Greenhouse Gases Mitigation CO₂ Capture and Utilization

Topic No: 5

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High temperature carbonate loop

- Principle = sequence of reversible carbonation/decarbonation reactions

  - ▶ Limestone is calcined at ca. 900 °C $CaCO_3 \rightarrow CaO + CO_2$
  - ▶ CaO is cooled down to ca. 650 °C
  - ▶ CaO is exposed to CO_2-containing gas $CaO + CO_2 \rightarrow CaCO_3$
  - ▶ $CaCO_3$ is calcined again, pure CO_2 i recovered ….. new cycle begins…

- The heat released by carbonation can (theoretically) be used for calcination

  - ▶ ΔH^0 ($CaCO_3 \leftrightarrow CaO + CO_2$) = ±178.2 kJ mol^{-1}

  - ▶ but ….. how this exchange can be provided?

- Very high theoretical adsorption capacity of limestone (100% calcite)

| Element	Molar mass	Compound	Molar mass	Theoretic capacity
Ca	40.08 g/mol	$CaCO_3$	100.09 g/mol	
O	16.00 g/mol			9.99 mmol/g = 43.97 g/100 g
C	12.01 g/mol	CO_2	44.01 g/mol	

High temperature carbonate loop: problems

■ **Problem 1 – limestone sintering**

► capacity drop due to the formation of an impermeable layer on the particles

► limited number of operation cycles $\Rightarrow$ increase of operation costs

■ **Problem 2 – suitable construction materials**

► high temperature combined with corrosive gases $\Rightarrow$ increase of capital costs

■ **Problem 3 – heat recovery**

► how to use the heat released by CO_2 sorption at 650 °C?

■ **Problem 4 – reaching the calcination temperature**

► heating source to reach 900 °C not available in standard power plants or another industrial technologies
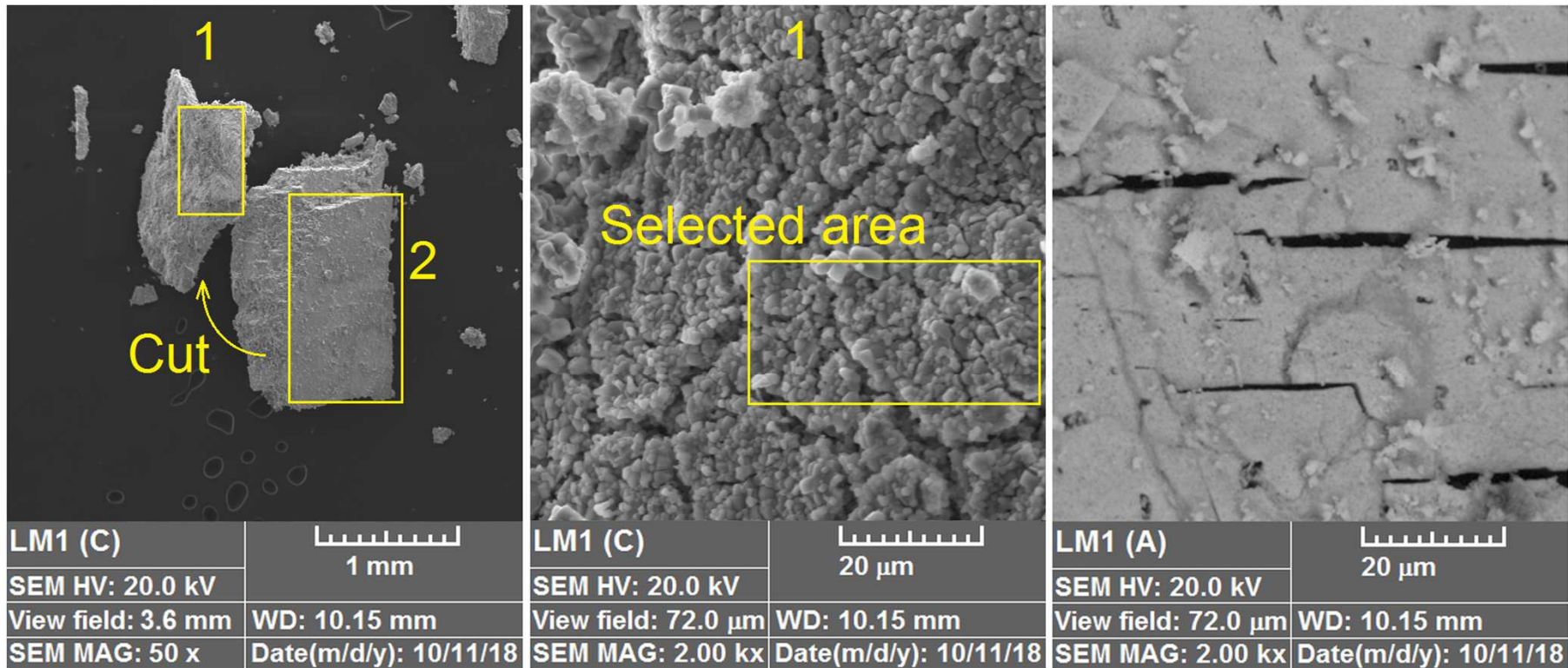
■ Alternation of temperatures sinters the surface of the particles.
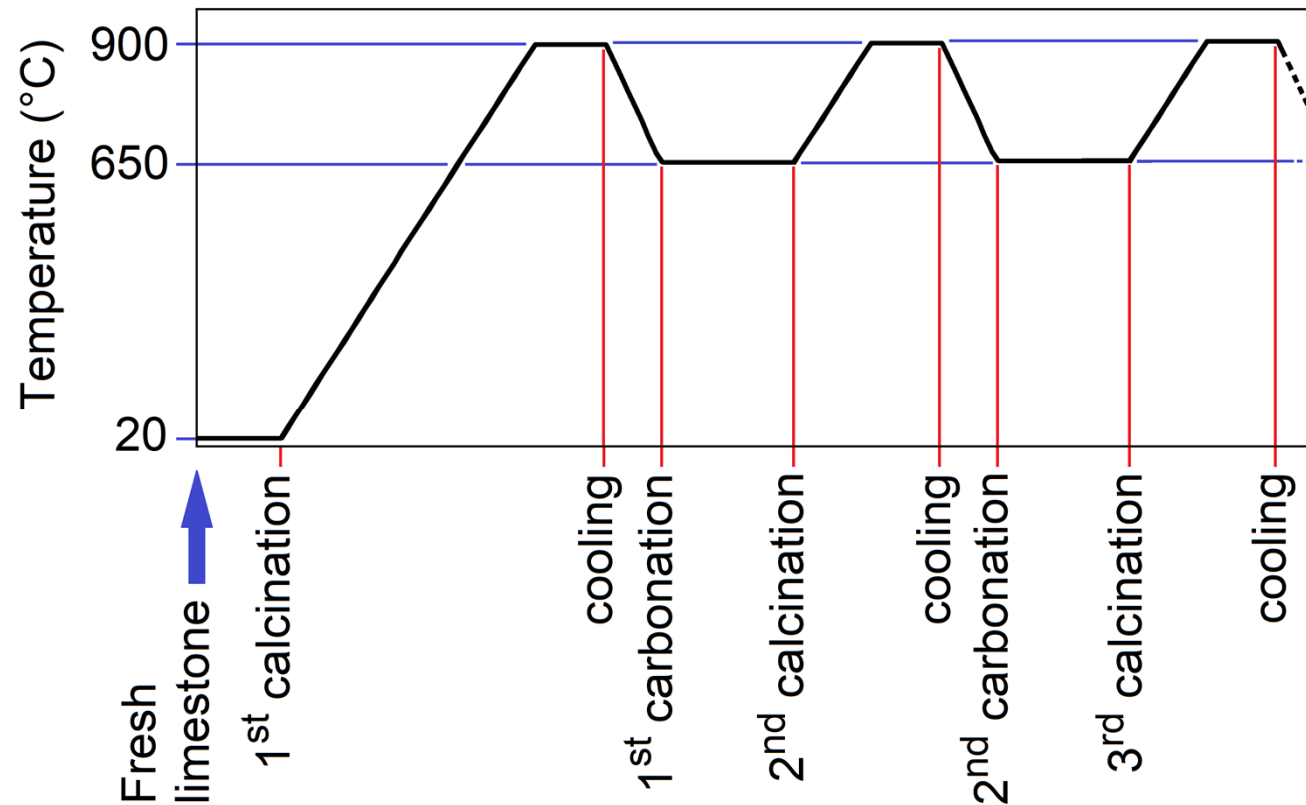
■ Calcite (trigonal $CaCO_3$) $\Rightarrow$ higher melting point $\Rightarrow$ more resistant

■ Aragonite (orthorhombic $CaCO_3$) $\Rightarrow$ lower m.p. ca. 825 °C $\Rightarrow$ less resistant

■ $MgCO_3 \Rightarrow$ lower m.p. ca. 350 °C $\Rightarrow$ less resistant

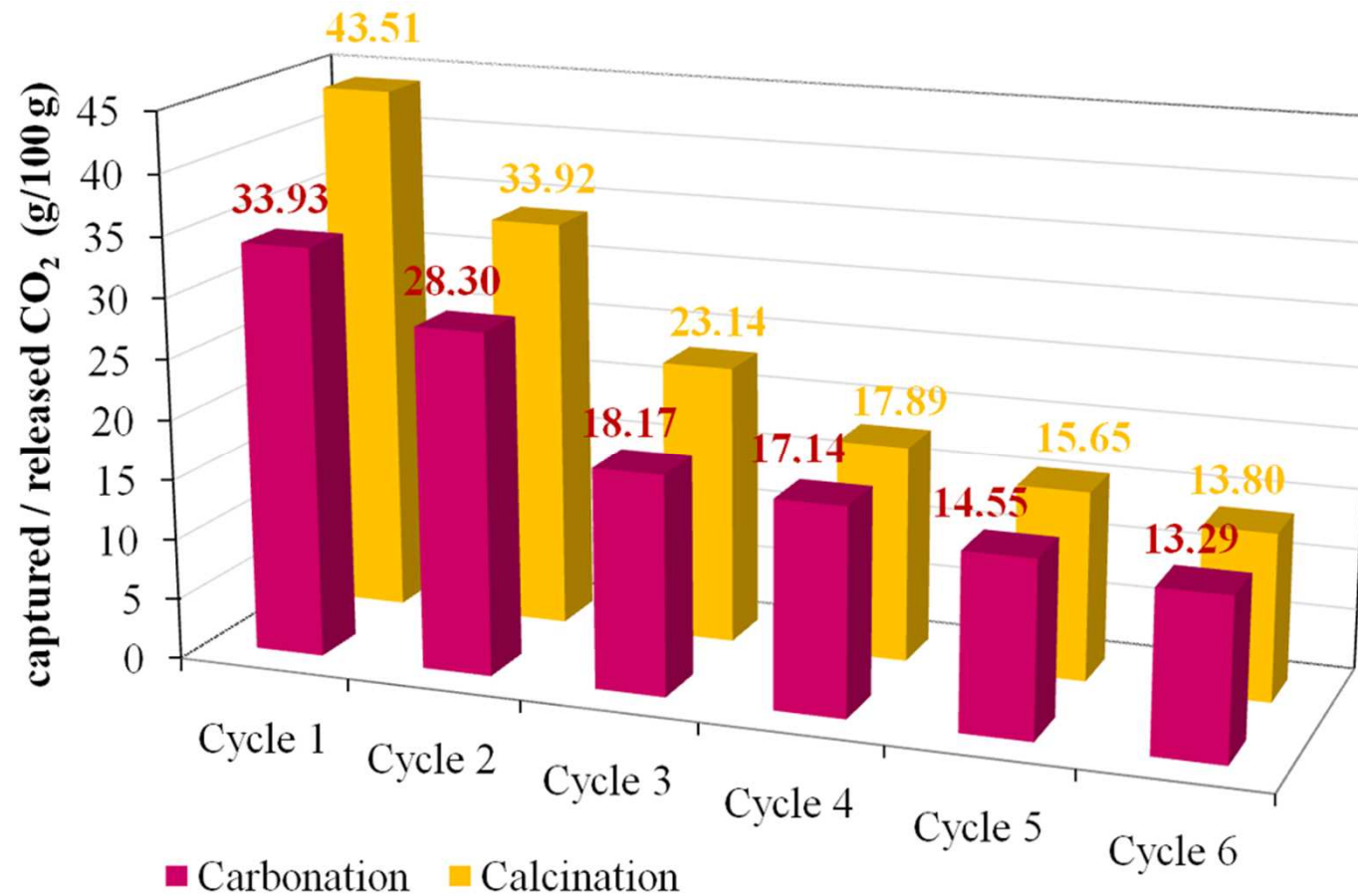- Alternation of temperatures sinters the surface of the particles.

Limestone particle ...   after 1st calcination   after 10th calcination

- Consequence: reduced diffusion of CO_2 molecules into particles $\Rightarrow$ decrease in capacity and worsening of sorption kinetics
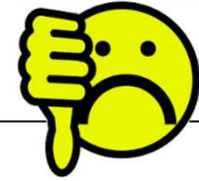
Example of the real limestone behavior (Branžovy quarry, central Bohemia)

Composition: $CaCO_3$ 98.22 % wt., $MgCO_3$ 0.93 % wt.

Theoretic capacity = 43.67 g/100g

■ Sintering + irreversible reaction $CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4$ =

■ LM1

Quarry Čertovy schody

$CaCO_3$ 98.86 % wt.

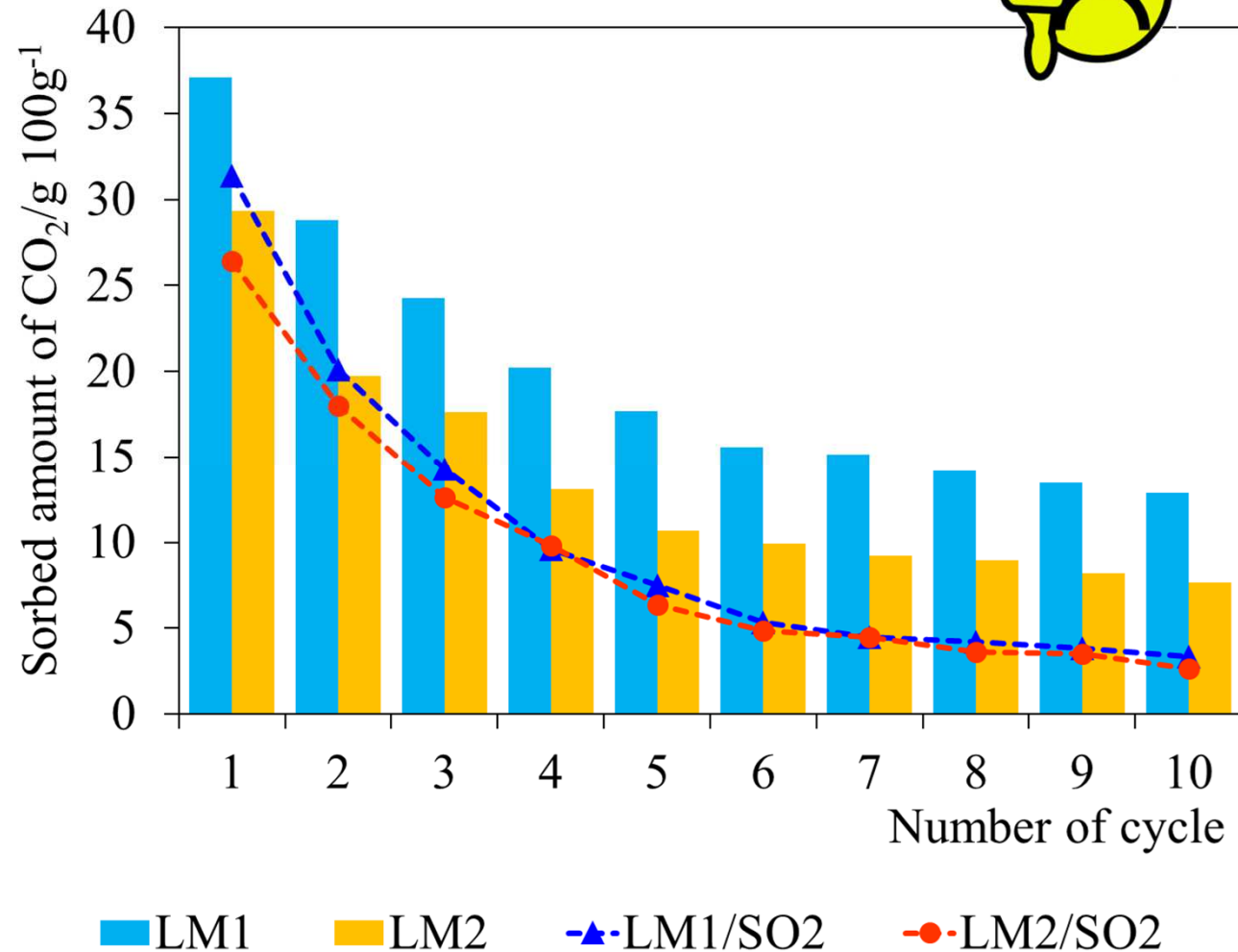$MgCO_3$ 0.75 % wt.

■ LM2

Quarry Libotín

$CaCO_3$ 96.47 % wt.

$MgCO_3$ 1.19 % wt.

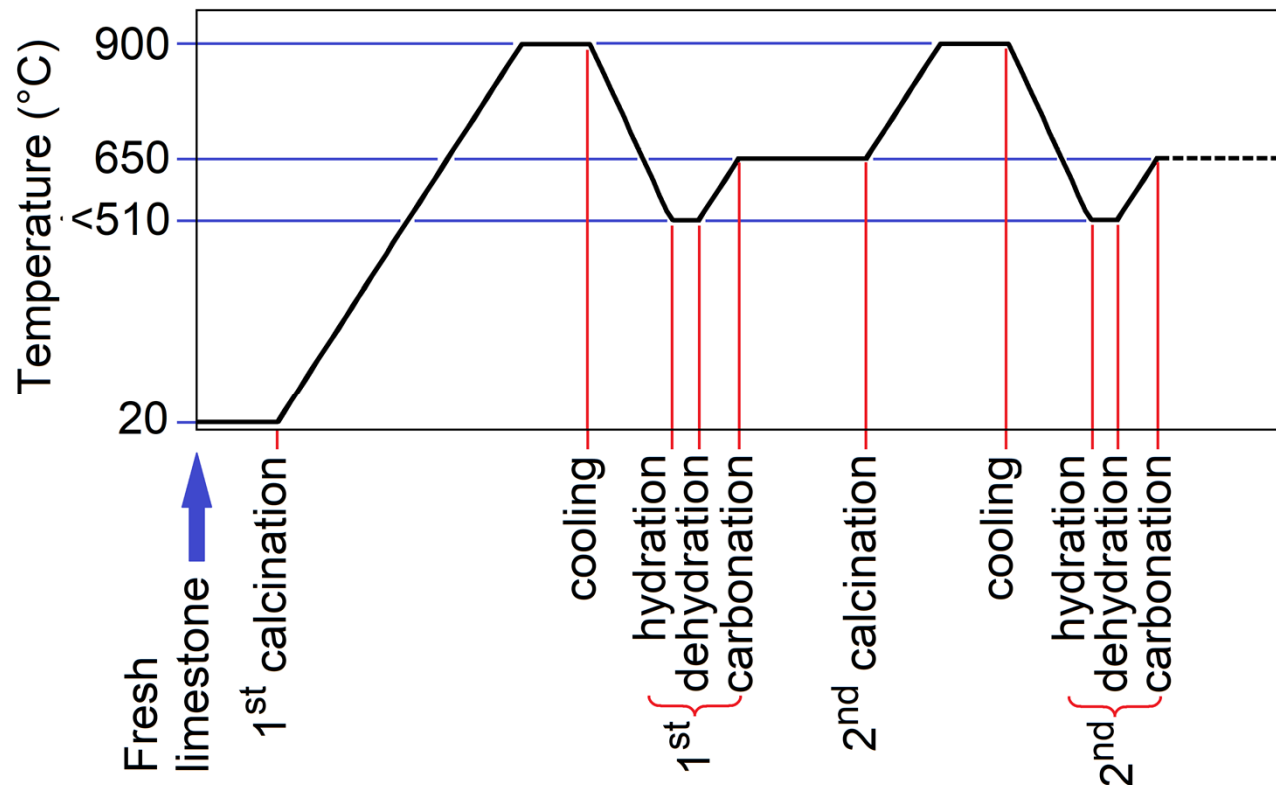■ SO_2 in gas

content 0.3 % vol.

■ Yes, 2 steps must be done

▶ SO$_2$ ⇒   must be deeply removed from the feed gas

▶ Sintering. ⇒   additional re-activation must be applied

possible reactivation based on the reaction with steam

$CaO + H_2O \rightarrow Ca(OH)_2$

molecular volume
increase by 53.8%
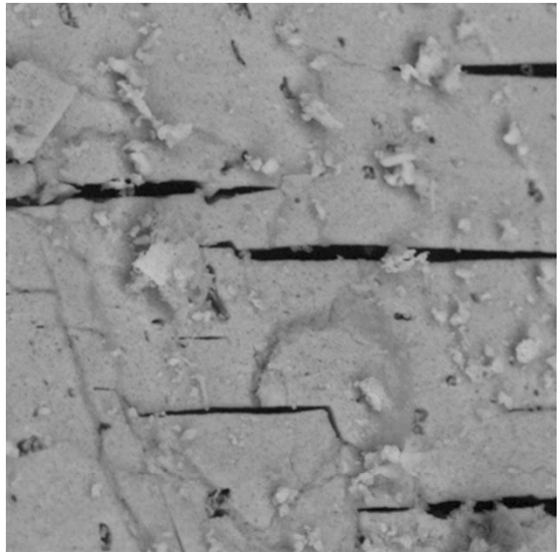disintegrates sintered sites
exothermic process
(94.6 kJ mol^{-1})

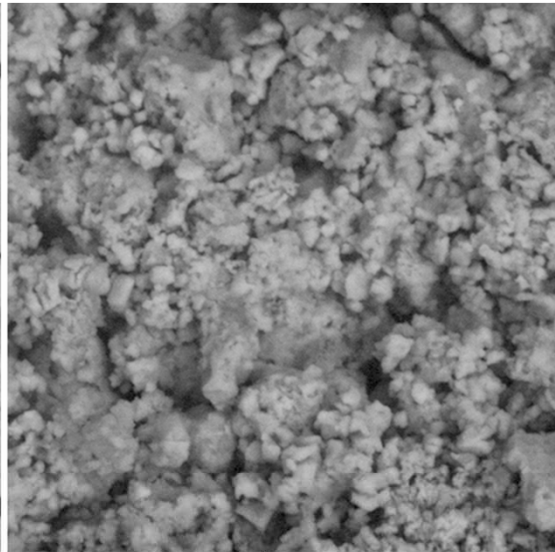■ Laboratory regenerability tests before scaling up to a industrial unit
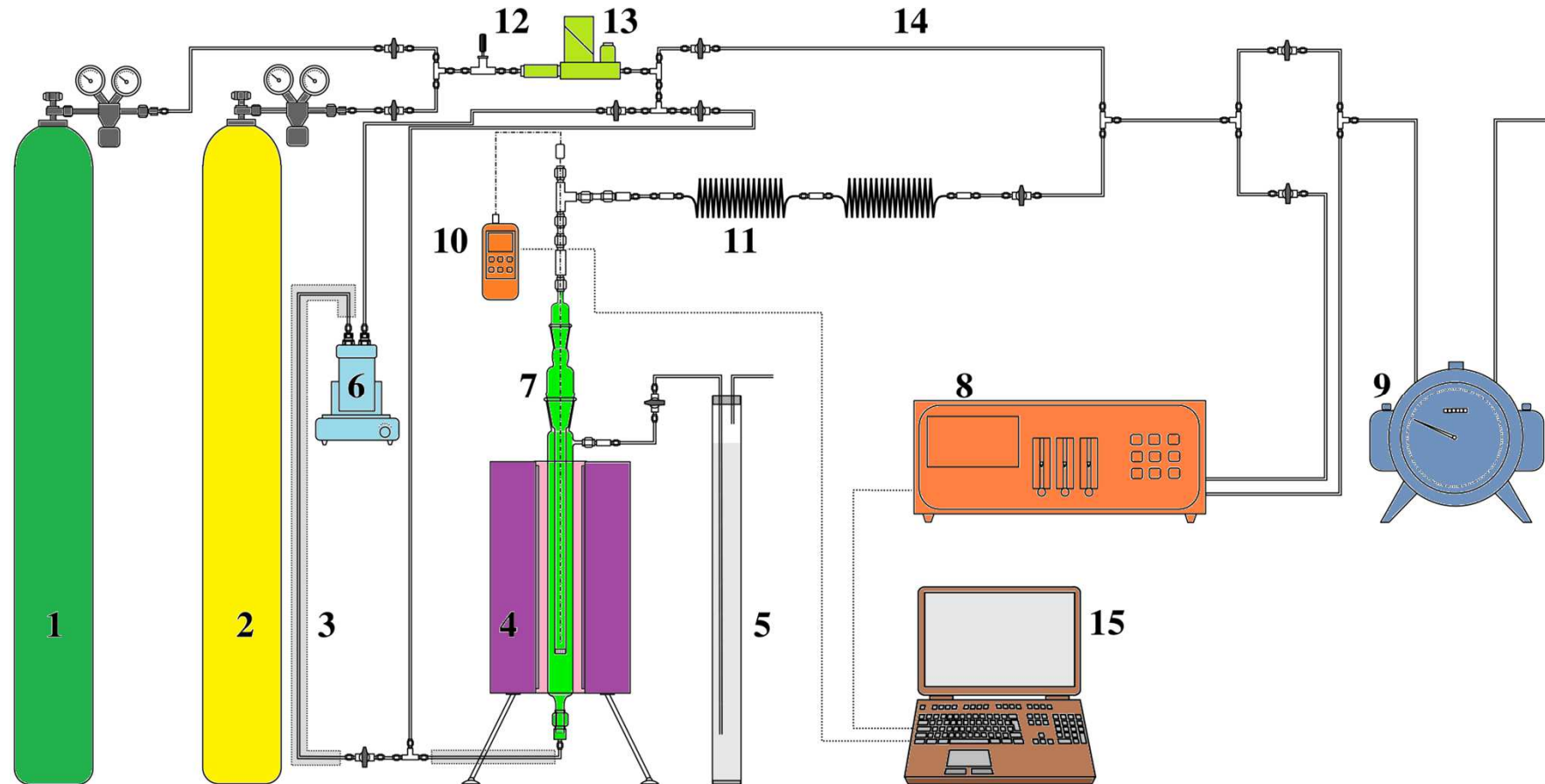
1, 2 – gases, 3 – heating mantle, 4 – oven, 5 –manostat, 6 – steam generator, 7 – fluidized bed adsorber, 8 – IR analyzer, 9 – gas meter, 10 – thermometer, 11 – coolers, 12 – needle valve, 13 – flow controller, 14 – bypass, 15 – PC

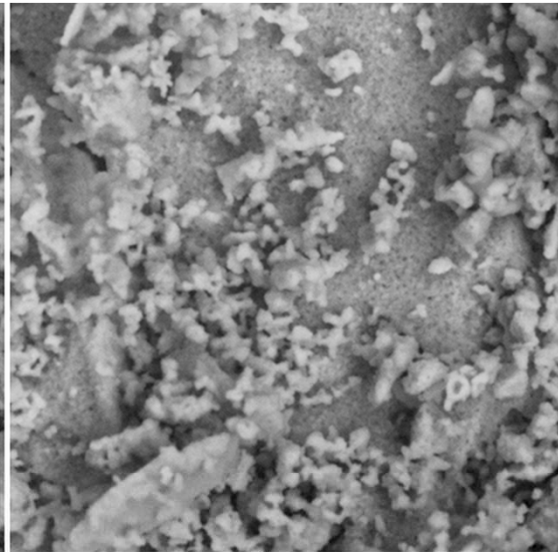- Steam restores porous surface (cauliflower-like structure).

LM1 (A)	20 µm
SEM HV: 20.0 kV	
View field: 72.0 µm	WD: 10.15 mm
SEM MAG: 2.00 kx	Date(m/d/y): 10/11/18

LM1 (B)	20 µm
SEM HV: 20.0 kV	
View field: 72.0 µm	WD: 10.15 mm
SEM MAG: 2.00 kx	Date(m/d/y): 10/11/18

LM1 (C)	20 µm
SEM HV: 20.0 kV	
View field: 72.0 µm	WD: 10.15 mm
SEM MAG: 2.00 kx	Date(m/d/y): 10/11/18

after 10th calcination
no activation

after 10th calcination
steam activation

after 10th calcination
steam activation
SO_2 contaminated

- Penalty for steam reactivation: energy loss for additional cooling/reheating

■ Steam suppresses capacity drop – but only if no SO_2 is present in the gas.

■ LM1
Quarry Čertovy schody
$CaCO_3$ 98.86 % wt.
$MgCO_3$ 0.75 % wt.
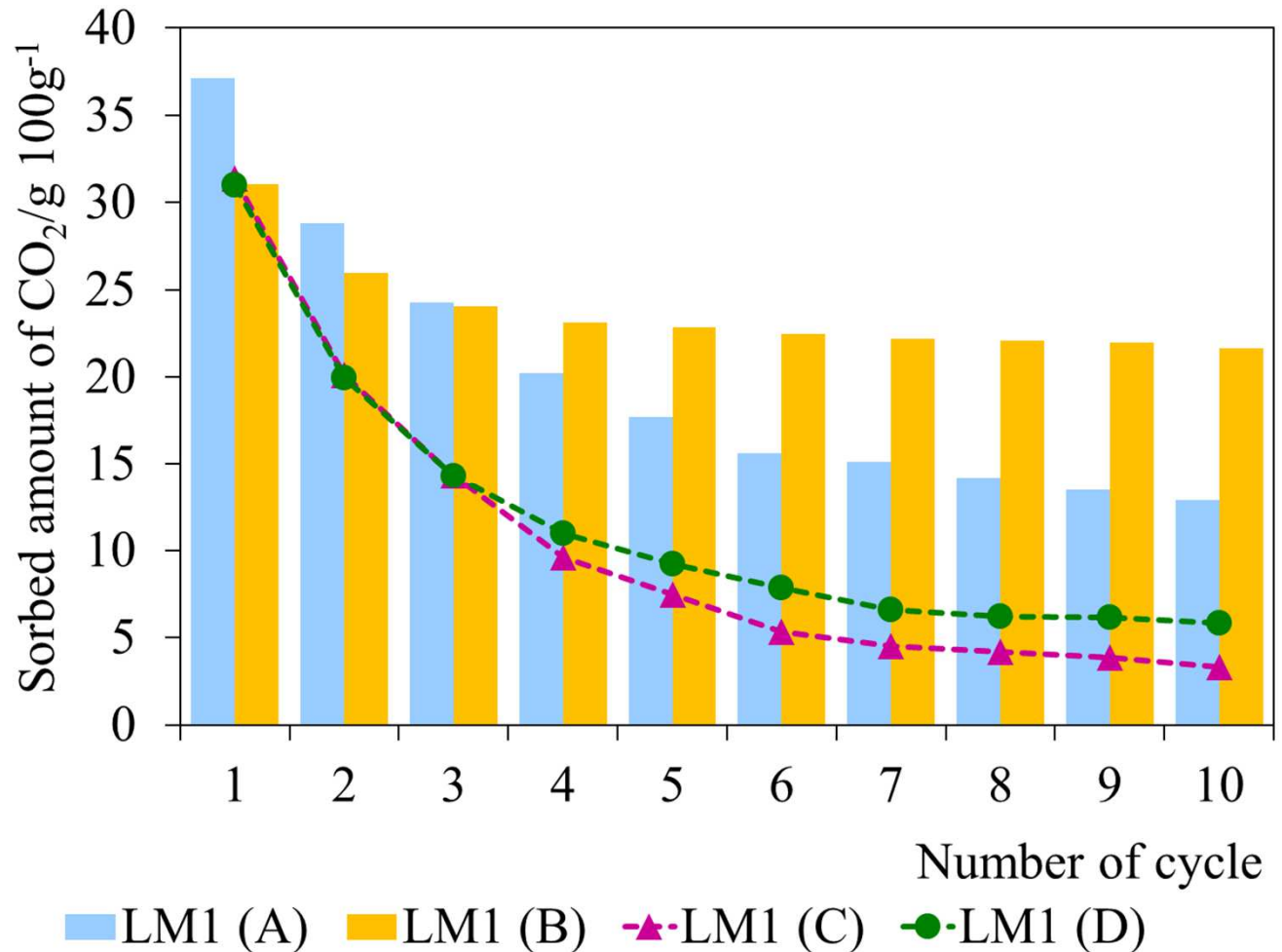
■ (A)
no steam
no SO_2

■ (B)
steam reactivation
no SO_2

■ (C)
no steam
0.3% SO_2

■ (D)
steam reactivation
0.3% SO_2

CO$_2$ Clean gas

900 °C   CALCINER   CARBONATOR   650 °C
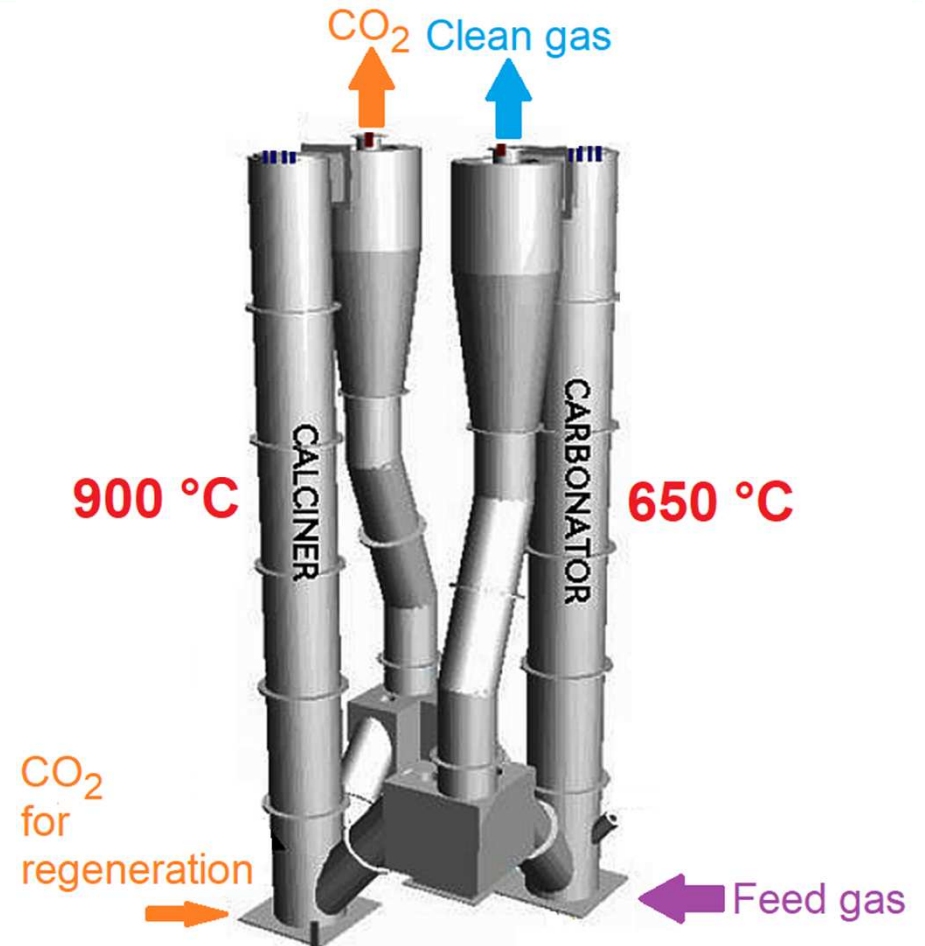
CO$_2$
for
regeneration

Feed gas

■ Available inox steels.

  ▶ AISI316L
      continuous use < 425 °C

  ▶ AISI316Ti
      continuous use < 425 °C

■ Available special alloys – expensive

  ▶ Kanthal Fe-Cr-Al   (Cr 20 – 30%, Al 4 – 7.5%)   < 1,500 °C
  ▶ Megapyr Fe-Cr-Al   (Cr 22%, Al 5.8%)   < 1,450 °C
  ▶ HASTELLOY alloy X (Ni 47.5%, Cr 21.8%, Fe 18.5%, Mo 9.0%)   < 1,204 °C

- **Sufficient heating source for calcination step**

  ▶ standard fluidised bed (e.g. for biomass combustion) – not enough

  ▶ cement rotary kilns – potentially yes

  ▶ blast furnaces in iron and steel industry – potentially yes

  ▶ already tested approach: additional source of heat = small oxy fuel burner

- **Utilization of heat generated during carbonation step**

 ▶ several conceptions – research and development still in progress

Cold adsorption

	Physical	Chemical
Forces	weak (van der Waals, hydrogen b.)	strong (sharing of electrons)
Specifity for gases	not specific (gases with higher boiling point sorbed better)	specific (according to chemical affinity to the adsorbent)
Adsorption heat	low, similar to condensation (< 40 kJ/mol)	high, as for chem. reaction (up to 400 kJ/mol)
No. of layers	multiple	single
Sorption rate	high	low at lower T (increasing with T)
Capacity	decreasing with increasing T	increasing with increasing T
Desorption	easy (decr. of p and increase of T)	difficult (high T, vacuum)

The most frequently used adsorbents

- **Silica gel**
  - ▶ chemical composition: SiO_2
  - ▶ specific surface area: $700 - 800$ m^2 g^{-1}
  - ▶ dominating pores: $3 - 30$ nm
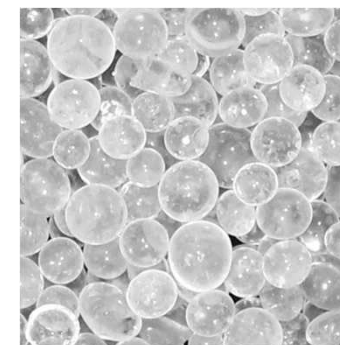
- **γ-alumina**
  - ▶ chemical composition: Al_2O_3
  - ▶ specific surface area: $200 - 350$ m^2 g^{-1}
  - ▶ dominating pores: $8 - 15$ nm

- **Natural zeolites**
  - ▶ chemical composition: $[(SiO_2)(AlO_2)_x]M_{x/n}^{n+} \cdot w\ H_2O$
  - ▶ specific surface area: $20 - 200$ m^2 g^{-1}
  - ▶ dominating pores: $10 - 80$ nm

- **Synthetic zeolites (molecular sieves)**

  ▶ chemical composition: $[(SiO_2)(AlO_2)_x]M_{x/n}^{n+} \cdot w\ H_2O$

  ▶ specific surface area: $400 - 800\ m^2\ g^{-1}$

  ▶ dominating pores: depending on type

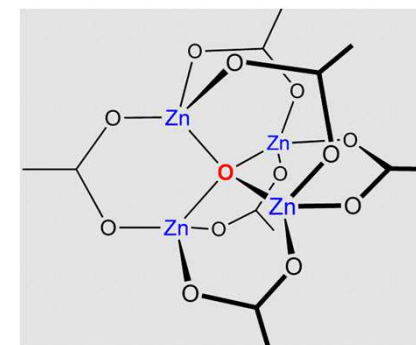- **Activated carbon**

  ▶ chemical composition: C

  ▶ specific surface area: $500 - 2{,}000\ m^2\ g^{-1}$
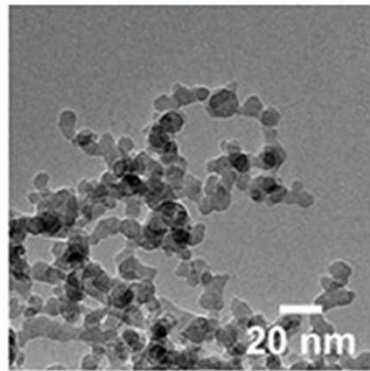
  ▶ dominating pores: $1 - 20\ nm$

- **Metal organic frameworks (MOFs)**

  ▶ chemical composition: hydrocarbon+metal

  ▶ specific surface area: $500 - 7{,}000\ m^2\ g^{-1}$
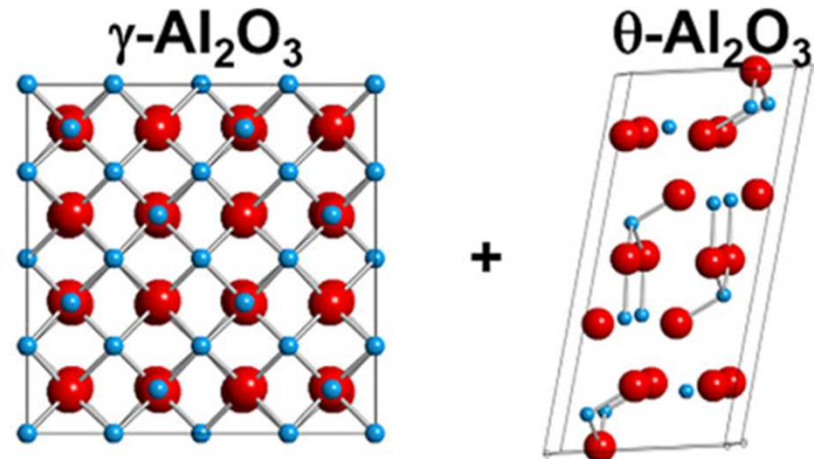
  ▶ dominating pores: depending on type

- Only γ–alumina offers significantly porous structure
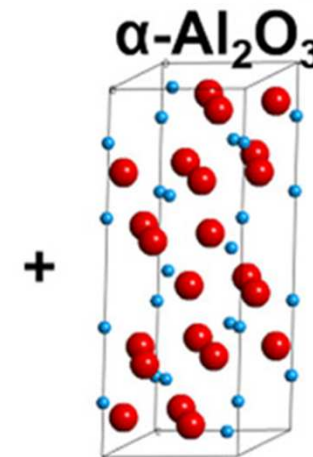 - ► crystalline modification depends on annealing procedure

Raw alumina conversion

Annealing

γ-Al$_2$O$_3$

θ-Al$_2$O$_3$

α-Al$_2$O$_3$

20 nm

+

+

Resuting crystalography
depends on:
    Annealing temperaure
    Annealing time

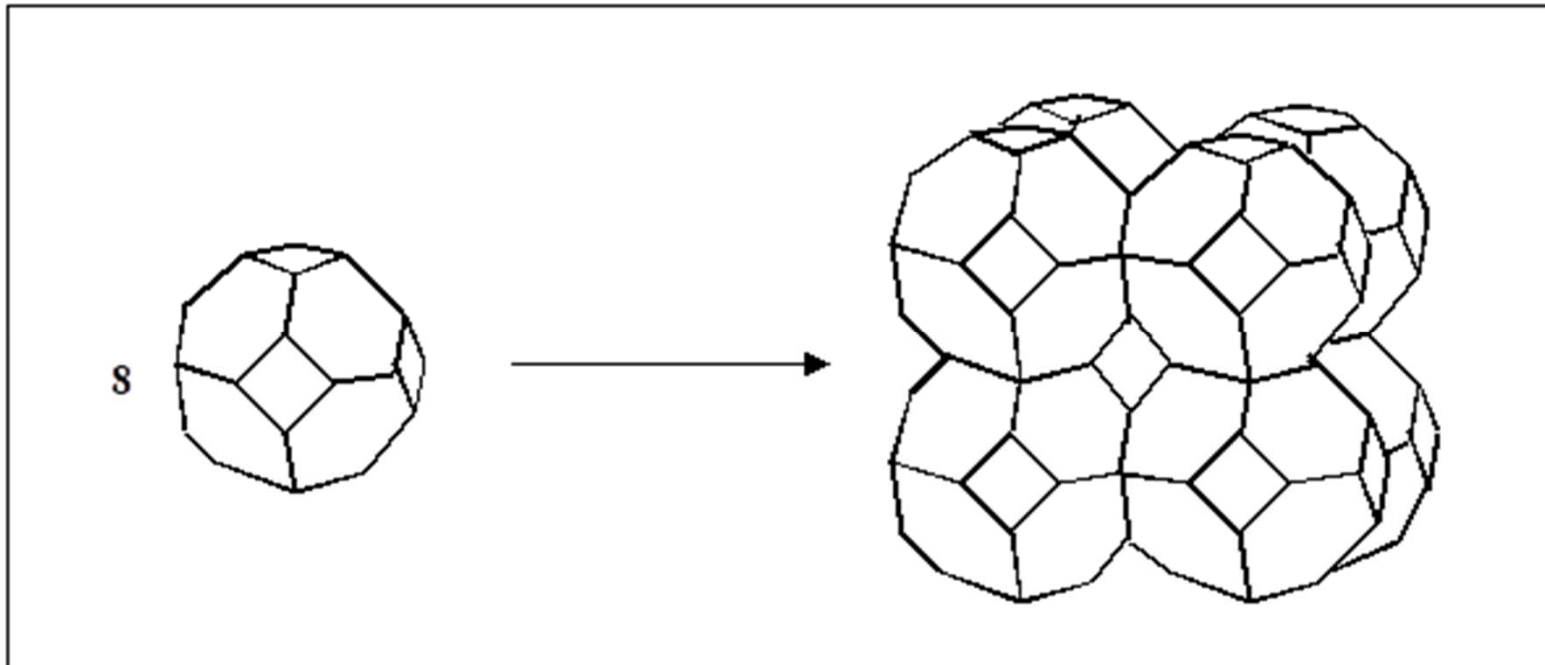e.g.high amount of "γ" at 1,100 °C / 18 hours

■ Natural zeolites with common formula $[(SiO_2)(AlO_2)_x]M_{x/n}^{n+} \cdot w\ H_2O$

▶ Cations (Na^+, K^+, Ba^{2+}) and water molecules located in the channels and cavities of $Si(Al)O_4$ tetrahedra

▶ Secondary building units of the structure (SBU) periodically repeated throughout the zeolite crystal $\Rightarrow$ precisely defined channel structure size

Example: eight sodalite SBUs forming structure of sodalite mineral

■ Analogous structures like natural zeolites are produced chemically

▶ raw materials: aluminosilicates – e.g. ashes from power stations

▶ process: hydrothermal alteration

▶ conditions: reaction with NaOH or KOH in an autoclave up to 130 °C
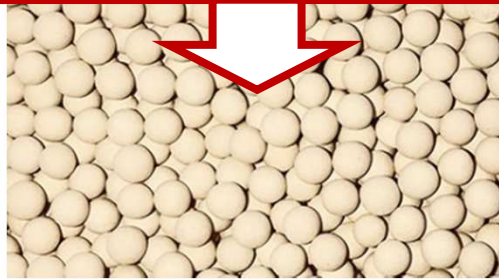
■ True density, apparent density

▶ true density ρ_t = weight of a sample referred to solid matter only V_s (solid skeleton without pores)

▶ apparent density ρ_a = weight of a sample referred to solid matter + pores

■ Specific surface area

▶ cm^2 (of internal pores) in 1 g of the adsorbent available for adsorption in a single layer

■ Total pore volume V_p

▶ cm^3 (of internal pores) present in 1 g of the adsorbent

$$\rho_a = \frac{V_s \cdot \rho_t}{V_s + V_p}$$

■ Pore size distribution

▶ percentual representation of volumes occupied by pores of different diameters

■ Adsorption capacity

▶ g (CO_2) captured by 1 g of the adsorbent

▶ mmol (CO_2) captured by 1 g of the adsorbent

■ **The principle of pycnometry**

▶ comparison of the amount (volume or weight) of fluid in an empty crucible and in a crucible with a known weigh of the sample

▶ Apparent density ρ_a liquid does not enter the pores (**mercury** used)

▶ True density ρ_t gas penetrates the pores (**helium** used)

▶ Total pore volume given by the formula:
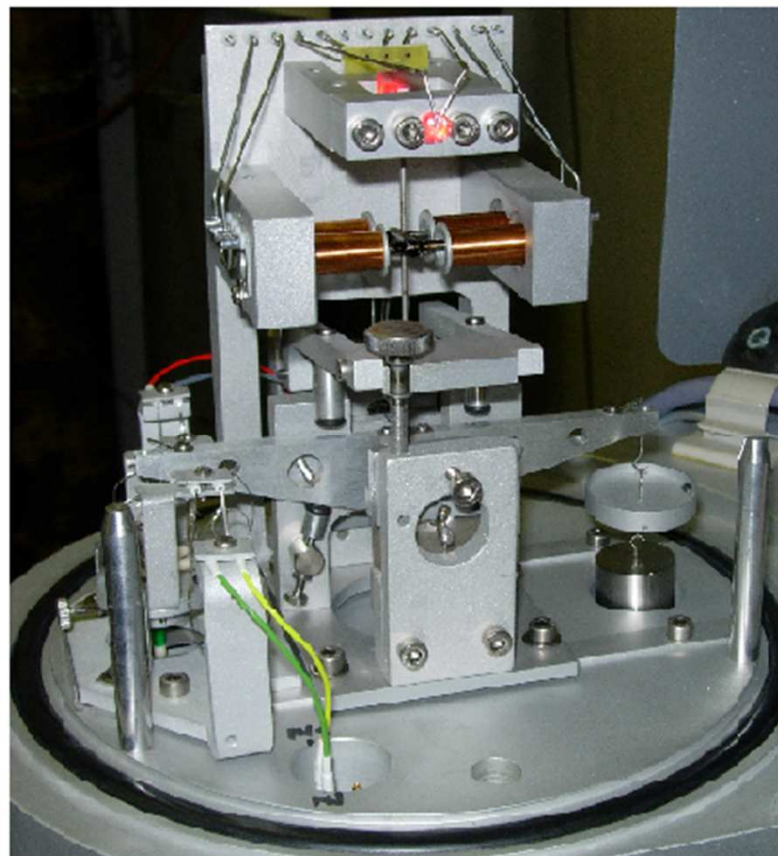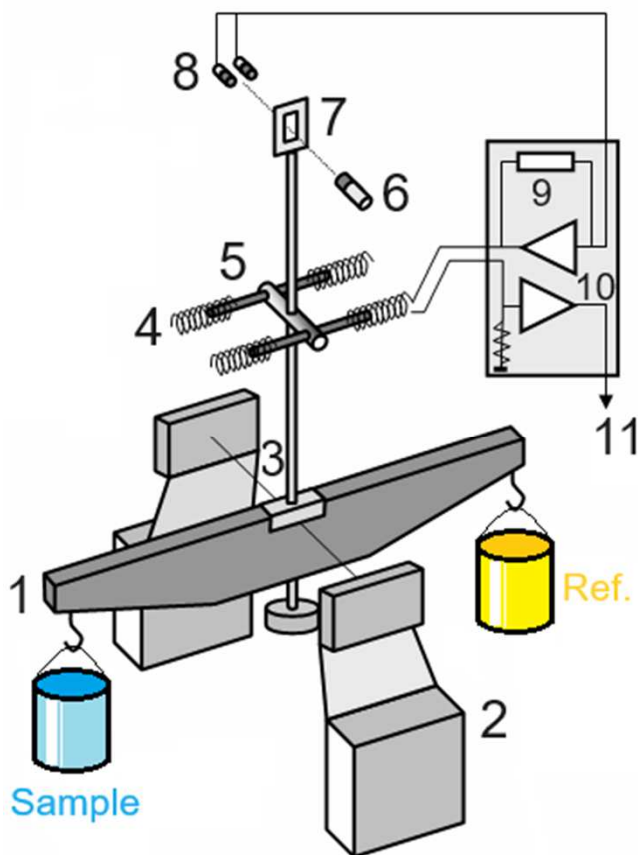
$$\rho_a = \frac{V_s \cdot \rho_t}{V_s + V_p}$$

A   B   C   D

ρ_a ρ_t
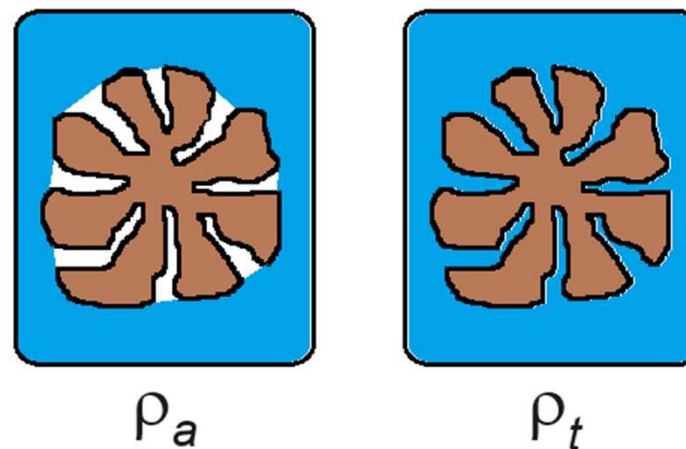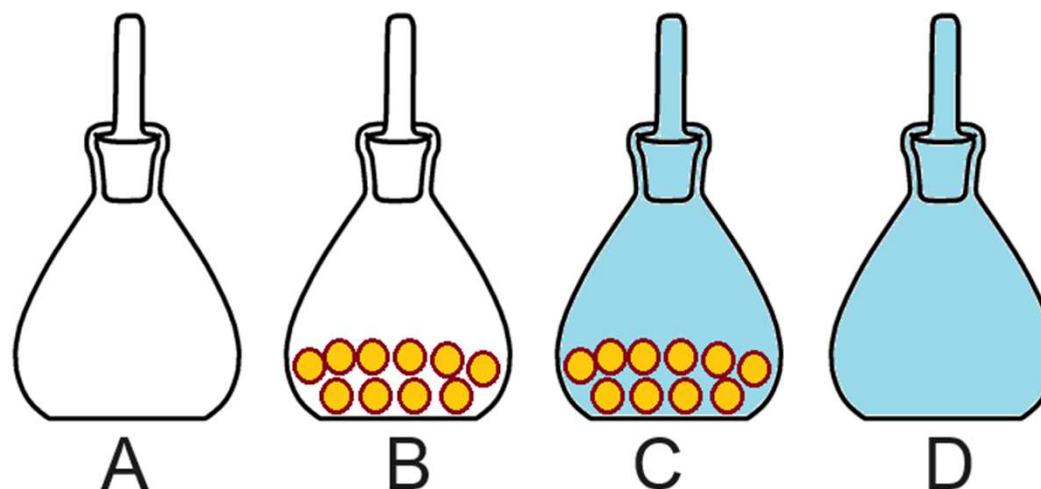
■ Adsorption capacity = the most important parameter of adsorbents

► depends on: pressure, temperature, gas mixture composition (competing gases)

► cannot be calculated $\Rightarrow$ must be measured
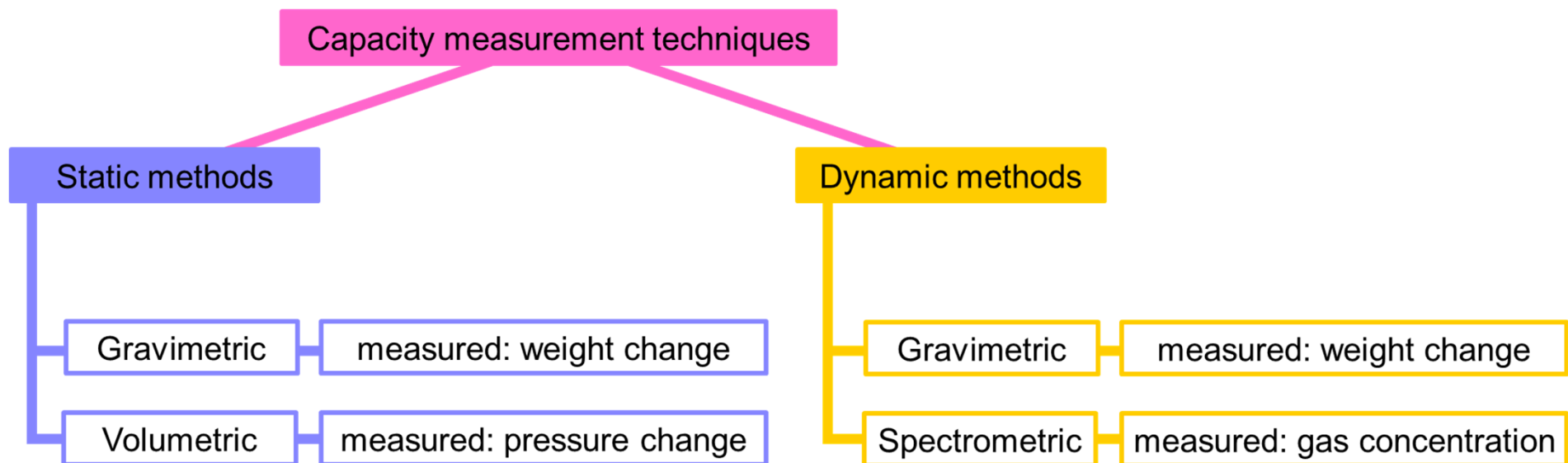
■ Microbalance with optical detection for static/dynamic measurements

1 – balance arm for sample and reference probes, 2 – torsion fiber tension spring, 3 – torsion fiber, 4 – solenoid, 5 – permanent magnet, 6 – light beam source, 7 – optical diaphragm, 8 – phototransistors, 9 – correction circuit, 10 – amplifiers, 11 – signal output

■ Principle: continuous measurement of the difference in CO_2 concentrations at the inlet and outlet of the adsorber

▶ other measured parameters: temperature, pressure, gas flow
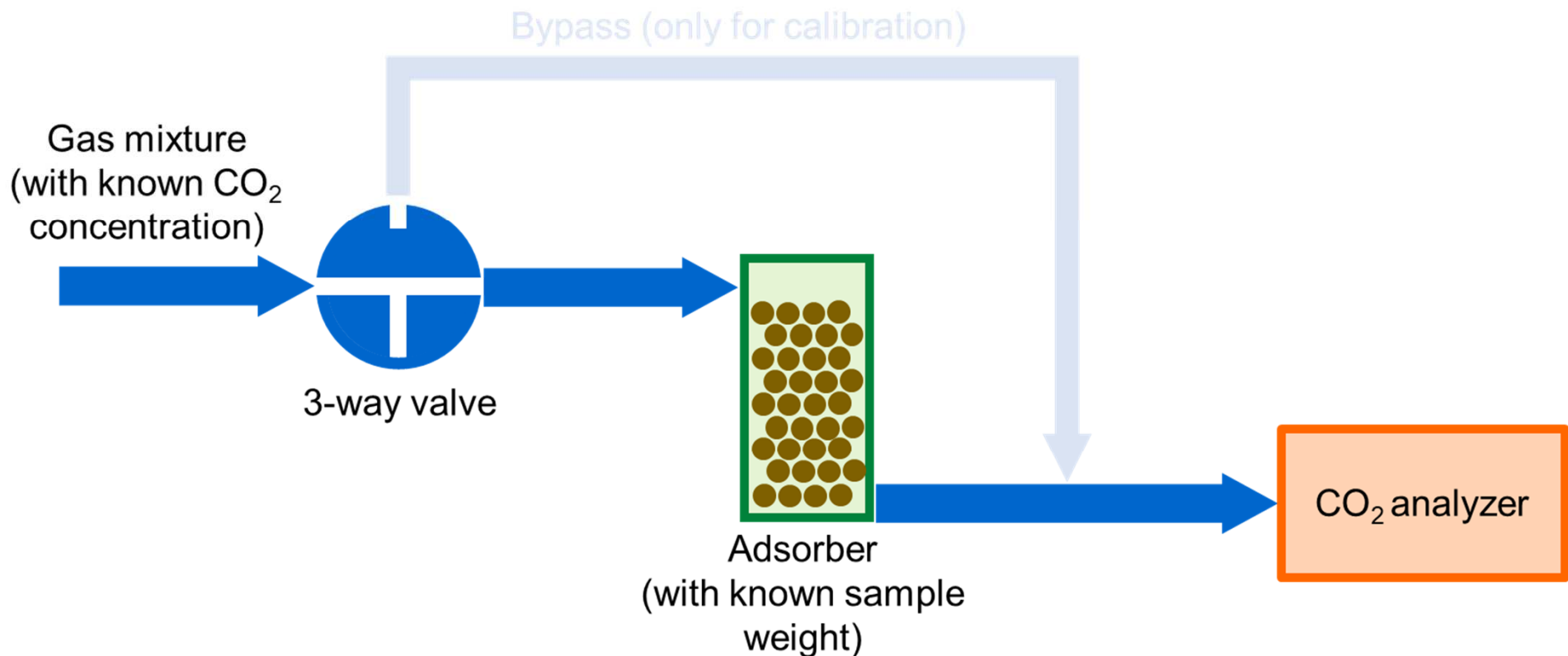
- Example of the spectrometric dynamic apparatus

1, 2 – model gases
3 – flow controller
4, 12 – three-way valves
5 – hygrometer
6 – safety vent
7 – manometer
8 – needle valves
9 – humidifiers
10 – humidity probe
11, 15 – coolers
13 – adsorber
14 – climate chamber
16 – condensate collector
17 – back-pressure regulator
18 – thermometer
19 – PC
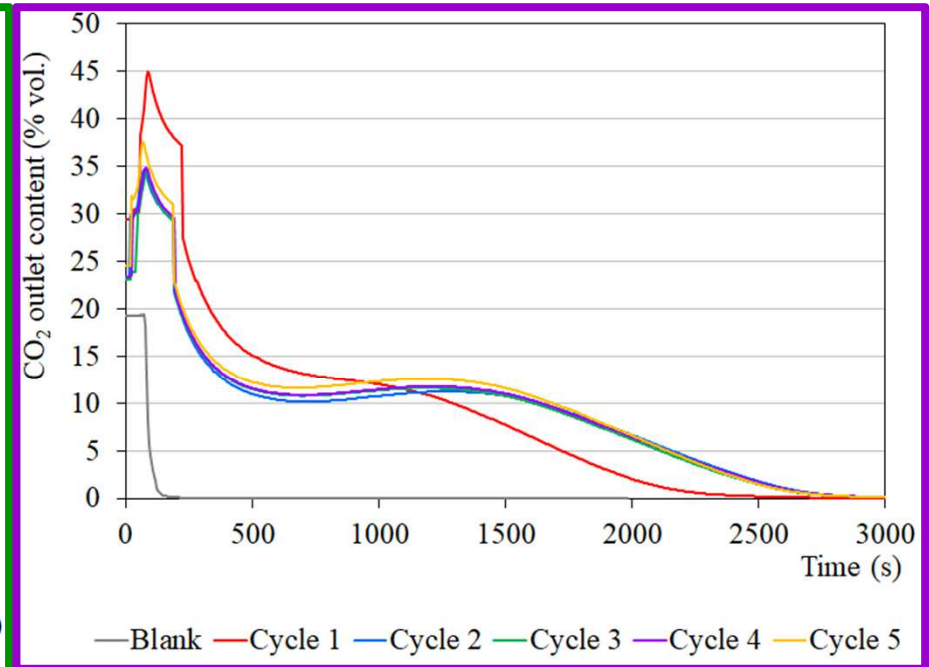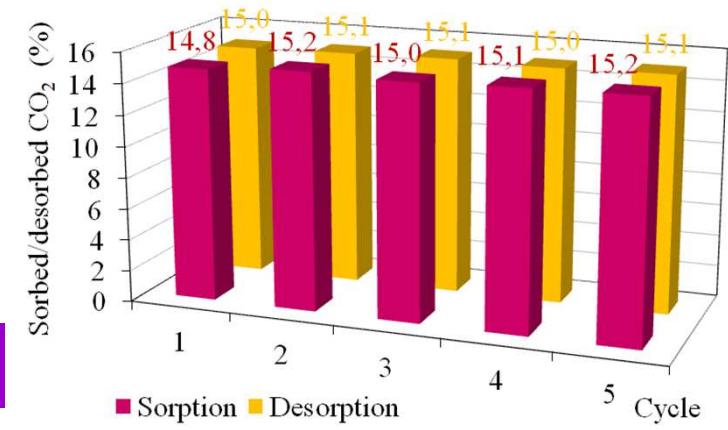20 – IR CO_2 analyzer
21 – bypass
22 – gas meter
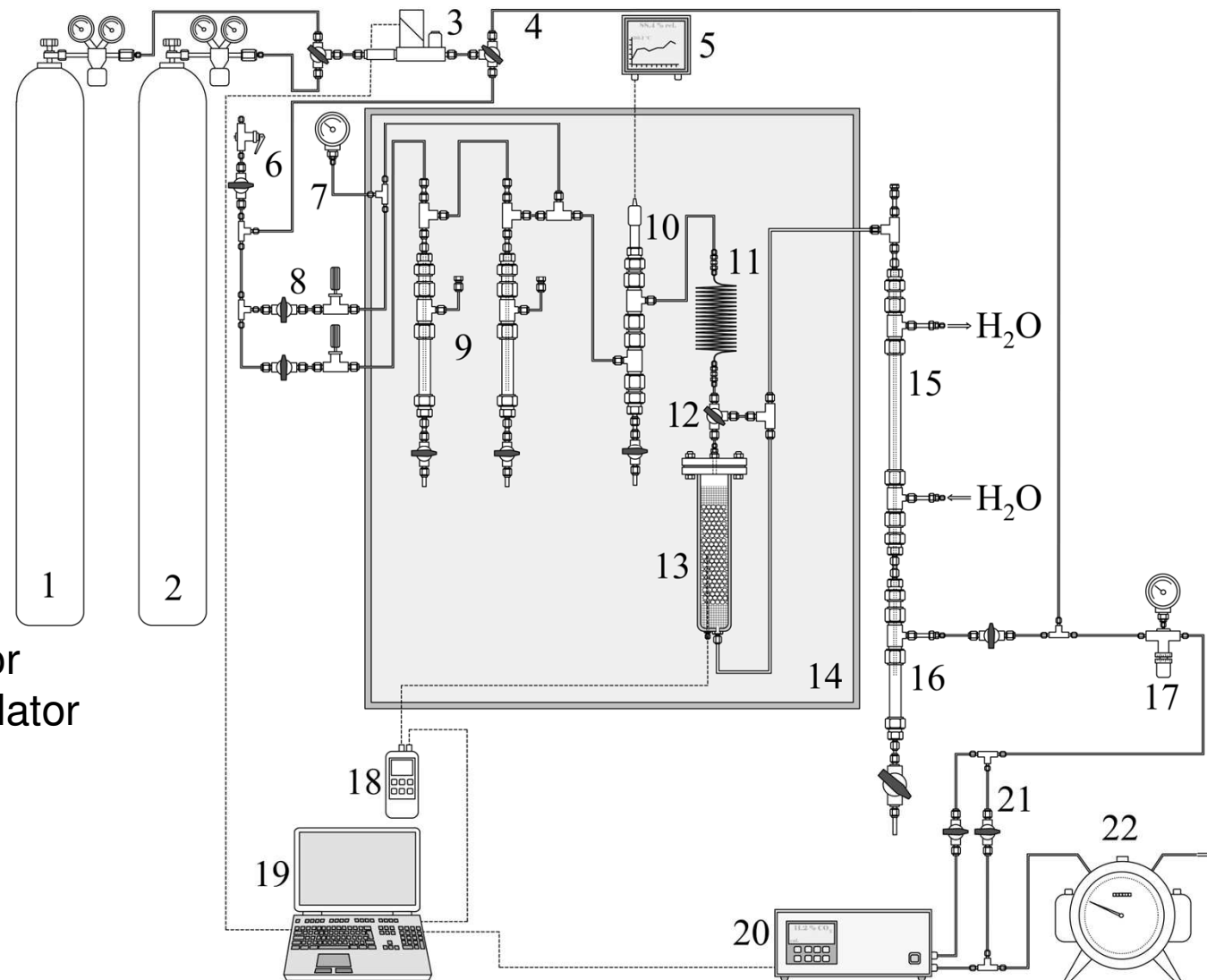
■ Example of the online data provided by the dynamic apparatus (13X, 5 bar, 20°C)
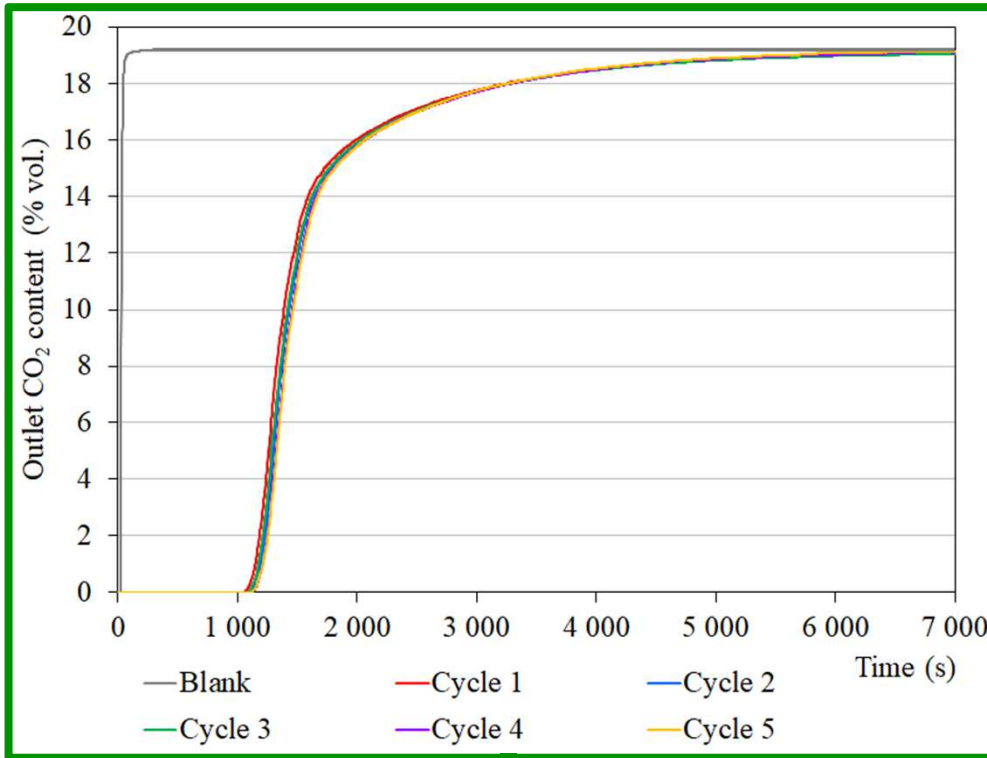
outlet CO_2 content during adsorption (so-called breakthrough curve)

outlet CO_2 content during desorption

■ Main ways of CO_2 storage (typically 800 m under the surface and deeper)

▶ deep saline aquifers

▶ extracted oil deposits

▶ extracted natural gas deposits

▶ non-minable coal seams

▶ enhancement of oil extraction (EOR) from nearly extracted deposits by CO_2 injection

▶ deep-sea disposal approx. 3,000 m below the water level and more

▶ in-situ carbonation by reaction of injected CO_2 with mafic and ultramafic minerals (ophiolite, basalt)

■ Main ways of CO_2 use

CO_2

direct use
- alkali waste water neutralization
- impregnation of wood with supercritical CO_2
- extraction of hop, coffee etc.
- drinks saturation

materials
- inorganic products: $NaHCO_3$, $CO(NH_2)_2$
- salicylic acid (Kolbe-Schmitt)
- carbonates (cyclical and linear)
- methanol (syngas + conversion to CH_3OH)

fuels
- methane (Sabatier reaction),
- liquid fuels (syngas + Fischer-Tropsch)
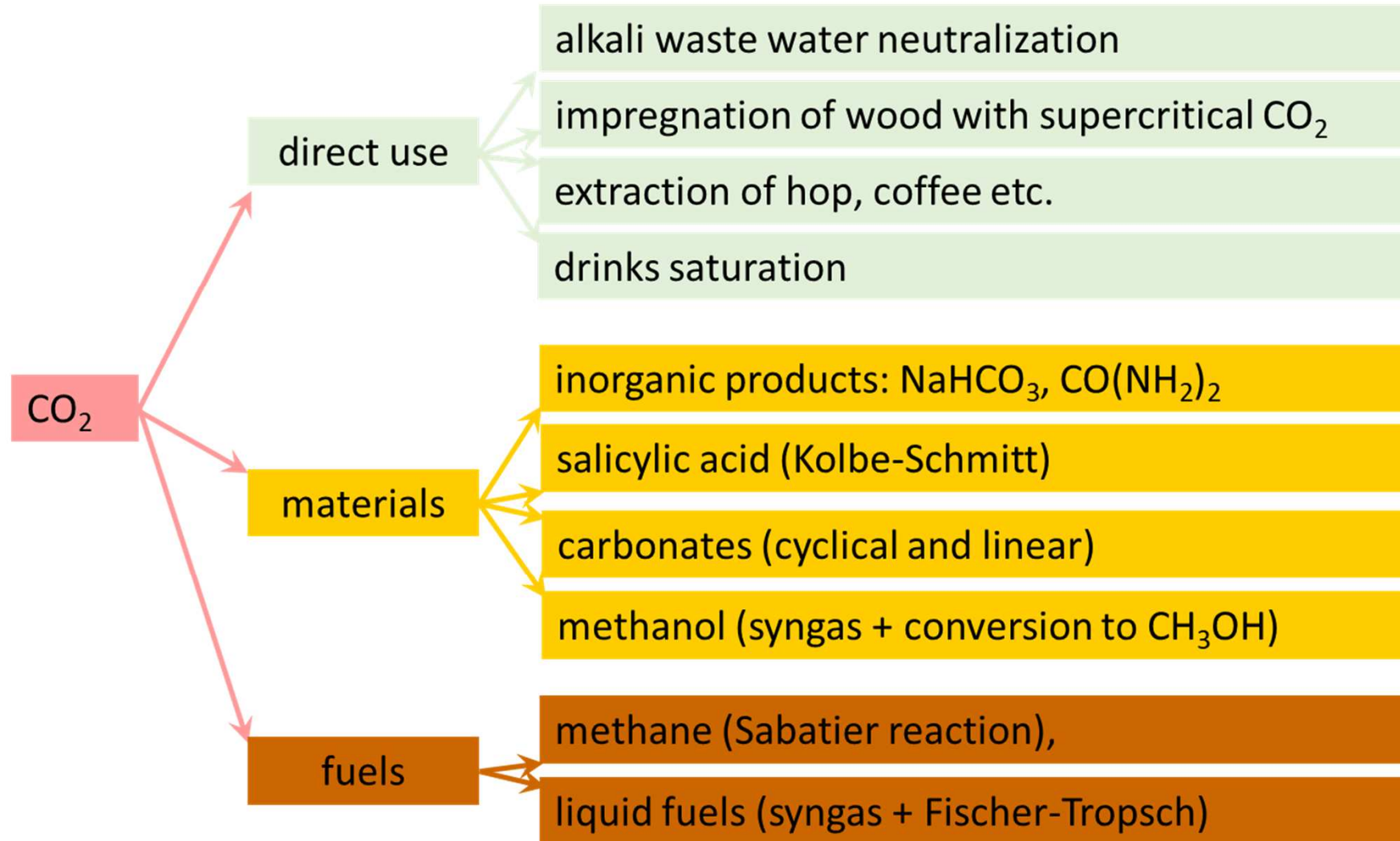
1. Li et al. Energy Fuels 2010, 24, 3698-3703. DOI: 10.1021/ef100245q.

2. Staf M., Miklová B., Kyselová V. The impact of variable carbonation and decarbonation conditions on the CO2 sorption capacity of CaO-based sorbents. Chemical Papers 2019, 73 (12), 3031–3042.

3. https://cordis.europa.eu/docs/results/241302/final1-caoling-final-report-en-publishable-report-doc.pdf

4. https://www.vskprofi.cz/katalog/silikagel-sgr

5. https://pubs.acs.org/doi/10.1021/acsomega.0c03353