MINISTERIO DE ECONOMÍA, INDUSTRIA Y COMPETITIVIDAD

CSIC
INSTITUTO NACIONAL DEL CARBÓN

HiPerCap CO_2

HiPerCap: Adsorption Technologies – Overview & Results

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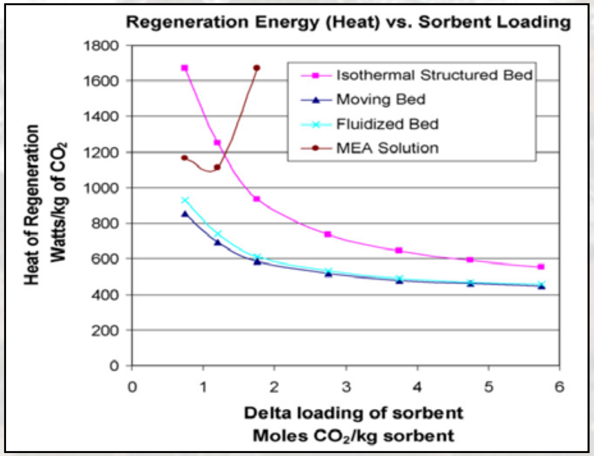
Solid sorbents: *Why?*

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

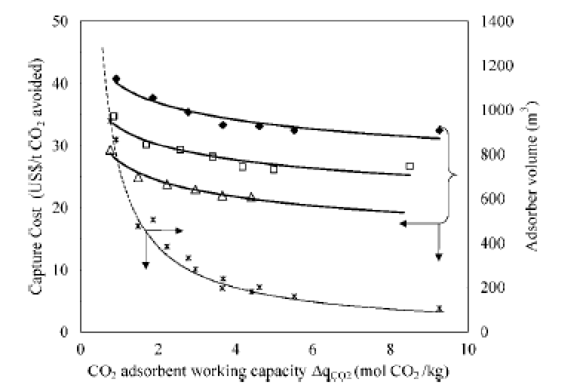


Figure 7. Effect on CO_2 capture cost (—) and total adsorber volume (---) of CO_2 adsorbent working capacity at three CO_2/N_2 selectivities: 50 (♦), 100 (□), and 500 (Δ), at 85% CO_2 recovery.

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

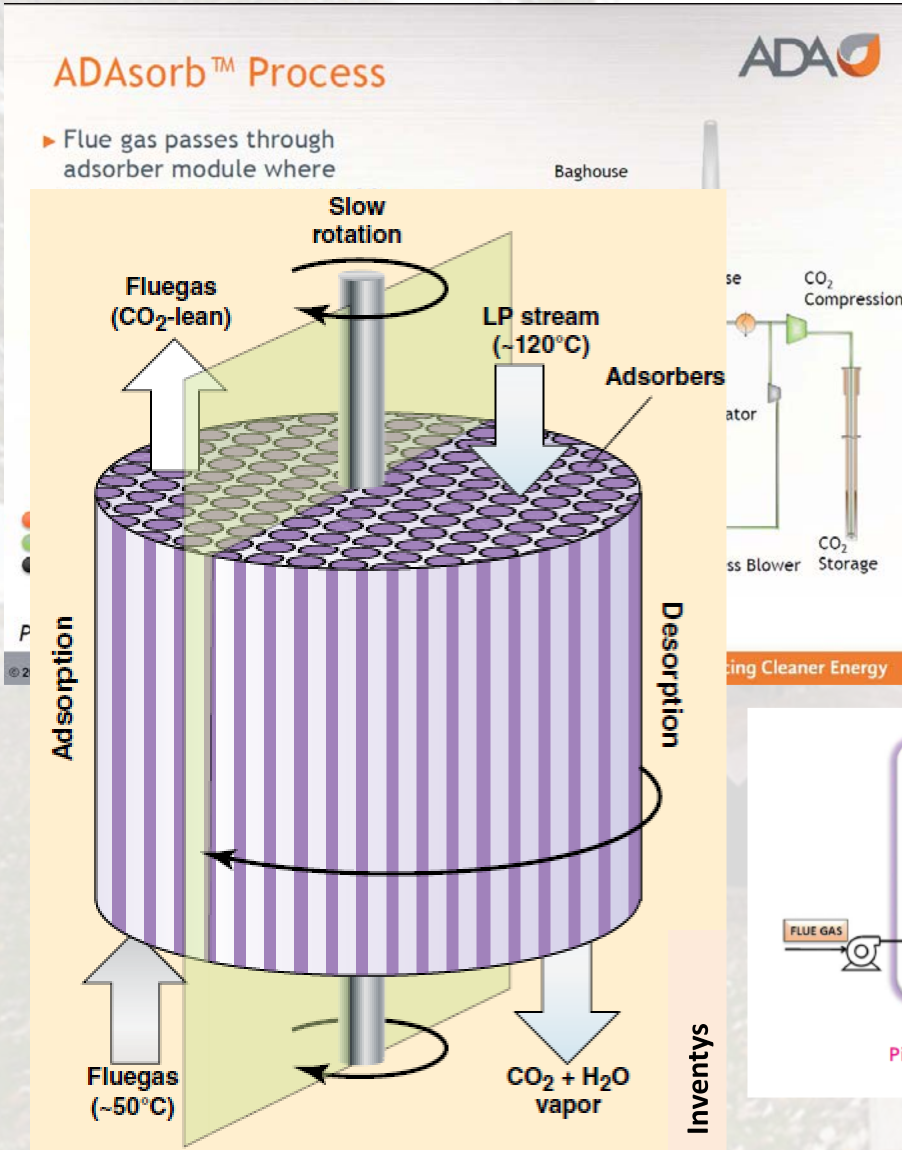
Post-combustion capture application- challenges

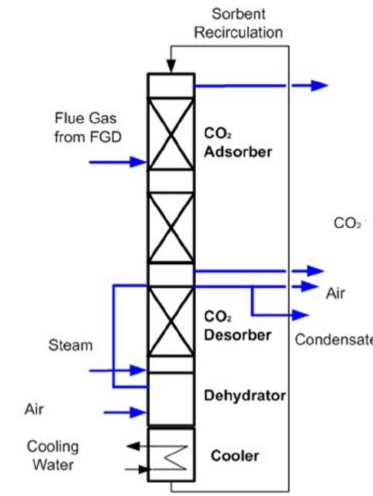
HiPerCap CO_2

	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)	90	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	

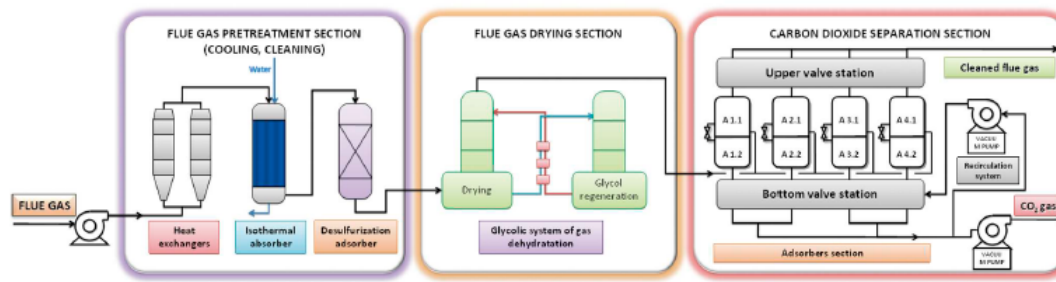
- Very large: pressure drop
- Very low: no driving force
- Relatively high for adsorption
- Ranges from 12 to 63% (wet basis)
- High water content
- SOx, NOx, ash, heavy metals, etc. present

Post-combustion capture applications





SRI Advanced Carbon Sorbent (ACS) technology



Pilot DR-VPSA installation – technological diagram

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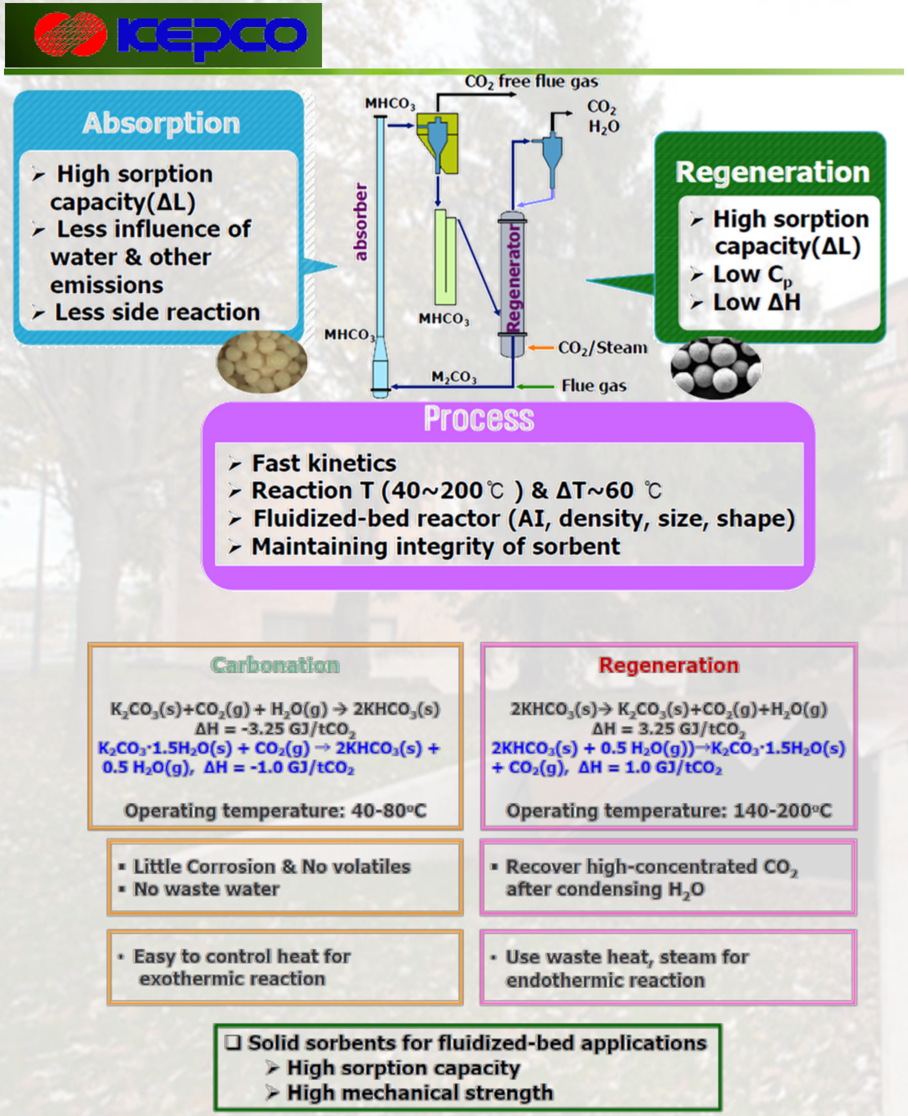
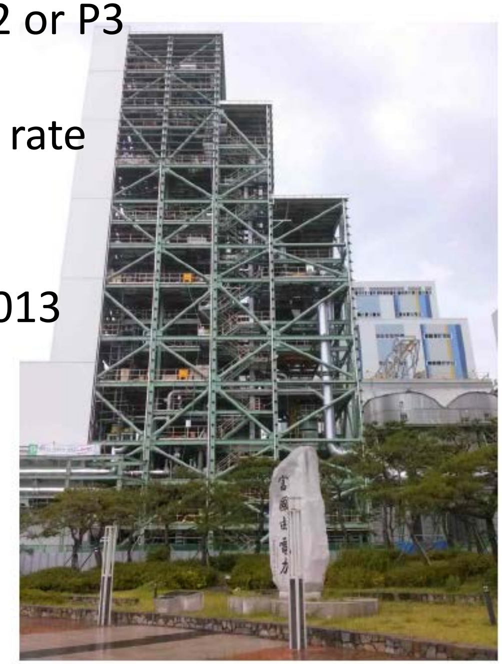
Post-combustion capture applications



- 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

HiPerCap CO_2

The main objective was 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

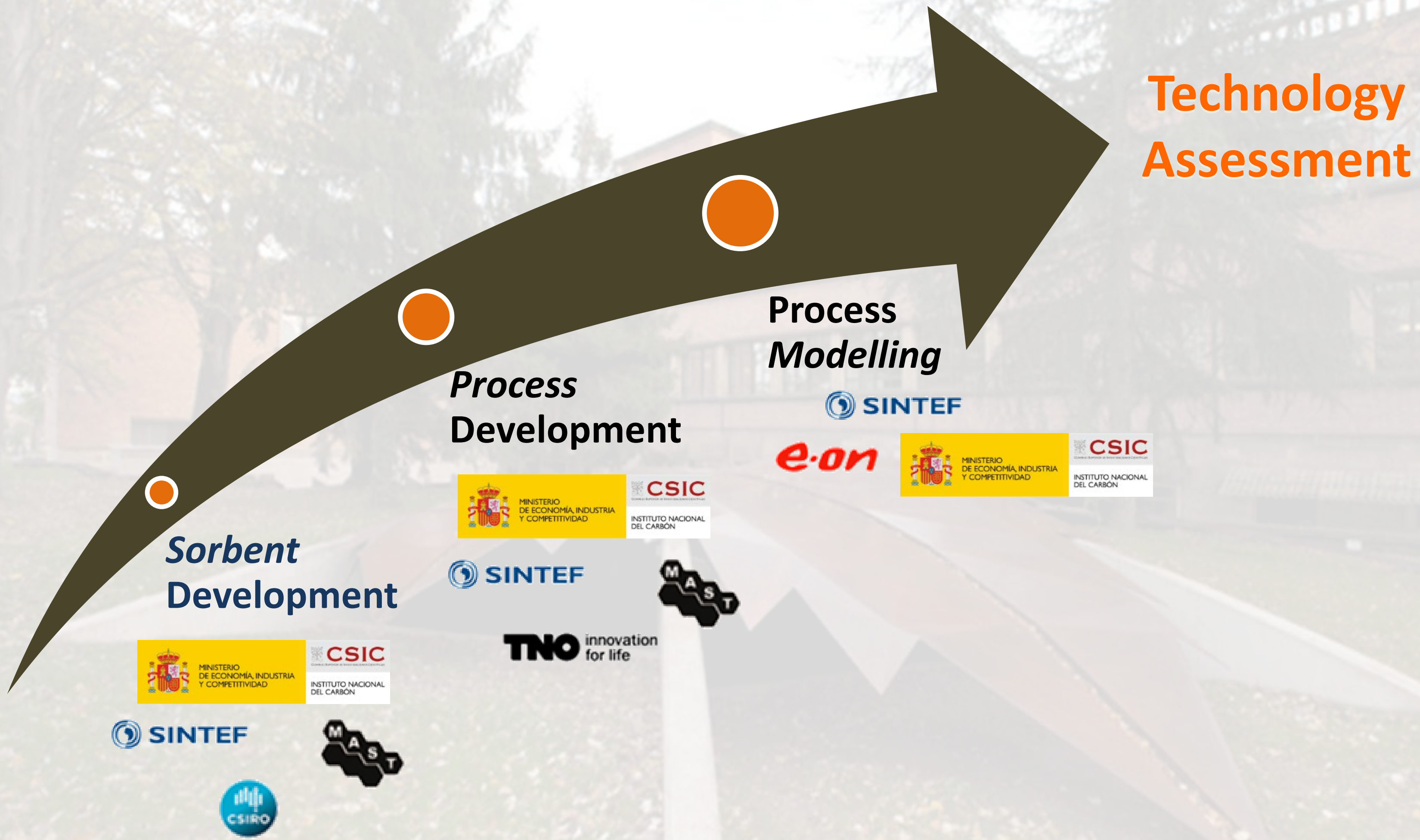
- Produce a **particulate solid adsorbent** for a moving bed reactor having suitable cyclic capacity under post-combustion conditions (e.g. >2.5 mmol/g for the high surface area sorbents) and that can withstand a 100°C temperature change within 3-4 minutes.

- 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.

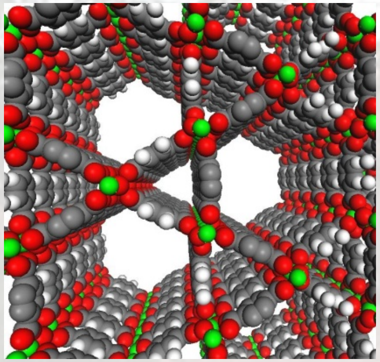
- **Evaluate** and **model moving** and **fixed bed** based adsorption processes that combine low pressure drop and high thermal efficiency and determine the process performance.

Data generated were transferred for process assessment in WP4

Partners/tasks in WP2

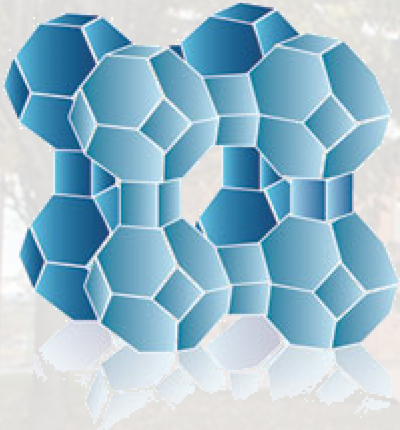


Porous solid sorbents: low temperature



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.

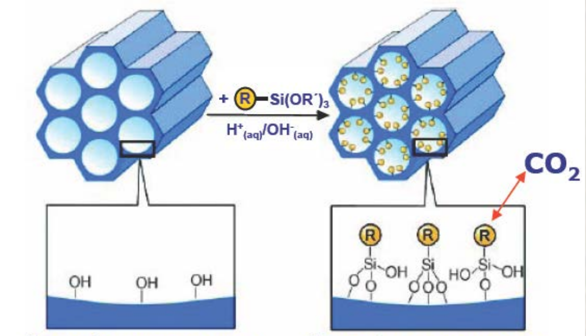


Zeolites

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

I. Sorbent Production

II. Evaluation & Modelling

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

Thermodynamics of adsorption

- ➢ Multicomponent adsorption experiments

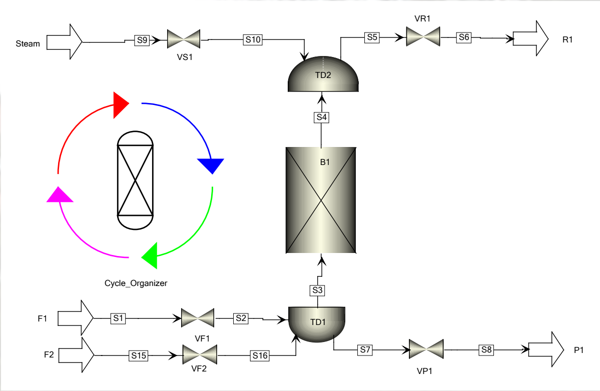
Selectivity
Kinetics of adsorption
Evaluation of operating conditions
Influence of impurities
Validation of adsorption model

Fixed-bed adsorption-desorption

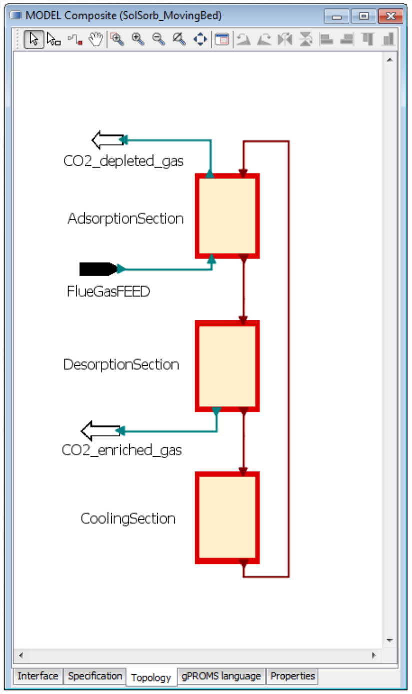
III. Simulation

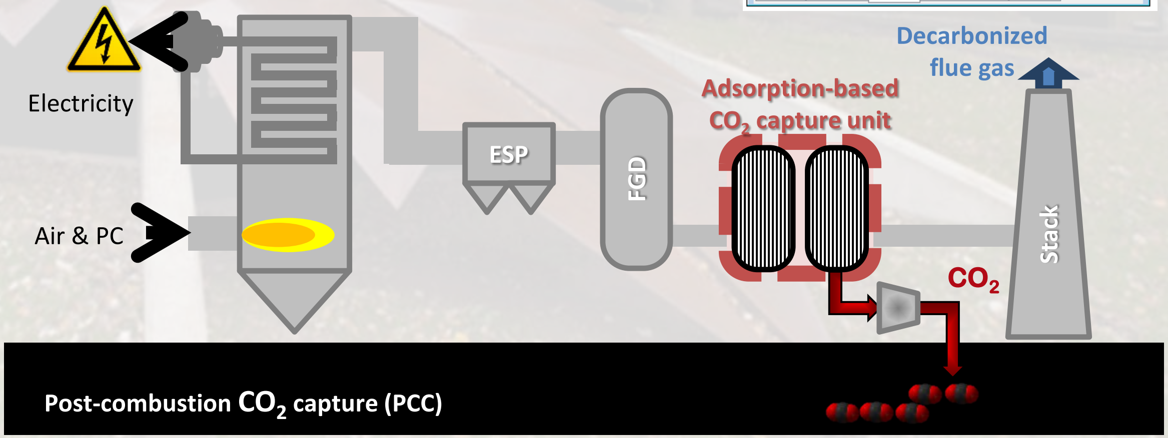
Design of adsorption-based CO_2 capture unit

Fixed-bed: *Aspen Adsorption*



Moving-bed: *gPROMS*





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Sorbent & Process development

HiPerCap CO_2

Fixed-bed TSA (FBTSA)

Phenolic resin honeycomb carbon monolith:

- ✓ Low pressure drop
- ✓ Effective heat transfer
- ✓ High stability
- ➢ Challenges: throughput & working capacity

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Moving-bed TSA (MBTSA)

Phenolic resin carbon beads:

- ✓ Low pressure drop
- ✓ Hardly no attrition
- ✓ Uses heat in flue gas for regeneration
- ➢ Challenges: hydrodynamics & particle residence time in regeneration

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Sorbent & Process development

HiPerCap CO_2

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Adsorption properties

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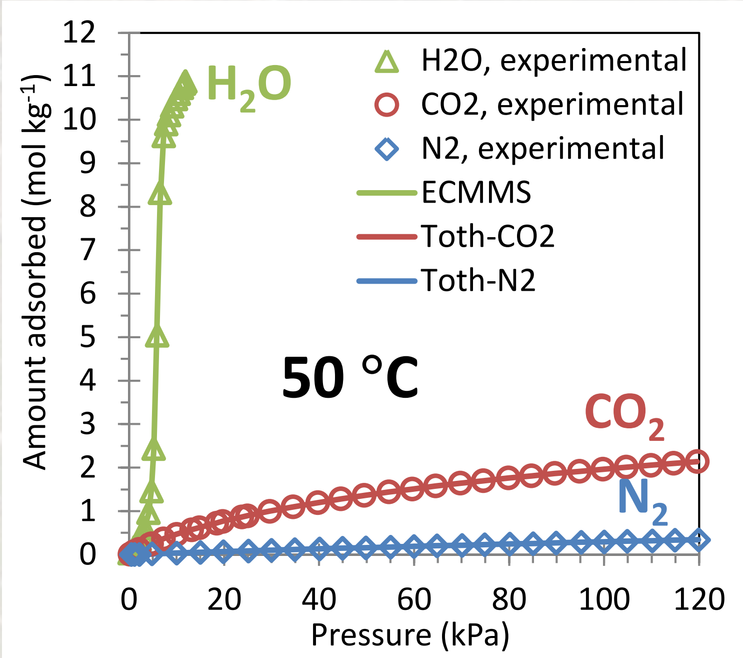
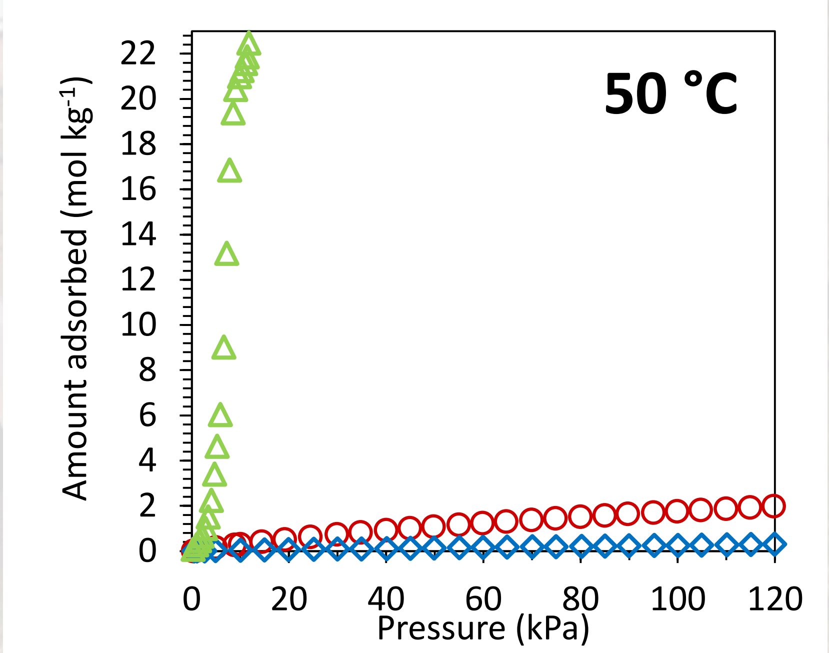
	Monolith	Beads	units
BET surface area	708	1314	$m^2\ g^{-1}$
Total pore volume	0.29	1.22	$cm^3\ g^{-1}$
Narrow micropore volume	0.29	0.22	$cm^3\ g^{-1}$
Narrow micropore width	0.57	0.79	nm





Process modelling: FBTSA

CSIC designed, developed and scaled up several **FBTSA post-combustion CO_2 capture** processes that meet the following specifications:

- ✓ ≥ 85% CO_2 capture rate from the 800 MW_e advanced supercritical coal reference plant
- ✓ The CO_2 product is delivered to the compression stage with a purity of ≥ 95% (dry basis) at 2 bar and 30 °C

TSA with steam stripping

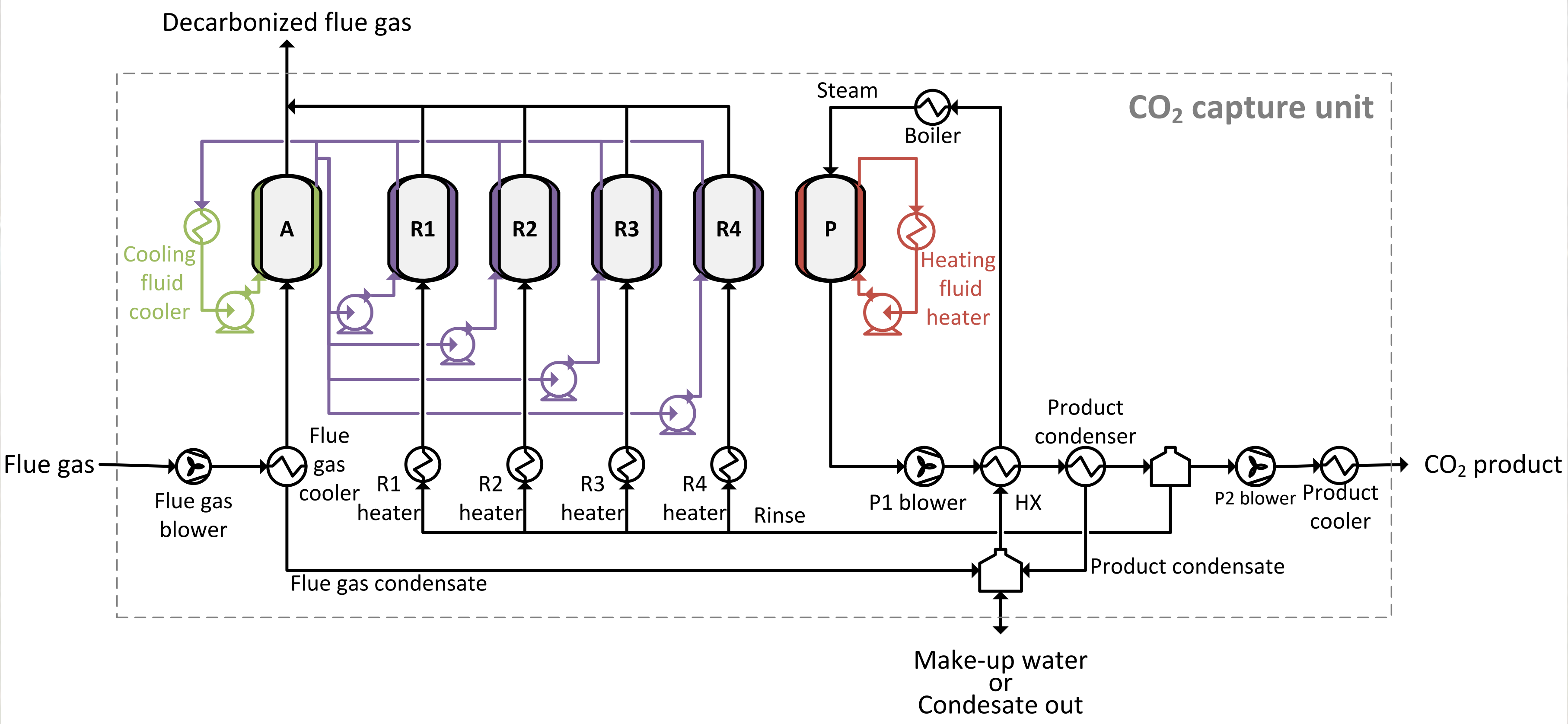
Carbon honeycomb monoliths (D = 3 cm; H = 0.7 m) installed in 24 adsorbers

Success cases:

- **Case 1**: the flue gas is fed to the adsorption capture unit directly after the desulfurization unit, at 47 ° C
- **Case 2**: the flue gas is cooled down to 30.78 °C prior to be fed to the adsorption capture unit

Process modelling: FBTSA

Case 2: flue gas is cooled down to 30.78 °C prior to adsorption unit



Process modelling: FBTSA

Parameter	Case 1	Case 2	Case 2b	Units
Purity of the CO_2 product (dry basis)	95.4	95.6	95.7	%
CO_2 capture rate	85.4	85.4	88.6	%
Productivity	0.35	0.40	0.52	$kg_{CO2}\ kg_{adsorbent}^{-1}\ h^{-1}$
Specific heat duty	4.89	3.59	2.89	$MJ_{th}\ kg^{-1}\ CO_2$
Specific cooling duty	4.40	3.36	2.79	$MJ_{th}\ kg^{-1}\ CO_2$
Specific electricity consumption	123	127	118	$kJ_e\ kg^{-1}\ CO_2$
Total amount of adsorbent	1428	1256	1005	tons

Case 2b *evaluates the influence of faster adsorption kinetics on Case 2 configuration*

Process modelling: MBTSA

SINTEF designed and scaled up several **MBTSA post-combustion CO_2 capture** processes that meet the following specification:

- ✓ ≥ 85% CO_2 capture rate from the 800 MW_e advanced supercritical coal reference plant

Moving bed TSA

Four units (D = 10 m; H = 25 m) installed in parallel

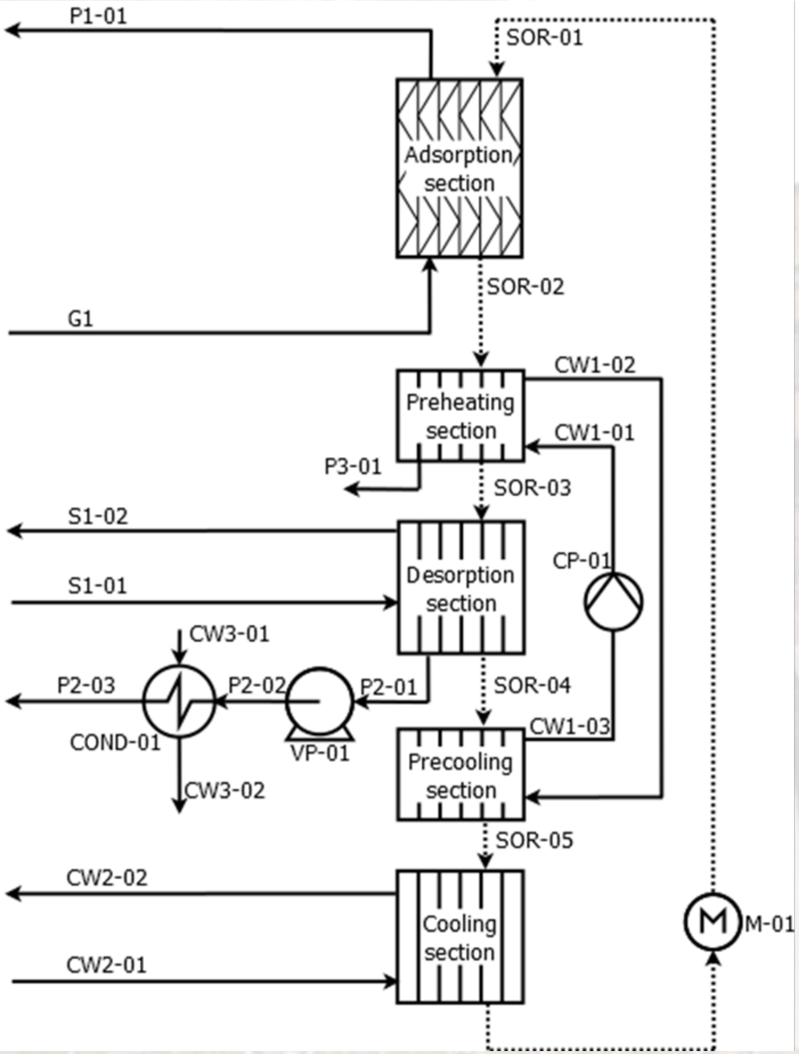
Basic configurations (A & B): CO_2 purity very low (<< 95%)

Success cases:

- **Configurations D**: includes preheating section and recycle of extracted gas from top of preheating section into the flue gas feed.

Process modelling: MBTSA

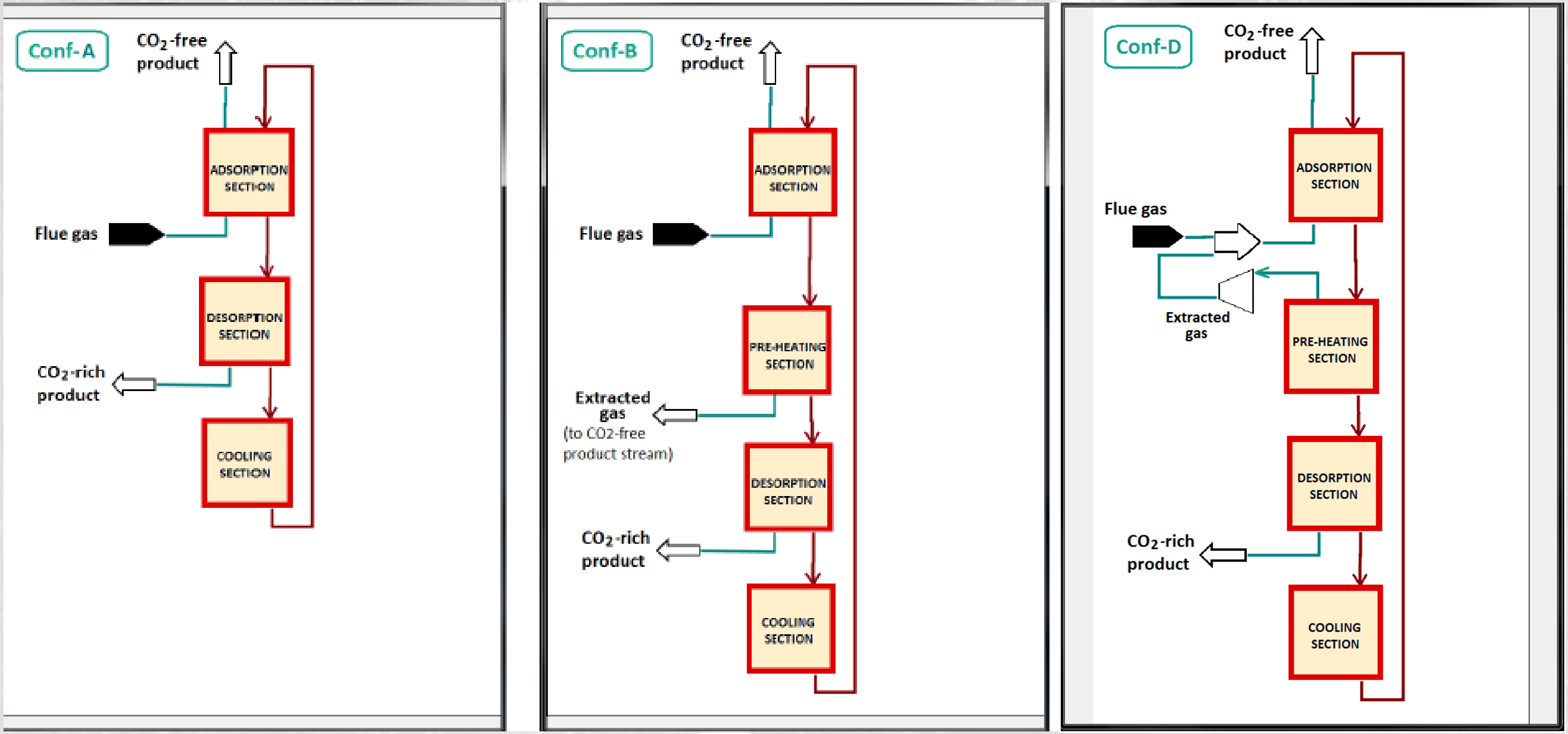
4 parallel moving bed TSA units



Name/tag	*info*
Stream	
CW1-01	Cooling water for heat recovery at preheater inlet (closed loop)
CW1-02	Water for heat recovery at preheater outlet (closed loop)
CW1-03	Water for heat recovery at precooler outlet (closed loop)
CW2-01	Cooling water from power plant for sorbent cooling (supply)
CW2-02	Cooling water used for sorbent cooling (supply)
CW3-01	Cooling water for condenser - drying of CO2-rich product (supply)
CW3-02	Cooling water for condenser - drying of CO2-rich product (return)
G1	Feed gas (flue gas from power plant)
P1-01	CO2-depleted product
P2-01	CO2-rich product (wet)
P2-02	CO2-rich product after condenser
SOR-01	Sorbent at adsorption section inlet
SOR-02	Sorbent at adsorption section outlet/preheating section inlet
SOR-03	Sorbent at preheating section outlet/desorption section inlet
SOR-04	Sorbent at desorption section outlet/precooling section inlet
SOR-05	Sorbent at precooling section outlet/cooling section inlet
S1-01	Steam from power plant (for sorbent regeneration)
S1-02	Exhaust steam back to power plant (after sorbent regeneration)
Separation equipment	
Adsorption section	
Preheating section (heat exchanger)	
Desorption section (heat exchanger)	
Cooling section (heat exchanger)	
Cooling section (heat exchanger)	
Auxiliary equipment	
M-01	Motor for sorbent circultation
CP-01	Circulating pump
VP-01	Vacuum pump
COND-01	Condenser (for drying of CO2-rich product)

Process modelling: MBTSA

4 parallel moving bed TSA units

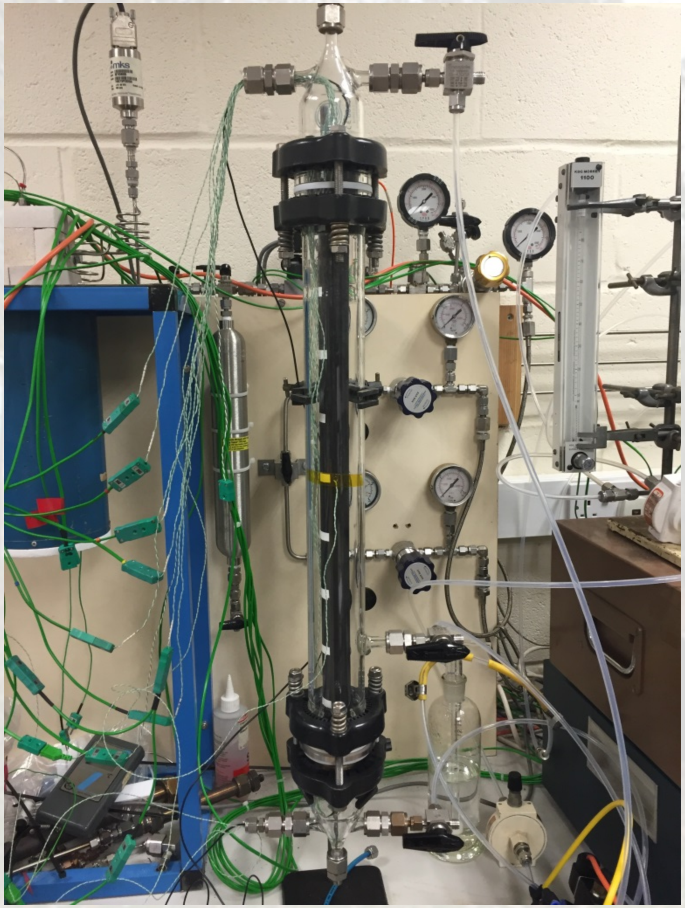


Process modelling: MBTSA

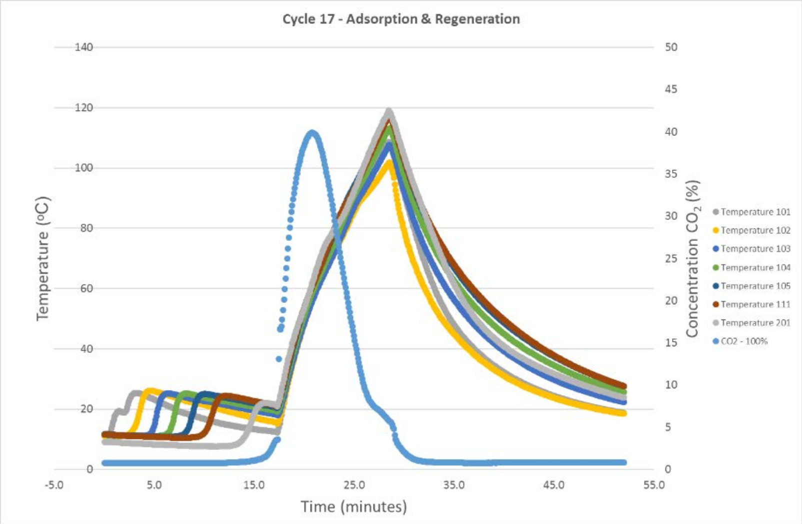
Parameter	Conf A	Conf B	Conf D	Units
Purity of the CO_2 product (dry basis)	65	72	94.6	%
CO_2 capture rate	86	78	85.6	%
Heat duty (external heat)	410	410	NA	MW_{th}
Recovered heat	660	660	NA	MW_{th}
Cooling duty	382	382	NA	MW_{th}
Specific electricity consumption	23.9	23.9	NA	$kJ_e\ kg^{-1}\ CO_2$
Amount of circulating sorbent (per unit)	2280	2280	2550	$kg\ s^{-1}$
Total amount of adsorbent	7982	7982	NA	tons

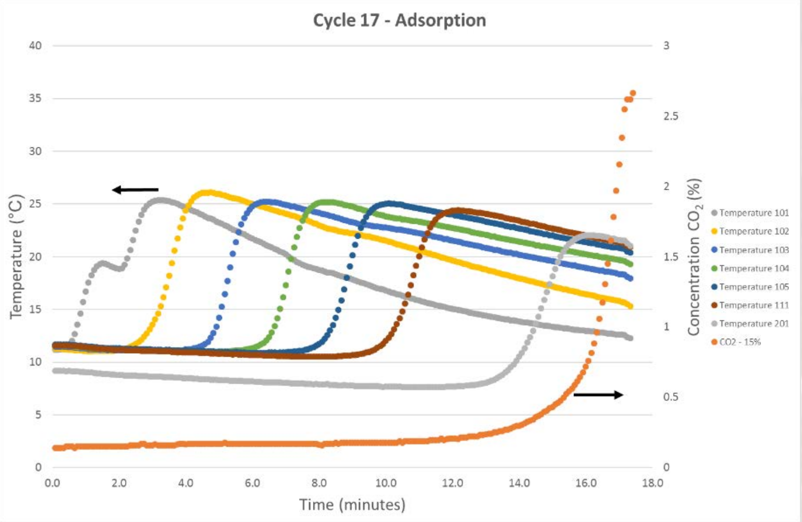
Testing with real flue gas from power plant

TNO innovation for life



MAST Carbon monolith module





Stable performance over 24 cycles of adsorption-regeneration

Conclusions

- Both MBTSA and FBTSA reach the targets defined in HiPerCap: ≥ 85% CO_2 capture rate with ≥ 95% CO_2 purity from the 800 MW_e advanced supercritical coal reference plant.
- Reducing the energy penalty of the TSA capture unit is challenging and requires action on the solid sorbent and engineering developments.
- Testing with real flue gas demonstrated the stability of the adsorption based system.

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