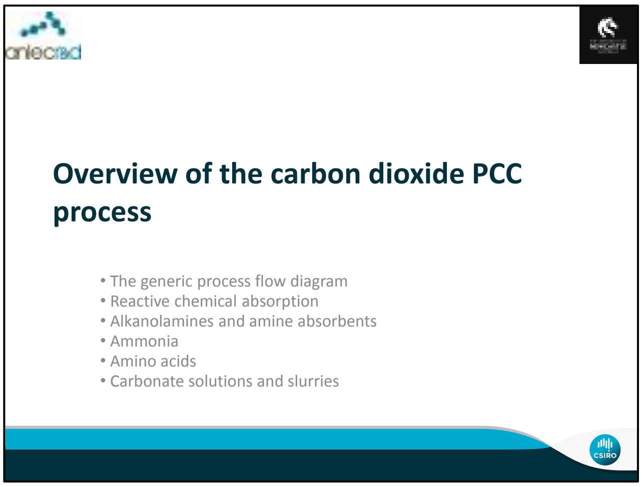
Overview PCC Process



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

Overview of the carbon dioxide PCC process

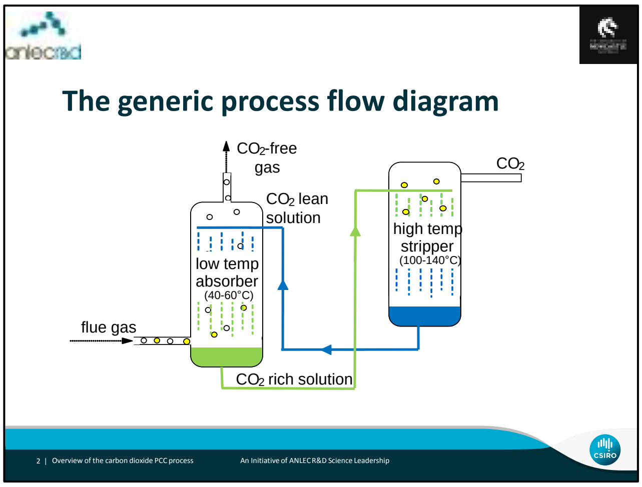
We start this section with a generic process flow diagram. It facilitates the understanding of the relatively simple process of cyclic and selective absorption of CO_2 from the flue gas stream of a power station. Included is an animation which further explains the process.

Subsequently the chemical principles of CO_2 absorption are introduced. First the nature of a chemical that selectively and reversibly reacts with CO_2 followed by the discussion of amines as such agents.

Classes of different amines are then introduced.

An interesting non-amine based process is using carbonate as the reactive component.

Overview PCC Process



The generic process flow diagram

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A schematic summary of the PCC process

a) The hot flue gas that is composed of mainly N_2 then CO_2, O_2, H_2O, and minor constituents like SO_2, NO_x, particulates etc. has to be cooled and then enters the bottom of the absorber column

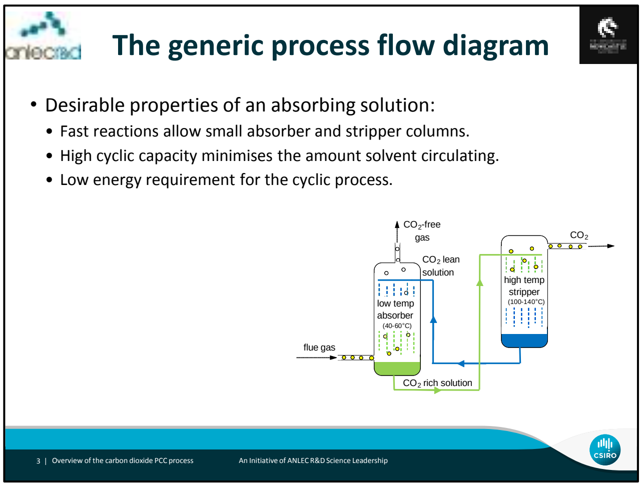
b) The gas mixture rises through the columns while the amine solution (blue) moves down. The counter current arrangement optimises the CO_2 uptake as the fresh amine solution interacts with the depleted gas at the top of the absorber.

c) The CO_2 rich amine solution (green) at the bottom of the absorber is pumped to the top of the stripper column from where it moves down.

d) The desorber column is much hotter than the absorber and as a result a certain fraction of the CO_2 is released and is collected at the top of the columns.

e) The depleted amine solution (blue) is collected at the bottom and the cycle is closed by re-introduction at the top of the absorber column.

Overview PCC Process



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.

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The important features of the PCC process

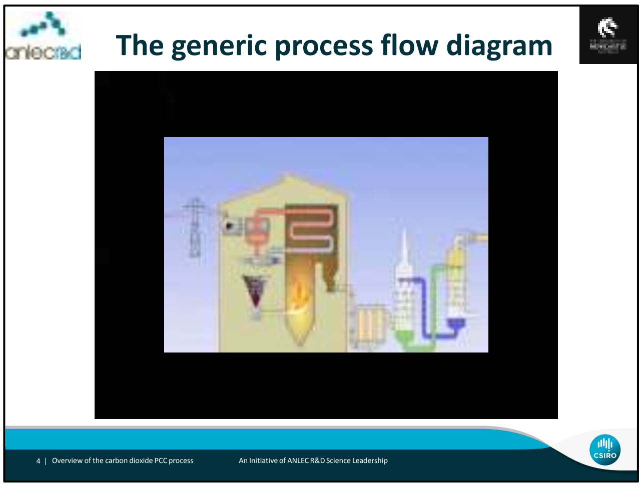
In the pursuit of improving PCC, there are two aspects that need attention:

a) The capital expenses to build the plant; the smaller the better. Fast reactions in the absorption allow smaller absorber columns and thus are advantageous

b) The energy requirement per unit of CO_2 is crucially important. Energy is required to pump the solutions but mainly for the heating of the amine solution in the stripper. Most important is a large swing in the CO_2 concentration of the solutions in the absorber and stripper; also very important is the total concentration of CO_2. The higher the concentration the less solution has to be bumped around and heated in the stripper.

c) Also important is the chemical stability of the amine. Constant replacement of decayed amine solution can be expensive ***(missing in slide)***

Overview PCC Process



The generic process flow diagram

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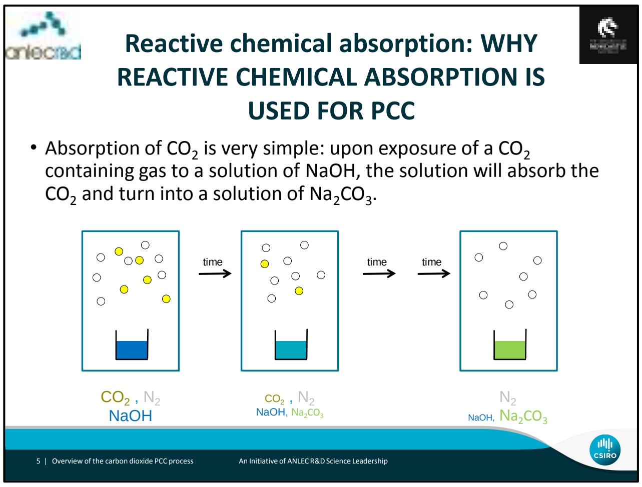
An animation of the PCC process

Unfortunately animations cannot be represented in printed matter (unless you live in the world of Harry Potter).

The power point presentation contains an animation which emphases the cyclic nature of the PCC process.



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.

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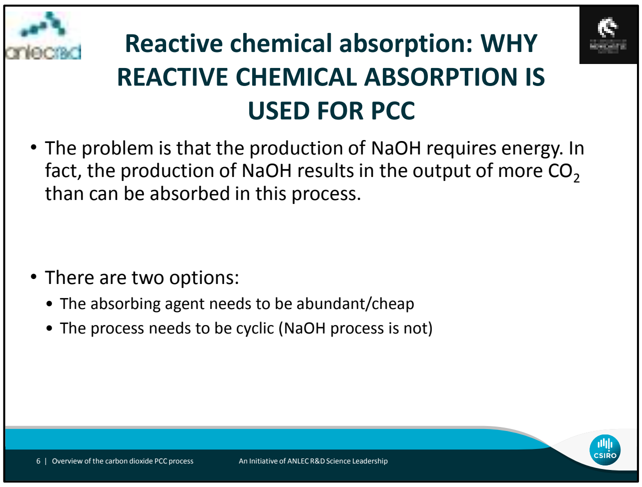
The basic principle of CO_2 absorption

This is an attempt to demonstrate the very basic principle of amine base PCC

a) Imagine a closed vessel with an atmosphere of a mixture of CO_2 and other unreactive gases, e.g. nitrogen; also in the vessel is an open container with sodium hydroxide solution
b) With time the CO_2 is absorbed into the NaOH solution which slowly is transformed into a solution of sodium carbonate, Na_2CO_3.
c) If there was enough NaOH to begin with all of the CO_2 will eventually be absorbed

Is this to solution to the greenhouse effect?



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)

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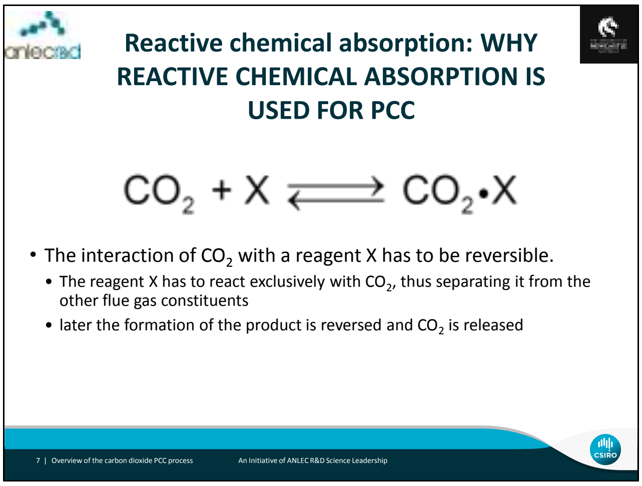
Absorption of CO_2 is easy, but not cheap

Absorption of CO_2 with a base like NaOH is very easy but does not make any sense in terms of CO_2 output. The production of NaOH requires a lot of energy and in the end more CO_2 is released in the production of the base than would be absorbed by it.

Are there alternative bases that are cheap/can be made with minimal energy input? The answer is: no! Thus, the only other option is to device a cyclic process where the reagent that captures the carbon dioxide is recycled.

The more efficient this cyclic process the better. Efficiency has several components, a process needs to be efficient in terms of energy requirement per unit of CO_2 captured, but also in terms financial requirements for plant construction and process maintenance.

Reactive Chemical Absorption



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

$$CO_2 + X \rightleftarrows CO_2{\cdot}X$$

- 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

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The Principle of the Cyclic Process

CO_2 reacts with an agent **X** to form a new molecule **$CO_2{\cdot}X$**. Crucially important is the fact that the reaction has to be reversible, i.e. the product **$CO_2{\cdot}X$** can also fall apart releasing the **CO_2**. In chemistry this reversibility is symbolised by the double arrow $\rightleftarrows$. Note that X has to react exclusively with CO_2 and not for example with the main flue gas component N_2. This requisite is easy to achieve as nitrogen in very inert, i.e. it tends not to react with anything.

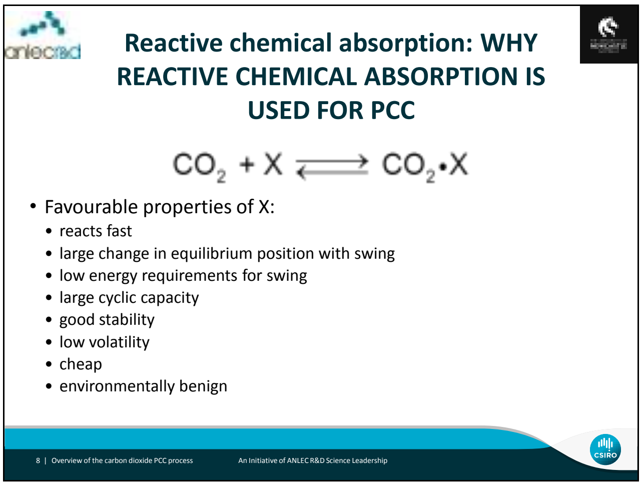
The position of the equilibrium has to be externally controllable. The most common such control parameter is the temperature. Generally, the lower the temperature the more the equilibrium lies to the right, on the side of the reaction product. Thus, at low temperature CO_2 is absorbed, at high temperature it is released.

An alternative external control is the pressure, at high pressure the formation of the product is favoured. For release of the CO_2 the pressure needs to be lowered.

It is also possible to use a third chemical that interacts with X (or CO_2) and thus influences the position of the equilibrium. The proton concentration or the pH is the most prominent example.

The temperature swing is by far the easiest of all above options.

Reactive Chemical Absorption



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

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Desirable properties of the reagent X

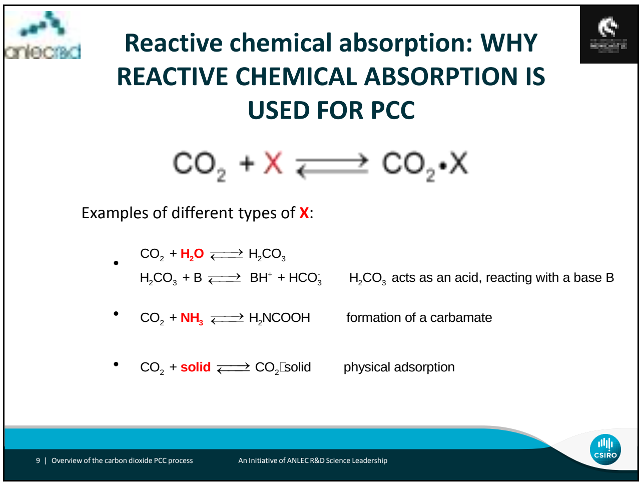
The ideal reagent reacts fast; the process requires less time and thus allows smaller absorber and desorber towers.

The larger the difference in the equilibrium position enforced by the temperature (or other) swing, the smaller the amount of solution has to be pumped, heated cooled. It is essentially the same as a large cyclic capacity, the amount of CO_2 separated per volume of solution cycled. The overall result is a small energy requirement, again per unit of CO_2 separated.

The ideal reagent X is stable, non-volatile and cheap. Most amines used for PCC decompose more or less rapidly and thus continuously need to be replaced. The exception is ammonia which however is very volatile and thus also needs continuous replacement.

Due to losses amines and their undesired reaction products escape the PCC process. At least they better do not harm the environment more than the CO_2 captured.

Reactive Chemical Absorption



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

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

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 + **solid** $\rightleftharpoons$ CO_2□solid physical adsorption

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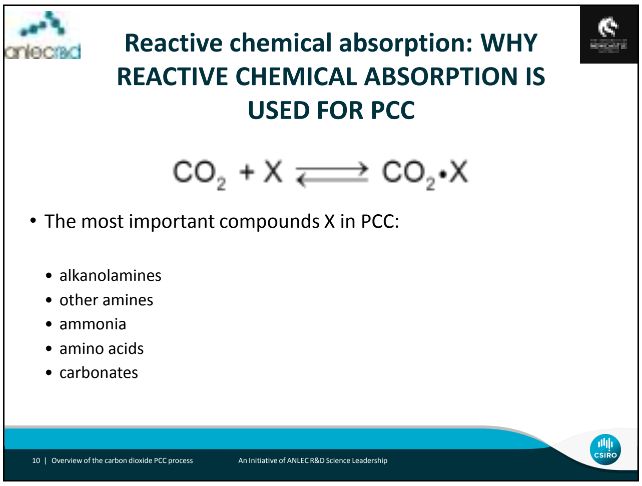
Examples of reactants X

A crucially important reactant is water! As it is the solvent for additional X's and is also a major component of any flue gas, its interactions with CO_2 cannot be ignored. Water reacts with CO_2 to form H_2CO_3, carbonic acid. Under normal conditions this equilibrium is on the left, thus the reaction itself is not important. However, H_2CO_3, as the name gives away, is an acid and reacts with bases by exchanging a proton, leaving HCO_3^-, the bicarbonate ion and protonated base. If the base is a tertiary amine this is the complete reaction.

With other amines an additional reaction occurs, e.g. CO_2 reacts with ammonia to form the carbamic acid, H_2NCOOH. It is the mono-amide of carbonic acid. This acid too releases a proton which is picked up by a base. As we will see later this reaction has major advantages as well as disadvantages.

The reactant X does not need to be in a solution, it can be attached to the surface of a solid. This appears to be a very attractive option, at least from the point of view of volatility. The main disadvantage is that such reactions tend to be far too slow for the required amounts of CO_2 to be captured.



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

$$CO_2 + X \rightleftarrows CO_2{\cdot}X$$

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

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Amines and other bases in aqueous solution as absorbents

Historically the most important amine is Mono-Ethanol-Amine, MEA, see its structure and properties on the next page. It is natural (for a chemist) to play with the motive of alkanolamines and investigate their properties.

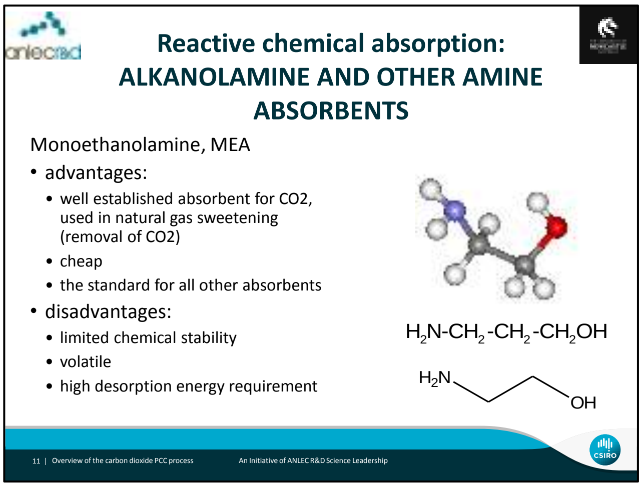
There is no need to restrict the playing to alkanolamines, to date many other amines have been tested; always in view of rate of reaction and ultimately energy requirement for the PCC process. There is almost no limit to the imagination of the chemist. Not to mention the possibility of using mixtures of amines.

A very special amine is ammonia, NH_3. Its main strengths are price, and stability, it almost cannot be destroyed. The main disadvantage is its volatility. At the top of the stripper column the separation of NH_3 from CO_2 is a formidable task in itself.

Amine acids form another interesting group. Due to their zwitter ionic nature they always exist as charged molecules and thus their volatility is negligible.

As mentioned before the base X does not need to be an amine. The most prominent base is the carbonate ion, CO_3^{2-}, it is doubly de-protonated carbonic acid. The net reaction with CO_2 is the formation of two molecules of bicarbonate. Carbonate is indestructible, very cheap and non-volatile. Its main disadvantage is the slow reactivity.

Amines, MEA and substitutions



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

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

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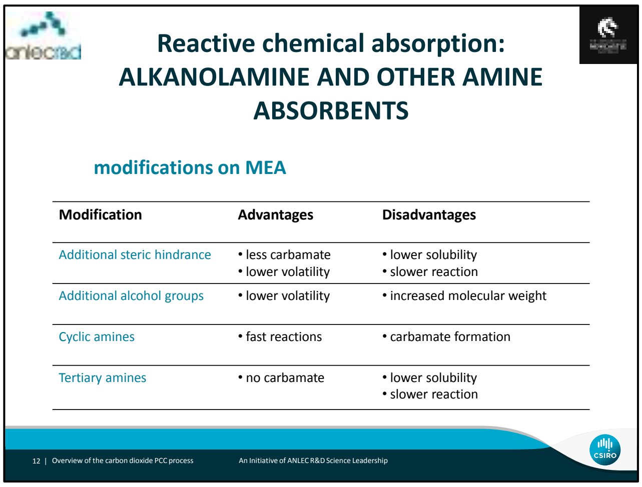
Monoethanolamine, MEA

MEA has been used to separate CO_2 from natural gas streams for many decades. The process here is called ‘gas sweetening’, as it is the removal of acidic gases. This had nothing to do with the greenhouse effect, it is just not viable to pump CO_2 through pipelines instead of the pure natural gas.

MEA is some sort of compromise between price, stability, reactivity, volatility and energy requirement for the cyclic process. It is a small molecule that means a high concentration can be achieved in water; the amine group does the work and the hydroxy group keeps the volatility reasonably under control.

Altogether, MEA as a PCC agent is well known and understood. MEA is the benchmark against which any other absorber is measured.

Amines, MEA and substitutions



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

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Modifications on MEA

As mentioned before it is the chemist's enjoyment to 'play' with molecules, here in the sense of adjusting the structure in all sorts of ways with the goal of improving its properties.

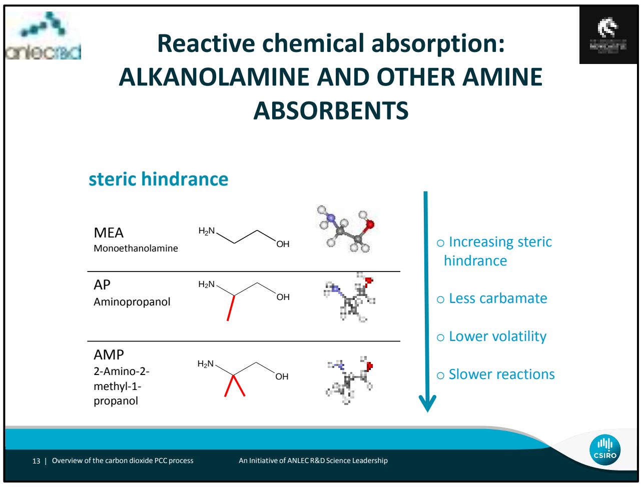
It has been mentioned before and will be discussed in detail in the section on the chemistry of PCC, carbamate formation is crucially important. And interestingly enough it has both advantages (it is fast) and disadvantages (low cyclic capacity).

Carbamate formation is reduced by the introduction of steric hindrance, i.e. reducing the space around the amine group so the CO_2 is hampered in accessing it. Additional steric hindrance automatically makes the molecule larger and reduced the solubility. The ultimate sterically hindered amine is the tertiary amine with no carbamate formation.

The alcohol group is valuable in reducing volatility, however its introduction increases the molecular weight and thus solubility.

Cyclic amines react very fast forming the carbamate with of course concomitant reduction in capacity.

Amines, MEA and substitutions



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

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Playing with steric hindrance

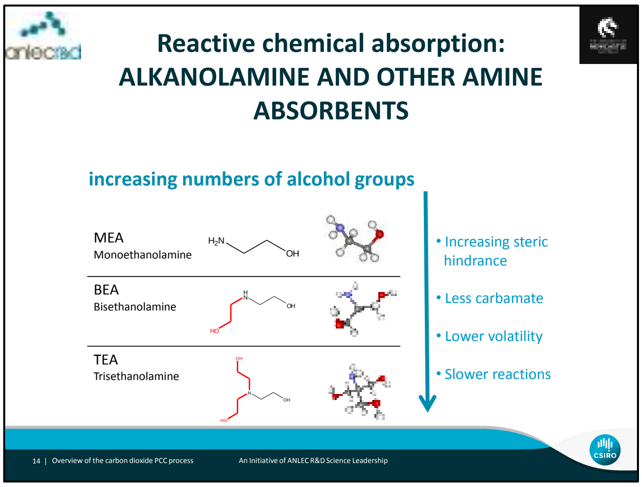
The easiest way to increase the steric hindrance around the amine is to replace a hydrogen on a neighbouring carbon with a methyl group(-CH_3). Chemists represent the methyl group with a short line, in the slide highlighted in red.

Starting with MEA, there are two hydrogens on the neighbouring CH_2 group; one or both can be replaced with a methyl group.

This process results in the planned increase in steric hindrance with the reduction in carbamate formation, concomitant slower reactivity and desirable lower volatility.

Aminopropanol, AP, is an important amine in modern PCC.

Amines, MEA and substitutions



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

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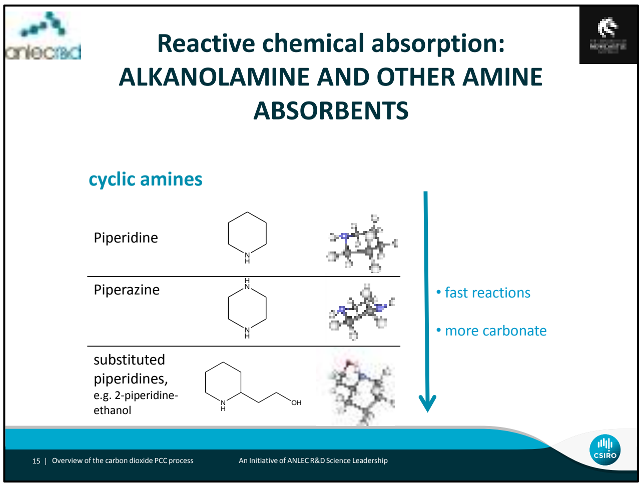
Number of alcohol groups

Increasing the number of alcohol groups can be achieved in the way shown in the slide. Starting with MEA, the nitrogen can be turned into a secondary and tertiary nitrogen by substituting the amine nitrogens with the ethanol group.

The results are similar to the increase in steric hindrance with reduction of carbamate formation, reduction in reaction speed and improved volatility.

None of the substitution products play an important role in PCC.

Amines, MEA and substitutions



Reactive chemical absorption:
ALKANOLAMINE AND OTHER AMINE ABSORBENTS

cyclic amines

Piperidine

Piperazine

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

- fast reactions
- more carbonate

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Cyclic amines

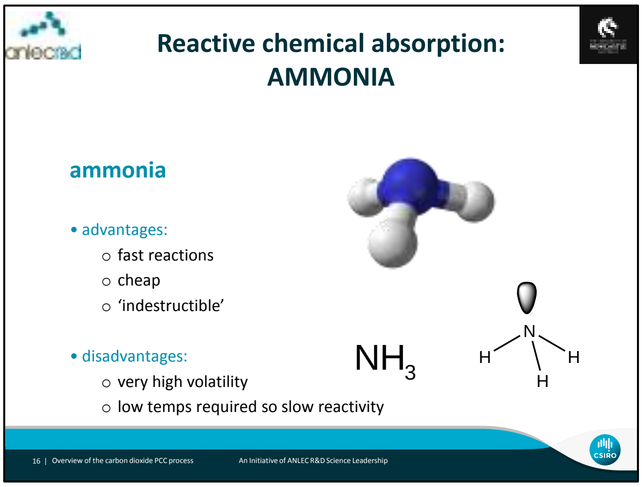
Presently, cyclic amines attract much interest.

As the structure of the molecules indicate, the substituents on the amine nitrogen and ‘bound back’ exposing the nitrogen and rendering the reaction with CO_2 to form the carbamate very fast. Indeed the cyclic amines are amongst the fastest of all amines.

Of particular interest is piperazine as it is a di-amine, one molecule of piperazine can potentially react with twice as many CO_2 molecules as the mono-amine piperazine or say MEA. Piperazine can form the di-carbamate but also the mono-carbamate with the second amine group absorbing the proton released by the carbamic acid.

Of particular interest are mixed amine solutions containing piperazine, the piperazine reacts fast while the other amine will not form the carbamate and only act as a base.

Naturally, ideas can be combined and the cyclic amines can be modified with other groups such as the ethanol group. Such substituted cyclic amines can feature very interesting and surprising properties.



Reactive chemical absorption:
AMMONIA

ammonia

- advantages:
  - fast reactions
  - cheap
  - 'indestructible'
- disadvantages:
  - very high volatility
  - low temps required so slow reactivity

NH_3

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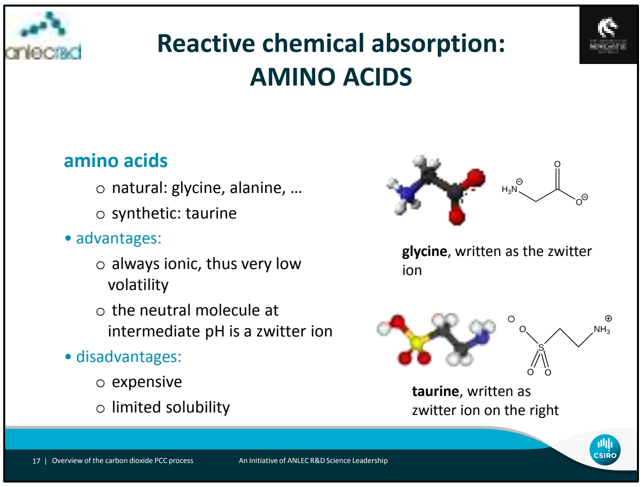
Ammonia

For several reasons ammonia is a very interesting amine and recently attracted a lot of interest for PCC applications:

- Ammonia is very stable, it essentially cannot be destroyed
- it is very cheap
- it reacts fast with CO_2 to form the carbamate
- it has good energetic properties, i.e. the energy required to separate a unit of CO_2 is relatively low

The main disadvantage if ammonia is its very high volatility. At the high temperatures of the stripper, ammonia is extremely volatile and thus it is difficult to prevent its escape together with the supposedly pure CO_2.

Amines, MEA and substitutions



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

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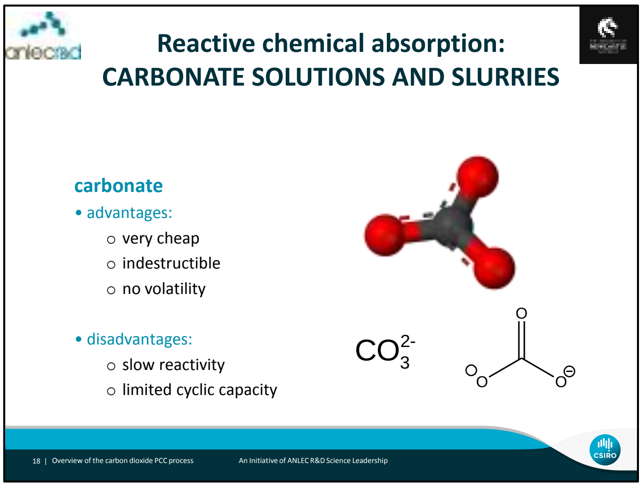
Amino Acids

Many amino acids are naturally occurring compounds and thus certainly environmentally friendly; there are also synthetic amino acids such as taurine that are explored for their properties as PCC solvents.

Amino acids have the interesting property of always existing in ionic form, irrespective of the pH: at low pH they are cations, at high pH they are anions and at intermediate pH they exist as zwitter ions, i.e. one end of the molecule carries a positive and one end a negative charge. This ensures a very low volatility under all conditions.

Disadvantages include a relatively high price, but large demand will allow large scale and thus cheap synthesis. Limited solubility is a more serious restriction as it requires large volumes of solution per unit of CO_2 removed from the gas stream.

Carbonate, CO_3^{2-}



Reactive chemical absorption:
CARBONATE SOLUTIONS AND SLURRIES

carbonate

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

CO_3^{2-}

Carbonate CO_3^{2-}

The carbonate ion is a very attractive base. It is the only base that is not an amine. As with ammonia, carbonate is very cheap and indestructible. Potassium carbonate has a very good solubility. Being an ion it is also completely non-volatile. Quite deservedly it attracts a lot of interest for PCC.

What is the problem? Not being an amine it cannot form the carbamate in a fast reaction and thus the absorption of CO_2 overall is relatively slow. Its cyclic capacity is also limited and thus a large amount of solution is required per unit of CO_2.

There are many attempts to find and/or develop catalysts that accelerate the uptake of CO_2 and thus would combine the advantages of the carbonate solution with the fast kinetics enabled by the catalyst. Naturally occurring enzymes, such as carbonic anhydrases, are extremely efficient catalysts for the reaction of CO_2 with water to form carbonic acid, whoever they are not stable under PC conditions, particularly in the stripper. Inorganic catalysts are also investigated.