Greenhouse Gases Mitigation CO_2 Capture and Utilization

Topic No: 4

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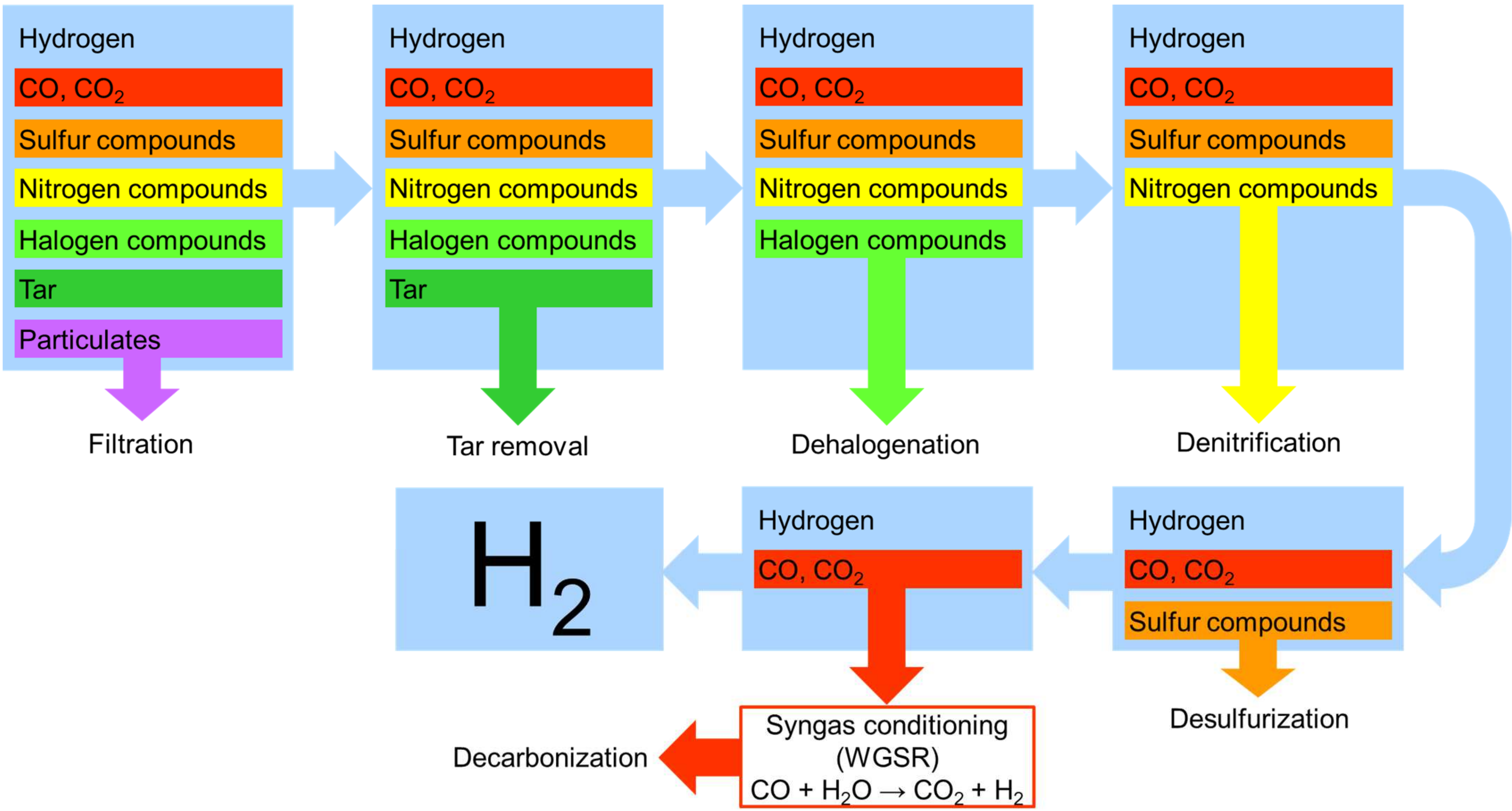
Pure H_2 = main step of pre-combustion proc.

- A typical sequence of syngas cleaning and conditioning steps:



Syngas cleaning in pre-combustion proc.

- In general, processes are divided into:
  - cold syngas cleaning
  - hot syngas cleaning
- Cold syngas cleaning – wet (absorption, scrubbing) or dry methods (adsorption….)
- Hot syngas cleaning – mostly dry methods (catalysis, adsorption…)
- A combination of hot and cold cleaning also possible
  - when switching to the cold method, the next hot step cannot be included

Why?

cooling down ↓ and **heating up** ↑ **again** makes no sense

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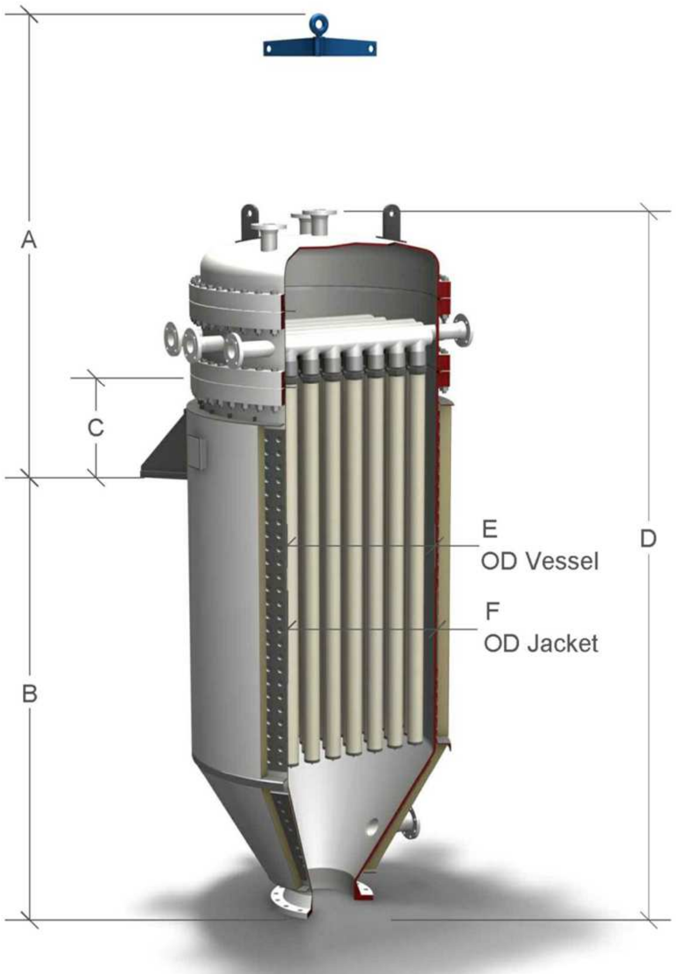
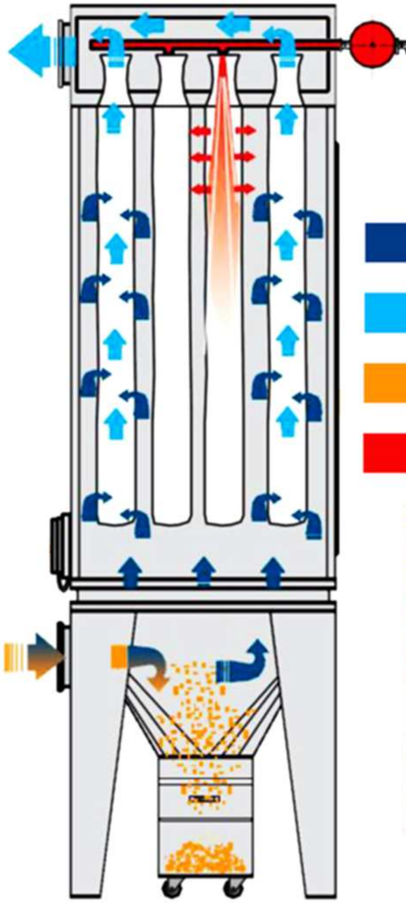
- In general, PM removal processes are divided into:
  - dry methods
  - wet methods
- According to principle, PM removal processes are divided into:
  - inertial separation
    - cyclones
  - barrier filtration
    - ceramic candle filters
    - textile baghouse filters
    - granular bed filters
  - electrostatic separation

+

- scrubbing (combined techniques for removal of PM + other specific contaminants)

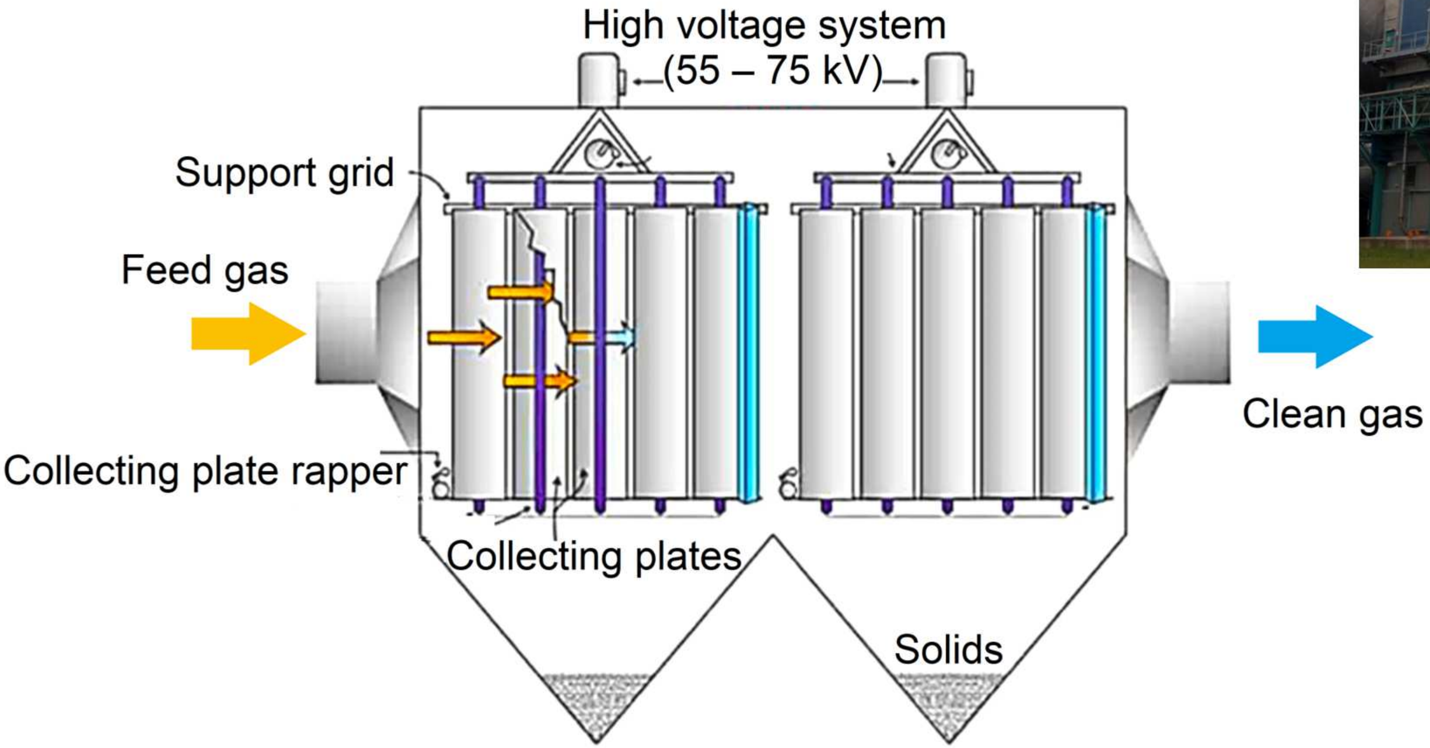




Ceramic candle filter
(up to 900 °C)

Teflon baghouse filter
(up to 280 °C)

- Electrostatic precipitator (ESP)
  - ► PM transport between 2 electrodes
  - ► internal (wire) electrode produces corona discharge
  - ► no electric arc !



Tar removal in pre-combustion proc.

- In general, tar removal processes are divided into:
  - ► cold syngas cleaning = scrubbing with liquids
    - water
    - engine oil
    - diesel fuel
    - fatty acid methyl esters derived from vegetable oil
  - ► hot syngas cleaning (metallic catalysts needed)
    - thermal cracking
      $$\text{hydrocarbons} \rightarrow C + H_2$$
    - hydrocracking
      $$\text{hydrocarbons} + H_2 \rightarrow \text{methane}$$
    - steam reforming
      $$\text{hydrocarbons} + H_2O \rightarrow CO + H_2$$
    - dry reforming
      $$\text{hydrocarbons} + CO_2 \rightarrow CO + H_2$$

Dehalogenation in pre-combustion proc.

- In general, hydrogen halides removal processes are divided into:
  - wet methods = scrubbing
    - water
    - NaOH solution
  - dry methods = physical and chemical adsorption
    - sodium aluminate ($NaAlO_4$)
    - CaO
    - limestone ($CaCO_3$)
    - Na_2CO_3
    - $NaHCO_3$
    - K_2CO_3

Denitrification in pre-combustion proc.

- In general, denitrification processes are divided into:
  - cold proceses = wet scrubbing
  - hot processes = catalytic thermal decomposition
  - hot or cold sorption (chemisorption as well as physical adsorption)

Desulfurization in pre-combustion proc.

- Hot processes
  - adsorption primarily chemical reaction with metal oxides
    Fe_2O_3, ZnO, Mn_2O_3, CuO, CaO
  - hot catalysis e.g. 10Ni-1Nb-1Ca/Al_2O_3
    sometimes not clear if the process is adsorptive or catalytic
  - in situ addition of alkaline compounds
    limestone for fluidized bed; K_2CO_3 for hydrothermal gasification
  - feeding material impregnation (coal, biomass, waste …)
    wet impregnation with Na_2CO_3 before gasification
- Cold processes
  - cryogenic distillation
  - cold catalysis system Lo-Cat™ with chelated Fe
  - oxidative desulfurization
    conversion of H_2S to elemental S using polyoxometalate
  - absorption (see the next slide)

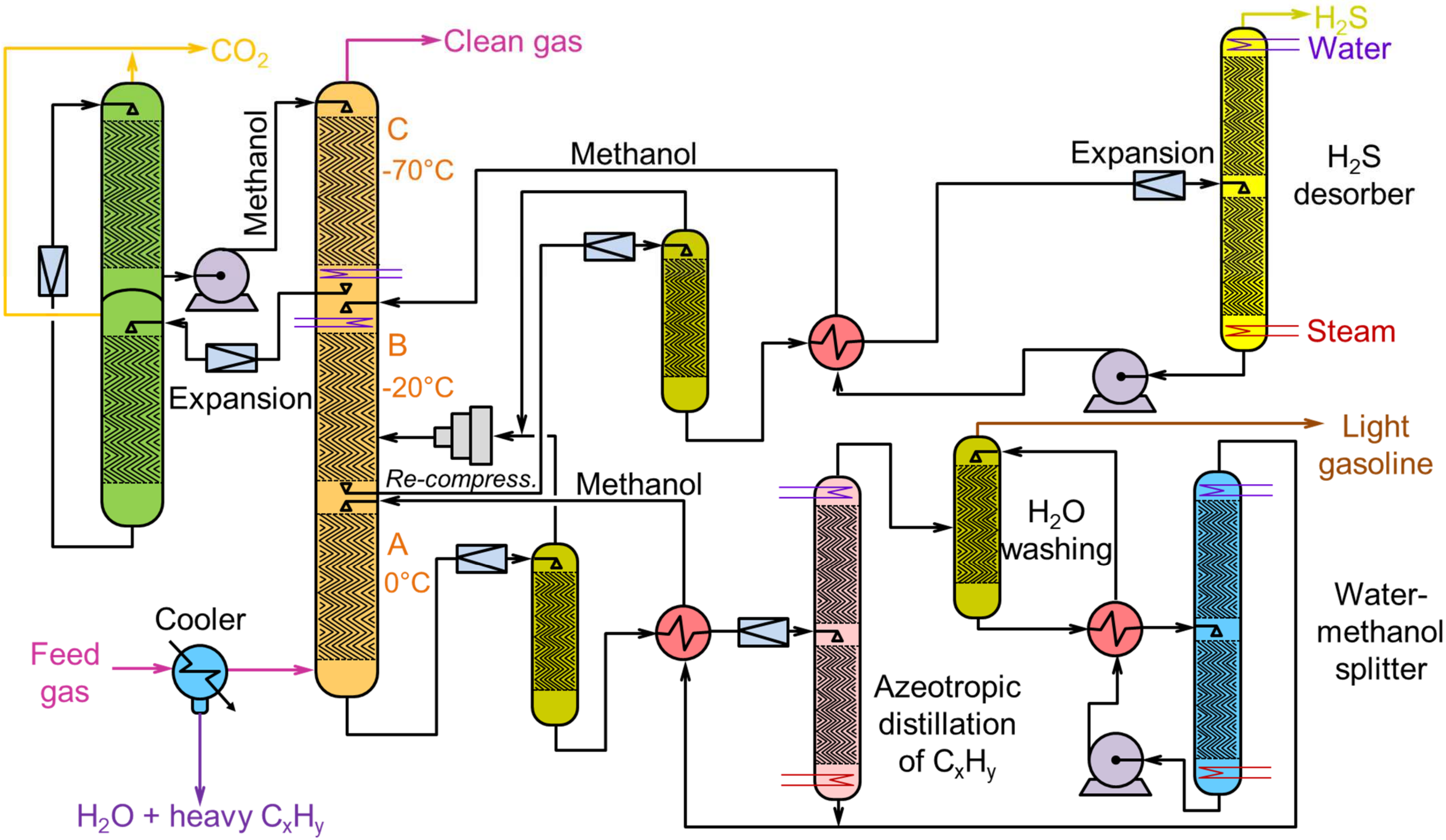
Desulfurization in pre-combustion proc.

- Wet processes overview (specific design enables also CO_2 separation)

Absorption type	Solvent	Commercial name
Physical absorption	Polyethylene glycol alkyl ethers	Selexol, Coastal AGR, Genosorb
	N-methyl-2-pyrrolidone	Purisol
	Methanol	Rectisol, Ifpexol
	Propylene carbonate	Jeffsol
Chemical absorption	Primary amines (MEA, DGA)	
	Secondary amines (DEA, DIPA)	
	Tertiary amines (MDEA, TEA)	
	Potassium carbonate	
Hybrid absorption	MEA + sulfolane	Sulfinol-M
	DIPA + sulfolane	Sulfinol-D
	Methanol + MDEA	Amisol
	Sterically hindered amines	Flexsorb

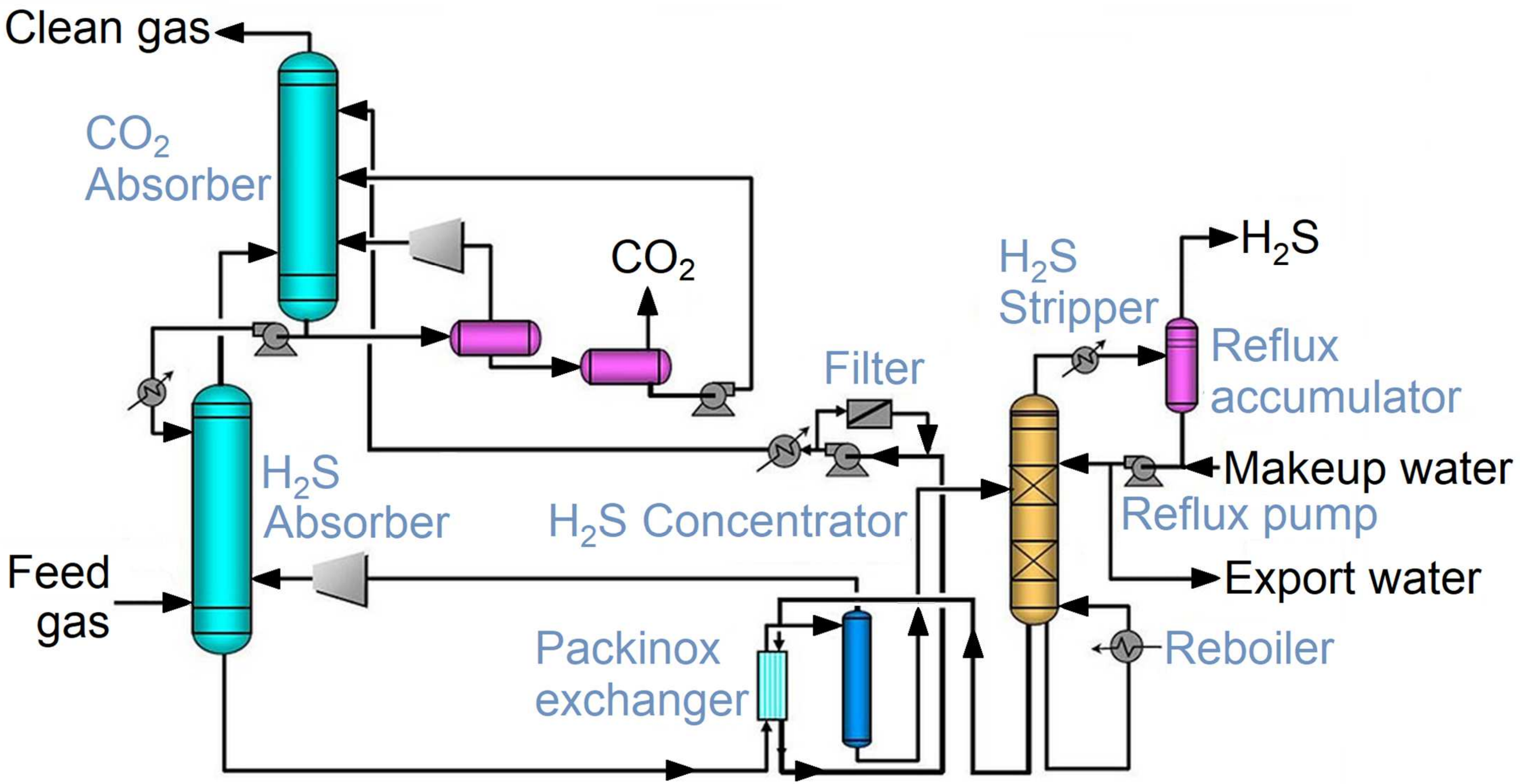
Rectisol process (by Lurgi company)

High pressure method: **A** – C_xH_y removal, **B** – H_2S removal, **C** – CO_2 removal

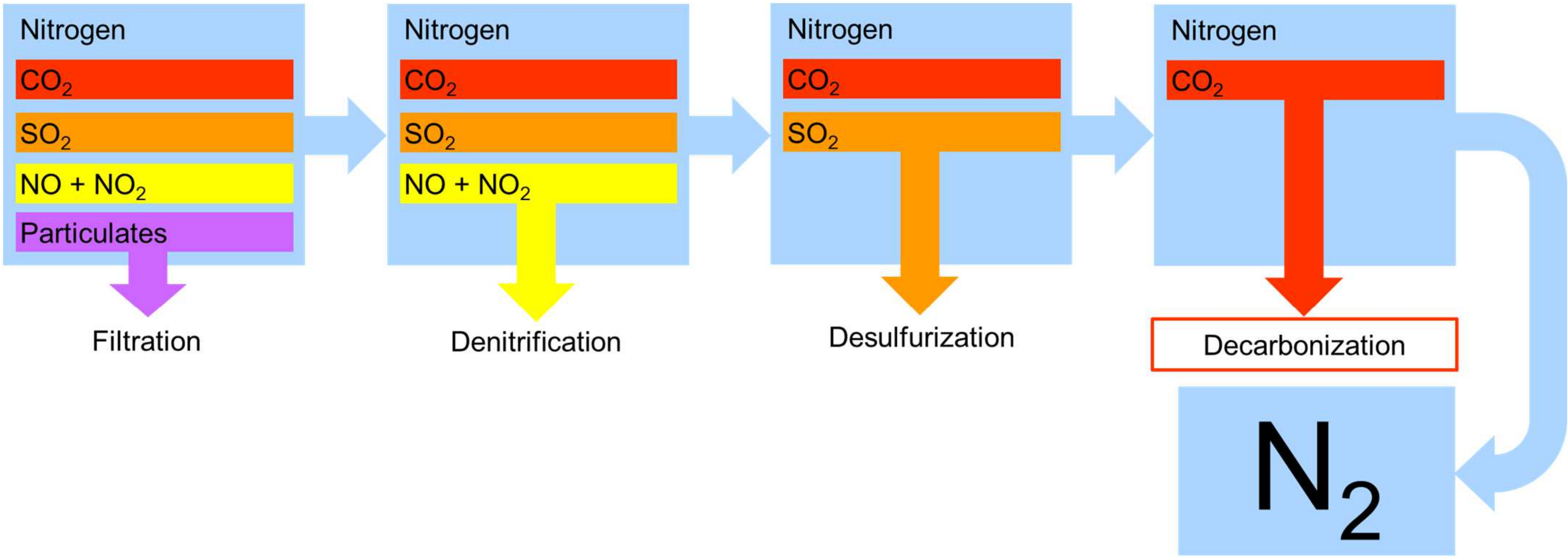


Selexol process

High pressure method (2 – 14 MPa) for acid gases removal H_2S and CO_2

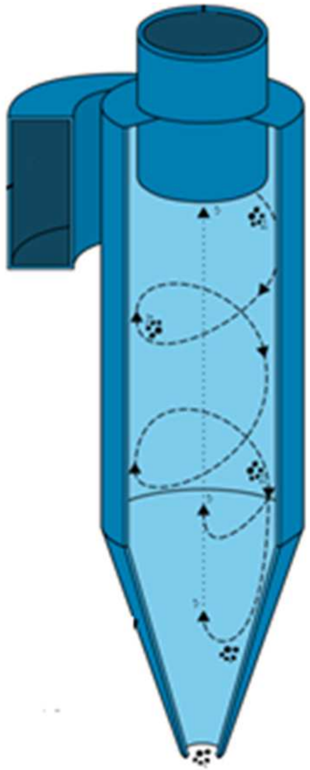


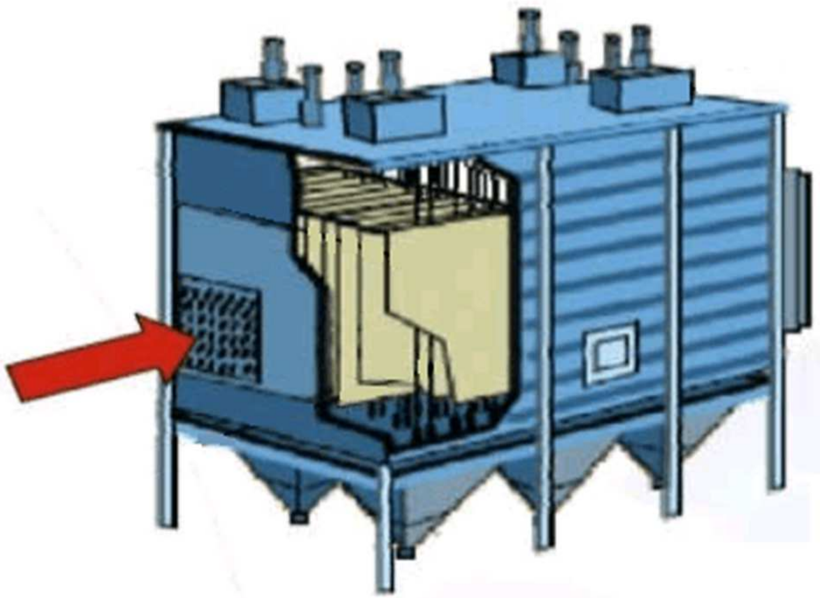
- A typical sequence of flue gas cleaning steps
  - lower number of contaminants compared to pre-combustion processes
  - but huge volume flows

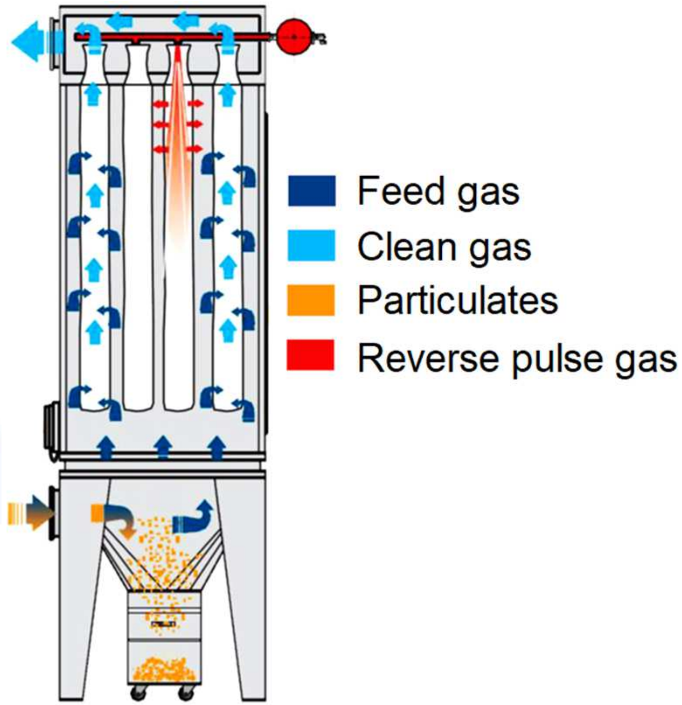


Particulates removal in post-combustion proc.

- Basically, only 3 methods widespread in the industrial practice
  - cyclones (typical pre-separators for fluidized bed combustors)
  - electrostatic separation (precipitation), ESP
  - barrier filtration – baghouse filters

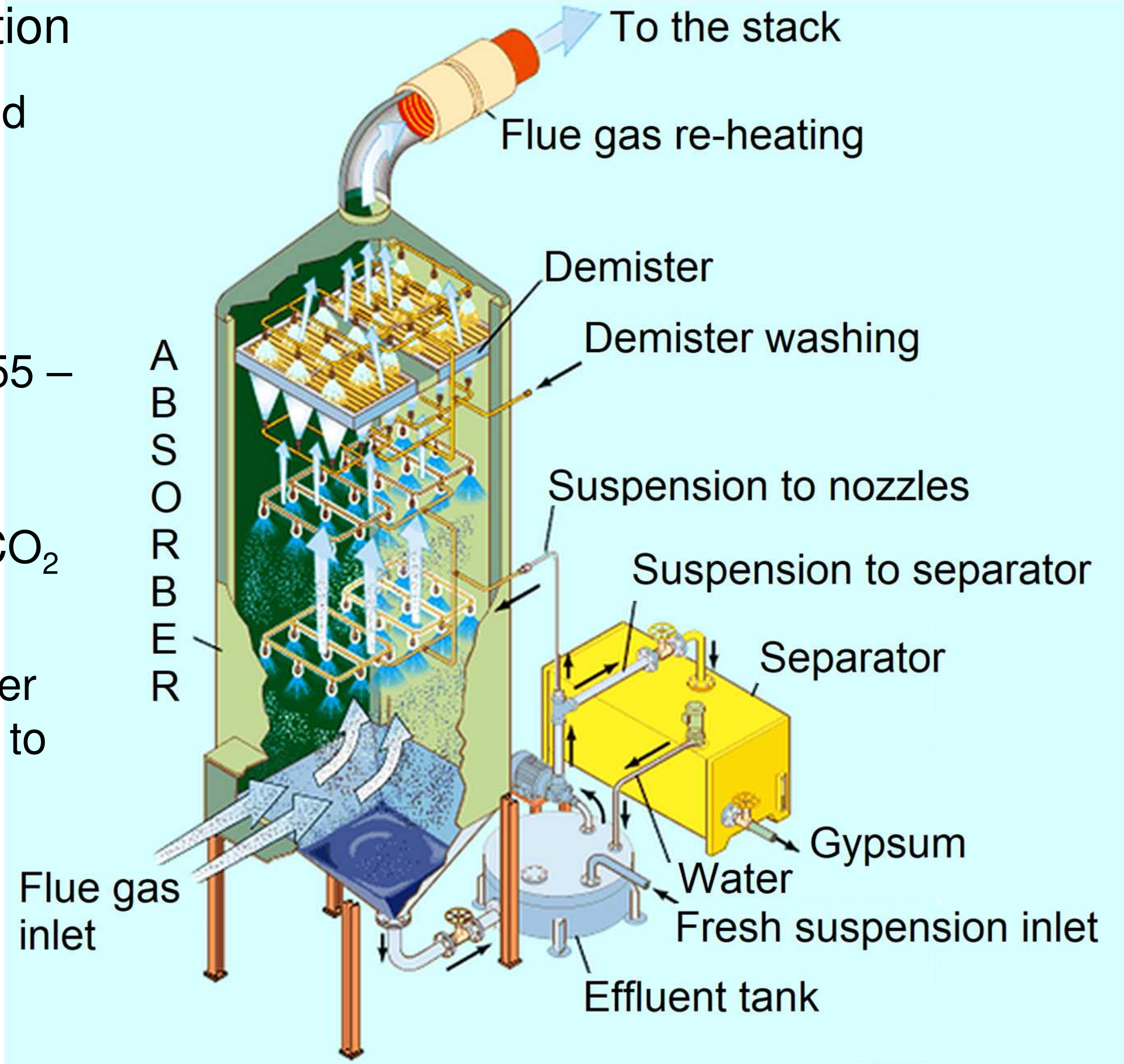






Desulfurization in post-combustion proc.

- Wet flue gas desulfurization
  - the most frequent method
  - except fluidized bed combustors
  - inlet t = 110 – 140 °C
  - optimal t for absorption 55 – 60 °C
  - Based on reaction
    $SO_2 + CaCO_3 \rightarrow CaSO_3 + CO_2$
    $2CaSO_3 + O_2 \rightarrow 2CaSO_4$
  - After passing the demister clean flue gas re-heated to ca. 75 – 95 °C



CO_2 capture in pre-/post-combustion proc.

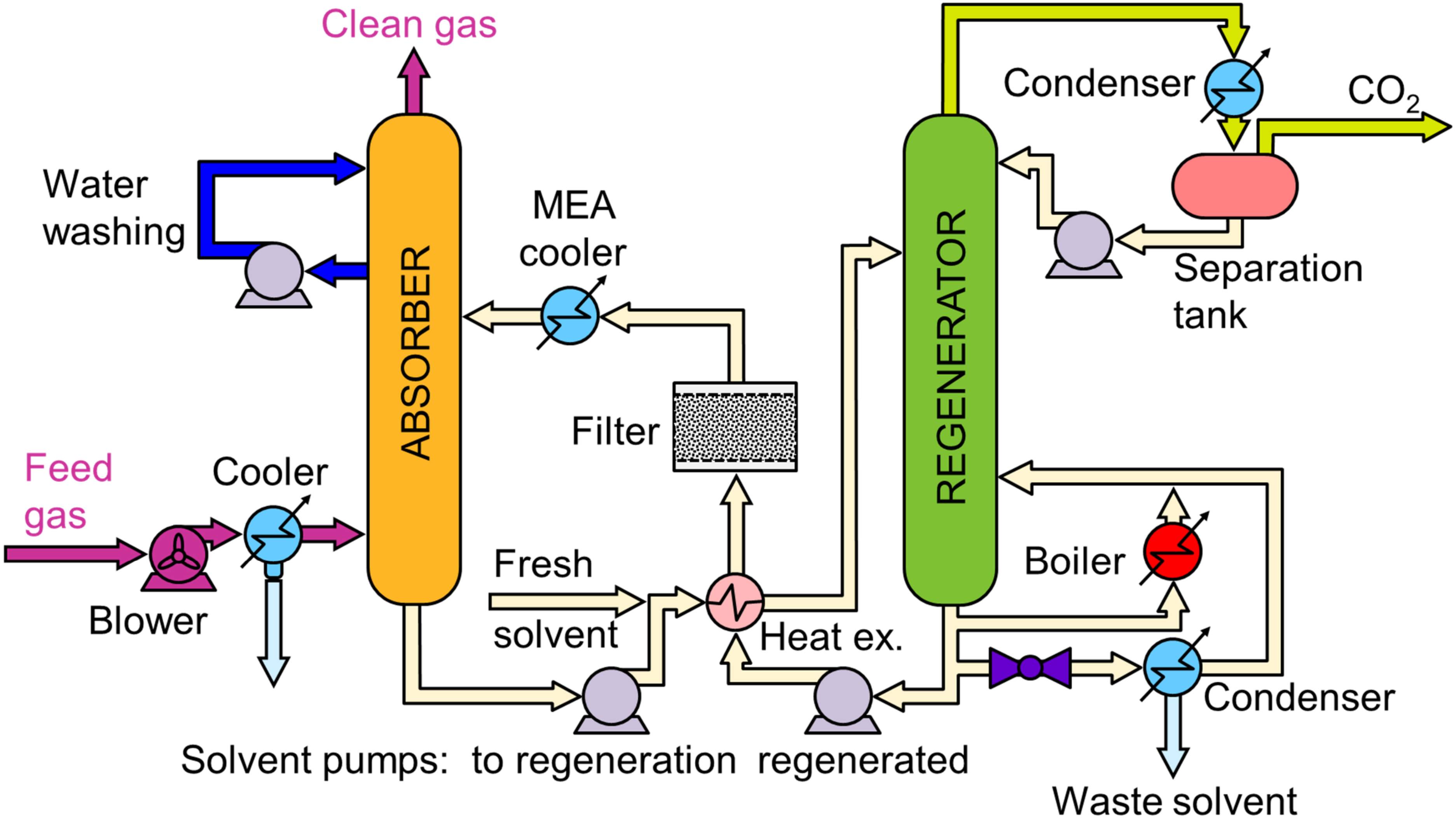
- Note: Some processes also common to desulfurization

3 main ways

Absorption	Adsorption	Membrane separation
Chemical absorption	Adsorption bed	Gas separation
MEA	Alumina	Polyphenylene oxide
NH_3 solution	Zeolites	Polydimethylsiloxane
Two-alkali system	Activated carbon	Gas absorption
Physical absorption	Regeneration method	Polypropylene
Selexol	Pressure swing	Ceramic-based systems
Rectisol	Temperature swing	
Propylene-carbonate F-process	Electric swing	Membrane / DEA
Purisol	Washing	

Methylethanolamine (MEA) process

Very similar arrangement for wide range of amine-based solvents



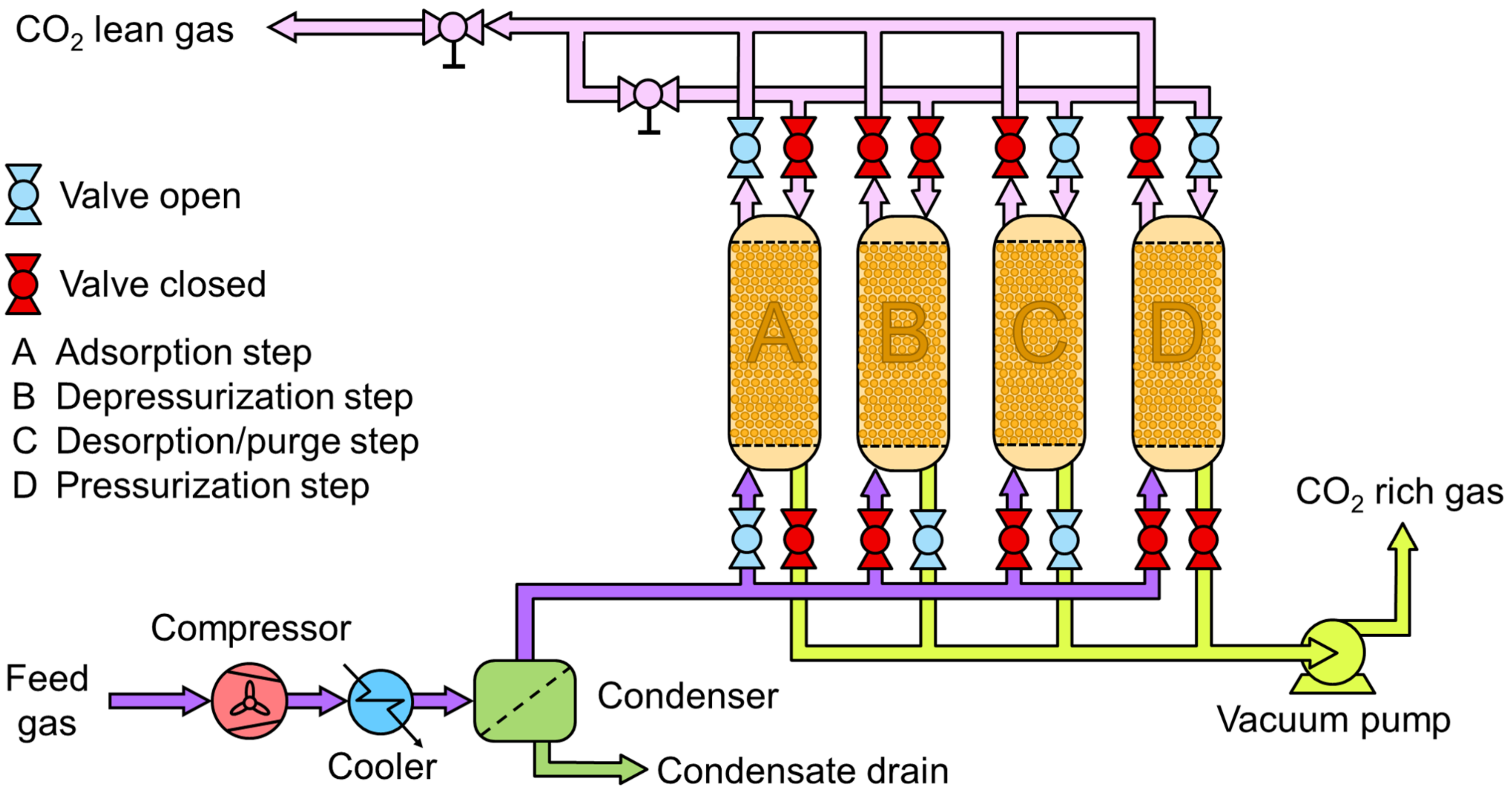
- Absorption columns filled with various packing materials (to enhance the mass exchanging surface)

Structured packing

Various types of bulk materials (Raschig rings etc.)

Pressure swing adsorption (PSA)

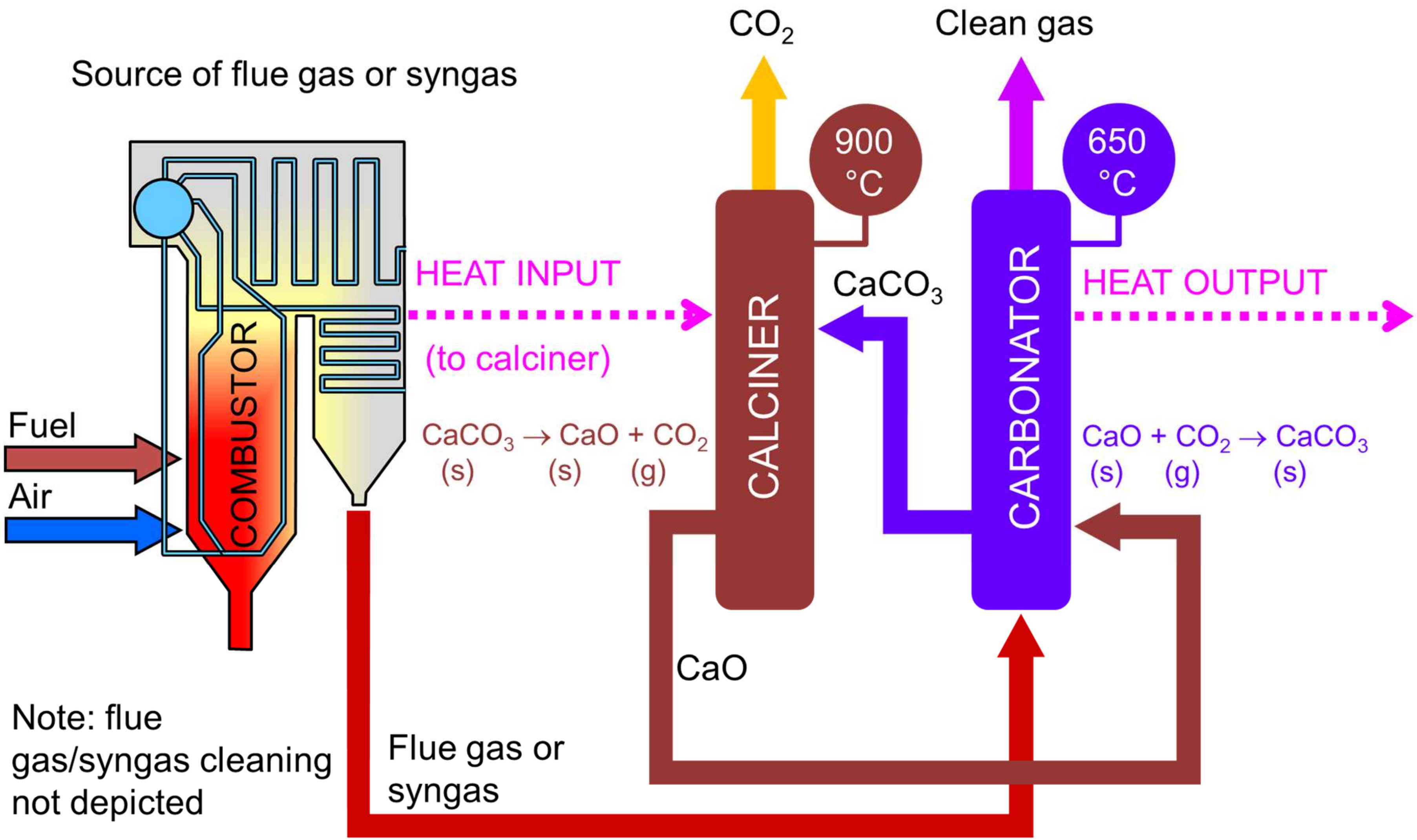
General scheme common for many gas mixtures – specific conditions and sorbents required



Pressure swing adsorption (PSA)

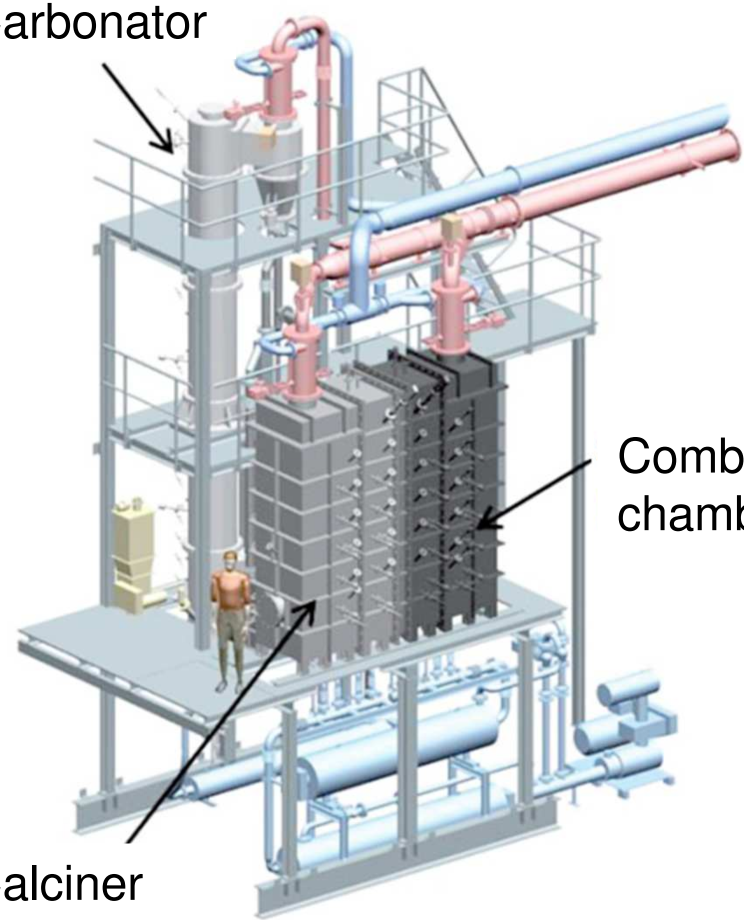
- Industrial scale unit Pioneer Technology Co.
  - Applied zeolites 5A, 13X, APGIII and activated carbon
  - H_2O and H_2S removed before PSA, CO_2 content in feed gas 13 – 15%
  - CO_2 removal efficiency 74 – 98%, CO_2 output purity 94 – 96%
  - adsorption pressure 1 – 3.5 bar / regeneration pressure 0.02 – 0.15 bar

Special example of the high-temperature chemical adsorption process



Carbonate looping adsorption (CLA)

- Pilot scale unit: Technische Universität Darmstadt
  - circulating adsorbent: $CaCO_3$ rich limestone
  - adsorption (carbonation) t = 650 °C; regeneration (calcination) t = 950 °C



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