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Carbon dioxide capture and storage to mitigate climate change

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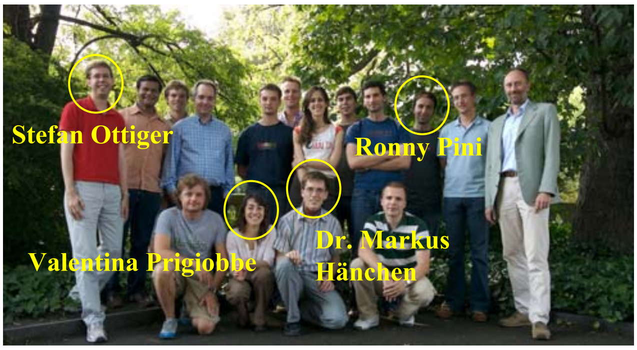
Acknowledgements

- Prof. Giuseppe Storti, Politecnico di Milano
- Prof. Renato Baciocchi, Università di Roma „Tor Vergata“



- Fondation Claude et Giuliana
- Swiss National Science Foundation

Outline

1. Separation technology for zero emission power plants
2. Carbon dioxide storage by mineral carbonation
3. Concluding remarks

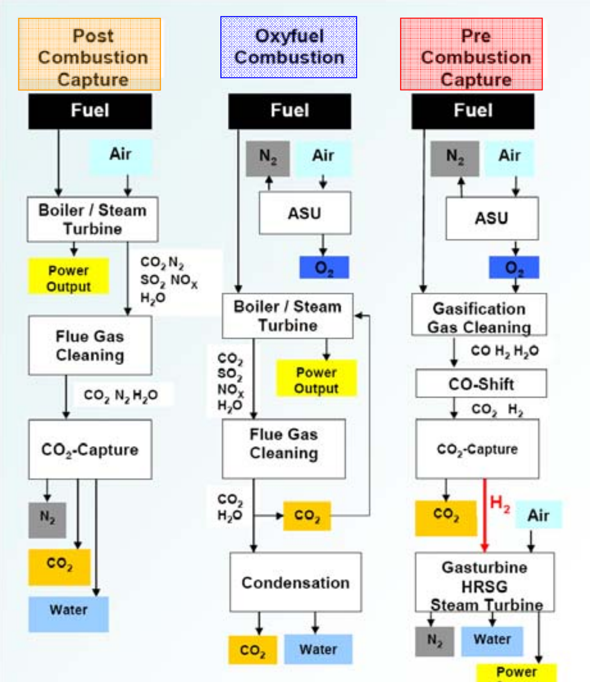
Overview of CO_2 capture systems

CO_2 (3-15%) / N_2

O_2 (21%) / N_2 (78%)

CO_2/H_2
O_2/N_2

CO_2 (5-50%) / CH_4



Source: Dr. Peter Radgen, Fraunhofer ISI (2006)

Unit operations for CO_2 capture

Distillation

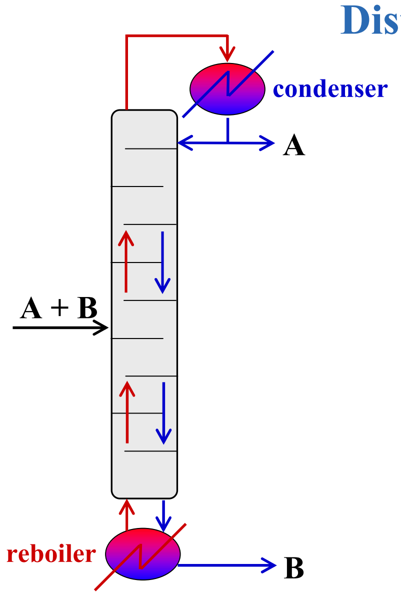
Absorption

Adsorption

Membrane

CO_2/N_2 **O_2/N_2** **CO_2/H_2** **CO_2/CH_4**

Distillation

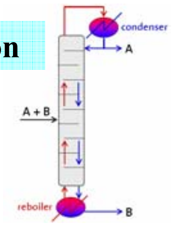


- Multi-stage countercurrent
- No additional phase/agent
- Energy intensive (cryogenic)
- Good for bulk separations

Gas	T_b (°C@1 bar)	T_{triple} (°C, bar)
CO_2	sublimation	-57, 5.18
CH_4	-162	-183, 0.12
O_2	-183	-219, 0.0015
N_2	-196	-210, 0.125

Unit operations for CO_2 capture

Distillation



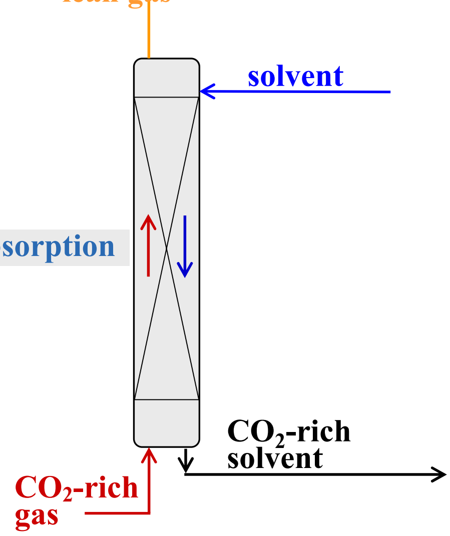
Absorption

Adsorption

Membrane

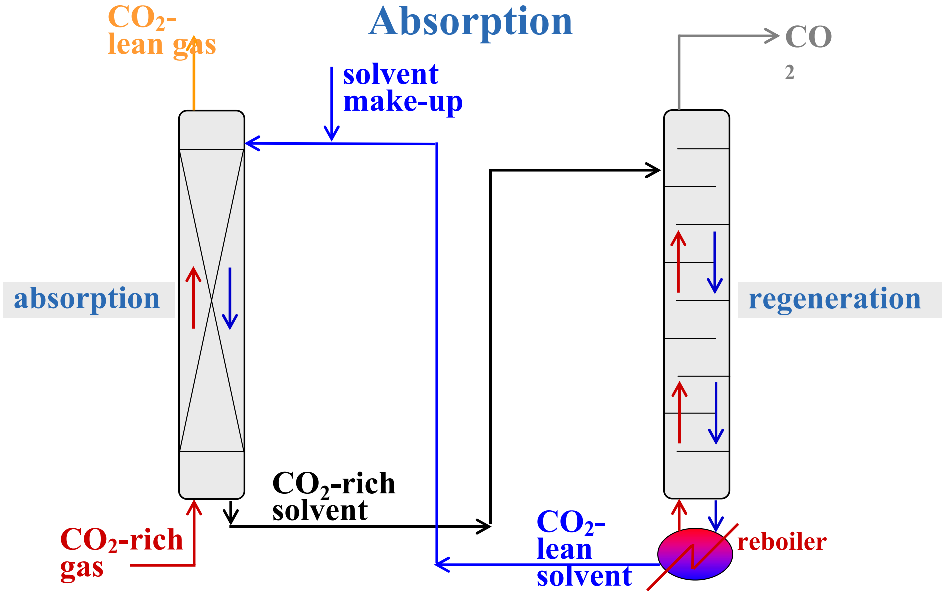
CO_2/N_2 **O_2/N_2** **CO_2/H_2** **CO_2/CH_4**

Absorption



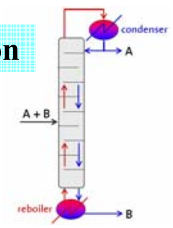
- Multi-stage countercurrent
- Chemical/physical solvents
  - Amines for CO_2 (chemical)
  - Selexol® (physical)
- Issues
  - Solvent losses/degradation
  - Need for trade-off between selectivity and energy cost of solvent regeneration

Absorption

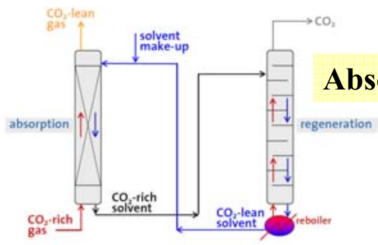


Unit operations for CO_2 capture

Distillation



Absorption



Adsorption

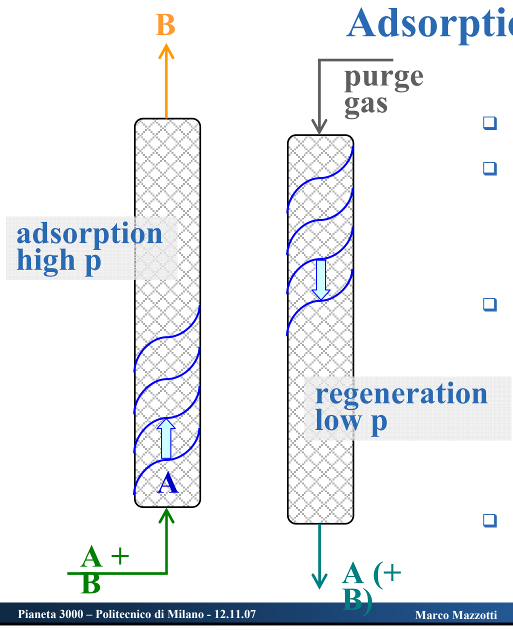
Membrane

CO_2/N_2	O_2/N_2	CO_2/H_2	CO_2/CH_4

Adsorption

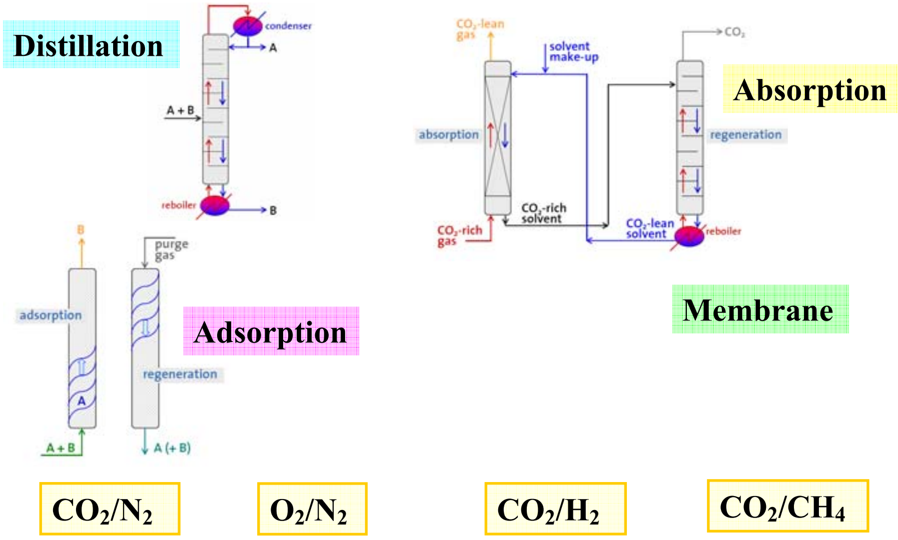
- Chemical/physical sorbents
  - Zeolites for pure O_2 (physical)
  - AC, zeolites or CaO for CO_2
- Multi-stage fixed-bed
- Issues
  - Cycled operation: high p for adsorption; low p for regeneration (trade-off)
  - High purity+recovery not easy

Adsorption



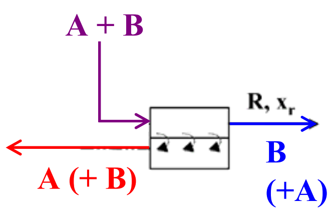
- Multi-stage fixed-bed
- Chemical/physical sorbents
  - Zeolites for pure O_2 (physical)
  - AC, zeolites or CaO for CO_2
- Issues
  - Cycled operation: high p for adsorption; low p for regeneration
  - High purity+recovery not easy
- Pressure Swing Adsorption (PSA)

Unit operations for CO_2 capture

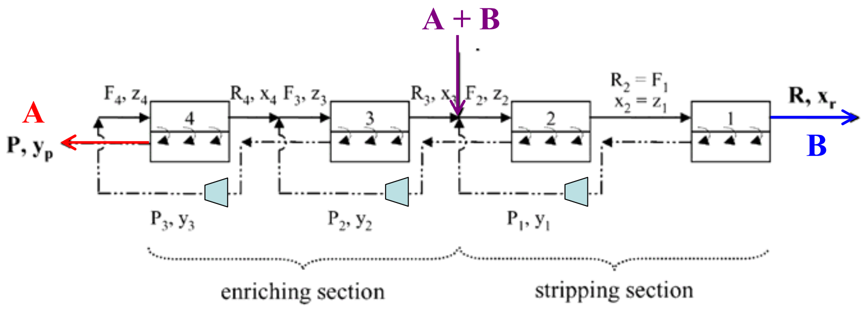


Membrane

- Single-stage
- Polymeric membranes (low T), ceramic membranes (high T)
- Trade-off between selectivity and permeability
- Need for multi-stage with recompression for high purity and recovery
- Energy intensive

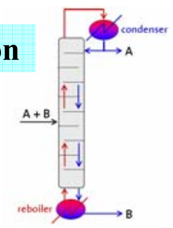


Membrane

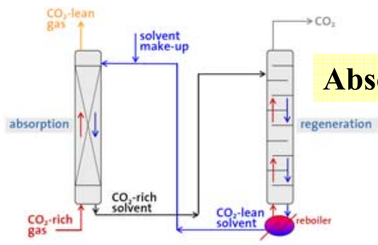


Unit operations for CO_2 capture

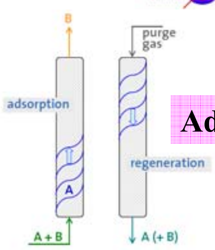
Distillation



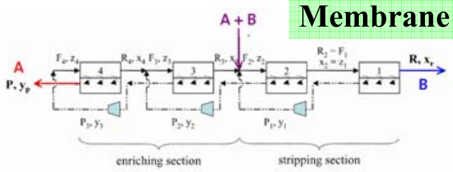
Absorption



Adsorption



Membrane



CO_2/N_2 O_2/N_2 CO_2/H_2 CO_2/CH_4

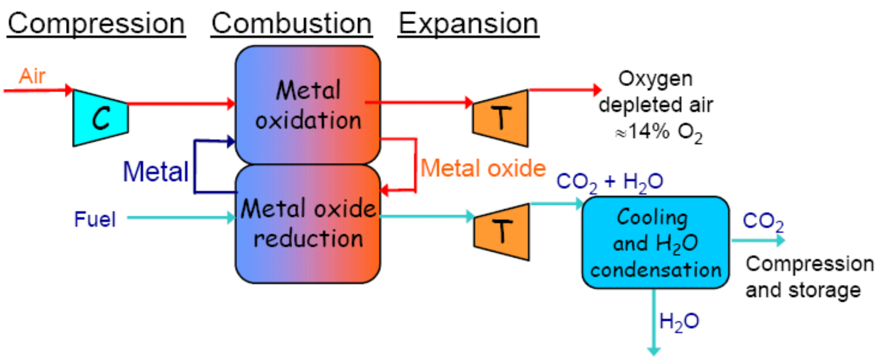
Unit operations for CO_2 capture

CO_2/N_2	O_2/N_2	CO_2/H_2	CO_2/CH_4
Absorption (chemical)	Distillation (cryogenic, large scale)	Absorption (chemical / physical)	Absorption (chemical / physical)
	Adsorption (PSA, small scale)		

Research

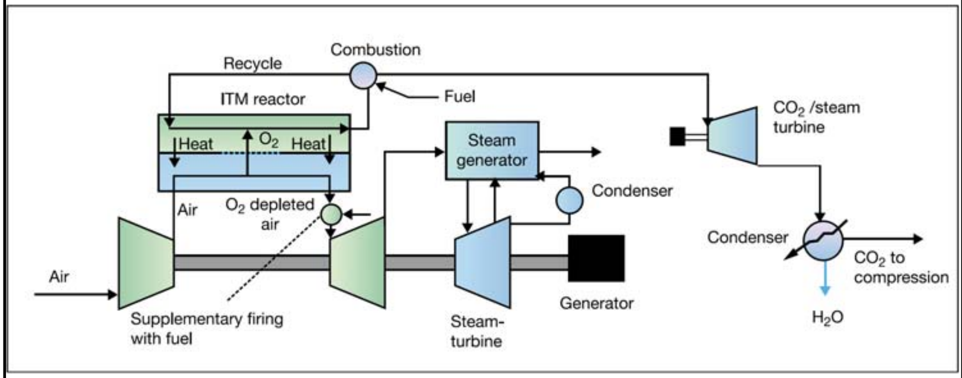
- Improved solvents
- New materials for membranes and adsorbents
- Improved process design
- Hybrid systems
- New advanced concepts

Chemical looping combustion



Source: IPCC Special Report on Carbon Dioxide Capture and Storage (2005)

Advanced zero emission power plant (AZEP)



Source: IPCC Special Report on Carbon Dioxide Capture and Storage (2005)

Outline

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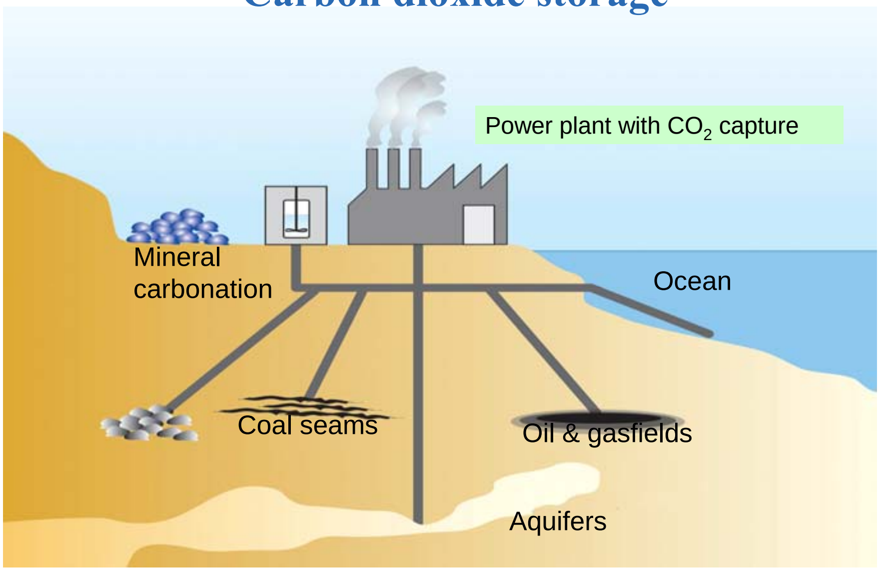
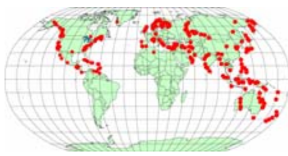
Carbon dioxide storage



Mineral carbonation

$C + O_2 \leftrightarrow CO_2$ + 394 kJ/mol CO_2

$MO + CO_2 \leftrightarrow MCO_3$ + 60 ÷ 90 kJ/mol CO_2



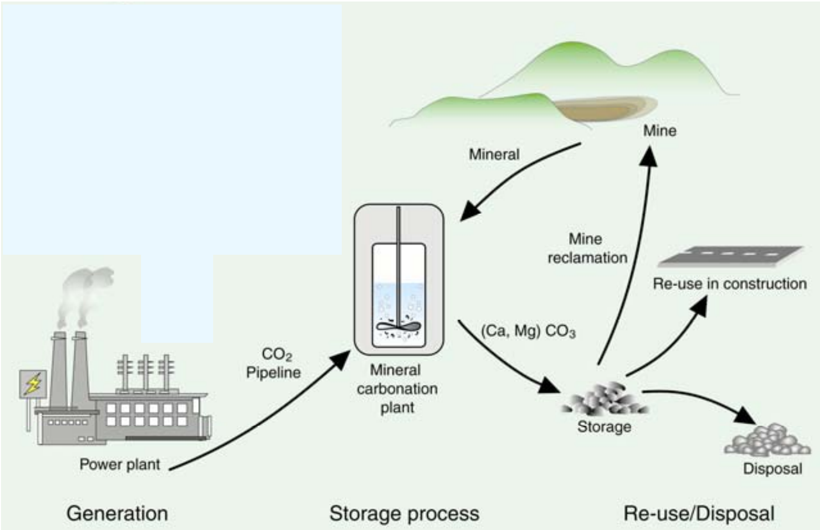
Total silicate deposits can fix CO_2 produced by all fossil fuel resources

<u>*Olivine*</u>
$Mg_2SiO_4 + 2CO_2 \leftrightarrow 2MgCO_3 + SiO_2$ + 89 kJ/mol CO_2

<u>*Serpentine*</u>
$Mg_3Si_2O_5(OH)_4 + 3CO_2 \leftrightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$ + 64 kJ/mol CO_2

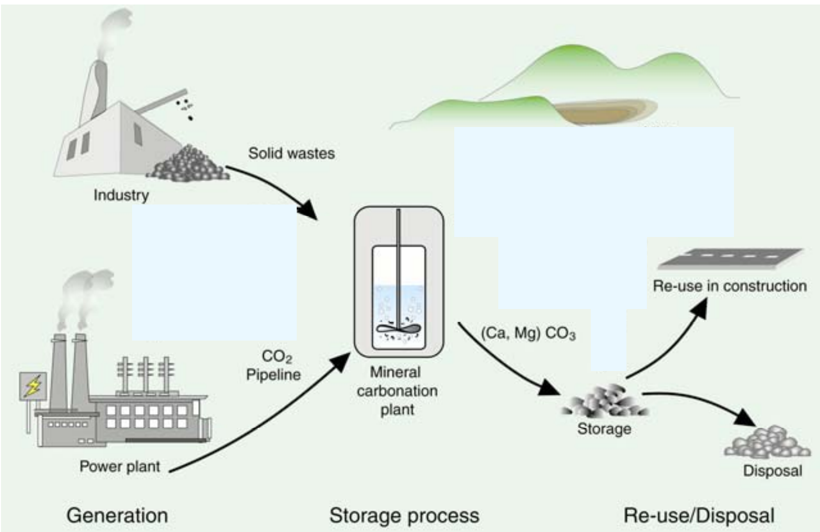
<u>*Wollastonite*</u>
$CaSiO_3 + CO_2 \leftrightarrow CaCO_3 + SiO_2$ + 90 kJ/mol CO_2

Mineral carbonation of natural silicates



Source: IPCC Special Report on Carbon Dioxide Capture and Storage (2005)

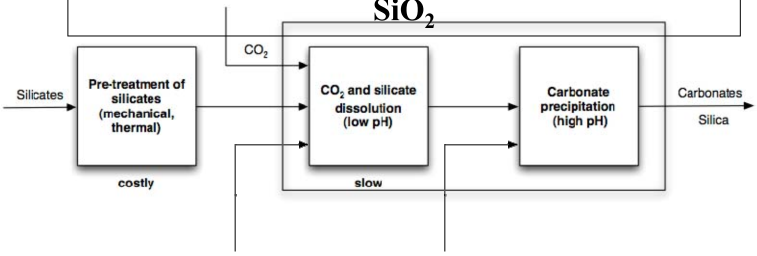
Mineral carbonation of industrial residues



Source: IPCC Special Report on Carbon Dioxide Capture and Storage (2005)

Mineral carbonation - the aqueous process

Olivine: $Mg_2SiO_4 + 2\ CO_2 \leftrightarrow 2\ MgCO_3 + SiO_2$



Accelerating dissolution:
- Strong acids
- Weak acids/ligands
- High surface area

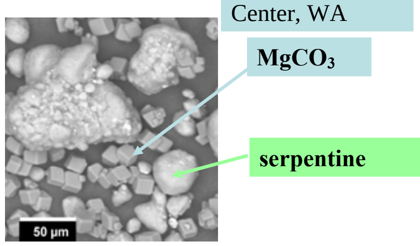
Accelerating precipitation:
- High pH
- High CO_2 pressure
- Seeding?

Operating conditions

Feasibility study

Albany Research Center, WA

- **Aqueous process, batch**
- **Parallel dissolution/ precipitation**
- **Particle size: 37 micron**
- **Solid concentration: 30 wt.%**
- **Residence time: 1h**



Mineral	Carbonation conditions		
	T, °C	P_{CO2}, atm	Carrier solution
Olivine	185	150	0.64 M $NaHCO_3$, 1 M NaCl
Wollastonite	100	40	Distilled water
HT serpentine	155	115	0.64 M $NaHCO_3$, 1 M NaCl

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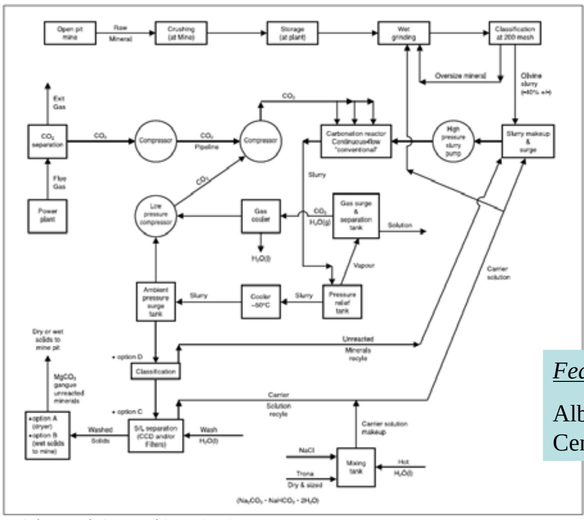
Aqueous mineral carbonation of olivine



Feasibility study

Albany Research Center, WA

Source: IPCC Special Report on Carbon Dioxide Capture and Storage (2005)

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Assessment and costs

Feasibility study

Albany Research Center, WA

Best option: Olivine

- **Cost: \$ 50 - 100 / t CO_2 stored**
- **30 - 50% additional energy requirements**
- **Scale: 1.6 - 3.7 t mineral / t CO_2 stored (similar scale as corresponding coal mining)**

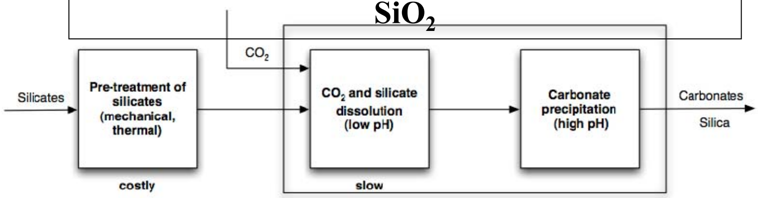
For comparison:

- **Capture & transport: \$ 15 ÷ \$ 80 / t net CO_2 captured**
- **Geological storage: \$ 0.5 ÷ \$ 8 / t CO_2 stored**

We are seeking a 2-fold to 5-fold improvement!

Mineral carbonation - the aqueous process

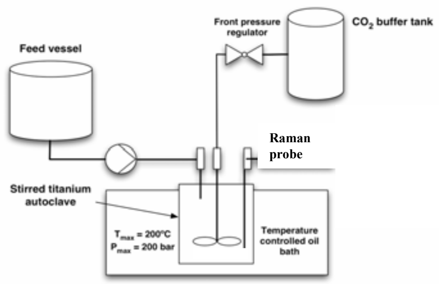
Olivine: $Mg_2SiO_4 + 2\ CO_2 \leftrightarrow 2\ MgCO_3 + SiO_2$



Experimental set-up

Low pressure and temperature reactor

High pressure and temperature reactor



$$MgCl_2(aq) + Na_2CO_3(aq) \rightarrow MgCO_3\downarrow + 2NaCl(aq)$$

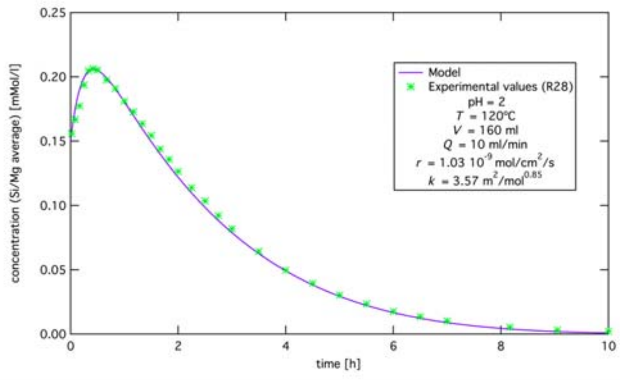
<u>Procedure</u>:

- Heating up of $Na_2CO_3 + H_2O$
- pressurization with CO_2
- dosage of $MgCl_2$

<u>Measurements</u>:

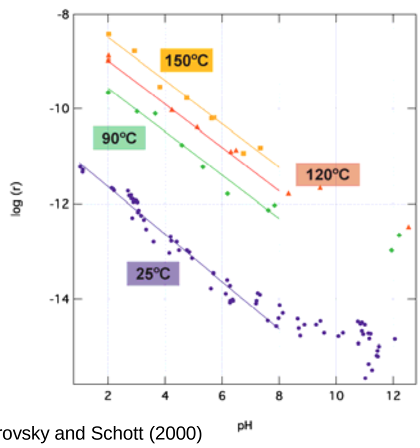
- On-line: Raman
- Off-line: SEM and XRD

Olivine dissolution (low pH, fast)



- **Population balance equation**: $$\frac{\partial f}{\partial t} - D\frac{\partial f}{\partial L} = 0$$

Olivine dissolution rate vs. pH and T



$\log(r) = $ -n pH $- E_A/(RT) + C$

T = 150°C: $\log(r) = -0.46$ pH $- 7.58$

T = 120°C: $\log(r) = -0.46$ pH $- 8.07$

T = 90°C: $\log(r) = -0.46$ pH $- 8.66$

T = 25°C:* $\log(r) = -0.50$ pH $- 10.64$

r = [mol/cm²/s]

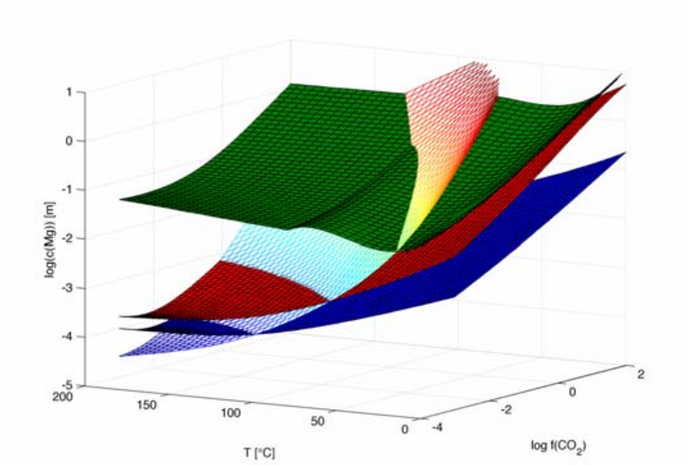
Activation energy:

E_A = 52.9 kJ/mol

* Pokrovsky and Schott (2000)

Hänchen et al., Geochim. Cosmochim. Acta 70 (2006) 4403-4416

Solubility of Mg-carbonates vs. T and P(CO_2)



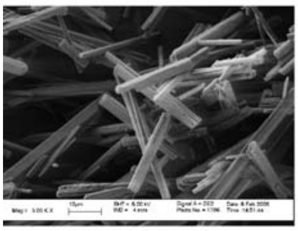
Nesquehonite
$MgCO_3{\bullet}3H_2O$

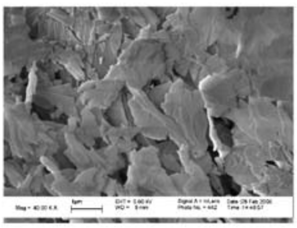
Hydromagnesite
$(MgCO_3)_4Mg(OH)_2$
$\bullet 4H_2O$

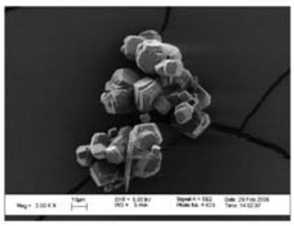
Magnesite: $MgCO_3$

Brucite: $Mg(OH)_2$

Formation of Mg-carbonates







Nesquehonite
$MgCO_3{\bullet}3H_2O$
T=25ºC, P_{CO2} = 1 bar

Hydromagnesite
$(MgCO_3)_4Mg(OH)_2 \bullet 4H_2O$
T=120ºC, P_{CO2} = 3 bar
t_{exp} < 4 h

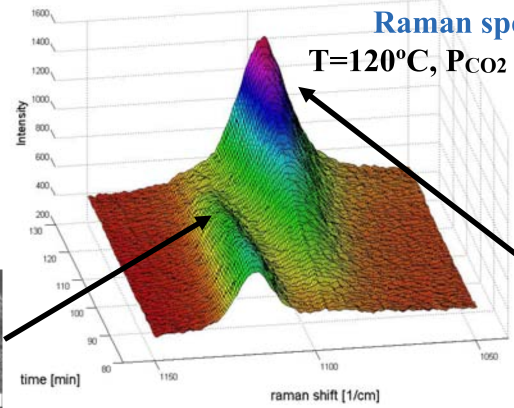
Magnesite
$MgCO_3$
T=120ºC, P_{CO2} = 3 bar
t_{exp} > 12 h

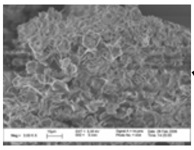
Hänchen et al., Chem. Eng. Sci. (2007) in press

Precipitation: high T, high P_{CO2}

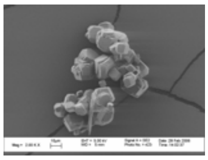
Time-resolved Raman spectra

T=120°C, P_{CO2} = 100 bar





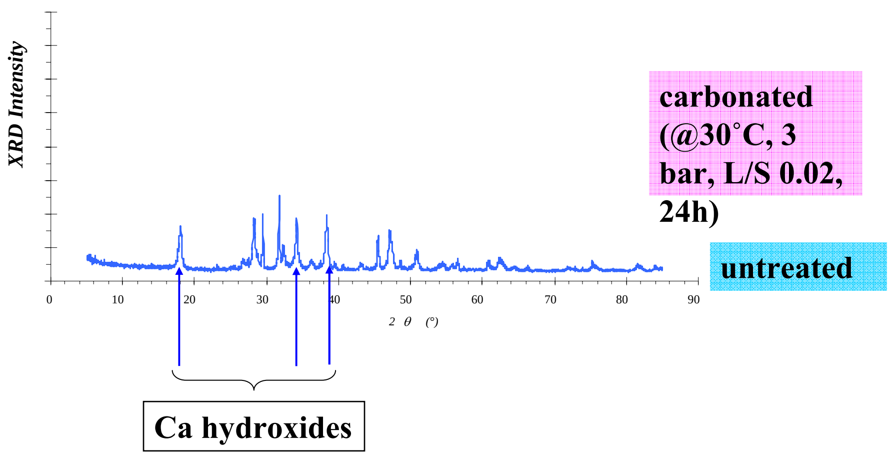
Hydromagnesite



Magnesite

Hänchen et al., Chem. Eng. Sci. (2007) in press

Mineral carbonation of APC fly ash



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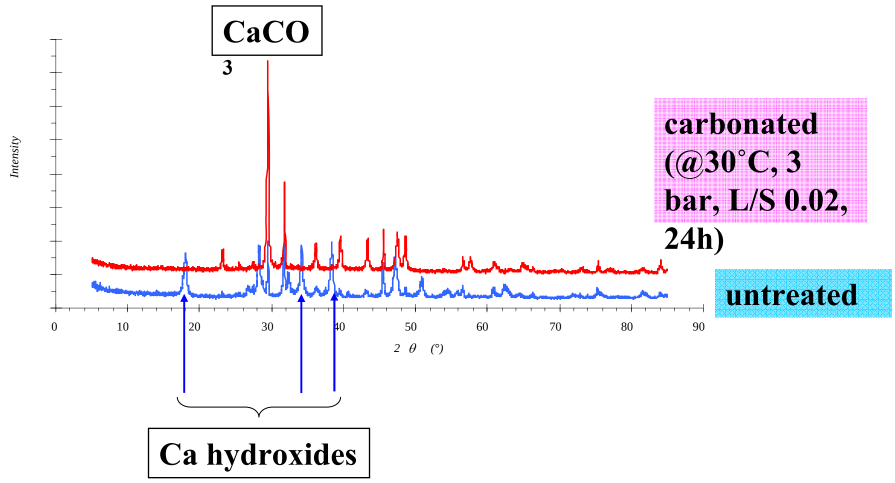

Outline

1. **Separation technology for zero emission power plants**
2. **Carbon dioxide storage by mineral carbonation**
3. **Concluding remarks**

Concluding remarks

- "Technologies are available to reduce greenhouse gas emissions but policies and measures are needed to realize the technological potential" (IPCC, 2001)
- Achievement of emission reduction targets require that all options be exploited (renewables, efficiency, savings, nuclear , CCS). Without CCS targets will not be achieved.
- CCS is expensive, particularly at this early deployment stage (6 Mt CO_2/y out of 25 Gt CO_2/y). We need new global and local regulatory, fiscal and financial instruments to make it possible.