



Maps for the Evaluation of Membrane Performances in CO₂ Post-Combustion Capture

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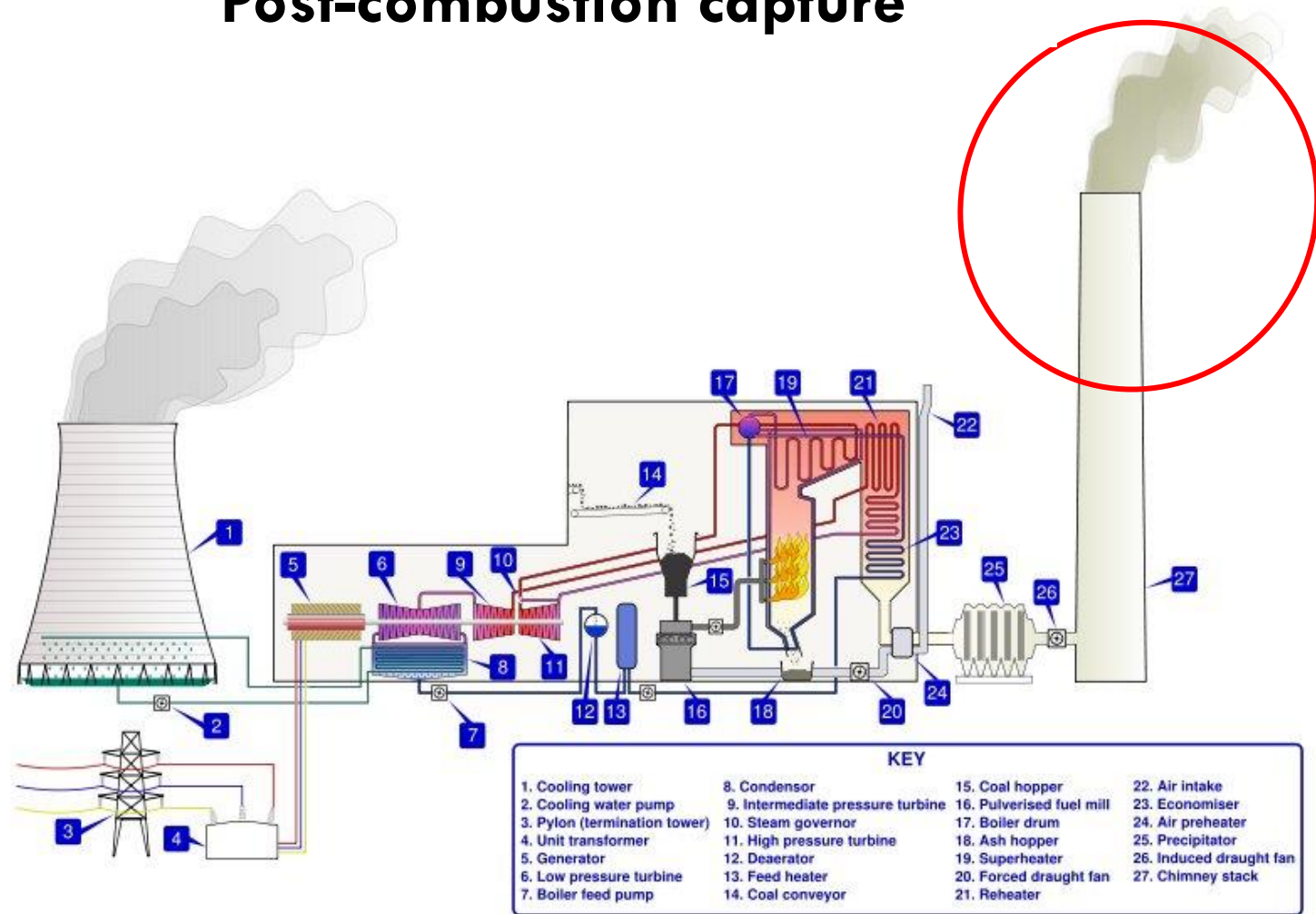


Summary

- Introduction
- Elaboration of Global Maps by 1-D theoretical model and comparison with literature data
- Conclusions



Post-combustion capture

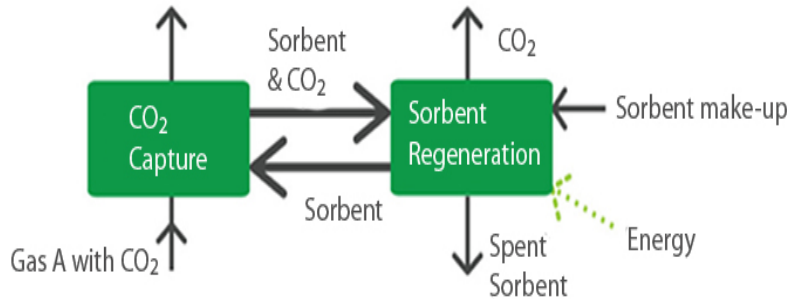


CO₂ (concentration of ca. 5–25%) has to be separated, at relatively low temperature and atmospheric pressure, from the flue gas emitted after the combustion of fossil fuels.

This possibility shows the essential advantage of being compatible to a retrofit strategy (i.e. an already existing installation can be, in principle, subject to this type of adaptation).

Traditional operations for CO₂ Separation

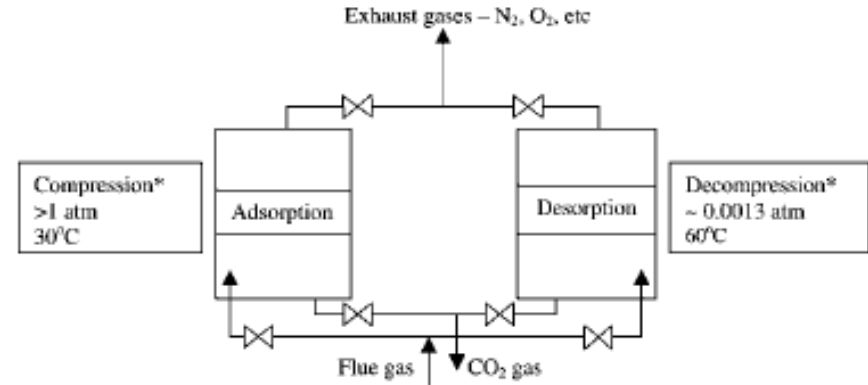
ABSORPTION



Use monoethanolamine (MEA) to dissolve CO₂. The CO₂-rich solution (i.e. >90%) is pumped to a regeneration column, where the CO₂ is stripped from the solution and the solvent recycled.

High amount of energy is consumed for the regeneration of solvent. Solvent is degraded in oxidising environment of flue gas

ADSORPTION



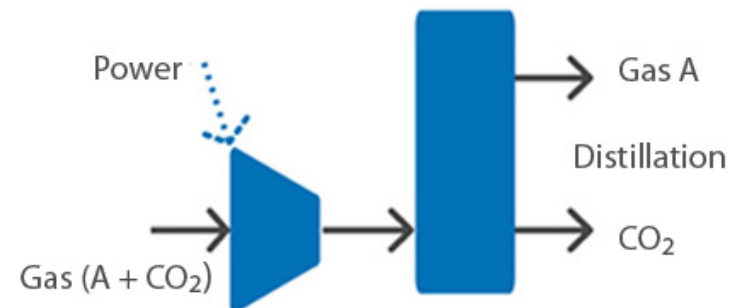
CO₂ is adsorbed onto the sorbent particles. In PSA, the gas mixture flows through a packed bed until the desired gas concentration approaches equilibrium. A vacuum can then be applied to liberate the CO₂ from the sorbent.

High pressure is required.

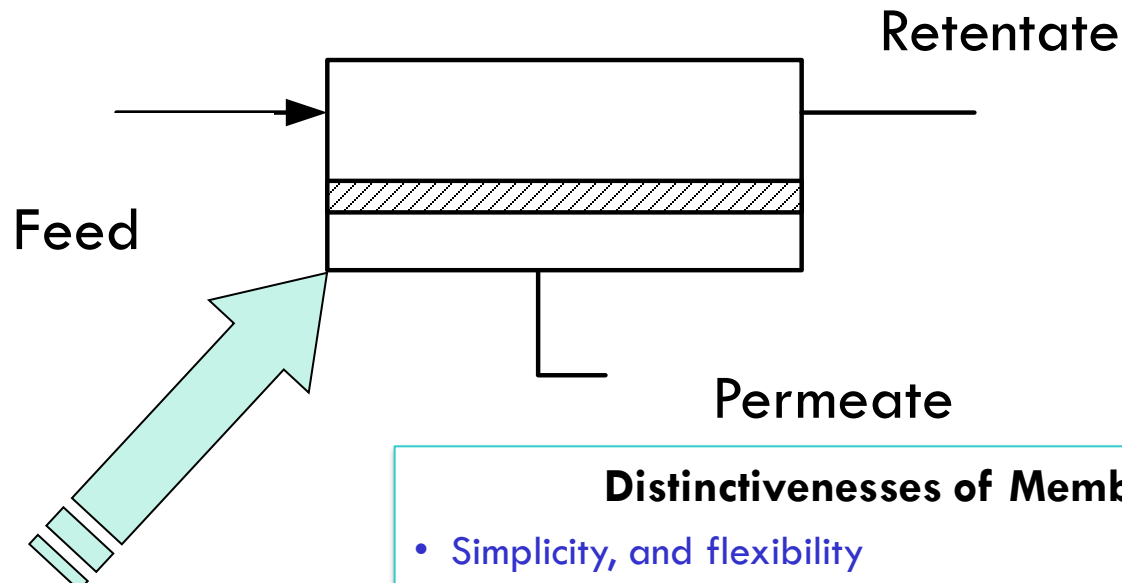
After the removal of all of the other gases and particulates a mixture of CO₂ (i.e. at high concentration) and N₂ is fed into a cryogenic chamber where liquid CO₂ can be separated by cooling and condensation whereas N₂ remains as a gas.

High amount of energy is consumed in refrigeration process. Pre - treatment stages for the water removal are necessary to avoid blockages in the system

CRYOGENIC



Membrane Gas Separation



Distinctivenesses of Membranes

- Simplicity, and flexibility
- Modularity, and ease of scale-up
- Reduced Equipment Size
- Low Investment Costs
- Ease of installation and incorporation of new membrane developments
- A flue gas compression much smaller than that for PSA is required.
- No extreme temperature (*i.e.* as in cryogenic separation)



C. E. Powell, G. G. Qiao, *Journal of Membrane Science*, 279 (2006) 1



Comparison among the different separation technologies

ABSORPTION		ADSORPTION		CRYOGENIC		MEMBRANE GS	
Advantages	Drawbacks	Advantages	Drawbacks	Advantages	Drawbacks	Advantages	Drawbacks
Recycling of the sorbent	Corrosion of carbon steel facilities due to oxygen	Recycling of the sorbent	Not able to handle large concentrations of CO ₂	No requirement of chemical absorbents	Several costly steps required to remove all water traces	No moving parts and modularity	Current low selectivity of membrane materials
Non-dependence on human operators	Degradation of the solvent due to SO _x and NO _x	High operating flexibility	Adsorption also of gases smaller than CO ₂	Atmospheric pressures	Increasing layer of solid CO ₂ onto heat exchanger surfaces	Istantaneous response to variations	Limitation on the suitable operating temperature for polymeric membranes
Consolidated know how of the technology	Energetic load for solvent recovery		Slow process		Complex control systems	Easy of expansion	



A Simple Tool for a preliminary analysis in one-stage membrane system

Feed/Retentate side

$$\frac{d\phi_{\text{CO}_2}^{\text{Retentate}}}{d\zeta} = -\Theta_{\text{CO}_2} \left(\phi X_{\text{CO}_2}^{\text{Retentate}} - X_{\text{CO}_2}^{\text{Permeate}} \right)$$

$$\frac{d\phi_{\text{N}_2}^{\text{Retentate}}}{d\zeta} = -\frac{X_{\text{CO}_2}^{\text{Feed}}}{X_{\text{N}_2}^{\text{Feed}}} \frac{1}{\alpha_{\text{CO}_2/\text{N}_2}} \Theta_{\text{CO}_2} \left(\phi X_{\text{N}_2}^{\text{Retentate}} - X_{\text{N}_2}^{\text{Permeate}} \right)$$

Permeate side

$$\phi_{\text{CO}_2}^{\text{Permeate}}(\zeta) = \phi_{\text{CO}_2}^{\text{Feed}} - \phi_{\text{CO}_2}^{\text{Retentate}}(\zeta)$$

$$\phi_{\text{N}_2}^{\text{Permeate}}(\zeta) = \phi_{\text{N}_2}^{\text{Feed}} - \phi_{\text{N}_2}^{\text{Retentate}}(\zeta)$$

- 1-D model
 - steady-state permeation
 - no sweep mode
 - co-current configuration
 - Flue gas stream containing **13% of CO₂**

Parameters used in simulation tests	
Flue gas composition	13% CO ₂ ; 87% N ₂
Flue gas feed pressure	1 bar
Membrane Selectivity	30-300
Pressures ratio	5-50
Number of stages	1



dimensionless molar flow rate
(i.e. for CO₂ and N₂)

$$\varphi_i = \frac{Q_i}{Q_i^{Feed}}$$

dimensionless module length

$$\zeta = \frac{z}{L}$$

Pressures Ratio

$$\Phi = \frac{P^{Feed}}{P^{Permeate}}$$

Permeation number

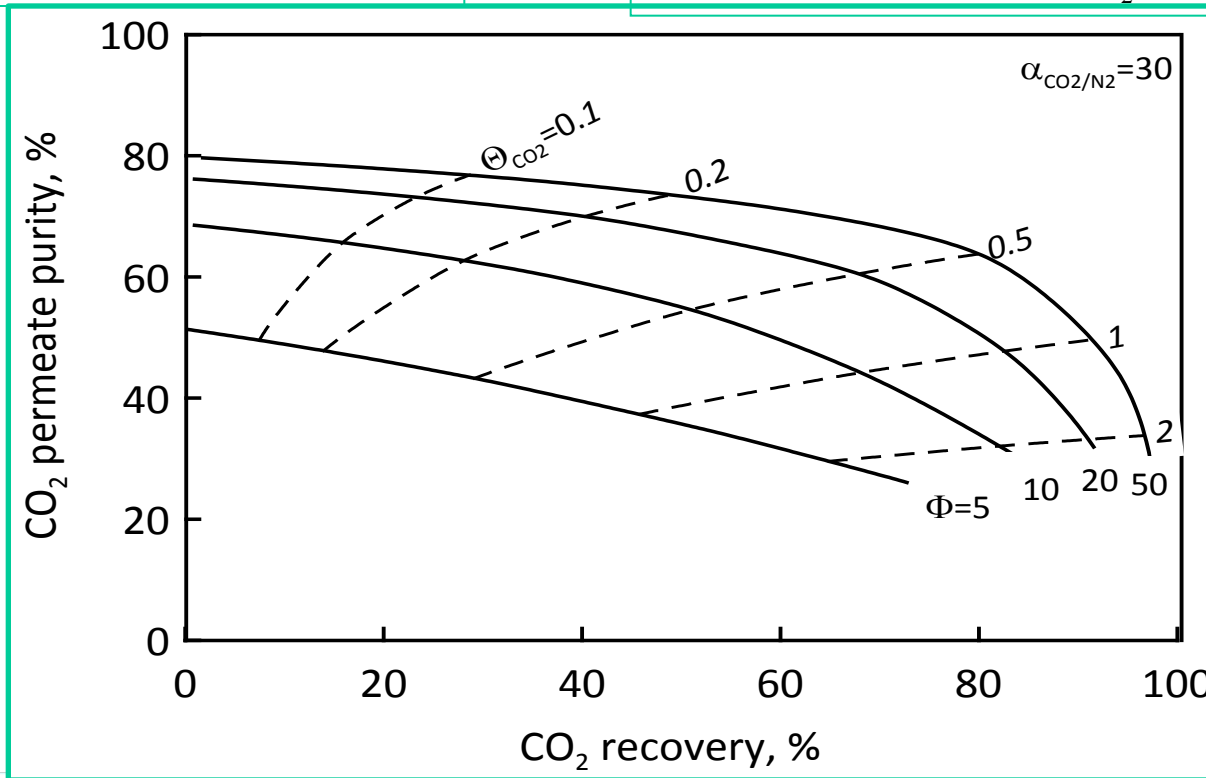
$$\Theta_{CO_2} = \frac{Permeance_{CO_2} A^{Membrane} P^{Feed}}{x_{CO_2}^{Feed} Q^{Feed} \Phi}$$

Θ_i compares two main mass transport mechanisms involved. It affects the performance of a one-stage membrane system as well as ϕ_i . A high Θ_i corresponds to a high residence time for the stream and, then, to a high permeation rate through the membrane with the respect to the convective flux along the module.

Global Maps: Modelling Results

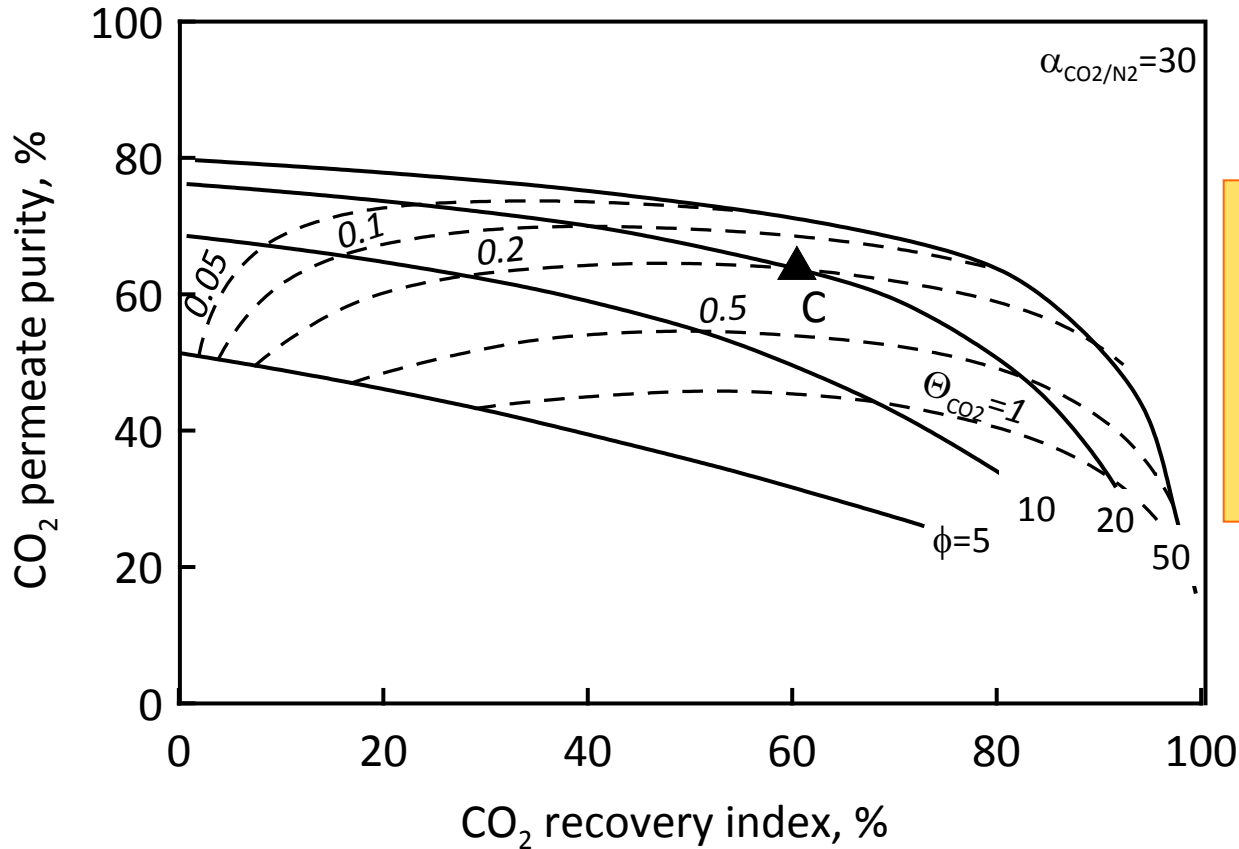
$$\text{Stage Cut} = \frac{\text{Permeate flow rate}}{\text{Feed flow rate}}$$

$$\text{CO}_2 \text{ recovery index} = \frac{\text{CO}_2 \text{ Permeate flow rate}}{\text{CO}_2 \text{ Feed flow rate}}$$



At a given permeation number (dashed lines), CO₂ purity increases with the recovery. A high permeation number leads to a higher recovery but lower purity: the main part of the feed flow rate permeates, preferentially in the first part of the module, through the membrane and N₂ dilutes the CO₂ permeated.

Use of Global Maps



Global maps could be considered a starting point in the Carbon Capture and storage process design

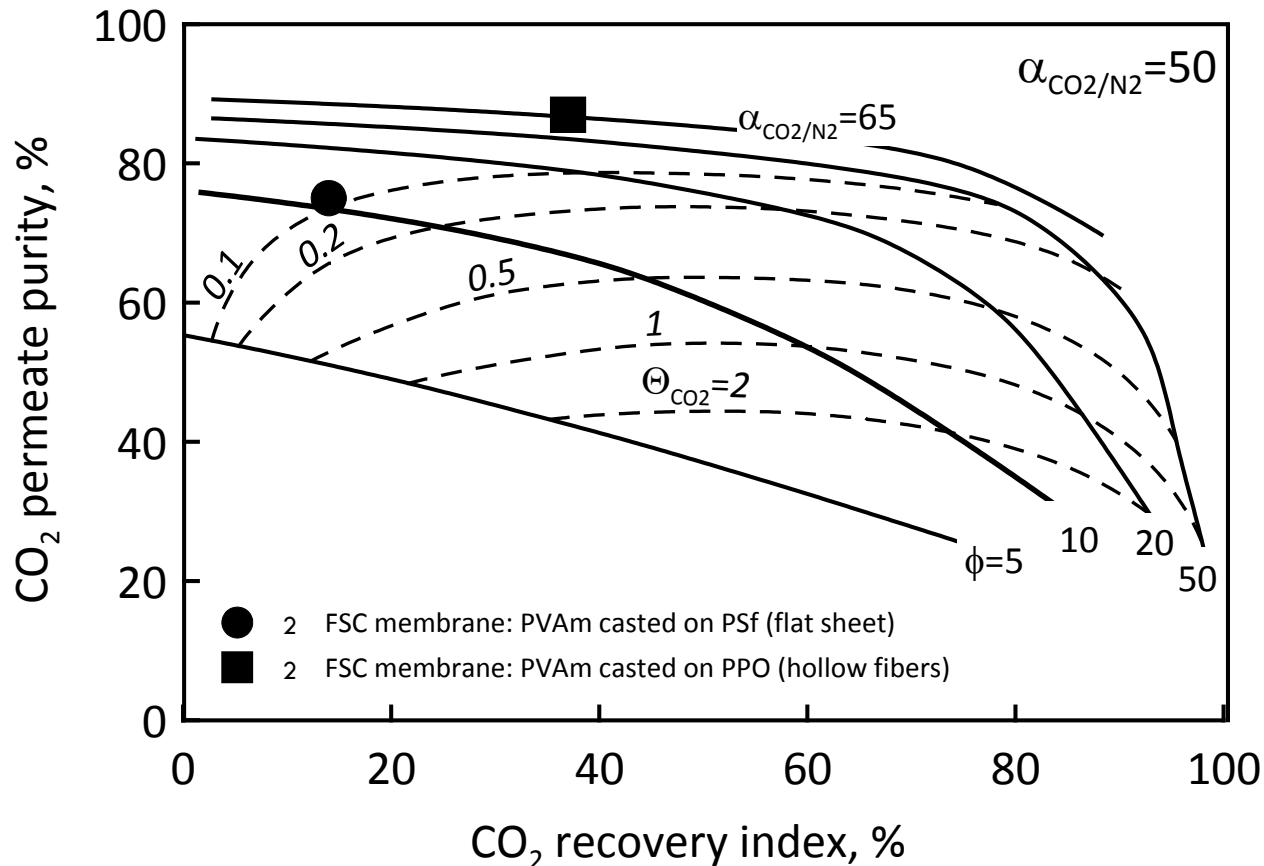
For a given membrane geometry and properties Θ_{CO_2} and Φ are obtained by infinite couples of operating conditions
For instance, 64% CO₂ purity and 61% recovery corresponds to a system having a Φ of 20 and a Θ_{CO_2} of 0.2.



Use of Global Maps

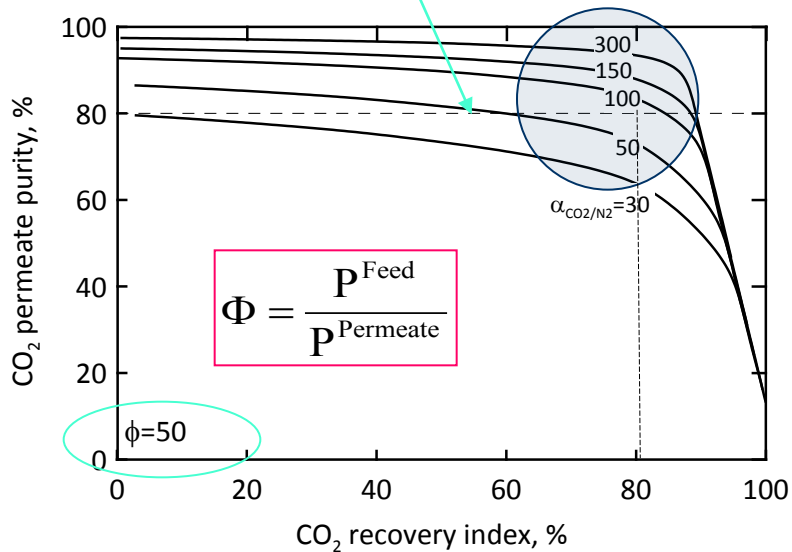
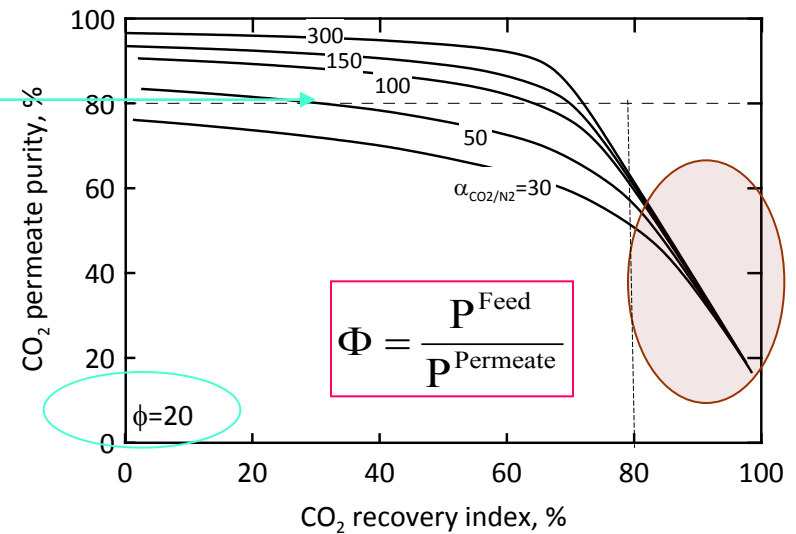
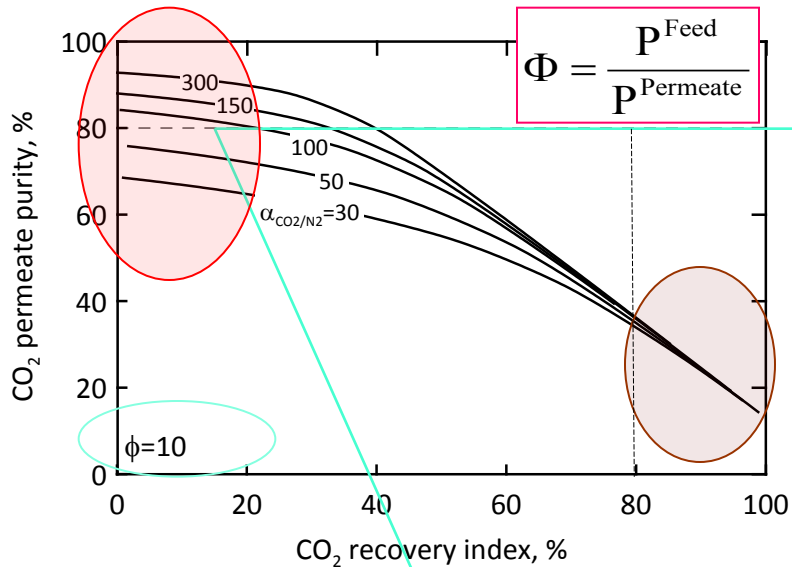
¹ Brunetti A., Scura F., Barbieri G., Drioli E., *Journal of Membrane Science*, 359 (2010) 115

² M.Sandru, *PhD Thesis*, Dep. of Chem. Eng. Faculty of Natural Sci. and Tech., Norwegian University of Science and Technology



For a pressure ratio of 10, the simulation provides a maximum achievable purity of CO₂ in permeate stream of around 76% at low recovery (i.e. close to zero). The purity decreases monotonically down to 39% when recovery is, instead, 76%.

Effect of ideal selectivity and pressure ratio on the membrane module performance



A value of **80%** is the **minimum purity** (corresponding to a recovery of 80%) **admitted for the storage** by the International Energy Agency¹ (i.e. dashed line in figures)

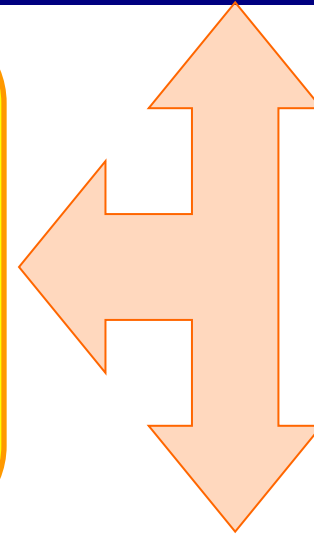
¹Bounaceur R., Lape D., Roizard D., Vallieres C., Favre E., *Energy*, 31 (2006) 2556

²Brunetti A., Scura F., Barbieri G., Drioli E., *Journal of Membrane Science*, 359 (2010) 115

CONCLUSIONS

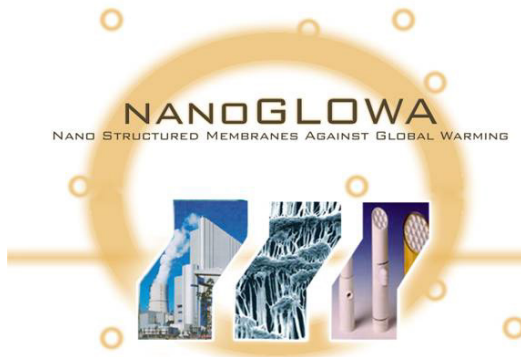
Some general guidelines to drive the application of Membrane Gas Separation Technology in an one-stage has been given for CO₂ – Post Combustion Capture.

For currently available membranes ($\alpha_{\text{CO}_2/\text{N}_2}=50$) it is not possible to get, simultaneously, an interesting CO₂ recovery and purity (i.e. 80% CO₂ in permeate stream). **Two membrane stages will give the required separation but higher costs will be obtained for compression intermediate stages**.



When high recoveries have to be approached pressure ratio (Φ) has a role much more determining than selectivity. In fact, for a selectivity of 100, **an increase of the pressure ratio from 10 to 50 shifts CO₂ recovery from 22% to 80%.**





Thank you for your attention

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