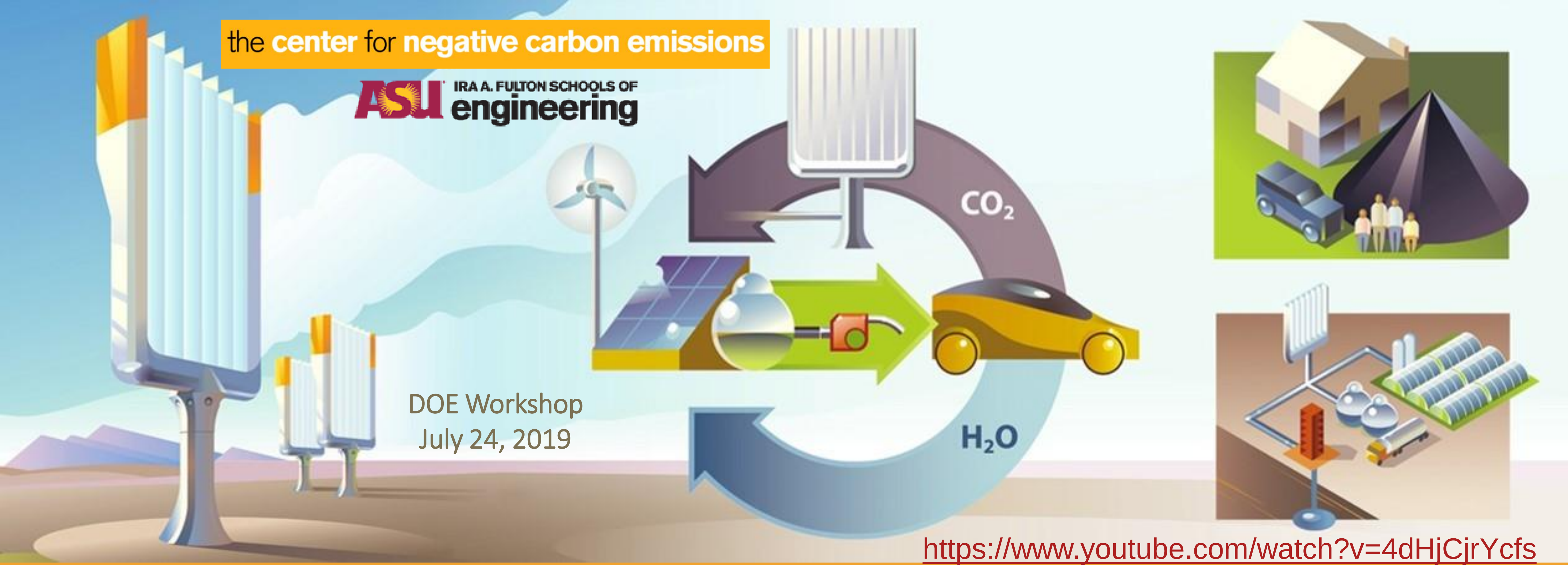


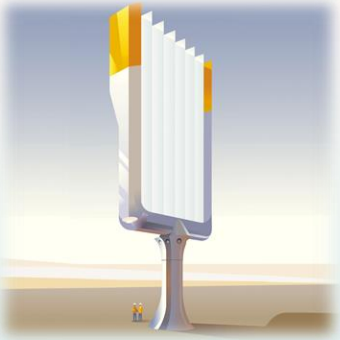
DOE Workshop
July 24, 2019

https://www.youtube.com/watch?v=4dHjCjrYcfs

Research Needs for Direct Air Capture

Klaus S Lackner

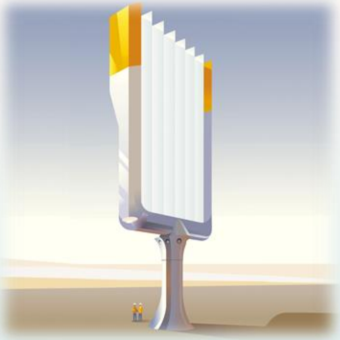
July, 2019



Direct Air Capture: Closing the Carbon Cycle on the Teraton-Scale

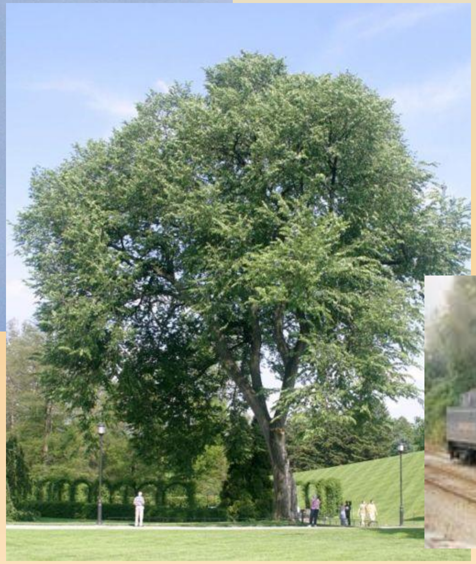
- Air capture can produce feedstock for fuels and chemicals (DACCU)
  - Current rate of oil consumption generates 1.5 Teraton CO_2 in the 21st century
  - DAC can promote solar energy to become the dominant primary energy source
- Air capture can collect waste from past and future emissions (DACCS)
  - Collecting 100 ppm from the atmosphere requires 1.5 Teraton of CO_2 capture
  - Sequestration cannot be avoided anymore
- What else can reach this scale? (Trillion dollar annual revenue industry)
  - Without competing with food production
  - Without large environmental footprints

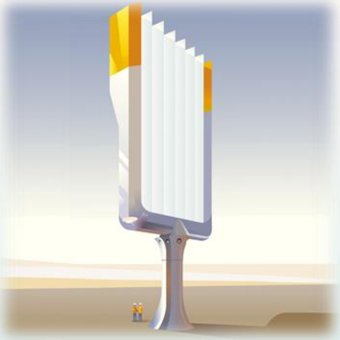
We better figure it out!



What took so long?

- Too different from established technologies
  - Heavier-than-air flight and direct air capture are nearly impossible with off-the-shelf technology

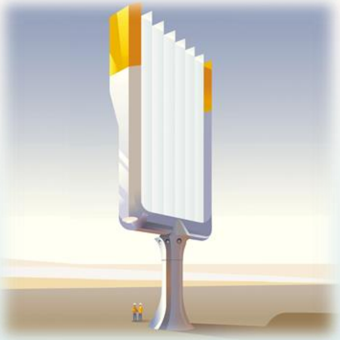




New Engineering Field

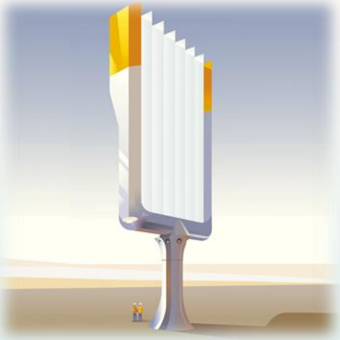
- Closing the anthropogenic carbon cycle the environment
  - Decoupling fuels from fossil carbon
    - *Tapping into a sustainable inexhaustible source of energy*
    - *Energy security; Supply stability; Sustainable use*
    - *Stabilizing the carbon level in the environment*
- Integrative, interdisciplinary and novel engineering
  - Disciplines formed around need and topic
    - *Mining engineering*
    - *Environmental engineering*
    - *Cybernetics*
    - *Carbonetics*

Carbonetics: The new engineering science for a stable climate and a permanent and secure energy supply support by the most versatile storage and transport system



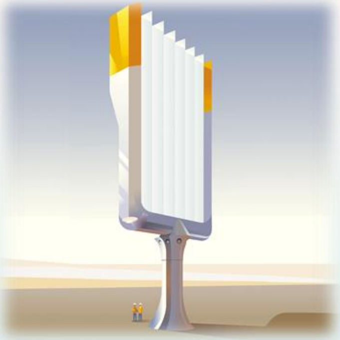
Aspects of Carbonetics

- Systems Design
- Techno-economics
- Aerodynamics of air contactors
- Sorbent material engineering
- Science of dilute separation
- Separation Membranes
- Application interfaces
- ….



Material Science of CO_2 Sorbents and Membranes

- Highly selective
  - N_2 + O_2 is 2500 times as abundant, H_2O – 10 – 100 times
- Minimal binding energy
  - $\Delta G_0 \leq -22 \frac{kJ}{mol}$ (implies chemical binding)
- Fast kinetics
  - But tempered by inherently slow air-side transport
- High capacity
  - Particularly for thermal activation (lots of energy wasted in the bulk material)
- Dirt cheap
  - 1 ton CO_2 per kg of sorbent requires 10,000 to 100,000 cycles
- Tough as nails
  - Must survive 100K capture and regeneration cycles, sunshine, heat, cold, wind, dust, …



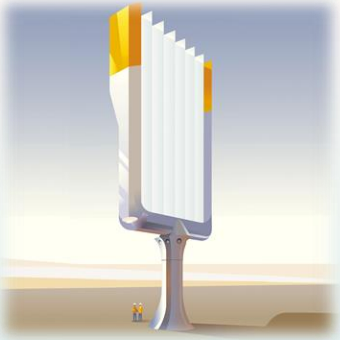
Sorbents and Membranes

- Membranes can increase selectivity of sorbent
  - Enhance selectivity against water
  - Challenge is exceedingly low partial pressure
  - Flux limitation:

$$F_{max} = \rho_{CO_2} c \sim 5\text{mol}/(\text{m}^2\ \text{sec})$$

    - *Density times sound velocity, evaluated at 40 Pa, and ambient temperature*
    - *Better than an electrolyzer membrane*
      - 1 Amp/cm^2/sec ~ 0.1 mol/m^2/sec for a singly charged ion
- Actively pumping membranes can eliminate need for batch process
  - Couples two different transports
    - *E.g., Water following a chemical potential pushes CO_2 up against a chemical potential*
    - *Analogous to the thermo-electric effect*
  - Game changer

Membranes are sorbents with two sides



Sorbent Thermodynamics

- **Sorbent is characterized by ΔH_0 and ΔS_0**
  - Enthalpy and entropy change of the sorbent reaction

$$Abs + CO_2 \leftrightarrow (Abs \cdot CO_2)$$

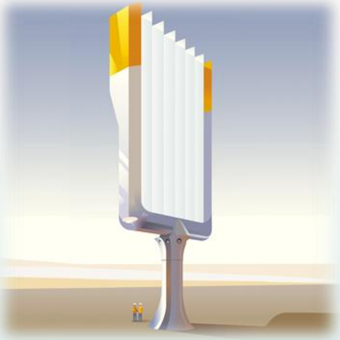
  - Free energy change determines direction of reaction

$$\Delta G = \Delta H_0 - T\left(\Delta S_0 + R \log \frac{P}{P_0}\right)$$

P is the pressure over the sorbent, T is the temperature, P_0 is the standard pressure at which thermodynamic quantities have been determined.

$\Delta G < 0$ for capture

$\Delta G > 0$ for regeneration



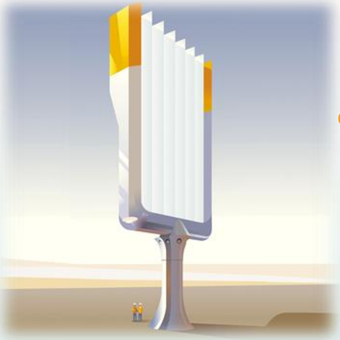
Estimating the size of things

$$\Delta G = \Delta H_0 - T\left(\Delta S_0 + R\log\frac{P}{P_0}\right)$$

- ΔH_0 is free for the choosing (needs to be negative)
- ΔS_0 is negative for all sorbents (gas has more entropy)
- $R\log\frac{P}{P_0}$ accounts for entropy change in the gas with pressure
  - $R\log\frac{P}{P_0} \approx -65\ \frac{J}{mol \cdot K}$ for air capture $P = 40\ Pa$
    - *Increases logarithmically with pressure, zero at 1 bar*

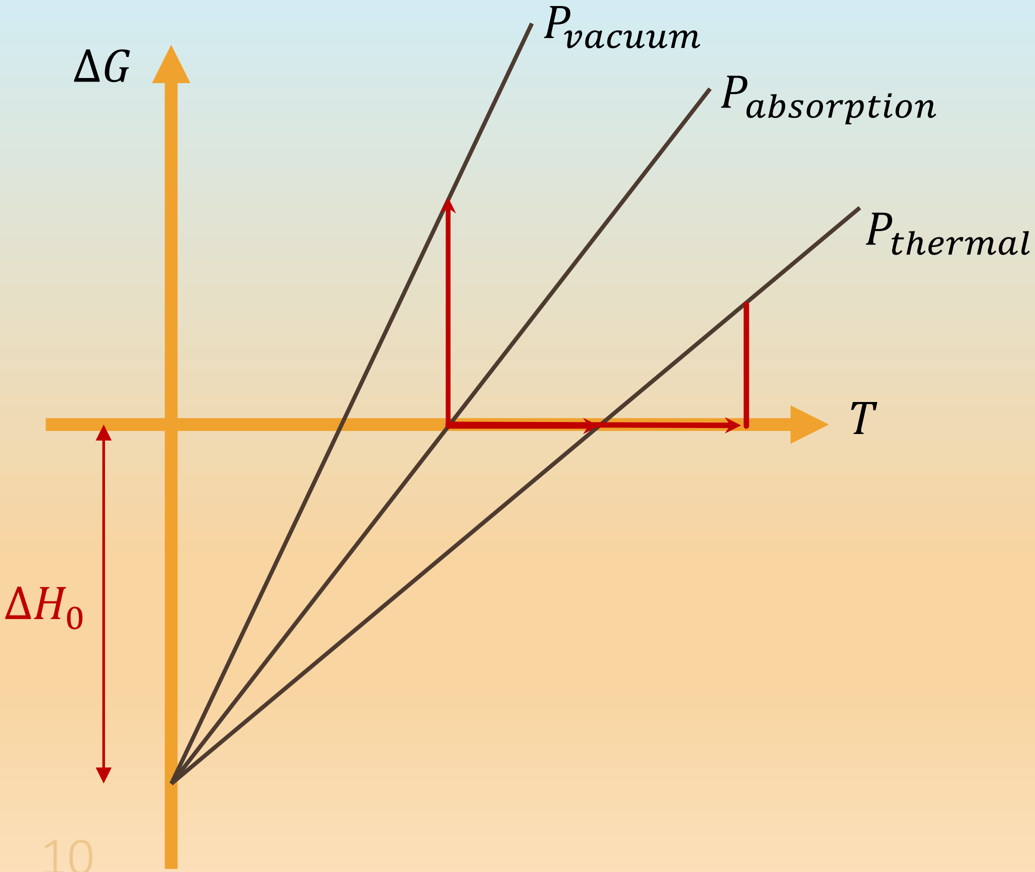
For solid sorbents the range of ΔS_0 is limited

$$-250\ J\ mol^{-1}K^{-1} < \Delta S_0 < -100\ J\ mol^{-1}K^{-1}$$

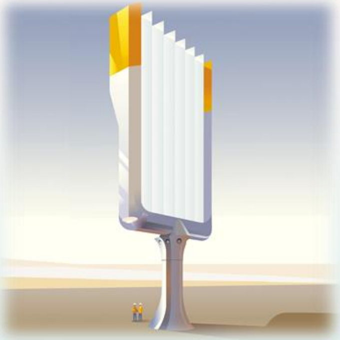


Thermal and Pressure swings

$$\Delta G = \Delta H_0 - T\left(\Delta S_0 + R\log\frac{P}{P_0}\right)$$



- Vacuum swings lower $\boldsymbol{P}$ to increase $\Delta\boldsymbol{G}$
- Thermal swings raise $\boldsymbol{T}$ to increase $\Delta\boldsymbol{G}$
- The moisture swing throws a switch and changes $\Delta\boldsymbol{H_0}$ and $\Delta\boldsymbol{S_0}$
  - Interaction of water, sorbent and CO_2

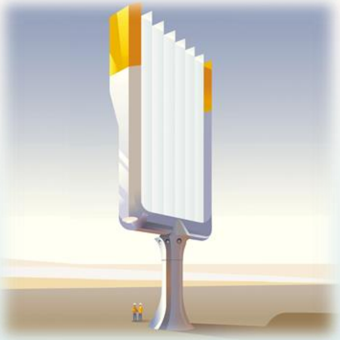


Optimizing a P-T Swing

- Starting point is ambient air
  - $P_1 = 40\ Pa, \quad T_1 \sim 300K$
  - $Release\ at\ higher\ P\ and\ higher\ T\text{:}\ \ (P_2, T_2)$
  - Estimate the achievable pressure given T_2 or the achievable temperature given P_2

$$\log\frac{P_2}{P_1} = -\left(\frac{\Delta S_0}{R} + \log\frac{P_1}{P_0}\right)\frac{T_2 - T_1}{T_2} \qquad \text{or} \qquad T_2 = T_1\left(1 - \frac{R\log\frac{P_2}{P_1}}{\Delta S_0 + R\log\frac{P_2}{P_0}}\right)$$

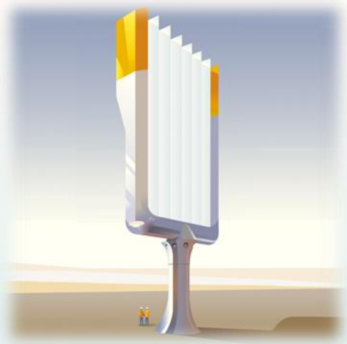
- A 50K temperature rise could reach a regeneration pressure between 0.006 and 0.1 atm
- To get to 1 atm requires between 90 and 120K temperature rise



Moisture swings are new

- Opens a new door for optimization
  - Barely understood
  - Relating to fundamental properties of water
  - Interactions of ions, hydrophobic resins

Furthermore moisture swing resins are tough, cheap, and fast



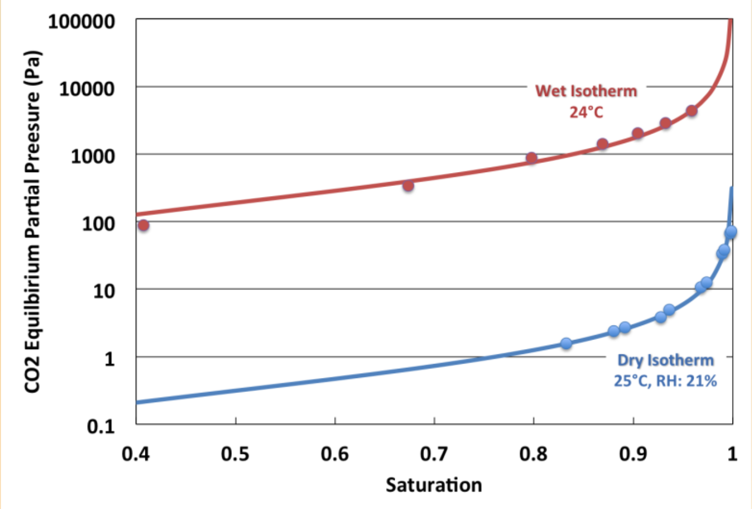
Moisture Swing Sorbent for Low Energy Air Capture

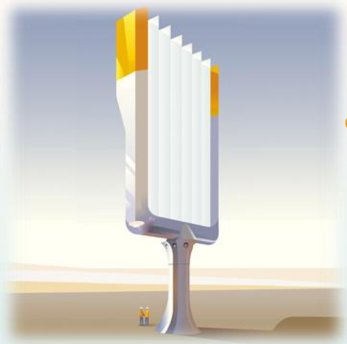
Anionic Exchange Resin: Solid carbonate “solution”
Quaternary ammonium ions form strong-base resin

Type I Strong Base Resin

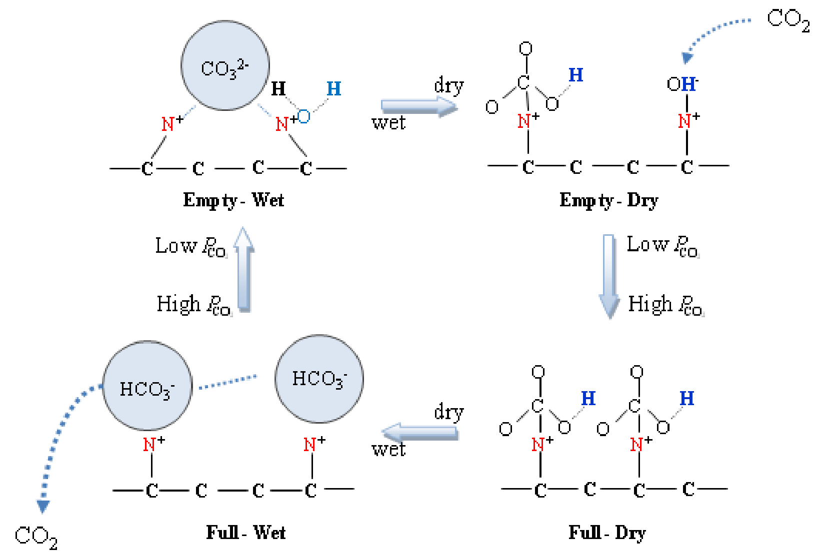
2 to 2.5 mol/kg of charge
1 to 1.25 mol/kg of CO_2 capacity
Durable, life time 10 to 20 years

- Positive ions fixed to polymer matrix
  - Negative ions are free to move
  - Negative ions are hydroxides, OH^-
- Dry resin loads up to bicarbonate
  - $OH^- + CO_2 \rightarrow HCO_3^-$ (hydroxide → bicarbonate)
- Wet resin releases CO_2 and unloads to carbonate
  - $2HCO_3^- \rightarrow CO_3^{--} + CO_2 + H_2O$
- Intermediate product stream is air with 5% CO_2
- Ion hydration drives CO_2 affinity
- $CO_3^{--} + H_2O \rightarrow HCO_3^- + OH^-$
  equilibrium is driven by water content

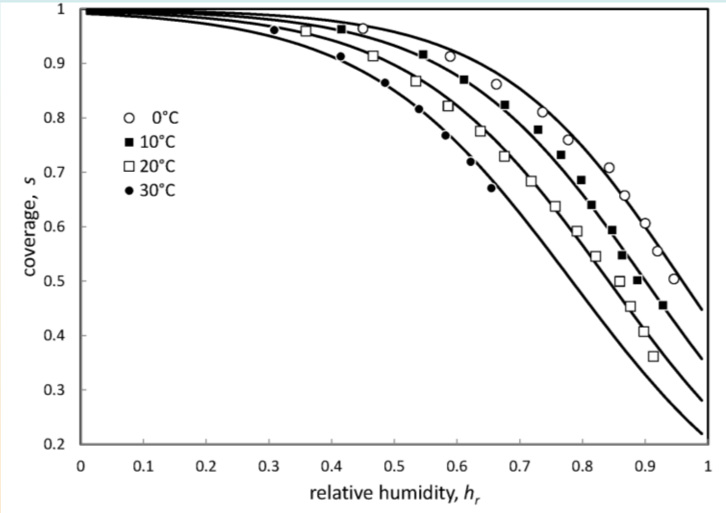




The moisture swing

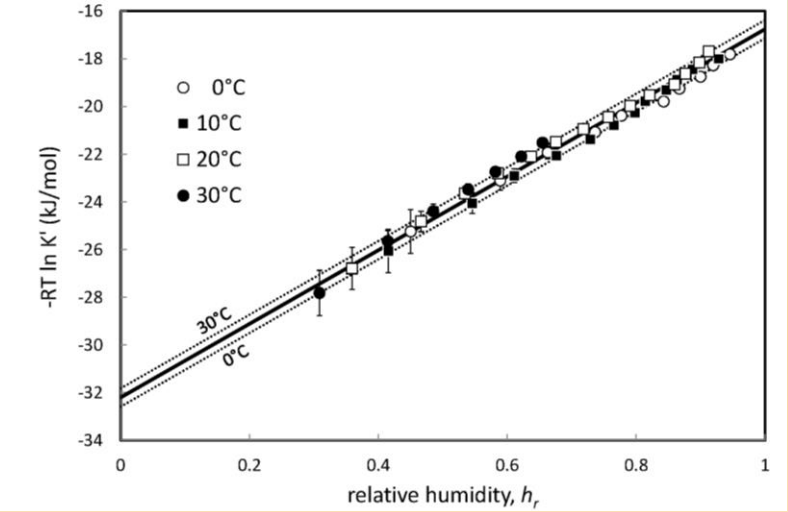


The effect of relative humidity

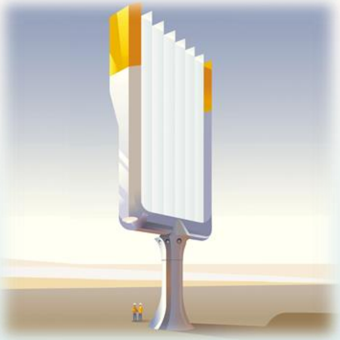


Sorbent loading at 400 ppm and room temperature

Free energy of binding CO_2

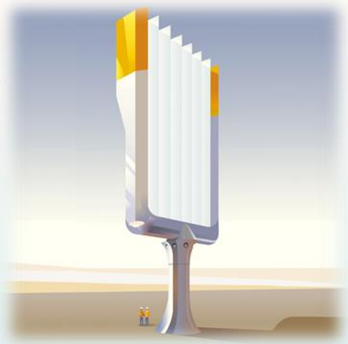


Reaction proceeds at constant P_{H_2O}



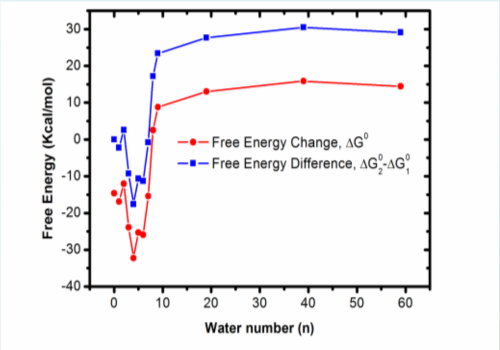
ASU's Direct Air Capture

- Passive System
- Moisture Swing Sorbent
- Mass Manufacturing Design
- Two Stage Concentrator



Multi-Scale Physical Modeling
I. From atoms to materials

- Density Functional Theory
  - Quantum-level understanding of sorbents on the molecular scale
  - Modeling the interaction of water, ions, and polymers

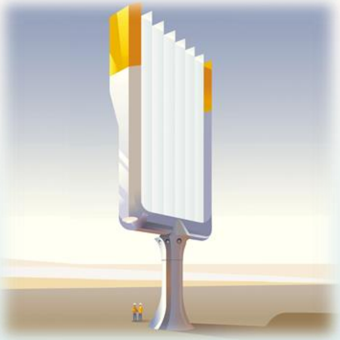


- Continuum models of the polymer matrix
  - Transport of H_2O, CO_2, and (OH^-, CO_2^{--}, HCO_3^-)
  - Diffusion under concentration gradients
  - Response to electric fields
  - Chemical equilibria depend on background water content
  - Understanding moisture driven carbon dioxide pumps

$$\frac{\partial n_i}{\partial t} + \vec{\nabla}\vec{j}_i = C_i$$

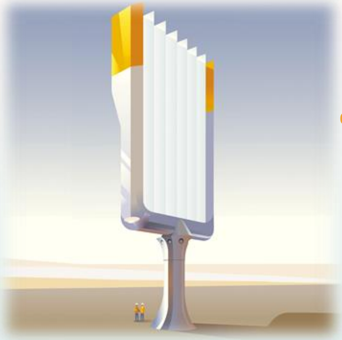
$$\vec{j}_i = -D_i\vec{\nabla}n_i + D_i q_i n_i \frac{\sum_k q_k D_k \vec{\nabla} n_k}{\sum_k D_k q_k n_k}$$

$$\frac{n_{H_2O} n_{CO_3^{2-}}}{n_{HCO_3^-} n_{OH^-}} = K(n_{H_2O}) \Rightarrow C_i$$



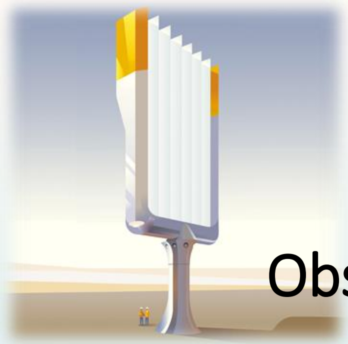
Multi-Scale Physical Modeling
II. From microstructure to device scale and beyond

- Multiphase models of composite filter/sorbent materials
  - Porous flow heat transfer in composites, textiles, porous materials
  - Structural characteristics, strength, brittleness,
  - Thermal, chemical and UV resistance
- Fluid dynamics and structural modeling of DAC structures
  - Passive air flows designs
  - response to wind loading
  - Installation scale air flows
- Energy and material flows
  - Heat, water, electric power, interaction with weather
  - Utilization rate as function of ambient conditions
- Interfaces with storage and utilization systems



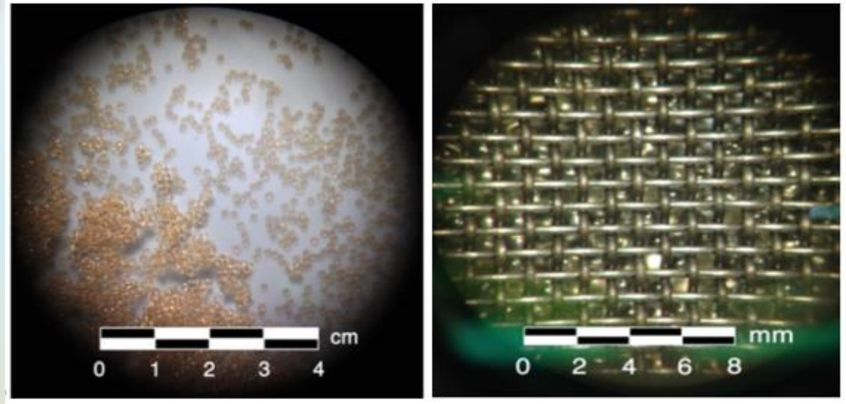
Techno-economic and LCA modeling

- Sorbent & membrane evaluations
  - Importance and valuation of different characteristics
- Techno-economic assessments
  - Bottom-up, top-down approaches
  - Costing and scaling
  - Assessment of learning curves
- Environmental impact assessments
  - Life cycle assessments
  - Water consumption
- Scaling approaches
  - Numbering up or scaling up?

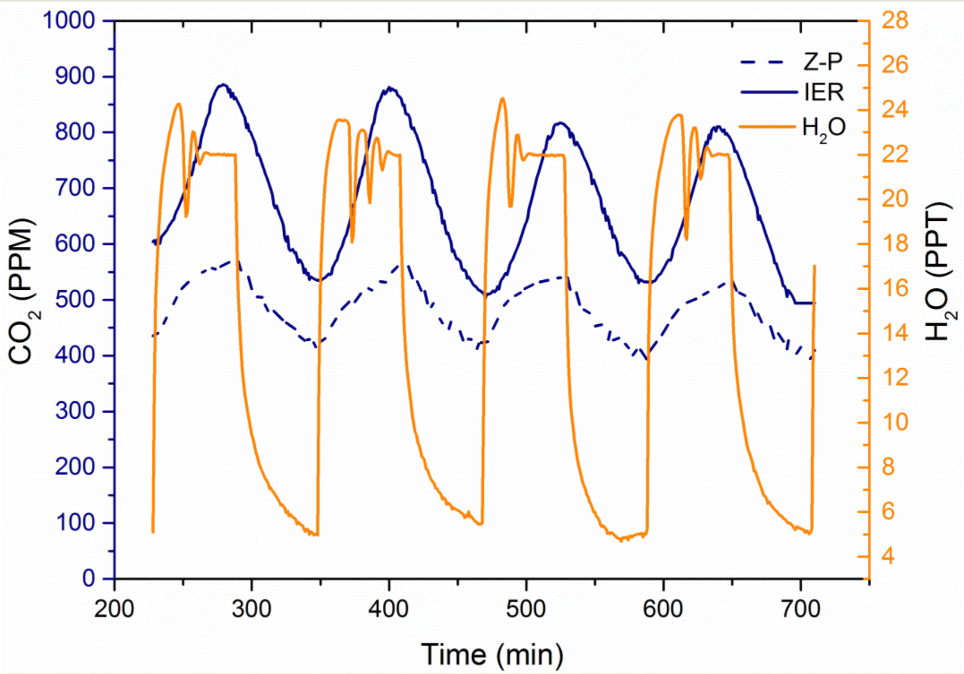


Moisture swing CO_2 capture & release

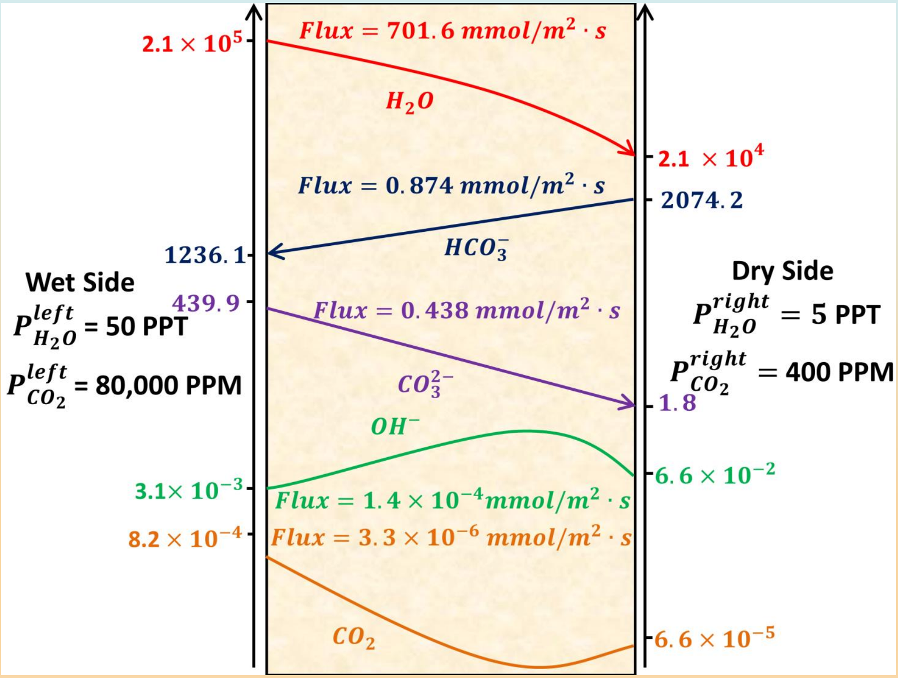
Observe what happens in a sorbent sphere



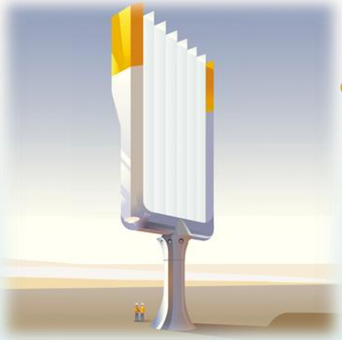
Moisture Pulse Drives CO_2 release



Predict what happens in a membrane?



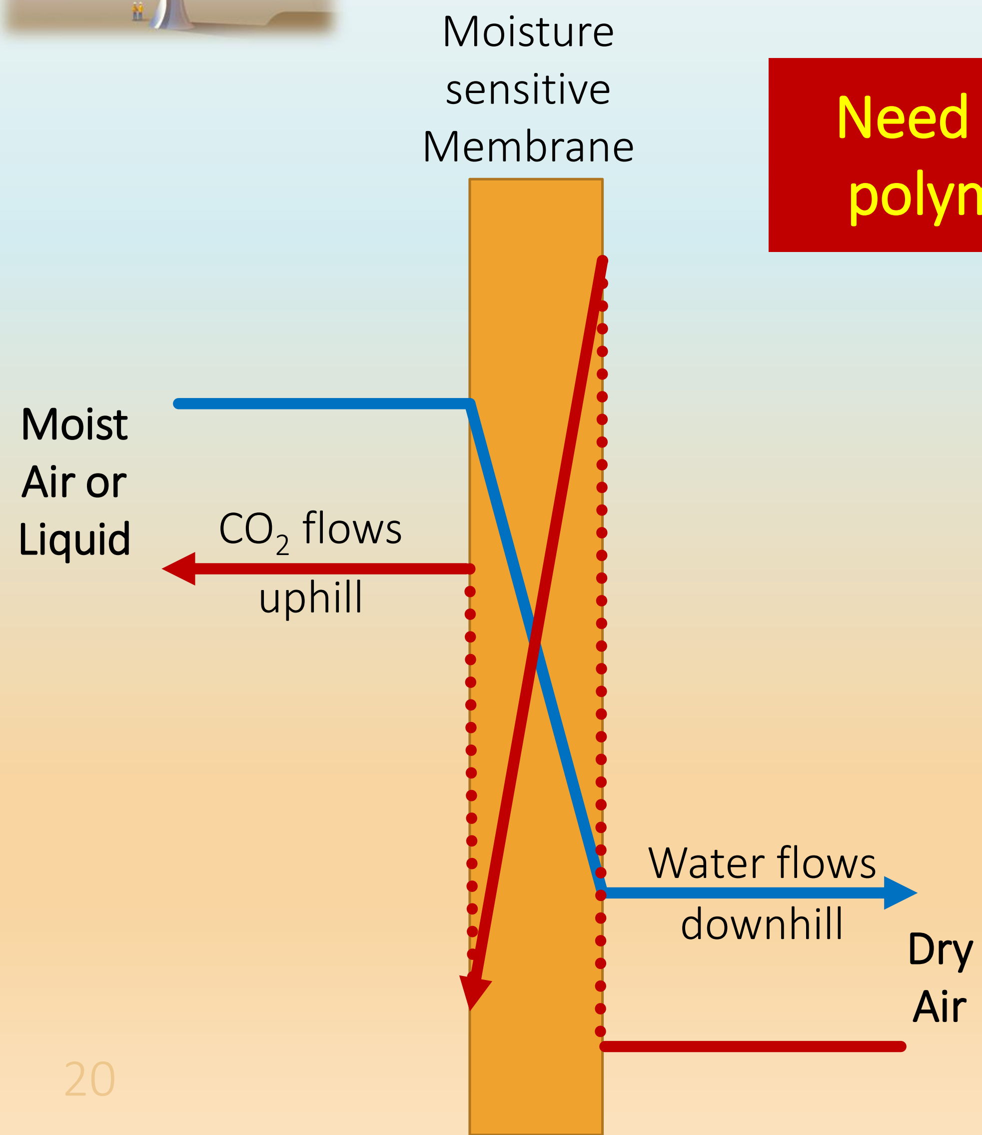
Model Calculations

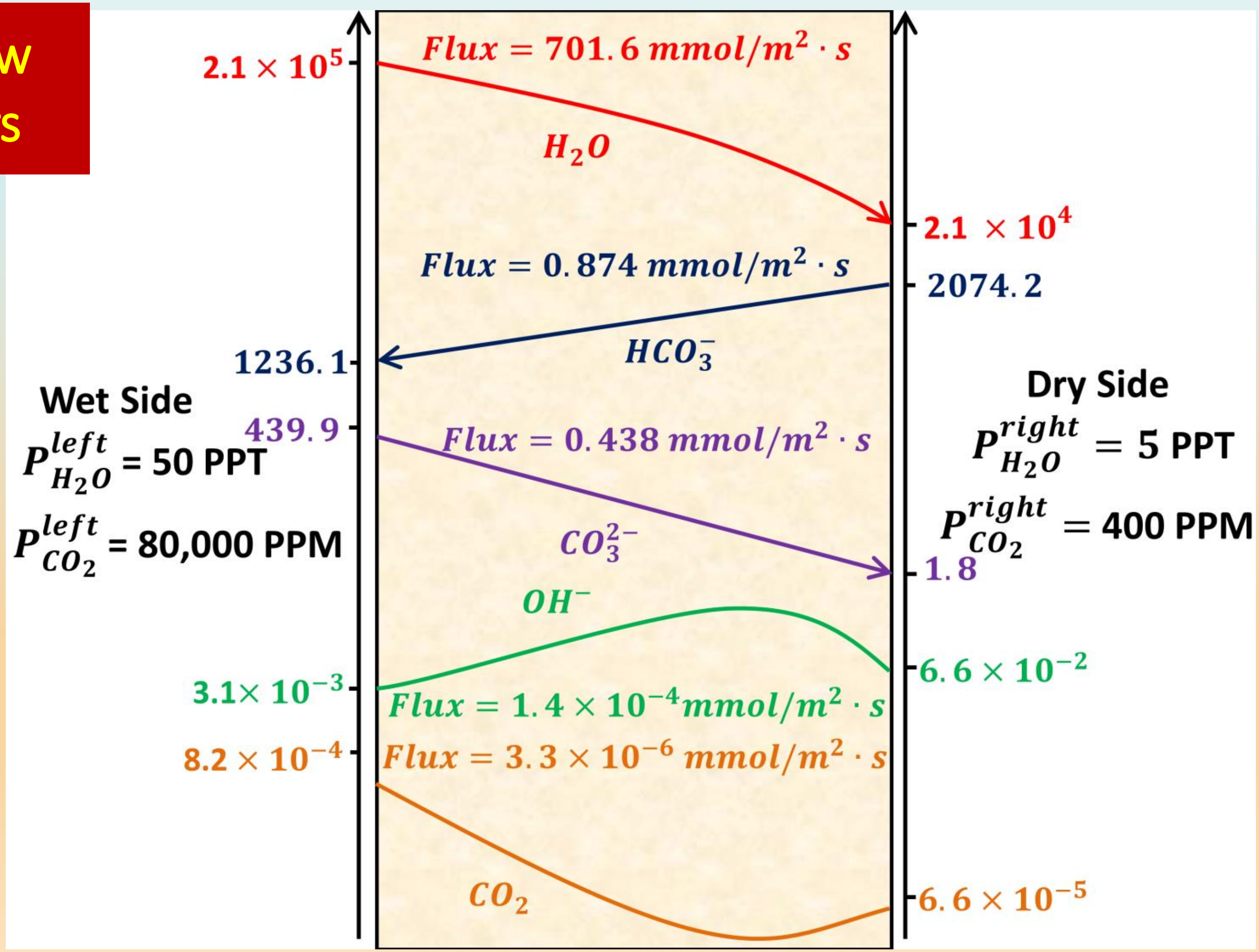


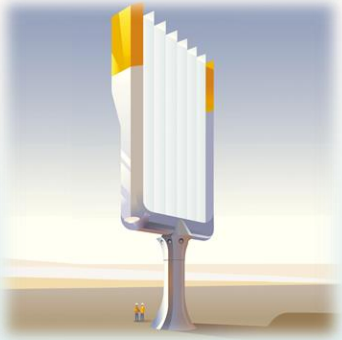
Transport Model Predicts Active Pumping

As water flows from the wet side to the dry side of the membrane, it pushes CO_2 to the wet side against a chemical potential

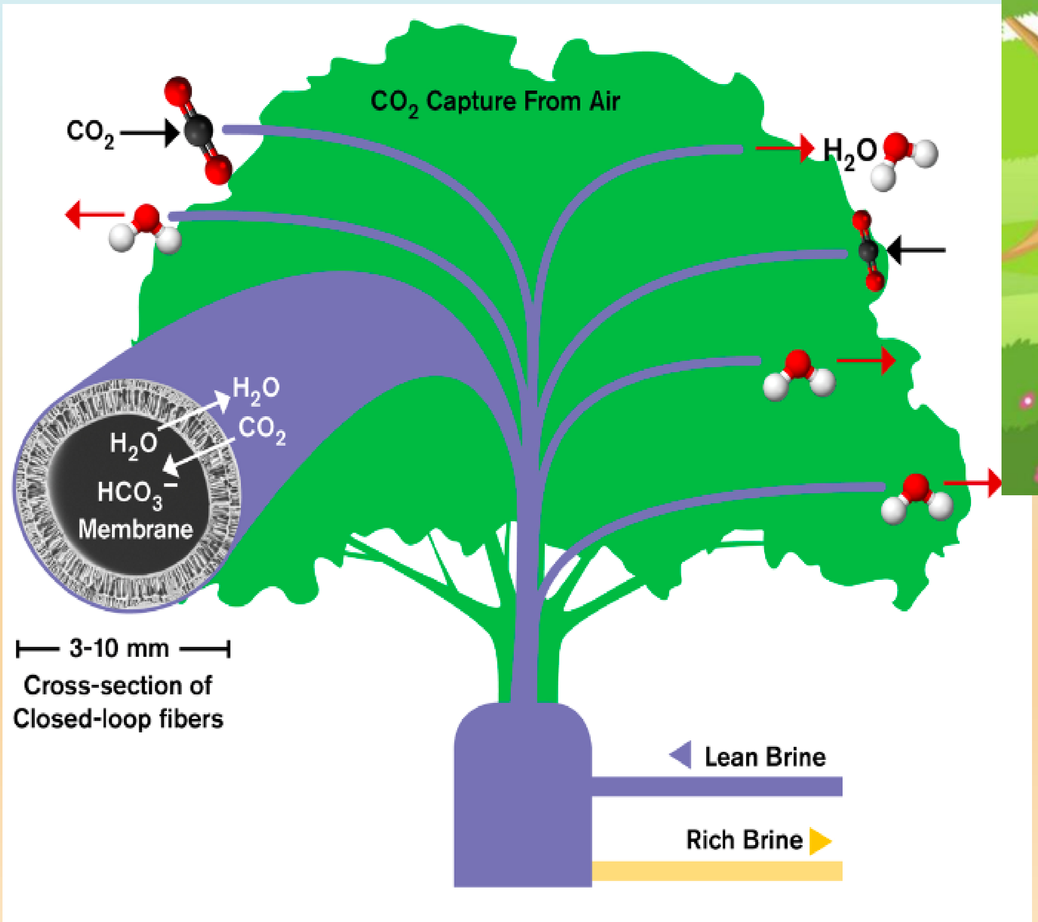
Need new polymers

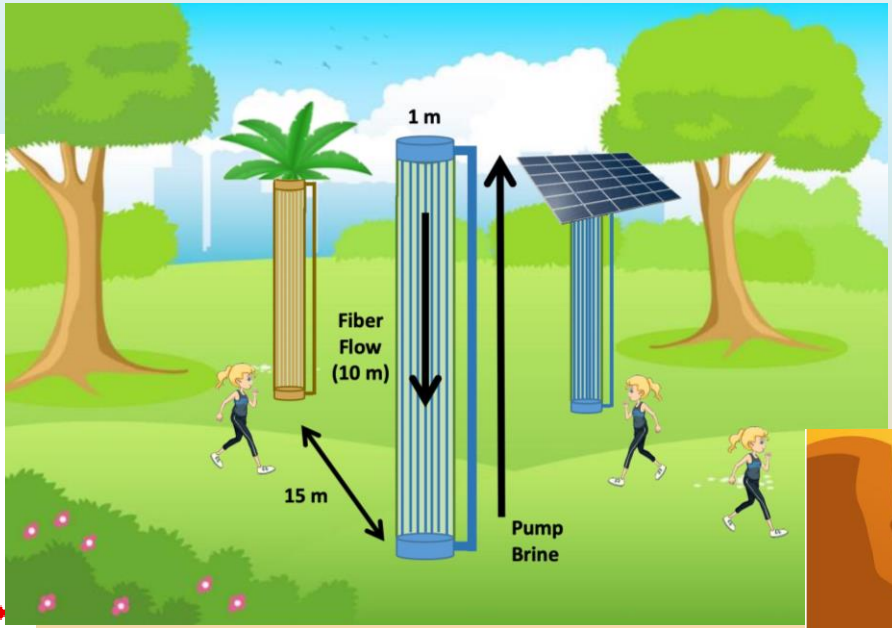




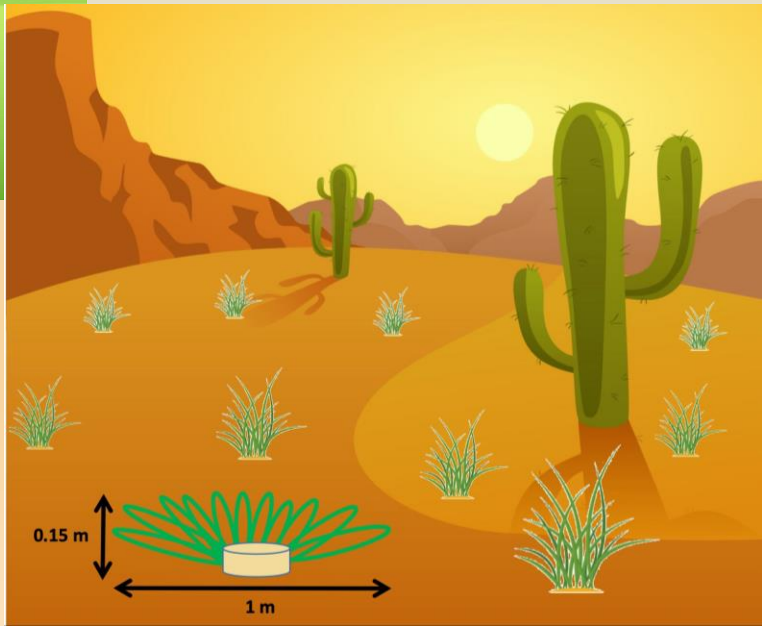


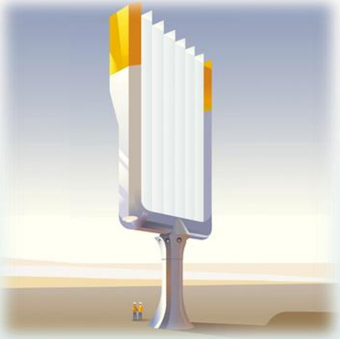
Active Membrane with Passive Air Flow Moisture Driven Transport





New ARPA-E Project will demonstrate the concept

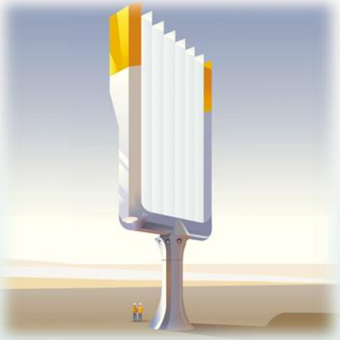




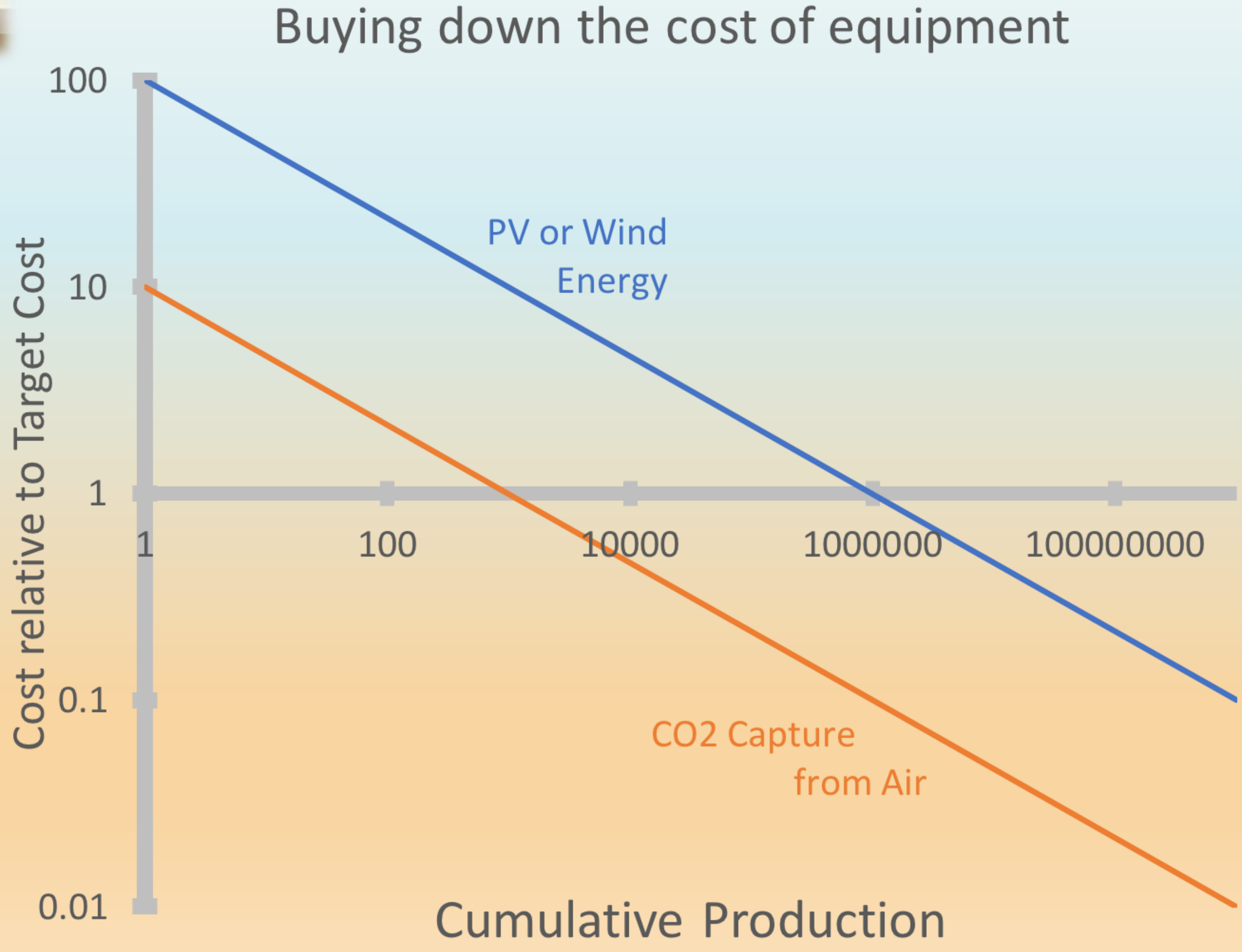
Carbonetics

- Air capture is at the beginning of a long road
  - Concepts are changing rapidly
  - Formal scientific support has not yet materialized
  - Need to move away from brute force to elegant solutions
- Advances needed
  - Passive or near passive systems to beat Sherwood's Rule
  - Advanced sorbents for efficient collection
  - Pumping membranes for integration
  - Moisture swing sorption is brand new and unexplored

Science can make a difference and cost can come down dramatically



Different Starting Points



Conventional Power Law:

$$\log_2 \varepsilon = -1/3$$

Unit cost:

$$c_n = c_1 n^{\log_2 \varepsilon}$$