

Pre- and post-combustion capture of CO₂



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China Australia Geological
Storage of CO₂

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CO2CRC Participants



 Supporting Partners: The Global CCS Institute, The University of Queensland, Process Group

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Outline

- Capturing CO₂ from fossil fuels
- CO₂ Capture Technologies
 - Absorption (吸收)
 - Adsorption (吸附)
 - Membrane Separation
 - Other Technologies



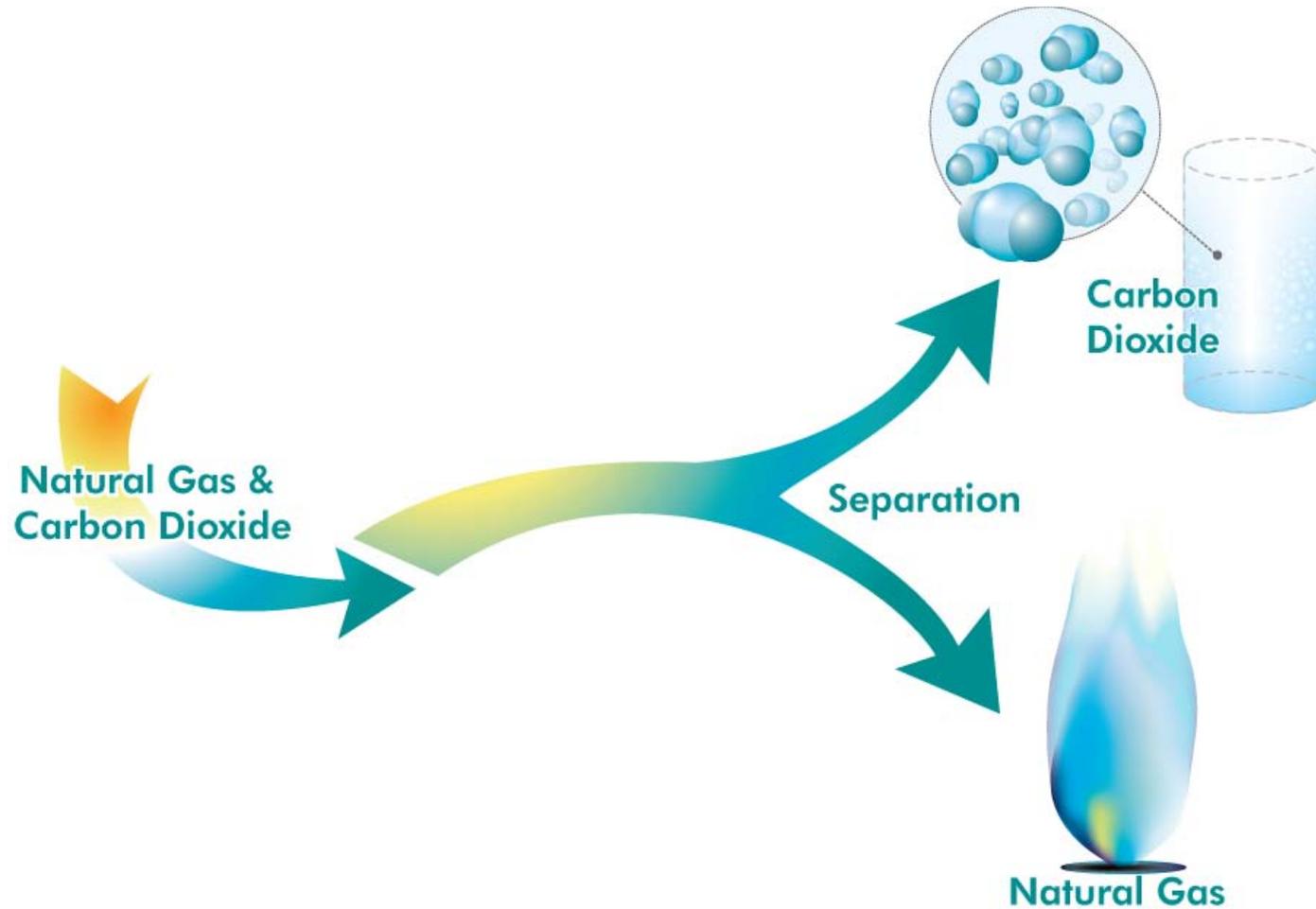
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Natural gas separation



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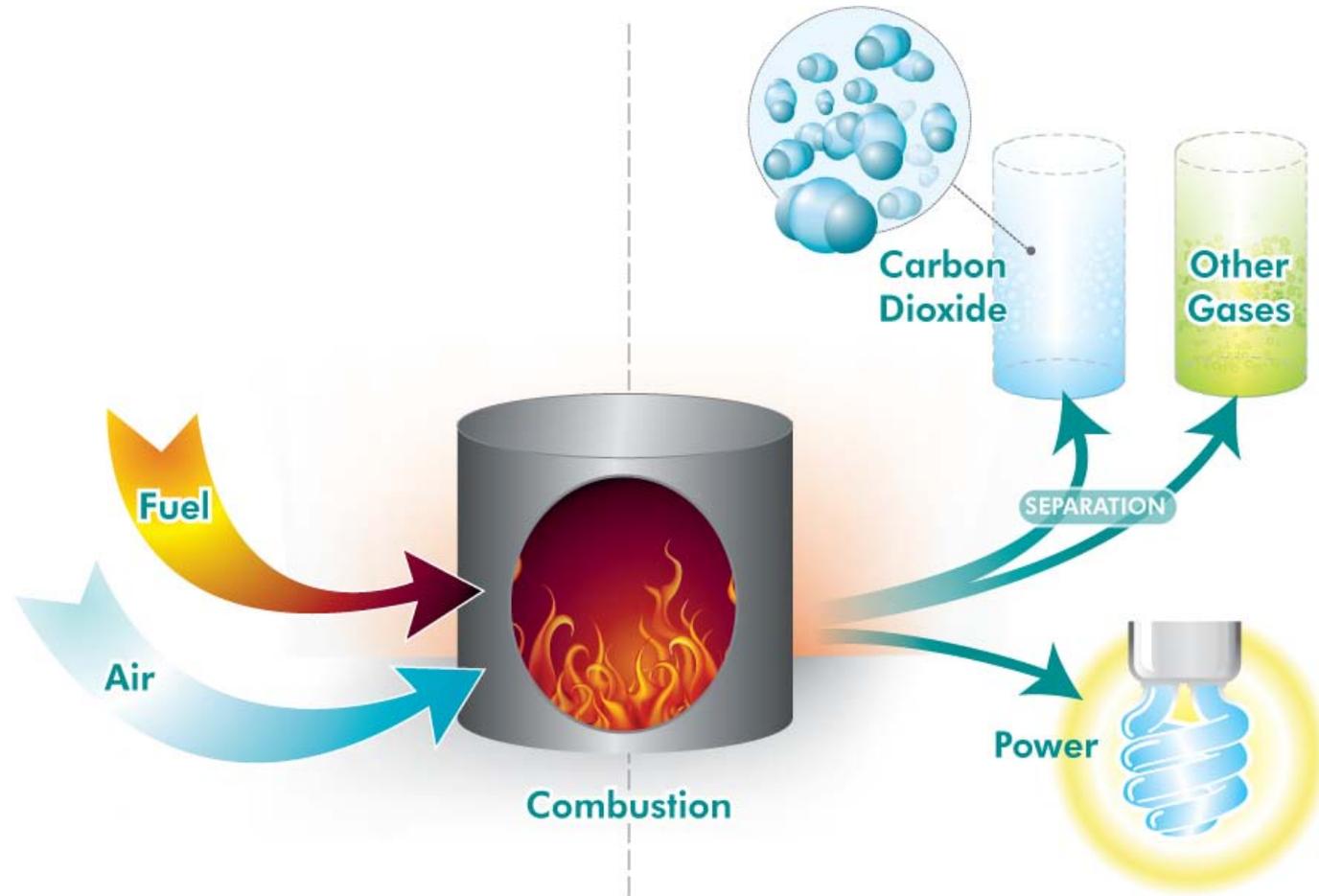
Natural Gas

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Post combustion capture



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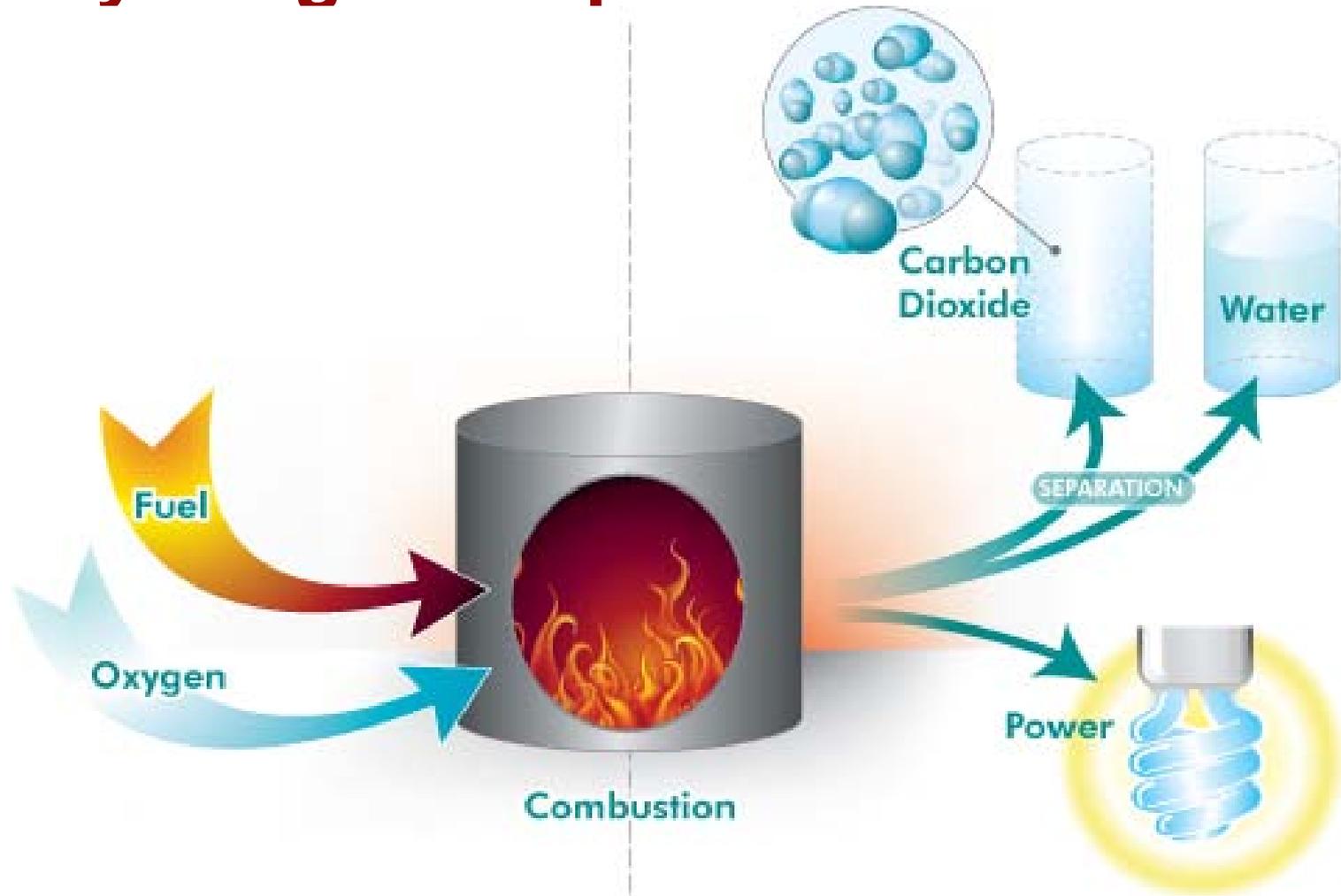
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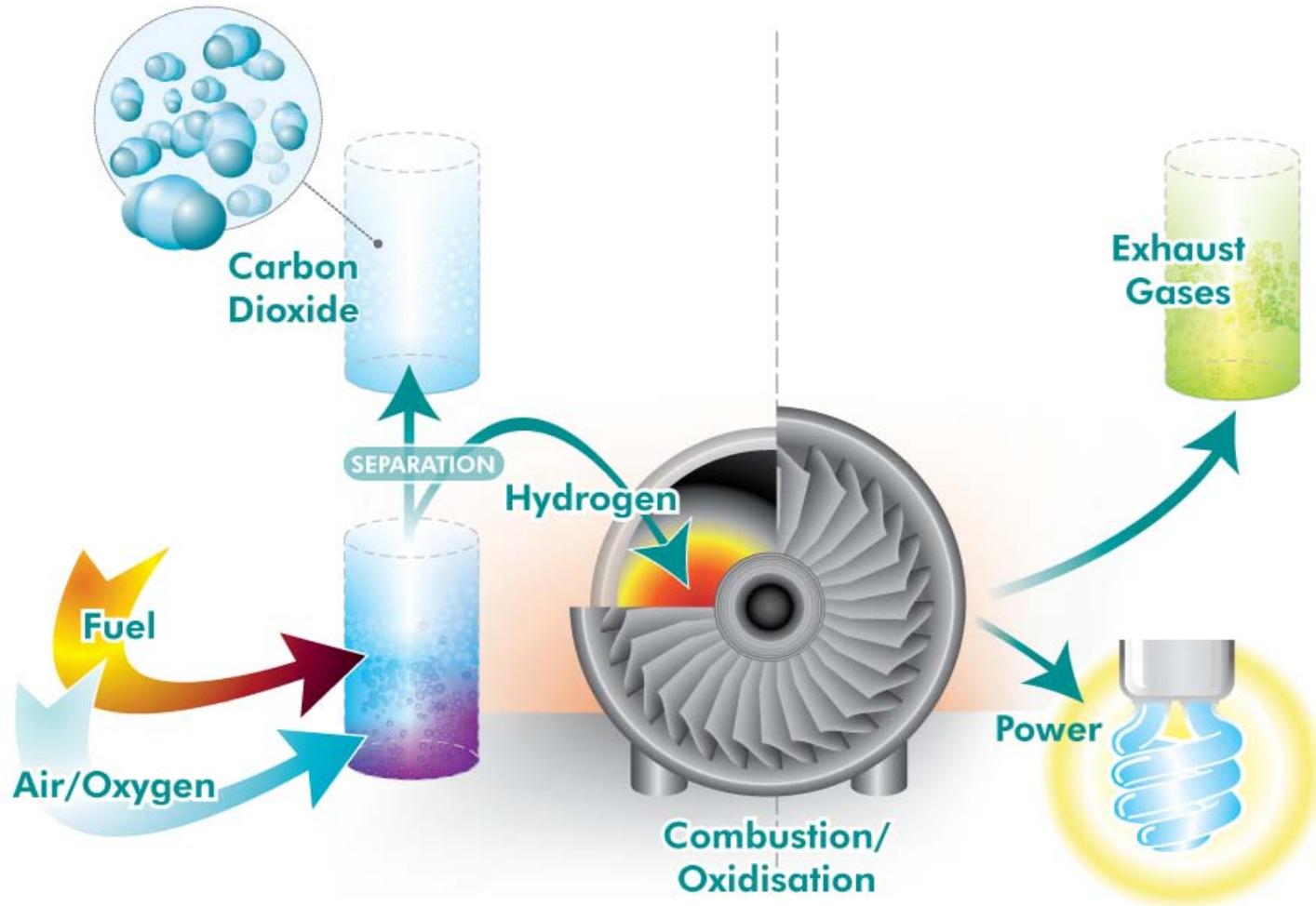
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Oxyfiring for capture



Gasification – pre-combustion capture



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Pre-combustion capture with IGCC

- Syngas is reacted with water convert the CO into CO₂
- $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$
- Leaves CO₂ which is captured for storage, and H₂ which can be used in a gas turbine
- Other uses for hydrogen: fuel cells and ammonia production



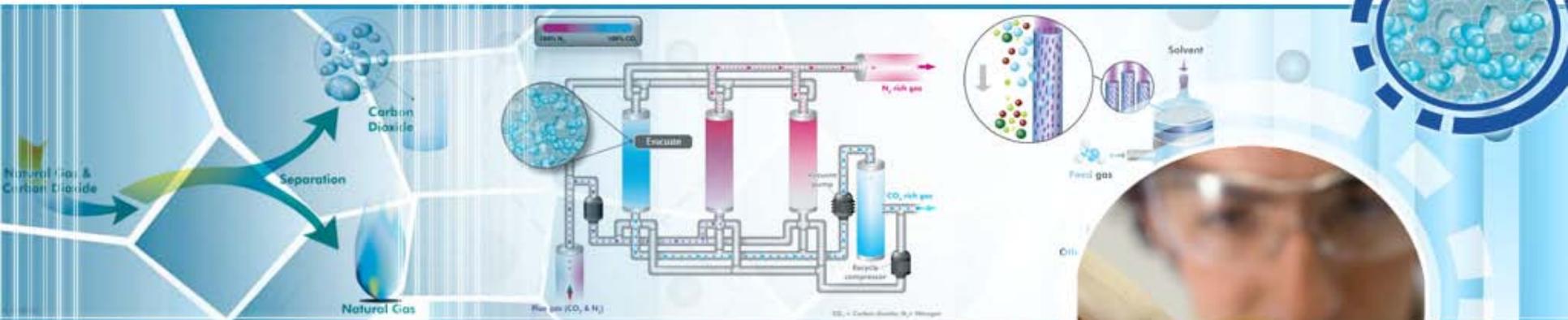
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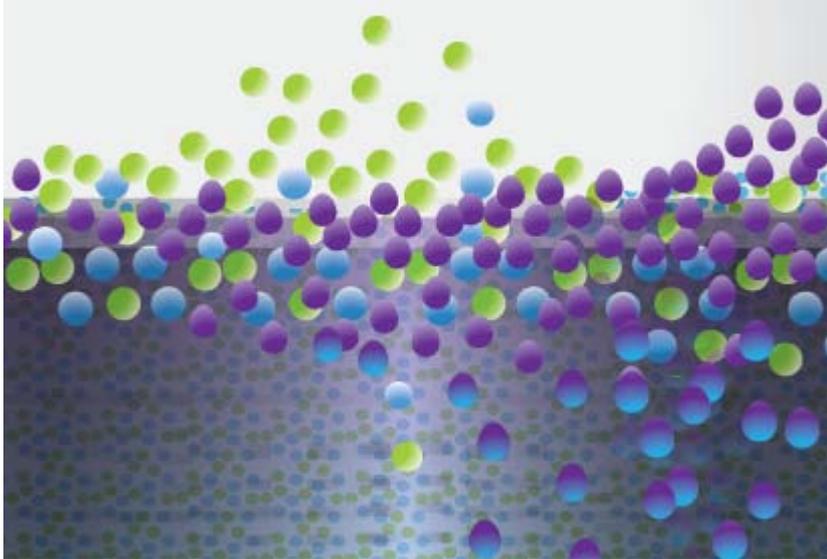


CO₂ capture technologies – Absorption (吸收)



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The absorption process



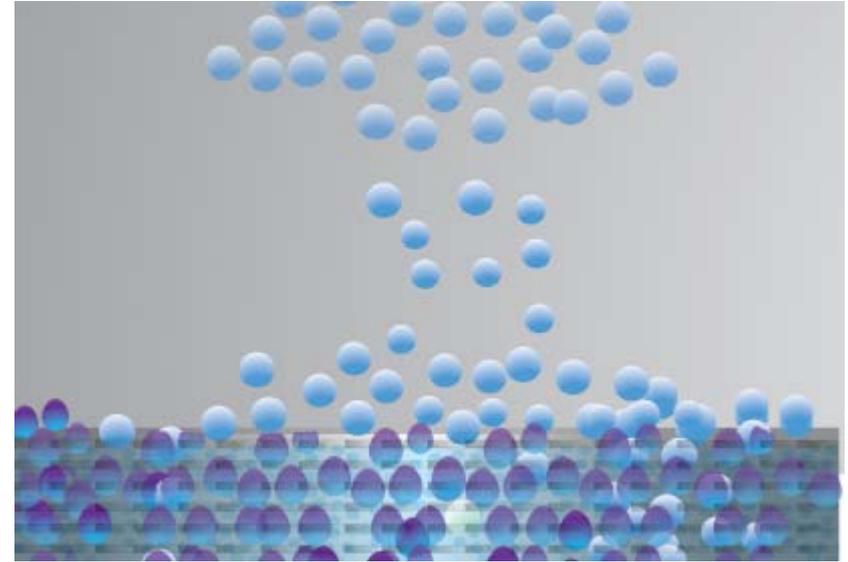
Absorption

- Contact with liquid

Nitrogen green, solvent purple, carbon dioxide blue

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Desorption

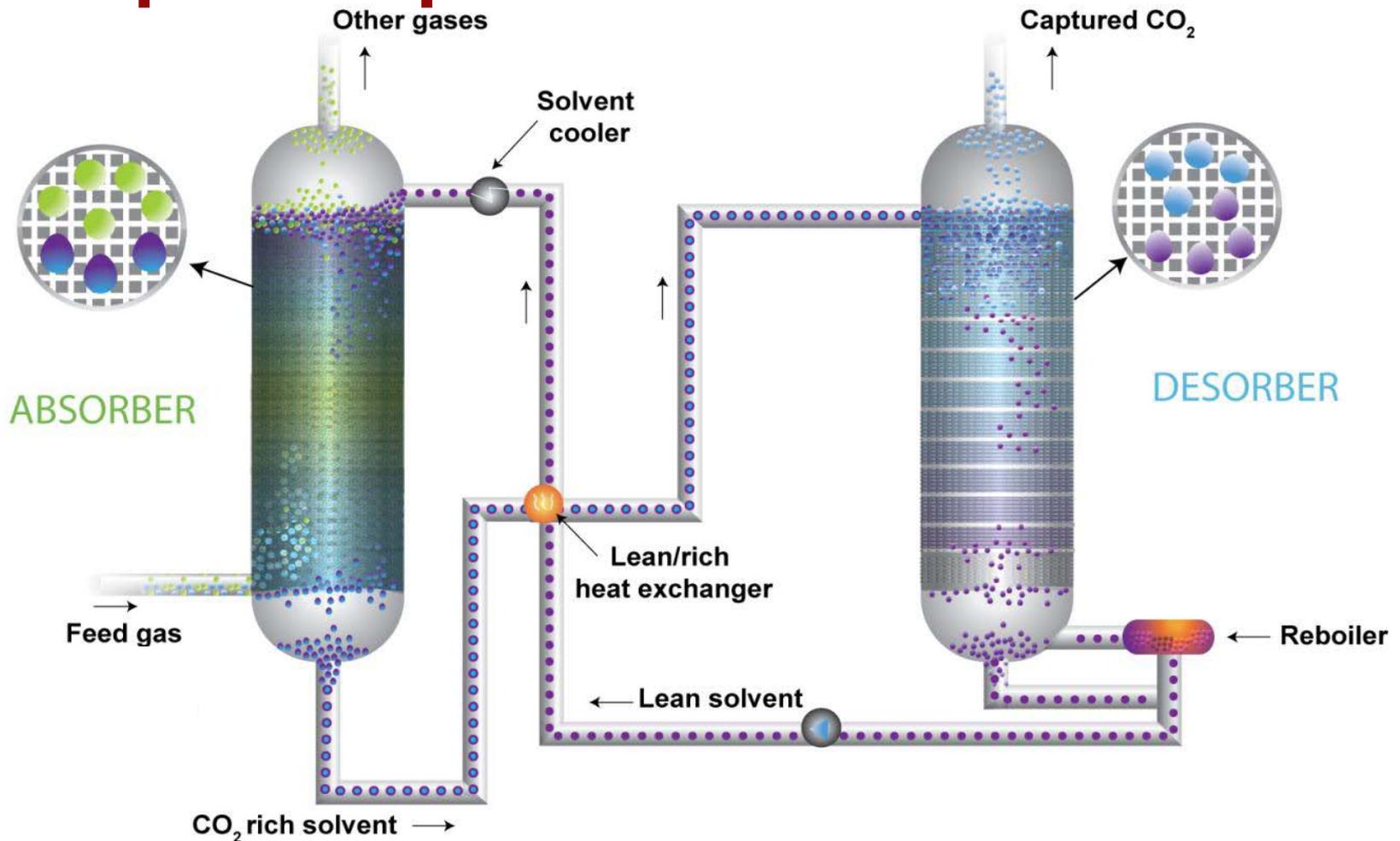
- Change T or P

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Absorption equipment



>> [Animation of absorption and desorption cycle](http://www.co2crc.com.au/misc/Schematic_1_animation/absorption_n_desorption_animation.html)

(http://www.co2crc.com.au/misc/Schematic_1_animation/absorption_n_desorption_animation.html)

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Solvent Absorption

- Countercurrent flow through a packed column is most common
- Plate towers are also used

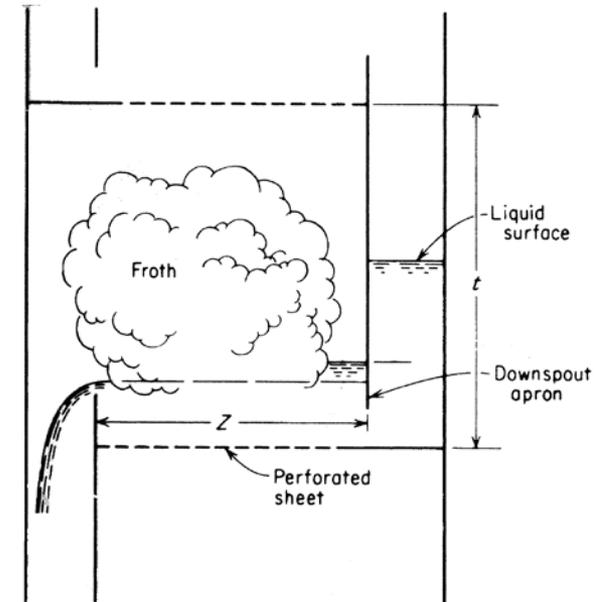


Image source: Mass Transfer Operations, R.E. Treybal, (1980) McGraw-Hill



Solvents

- **Physical Solvents – Selexol**
- **Chemical Solvents –**
 - **Primary and secondary amines – MEA, DEA, ammonia**
 - **Tertiary and hindered amines – MDEA, KS1**
 - **Amino acid salts – BASF Puratreat, Siemens/TNO**
 - **Potassium Carbonate**



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Solvent Degradation

- Environmental impact
 - Waste disposal
 - Possible releases
- Economic losses
 - Purification/Replacement
 - Equipment corrosion
 - Waste disposal
- Performance losses
 - Reduced capacity for CO₂
 - Increased heat duty for reclaimer



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Comparison of Solvent Properties

	Cost (US\$/lb)	Volatility (atm x 10 ³ at 40C)	Degradation	Corrosion	Stripper Steam Requirement (MJ/kg CO ₂)
MEA	40	0.1	High 1.5 kg/t CO ₂	High	4.2
MDEA	300	0.003	Moderate	Moderate	3.3
Chilled Ammonia	5	200	None	High	2.2
Potassium Carbonate	40	0	None	High	3.5



Source: Rochelle, 2007
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Solvent absorption demonstration plants

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Pre-Combustion
HRL, Mulgrave



Post-Combustion
International Power,
Hazelwood



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An Amine-Based CO₂ Capture System Used to Purify Natural Gas at BP's In Salah Plant in Algeria



Source: Photo courtesy of IEA Greenhouse Gas Programme.



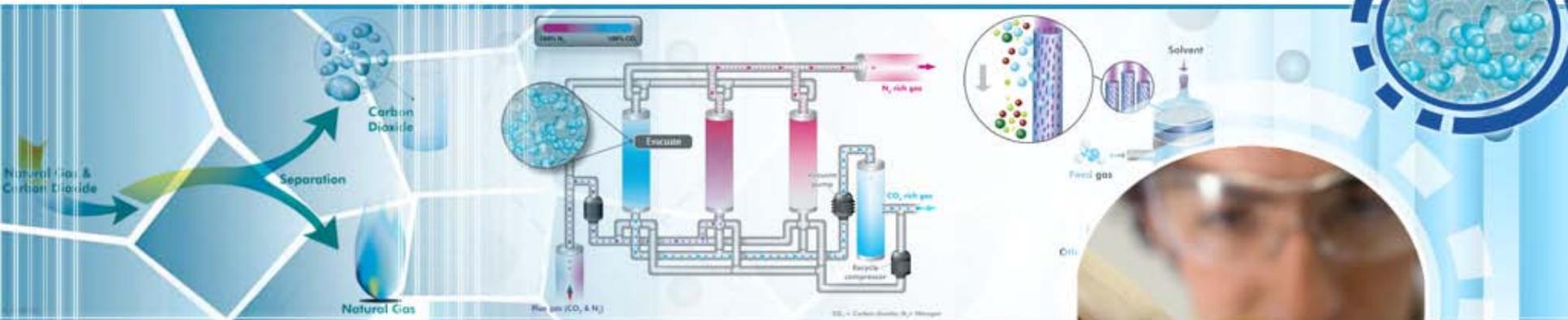
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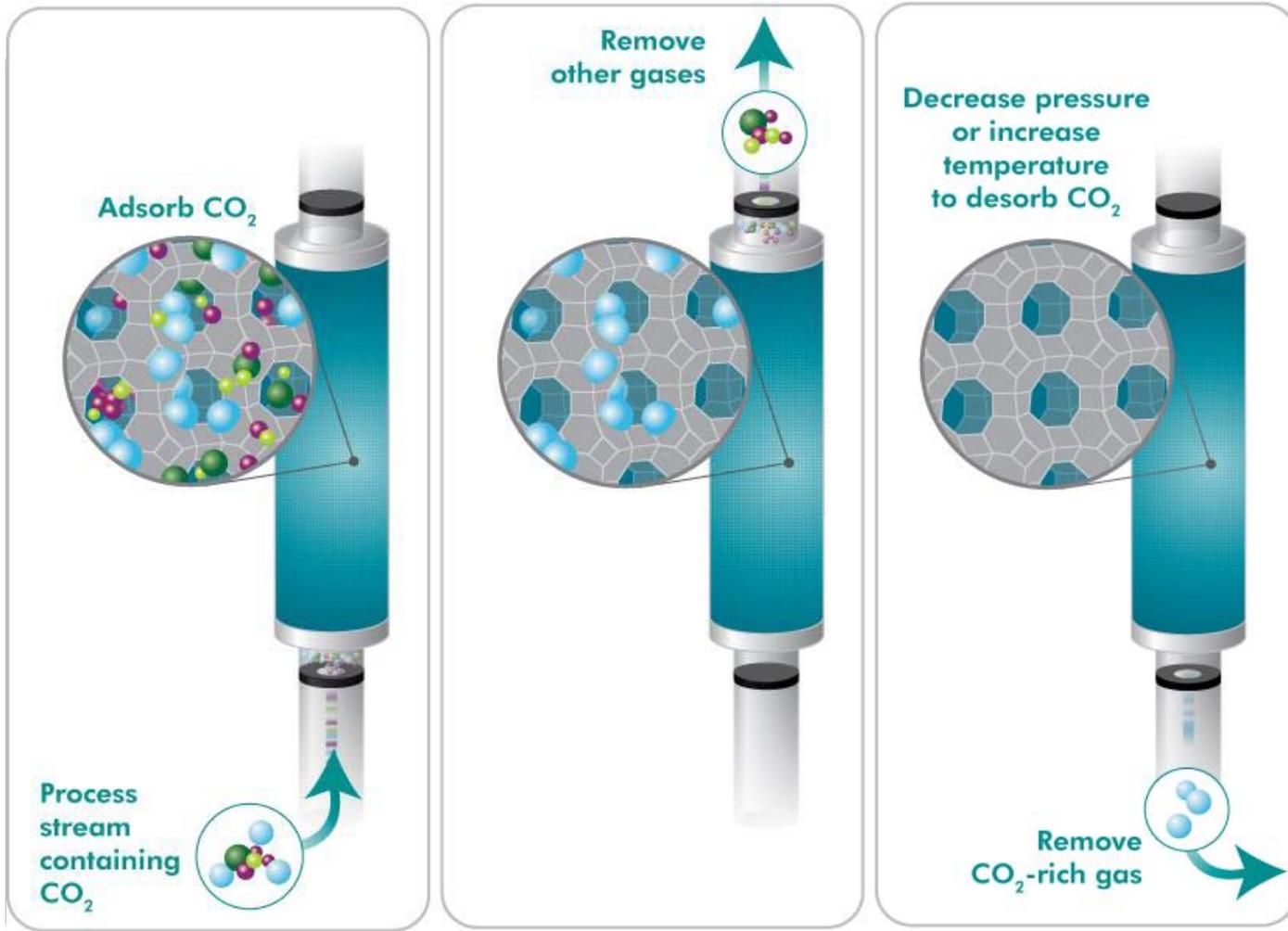


CO₂ capture technologies – Adsorption (吸附)



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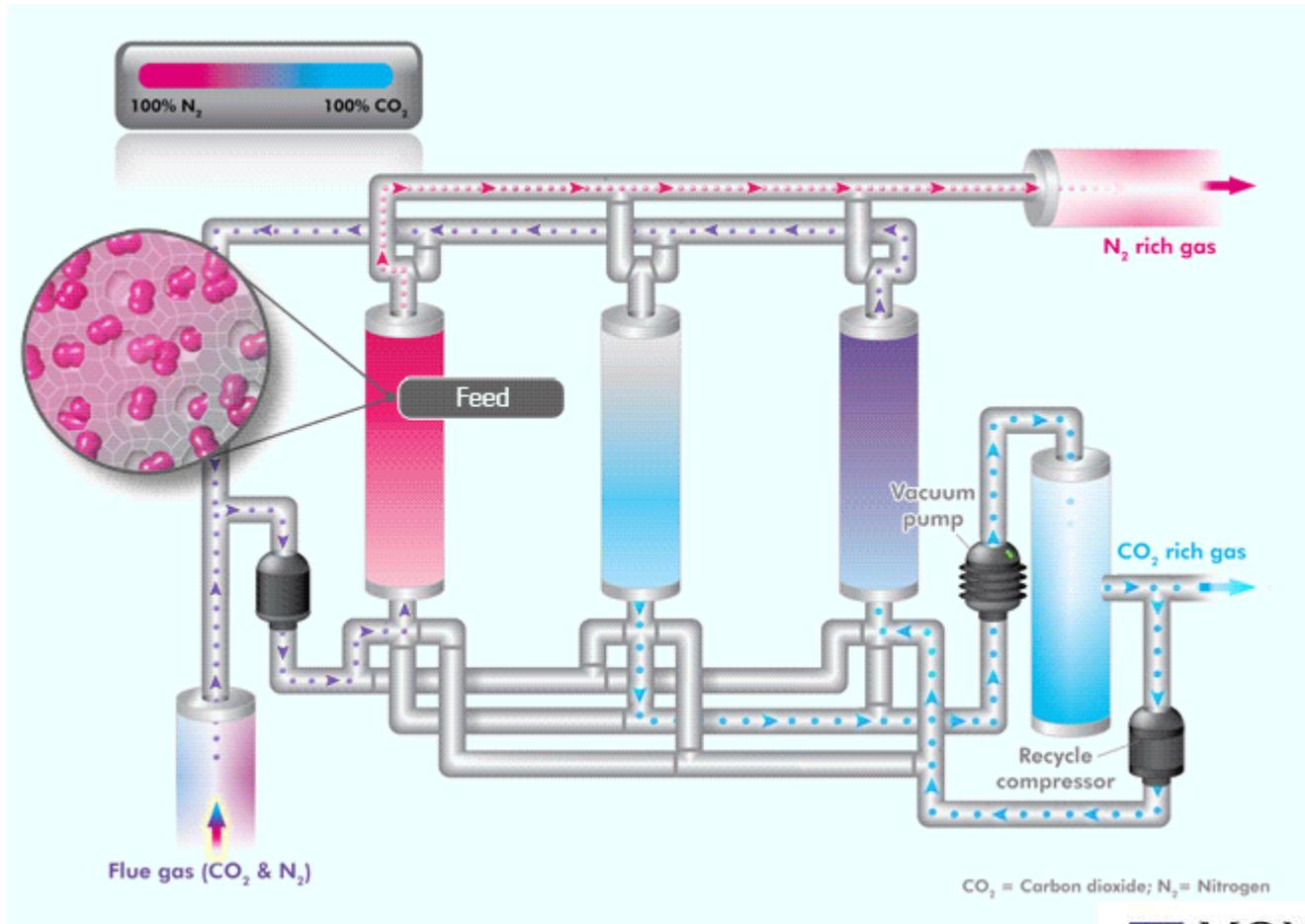
Principle of Adsorption Capture



 Carbon dioxide (CO₂)  Other gases



Adsorption process cycle



>> [Animation](http://www.co2crc.com.au/misc/anim_adsorption_process.html) http://www.co2crc.com.au/misc/anim_adsorption_process.html



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Adsorption Technology

- Gas solid interaction
 - Physical bonding
 - Chemical bonding
- Simple, robust and energy efficient
- Regeneration methods
 - Pressure/vacuum swing (P/VSA)
 - Temperature swing (TSA)
 - Electrical swing adsorption (ESA)



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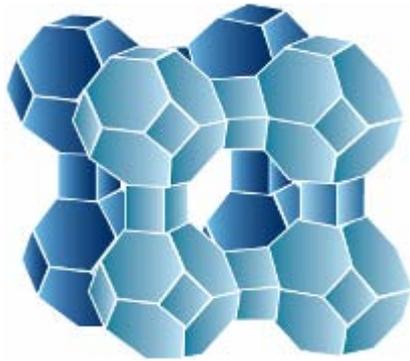


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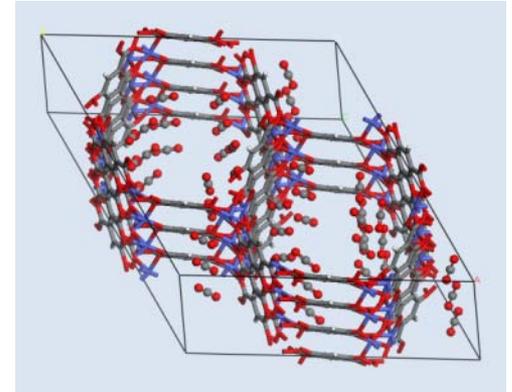


Adsorbent examples

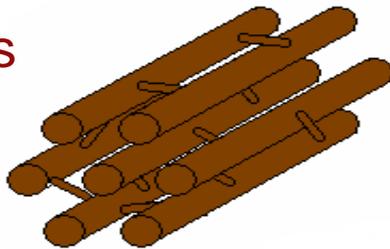
Zeolites



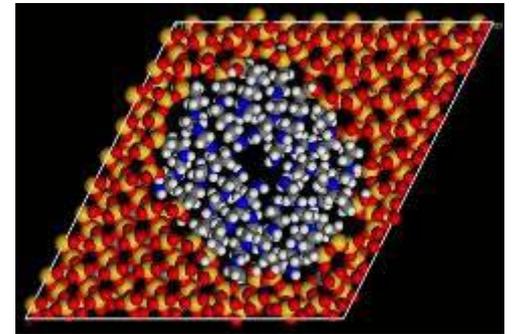
Metal Organic Frameworks (MOF)



Mesoporous Carbons



Inorganic-Organic Hybrids



Adsorption Technology

- Commercial process
 - Hydrogen PSA
 - Oxygen VSA
 - Landfill P/VSA
 - Air drying
 - Natural gas drying/purification
 - Syn-gas sweetening
 - Medical oxygen generator
 - VOC removal



Hydrogen PSA

Stocker and Whysall, UOP. 1998 30 years of PSA Technology for Hydrogen Purification



Oxygen VSA.

Image courtesy of Air Products and Chemicals, Inc .



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Three bed full cycle CO₂ capture VSA unit for wet flue gases in Monash Uni



95% purity,
80% recovery

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Adsorption demonstration plants



Pressure swing
adsorption
Pre-Combustion



Vacuum swing
adsorption
Post-combustion



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Advantages for adsorption in post-combustion CO₂ capture

- **Easy handling – using solid sorbents instead of liquid**
- **Low energy cost, ~1-2 MJ/kg CO₂**
- **Low cost adsorbent – Activated carbon, zeolites**
- **Simple process control logic**
- **Possibility of direct high temperature flue gas capture**



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Challenges for adsorption in post-combustion CO₂ capture

- **Scale-up**
 - Large throughput, million m³ per hour
 - Large rotary equipment, blower, pumps etc.
- **Impurity effects**
 - Water vapor
 - SO_x/NO_x
- **Pressure drop**



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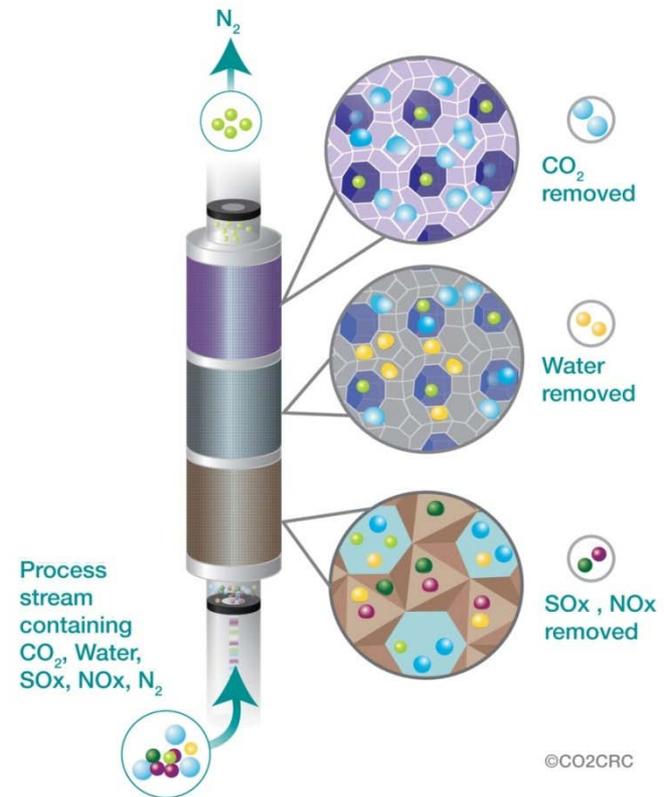


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Advances in adsorption technologies

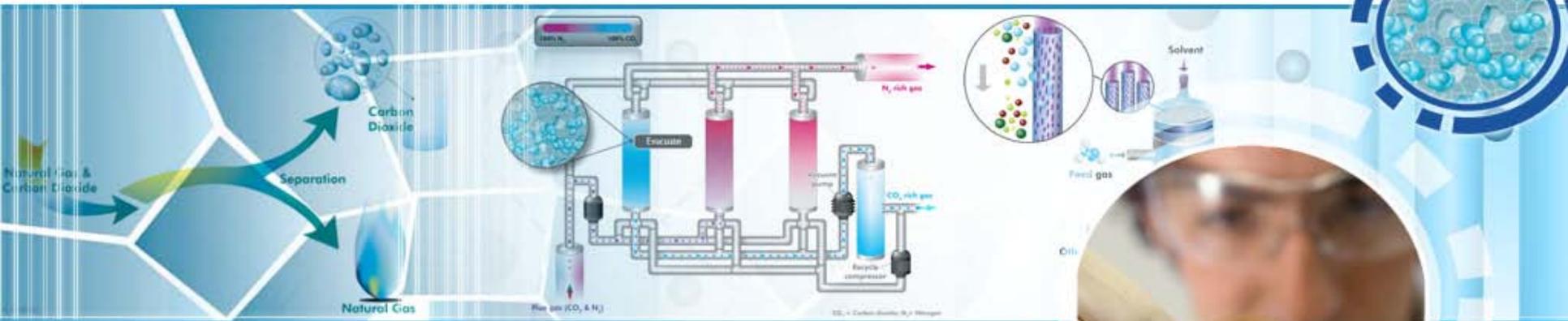
- Process improvement
 - New vacuum swing adsorption cycles
 - Temperature-assisted vacuum swing adsorption
 - Electrical swing adsorption
 - Heat integration
 - Multiple-layered column



Dong Xu, et al., *Adsorption*, in revision.



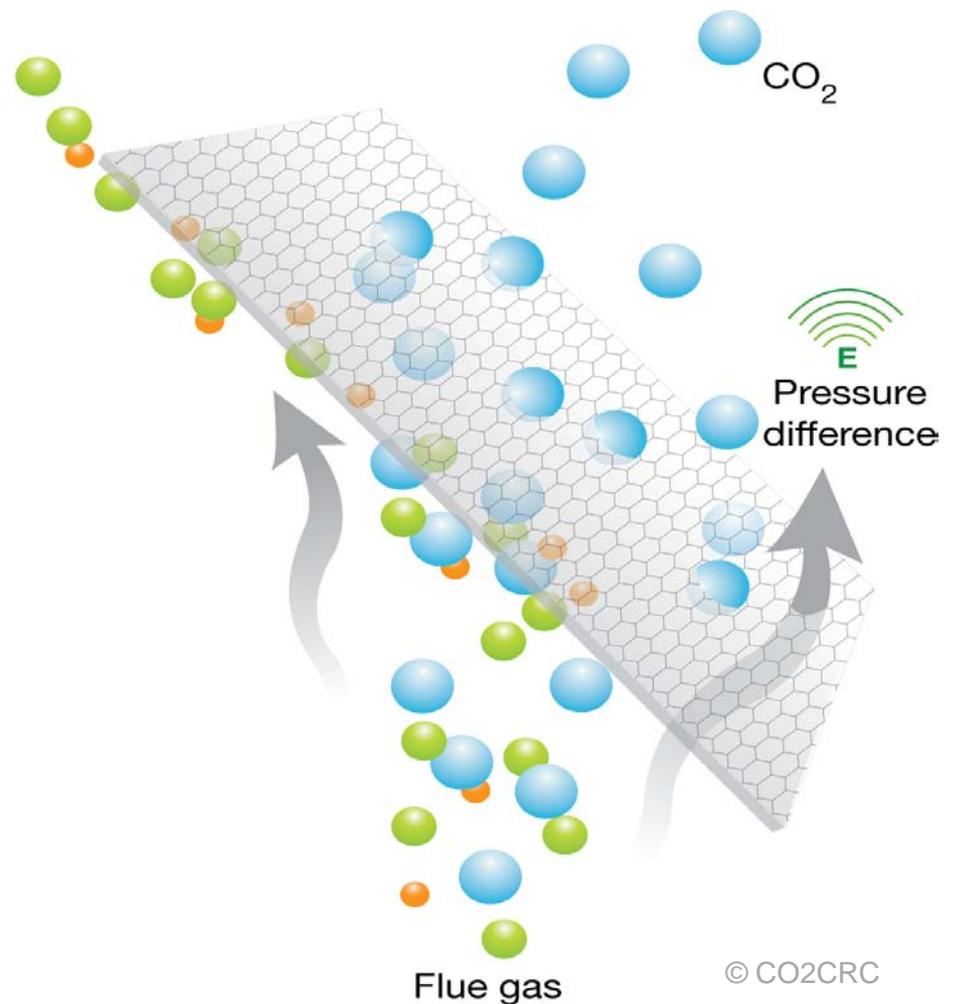
CO₂ capture technologies – Membrane Separation



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Membranes

CO₂ can selectively pass through gas separation membranes to be removed from the flue gas.



>> [Animation](#)

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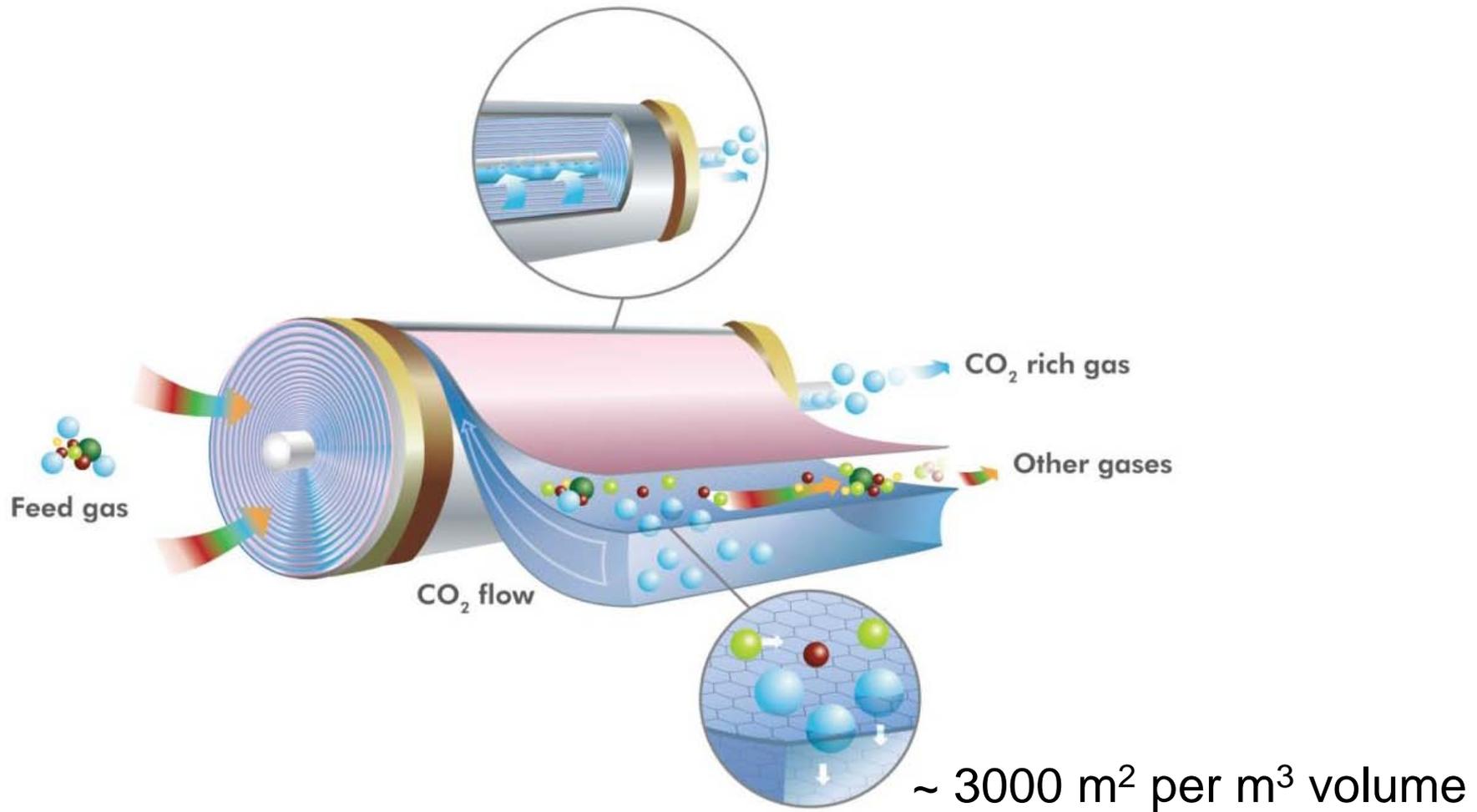
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Spiral Wound Module



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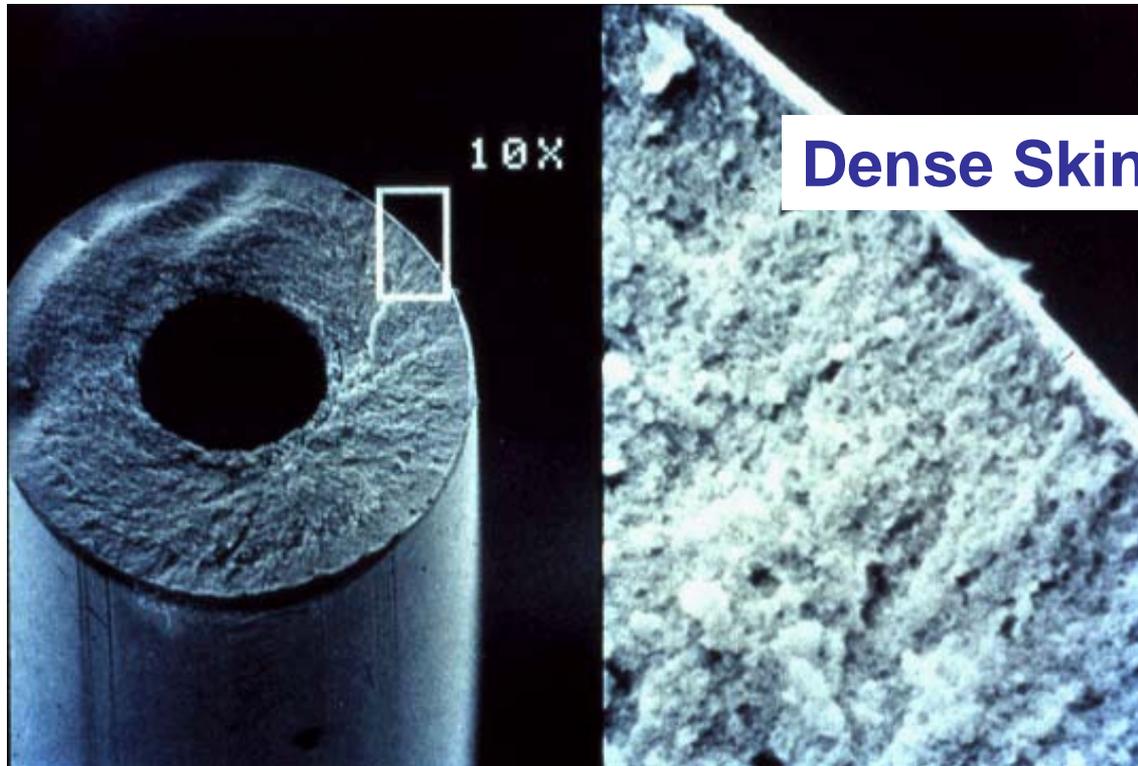
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Hollow Fibre Membrane



Fibre diameter 0.1 to 0.5 mm diameter

Skin layer ~0.1 micron thick



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Polymer Membranes for CO₂ removal

- **First Generation:**
 - Cellulose acetate (Cynara by Natco, Grace)
 - Polysulfone (Prism by Air Products)Generally spiral wound
- **Second Generation:**
 - Polyimides (MEDAL by Air Liquide)
 - Perfluoropolymers (Z-Top by MTR)
 - Poly ether ether ketone (PEEK by Porogen)More likely to be hollow fibre
- **Third Generation??**
 - Polaris by MTR



When are Membranes Competitive?

- When the feed contain moderate concentrations (10% to 85% vol) of the more permeable gas.
- When the feed is already at moderate to high pressure (15 to 150 bar gauge) and for polymeric membranes at moderate temperature (0° to 70° C)
- When the product gases are not required at very high purities or with 100% recovery.
- Polymeric membranes are proven in the capture of CO₂ from natural gas



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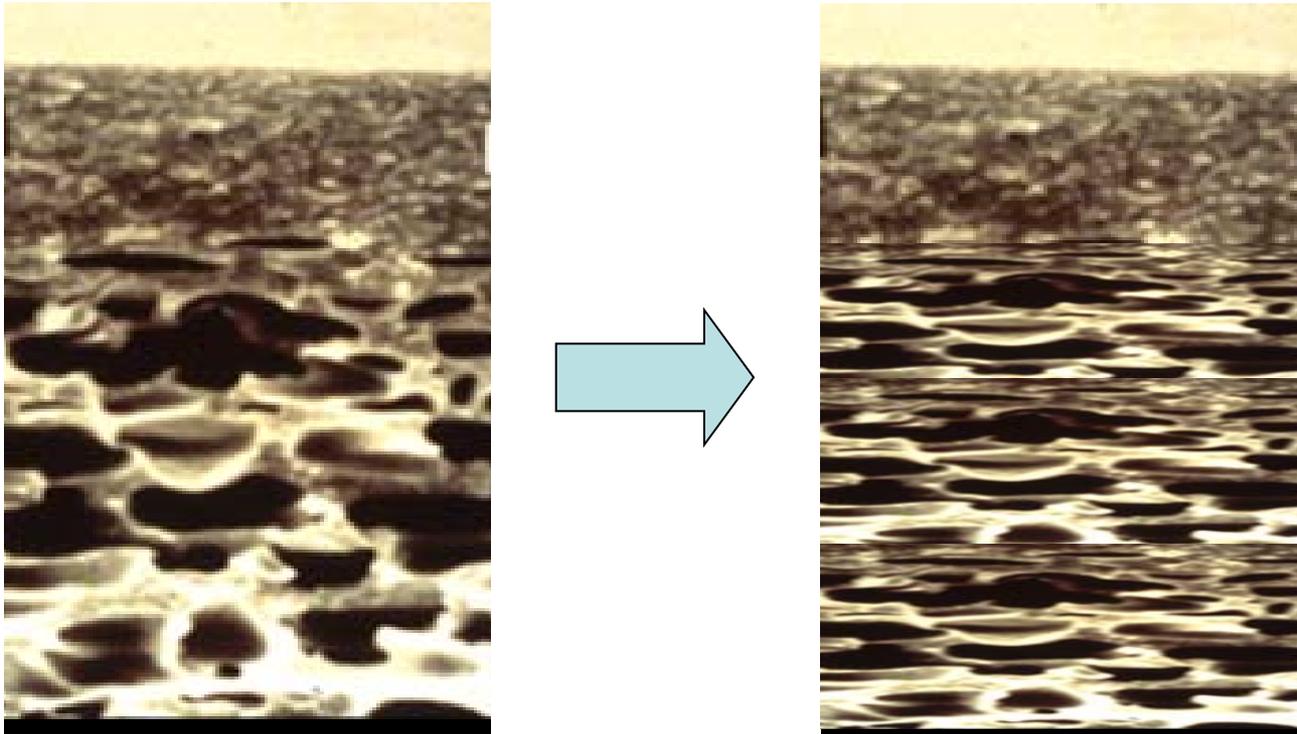
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Operational Performance Issues

Compaction

Collapse of the porous support layer adjacent to the selective layer.



- Mechanical compression due to high transmembrane pressure
- Evaporation of liquid contaminants causing capillary pressures



Plasticization

Polymer swelling due to sorption of condensable gases (water, aromatics, hydrocarbons)

- Plasticization causes:
 - Increases in permeability/losses in selectivity
 - Time dependent permeation behavior (hours to days)
 - Loss of mechanical strength
 - Increased rates of compaction



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Physical Aging – diffusion of ‘excess’ free volume out of a glassy polymer over time (weeks to years)

Fouling – Liquid and solid contaminants can coat the membrane surface with a film that adds an additional mass transfer resistance e.g. compressor oil, fine particulates

Chemical Interactions – Some contaminants can chemically interact with the polymer e.g. HCl with cellulose acetate.



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Membrane demonstration plants CO2CRC



Membrane separation
Pre-combustion



Membrane separation
Post-combustion



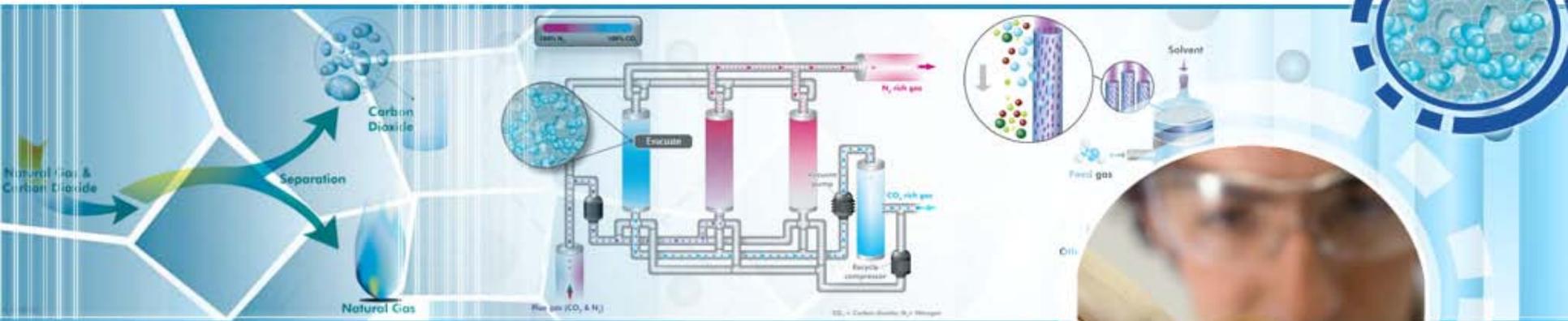
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CO₂ capture technologies – Other technologies



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Other Capture Technologies

- Membrane gas absorption
- Low temperature separation
 - Chilled water
 - Cryogenic distillation
- Oxy combustion
- Chemical looping
- Algae (bio-fuel)
- Enzymes



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