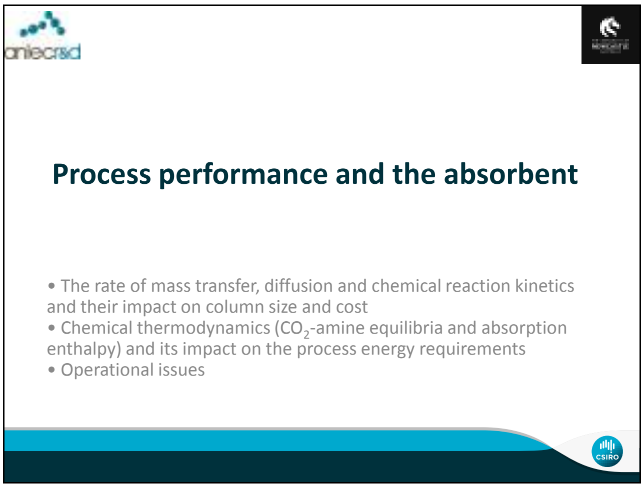
# Process performance and the absorbent



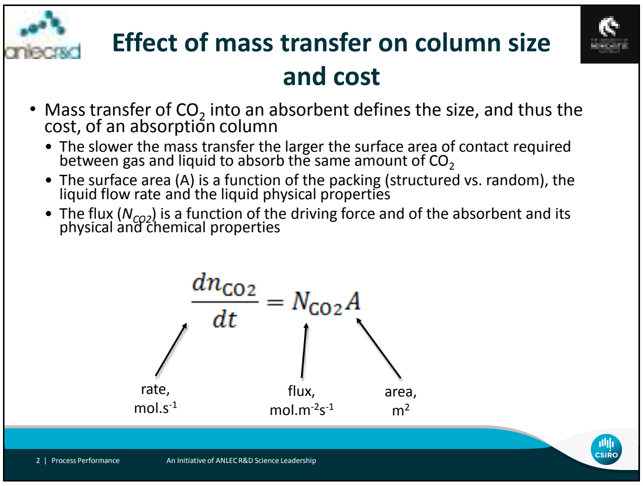
Process performance and the absorbent

- The rate of mass transfer, diffusion and chemical reaction kinetics and their impact on column size and cost
- Chemical thermodynamics ($CO_2$-amine equilibria and absorption enthalpy) and its impact on the process energy requirements
- Operational issues

The way a capture process performs is controlled by the complex interplay between a number of factors. There is: the rate at which $CO_2$ is absorbed and the amount that can be absorbed; the energy that must be input to heat the solvent and release $CO_2$; degradation of the solvent via oxidation, heating and reactions with $SO_x$ and $NO_x$; corrosion of the plant; and many more.

Dealing with these factors and the interplay between them is a challenging task.

# Effect of mass transfer on column size and cost



## Effect of mass transfer on column size and cost

- Mass transfer of $CO_2$ into an absorbent defines the size, and thus the cost, of an absorption column
  - The slower the mass transfer the larger the surface area of contact required between gas and liquid to absorb the same amount of $CO_2$
  - The surface area (A) is a function of the packing (structured vs. random), the liquid flow rate and the liquid physical properties
  - The flux ($N_{CO2}$) is a function of the driving force and of the absorbent and its physical and chemical properties

$$\frac{dn_{\mathrm{CO2}}}{dt} = N_{\mathrm{CO2}}A$$

rate, mol.$s^{-1}$

flux, mol.$m^{-2}s^{-1}$

area, $m^2$

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In terms of the capital cost of a $CO_2$ capture plant, it is typically the absorber that is the most expensive component in the gas path. They are usually made from steel. The smaller the absorber required the lower the capital cost.

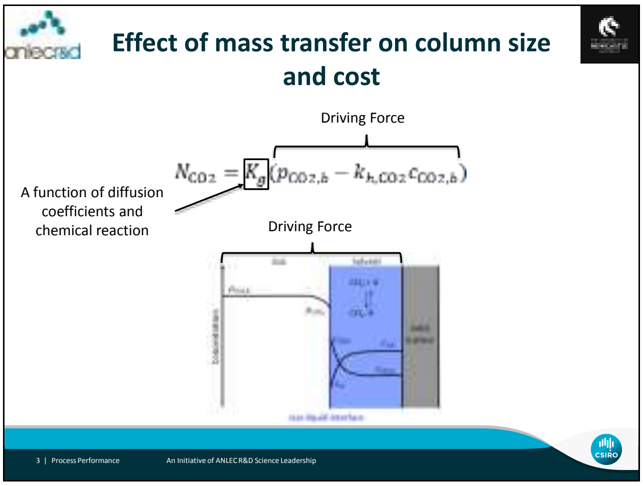
The rate at which $CO_2$ can be absorbed is governed by the mass transfer properties (the absorption flux, $N_{\mathrm{CO2}}$) and the surface area of contact between the gas and liquid $A$.

$$\frac{dn_{\mathrm{CO2}}}{dt} = N_{\mathrm{CO2}}A$$

As was described in section 5, the absorption flux is defined by a combination of driving force, diffusion and chemical reaction of $CO_2$. The surface area of contact is defined by the column dimensions, the type of packing (structured vs. random), and the flow properties of the absorbent (flow rate and physical properties).

In effect the surface area can be controlled by column design and operation while the flux is controlled by the solvent chemistry and viscosity, the extent of stripping and the $CO_2$ content of the flue gas.

# Effect of mass transfer on column size and cost



**Effect of mass transfer on column size and cost**

Driving Force

$$N_{CO2} = \boxed{K_g}(p_{CO2,b} - k_{h,CO2}c_{CO2,b})$$

A function of diffusion coefficients and chemical reaction

Driving Force

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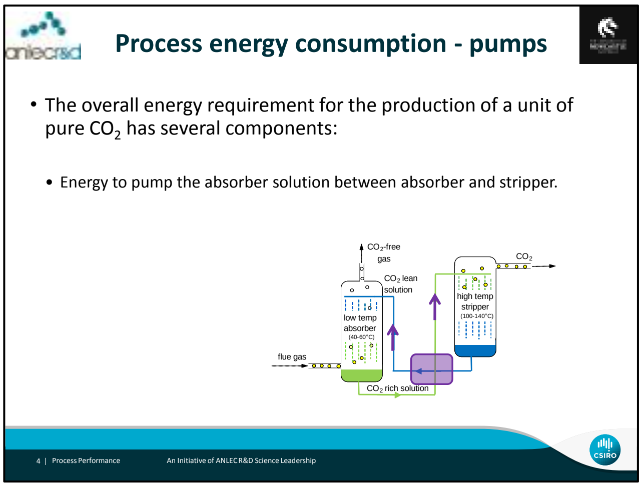
If the steady-state example is considered from section 5, the flux of $CO_2$ from the gas to the liquid, $N_{CO2}$ (mol.m$^2$.s$^{-1}$), can be described by the equation below.

$$N_{CO2} = K_g(p_{CO2,b} - k_{h,CO2}c_{CO2,b})$$

$K_g$ is the overall mass transfer coefficient from the gas to the liquid. It depends on gas phase diffusion, liquid phase diffusion and chemical reaction. The driving force is the concentration gradient from the bulk gas to the bulk liquid. If it is expressed in partial pressure it is the difference between the bulk gas partial pressure, and the partial pressure of $CO_2$ that would need to be over the bulk liquid to give the dissolved $CO_2$ concentration. This is calculated from the Henry constant $k_{h,CO2}$ which defines the solubility of $CO_2$.

$$k_{h,CO2} = \frac{p_{CO2}}{c_{CO2}}$$

# Process Energy Consumption



Process energy consumption - pumps

- The overall energy requirement for the production of a unit of pure $CO_2$ has several components:
  - Energy to pump the absorber solution between absorber and stripper.

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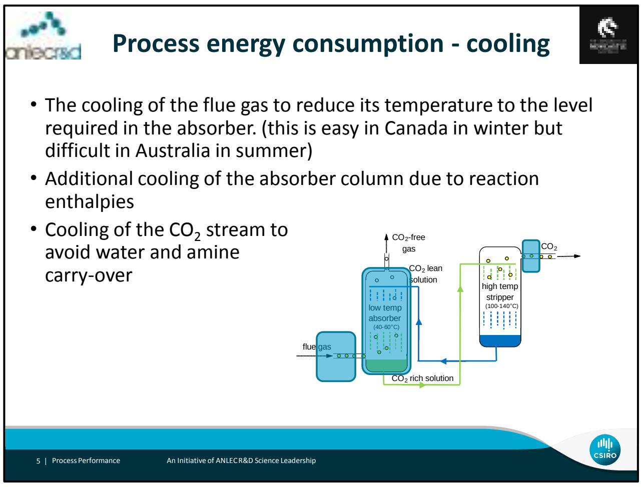
## Pumping

Large amounts of solution need to be pumped through the closed loop between absorber and stripper.

As the solution flowing to the stripper is relatively cool and needs to be heated while the solution from the stripper is hot and needs to be cooled. A heat exchanger, indicated by the purple square, that exchanges the heats between these two flows is essential but the restricted flow in the exchanger unit requires substantial additional pumping energy.

# Process Energy Consumption



## Process energy consumption - cooling

- The cooling of the flue gas to reduce its temperature to the level required in the absorber. (this is easy in Canada in winter but difficult in Australia in summer)
- Additional cooling of the absorber column due to reaction enthalpies
- Cooling of the $CO_2$ stream to avoid water and amine carry-over

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## Cooling

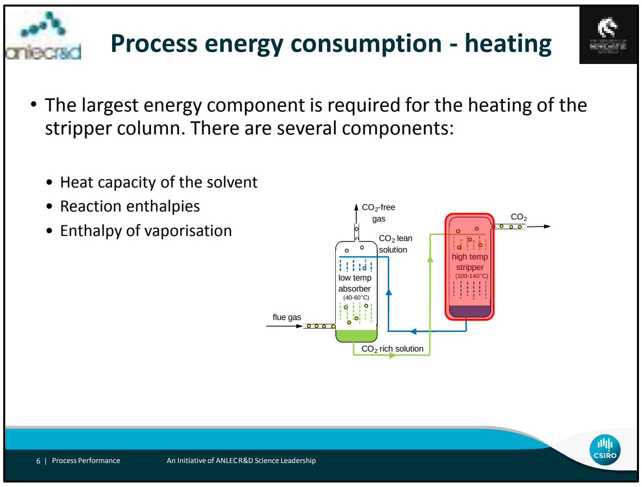
The flue gases coming from the powerstation are hot and need to be cooled before they are injected into the absorber column in order to react with the amine solution. In winter in the north of Canada this is much easier than on a hot summer day in Australia, and in Australia even water for such a purpose is rare.

The interactions of $CO_2$ with the absorber solution produce a lot of energy, they are exothermic, and thus additional cooling in required, with of course the same problems as with the cooling of the flue gases.

The $CO_2$ stream at the top of the stripper column is also hot and there is a substantial amount of steam and volatile amines in this mixture. Cooling results in water condensation and most of the amines will dissolve in this water.

Additional heat exchange units could use this waste energy for the heating in other sections of the process but this requires additional heat exchange units and pumping energy.

# Process Energy Consumption



**Process energy consumption - heating**

- The largest energy component is required for the heating of the stripper column. There are several components:
  - Heat capacity of the solvent
  - Reaction enthalpies
  - Enthalpy of vaporisation

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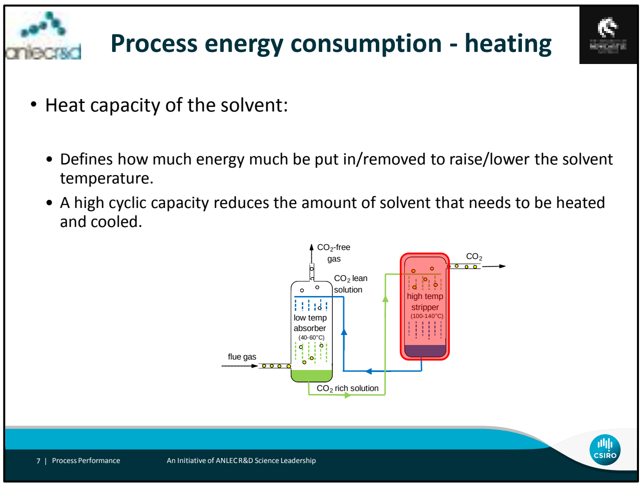
## Heating

By far the largest amount of energy required for the PCC process is used to heat the stripper column to sufficiently high temperatures, typically 100-140°C.

An interesting question is where this energy should come from.

- The idea of using solar heat is very attractive but clearly difficult from the continuity point of view: there is no sun at night and not sufficient at overcast days. As the sole energy source solar heat would require additional large energy storage facilities.
- Electric energy is plentiful in a powerstation but selling the electricity is the preferred option.
- The best option seems to be to use some of the overheated steam produced in the boiler. While this will result in reduced electricity production, it is still the most efficient way of providing the heat energy.

# Process Energy Consumption



**Process energy consumption - heating**

- Heat capacity of the solvent:
  - Defines how much energy much be put in/removed to raise/lower the solvent temperature.
  - A high cyclic capacity reduces the amount of solvent that needs to be heated and cooled.

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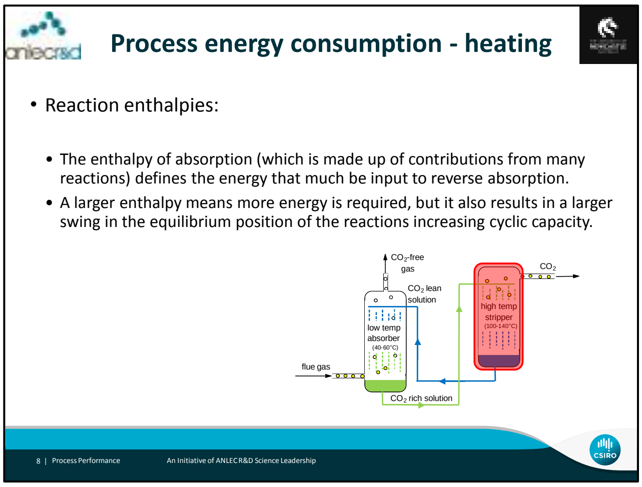
## Heating

There are several components to the energy requirements in the stripper, an important one is the heat capacity of the solvent which of course is mainly water.

Obviously, the less water required to process a ton of $CO_2$ the better. This is the main reason why absorber solution are as concentrated as possible, the more amine in the solution the more can react with $CO_2$. And the higher the stoichiometric ratio between amine and absorbed $CO_2$ is the better, this is what makes tertiary and sterically hindered amines attractive as they do not form carbamates and thus react 1:1 with $CO_2$. Unfortunately the reactions in the absorber are slow for these amines, the price to pay for that advantage in the stripper is the necessity to build a larger absorber column.

# Process Energy Consumption



**Process energy consumption - heating**

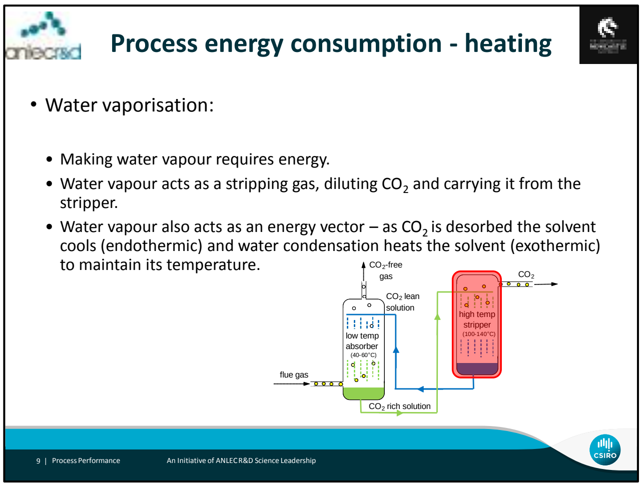
- Reaction enthalpies:
  - The enthalpy of absorption (which is made up of contributions from many reactions) defines the energy that much be input to reverse absorption.
  - A larger enthalpy means more energy is required, but it also results in a larger swing in the equilibrium position of the reactions increasing cyclic capacity.

## Heating

The equilibrium between the different forms of $CO_2$ (carbonates and carbamates) and the amine that is established in the absorber is shifted at the higher temperatures of the stripper and $CO_2$ is released. All the energy that has been released in the absorber column, and it was not welcome there, now needs to be supplied in the stripper and this is expensive now.

The reaction enthalpies for the reactions of $CO_2$ in the absorber solutions are different for different amines. Amines with small reaction enthalpies appear to be attractive, however small reaction enthalpies results in small shifts in the equilibrium positions at low and high temperatures and thus small cyclic capacities. More solution has to be pumped and the parasitic heating of the solvent gains importance.

# Process Energy Consumption



## Process energy consumption - heating

- Water vaporisation:
  - Making water vapour requires energy.
  - Water vapour acts as a stripping gas, diluting $CO_2$ and carrying it from the stripper.
  - Water vapour also acts as an energy vector – as $CO_2$ is desorbed the solvent cools (endothermic) and water condensation heats the solvent (exothermic) to maintain its temperature.

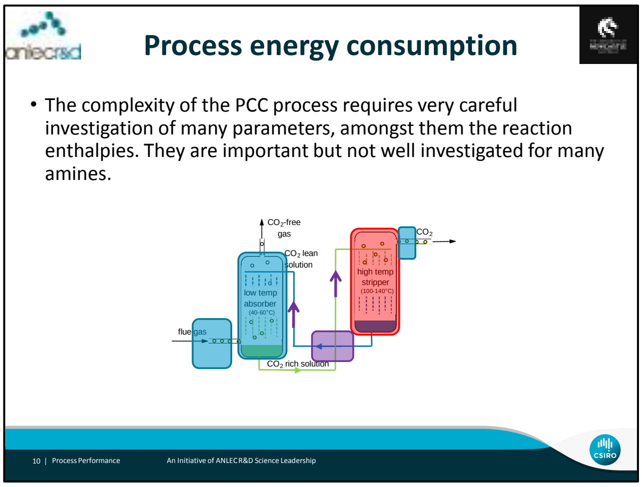
## Heating

Another interesting component of the energy requirement for heating in the stripper is the following.

The heat or enthalpy of vaporisation for water is very high thus it appears that this process should be avoided. According to Henry's law there is a clearly defined equilibrium between the $CO_2$ concentration in the gas phase and in the liquid phase; if the $CO_2$ would accumulate in the gas phase the process of its release from the solvent would quickly come to a halt. Interestingly, the water vapour that is produced in the stripper plays a very important role as a carrier gas that moves the $CO_2$ away from the interface between the solution and the gas phase, reducing the $CO_2$ concentration at the interface and thus maintaining the release of $CO_2$ from the solvent.

An additional effect of the steam in the stripper column is its property of distributing the heat throughout the complete volume.

# Process Energy Consumption



### Process energy consumption

- The complexity of the PCC process requires very careful investigation of many parameters, amongst them the reaction enthalpies. They are important but not well investigated for many amines.

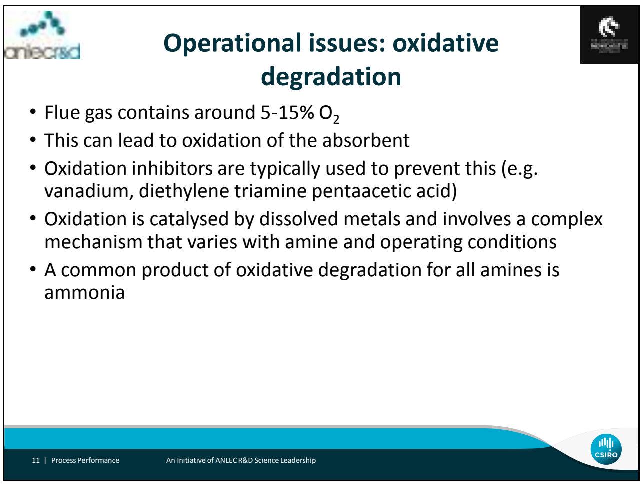
## Overall energy consumption

The PCC process is very complex and there are many components that require very careful consideration in order to minimise the cost per unit of $CO_2$ that is captured.

None of these can be discussed in any detail in this text. One which is particularly intriguing is the choice of an amine that either is reactive, i.e. it forms the carbamate, or not. Carbamate formation always results in faster absorption in the absorber column which thus can be constructed smaller, but it also results in an unfavourable 1:2 reaction, i.e. 2 amines are required per $CO_2$ absorbed. This translates into reduced capacity and thus larger volumes of solvent that need to be pumped and heated and cooled.

To find the perfect compromise is clearly not easy.

# Operational issues: oxidative degradation



Operational issues: oxidative degradation

- Flue gas contains around 5-15% $O_2$
- This can lead to oxidation of the absorbent
- Oxidation inhibitors are typically used to prevent this (e.g. vanadium, diethylene triamine pentaacetic acid)
- Oxidation is catalysed by dissolved metals and involves a complex mechanism that varies with amine and operating conditions
- A common product of oxidative degradation for all amines is ammonia

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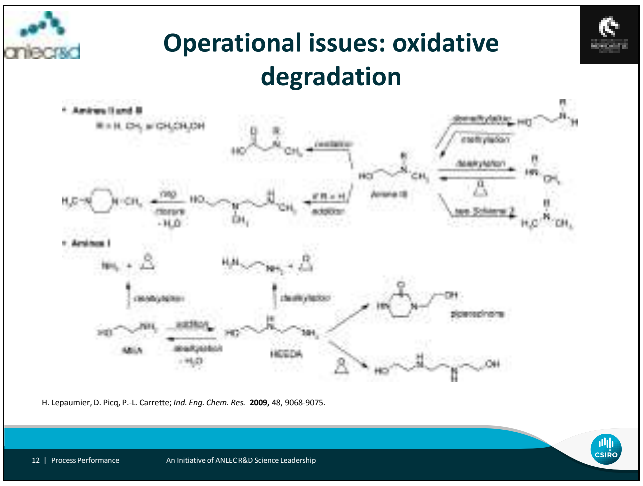
The original $CO_2$ capture process was developed for $CO_2$ from oxygen free environments. For example from natural gas or from a mixture with $H_2$ as part of ammonia synthesis. Power station flue gas contains between 5-15% residual $O_2$ following combustion. For susceptible absorbents like amines this leads to oxidation.

Oxidation reactions are very complex and typically involve the formation of radical species as intermediates. One way of reducing oxidative degradation is to add radical scavengers such as vanadium complexes.

Dissolved metals, particularly iron(II), play a role in the catalysis of oxidation. Reducing the amount of dissolved metals by limiting corrosion can reduced oxidation rates.

There are many compounds that result from the oxidative degradation of amines. However, a common product is ammonia and ammonia production can be used as a way to indirectly monitor the extent of oxidative degradation.

# Operational issues: oxidative degradation



Operational issues: oxidative degradation

H. Lepaumier, D. Picq, P.-L. Carrette; *Ind. Eng. Chem. Res.* **2009**, 48, 9068-9075.

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There are many different chemical pathways taken by oxidative degradation. It depends upon the amine structure and the conditions. These scheme summarises the different pathways for primary (I), secondary (II) and tertiary (III) amines.