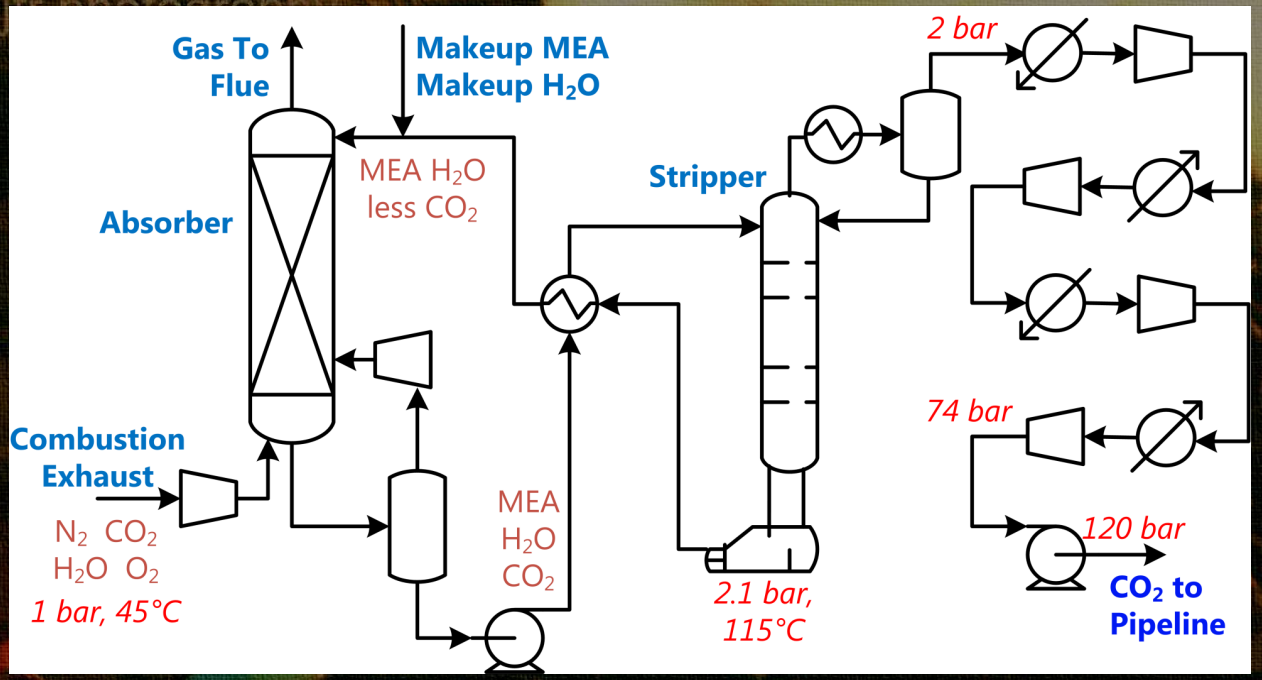
CO_2 Capture and Sequestration

For Current and Near-Commercial Technologies



Thomas A. Adams II
McMaster University
Department of Chemical Engineering
McMaster Advanced Control Consortium
McMaster Institute for Energy Studies

Lecture 4.2 – 2018 Edition

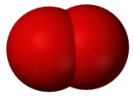
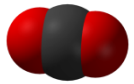
Post Combustion Carbon Capture

(What we can do now)

Fundamental Problem of CO_2 Capture and Sequestration

- Fundamental problem: separation of CO_2 and N_2 in flue gases:
  - We need to go from dilute to high purity
- We need to go from low pressure to high pressure
- And there's an awful lot of it (~7 million ton/yr per coal power plant).

TYPICAL COAL POWER FLUE EXHAUST, 1 BAR

	Mol %	Kinetic Diameter (Images to Scale)
N_2 (&Ar)	68%	3.6 Å
O_2	2%	 3.45 Å
CO_2	13%	 3.30 Å
H_2O	17%	2.7 Å

CO_2 PIPELINE LIMITS, 120 BAR

	Kinder Morgan	Sleipner
N_2 (&Ar)	<4%	3-5%
O_2	<50ppm	<50ppm
CO_2	>95%	93-96%
H_2O	<690ppm	<Saturated

Sources: NETL 2007 - Bituminous Baseline Report (see required reading). Adams & Barton, AIChE J (2010)
deVisser E., et al. Dynamis CO2 quality recommendations. Int. J. Greenhouse Gas Cont. 2008, 2, 478–484
Molecule Images from chemistry.about.com. Sizes from Angew. Chem. Int. Ed. 2010, 49, 6058 – 6082.

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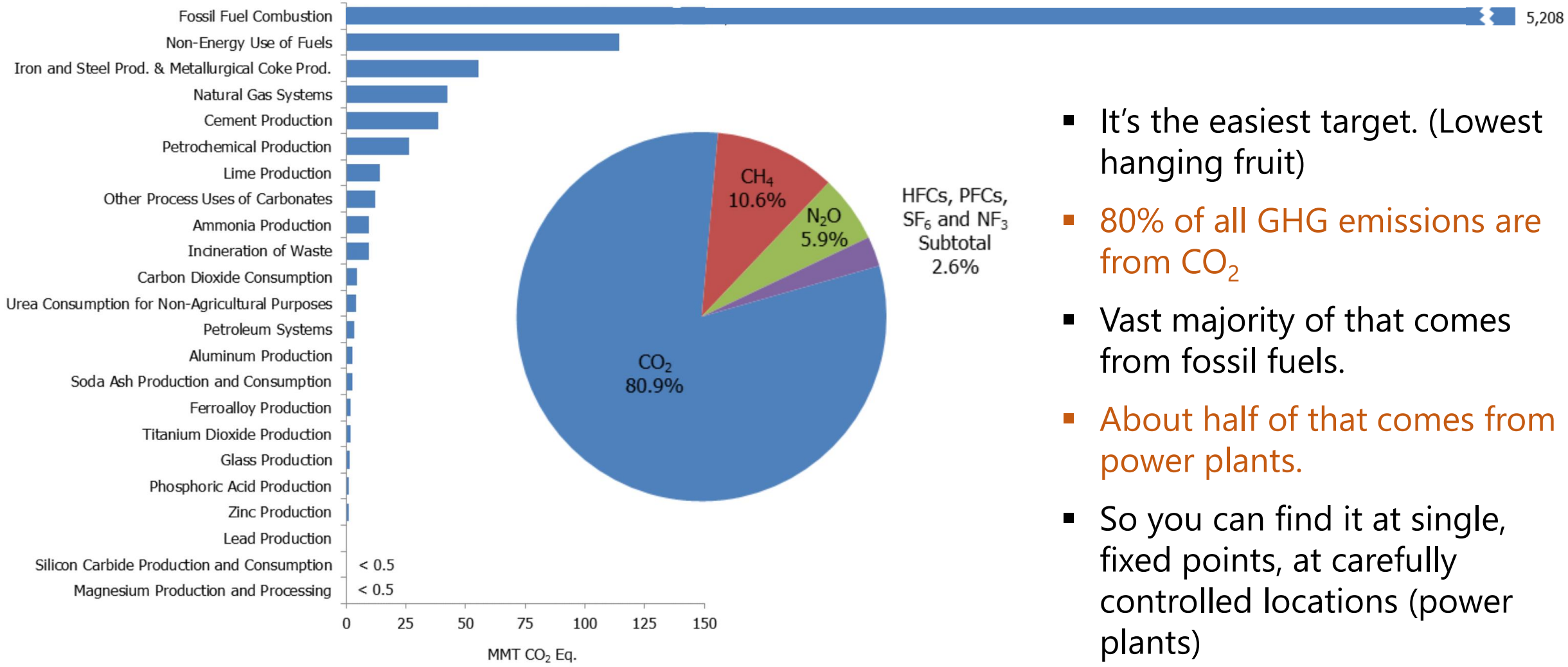
Why focus on CO_2 and not other GWGs?



- It's the easiest target. (Lowest hanging fruit)
- 80% of all GHG emissions are from CO_2
- Vast majority of that comes from fossil fuels.
- About half of that comes from power plants.
- So you can find it at single, fixed points, at carefully controlled locations (power plants)

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Sources: US EPA: US Greenhouse Gas Inventory 2016 (1990-2014)

Once-Through Approaches

- Possible strategy: react the CO_2 into a solid, stable form.
- Example: "Skyonic" process:

$$2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2$$

salt — sodium hydroxide — hydrogen — chlorine

$$2NaOH + CO_2 \rightarrow Na_2HCO_3 + H_2O$$

sodium hydroxide — washing soda

$$Na_2HCO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$$

washing soda — baking soda (solid precipitate)

- Discuss: what challenges do you see? Is this a good or bad idea? Is it profitable? Will it help the environment? Energy balances?
  - June 25, 2012: Skyonic raises $9 million. BP and Conoco backed.

Sources: http://www.reuters.com/article/2012/06/25/us-skyonic-carboncapture-idUSBRE85O1C920120625

Once-Through Discussion Notes

- To form sodium hydroxide, you produce H_2 from low-energy reagents
  - need energy input (electrolysis process)
- What do you do with the baking soda?
  - water soluble
  - biodegradable ($2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$), ($Na_2Co_3 \rightarrow NaO + CO_2$)
- CO_2 from one supercrit. coal plant: ~7 million ton/year
- Baking soda from one plant: ~13 million ton/year
- North American baking soda market: ~0.7 million ton/year
- Baking soda from all coal in North America: ~8,000 million ton/year
- World Salt Production: ~250 million ton/year

Sources: http://www.gjsentinel.com/news/articles/high_demand_for_baking_soda_dr/. http://www.saltinstitute.org/Production-industry/
NETL 2007 - Bituminous Baseline Report (see required reading).

Absorption-based Methods

- Physical Solvents
  - Think of it as the solute (CO_2) fitting in the spaces between solvent molecules in solution. Van der Waals forces, etc.
  - Rectisol™ (methanol), Selexol™ (Dimethyl ethers and glycols), 40 years of experience
  - Ionic liquids: future possibility.
    - Ions in solution (molten organic salts) have very low volatility, easier to r
    - Thus easier to regenerate.
    - Weak association between ionic liquid and CO_2 molecules
- Chemical Solvents
  - The solute form ionic bonds to the solvent molecules, forms intermediate species in solution. Like a chemical reaction.
  - Monoethanolamine (MEA, 50 years of experience), Diethanolamine (DEA), Methyldiethanol Amine (MDEA),

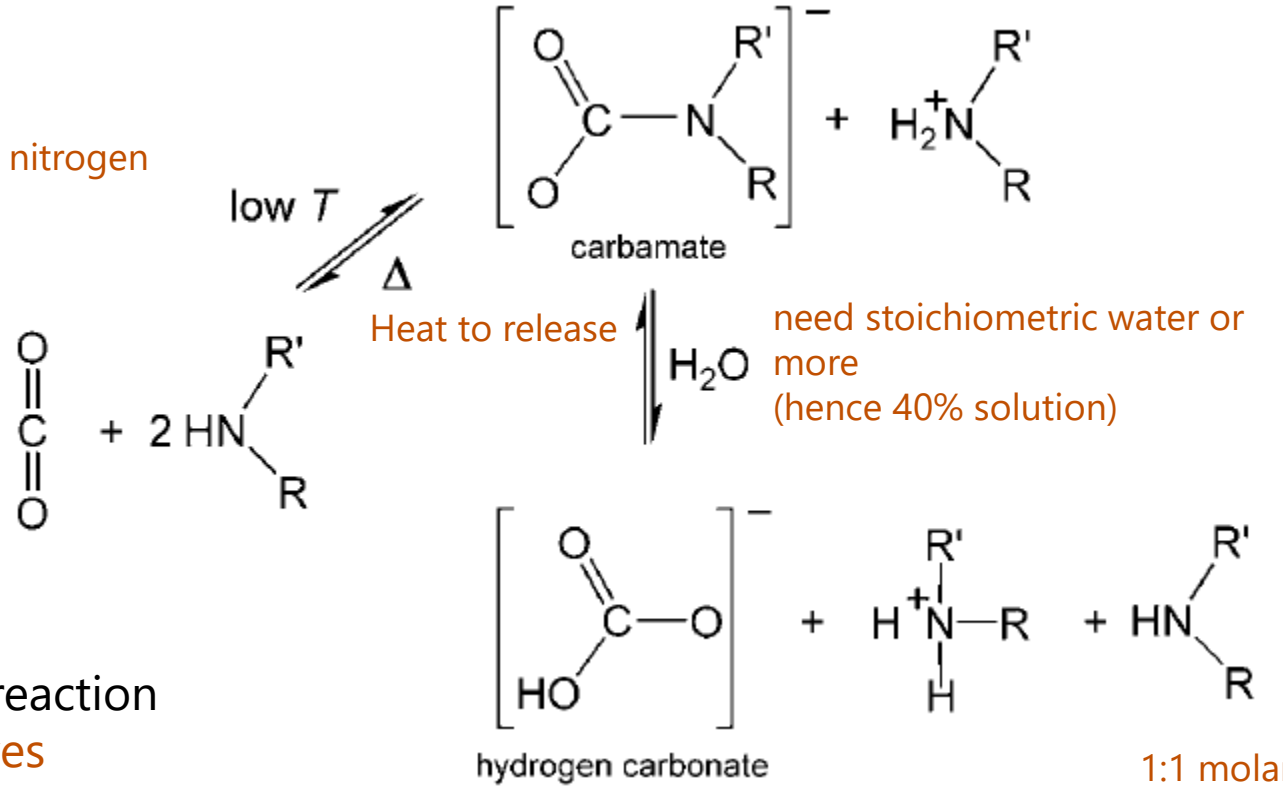
Sources: D'Alessandro et al. Angew Chem Int Ed, 49, 6058-6082 (2010)

MEA Chemical Absorption

- Aqueous MEA (40% solution) is the solvent

Forms a carbamate ion

CO_2 reacts with nitrogen



need stoichiometric water or more
(hence 40% solution)

The chemical reaction framework gives excellent selectivity for CO_2

And in aqueous solution forms the carbonate

1:1 molar capacity ratio (at 100% solvent efficiency)

Sources: D'Alessandro et al. Angew Chem Int Ed, 49, 6058-6082 (2010)

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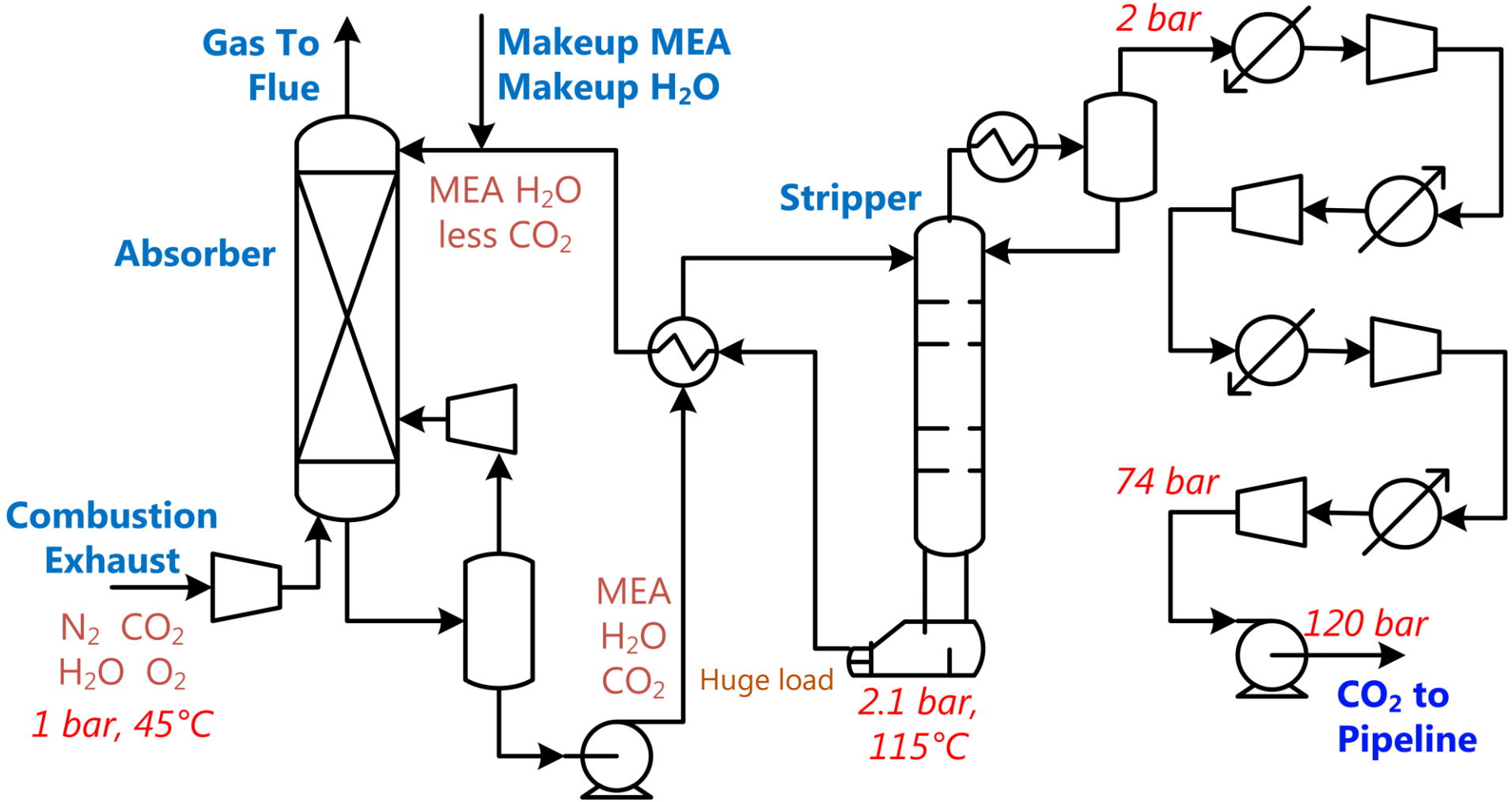
MEA Example



Sources: NETL Bituminous Baseline (2007), see required reading. Adams and Barton, AIChE J (2010).
Xu et al, App Mech Maters Vols 130-124,3807-3811 (2012)

We do this now! Canada world's leader!

- Built in 2014.
  - 109 MW scale average as of 2017
  - 83% Uptime
  - 58% Capture Rate
- Captured CO_2 Pipelined.
  - About half for EOR
  - Half for sequestration
- Note large CO_2 capture footprint

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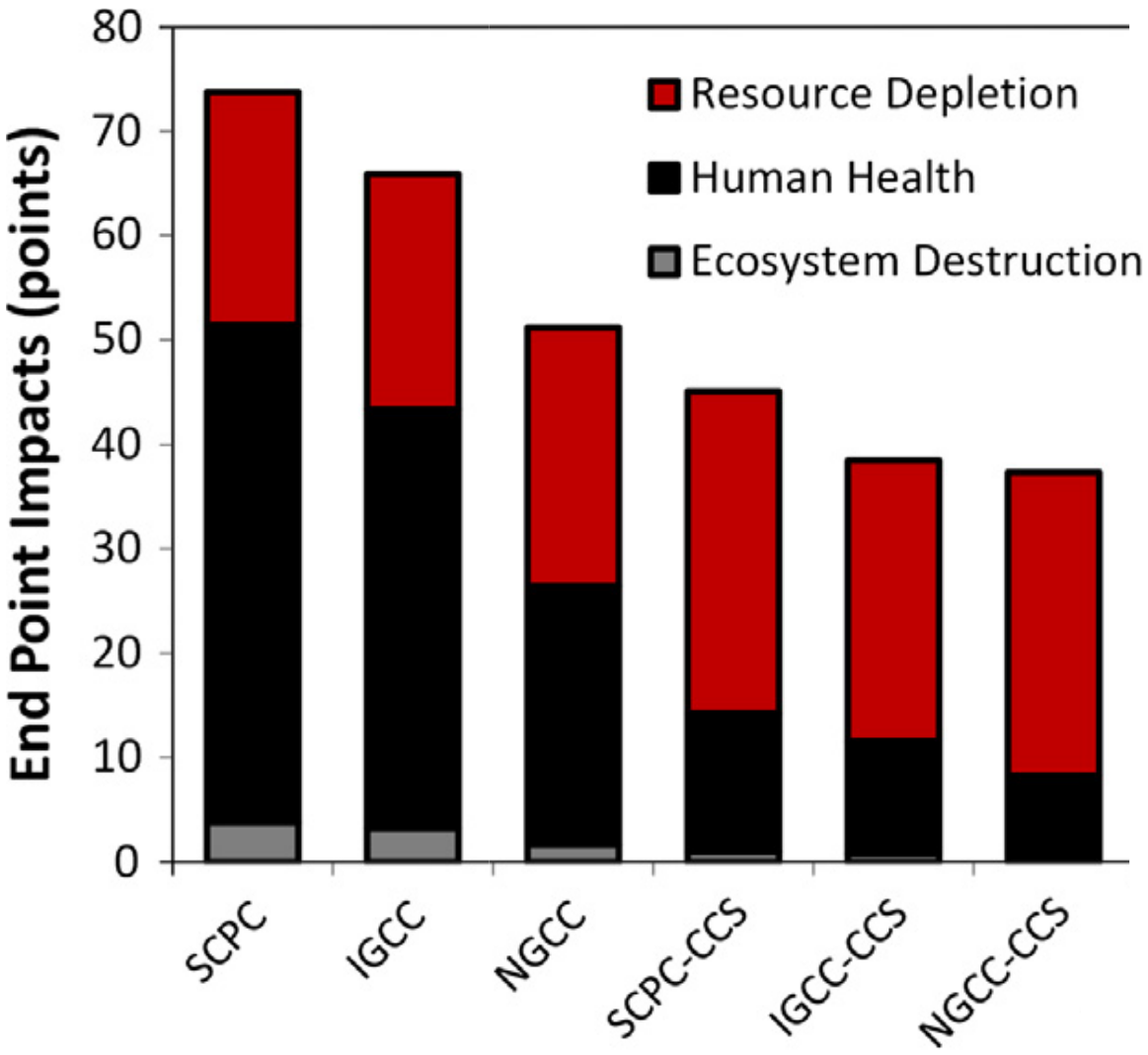
Sources: SaskPower.com, Boundary Dam Carbon Capture Project
Adams TA II, Hoseinzade L, Okeke IJ, Madabhushi P. *Processes 5*, 44. (2017). doi:10.3390/pr5030044

Life Cycle Impacts Must be Considered

Capturing 90% of the CO_2:

1. Reduces efficiency from about 38% to 25% (HHV)
2. Reduces CO_2 emissions only by 80% because you have to burn more coal to make up for the power loss.
3. Total life cycle impacts only reduce 25-35%



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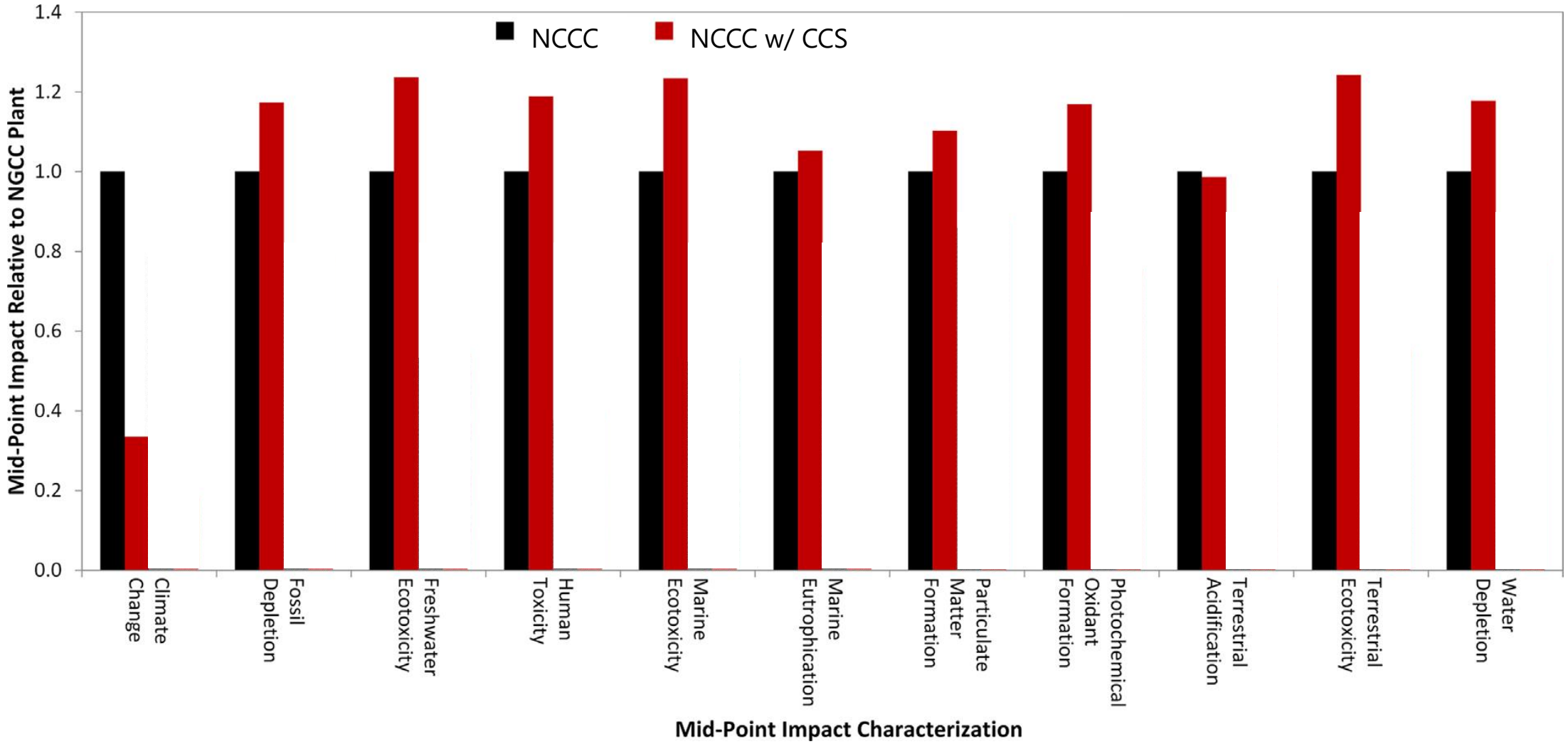
Sources: Nease J, Adams TA II. *Applied Energy* 150:161-175 (2015).
Adams TA II, Barton PI. *J Power Sources* (2010)

CCS is worse in *almost* every impact category.



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Sources: Nease J, Adams TA II. Life Cycle Analyses of Bulk-Scale Solid Oxide Fuel Cell Power Plants and Comparisons to the Natural Gas Combined Cycle. *Canadian J Chem Eng*, 93:1349-1363 (2015).

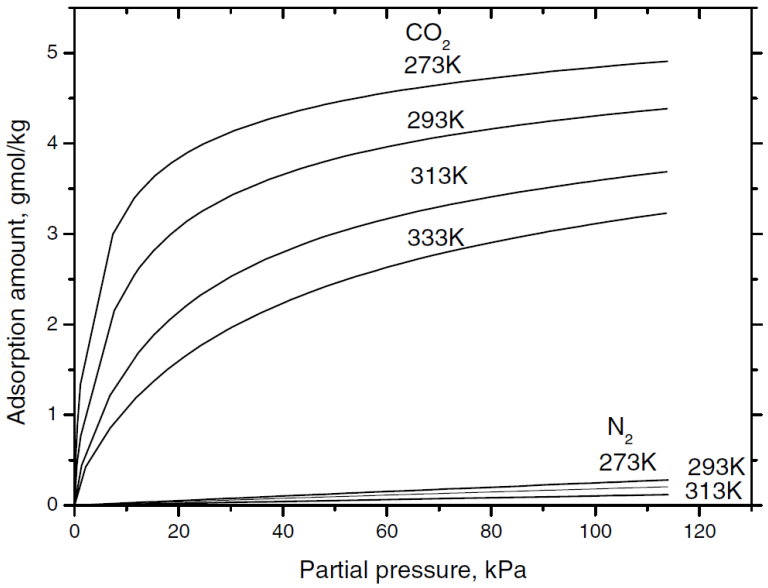
Adsorption-based Methods

- Typical adsorbant materials include:
  - Activated carbon (physical)
  - Zeolites (physical)
  - Titanosilicates
  - Alumina
  - Calcium Oxide (chemiosorption)
- Pressure Swing and Temperature Swing methods possible
- However! Almost nothing being used for post-combustion flue gases commercially.
  - Not developed yet? Not a good idea?

Sources: Ebner & Ritter. Sep Sci Tech, 44, 1273-1421 (2009). See esp. p1297. D'Alessandro et al. Angew Chem Int Ed, 49, 6058-6082 (2010)

TSA vs. PSA

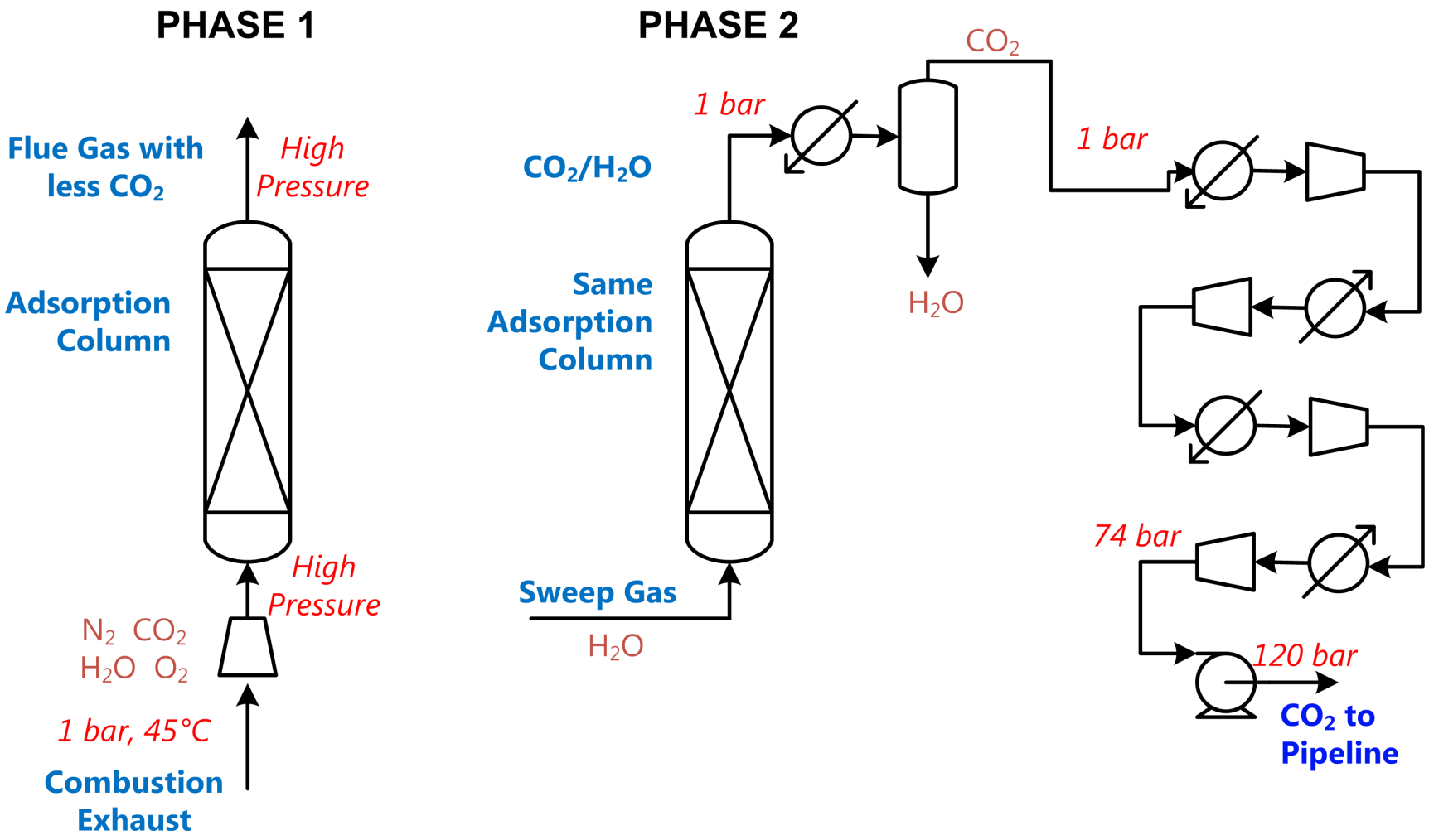
- PSA is hard because:
  - Adsorb at high pressure, but we start with low pressure flue gas!
    - (A) Some adsorbants work at atmospheric pressure
  - Desorb at low pressure, but we want high pressure CO_2!
    - (A continued) But… then you need to desorb at vacuum!
- TSA is hard because:
  - Adsorb at low temperature:
    - Have to cool down the hot flue gas
  - Desorb at high temperature:
    - Have to cool down the hot effluent
  - Continual thermal cycling of the beds is also expensive



Sources: Zhang et al, Energy Convers Manage 49, 346-356 (2008). Plot shown for adsorbent "NaX-UOP"

Overly Simple Pressure Swing Adsorption Example

- Switch when column full
- Use multiple columns in parallel
- Need sweep gas which is "easy" to separate from the CO_2



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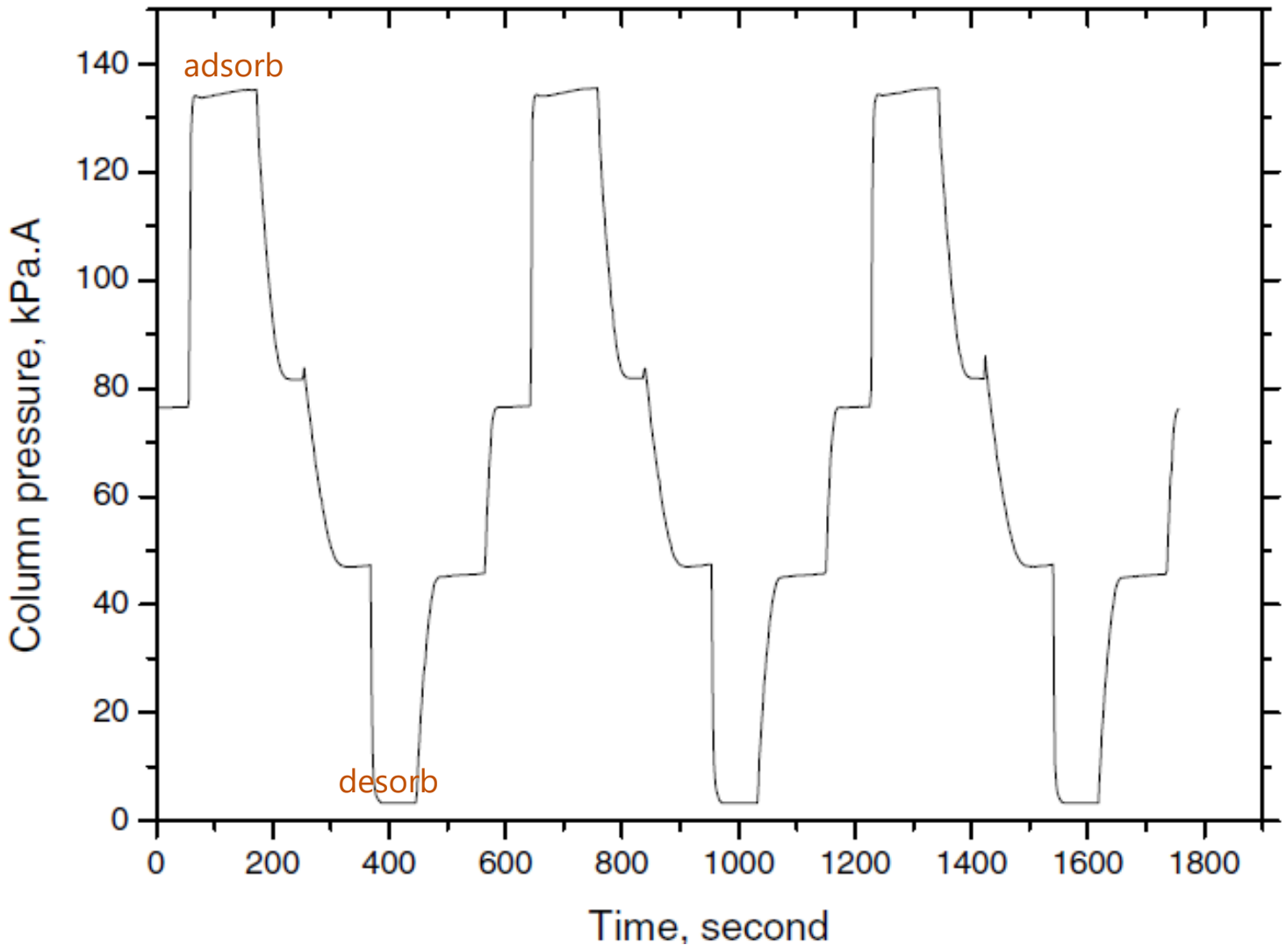
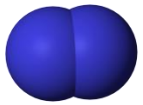
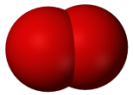
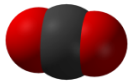
PSA Continued



Sources: Zhang et al, Energy Convers Manage 49, 346-356 (2008). Plot shown for adsorbent "NaX-UOP"

Molecular Sieves / Membranes?

Sources: Mitarien M. Economic N2 Removal. Hydrocarbon Engineering Magazine, Jan 2009.. Ebner & Ritter. Sep Sci Tech, 44, 1273-1421 (2009).

	Mol %	Kinetic Diameter (Images to Scale)
N_2 (&Ar)	68%	 3.6 Å
O_2	2%	 3.45 Å
CO_2	13%	 3.30 Å
H_2O	17%	2.7 Å

- Can we use molecular sieves based on size differences?
- Get something with pores about 3.38 ± 0.2 Å (very difficult!)
  - Have to get enough CO_2 through to be worth it
  - Have to maintain CO_2 purity! (O_2 purities limited to ppm levels)
- Have capability to create pore openings within 0.1 Å! (In different contexts)
- CO_2 has highest MW:size ratio of the bunch → fast permeating, high selectivity
- Yet not yet commercialized for post combustion flue gas capture.
  - (More common for removing CO_2 from natural gas, but still small)
- Basic challenge: CO_2 purity constraints high, volumes are huge. Membranes not good at hitting both targets.

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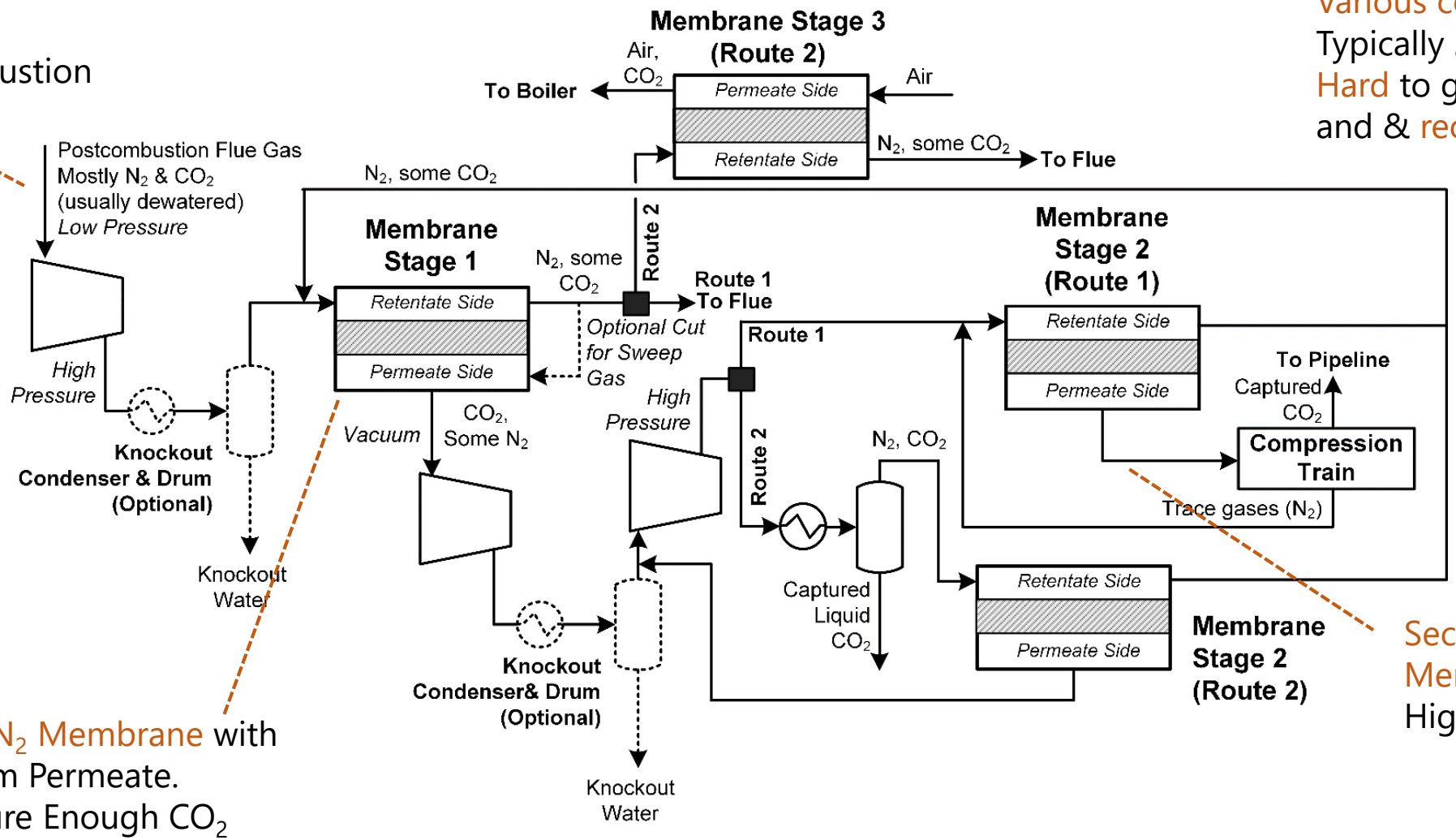
Post-Combustion Membrane-Based Capture

Flue Gas from
Upstream Combustion

Various configurations
Typically 2 or 3 stages
Hard to get both purity
and & recovery



CO_2 / N_2 Membrane with
Vacuum Permeate.
Not Pure Enough CO_2

Second CO_2 / N_2
Membrane
Higher Purity CO_2

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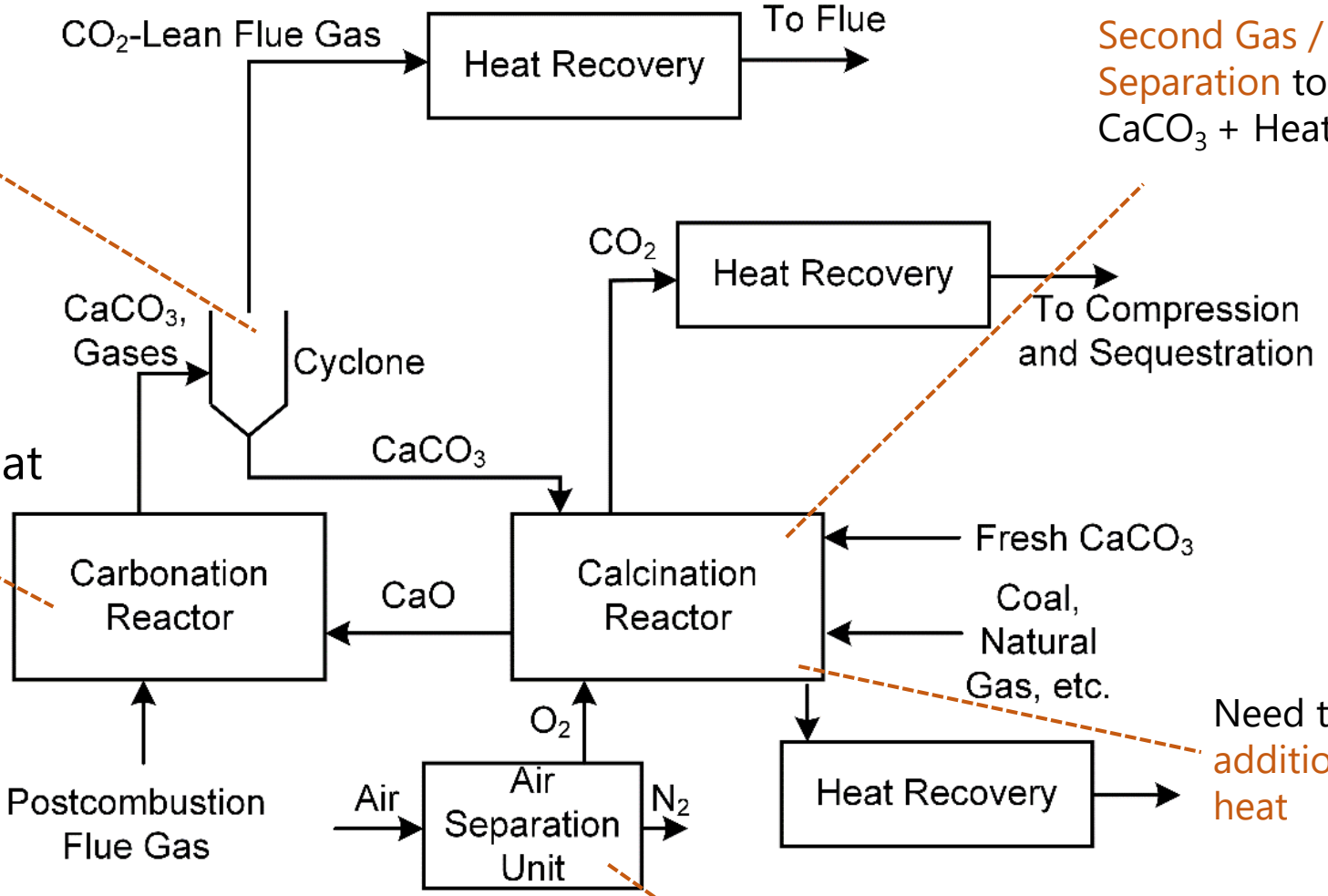
Source: Adams TA II, Hoseinzade L, Madabhushi P, Okeke IJ. Processes 5:44 (2017).

Post-Combustion Solid-Based Capture

Solid Calcium Carbonate
Cycloned from rest of flue gases

Second Gas / Solid Separation to release CO_2.
$CaCO_3 + Heat \rightarrow CaO + CO_2$

$CaO + CO_2 \rightarrow CaCO_3 + Heat$



Need to burn additional fuel for heat

Need High Purity Oxygen to prevent N_2 injection

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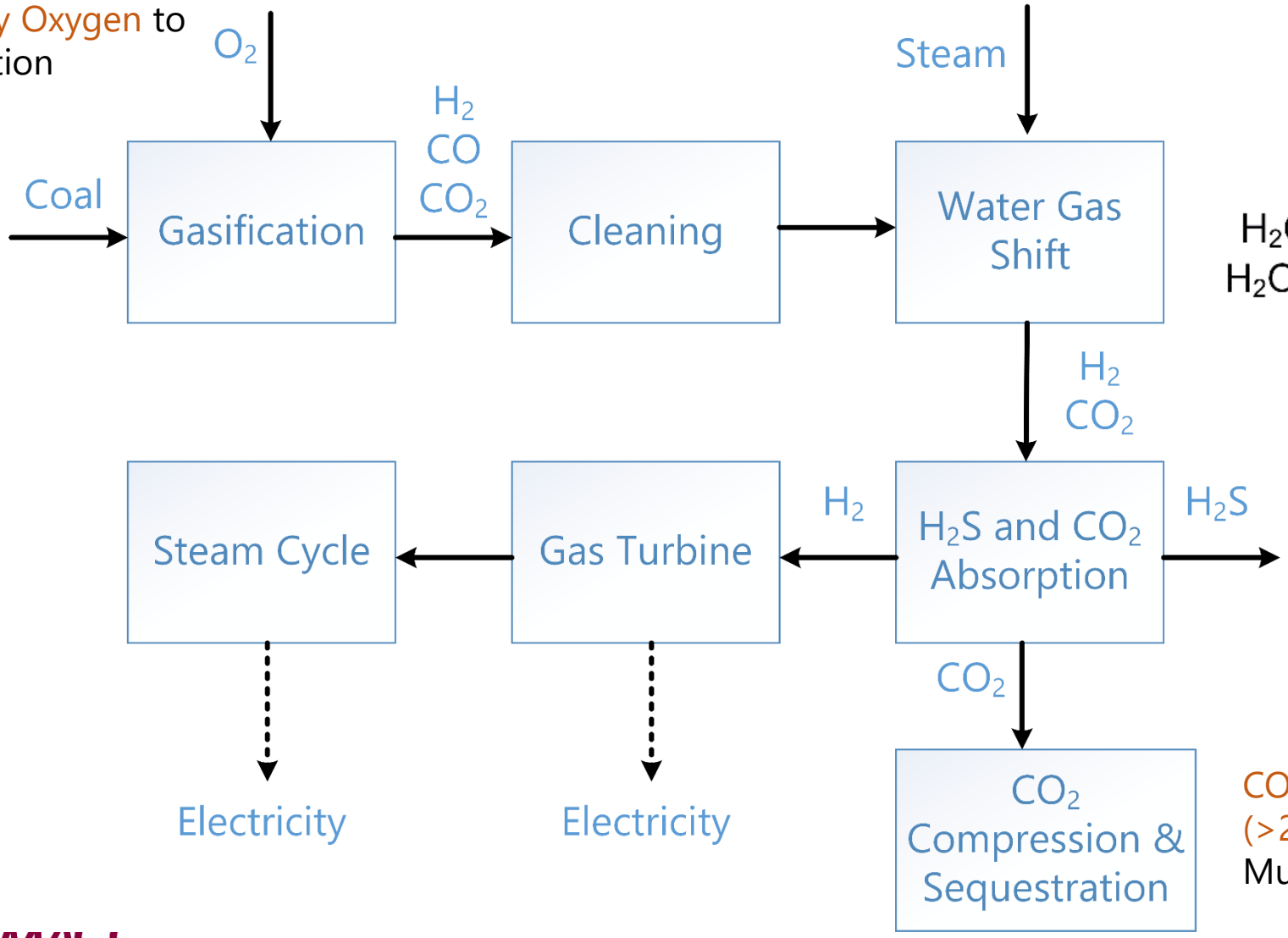
Source: Adams TA II, Hoseinzade L, Madabhushi P, Okeke IJ. Processes 5:44 (2017).

Pre-Combustion Solvent-Based Capture (IGCC)

Need High Purity Oxygen to prevent N_2 injection



WGS Reactors

$H_2O + CO \rightarrow CO_2 + H_2$

$H_2O + COS \rightarrow CO_2 + H_2S$

Selexol or Rectisol Solvents

Capture H_2S and CO_2 in separate stages

H_2/CO_2 Separation Principle

CO_2 captured at higher pressures (>20 bar)

Much lower compression costs

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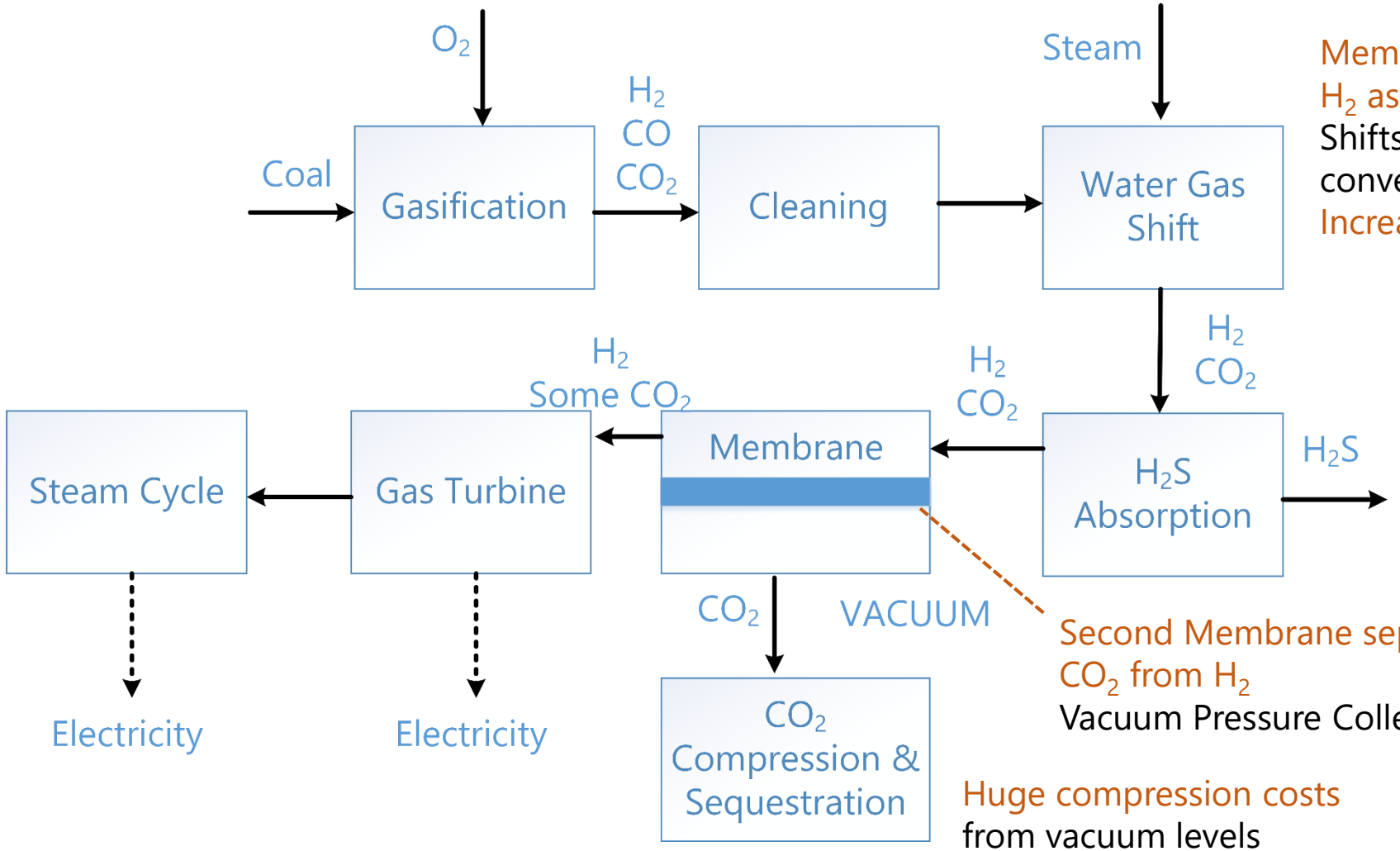
Pre-Combustion Membrane-Based Capture



Membrane-enhanced WGS removes H_2 as produced

Shifts equilibrium to toward higher conversion

Increases CO_2 concentration for later

Second Membrane separates CO_2 from H_2

Vacuum Pressure Collection

Huge compression costs from vacuum levels

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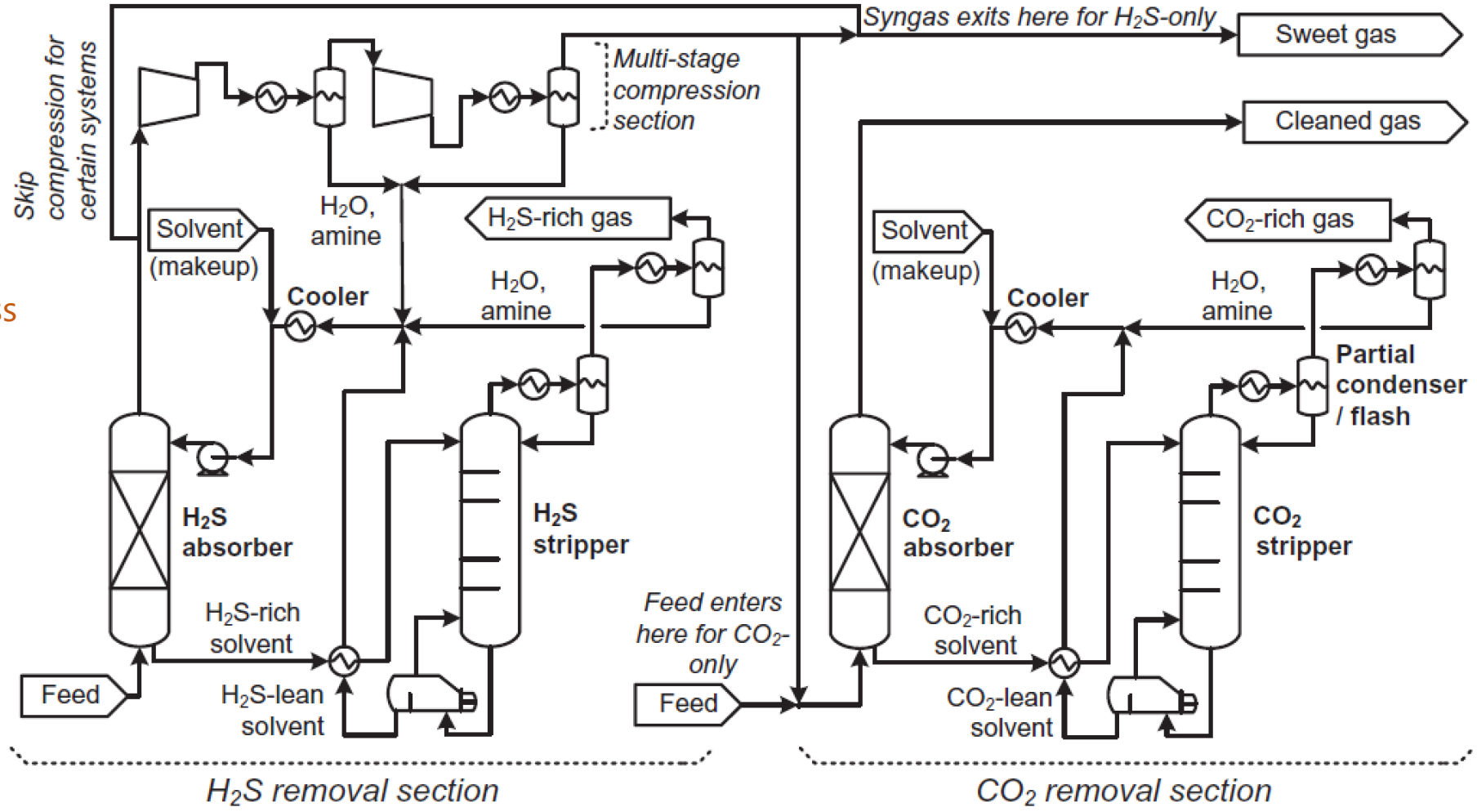
Source: Adams TA II, Hoseinzade L, Madabhushi P, Okeke IJ. Processes 5:44 (2017).

Dual Sulfur and CO_2 Removal - MDEA

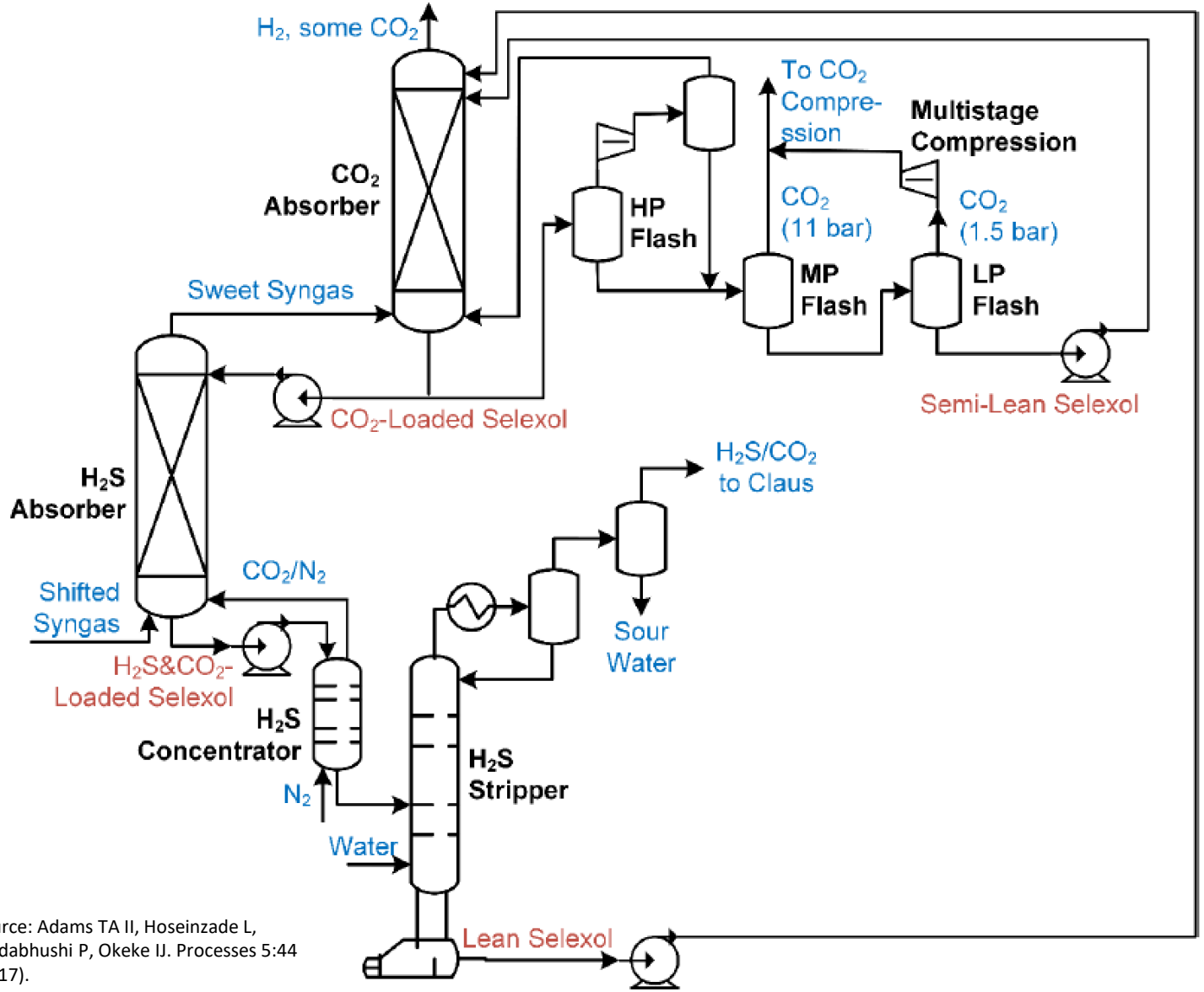
Split into two distinct process sections



Source: Adams TA II, Khojestah Salkuyeh Y, Nease J. Process and Simulations for Solvent-based CO2 Capture and Syngas Cleanup. In: Reactor and Process Design in Sustainable Energy Technology, ed: Fan Shi

Dual Sulfur and CO_2 Removal - Selexol

H_2S and CO_2 separation integrated together



Source: Adams TA II, Hoseinzade L, Madabhushi P, Okeke IJ. Processes 5:44 (2017).

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Summary of CO_2 Applications

45% MDEA, 5% Piperazine, 50% H_2O

Diglycolamine

	Application	Feed Pressure	H_2S to Claus	CO_2 to Vent	CO_2 to CCS	MDEA	MDEA/ PZ	MEA	DGA	Rectisol	Selexol
CO_2/H_2 Separation	IGCC	High	•		•					•	•
	Gas to liquids	Medium	•			•	•				
	Coal to liquids	High	•	•		•	•			•	•
	Coal to liquids	High	•		•					•	•
CO_2/N_2 Separation	Coal power plant	Low			•			•	•		
	NGCC, postcombustion	Low			•			•	•		
CO_2/H_2 Separation	NGCC, precombustion	Medium		•		•	•	•	•		
CO_2/H_2 Separation or CO_2/CH_4 Separation	Sweet gas cleaning	Varies		•			•				
	Sweet gas cleaning	Varies			•		•				•
	Sour gas cleaning, low CO_2 content	Varies	•			•	•	•	•		
	Sour gas cleaning, high CO_2 content	Varies	•	•		•	•				•
	Sour gas cleaning, high CO_2 content	Varies	•		•	•	•				•

Source: Adams TA II, Khojestah Salkuyeh Y, Nease J. Process and Simulations for Solvent-based CO2 Capture and Syngas Cleanup. In: Reactor and Process Design in Sustainable Energy Technology, ed: Fan Shi

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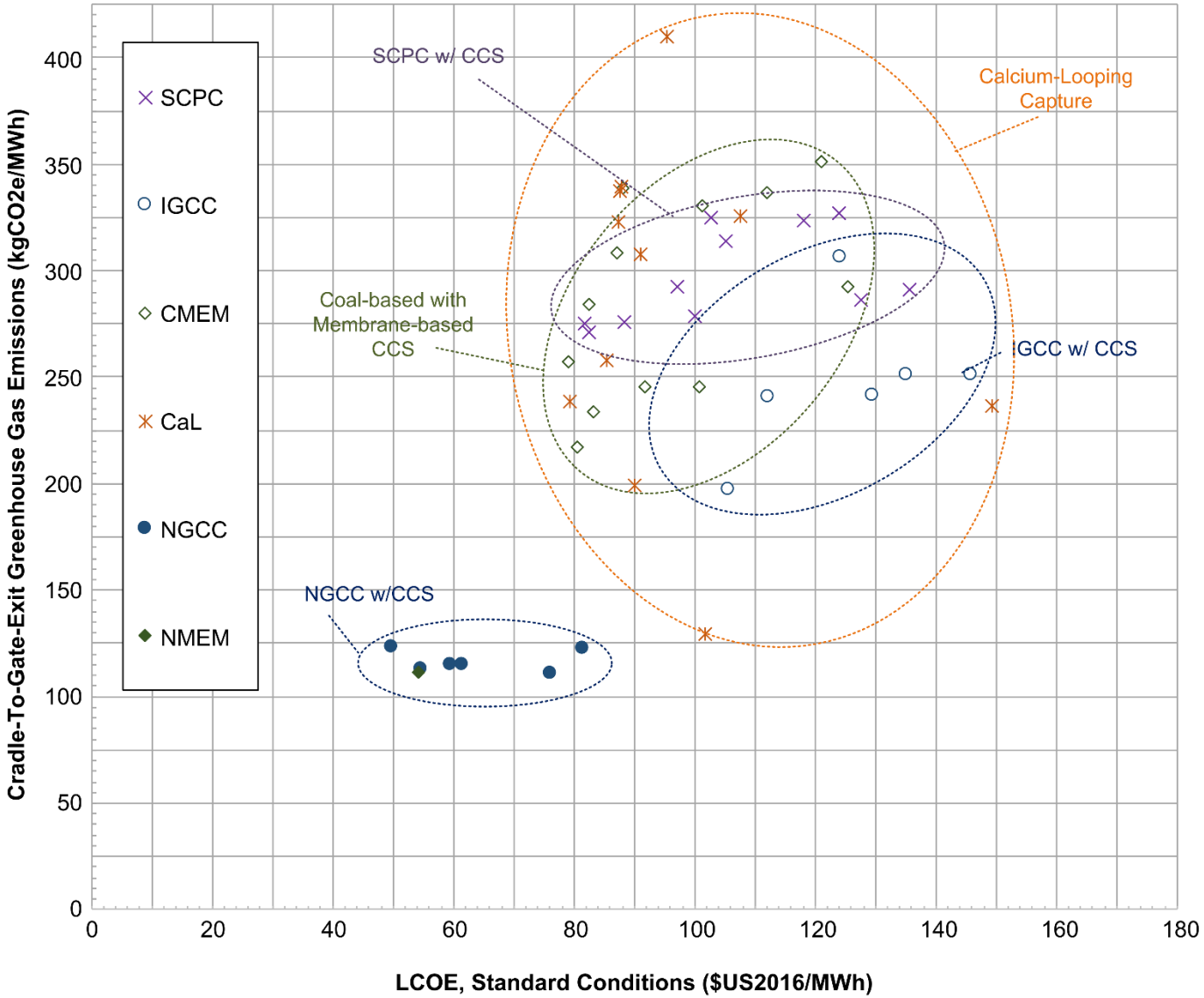
Cost Comparisons

- Analysis of 100 results in the literature for various power plants.
- Converted to standard size, location, fuel cost, fuel type, supply chan (for LCA), NOx considerations, project year, system boundaries, and captured CO2 settings.
- Only fair comparison that exists!



Source: Adams TA II, Hoseinzade L, Madabhushi P, Okeke IJ. Processes 5:44 (2017).

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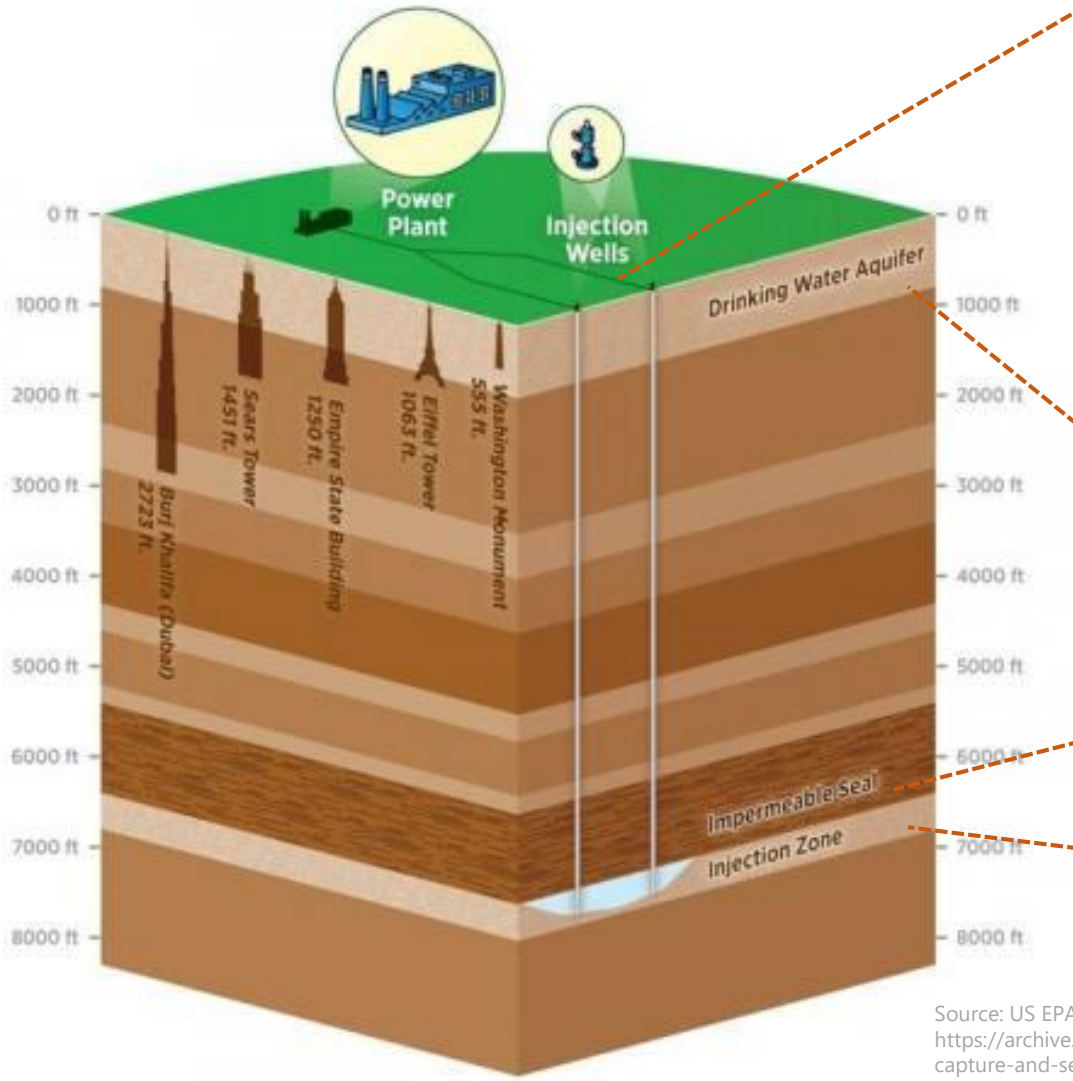
CO_2 Sequestration

Options going forward

Sequestration Basics



CO_2 pipeline needs to be constructed to transport captured CO_2 to sink.

An additional factor to consider with the optimal location problem.

Example: Is it better to place power plant on floating gas platform in ocean and generate, capture, and sequester there rather than placing power plant on shore and piping CH_4 & CO_2 across ocean?

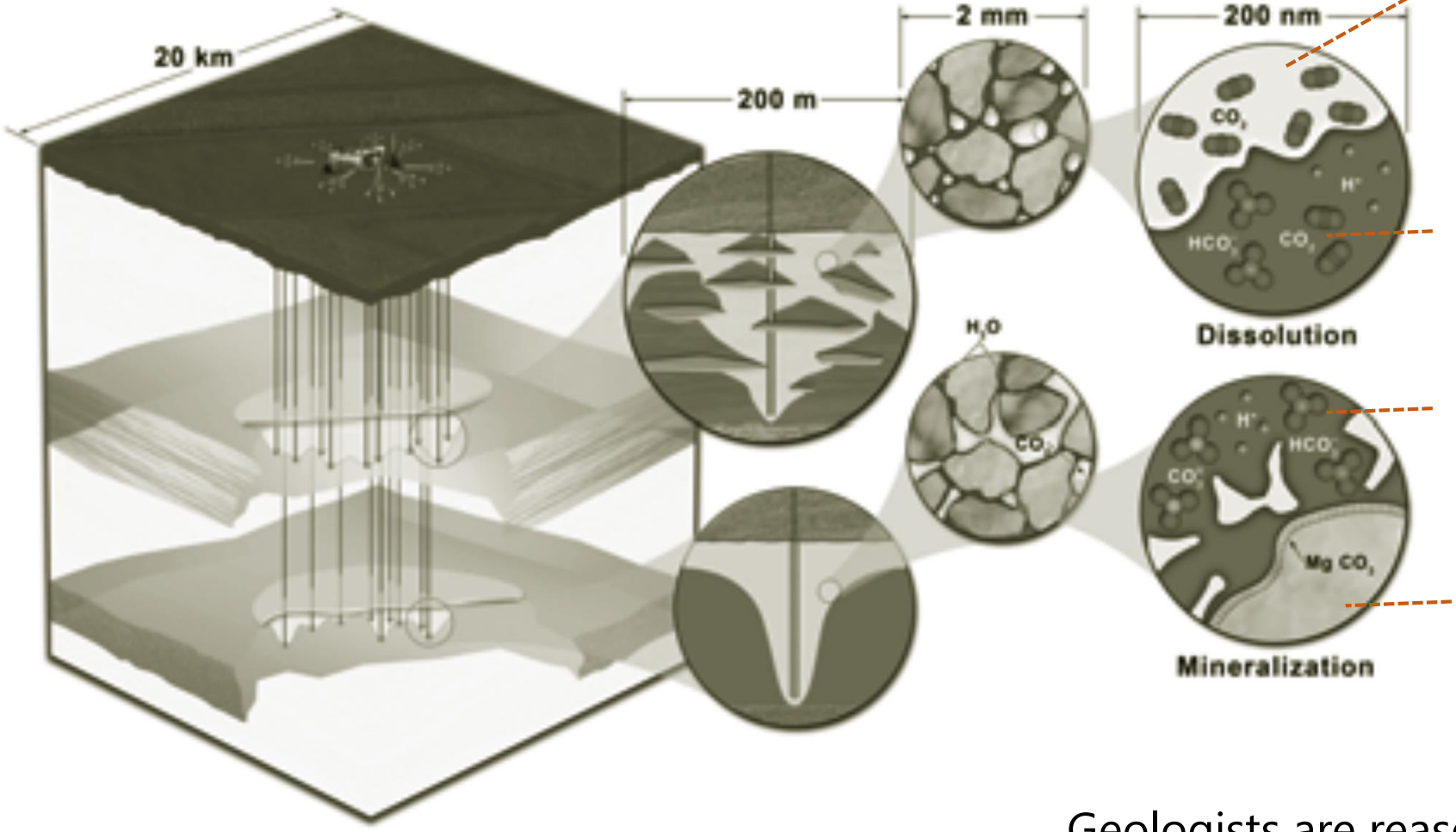
Aquifer level (drinking water)

Cap Rock (impermeable to gases)

Porous Rock (permeable to gases)

Source: US EPA. Carbon capture and sequestration overview. https://archive.epa.gov/epa/climatechange/carbon-dioxide-capture-and-sequestration-overview.html

Ground Level Resolution



Some rock layers are heterogeneous and can store CO2 in the pores, but only a small percentage is available. This means that very large areas are required.

After 10-100 years, CO_2 will dissolve into other fluids, like water, oil, or natural gas.

Homogenous layers have more space, but would be shared with other fluids (like water).

After 100-1000 years, CO_2 will mineralize and precipitate into a solid by reacting with the minerals in the rock itself.

Geologists are reasonably confident that over 99% of the CO_2 will remain trapped after 1000 years.

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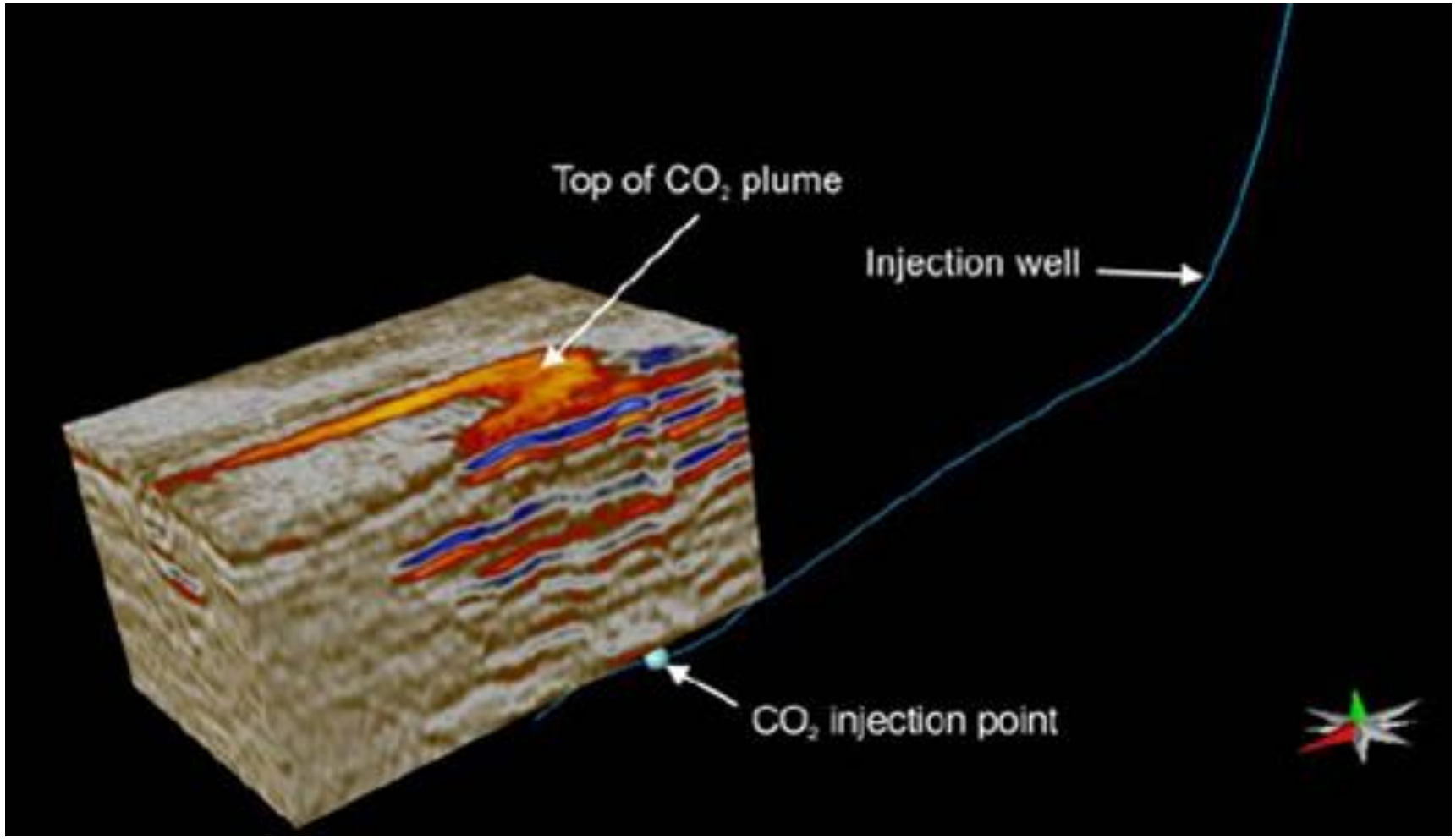
Source: MIT, The Future of Coal (2007).

Example: Sleipner Field (Norway)



Norway world's leader in non-EOR sequestration

Sleipner and Snovit fields first demonstrations.

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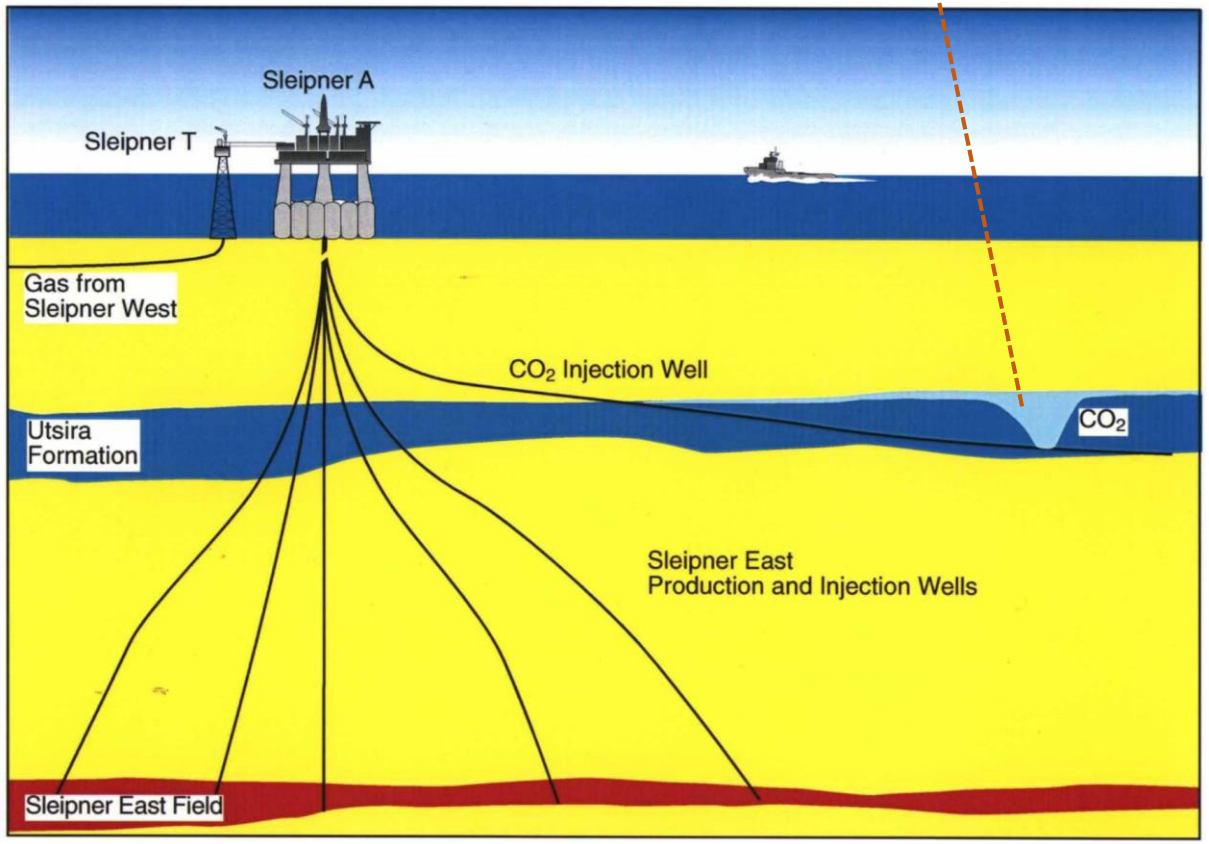
Source: British Geological Survey. Why monitor CO2 storage projects?

Example: Sleipner Field (Norway)

Shape of CO_2 plume here
(Rises upward more easily than horizontal movement)



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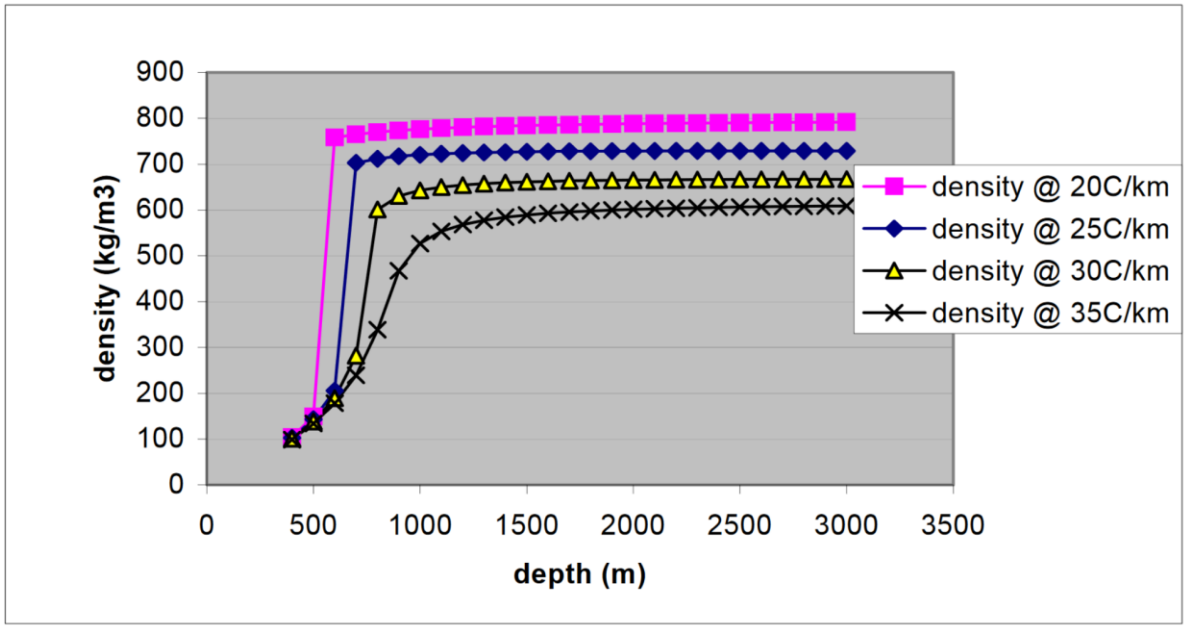
Source: Halloway S. Sequestration – The underground storage of carbon dioxide. British Geological Survey. Images originated from Eqinor (then called Statoil)

Density of CO_2



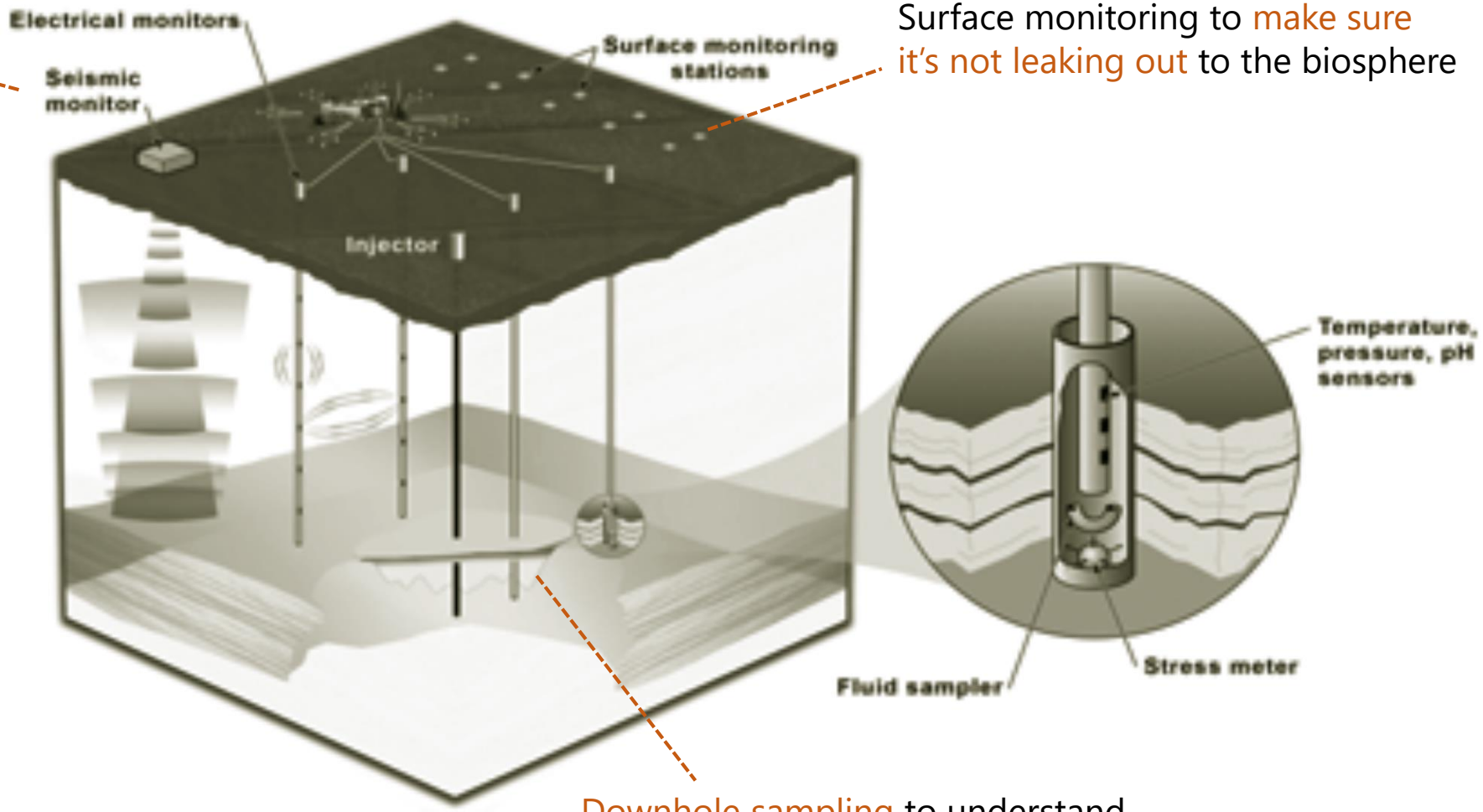
- About 80% of the density of water at 20°C and sufficient depth.
- But varies greatly with temperature.
- Pressure limits dictated by rock strength.
  - Alberta: You can put back into hydrofracked pore spaces if you are below 90% of the pressure needed to fracture it. (Makes sense).

Source: Halloway S. Sequestration – The underground storage of carbon dioxide. British Geological Survey.

Monitoring Systems

Check for seismic activity (earthquakes!!!!)

Surface monitoring to make sure it's not leaking out to the biosphere



Need to monitor for the next 1,000-10,000 years or so.

NO PROBLEM

Oldest organizations
Kongō Gumi (construction, 1428 yrs)
Catholic Church (<2000 yrs)
Ancient Rome (2206 yrs)
Ancient Egypt (2400 yrs)
Ancient Sumer (2600 yrs)
Japanese Monarchy (>2675 yrs)
Buddist Monastic Tradition (~3000yrs)
Jewish Priesthood (~3000-4000yrs)?
China (>4050 yrs)

Downhole sampling to understand temperature, pH, pressure, etc.

McMaster University ENGINEERING
MACC McMaster Advanced Control Consortium

Source: MIT, The Future of Coal (2007).

Summary

- Pulverized coal is ubiquitous, but problematic.
- Natural gas power is increasing but its concentrations of CO_2 are even worse
- CO_2 capture is a huge challenge:
  - Once-through – not practical
  - Solvent based – incredibly expensive, but mature
  - Adsorption based – futuristic, probably expensive (lack of data)
  - Membrane based - futuristic, comparable with solvents, not much room for growth
- Basically CO_2 capture is so difficult that it motivates a huge body of development in alternative electricity generation… (coming up next!)
- Then you have to sequester the CO_2. Easier said than done!
  - But we know how to do it.