The 10th Trondheim Conference on
CO_2 Capture, Transport and Storage

KCRC

A Heat Integrated Solid-sorbent Based Fluidized Bed Process for Post-Combustion CO_2 Capture

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Dry sorption vs. amine scrubbing

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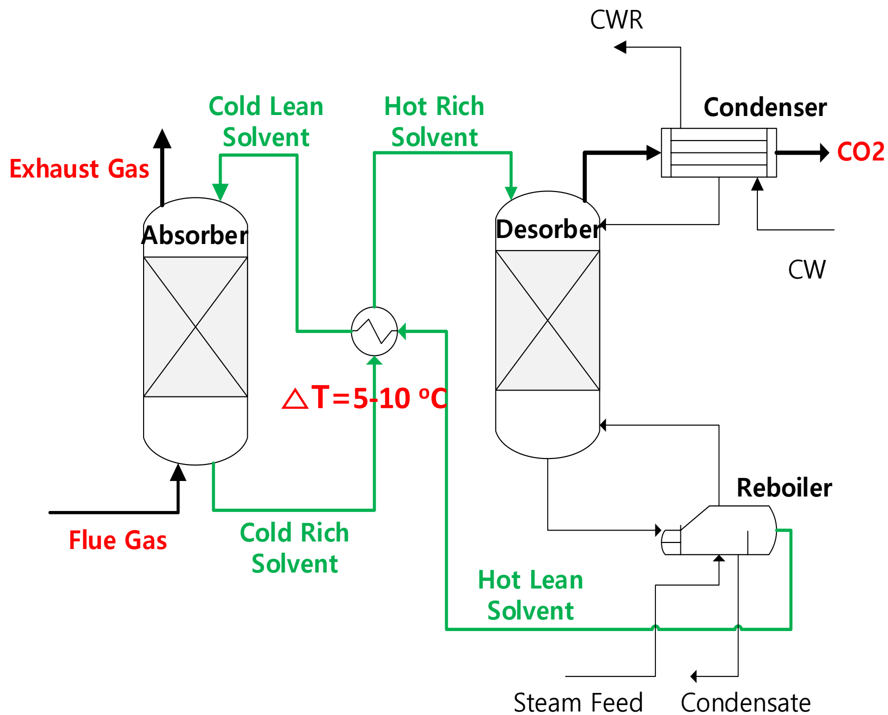
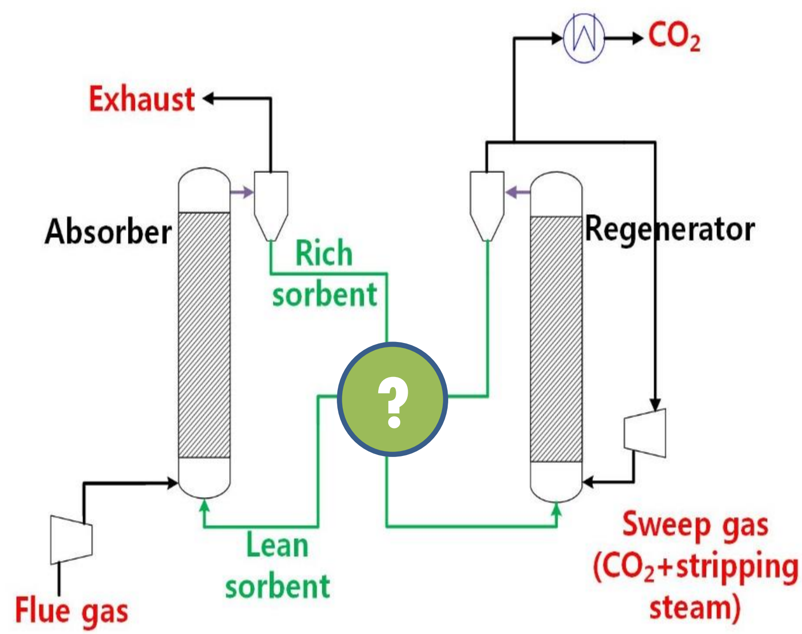
Amine Scrubbing Process



Solid Sorbent-based Process



- **Advantage of dry-sorbent process**

  Low degradation / corrosiveness / volatility

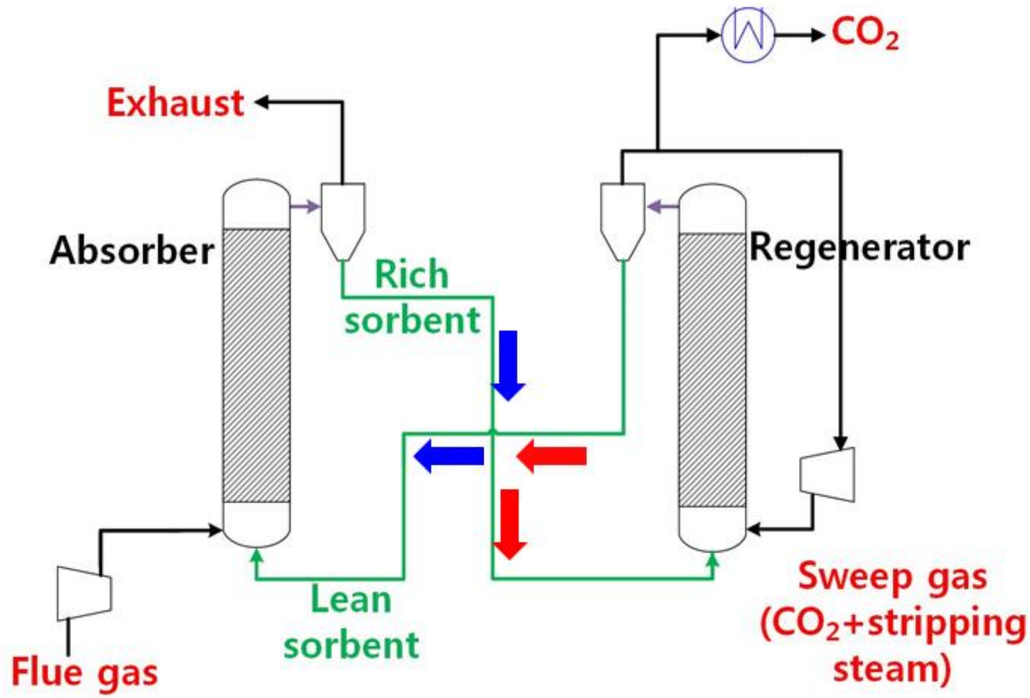
- **Main issue**

  1) Difficult heat exchange between lean/rich sorbents

  2) Low fluidity

Dry sorption process developed by KRICT & KAIST

- Low temperature process with sensible heat exchange



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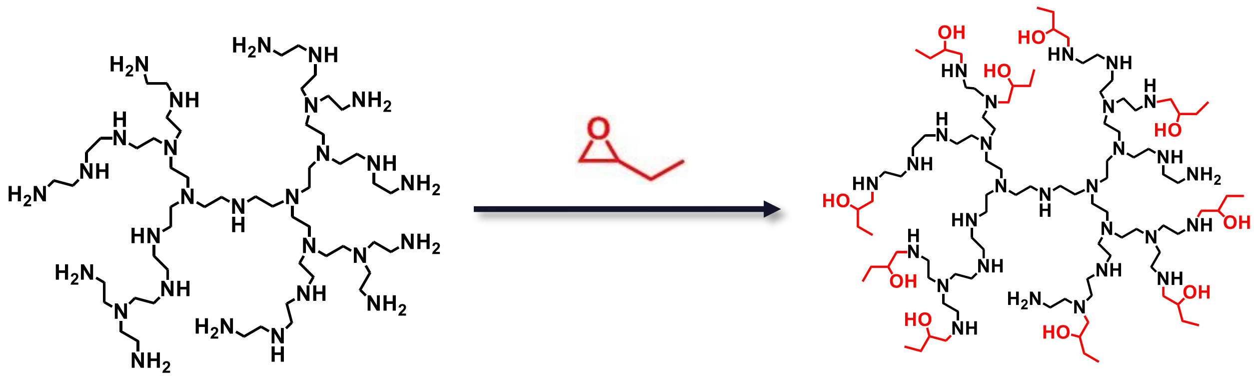
- Epoxy functionalized sorbent with a low heat of absorption

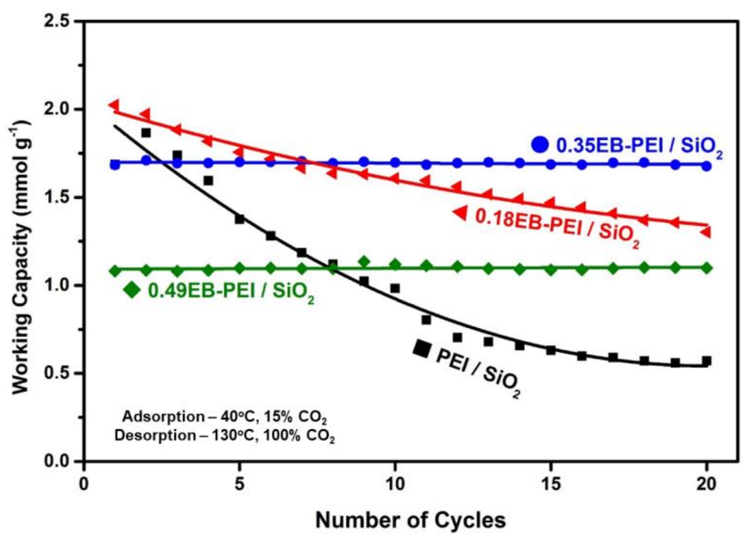
KRICT
(Dr. Yong Ki Park)
- Process development
- Sorbent shaping & scale-up

KAIST
(Prof. Minkee Choi)
- Sorbent development

(KAIST) Epoxybutane-functionalized PEI (EB-PEI)

- Epoxy-functionalization of primary amines in PEI
  - → Resistant to urea formation (less steam demand in a desorption bed)
  - → Low heat of CO_2 absorption

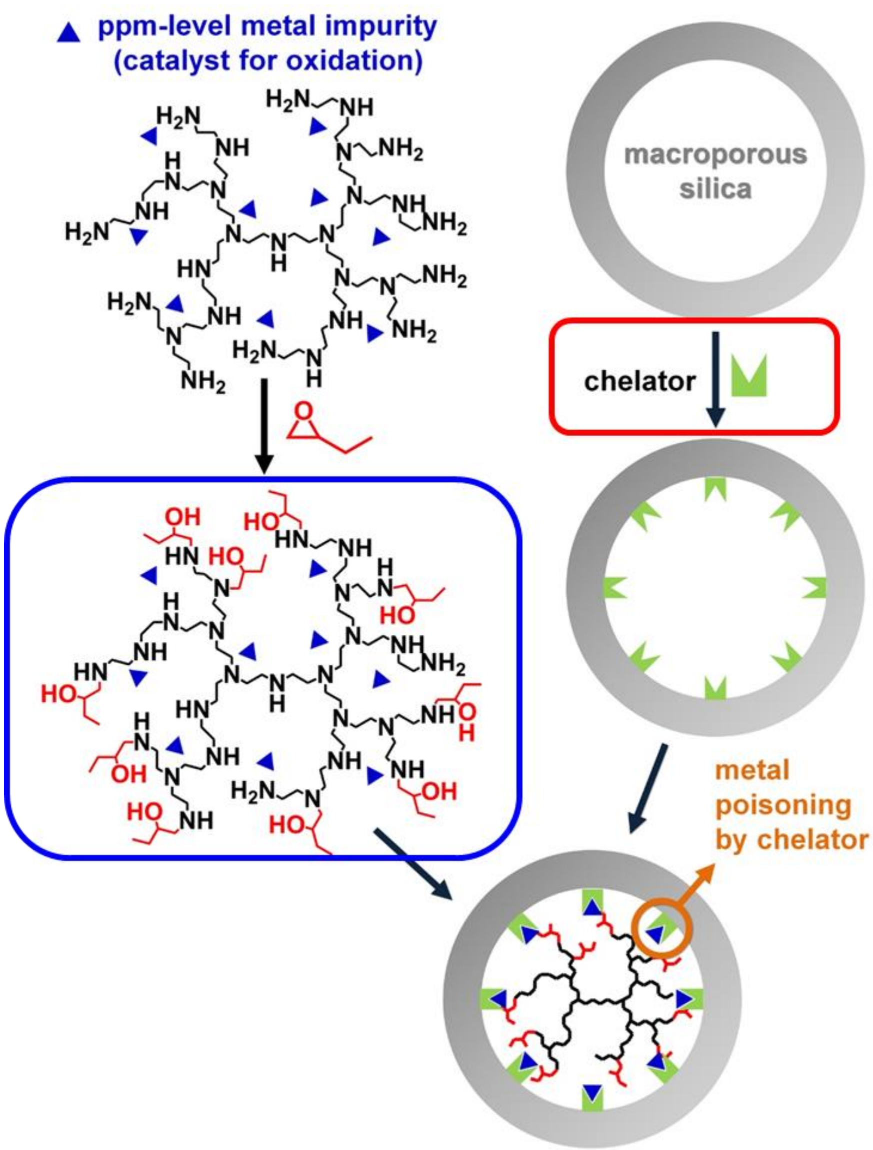


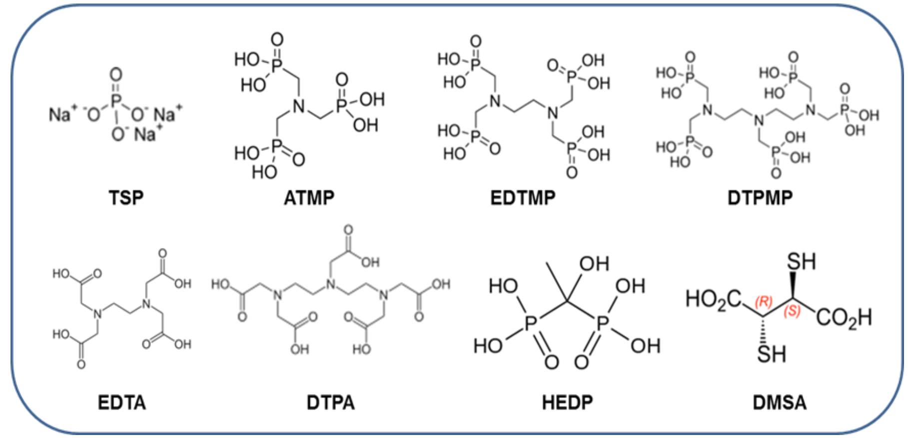


Sample	Heat of adsorption [GJ / ton-CO_2]
PEI	1.85
0.18EB-PEI	1.73
0.35EB-PEI	1.47
0.49EB-PEI	1.25

- *Nature Communications*, **2016,** *7*, 12640.
- Patents (KR 10-1738954, 10-1967508, US 15644924)

(KAIST) Oxidation stability of EB-PEI

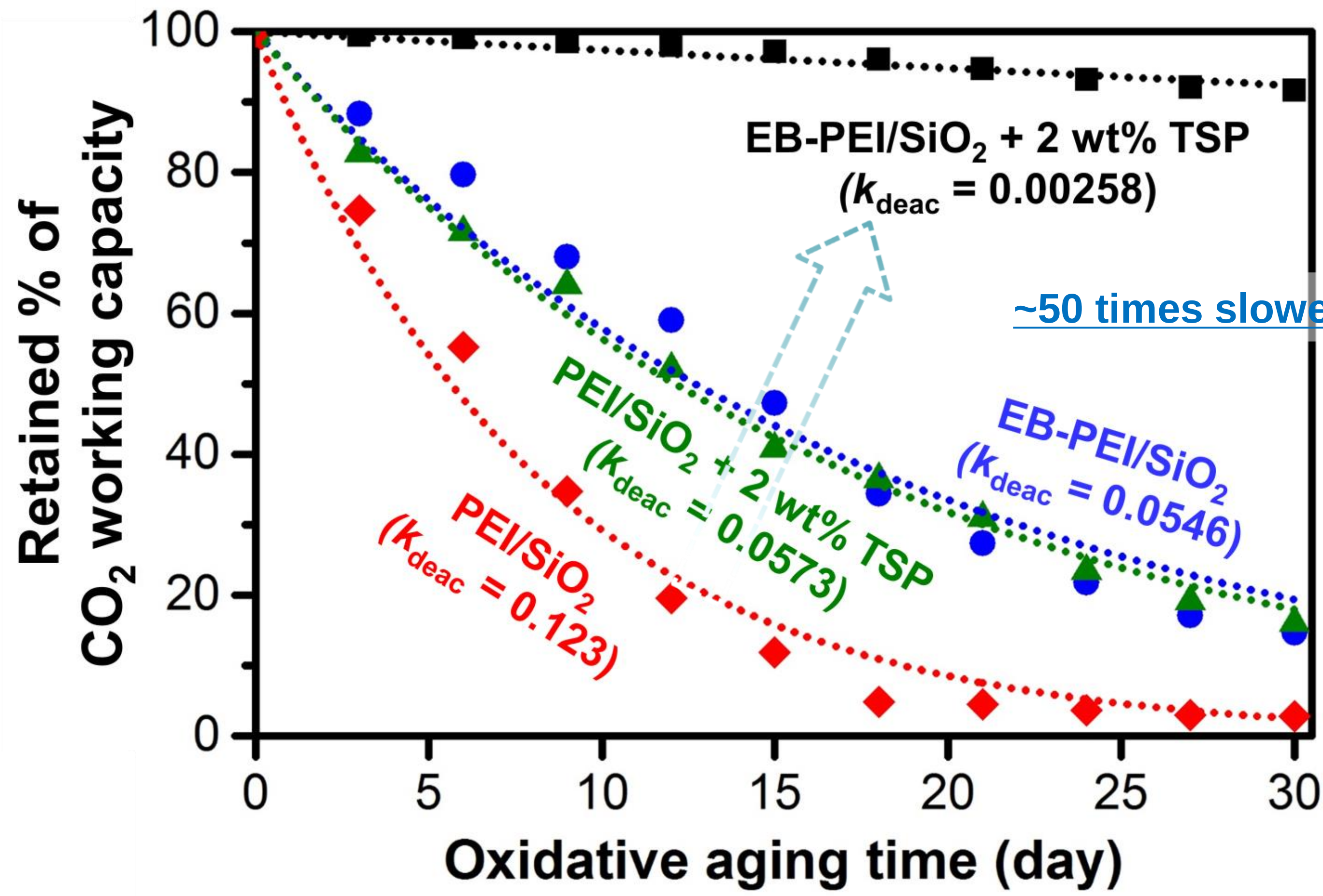




- Solid sorbents meet hot O_2-containing gas in a fluidized bed (standpipe & heat exchanger)
  → O_2 stability is very critical to successful operation of dry sorbent fluidized bed processes.
- Chelators for metal impurity & hydroxylation of PEI retard oxidation of the sorbent.

- *Nature Communications*, **2018,** *9,* 1-7
- Patents (KR 10-2017-0152380, US 2019-0143299)

(KAIST) Improvement of oxidation stability



~50 times slower deactivation

Oxidative aging condition (simulated flue gas)

- 15% CO_2, 10% H_2O, 3% O_2, balanced with N_2 at 110˚C for 30 day

(KAIST) Egg-shell type adsorbent with SO_2 resistance

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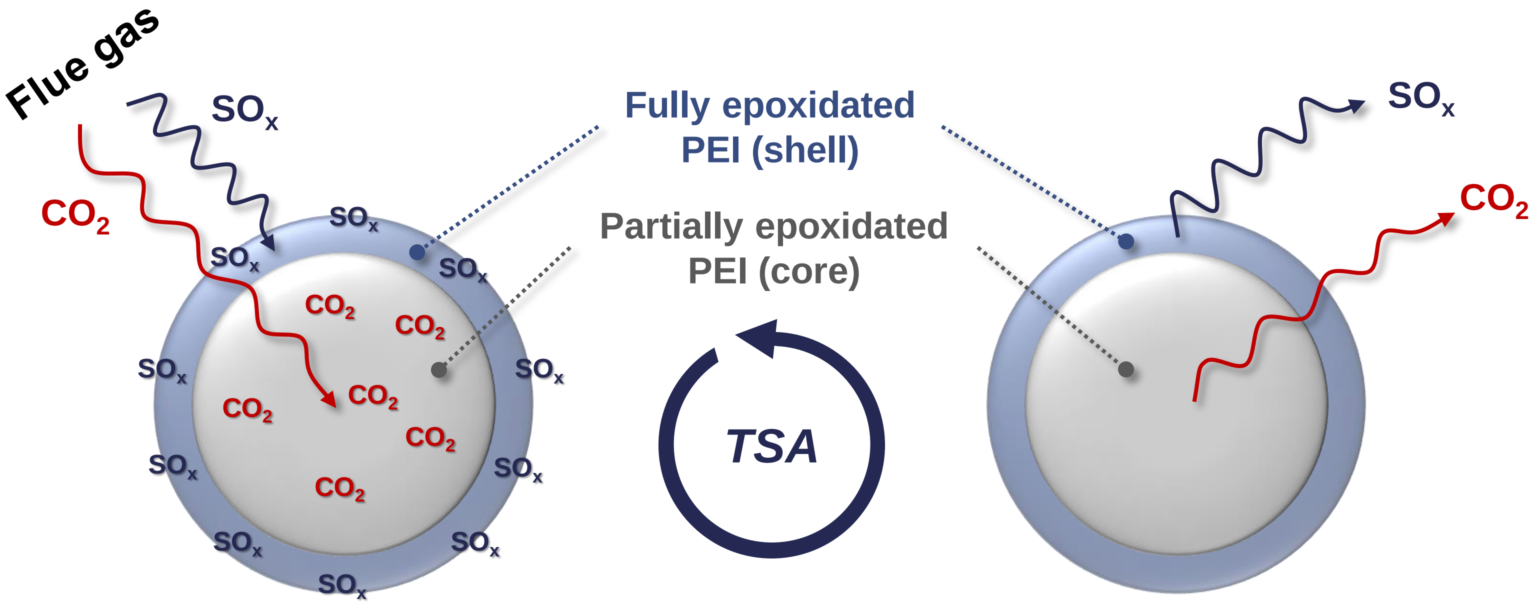


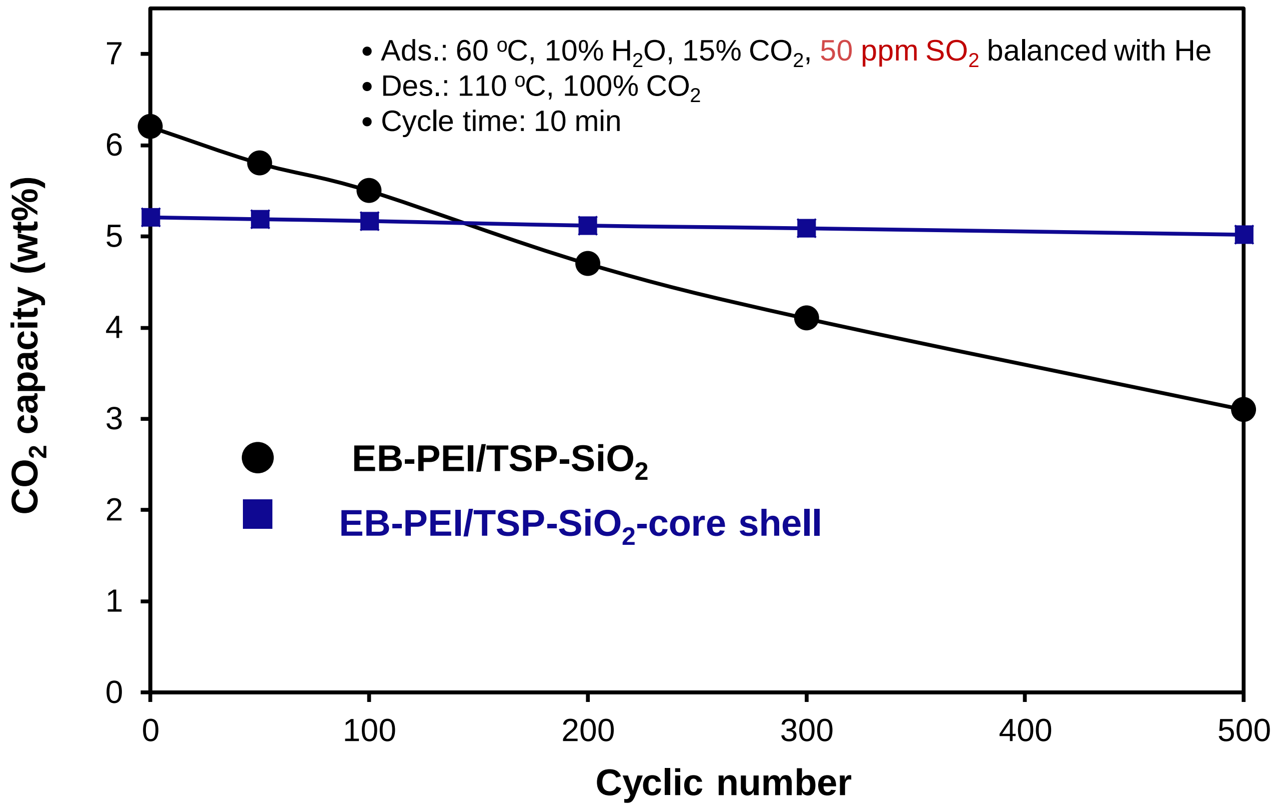
Egg-shell type CO_2 adsorbent

- **Core :** Partially epoxidated PEI
  - High CO_2 working capacity
  - Highly regenerable without the urea formation
  - Irreversible adsorption of SO_2 (SO_2-induced degradation)

- **Shell :** Fully epoxidated PEI (tertiary amines)
  - Selective adsorption of SO_2 over CO_2
  - SO_2 can be easily desorbed by increasing temperature (110 °C)
  - Protects core-amine (0.37EB-PEI) from the SO_2-induced degradation

ACS Appl. Mater. Interfaces, **2019,** *11,* 16586–16593

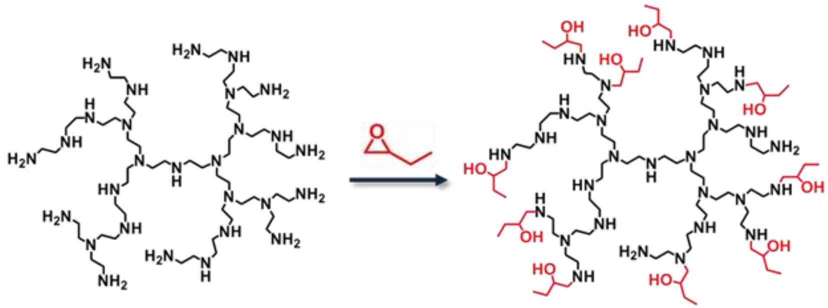
(KAIST) Cyclic stabilities at SO_2-containing environment



* Q_{CO2} : CO_2 adsorption capacity

Sample	CO_2 adsorption capacity (wt%)		$Q_{CO2}(SO_2\ treated)/Q_{CO2}(fresh)$*
	Fresh	After 500 cycles	
EB-PEI/TSP-SiO_2	6.2	3.1	0.50
EB-PEI/TSP-SiO_2-core shell	5.2	5.0	0.96

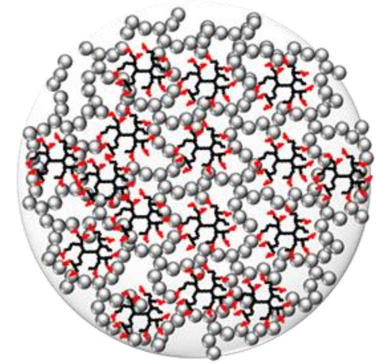
Development of spherical sorbents



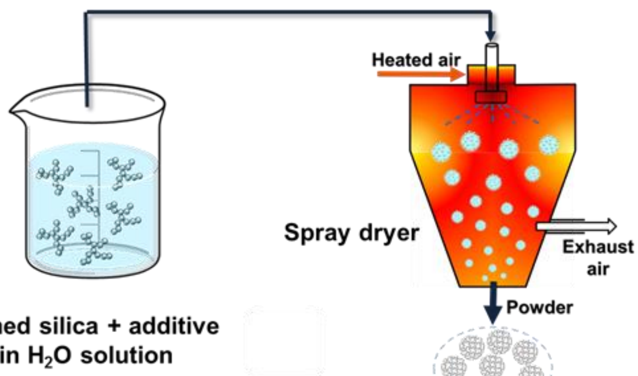
Reaction between epoxide & PEI

- capable of 500 kg/month manufacture

Impregnation & Drying



Functionalized PEI/silica composite adsorbent



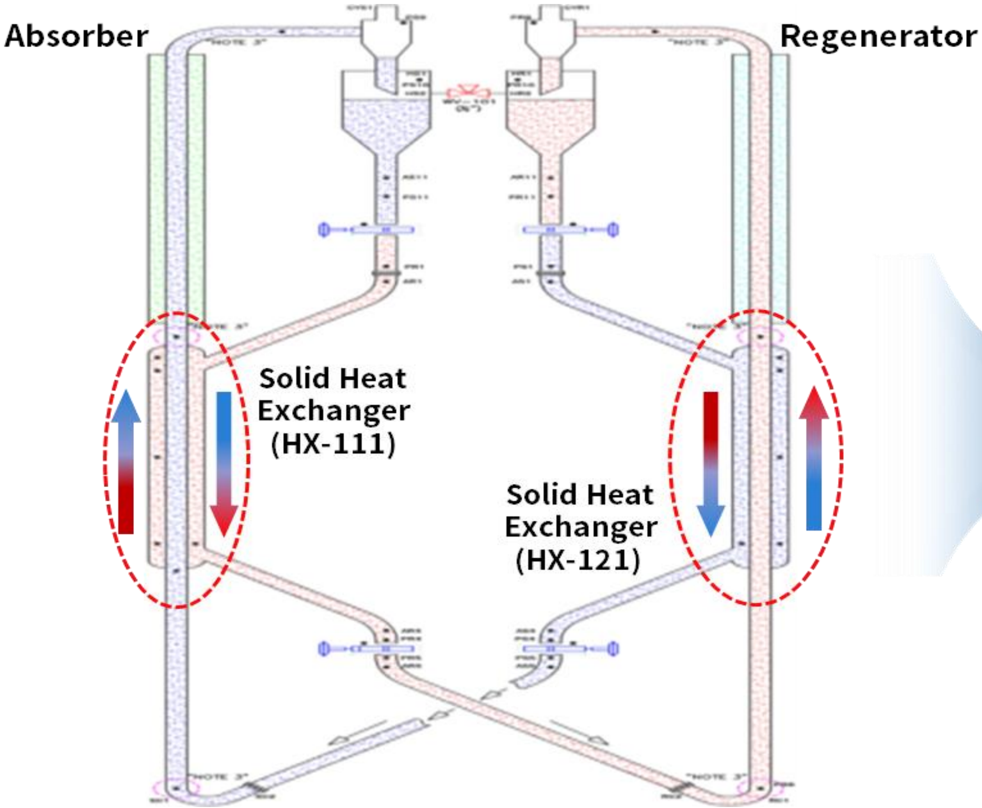
Silica support spray-drying

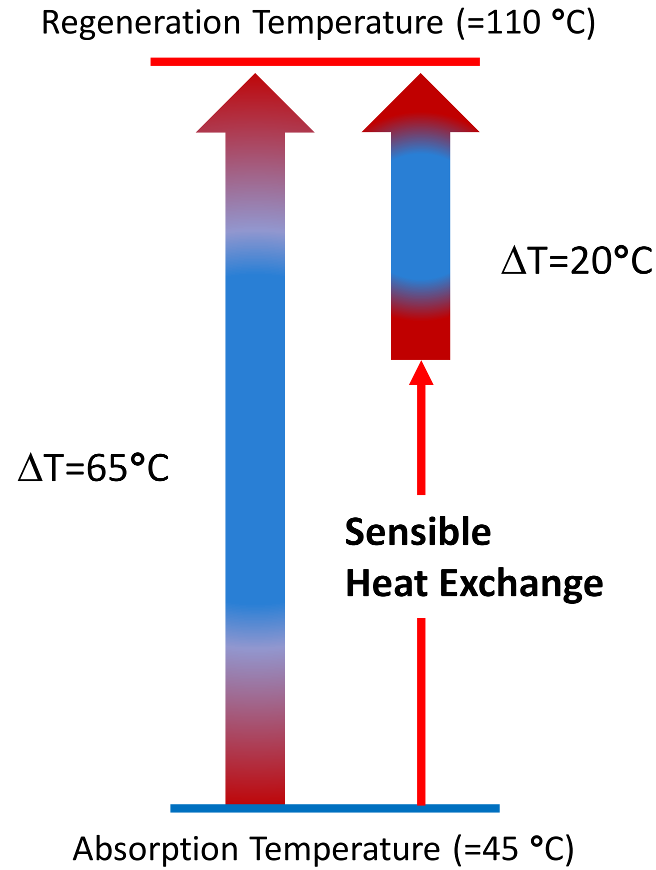
Sorbent properties	
Abs. capacity (wt%)	7.0*
Specific heat (J/g·K)	1.4
Heat of Abs. (GJ/tCO_2)	**1.47**
Mean particle size (μm)	150
Attrition Index	2.5

*150 mbar CO_2

Concept of solid-solid heat exchanger

100 Nm^3/hr bench-scale configuration

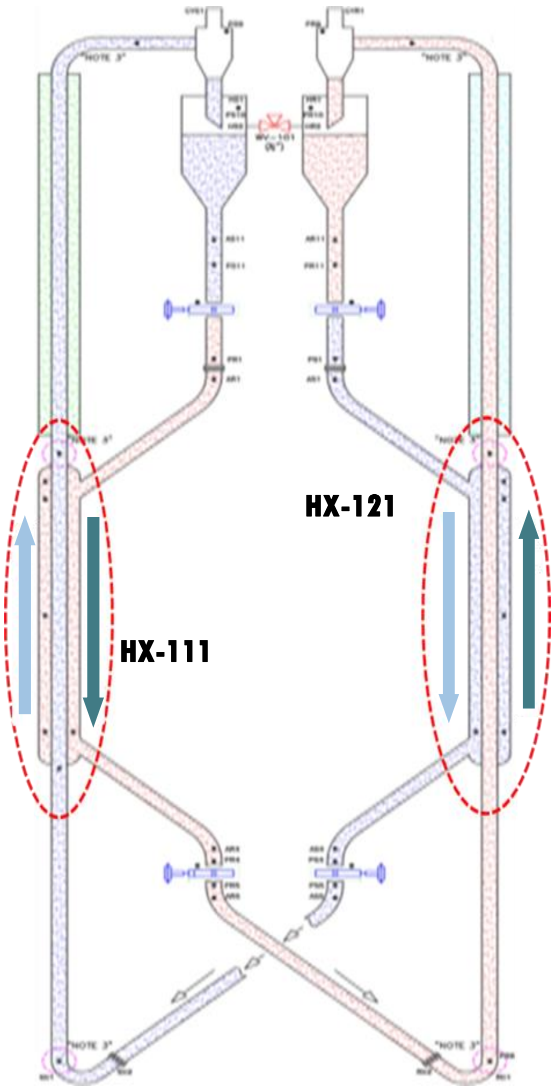




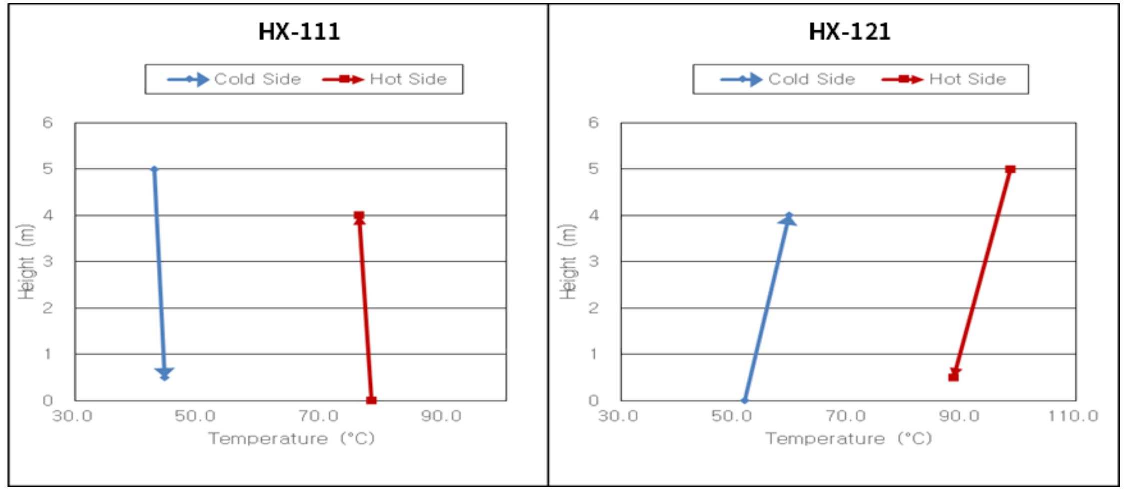
- Patent-pending (EU 14 762 615.4)
- Patent-registered (KR 10-1571966, US 9,694,312)

Recover sensible energy through direct solid-solid heat exchange
(△T: 65 → 20 °C)

Operation result – Solid heat exchanger



Solid-Solid Heat Exchanger Temperature Profile



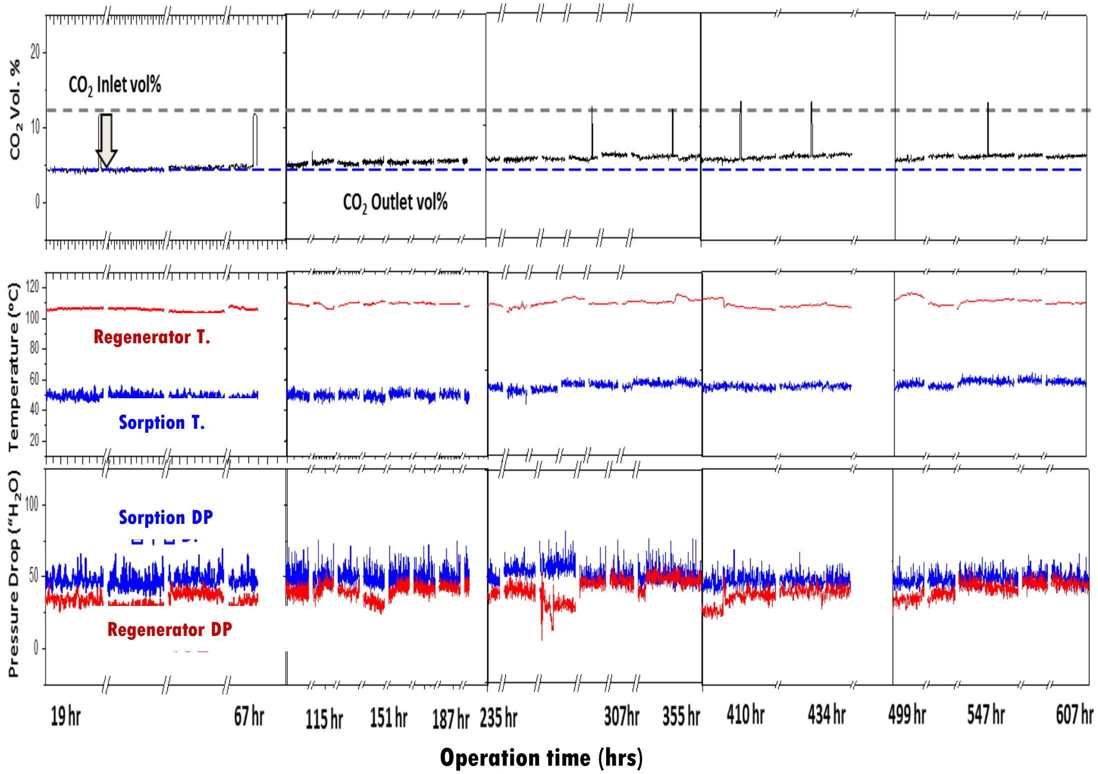
	w/o Solid HX	w/ Solid HX	0.5 MW (Target)
MTA (°C)	65	45	30
Sensible E. (GJ/tCO_2)	2.6	1.9	1.3

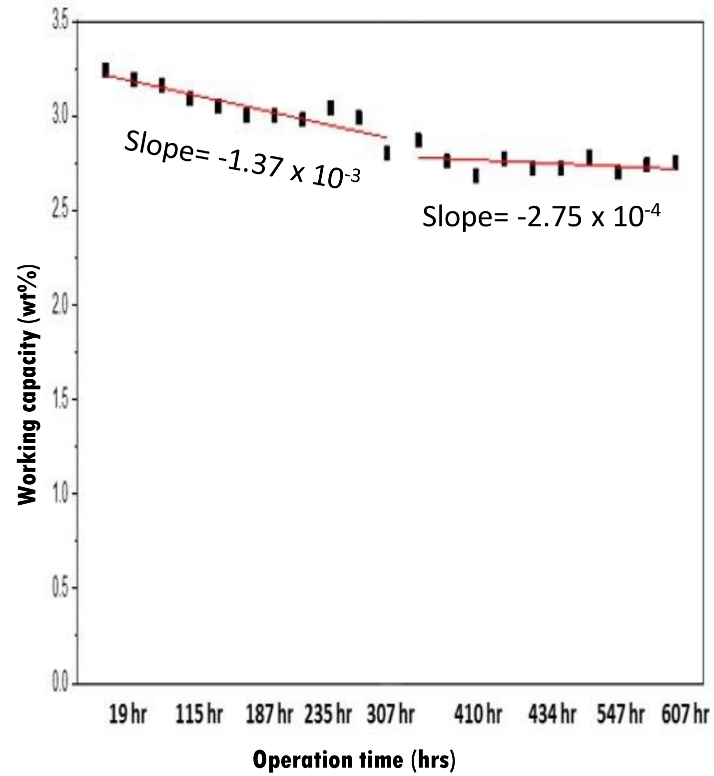
- 20 °C recovered by solid heat exchanger

  → 30% sensible energy reduction
- MTA (minimum temp. approach): 45 °C

Sorbent stability test and cost

- **Bench-scale operation to test stability**

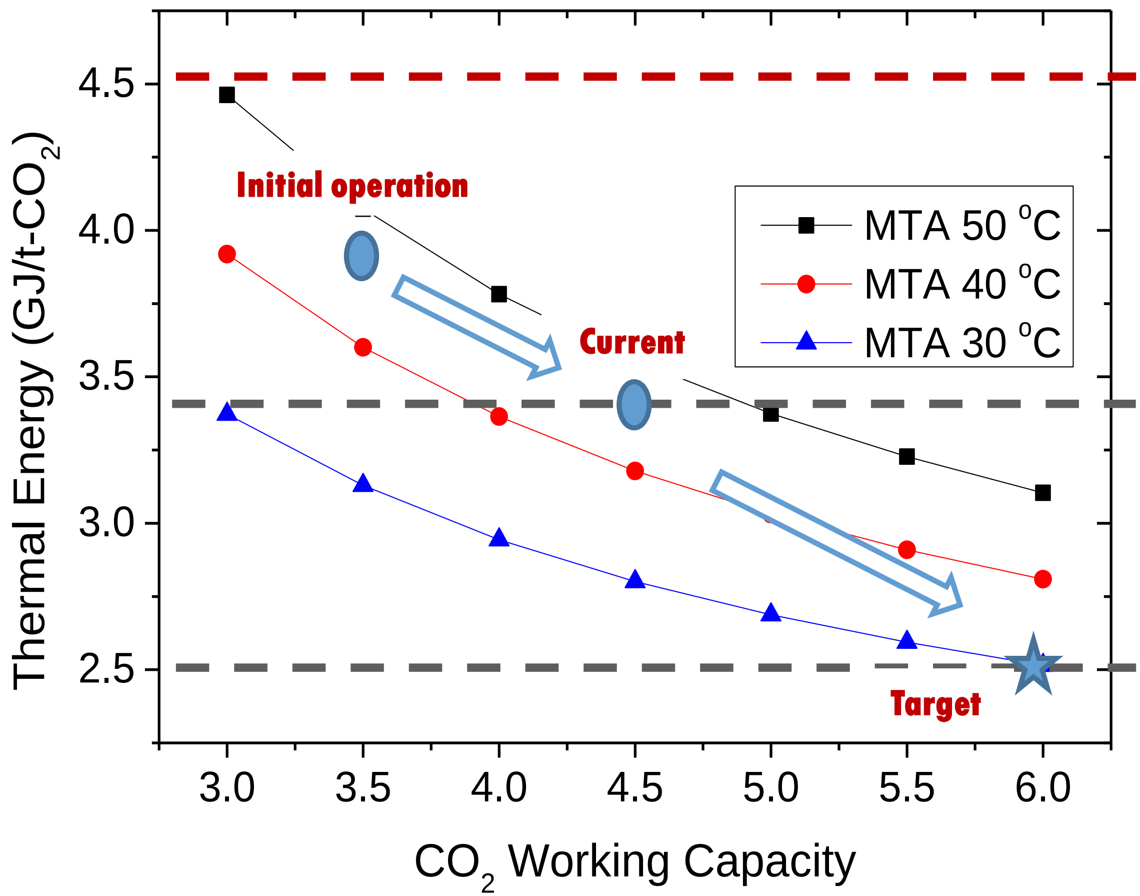


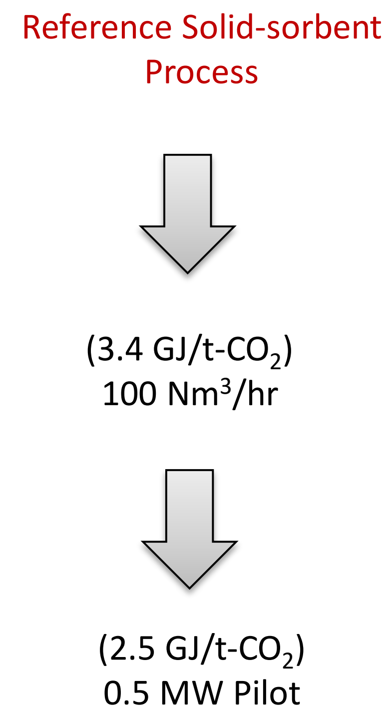


Solvent Type	MEA (Fluor)	KS-1 (MHI)	Benfield (UOP)	EB-PEI
Make up (kg/t-CO_2)	1.5	0.35 ~ 0.40	2.4	*1.14 (0.5% make-up/day)
Cost (USD/kg)	1.2	16.5	-	12 (raw material cost)

*Basis: attrition loss 0.5wt%/day, sorption working capacity 5wt%

Critical Factors affecting thermal energy





- Improving MTA by -10 °C ------▸ Energy reduced by 0.7 GJ/t-CO_2
- Increasing working capacity by +1wt% ------▸ Energy reduced by 0.5 GJ/t-CO_2

Process scale-up to 0.5 MWe pilot plant

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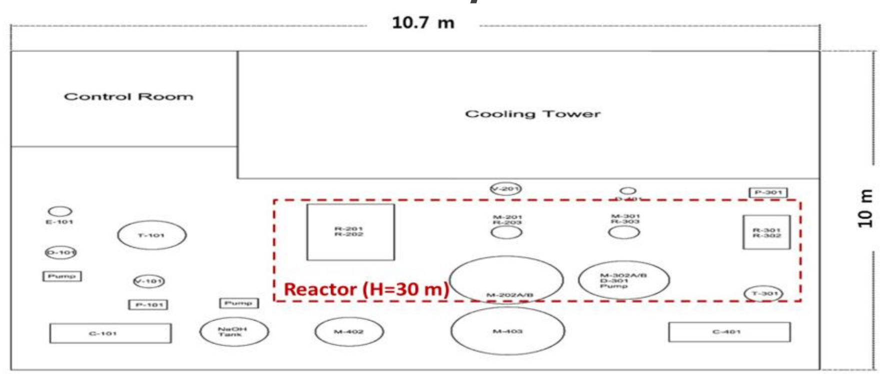
Project Site	**Dae-gu Dyeing Industrial Center, South Korea (75 MWe PC Power Plant)**
CO_2 Capture Capacity	2,000 Nm^3/hr (~0.5 MWe Power Plant)
Start-up Date	From October 2019

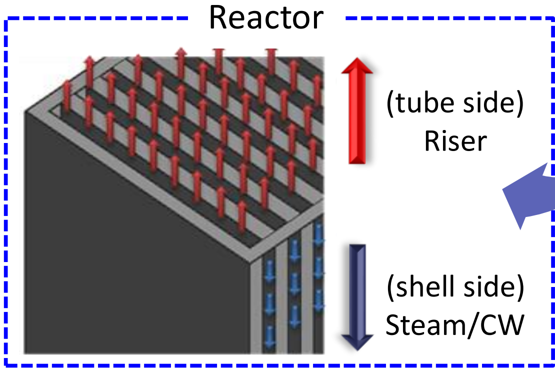
Reference Power Plants

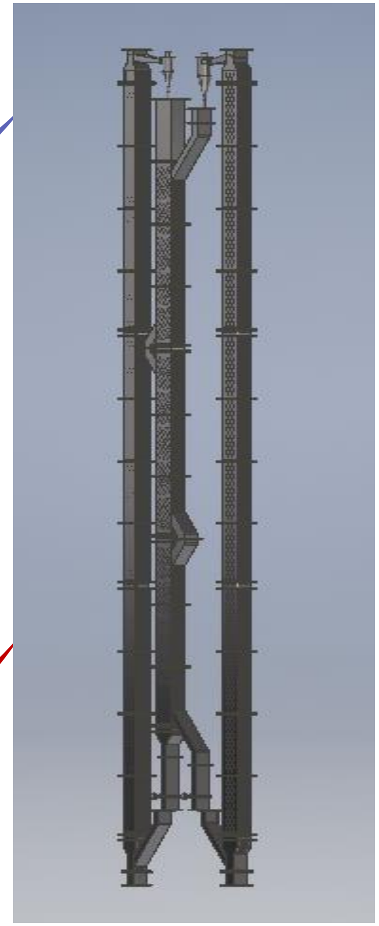
CO_2 Capture Plant EPC Site

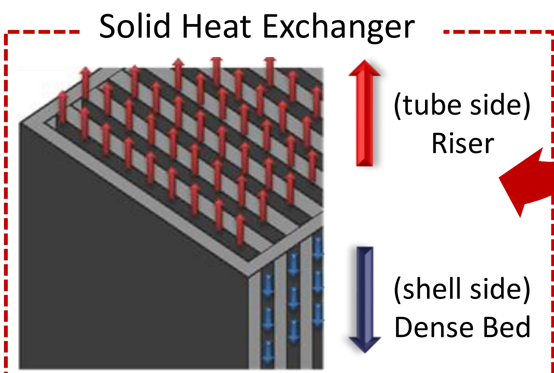
Plant Layout



0.5 MWe pilot plant – reactor design







		Absorber	Desorber	Units
Reactor	Heat duty	417	360	kW
	Overall U	35.6	65.1	W/m²·K
	Designed Area	613	452	m²
Solid HX	Heat duty	127	113	kW
	Overall U	15	15	W/m²·K
	Designed Area	212	156	m²
Plate Size	Depth	25	10	mm
	Width	570	570	mm
	Number of Plates	20	15	EA
Footprint		1.15 × 0.63 × 35	0.64 × 0.63 × 35	m³

- Reactor : plate-type fluidized bed → easy scale-up by modulation

0.5 MWe pilot plant – CFD analysis

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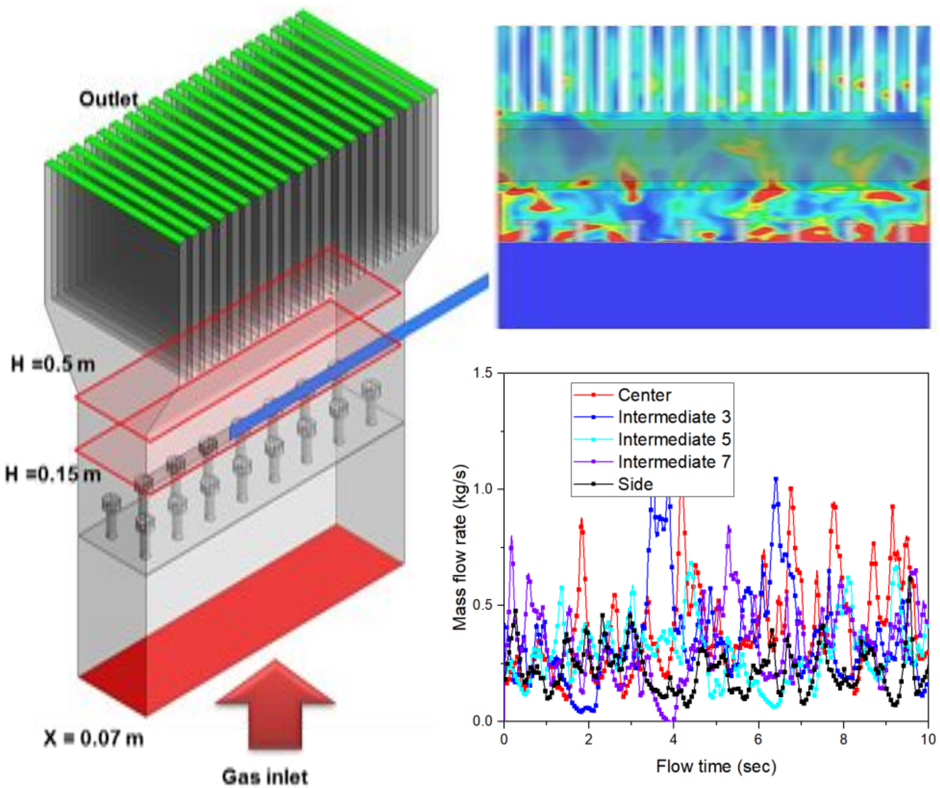
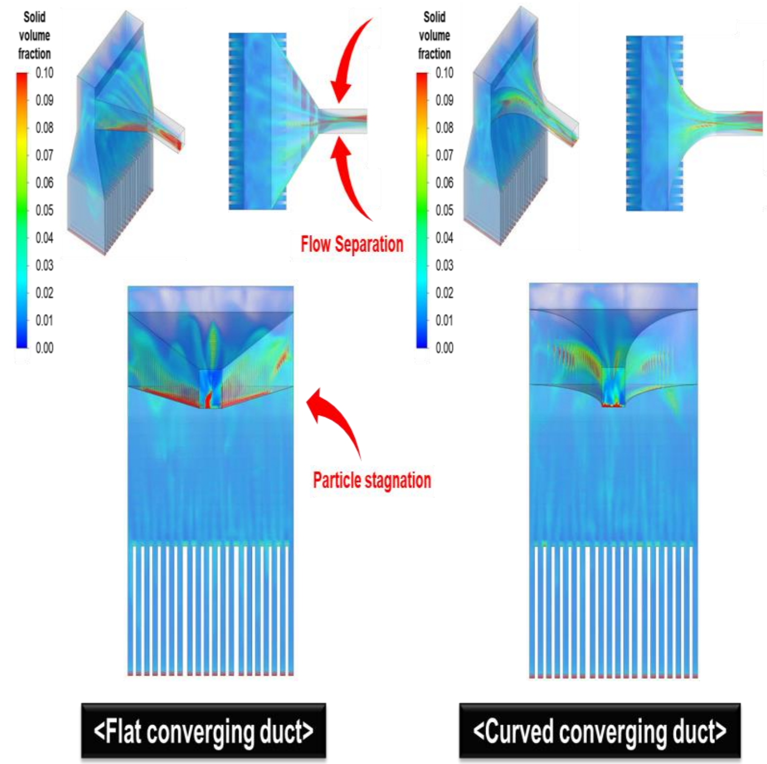
• Distributor



• Reactor Outlet

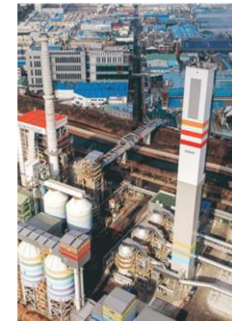


- Refer to distributor in CFBC (equipped with Plate-type Super Heater)
- Distributor and reactor outlet designs are under tuned through CFD simulation

Current status of the process development

20 Nm^3/hr scale operation with restricted heat exchange

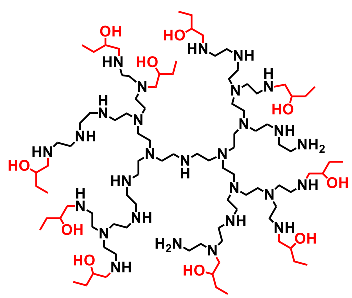
100 Nm^3/hr scale operation with improved heat exchange



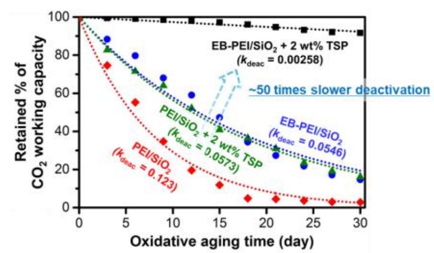
0.5MW pilot test with real flue gas (Target : 2.5 GJ/tCO_2)

2012 — 2014 — 2017 — 2018 — 2019 — 2020

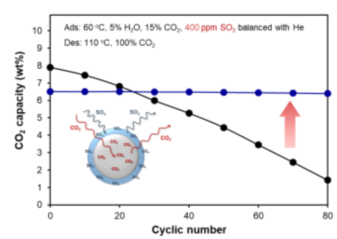
current (2019)



EB-PEI



Enhanced O_2 stability



Enhanced SO_2 stability

Manufacture of 6 tons of sorbent for pilot test

Summary

- A circulating fluidized bed process with a novel solid heat exchanger was developed and it shows 30 % of sensible heat recovery from lean sorbent stream.

- Amine impregnated sorbent with a low heat of sorption was developed and optimized to prevent from thermal and oxidative degradation.
- 1 month continuous operation demonstrates its stability.

- Bench scale process of 20 Nm^3/hr and 100 Nm^3/hr were constructed and operated.
- Its performance shows 3.4 GJ/t-CO_2 and 4.5 wt% of sorption working capacity.
- 2,000 Nm^3/hr (0.5 MW scale) CO_2 capture plant is under constructed and the startup will be from October 2019.

Acknowledgments

Reactor development

Prof. Hyung Hee Cho (Yeonsei Univ.)

Amine based sorbent development

Prof. Minkee Choi (KAIST)

Prof. Young Soo Ko (Kongju Natl. Univ.)

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T H A N K

Y O U

Questions & Comments ?