CO2 Summit III: Pathways to Carbon Capture, Utilization, and Storage Deployment

Proceedings

5-24-2017

Adsorption Processes for CO2 Capture: An Overview

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Recommended Citation

Paul Webley, Ranjeet Singh, and Penny Xiao, "Adsorption Processes for CO2 Capture: An Overview" in "CO2 Summit III: Pathways to Carbon Capture, Utilization, and Storage Deployment", Jen Wilcox (Colorado School of Mines, USA) Holly Krutka (Tri-State Generation and Transmission Association, USA) Simona Liguori (Colorado School of Mines, USA) Niall Mac Dowell (Imperial College, United Kingdom) Eds, ECI Symposium Series, (2017). http://dc.engconfintl.org/co2_summit3/41

ADSORPTION PROCESS FOR CO_2 CAPTURE: AN OVERVIEW

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CO2 Summit III
May 22-26, 2017

Questions

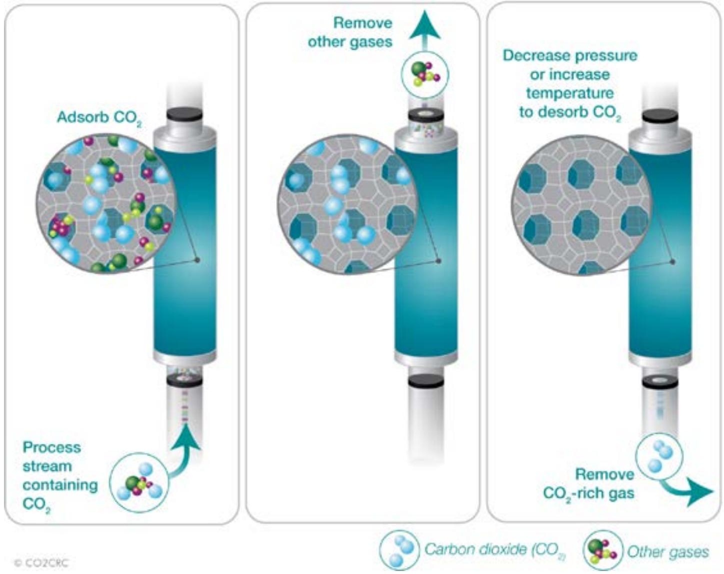
- What is adsorption based capture and how does it work?
- What does it depend upon?
- Where is it used (applications) and how does it perform?
- Why should we use it? - What are advantages of adsorbents over conventional capture systems (CAPEX, OPEX)?
- What are the problems?
- Potential Application areas?
- What are RD&D areas for future?

What is Adsorption based Capture?

- Expose process gas to porous, dry solid selective to CO_2, removing non-CO_2 gases

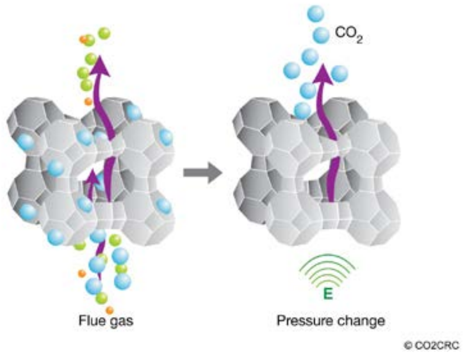
- Regenerate solid (temperature, pressure, steam etc) and recover pure CO_2

- Repeat with multiple beds (move the gas or move the adsorbent)



What does it depend upon?

- Excellent adsorbent material (cheap, high working capacity and selectivity to CO_2)
- Effective gas-solid contactor
- Energy efficient regeneration scheme
- Well engineered process and cycle
- Strong relationship between adsorbent, process design and feed properties



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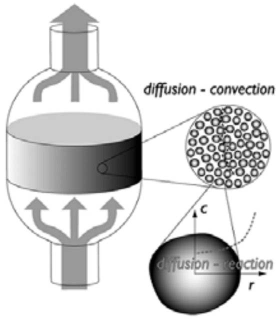

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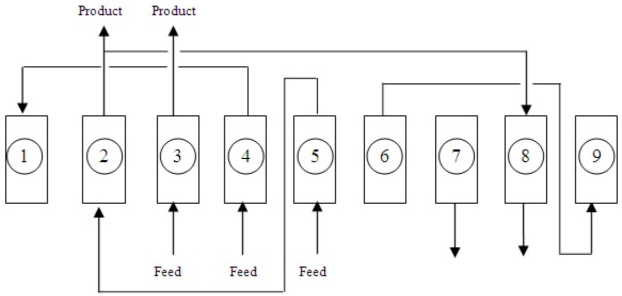


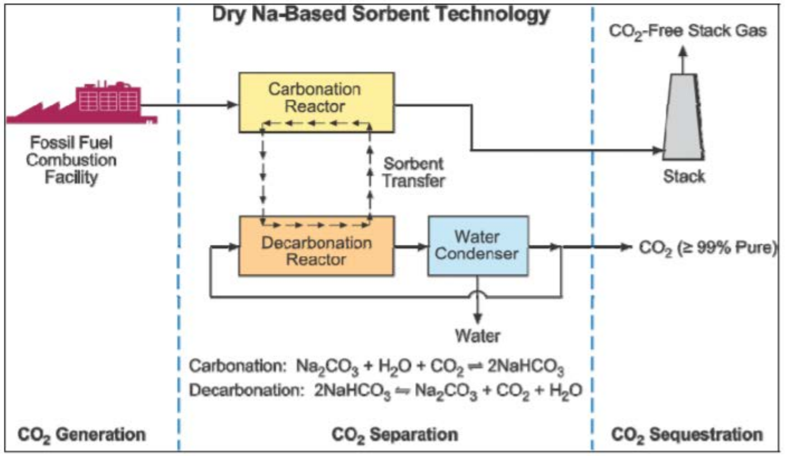
Where is it used (applications) and how does it perform?

- Temperature Swing Adsorbent Systems (steam regenerated) – chemisorbents in rotary beds or circulating beds
  - RTI Research (Research Triangle Ins)
  - KIER (Korean Inst Energy Res)
  - Climeworks
  - Inventys VeloxoTherm
  - TDA alumina sorbents (fixed bed, steam regen)
  - Seibu Giku ceramic wheel

- Pressure and Vacuum Swing Adsorbent Systems (physisorbents in fixed beds)
  - Numerous vendors

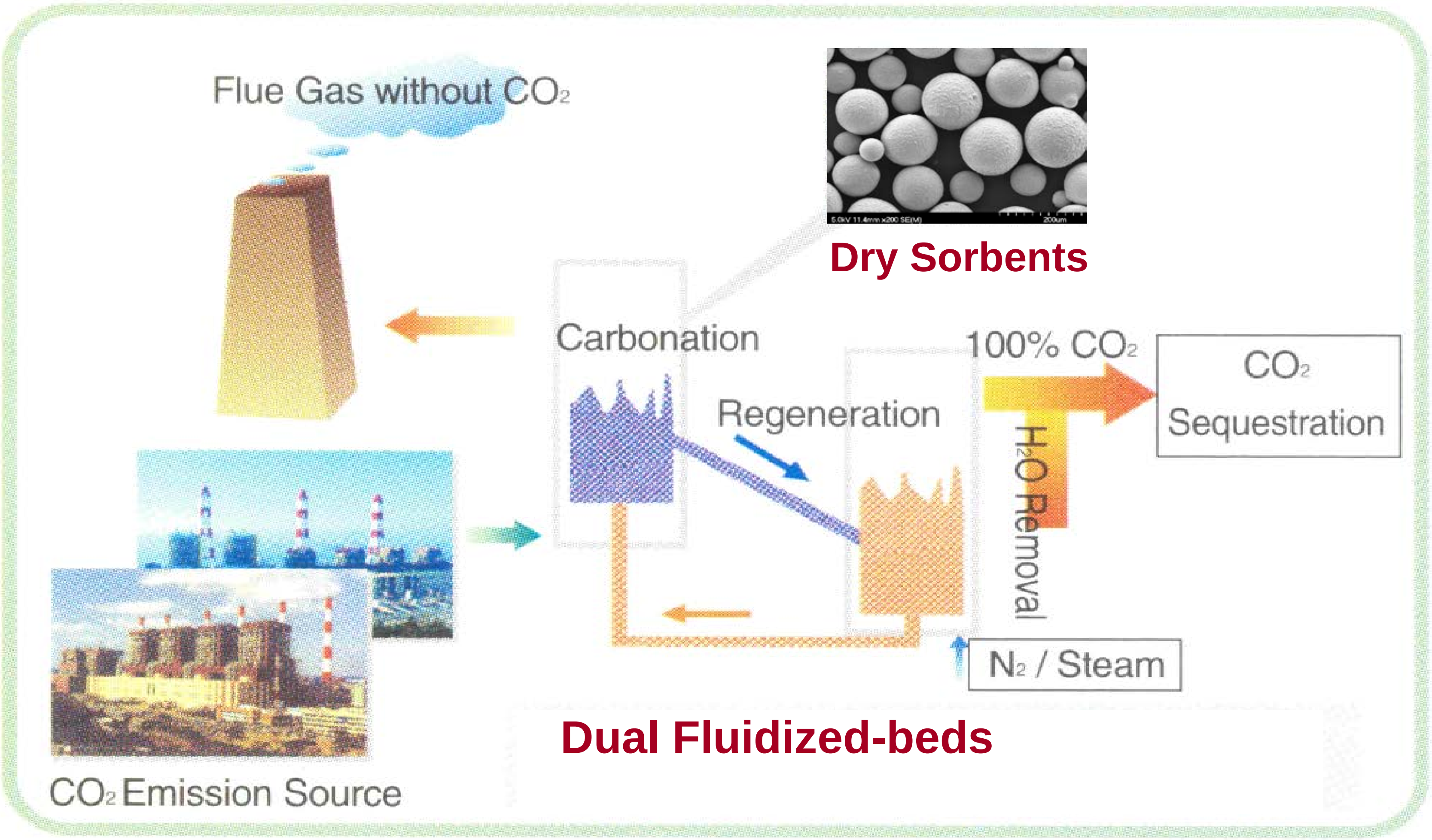
RTI International

- RTI's CO2 capture process – the Dry Carbonate Process – sodium carbonate to sodium bicarbonate reaction



- RTI conducted cycle testing (adsorption and regeneration) of entrained-bed tests at CANMET
- > 90% CO2 removal was demonstrated in the reactor
- The temperature rise (due to exothermic reaction) was limited to ~ 10ºC
- Sorbent reactivity was maintained over 7 cycles (consistent >90% removal) - fully regenerated upon heating to 120ºC

Korea Institute of Energy Research (KIER)



Dry Sorbents

Dual Fluidized-beds

Process Development

2003

$2\ Nm^3/hr$

x 50

2006

0.025 MWe
$100\ Nm^3/hr$

x 20

2010

0.5 MWe
$2{,}000\ Nm^3/hr$

x 20

2013

10 MWe
$35{,}000\ Nm^3/hr$

Road Map

(2008~2010)

Test bed

(0.5 MWe)

2,000 Nm^3/h

(3,000ton CO$_2$/yr)

(2011~2014)

Pilot plant (10 MWe)

Spin-off

35,000 Nm^3/h

60,000 tCO$_2$/y

(2015~2017)

Pilot plant (10 MWe)

Optimization

35,000 Nm^3/h

60,000 tCO$_2$/y

(~2020)

Coal fired power plant (>150 MWe)

1,500,000 Nm^3/h

(3 Mton CO$_2$/yr)

Economics of KIERS Capture Process

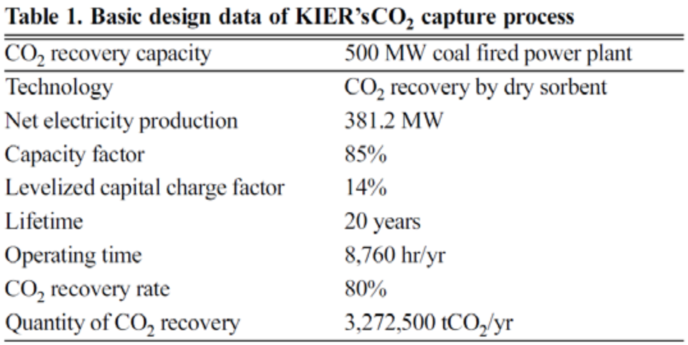


Table 1. Basic design data of KIER'sCO$_2$ capture process

CO$_2$ recovery capacity	500 MW coal fired power plant
Technology	CO$_2$ recovery by dry sorbent
Net electricity production	381.2 MW
Capacity factor	85%
Levelized capital charge factor	14%
Lifetime	20 years
Operating time	8,760 hr/yr
CO$_2$ recovery rate	80%
Quantity of CO$_2$ recovery	3,272,500 tCO$_2$/yr

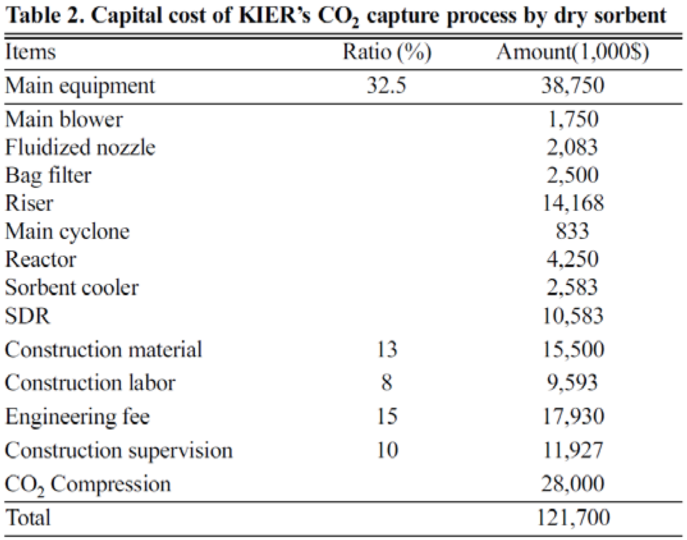


Table 2. Capital cost of KIER's CO$_2$ capture process by dry sorbent

Items	Ratio (%)	Amount(1,000$)
Main equipment	32.5	38,750
Main blower		1,750
Fluidized nozzle		2,083
Bag filter		2,500
Riser		14,168
Main cyclone		833
Reactor		4,250
Sorbent cooler		2,583
SDR		10,583
Construction material	13	15,500
Construction labor	8	9,593
Engineering fee	15	17,930
Construction supervision	10	11,927
CO$_2$ Compression		28,000
Total		121,700

Cost Profile

- KIER’s cost estimation

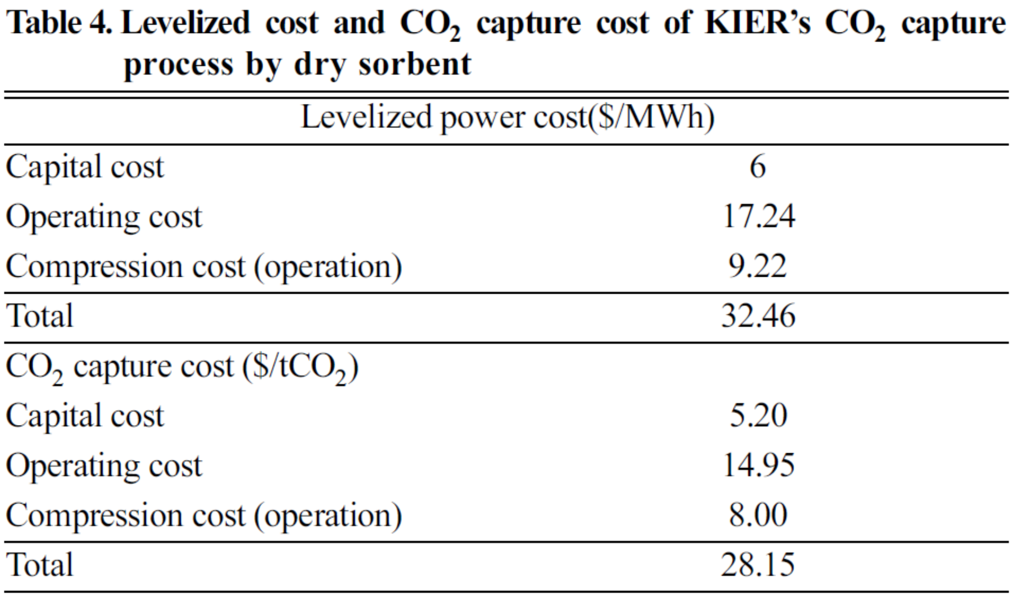


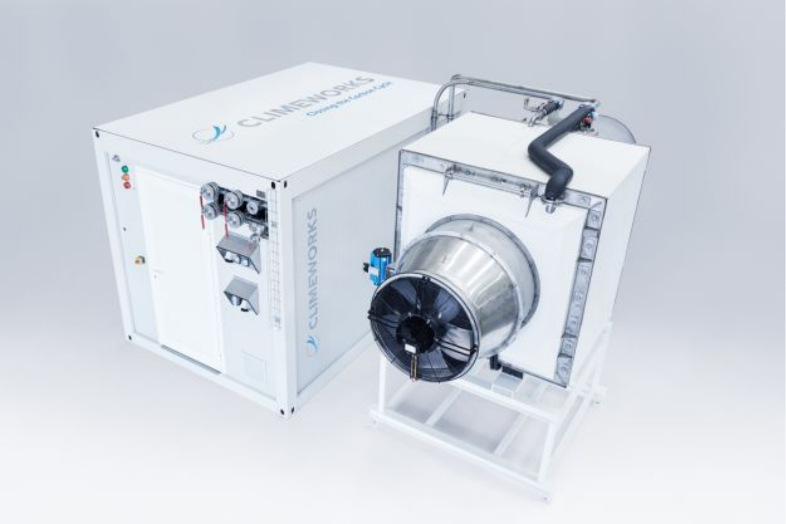
Table 4. Levelized cost and CO_2 capture cost of KIER’s CO_2 capture process by dry sorbent

Levelized power cost($/MWh)	
Capital cost	6
Operating cost	17.24
Compression cost (operation)	9.22
Total	32.46
CO_2 capture cost ($/t$CO_2$)	
Capital cost	5.20
Operating cost	14.95
Compression cost (operation)	8.00
Total	28.15

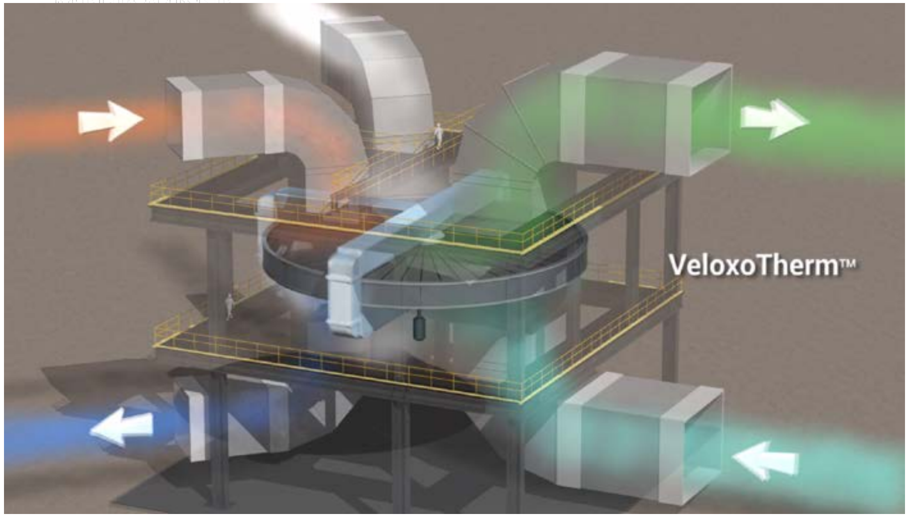
Korean Chem. Eng. Res., Vol. 50, No. 4, August, 2012

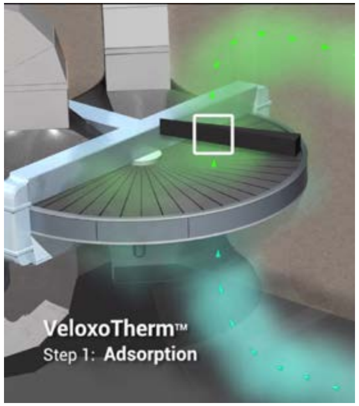
Climeworks

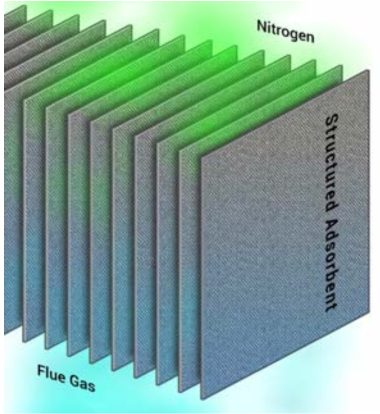
- Direct capture from air
- Amine impregnated cellulose fibres
- Pilot in Hinwil (18 units)
- Adsorbent regenerated by waste heat (95C) and pressure reduced to 0.2 atm
- Fan power requirement 200-300 kWh/t CO2
- Capture 900 t/yr CO2
- 5 cycles/day
- Greenhouses, etc



Inventys VeloxoTherm







- Steam regenerated rotary wheel adsorbent
- diamine-functionalized commercial silica gel
- “1.5 GJ/t CO2”
- Pilot with NRG underway

Pressure and Vacuum Swing Adsorption

- CO_2 recovery from H2PSA tail gas, beverage plant, landfill gas
- Vacuum to 0.1-2 atm
- Physisorbents
- Sophisticated cycles to enhance purity to >95%

Why should we use it?

- Relatively simple, no chemical emissions (low env. footprint), no disposal
- Great flexibility in choosing adsorbents to match feed gas stream properties
- Quick start-up and shut down and offers load following and flexible capture
- Flexible regeneration modes (pressure, temperature, steam, etc) depending on what is available –either thermal or mechanical energy (or both) can be used
- In principle, low energy is possible (absence of water, low Cp of adsorbents, good heat recovery) – esp. calcium looping.

What are the problems ? - Scalability

- Scalability – conventional configurations (fixed beds, switching valves, blowers) reach their limit at about 400,000 Nm^3/h

- A CO2VSA sized for PCC using maximum bed sizes, valves, vacuum blowers, equates to about 80 MW power plant – will need 7 trains for 500MW plant. Limit is low vacuum levels needed lead to large vacuum pumps

- Much better matched to high pressure and high concentration streams with smaller throughput

- TSA processes can be slow in fixed beds and only scale for other configurations (heat transfer limitation) – then have solids handling challenges

What are the problems? - Adsorbents

- Most adsorbents selective for CO_2 are also selective for impurities such as SOx, HCl, etc – these are often irreversibly adsorbed (may need to remove these before the process)
- Some adsorbents referentially adsorb water reducing their CO_2 capacity. In addition, some may collapse upon exposure to moisture
- Adsorbent cost and manufacturing – usually, these are 20-30% of the plant cost (when they are \$2-3/kg). Exotic adsorbents (\$100/kg or more) which are difficult to make in bulk are not realistic for large scale application
- Adsorbent working capacity and working selectivity are key – coadsorption of non-CO2 gases contaminate the CO2 product

What are the problems? - Energy

- VSA processes consume electrical energy – values range from 1-5 GJ/t CO_2. Equivalent to 3-15 GJ/t CO_2, thermal

- TSA processes suffer from slow heat transfer rates and low thermal efficiency – fluidized bed arrangements give low loadings since bed and gas flow is co-current. Best reported energies are in the range 2-5 GJ_{th}/t CO2. Limit is ~ 1 GJ/t CO_2 for fixed bed processes

- Exception is calcium looping in which high combustion temperatures can be utilized for regeneration

Opportunities for adsorbent based CO_2 capture

Rejecting CO_2 from high CO_2 content wells (> 50% CO_2)

coal or biomass gasification

High pressure CO_2 removal at high temperature

CO_2 recovery and reuse from dry ice manufacture and food industry

CO_2 recovery from petrochemical, oil, steel, cement, landfill gas, etc

Natural Gas

Rejecting CO_2 from high CO_2 content wells (> 50% CO_2)

enrich CH_4 to high enough value on an off shore platform to pipe to shore for further processing

Desirable features?

- Small footprint is key -> high working capacity
- Minimize loss of valuable component -> **<u>high selectivity</u>** at high pressure
- Low energy, capital is secondary (use pressure in the stream to do the separation)

Otway Capture Project

Location: Otway Basin CO2CRC facility

Cost : just over \$3m for the whole project

Main Objectives

- To develop cost effective, compact technologies to capture CO_2 mainly from high CO_2 content wells.
- To test new capture materials (membranes and adsorbents) and develop new capture processes

Main Features

- Feed Pressure: 90 to 20 bar
- Feed CO_2 Concentration: 5% to 80% achieved by CH_4 addition (existing is ~80% CH_4 and 19% CO_2)
- H_2S addition for impurities effect tests

High Selectivity Adsorbents. Nat Gas CO2 Capture

CO2 Capture from Nat Gas – Otway Test skid

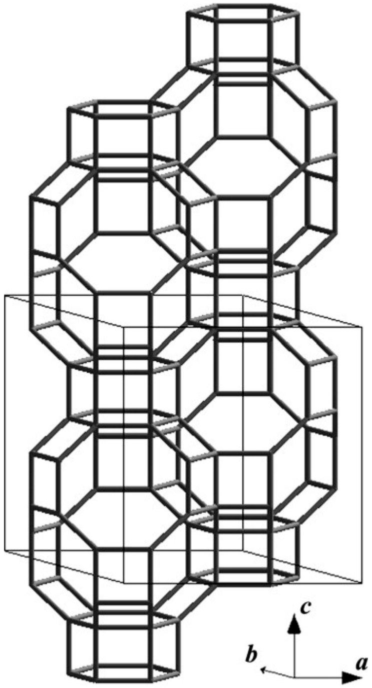
Highly Selective Adsorbents

- What adsorbents to use? Need CO_2 (3.4 A) adsorption and no CH_4 (3.8A) adsorption

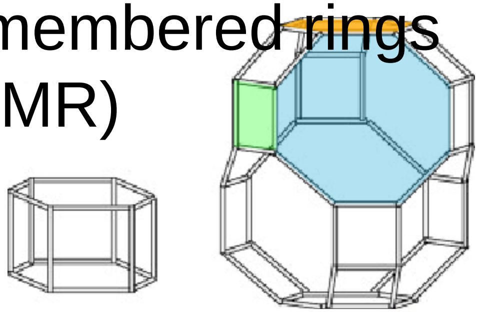
- Research program commenced in 2008 to find suitable adsorbents: $CO_2/N_2/CH_4$ adsorption in ion-exchanged chabazite (& LTA)
  - Low temperature pore-blockage by cations
  - CO_2 adsorption via ***molecular trapdoor mechanism***

$CO_2/N_2/CH_4$ adsorption in CHA

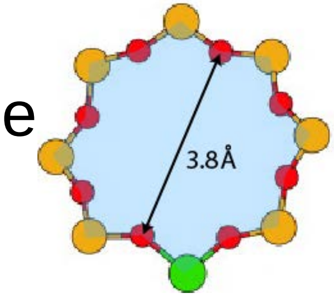
Chabazite ($M_iAl_xSi_{36-x}O_{72}$)



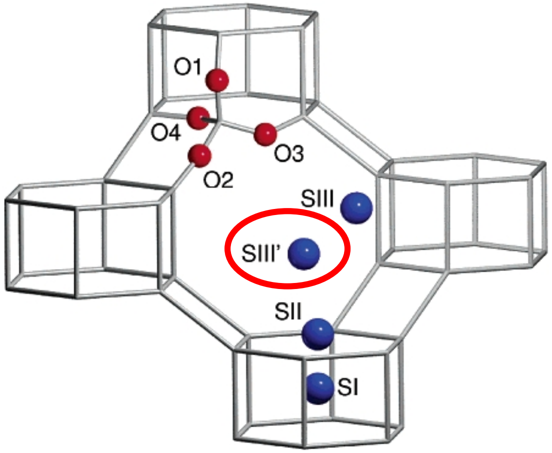
- 8-, 6-, and 4-membered rings (MR)



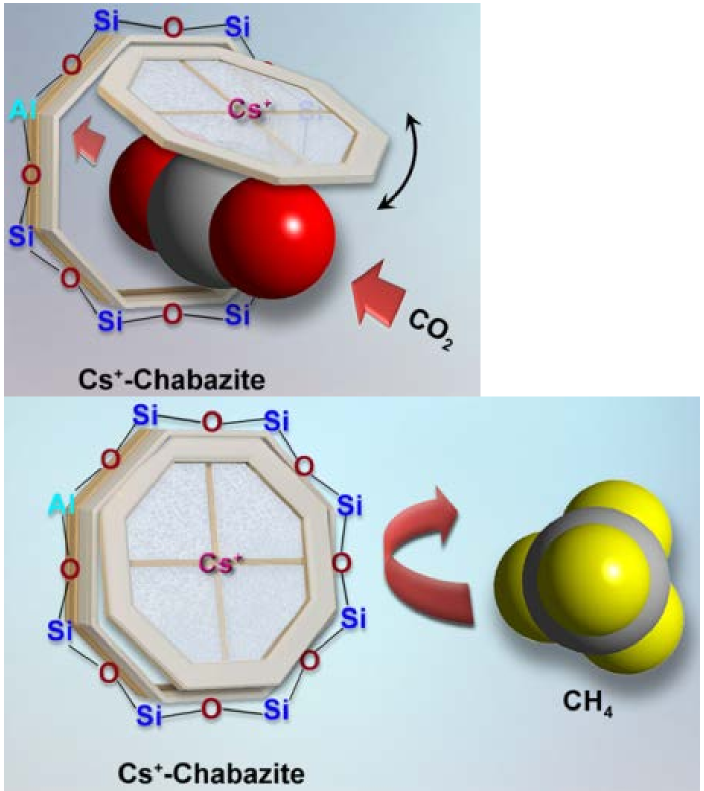
- 8MR: the only access to interior

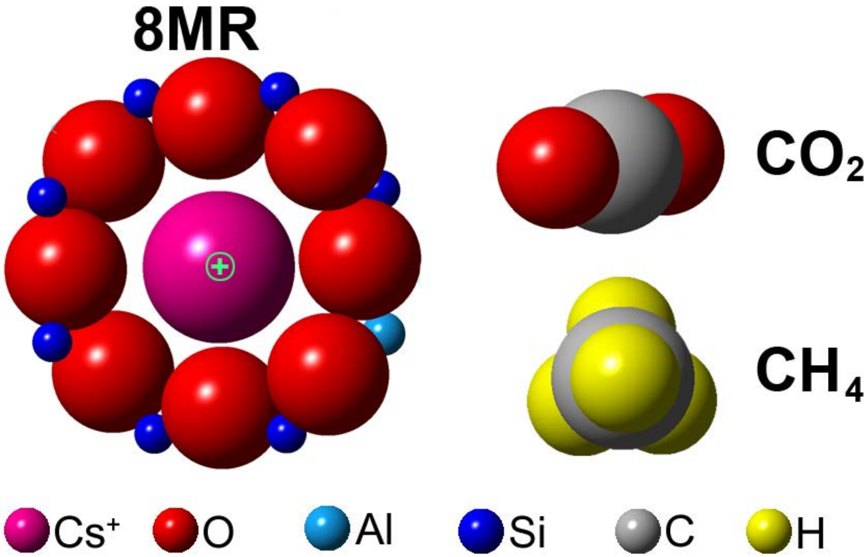


- Extraframework cation sites



CO_2/CH_4 separation on Chabazite Zeolite – “Trapdoor” Sieving



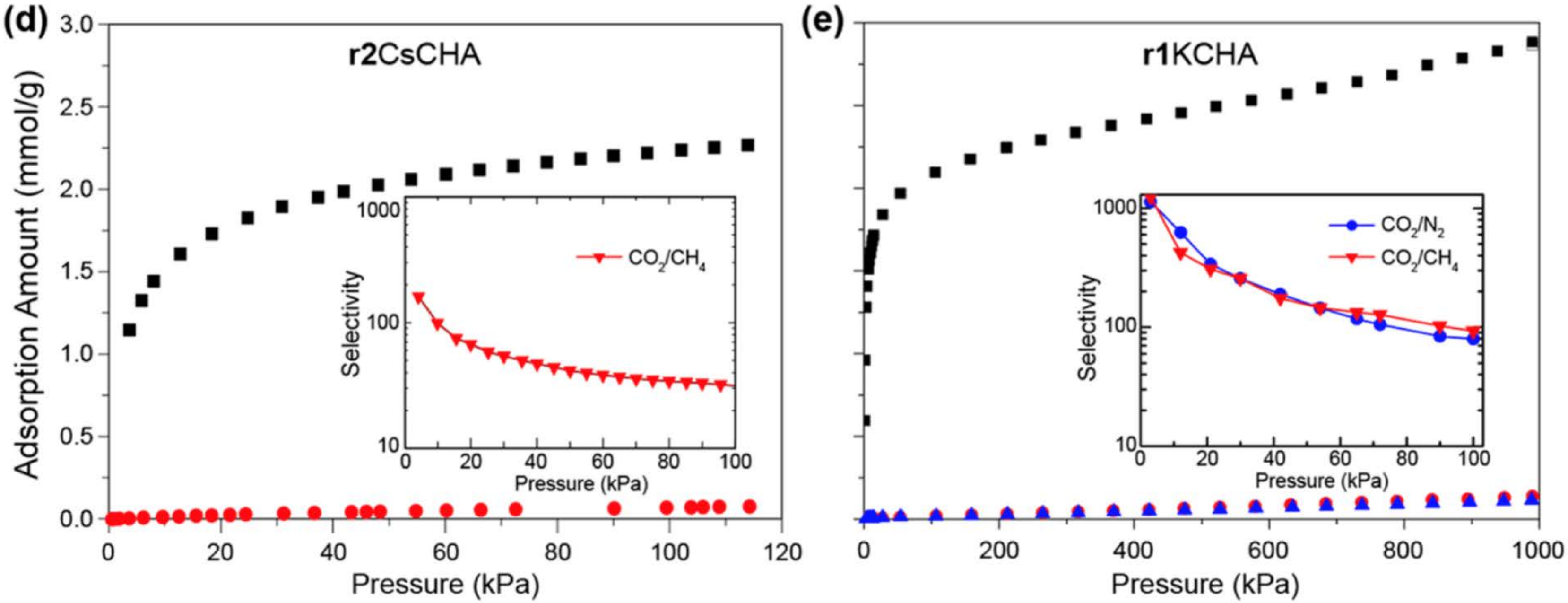


- “Infinite” CO2/CH4 selectivity

Molecular Trapdoor Mechanism

- A brief summary
  - Gas molecules can be classified into “strong” or “weak”, depending on their interaction strength with the door-keeping cations
  - Below T_S, a “strong molecule” can be admitted by inducing cation deviation from pore aperture whereas “weak” molecules cannot, regardless of size, thus discriminating between molecules
  - Temporary cation deviation allows one molecule to pass through each time – works for separation of mixture gases

High working selectivity of gas separation



$S_{CO2/CH4}$ = 31 at P= 1 bar

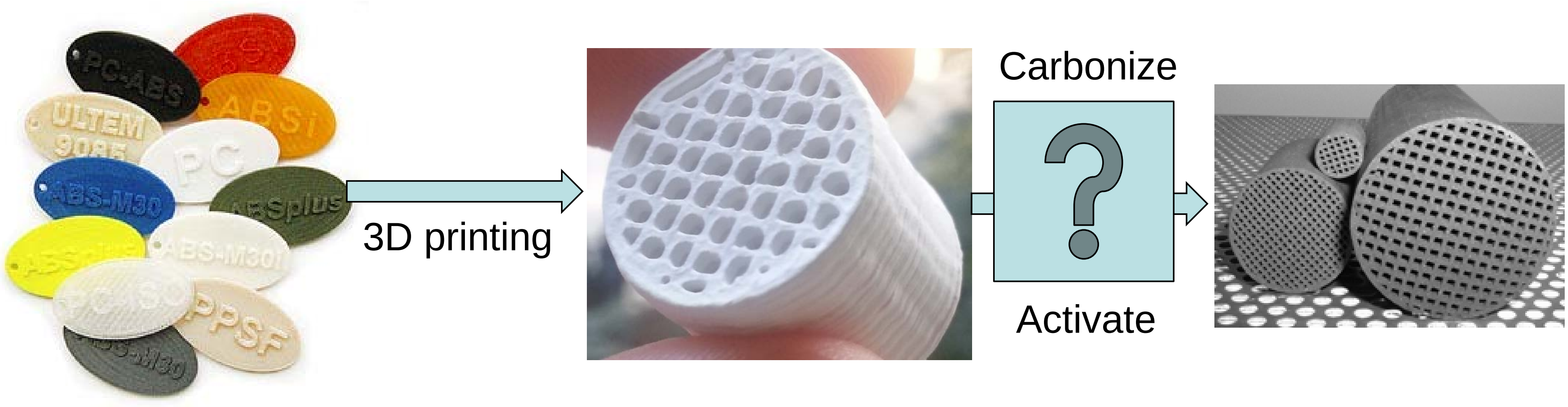
$S_{CO2/CH4}$ = 93 $S_{CO2/N2}$ = 80 at P= 1 bar
$S_{CO2/CH4}$ = 21 $S_{CO2/N2}$ = 23 at P= 10 bar

What are future R&D needs?

- Improved adsorbents:
  - Higher working capacity and selectivity for CO_2
  - High strength, durability
  - Improved tolerance for impurities
  - LOW COST
  - Low environmental impact of synthesis
- Eg. amine supported adsorbents
- Formed Adsorbents
  - Monoliths
  - Laminates
  - Micron and sub-micron for fluidised bed applications

3D Printing for CO2 Capture

Using 3D Printing technology to build the monolith, and then carbonize and activate to capture CO2.

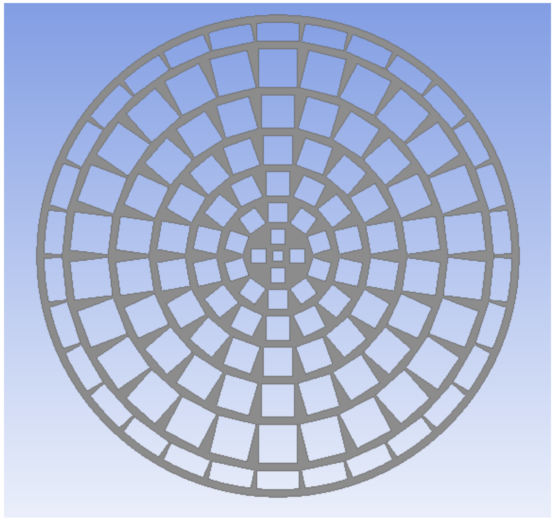


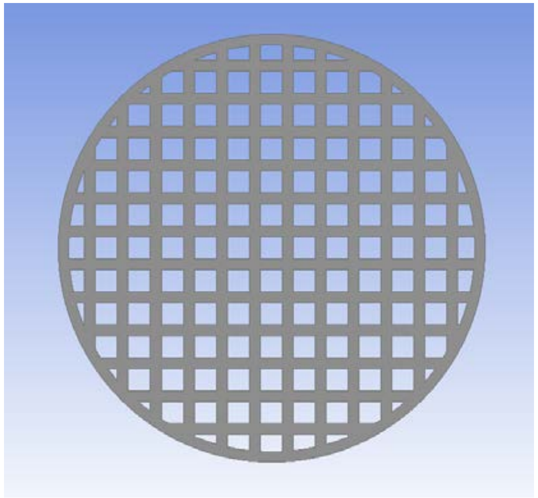
3D printing

Carbonize

Activate

3D Printing for CO2 Capture





and other geometries

How does CO2 capture efficiency vary with channel geometry?

What are future R&D needs?

- Adsorbent contactors
  - Fixed bed: low cost, “Small scale”, rotary valves, radial beds
  - Structured adsorbents: rapid swing materials for rapid TSA (hollow fibre with adsorbents embedded), rotary beds
  - Fluidised bed contactors for large scale deployment

What are future R&D needs?

- Process Design
  - Improved cycles for high purity CO_2 at modest vacuum
  - Integration of adsorption process with plant producing CO2 (waste heat, combustion heat)
  - Hybrid separation processes
    - Upstream “rough” separation by VSA to concentrate to 70% CO2
    - Downstream low temperature process to produce liquid CO2
    - Recycle vent gas from low temperature process to upstream VSA

Eg. VSA for flue gas CO2 capture

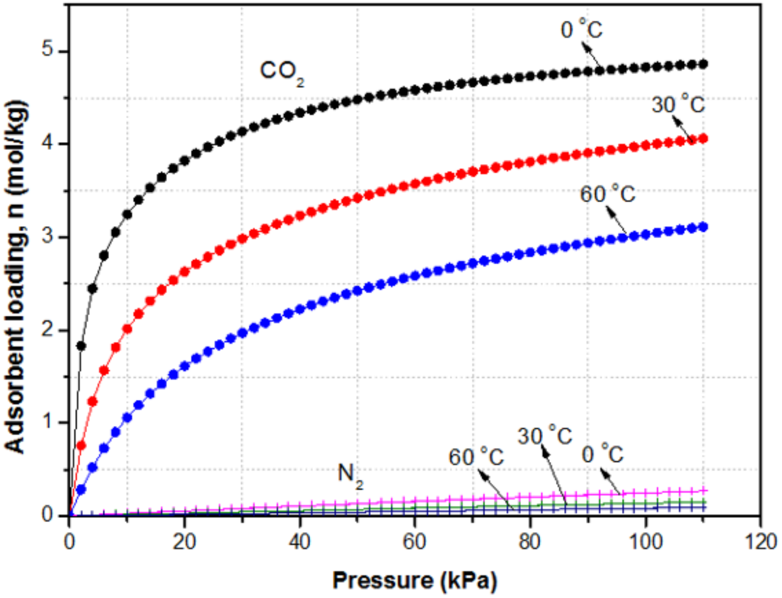
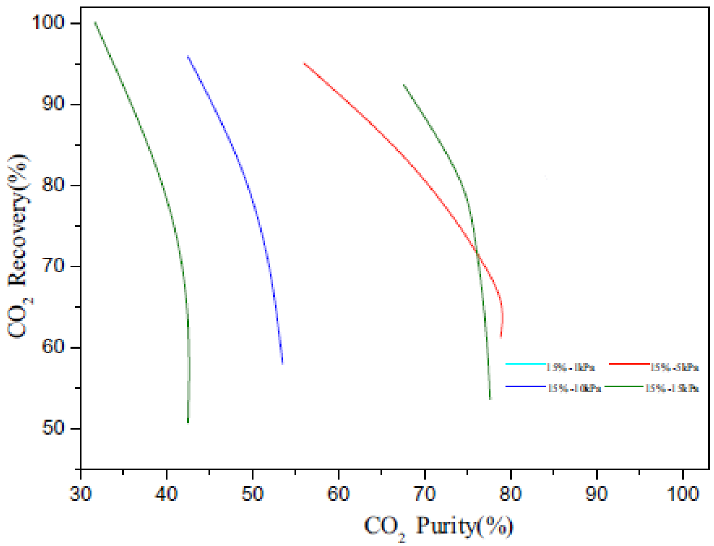


Fig. 1. Adsorption isotherms for CO_2 and N_2 on zeolite 13X at 0, 30 and 60°C.

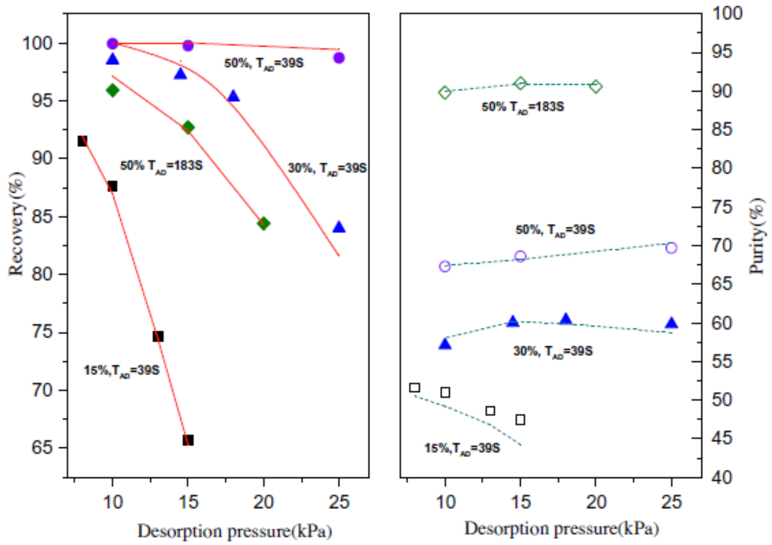
- Very steep isotherm slope at low partial pressure means deep vacuum (< 3kPa) is needed to produce high purity in simple cycles
  - Excessive power and volume flow rate
- Need to increase the gas phase partial pressure of CO_2 before application of vacuum
- Opportunities for novel cycle design

Purity/Recovery Trade off



Recovery/Purity trade-off

Desorption Pressure of 1kPa needed to achieve 95% purity with simple 6 step cycle



Effect of desorption pressure on recovery and purity – different feed concentration

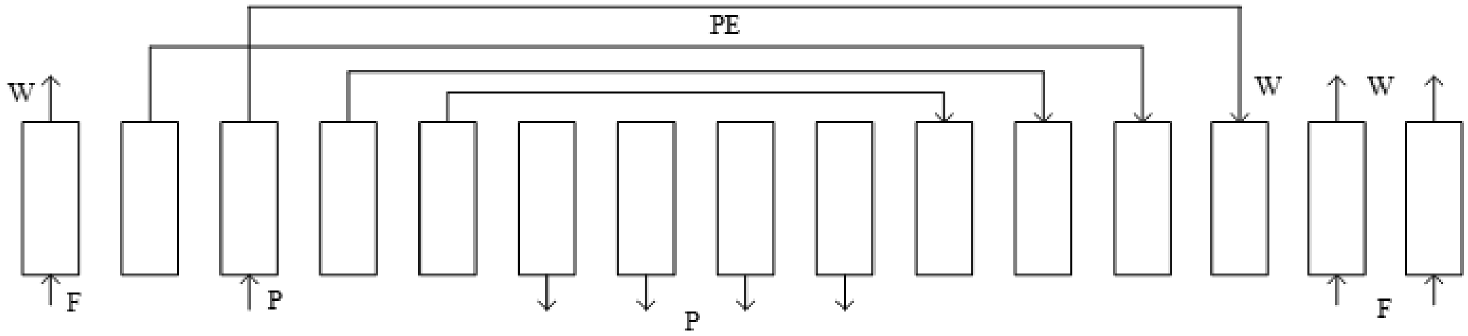
Webley et al., Chem.Eng.J., 2015, 265, 47

Cycle Design Principles

- Multiple reflux streams (pressure equalisation) to enhance recovery and reduce power
- Heavy Reflux to enhance purity before pumpdown
- Recovery of heavy reflux effluent
- Intermediate pressure heavy reflux

Cycle Design

(a)

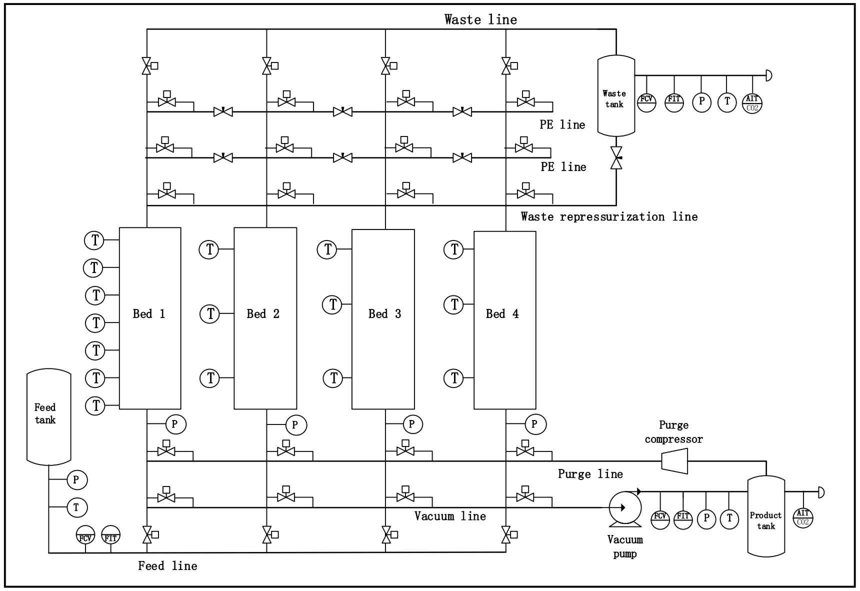


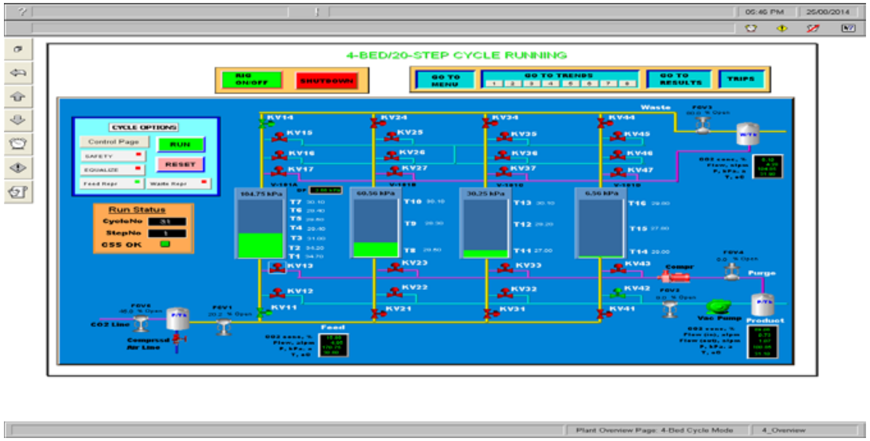
(b)

B1	F	PE	RN	PE	PE	EV				PE	ID			PE	ID		PE	Rp	F	
B2	ID	PE	Rp	F			PE	RN	PE	PE	EV				PE	ID			PE	ID
B3	EV				PE	ID			PE	ID		PE	Rp	F			PE	RN	PE	PE
B4	ID			PE	ID		PE	Rp	F			PE	RN	PE	PE	EV				PE
t(s)	60	10	10	10	10	60	10	10	10	10	60	10	10	10	10	60	10	10	10	10

Step times are shown for a cycle run with a total of 80 seconds for adsorption

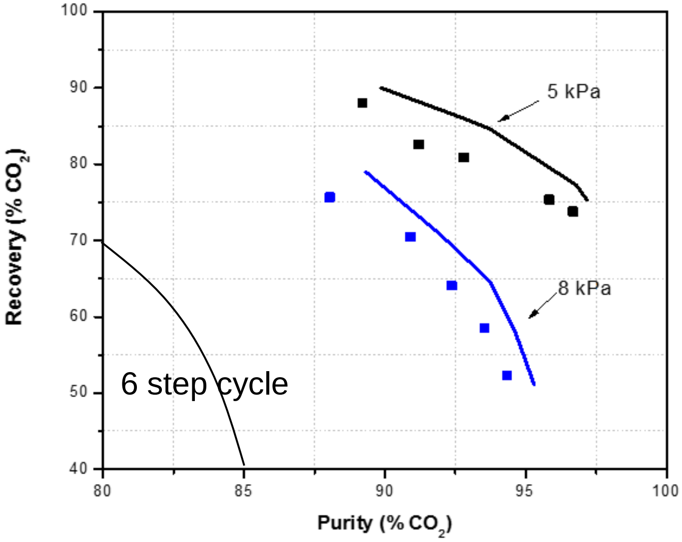
4-bed PSA/VSA experimental equipment

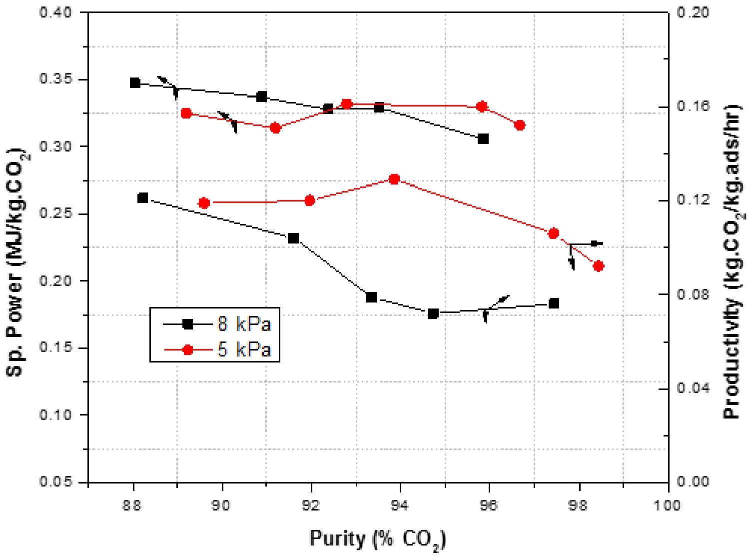




- 4 column PSA/VSA rig, custom-built
- Packing height 900 mm
- Diameter 20 mm
- Qnty of adsorbent 200 g per column
- Fully automated via PLC/SCADA system

Recovery, Productivity, Power





- Purity and Recovery significantly higher than best cycles to date
- Specific Power about 30% lower

Summary

- Adsorption processes for CO_2 capture have developed rapidly over last 20 years – only starting to see commercial developments now
- PCC not first target – there are much better fits elsewhere (high CO2 partial pressure, smaller throughput)
- Considerable opportunities to further develop the technology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