HiPerCap WP2: Adsorption Technologies

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HiPerCap CO_2

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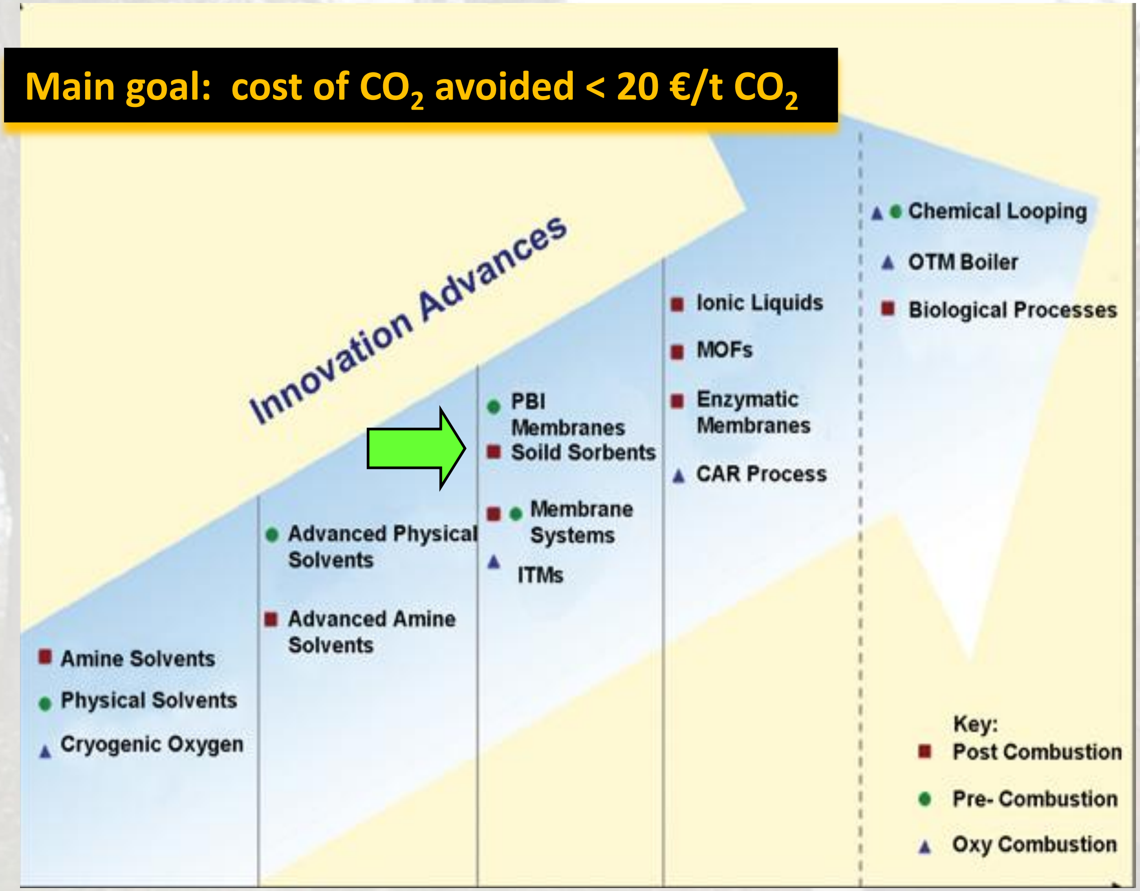
Alternative capture technologies



Cost reduction benefit →

Time to commercialisation →

- Technologies need to demonstrate clear competitive edge
- Technologies need to overcome challenges of other acids gases, SO_x and NO_x etc
- Rapid development required
- Risk that technologies will not scale up

Source: Figueroa *et al*. Int. J. Greenhouse Gas Control 2, 9-20 (2008)

Solid sorbents: *Why?*

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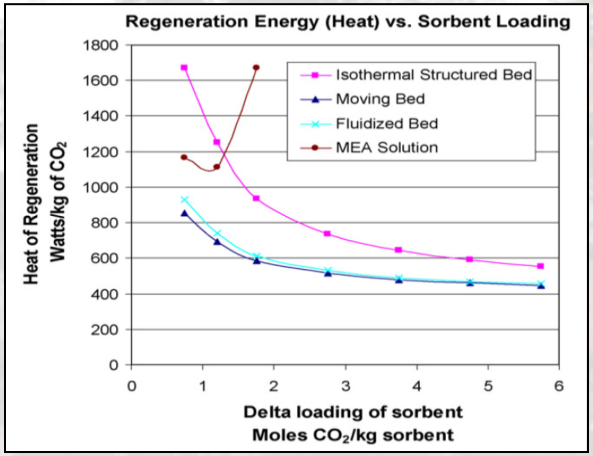
Advantages over *Absorption*

- ✓ Significantly increased contact area over solvent systems
- ✓ Reduced energy for regeneration and moving sorbent materials (if high capacity achieved)
- ✓ Elimination of liquid water (corrosion, etc.)
- ✓ Potential to reduce energy loading by 30-50%



Gray *et al*. J. Greenhouse Gas Control 2, :3-8 (2008)

Challenges of CO_2 adsorbents

- High capacity
- High selectivity
- Adequate adsorption/desorption kinetics
- Good stability / lifetime
- Mechanical strength
- Reasonable cost

< 25 \$/t CO_2 avoided

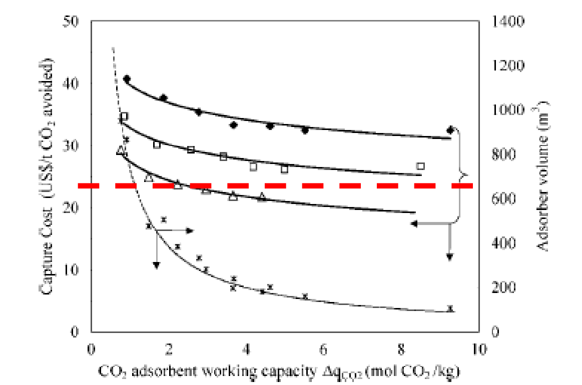


Figure 7. Effect on CO_2 capture cost (—) and total adsorber volume (---) of CO_2 adsorbent working capacity at three CO_2/N_2 selectivities: 50 (♦), 100 (□), and 500 (Δ), at 85% CO_2 recovery.

Ho *et al*. Ind. Eng. Chem. Res. 47, 4883-90 (2008)

Post-combustion capture application- challenges

	PC (w FGD)	NGCC	Oxyfuel
Volume flow (m^3/h)	2.2×10^6	3.8×10^6	0.5×10^6
Pressure (barg)	0.05	0.05	0.05
Temperature (^oC)	70-90	70-90	170
N_2 (%)	71	75	
CO_2 (%)	12.6	3.4	62.6
Water (%)	11.1	6.9	31.5
Oxygen (%)	4.4	13.8	4.5
SO_2 (ppm)	200		
NOx (ppm)	670	25	

- Very large: pressure drop
- Very low: no driving force
- Relatively high for adsorption
- Ranges from 12 to 63% (wet basis)
- High water content
- SOx, NOx, ash, heavy metals, etc. present

Source: Webley, P.A. (2010). *CO_2 capture by adsorption processes: from materials to process development to practical implementation.*

Post-combustion capture applications

Power generation

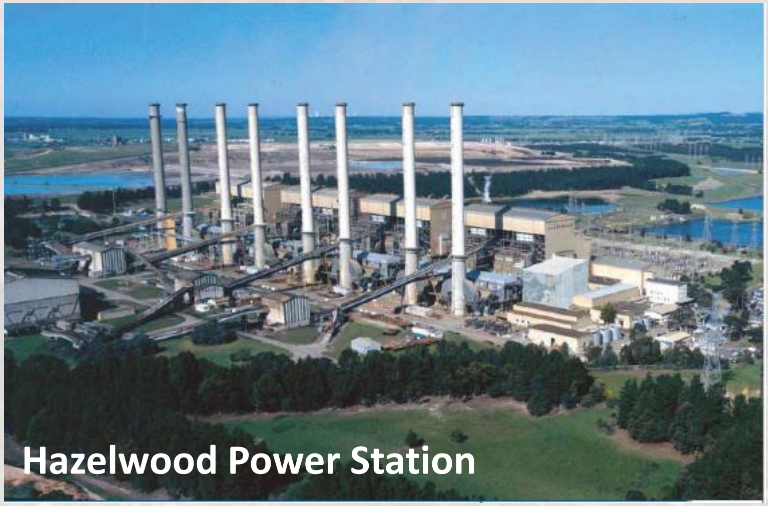
The **CO2CRC H3 Capture Project** at International Power's Hazelwood Power Station, completed in 2011, conducted research into adsorption technologies for CO_2 capture.

Goal:

- demonstrate adsorption for CO_2 capture from flue gas;
- assess adsorption process, equipment and different adsorbents under various working conditions and equipment configurations;
- assess the effect of impurities, temperature and load on the vacuum swing adsorption process;
- assess economic and engineering issues for scale-up

The H3 project was part of the Latrobe Valley Post-combustion Capture Project, supported by the Victorian Government, through the Energy Technology Innovation Strategy (ETIS) Brown Coal R&D funding.

CO2CRC H3 Capture Project


Hazelwood Power Station

Post-combustion capture applications

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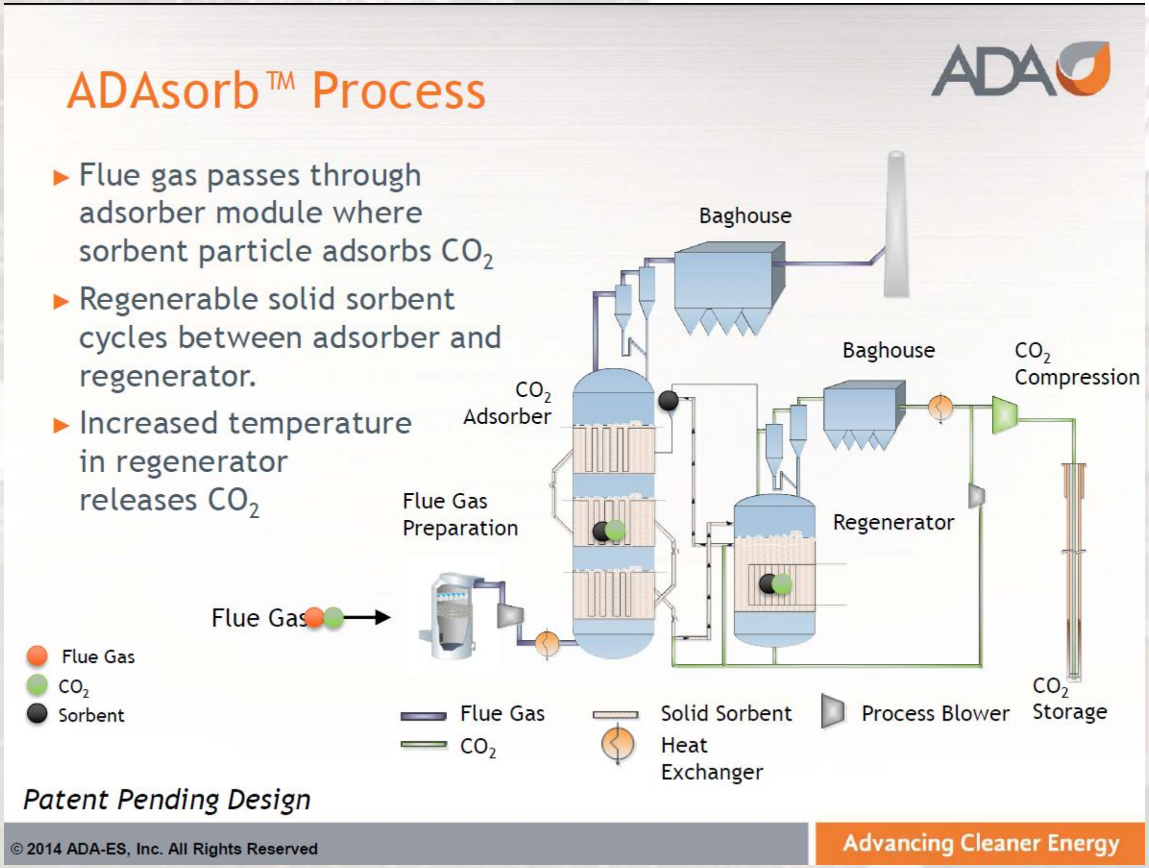
Power generation



- Over 250 potential CO_2 adsorbents have been evaluated by ADA to date (including INCAR-CSIC)
- Slipstream of flue gas from a coal-fired power plant
- A 1MWe pilot plant being designed and installed to validate performance for this novel technology. The current EPC schedule indicated the pilot should be ready for operation in early 2014

Post-combustion capture applications

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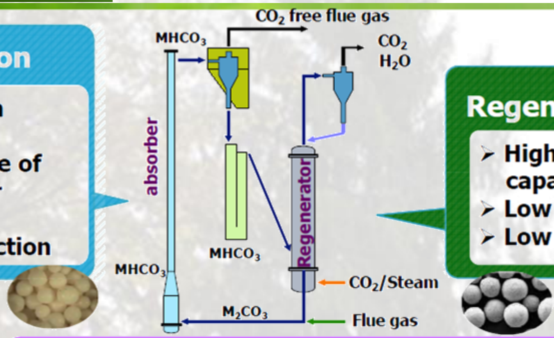
KEPCO

Absorption

- High sorption capacity(ΔL)
- Less influence of water & other emissions
- Less side reaction



Regeneration

- High sorption capacity(ΔL)
- Low C_p
- Low ΔH

Process

- Fast kinetics
- Reaction T (40~200℃) & ΔT~60 ℃
- Fluidized-bed reactor (AI, density, size, shape)
- Maintaining integrity of sorbent

Carbonation

$K_2CO_3(s)+CO_2(g) + H_2O(g) \rightarrow 2KHCO_3(s)$
ΔH = -3.25 GJ/tCO_2
$K_2CO_3 \cdot 1.5H_2O(s) + CO_2(g) \rightarrow 2KHCO_3(s) + 0.5\ H_2O(g)$, ΔH = -1.0 GJ/tCO_2

Operating temperature: 40-80°C

- Little Corrosion & No volatiles
- No waste water

- Easy to control heat for exothermic reaction

Regeneration

$2KHCO_3(s) \rightarrow K_2CO_3(s)+CO_2(g)+H_2O(g)$
ΔH = 3.25 GJ/tCO_2
$2KHCO_3(s) + 0.5\ H_2O(g) \rightarrow K_2CO_3 \cdot 1.5H_2O(s) + CO_2(g)$, ΔH = 1.0 GJ/tCO_2

Operating temperature: 140-200°C

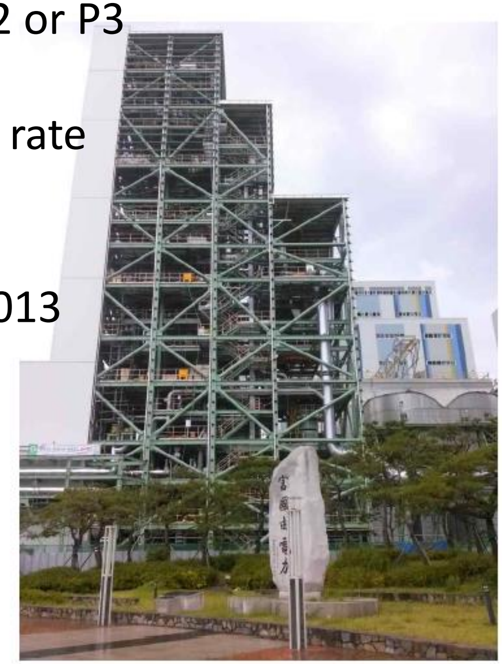
- Recover high-concentrated CO_2 after condensing H_2O

- Use waste heat, steam for endothermic reaction

❑ Solid sorbents for fluidized-bed applications
- High sorption capacity
- High mechanical strength

Power generation

- 10 MW slipstream from 500 MW coal-fired power plant
- Location: Hadong, Korea
- 200 t CO_2/d
- Sorbent: KEP-CO2P2 or P3
- Targets:
  - > 80% CO_2 capture rate
  - <95% CO_2 purity
  - US$ 30/t CO_2
- Start up: October 2013



10 MW Pilot Plant at KOSPO's Hadong coal-fired power plant, Unit # 8

WP2 Objectives

The main objective in WP2 is to prove **adsorption** with **low-temperature solid sorbents** as a high efficiency and environmentally benign technology for post-combustion CO_2 capture by means of experimental and modelling work.

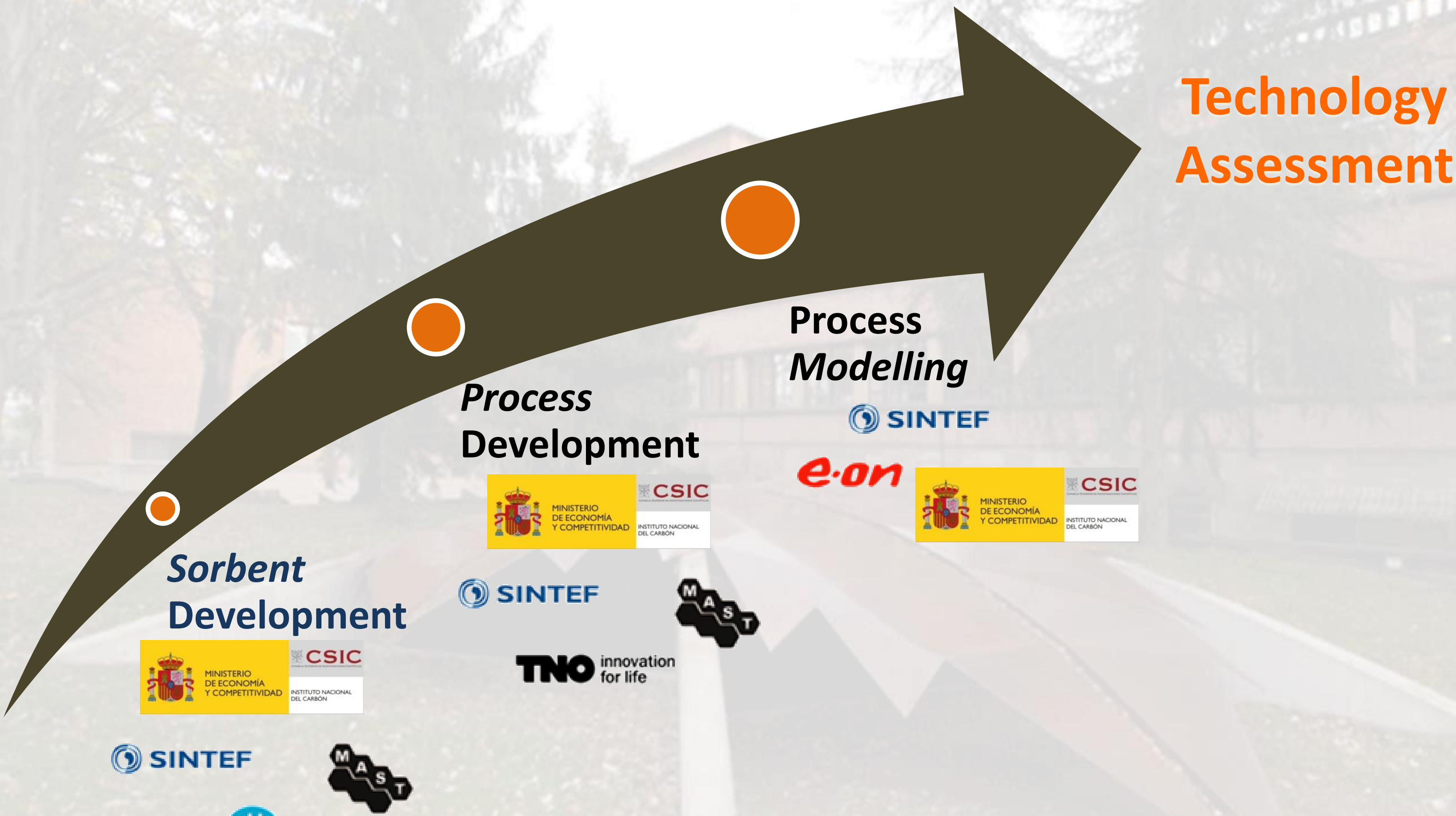
- Produce a **particulate solid adsorbent** for a moving bed reactor having suitable cyclic capacity under post-combustion conditions (e.g. >2.5 mmol/g for the high surface area sorbents) and that can withstand a 100°C temperature change within 3-4 minutes.

- Produce a structured **carbon monolith** sorbent with substantial equilibrium carbon dioxide uptake in high relative humidity environments (e.g. >1.5 mmol/g at 150 mbar CO_2 and 20°C) and with acceptable adsorption/desorption kinetics. The monoliths should also have enhanced thermal conductivity characteristics of better than 2W/mK.

- **Evaluate** and **model moving** and **fixed bed** based adsorption processes that combine low pressure drop and high thermal efficiency and determine the process performance.

Data will be generated, which allows the determination of the energy potential of the different concepts and benchmark the different concepts (WP4)

Partners/tasks in WP2



Porous solid sorbents: low temperature

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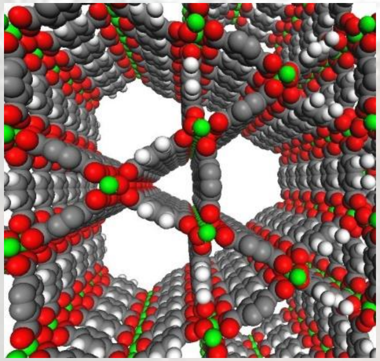
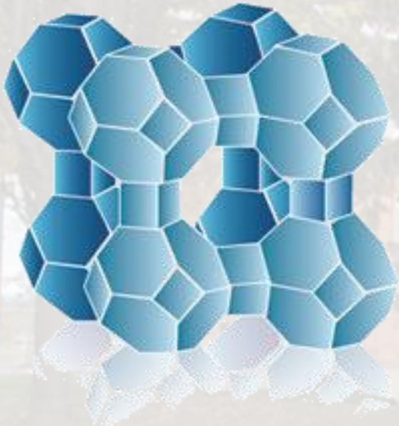


Metal-Organic Frameworks(MOF)

Cristaline compounds integrated by metal ions liked by organic ligands in a forming a porous network. Extremely high porosity suitable for gas storage and purification. Air/moisture sensitive.

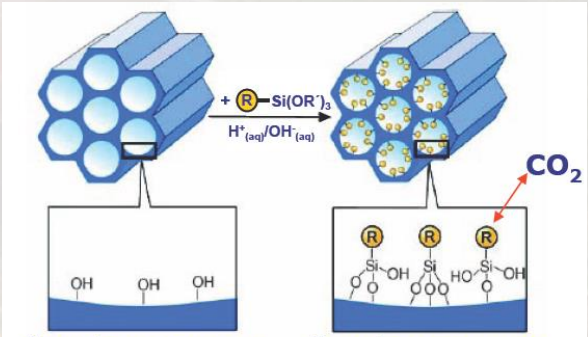


Zeolites

Aluminosilicate molecular sieves. High capacity and selective CO_2 sorbents in the higher pressure range. Very sensitive to water.

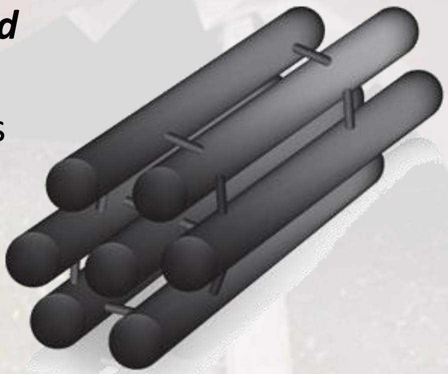
Functionalised porous materials

- Surface (e.g. amine grafted)
- Matrix (e.g. N containing polymer)



Carbon-based

From activated carbons to carbon molecular sieves. Less sensitiveness to water, easy regeneration and lower cost. Low temperature CO_2 sorption.



Sorbent selection

Ideal adsorbent:

- ✓ Low cost
- ✓ Availability
- ✓ High capacity
- ✓ High selectivity towards CO_2
- ✓ Ease of regeneration
- ✓ High stability/durability

Carbon materials	
Cost	✓
Ease of regeneration	✓
Water tolerance	✓
Durability	✓
Availability	✓

Carbon precursors selected within HiPerCap:

- Agricultural by-products
- Phenolic resins
- Natural polymers/precursors

Sorbent & Process development

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I. Sorbent Production

II. Evaluation

- ✓ Characterization
- ✓ Pure component adsorption isotherms at selected T: CO_2, N_2, H_2O

Equilibrium of adsorption

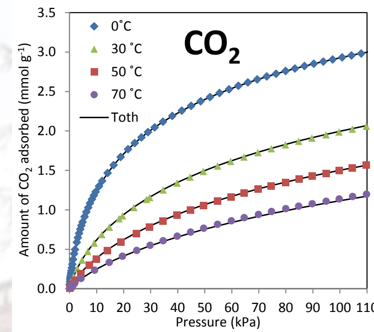
- ➢ Multicomponent adsorption experiments

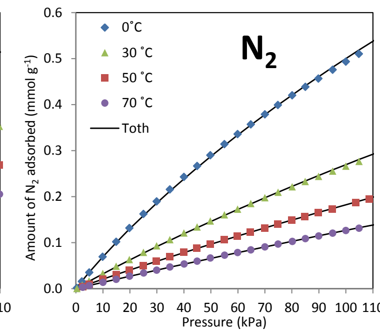
  Selectivity
  Kinetics of adsorption
  Evaluation of operating conditions
  Influence of impurities
  Validation of adsorption model

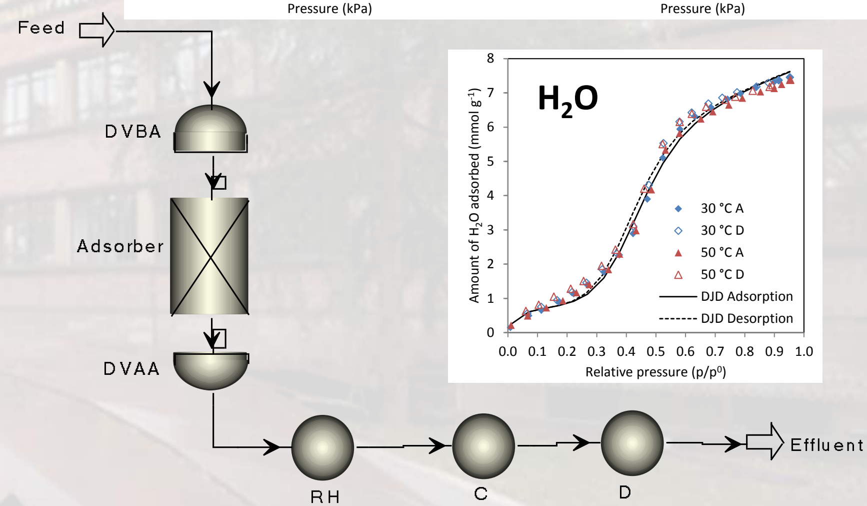
Dynamics of adsorption-desorption

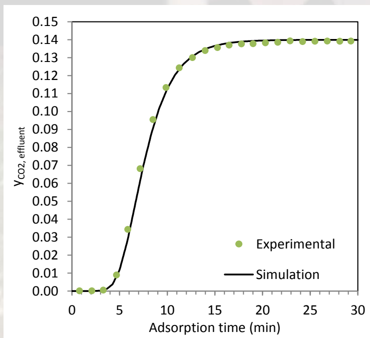
III. Modelling

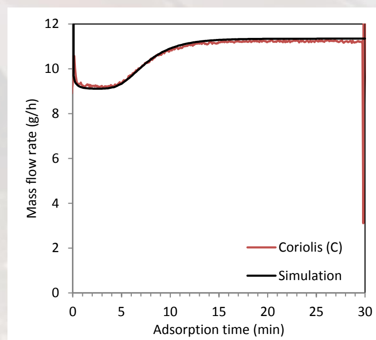
Design of adsorption-based CO_2 capture unit

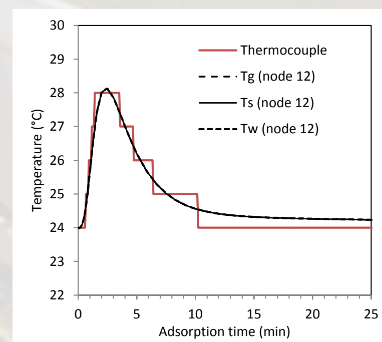












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Adsorbent requirements from process operation

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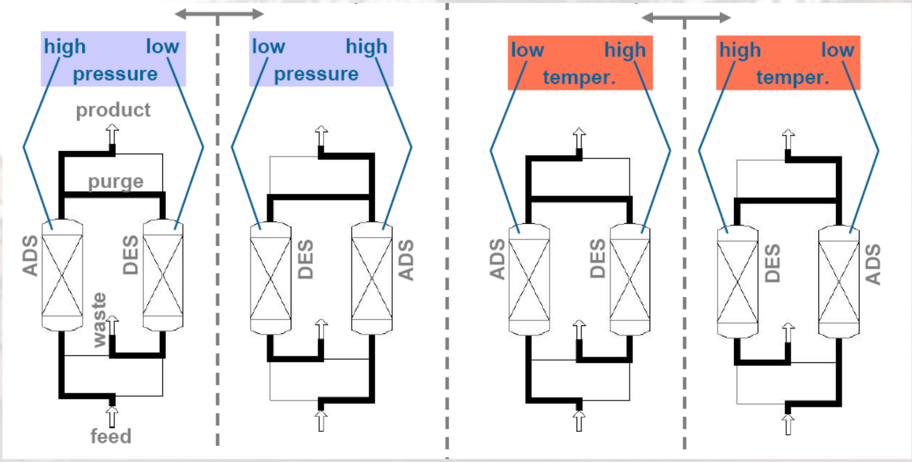
1. Minimal compression of flue gas (vacuum operation) needs large working capacities between 0 and 1 bar
2. Regeneration of the adsorbent is where the energy is needed
3. Difference between adsorption and desorption for CO_2 compared to other gases is key
4. Large adsorption amount is not necessarily better
5. Interaction of species is important (impurities)

Pressure Swing Adsorption (PSA/VSA)

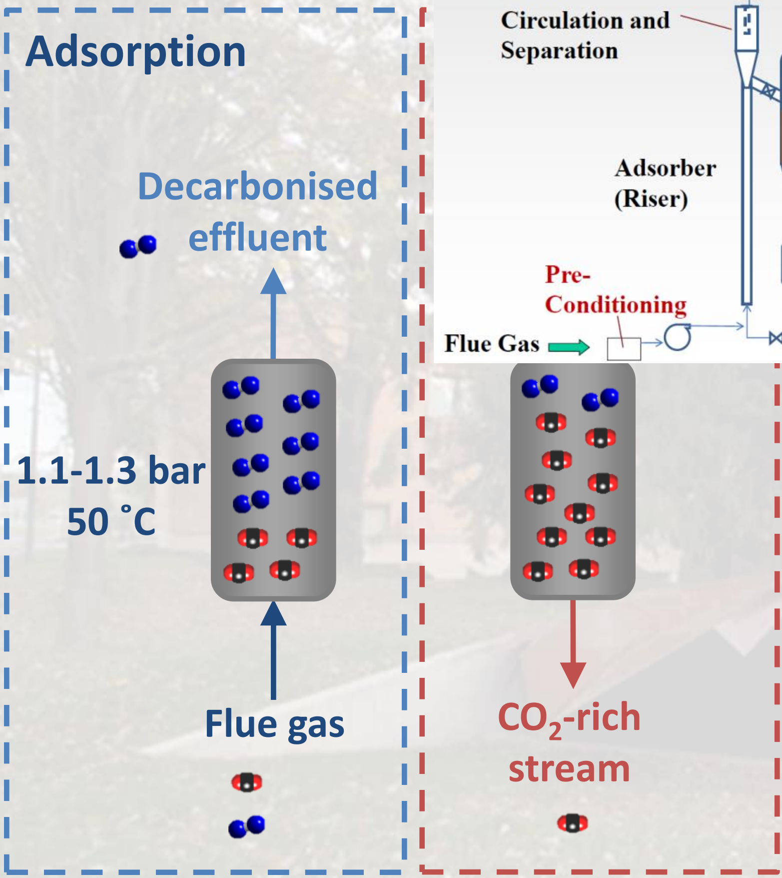


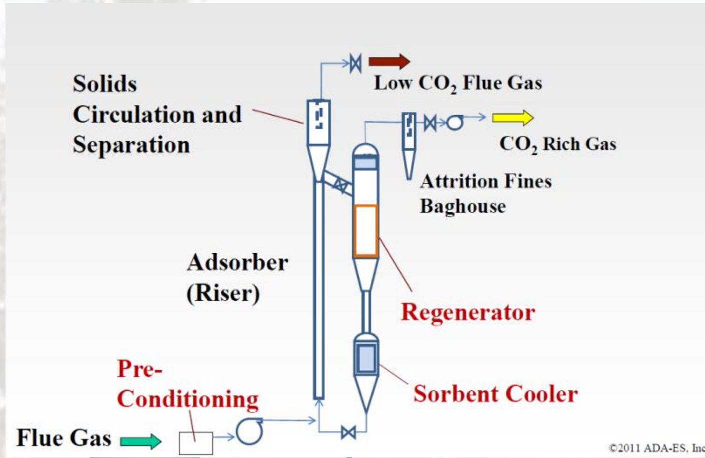
Temperature Swing Adsorption (TSA)

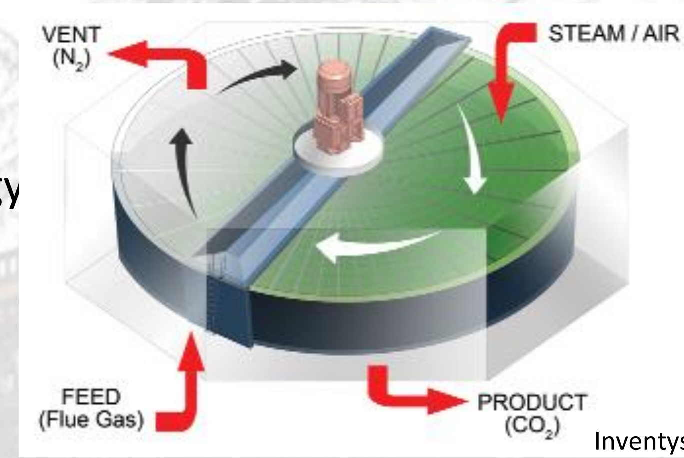
Process design parameters

- ***Adsorbent inventory***: scales with CO_2 working capacity
- ***Purity and recovery***: scales with CO_2 working selectivity
- Cycle should be optimized for specific feed gas-adsorbent combinations

Adsorption based processes







TSA

⊖ Longer cycles => lower productivity

=> Circulating solids (ADA-ES)

=> Rotating bed (Veloxotherm^{TM}, Inventys)

⊕ **$ 15 per tonne!**

VSA

⊕ Rapid swing cycles

Temperature Swing Adsorption based processes

Fixed –bed

Conventional heating (steam or hot gas) is lengthy

Mass transfer↔ Heat transfer

Cycle duration ↔ Productivity

How to heat and cool the adsorbent bed more rapidly and increase the productivity of a TSA process?

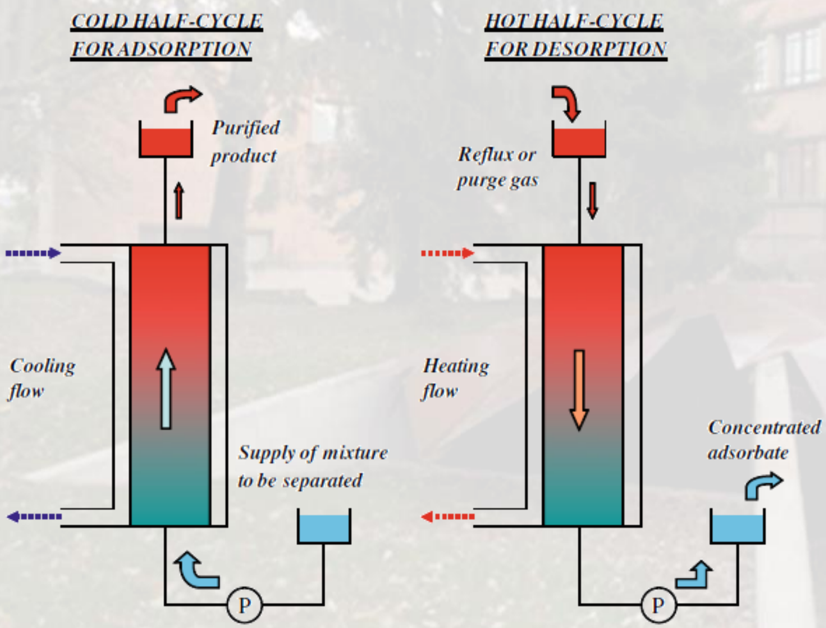
. Improve thermal conductivity: promoters

. Cycling -zone adsorption

. Circulating fluidized bed

How to heat and cool the adsorbent bed more rapidly and increase the separation efficiency of a TSA process?

. Electro-Thermal swing operation



Source: Luo, L. (2013). *Intensification of adsorption processes in porous media*. Chapter 2. Heat and mass transfer intensification and shape. A multi-scale approach.

Table 2.3 Physical, electrical, adsorption and cost properties of ACM, ACB, and ACFC (Luo et al. 2006) Carbon 44:2715–2723

Adsorbent Model	ACM RICD, Beijing, China	ACB Ambersorb 572 (Rohm and Hass)	ACFC ACFC-5092-20 (American Kynol Inc.)
Pressure drop at 0.1 m/s of superficial gas velocity (Pa/cm)	1.0	89.9	38.8
Permeability (m^2)	1.8×10^{-8}	2.0×10^{-10}	1.9×10^{-11}
Micropore volume (cm^3/g)	0.21	0.41	0.75
Adsorption capacity at $p/p_o = 0.9$ (g/g)	0.26	0.52	0.6
Throughput ratio	0.81	0.91	0.81
Length of unused bed	0.21	0.08	0.21
Electrical resistivity at 455 K (Ω-m)	3.9×10^{-1}	8.1×10^{-2}	4.8×10^{-3}
Max. achieved concentration factor	46	20	1,050
Cost ($/kg)	3.6	1,575	730

Monolith | Spherical Beads | Fiber cloth

Temperature Swing Adsorption based processes

Fixed –bed: Structured adsorbents

Advantages:

- Superior mass transfer kinetics
- Effective heat transfer: uniform T distribution
- Low pressure drop

Challenges:

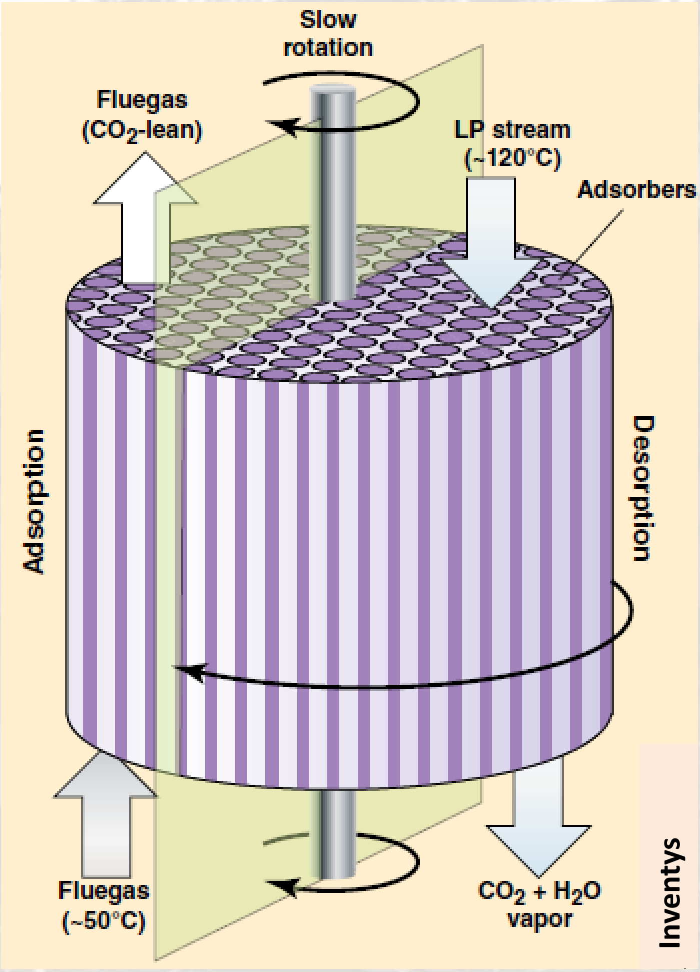
- Throughput: working capacity
- Working capacity: wall thickness and voidage

Conformations:

- Monoliths: HiPerCap focus
- Fabric structures
- Laminates

Monolith design parameters:

- Cell density: ensure high loading
- Wall thickness: mass transfer resistance (external film and pore diffusion)
- Bed length: sufficient residence time



Temperature Swing Adsorption based processes

Moving-bed: Particulates

Advantages:

- High working capacities
- Uses the heat contained in the flue gas for regeneration
- Low pressure drop

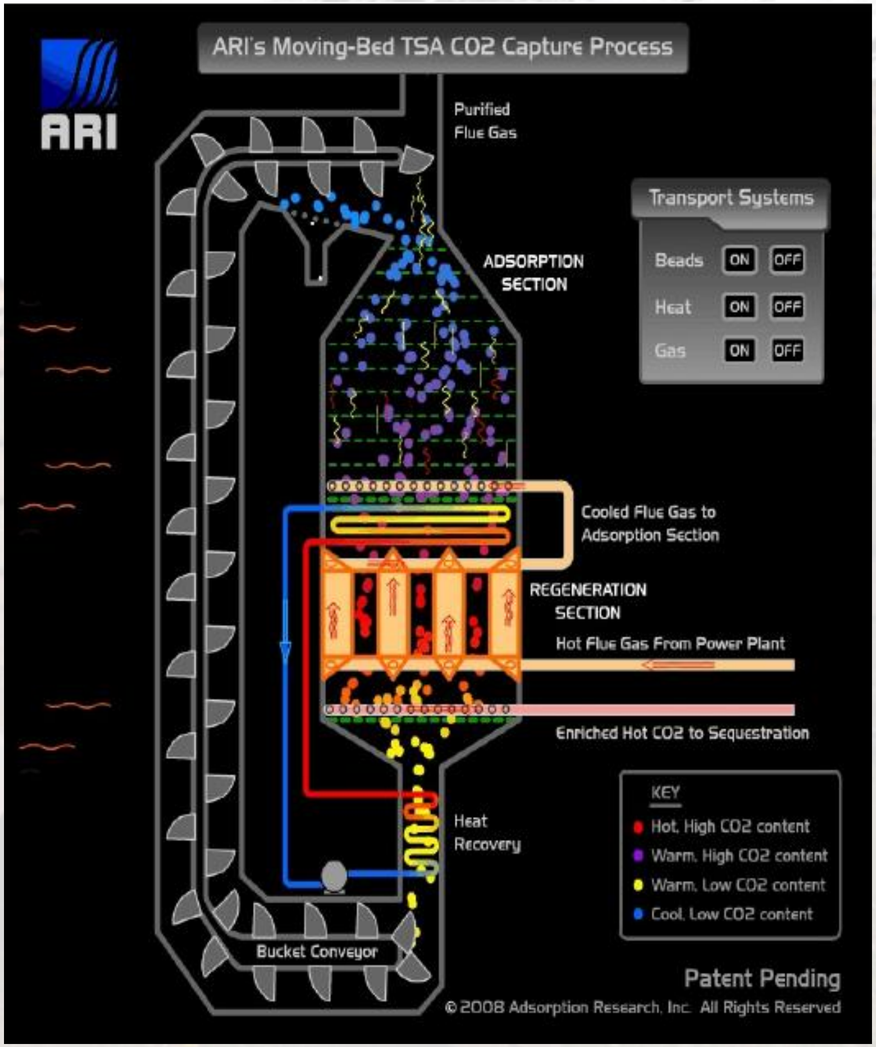
Challenges:

- Hydrodynamics: scarce data
- Velocity: limited by fluidization
- Particle residence time in the regeneration section

Table 4. Physical Properties and Parameters Employed in Moving Bed Design

Moving Bed Regenerator Design		
total flue gas flow	34 000	am^3/min
number of modules	5	
Sorbent Properties		
particle density	882	kg/m^3
packed void fraction	0.52	
particle heat capacity	1926	J/(kg·°K)
Thermal Conductivity		
gas (CO_2 @ 212 °F)	0.022	W/(m·°K)
solids (polypropylene)	0.138	W/(m·°K)
effective thermal conductivity	0.058	W/(m·°K)
alpha, α	2.59×10^{-4}	m^2/h
opening between panel, $2b$	50.8	mm
solid velocity, v_z	2.5	mm/s
sorbent circulating rate	4903	kg/min
cross-sectional area required	76	m^2

Source: Yang et al., Ind. Eng. Chem. Res., 2009, *48*, 341-351



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