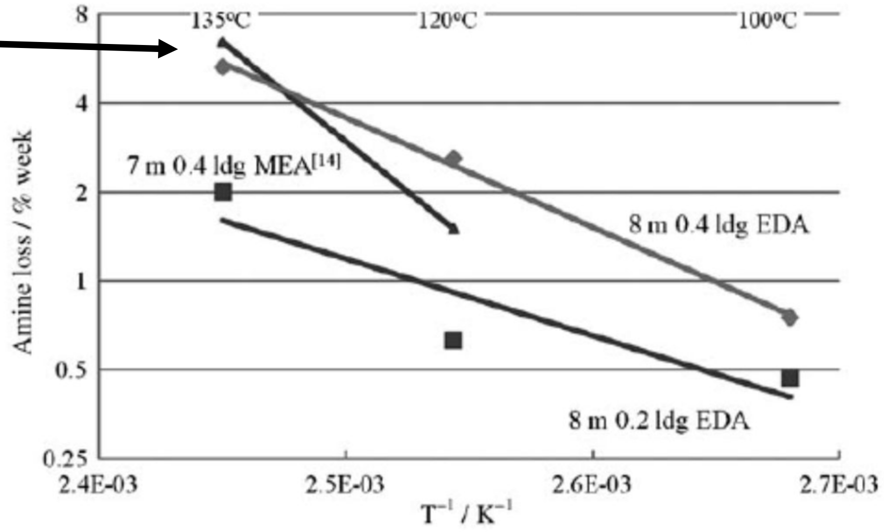


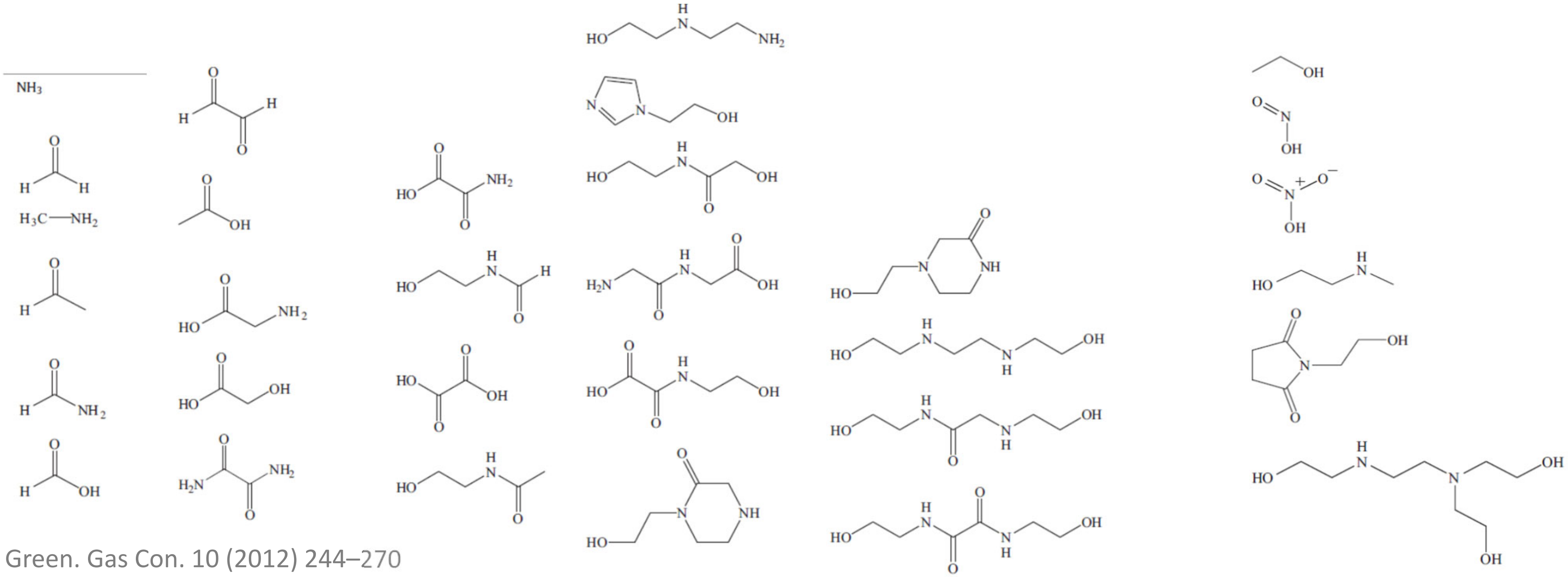
Figure 4. Thermal degradation rates of MEA and EDA.

Doi 10.1016/j.coche.2012.02.004

DOI: 10.1002/cssc.200900293

MEA- oxidative degradation

- Below are all the oxidative products.
- Anti-oxidants can be used to help prevent amine degradation

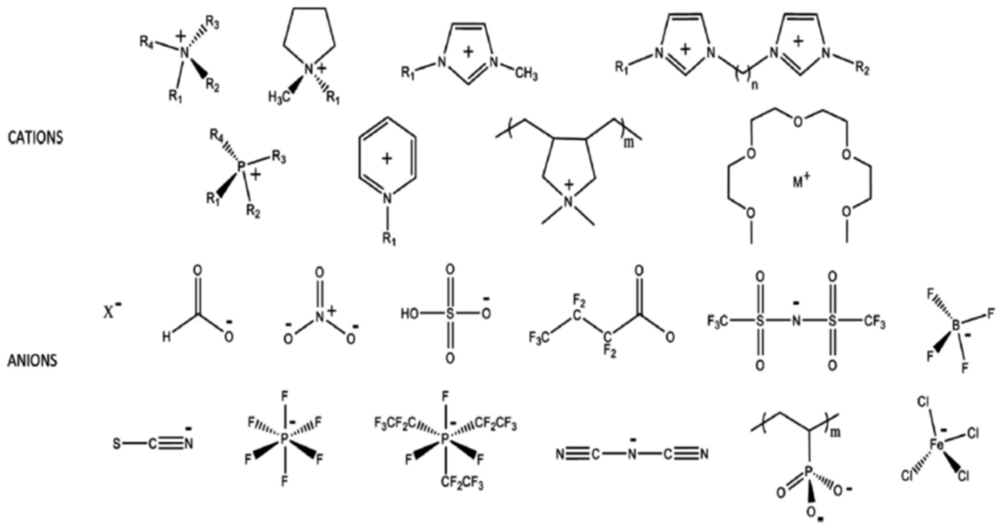


Int. J. Green. Gas Con. 10 (2012) 244–270

Ionic liquid approach

- Ionic liquids are ionic species that are liquid at room temperature
- The ionic nature entails they have low vapor pressures/ high boiling points
- This allows CO_2 to be absorbed at low temperatures/high pressures, and desorbed from solution at high temperatures/low pressures without evaporating the liquid

Or any gas, such as N_2 or O_2

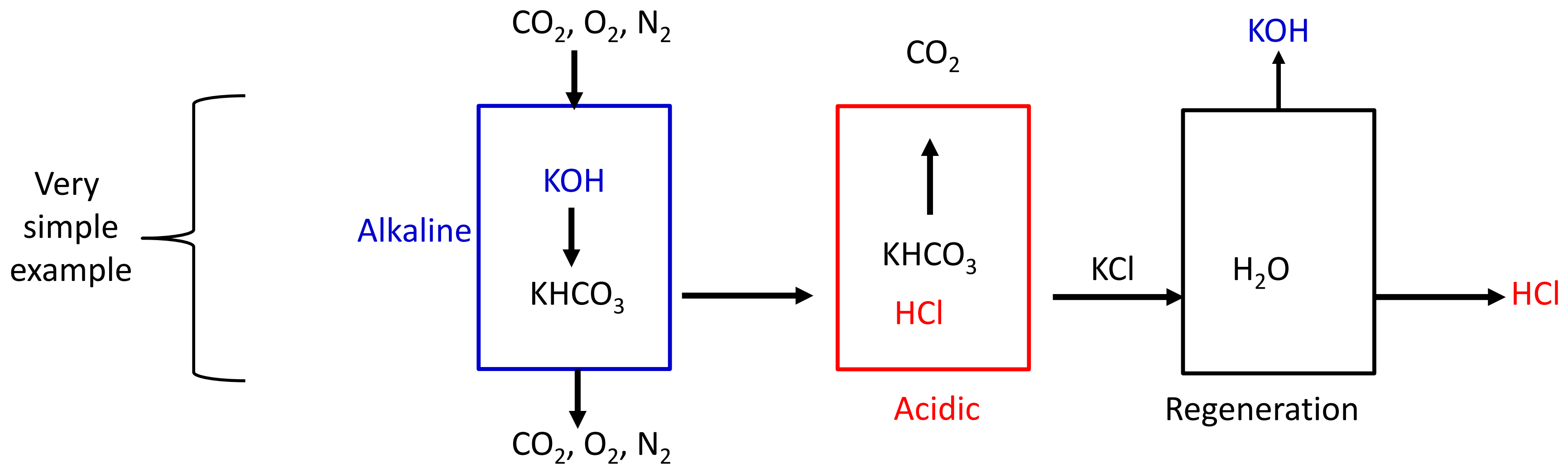


- Chemical stability is an issue.

10.1039/c7ee02342a

pH swing CO_2 capture

- The basis of this is that alkaline solutions absorb CO_2 and acidic solution degass CO_2.
- Same concept as ocean acidification and CO_2 crossover in CO_2 electrolysis.
- It is the regeneration of water to an acidic + basic solution that costs us energy.


Very simple example

Alkaline

CO_2, O_2, N_2

KOH

$KHCO_3$

CO_2, O_2, N_2

CO_2

$KHCO_3$

HCl

Acidic

KCl

KOH

H_2O

HCl

Regeneration

pH swing CO_2 capture - thermodynamics

- The pKa is the point where 50% of reactants and 50% of products.

pKa = 6.5

pKa = 10.6

$$CO_2 + H_2O \quad \leftrightarrow \quad H_2\,CO_3 \quad \leftrightarrow \quad H^+ + HCO_3^- \quad \leftrightarrow \quad 2H^+ + CO_3^{2-}$$

- In theory we could absorb CO_2 from air at pH 6.51 and desorb CO_2 at pH 6.49. Thermodynamically this would be very efficient. What are two reasons why this would be not useful?

  #1: Kinetics would be very slow

  #2: A pKa of 6.5 assumes pure CO_2 absorbed/desorbed. We want to absorb 400 ppm CO_2 and desorb 100% CO_2.

$$pKa = Log_{10}\frac{[HA]}{[A^-][H^+]}$$

pH swing CO_2 capture - thermodynamics

- How do we account for the 400 ppm to 100% CO_2 issue?
- We find the Gibbs Free Energy of the change in chemical equilibrium.
    - Already did this with ‘Entropic energy for CO_2 concentration problem’ at the beginning of the lecture. 19.4 kJ/mol CO_2.
- How do we relate pH to Gibbs free energy $H_2O \leftrightarrow H^+ + OH^-$

$$\Delta G = -RTln\left(\frac{[H^+][OH^-]}{[H_2O]}\right)_{Ref} = -5.71\frac{kJ}{mol} * (Log[H^+] + Log[OH^-])$$

$$\Delta G = 5.71\frac{kJ}{mol} * \Delta pH$$

This will effectively increase by a factor of 2, but will also change our pH by a factor of 2

pH swing CO_2 capture - thermodynamics

- From entropy we have 19.4 kJ/mol CO_2, and 1 pH unit gives us 5.7 kJ/mol.
- Thus the real minimum pH difference to go from 400 ppm to 100% CO_2 is:

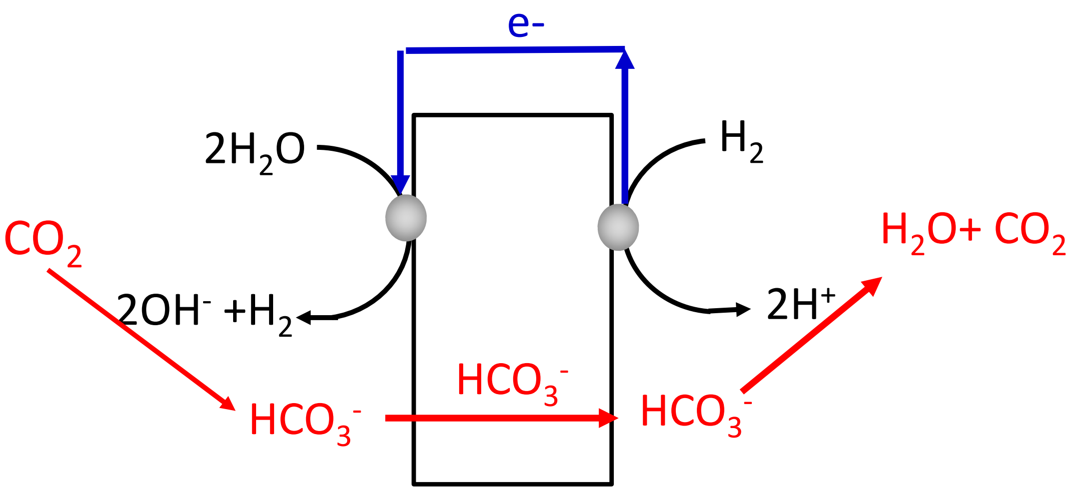
$$\Delta pH_{minimum} = \frac{19.4\,\frac{kJ}{mol}}{5.71\,\frac{kJ}{mol}} = 3.4$$

- If we want reasonable driving force, we are probably looking at pH 4.
- Given HCO_3/CO_2 has neglible catalytic barrier energetically we should have minimal energy losses if we can design a good system.

pH swing CO_2 capture – practical example

- From fuel cell/electrolyzers we know H^+/H_2 redox reaction has minimal overpotential with Pt. (We also know Pt use is so minimal to not have any notable cost issues.)

- We can make an ‘electrolyzer’ that uses H^+/H_2 as a redox couple to induce a pH build-up



Anion exchange membrane

- The H_2 produced at the cathode, is used at the anode, thus no change in hydrogen

pH swing CO_2 capture – practical example

- If I have no overpotential, and no membrane resistance, what voltage will my device need to operate if I want a pH gradient of 4?

Nernst Equation

$$\Delta E = -\frac{RT}{nF} ln\left(\frac{Products}{Reactants}\right) \Longrightarrow \Delta E = 59mV * pH$$

$$\Delta E = 236\,mV$$

- What practical issues would we get that would make this device unworkable? (Think fuel cells)
  - Answer: O_2 from the inlet stream would reduce to water instead of water to H_2 (It is 1.23V easier). To resolve this you would need a pre-step to remove O_2.

Direct Air Capture (DAC)

- A major issue with direct air capture is mass transfer. You need a lot of 400 ppm CO_2 air to capture 1 ton of CO_2.

- If I want a 2m x 2m device to capture 1 ton/day CO_2, what velocity of air at 25 °C do I need to run through it.

Rendering of CO_2 capture

doi: 10.1126/science.aau4107

$$1\ ton\ CO_2 = \frac{1{,}000 kg}{44\ \frac{kg}{kmol}} = 23\ kmol$$

$$V_{CO2} = \frac{nRT}{P} = \frac{23kmol * 0.082 \frac{L\ atm}{mol\ K} * 298K}{1atm} = 562{,}000L = 562\ m^3$$

$$\frac{V_{CO2}}{V_{Total}} = \frac{400}{1\ million} \Rightarrow V_{Total} = 1.4\ million\ m^3$$

Direct Air Capture (DAC)

$V_{Total} = 1.4\, million\, m^3$

Seconds in a day= 3600 s/hr *24 hr/day= 86,400 seconds = 0.0864 million seconds

Volumetric flow rate needed = 1.4/0,086 = 16,2 m^3/s

Area of device= 2m x 2m= $4m^2$

$$v = \frac{16\,\frac{m^3}{s}}{4m^2} = 4\,\frac{m}{s}$$

- How much power will that take to move the fans?

Density of air

~ 1.2 kg/m^3 at 25 °C

From Wind Energy lecture: $P_{wind} = P_{Fan} = {}^1/_2\, S\rho v^3$= ½*4*1.2*$4^3$= 154W

154W * 86400 s/day *1 kW/1000W = 13,271 KJ/day =3.7 kWh/day

This assumes no resistance due to the CO_2 absorber (unrealistic) ↗

- Do we need to consider Betz limit for fans?

  Ans = Yes, thus we need to divide power by 59% or lower (3.7/0.59= 6.3 kWh/day)

Direct Air Capture (DAC)- pore size

- The low CO_2 concentration means air resistance will be a much greater issue with DAC compared to flue gas capture
- Decreasing absorber density helps resolve this, but also means more volume (Capital costs) is needed

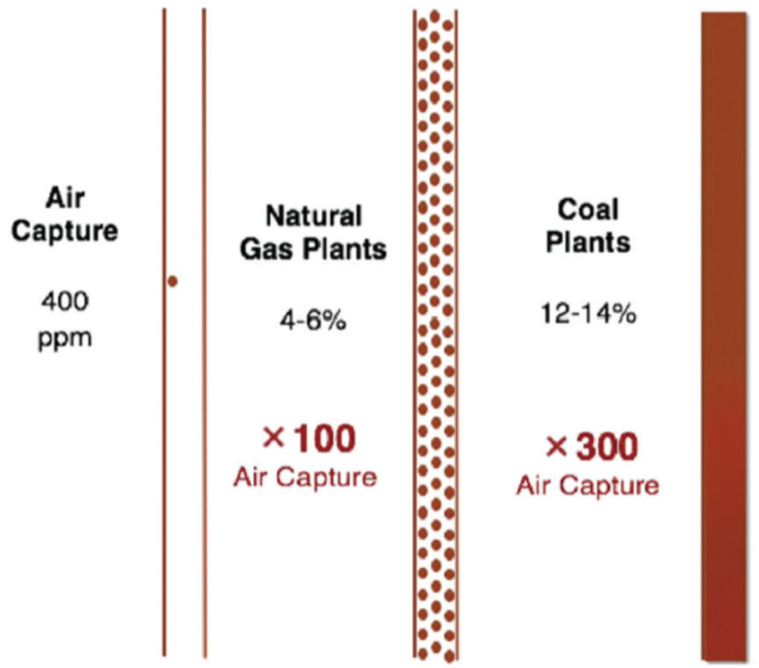


Fig. 26 In the case of adsorption, the optimal pore size depends upon the dilution of CO_2 in the gas mixture.

Doi: 10.1039/c7ee02342a

Biggest companies

climeworks

- Swiss company. First company in DAC started in 2009. Demo plants in 2017, full commercial plants in 2021. Use MOF catlayst produced by Svante.

Carbon Engineering

- Canadian company. Demo plant in 2015. KOH captures CO_2, then a Ca-K carbonate switch, and then heat $CaCO_3$ to release CO_2.

captura

- Focuses on ocean capture of CO_2/carbonate. Uses a bipolar membrane approach. USA company derived from CalTech

AKER CARBON CAPTURE

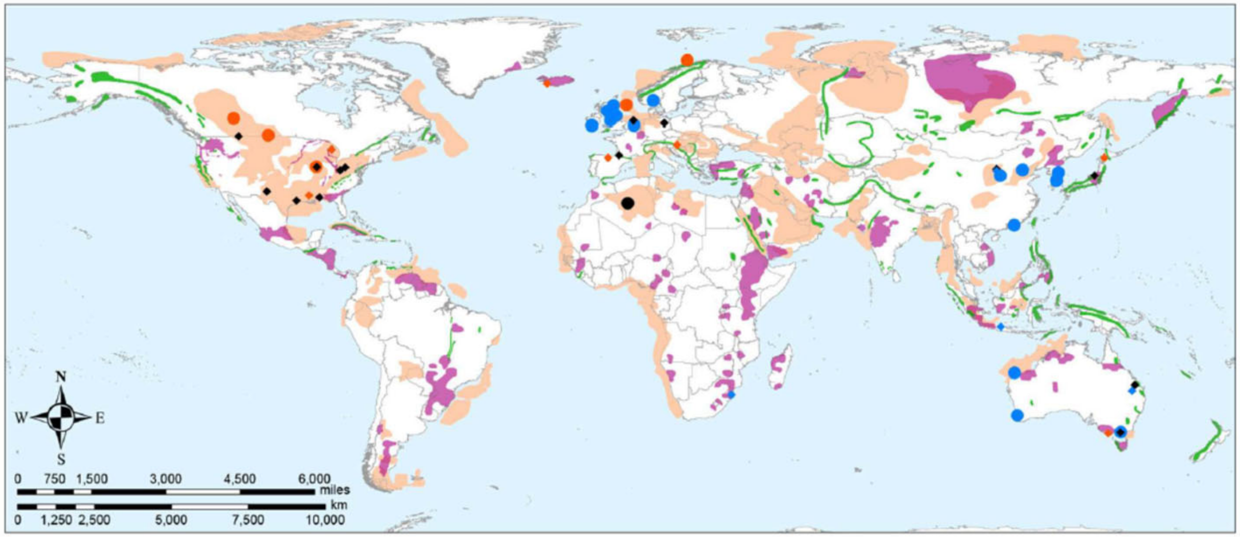
- Norweigian company (with branch in Denmark). Use organic amines. Lot of work with flue gas. Is doing CO2 capture in Kalundborg & Avedøre in Denmark.

CO_2 storage

There are better ideas than this

CO_2 storage – overall numbers

- According to IPCC to maintain 1.5 C, we should sequester 125 Gton by 2100.
- The combined underground storage capacity in saline aquifers and hydrocarbon reservoirs is estimated to range between 5,000 and 25,000 Gton CO_2.
- The cheapest storage costs are said to be 7-30 \$/ton CO_2.



CO_2 sequestration facilities, projects, and opportunities

Doi: 10.3389/fclim.2019.00009

CO_2 storage – Overall numbers

- According to IPCC to maintain 1.5 C, we should sequester 10 Gton/yr.
- Storing capacity is 64 MtonCO_2/year (as of July 2025) for pure CCS.
- 28 Mton/yr CO_2 'storage' for enhanced oil recovery

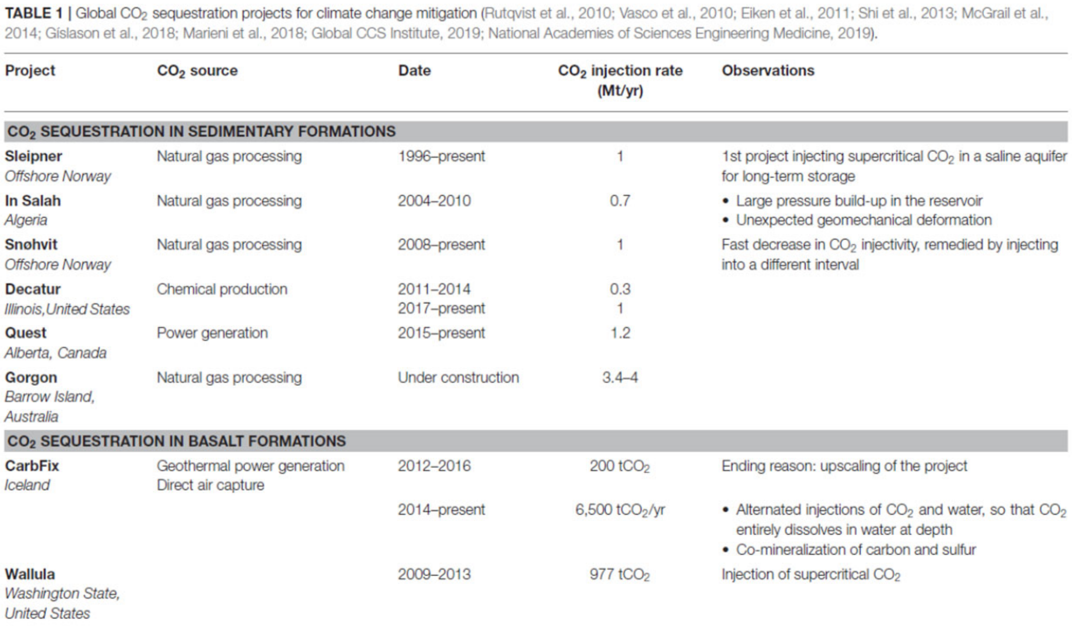
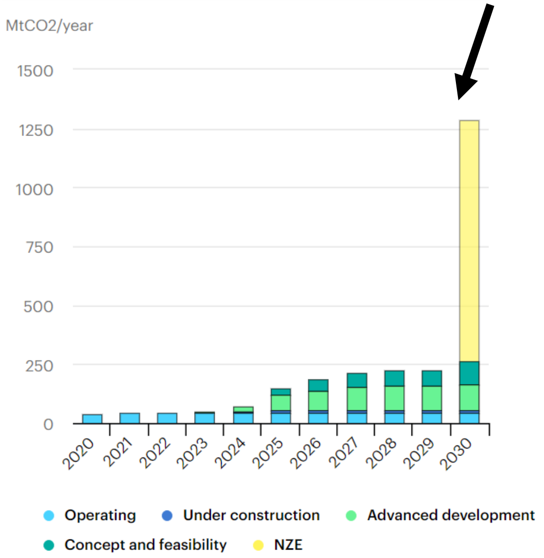


TABLE 1 | Global CO_2 sequestration projects for climate change mitigation (Rutqvist et al., 2010; Vasco et al., 2010; Eiken et al., 2011; Shi et al., 2013; McGrail et al., 2014; Gislason et al., 2018; Marieni et al., 2018; Global CCS Institute, 2019; National Academies of Sciences Engineering Medicine, 2019).

Project	CO_2 source	Date	CO_2 injection rate (Mt/yr)	Observations
CO_2 SEQUESTRATION IN SEDIMENTARY FORMATIONS				
Sleipner *Offshore Norway*	Natural gas processing	1996–present	1	1st project injecting supercritical CO_2 in a saline aquifer for long-term storage
In Salah *Algeria*	Natural gas processing	2004–2010	0.7	• Large pressure build-up in the reservoir • Unexpected geomechanical deformation
Snøhvit *Offshore Norway*	Natural gas processing	2008–present	1	Fast decrease in CO_2 injectivity, remedied by injecting into a different interval
Decatur *Illinois, United States*	Chemical production	2011–2014 2017–present	0.3 1	
Quest *Alberta, Canada*	Power generation	2015–present	1.2	
Gorgon *Barrow Island, Australia*	Natural gas processing	Under construction	3.4–4	
CO_2 SEQUESTRATION IN BASALT FORMATIONS				
CarbFix *Iceland*	Geothermal power generation Direct air capture	2012–2016	200 tCO_2	Ending reason: upscaling of the project
		2014–present	6,500 tCO_2/yr	• Alternated injections of CO_2 and water, so that CO_2 entirely dissolves in water at depth • Co-mineralization of carbon and sulfur
Wallula *Washington State, United States*		2009–2013	977 tCO_2	Injection of supercritical CO_2

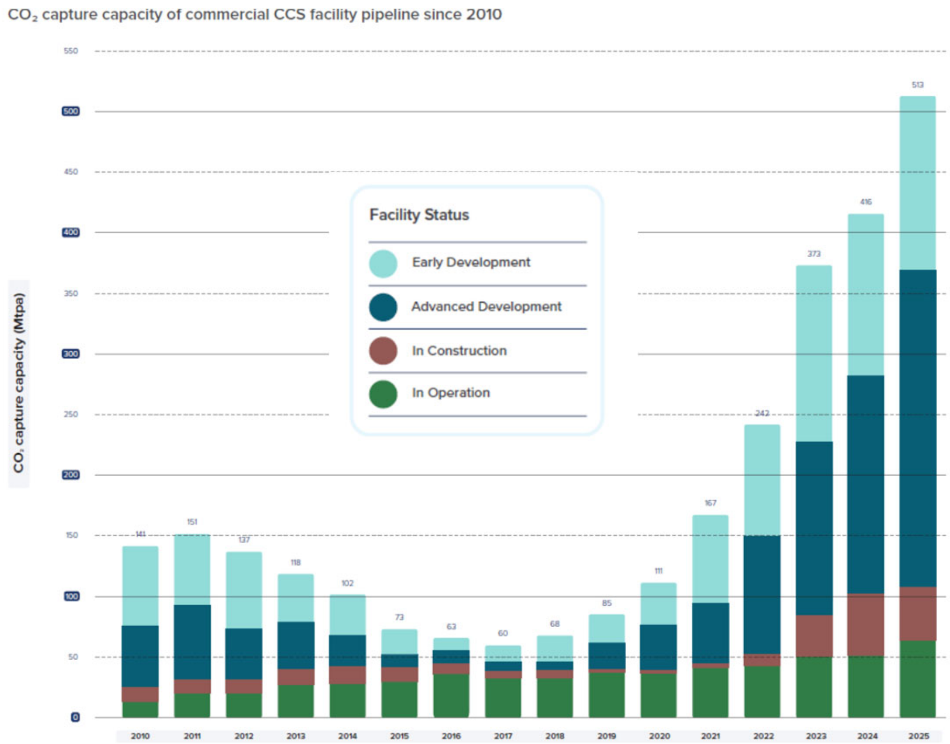
Doi: 10.3389/fclim.2019.00009

IEA version of net zero
(10x lower than IPCC value)

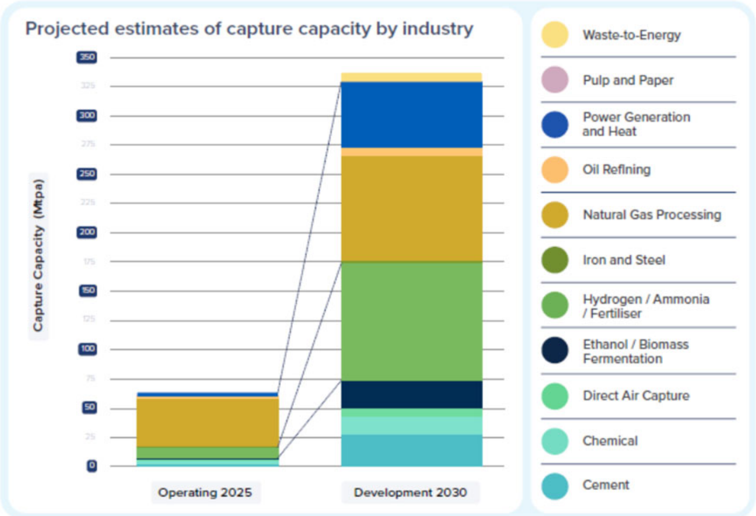


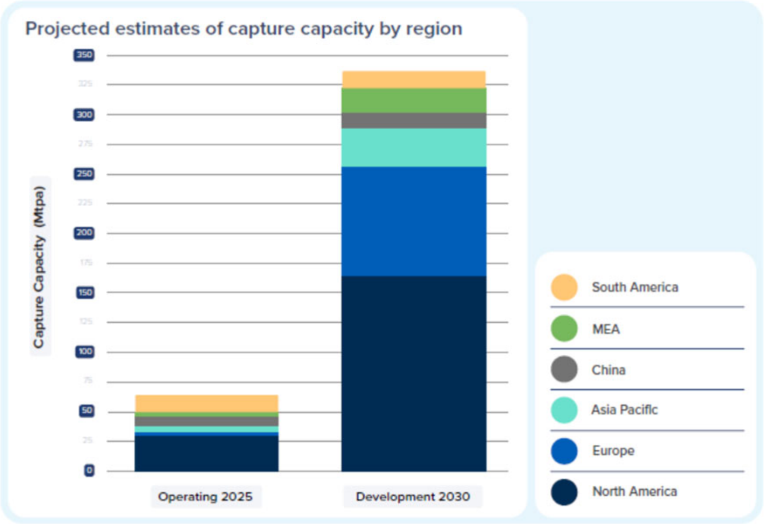
IEA Data

CO_2 storage – Overall numbers



[Global Status of CCS Report, 2025]



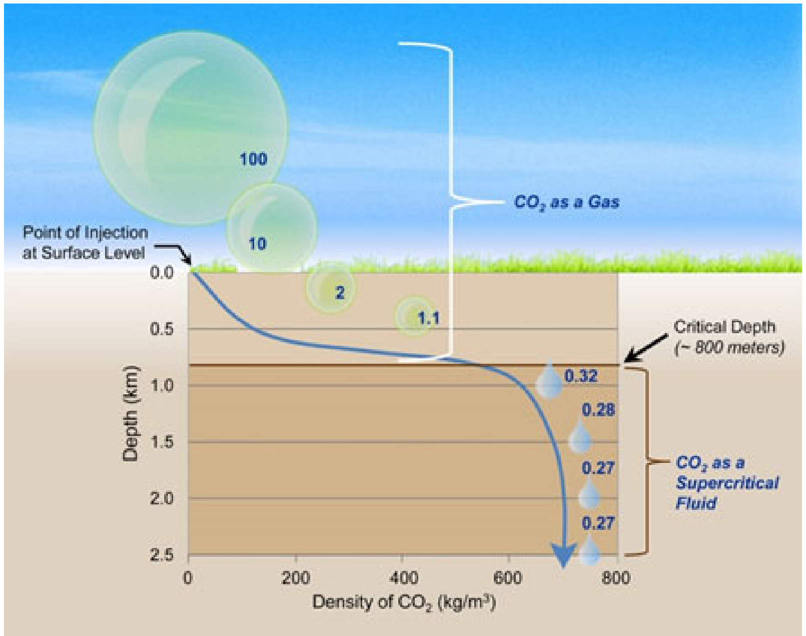


CO_2 storage - Underground

- CO_2 becomes supercritical at 31 °C and 73 atm

CO_2 State	Temperature (K)	Pressure (bar)	Density (kg/m^3)
Liquid	298	100	819
Supercritical	305	300	941
Supercritical	350	80	164

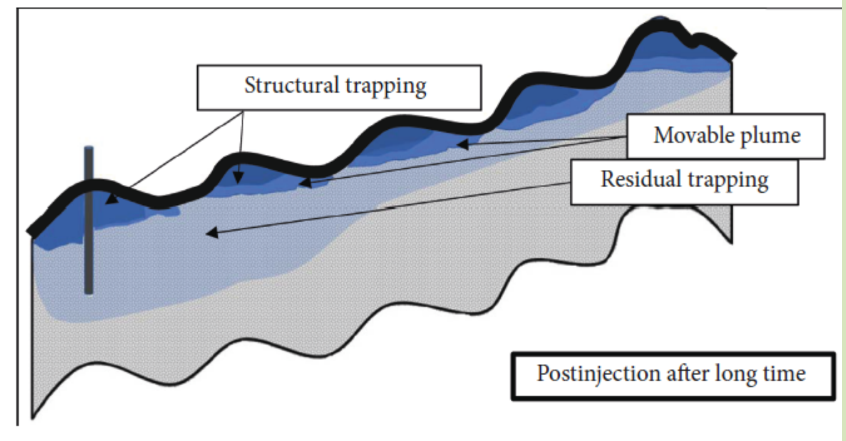
- The deeper we go into the Earth, the higher the natural temperature and pressure
- 800m into Earth, should give us a supercritical temperature (i.e > 31 ° C)



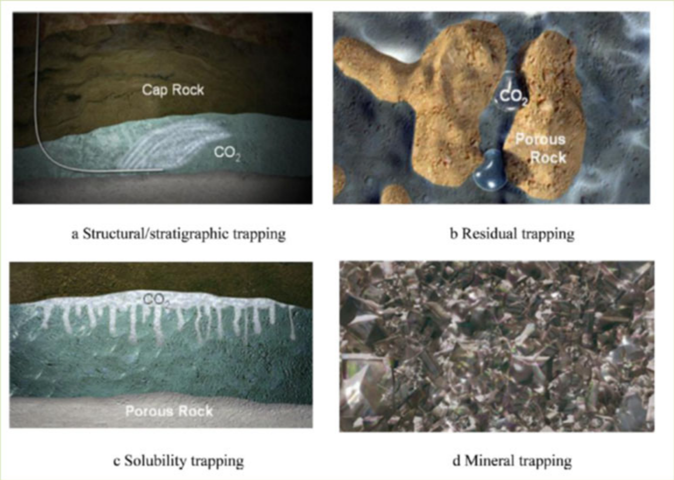
Netl.doe.gov

CO_2 Storage - methods

- The 4 major types of CO_2 storage are
  - Structural trapping
  - Residual trapping
  - Solubility trapping
  - Mineral trapping



Doi: [10.1155/2021/7762127](https://doi.org/10.1155/2021/7762127)



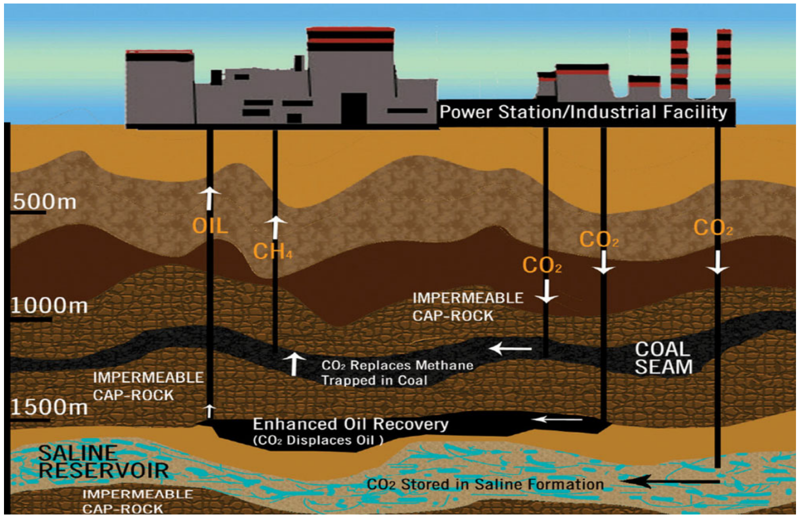
a Structural/stratigraphic trapping
b Residual trapping
c Solubility trapping
d Mineral trapping

Doi: [10.1016/j.joei.2014.03.032](https://doi.org/10.1016/j.joei.2014.03.032)

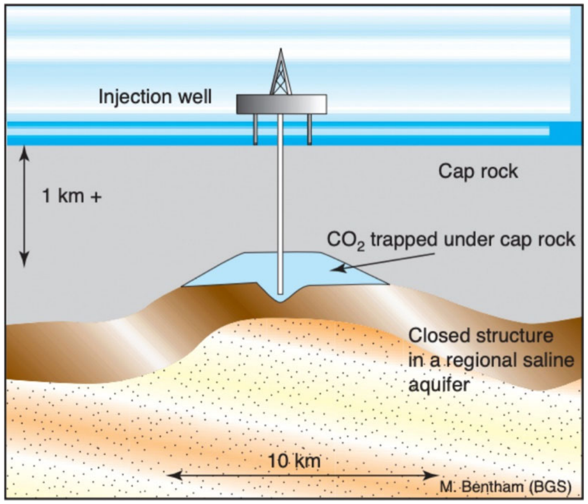
- Stuctural trapping is trapped like a bottle, whereas residual is trapped like in a sponge

Reservoir rocks vs. Caprocks

- Caprocks are solid and on top, whereas reservoir rocks are porous and on the bottom
- Caprocks are best as anhydrite ($CaSO_4$) or low permeability carbonate rocks.
- Reservoir rocks are best as sandstone (SiO_2), limestone ($CaCO_3$), dolomite ($CaMgCO_3$), or basalt (lava).



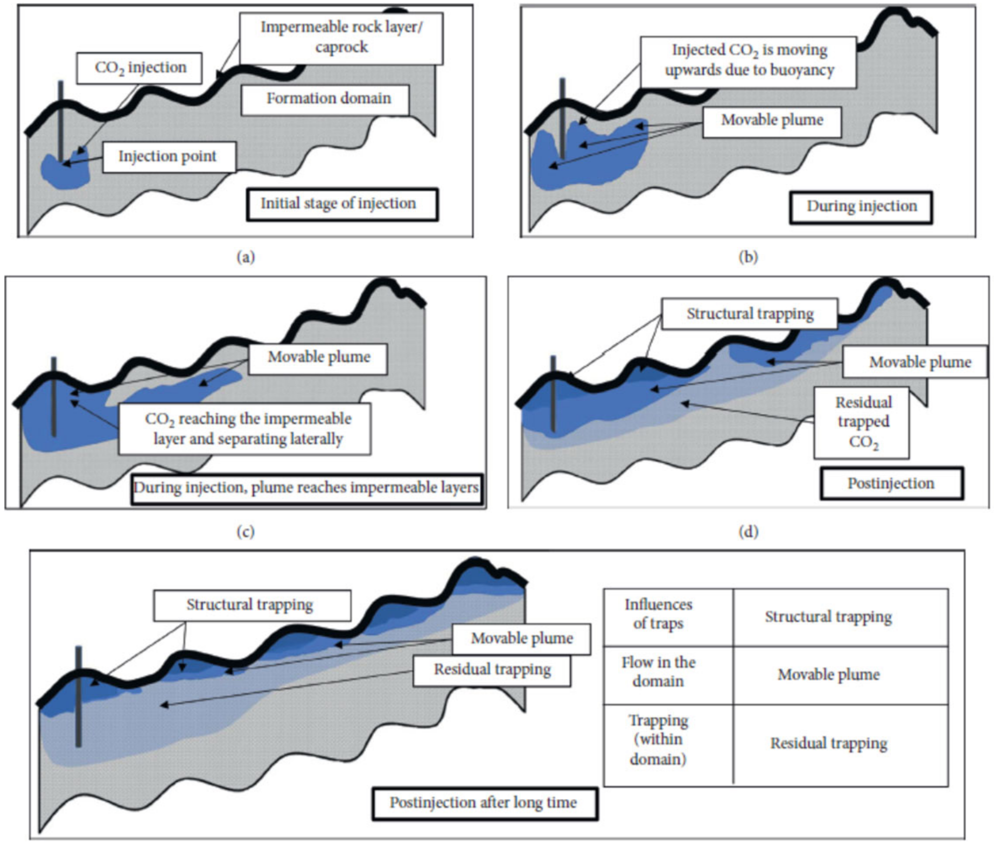
Link



Doi:10.2516/ogst:2005038

CO_2 plumes and modeling

- The mass transfer of CO_2 from pipe to throughout the resevoir is important.
- As every resevoir is different, thus each a unique CO_2 diffusion and thus storage rate.
- The general trend is a movable plume goes through and a slower residual trapping builds from that



Doi: 10.1155/2021/7762127

CO_2 storage - Underground

- CO_2 starts as physically stored, but then gets slowly mineralized

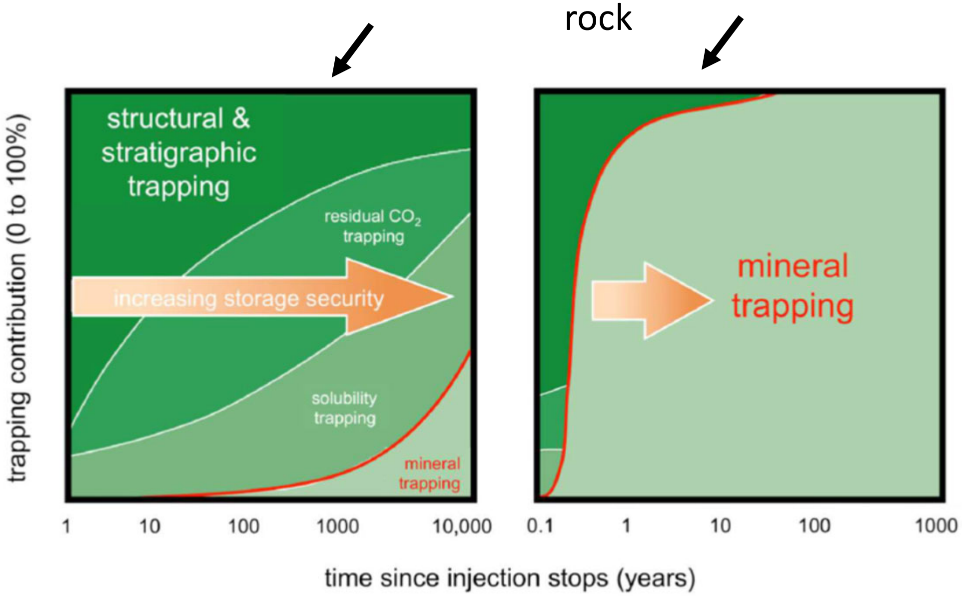
  - Residual trapping is replacing fluids that was in rock pores via capillary forces.

  - Once in the reservoir the CO_2 soubilizes in the aqueous solution

  - Finally it reacts to form stable carbonate species.

In SiO_2 dominated rock

In mafic (Mg, Fe dominant) rock



Doi: 10.3389/fclim.2019.00009

Learning Objectives

- How plants capture CO_2
- How industry captures CO_2 currently
- How direct air capture works
- How pH swing CO_2 capture works
- Physics behind CO_2 storage

Exercises

1. Determine the Gibbs free energy difference going from MnO and CO_2 to $MnCO_3$. This should give perspective on how effective CO_2 mineralization can be.

2. The drag coefficient for a species is $F_D = \frac{1}{2}\rho v^2 C_D A$ If I have a drag coefficient of 5, the density of air is 1.2 kg/m^3 , operating at the Betz limit and the fan is 1m thick, how much extra power will I need for the direct air capture fans that we calculated for as an in-class exercise? Assume same velocity and area of the device. If we double the air flow (i.e. amount of CO_2 captured/time) how would that effect the power of the fans?