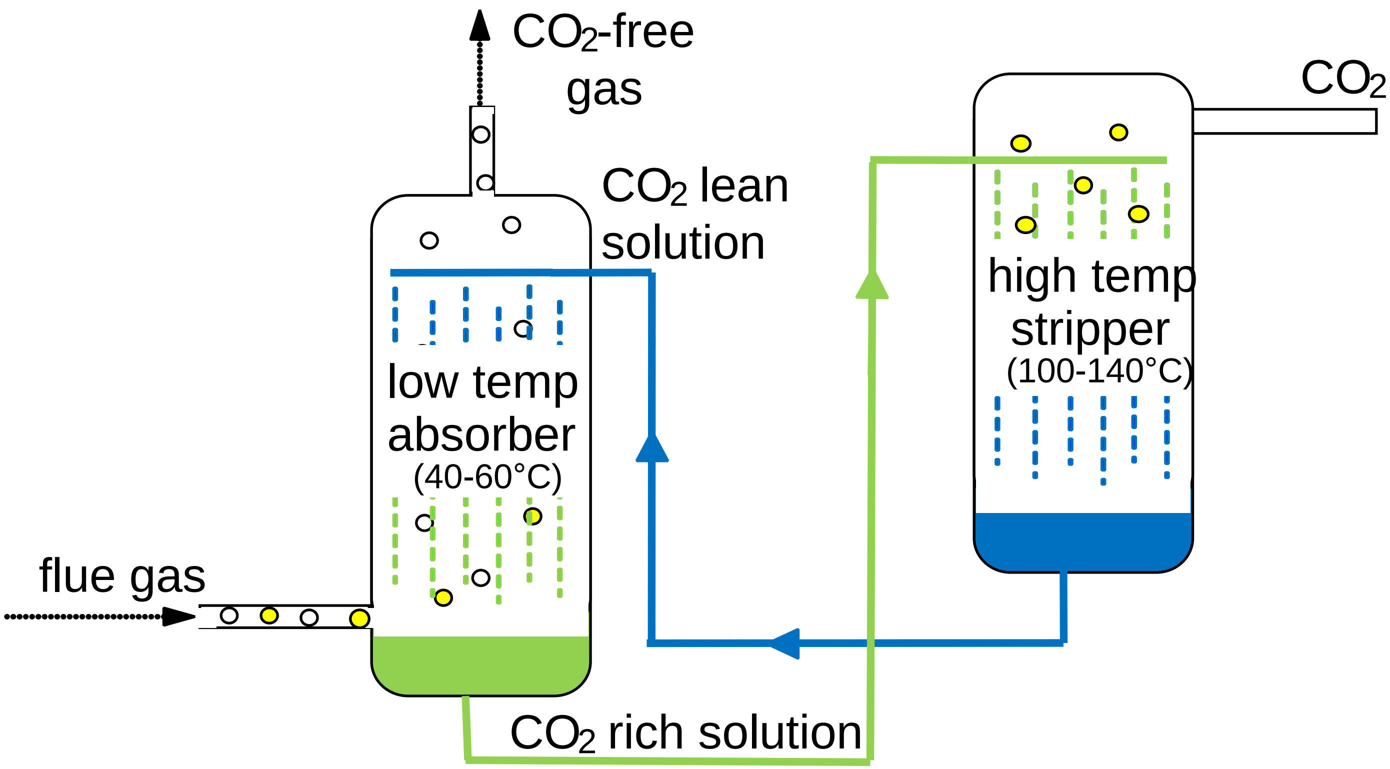
Overview of the carbon dioxide PCC process

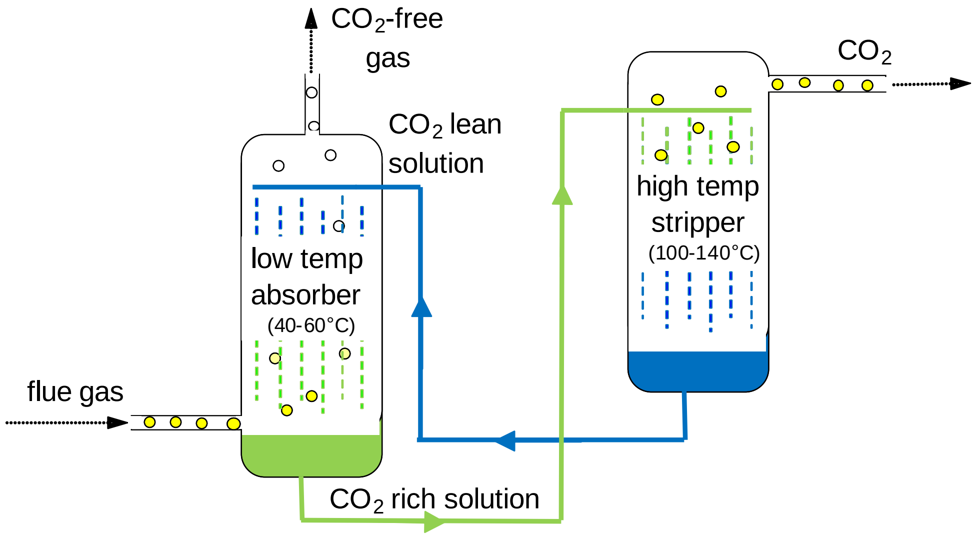
- The generic process flow diagram
- Reactive chemical absorption
- Alkanolamines and amine absorbents
- Ammonia
- Amino acids
- Carbonate solutions and slurries

The generic process flow diagram

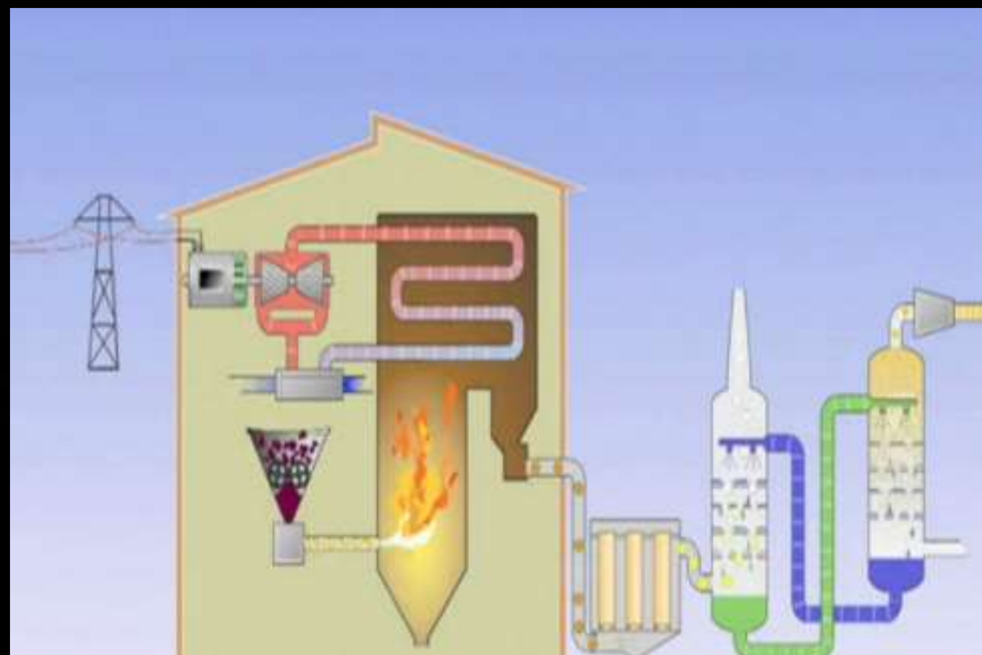


The generic process flow diagram

- Desirable properties of an absorbing solution:
  - Fast reactions allow small absorber and stripper columns.
  - High cyclic capacity minimises the amount solvent circulating.
  - Low energy requirement for the cyclic process.

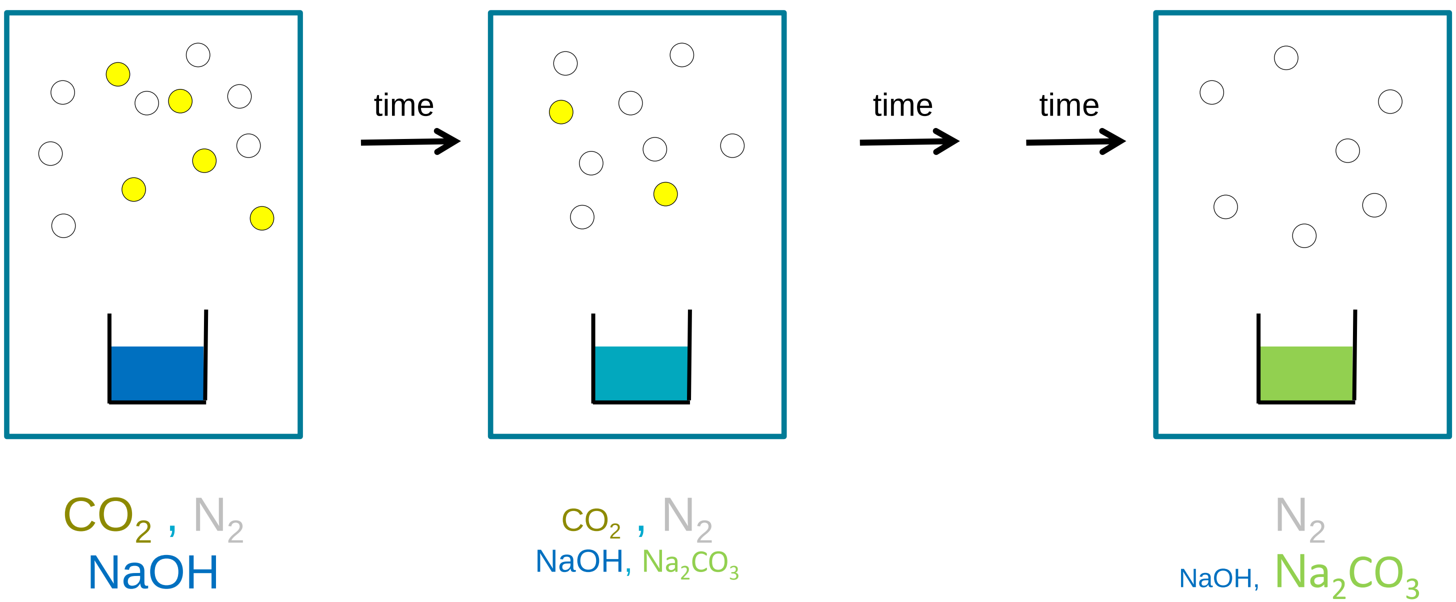


The generic process flow diagram



Reactive chemical absorption: WHY REACTIVE CHEMICAL ABSORPTION IS USED FOR PCC

- Absorption of CO_2 is very simple: upon exposure of a CO_2 containing gas to a solution of NaOH, the solution will absorb the CO_2 and turn into a solution of Na_2CO_3.



Reactive chemical absorption: WHY REACTIVE CHEMICAL ABSORPTION IS USED FOR PCC

- The problem is that the production of NaOH requires energy. In fact, the production of NaOH results in the output of more CO_2 than can be absorbed in this process.

- There are two options:
  - The absorbing agent needs to be abundant/cheap
  - The process needs to be cyclic (NaOH process is not)

Reactive chemical absorption: WHY REACTIVE CHEMICAL ABSORPTION IS USED FOR PCC

$$CO_2 + X \rightleftharpoons CO_2 \bullet X$$

- The interaction of CO_2 with a reagent X has to be reversible.
  - The reagent X has to react exclusively with CO_2, thus separating it from the other flue gas constituents
  - later the formation of the product is reversed and CO_2 is released

Reactive chemical absorption: WHY REACTIVE CHEMICAL ABSORPTION IS USED FOR PCC

$$CO_2 + X \rightleftharpoons CO_2 \cdot X$$

- Favourable properties of X:
  - reacts fast
  - large change in equilibrium position with swing
  - low energy requirements for swing
  - large cyclic capacity
  - good stability
  - low volatility
  - cheap
  - environmentally benign

Reactive chemical absorption: WHY REACTIVE CHEMICAL ABSORPTION IS USED FOR PCC

$$CO_2 + X \rightleftharpoons CO_2 \cdot X$$

Examples of different types of **X**:

- $CO_2 + H_2O \rightleftharpoons H_2CO_3$

  $H_2CO_3 + B \rightleftharpoons BH^+ + HCO_3^-$ — H_2CO_3 acts as an acid, reacting with a base B
- $CO_2 + NH_3 \rightleftharpoons H_2NCOOH$ — formation of a carbamate
- $CO_2 + \text{solid} \rightleftharpoons CO_2$solid — physical adsorption

Reactive chemical absorption: WHY REACTIVE CHEMICAL ABSORPTION IS USED FOR PCC

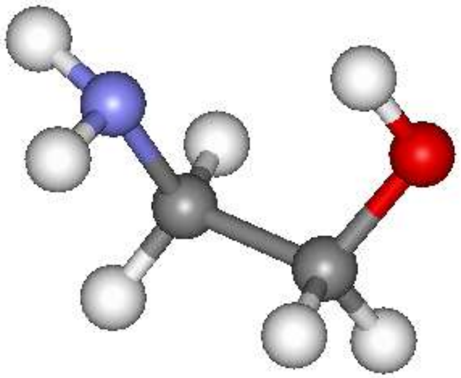
$$CO_2 + X \rightleftharpoons CO_2{\bullet}X$$

- The most important compounds X in PCC:
  - alkanolamines
  - other amines
  - ammonia
  - amino acids
  - carbonates

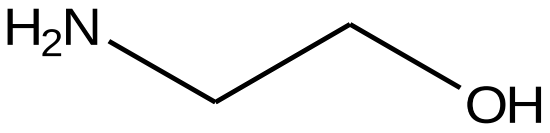
Reactive chemical absorption: ALKANOLAMINE AND OTHER AMINE ABSORBENTS

Monoethanolamine, MEA

- advantages:
  - well established absorbent for CO2, used in natural gas sweetening (removal of CO2)
  - cheap
  - the standard for all other absorbents
- disadvantages:
  - limited chemical stability
  - volatile
  - high desorption energy requirement



$H_2N\text{-}CH_2\text{-}CH_2\text{-}CH_2OH$



Reactive chemical absorption: ALKANOLAMINE AND OTHER AMINE ABSORBENTS

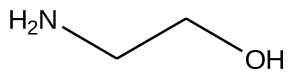
modifications on MEA

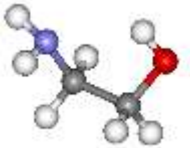
Modification	Advantages	Disadvantages
Additional steric hindrance	• less carbamate • lower volatility	• lower solubility • slower reaction
Additional alcohol groups	• lower volatility	• increased molecular weight
Cyclic amines	• fast reactions	• carbamate formation
Tertiary amines	• no carbamate	• lower solubility • slower reaction

Reactive chemical absorption: ALKANOLAMINE AND OTHER AMINE ABSORBENTS

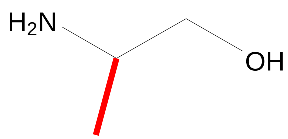
steric hindrance

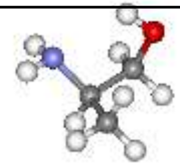
MEA
Monoethanolamine



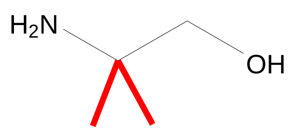


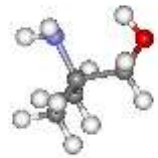
AP
Aminopropanol





AMP
2-Amino-2-methyl-1-propanol



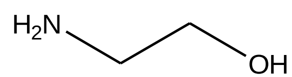


- Increasing steric hindrance
- Less carbamate
- Lower volatility
- Slower reactions

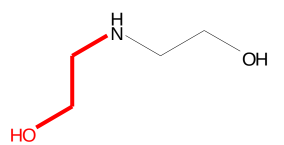
Reactive chemical absorption: ALKANOLAMINE AND OTHER AMINE ABSORBENTS

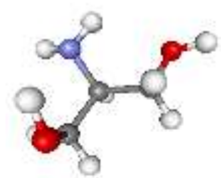
increasing numbers of alcohol groups

MEA
Monoethanolamine

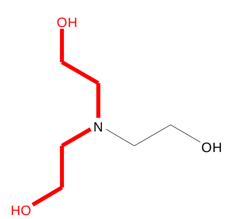


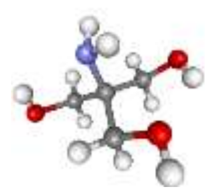
BEA
Bisethanolamine





TEA
Trisethanolamine



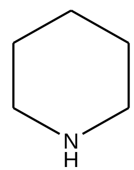


- Increasing steric hindrance
- Less carbamate
- Lower volatility
- Slower reactions

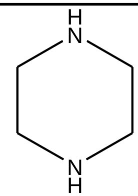
Reactive chemical absorption: ALKANOLAMINE AND OTHER AMINE ABSORBENTS

cyclic amines

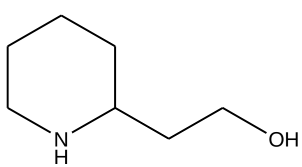
Piperidine

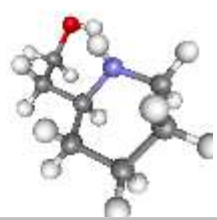


Piperazine



substituted piperidines,
e.g. 2-piperidine-ethanol

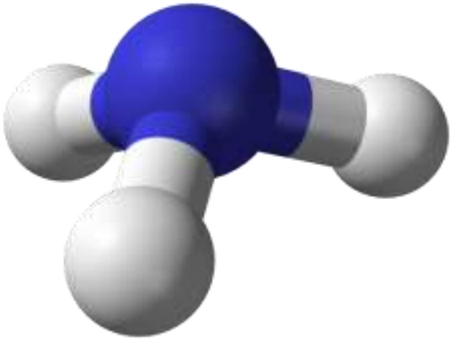




- fast reactions
- more carbonate

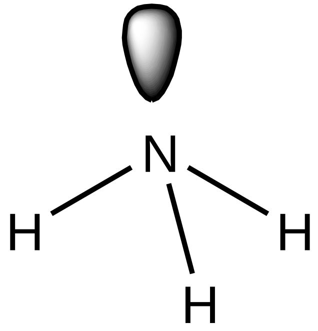
Reactive chemical absorption: AMMONIA

ammonia



- advantages:
  - fast reactions
  - cheap
  - ‘indestructible’

NH_3



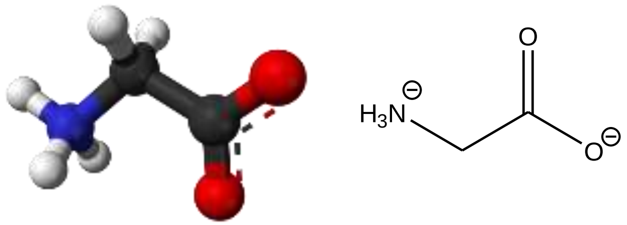
- disadvantages:
  - very high volatility
  - low temps required so slow reactivity

Reactive chemical absorption: AMINO ACIDS

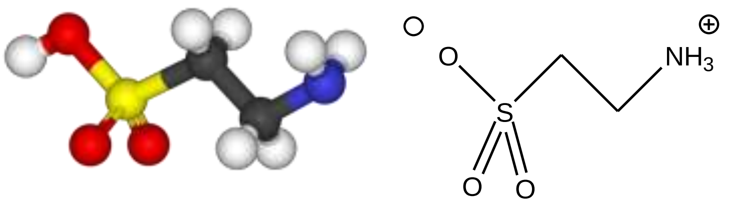
amino acids

- natural: glycine, alanine, …
- synthetic: taurine

- advantages:
  - always ionic, thus very low volatility
  - the neutral molecule at intermediate pH is a zwitter ion
- disadvantages:
  - expensive
  - limited solubility



glycine, written as the zwitter ion

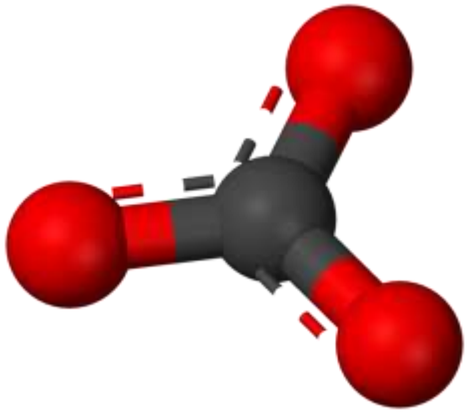


taurine, written as zwitter ion on the right

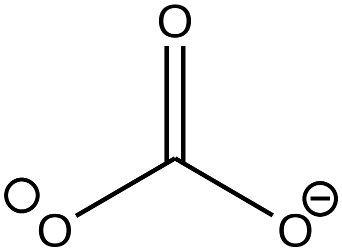
Reactive chemical absorption: CARBONATE SOLUTIONS AND SLURRIES

carbonate

- advantages:
  - very cheap
  - indestructible
  - no volatility
- disadvantages:
  - slow reactivity
  - limited cyclic capacity



CO_3^{2-}



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