

Technological Options of Carbon Capture

István Lakatos

Research Institute of Applied Earth Sciences
University of Miskolc, Hungary



General overview

The burning of fossil fuels, including coal, oil and gas (plus biofuels and waste materials) meets more than 85% of the world energy needs today. The associated CO₂ emission of power plants and transportation (~30 Gt/y) cause detrimental changes to the earth climate. The scientific community agrees that the solution for mitigating the CO₂ emission lies in a portfolio of strategies including the following two areas:

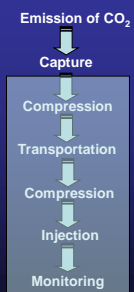
- Carbon capture and storage (CCS) and
- Carbon capture and utilization (CCU)

Mitigation of CO₂ through separation of gas mixture, mainly from power plant emission, will be a critical step toward stabilization of global warming. Therefore, the society of engineers, chemists, physicists, earth scientists, mathematicians, social representatives should advance to develop efficient separation technologies in the coming decades. The professionals also have a mission and vision that one day the advances CCS can take place in a single process, rather than the current three-step sequence of capture, compression, and storage.



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Sequence of carbon sequestration



Objectives of the presentation

Not discussed topics:

- Thermodynamics of CO₂
- Selection of geological formation
- Multiphase equilibrium in formation
- Gas tightness of formation
- In-situ barrier formation (leak-off)
- Social aspects of CCS
- OPEX and CAPEX



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CO₂ exhaust of different industry

- Power plants:
 - Coal : 12-15%
 - Oil : 3-8%
 - Gas : 3-5%
 - Waste : ≈20%
- Cement : 14-33%
- Refineries : 3-13%
- Iron and steel : ≈5%
- Chemical : 12-100%

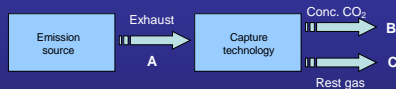
Storage of CO₂ needs substantial concentration, preferably up to >80%. Capture (CC), however, decreases plant efficiency:

	Without CC	With CC
■ Coal (subcritical)	33-39%	23-25%
■ Coal (supercritical)	38-44%	29-31%
■ Coal (ultrasupercritical)	43-47%	34-37%
■ Gas (combined cycle)	45-51%	38-43%
■ Gas (gasification comb.)	37-44%	32-39%



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Minimum thermodynamic work of CC



The minimum work required to separate CO₂ from gas mixture can be calculated by the combined first and second law of thermodynamics. The minimum work for isothermal and isobar processes is equal to the negative difference in Gibbs free energy of the separated final states (B+C) from the mixed initial state (A).

$$W_{\min} = \Delta G_{\text{sep}} = \Delta G_B + \Delta G_C - \Delta G_A$$

$$\frac{\partial G}{\partial n_i} = G_i + RT \ln \left(\frac{p_i}{p} \right)$$

$$G_{\text{total}} = \sum_i n_i \frac{\partial G}{\partial n_i}$$



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Types of carbon capture

As an emerging field, the carbon capture ranges many disciplines. Actually, no single source exists that explains the fundamentals of gas separation and enrichment process. The most frequented types of carbon captures are the following:

- Absorption (liquid/gas interaction)
- Adsorption (gas/solid interaction)
- Membrane (gas phase)
- Mineral carbonation (chemical process)
- Cryogenic (distillation)
- Algae transformation (photosynthesis)
- Catalytic reduction (chemical process)

Technologies usually consist of the two main elements:

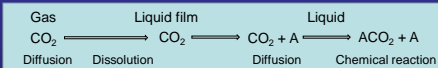
- Capture
- Stripping (regeneration)



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Thermodynamic aspects of CO₂ absorption

Solubility of CO₂ in different solvents is the major factor determining the equilibrium, mass transfer and kinetics of absorption/desorption:



Equilibrium conditions:

Roult law Ideal system: $\frac{y_{\text{CO}_2} \cdot p_{\text{a}}}{x_{\text{CO}_2} \cdot p}$ non-Ideal system: $\frac{y_{\text{CO}_2} \cdot f_{\text{a}}}{x_{\text{CO}_2} \cdot f}$

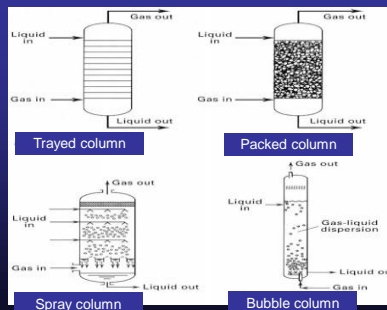
Henry's law Ideal system: $p_{\text{CO}_2} = H \cdot x_{\text{CO}_2}$ non-Ideal system: $f_{\text{CO}_2} = H \cdot x_{\text{CO}_2}$

Dirk W. van Krevelen $\log\left(\frac{H}{H_0}\right) = hI = \frac{1}{2} \sum_i \Delta_i c_i^2 \quad h = h_a + h_b + h_g$



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Types of standard absorption columns



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Solvent selection in absorption technology

- Desired properties of solvents:
- High CO₂ capacity
 - Fast kinetics with CO₂
 - Low volatility
 - Low viscosity
 - Nontoxic, inflammable, noncorrosive
 - High thermal stability resistance to oxidation

Amine-based solvents:

- Primary amines (MEA)
- Secondary amines (DEA)
- Tertiary amines (MDEA)
- t-Butanolamines (AMP)

Electrolyte solvents (0.1-1.4 mol/l):

- NaCl
- NaNO₃
- Na₂SO₄
- MgCl₂
- MgSO₄
- Mg(NO₃)₂

Pure organic solvents:

- Amyl alcohol
- t-Butanol
- Ethanol

Ionic liquid – melts of salts

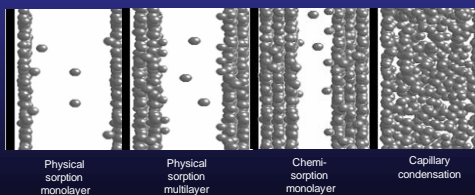


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Fundamentals of adsorption

In adsorption the gas mixture contacts with surface of solid phase, which selectively adsorb or complex with CO₂, removing thus it from the gas phase. The molecules in the fluid phase prior to adsorption is referred as **adsorptive**, once on the surface is defined as **adsorbate**, and the solid phase is called as **sorbent**.

Types of sorption processes:



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Features of different sorption processes

- Physical sorption: highly reversible, weak bonding forces (10-15 kcal/mol)
- Chemisorption : highly irreversible, covalent bonding (15-100 kcal/mol)
- Capillary condensation : reversible, adhesion forces between molecules

Thermodynamics of adsorption (isotherms):

Physical sorption: Freundlich equation (diluted system, monolayer)
Langmuir equation (concentrated systems, monolayer)
BET equation (concentrated system, multilayer)
Lennard-Jones equation (competitive adsorption)

Chemical sorption: Thiele and Jütner moduli

Physical/chemical sorption: Tóth's consistent equation (mono- and multilayer)
Capillary condensation: Thomson equation

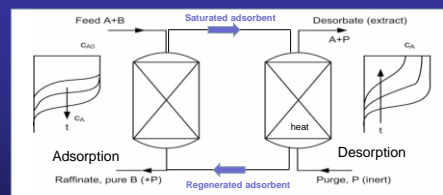
Basic Structure of sorbents (IUPAC classification):

- Micropores : < 20 Å (high hysteresis)
- Mesopores : 20-500 Å (slight hysteresis)
- Macropores : >500 Å (no hysteresis)

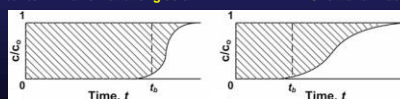


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Schematic of sorption technology



Breakthrough curves in **Narrow and long column** **Short and wide**



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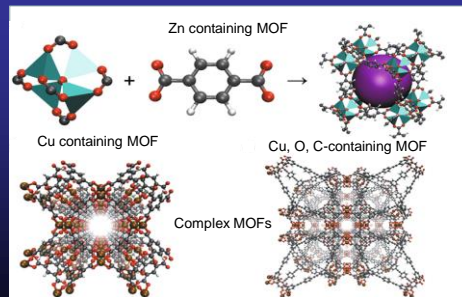
Frequently used sorbents

Sorbent	Pore diameter, nm	Density, kg/m ³	BET surface, m ² /g
Activated carbon:			
Small-pore	1-2.5	500-900	400-1200
Large-pore	>3	600-800	200-600
Zeolite			
Small-pore	0.3	670-740	700
Medium-pore	0.5	670-720	650
Large-pore	0.8	610-710	600
Silica gel			
Small-pore	2.2-2.6	1000	800
Large-pore	10-15	620	320
Activated alumina	1-7.5	800	320
MOFs	0.4-2.4	200-1000	150-6200
Hollow fibers	2.5-11	1250	450-1100
Hydrotalcite	2-20	150-550	5-500
Chemisorbents	0.2-20	2000	250-1250



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Structure of MOFs (metal-organic-frameworks)



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General feature of membrane separation

A semipermeable membrane allows for selective transport and subsequent of one or more components of a gas mixture. In terms of carbon capture, the membrane should be selective to CO₂ from other components (CH₄, O₂, N₂, H₂, etc.). The membrane technology requires durable, high mass-transfer flux, defect-free membrane fabrication into compact cost effective modules with high surface area per volume. In general, sharp separation are not achievable using semipermeable membranes.

Membrane separation has many advantages over absorption and adsorption:

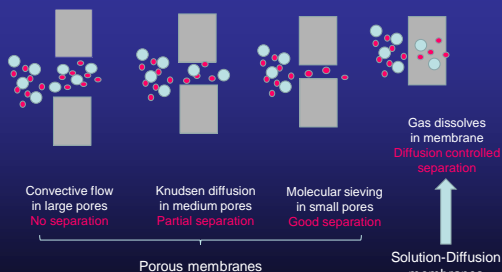
- No regeneration
- Ease of integration into power plants
- Process continuity
- Space efficiency
- Absence of phase changes

Disadvantages: sufficient driving force is required, e.g. diluted systems need pre-concentration, or CO₂ has to be the dominant species in gas mixtures



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Mechanism of membrane separation



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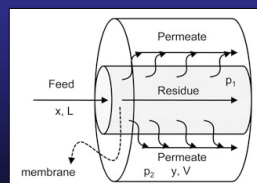
Membrane materials and constructions

CO₂-selective membranes can be synthesized from natural and synthetic polymers, like wool, rubber, cellulose, polyimide, polysulfone, etc. The membranes can be glassy, or rubbery fabricated as

- Asymmetric sheets
- Thin-composite sheets
- Tubules
- Hollow fibers

Membrane modules might be:

- Plane-and-frame
- Spiral-wound
- Hollow fiber
- Tubular
- Monolith



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Selectivity of gas mixtures in membranes

Membrane	Mixtures	Selectivity
Silicon rubber	CO ₂ /H ₂	4.9
	CO ₂ /O ₂	5.0
	CO ₂ /CH ₄	3.4
Polyether diimide (Kapton)	CO ₂ /H ₂	0.2
	CO ₂ /O ₂	3.1
Ethyl cellulose	CO ₂ /O ₂	6.1
	CO ₂ /CH ₄	11.0
Poly-methyl methacrylate	CO ₂ /O ₂	4.4
	CO ₂ /CH ₄	46.0
Polyimide (PMDA-4,4-ODA)	CO ₂ /O ₂	4.4
	CO ₂ /CH ₄	46.0
Polysulfone	CO ₂ /O ₂	4.1
	CO ₂ /CH ₄	23.3
Polydimethylsiloxane	CO ₂ /O ₂	5.8
	CO ₂ /CH ₄	3.2
Cellulose acetate	CO ₂ /O ₂	5.8
	CO ₂ /CH ₄	32.0

Permeability of gases in membranes

Membrane	H ₂	He	CH ₄	N ₂	O ₂	CO ₂
Silicone	940	560	1370	440	930	4600
Rubber	49	30	29	8.7	24	434
Polysulfone	14	13	0.27	0.25	1.5	6.5
Polycarbonate	-	14	0.28	0.26	1.5	6.5
Polyimide	2.3	-	0.007	0.018	0.13	0.41

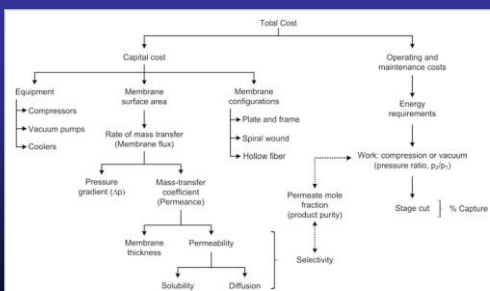
Gas permeability is expressed in Barrer at 25-30 °C

Separation factor:

$$\alpha = \left(\frac{D_A}{D_B} \right) \left(\frac{S_A}{S_B} \right)$$

here D_A/D_B mobility selectivity
S_A/S_B solubility selectivity

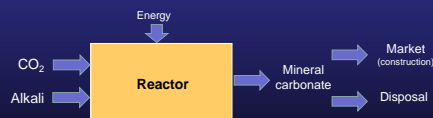
Cost assessment of membrane technology



Fundamentals of mineral carbonation

Mineral carbonation takes place through the reaction of CO₂ with an alkaline source that contains di- or multivalent cations like calcium, magnesium, iron, etc., as well as hydroxyl anions to form stable carbonate or hydro-carbonate minerals. The method has a practical potential to capture and long-term storage of CO₂.

Schematic of CO₂ capture and storage by carbonation:



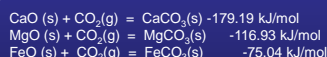
The process can take both as a single or a multiphase reaction. The alkaline material may be obtained from natural minerals and industrial byproducts

Thermodynamics of mineral carbonation

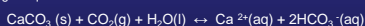
Two-phase reactions:



Basic gas-solid reactions at 298 K and 1 bar:



Natural gas-liquid/solid reactions at ambient condition:



Types of carbonation:

- Direct carbonation using natural minerals or industrial by-products
- Indirect carbonation using transformed (enriched) minerals or industrial byproducts
- Ultramafic carbonation using in-situ Ca-, Fe-, Mg-containing silicates
- Brine carbonation using high inorganic salt content

Carbonation with minerals and byproducts

Carbonation with minerals:

Mineral	T, °C	p _{CO2} , bar	Carrier phase
Olivine	185	150	0.6 M NaHCO ₃ , 1 M NaCl
Wollastine	100	40	Distilled water
Serpentine	155	115	0.6 M NaHCO ₃ , 1 M NaCl

Carbonation with industrial byproducts:

- Coal combustion: Fly ash
- Iron/steel making: Steel, blast slag, electric furnace slag
- Cement industry: Kiln dust, waste cement
- Asbestos mining: Mine tailings
- Aluminum industry: Bauxite residue
- Waste incineration: Incinerator ash

Reaction condition of carbonation with industrial byproducts:

Waste product	Size, μm	T, °C	p _{CO2} , bar	Conversion, %
Cement kiln dust	~3	25	0.8	77
Fly ash	~40	30	10-39	82
Steel slag	~38	100	19	74

Challenges of Mineral Carbonation with CCS

The upper limit of mitigation potential of mineral carbonation for CCS is dictated by the availability of alkaline materials. The availability is limited due to the energy intensity of mineral recovery and slow kinetics of dissolution in silicate-based technology. Source of industrial byproducts are also limited. The carbonation potential is on order of 10Mt/y CO₂. Thus, the carbonation potential in CCS may not serve to mitigate large volume of CO₂, it may be one aspect comprising the portfolio of strategies and has additional benefits of simultaneous sequestration of other hazardous materials (e.g. heavy metal compounds)



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Conclusions

- The carbon capture (CC) is inseparable, fundamental element of carbon sequestration (CCS) and carbon utilization (CCU) projects.
- Numerous CC technology have been developed on the past decades, but none of all can be applied for enrichment of CO₂ prior to storage.
- Absorption, adsorption and membrane technology is recommended for separation and concentration of CO₂ in gas to be injected into the geological formation.
- All capture technology is based on chemical engineering fundamentals and sophisticated design is needed to construct complete facilities.
- The cost of capture, whatever is the technology, is significant. That is one of the reasons why the CCS and CCU projects, even in case of pilot tests, should be supported.



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Thank you for your attention
and patience



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