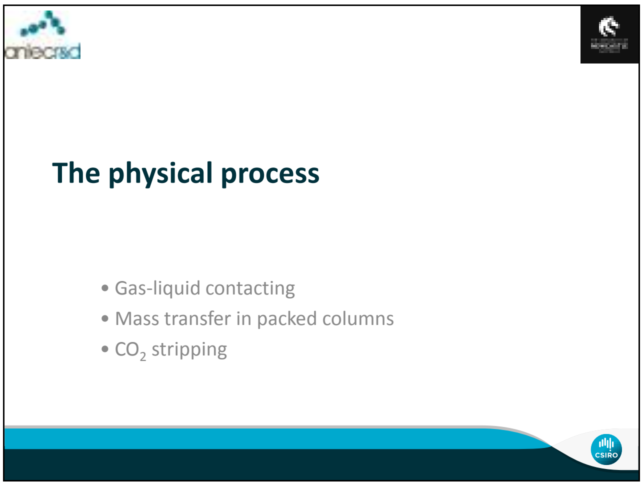
The physical process



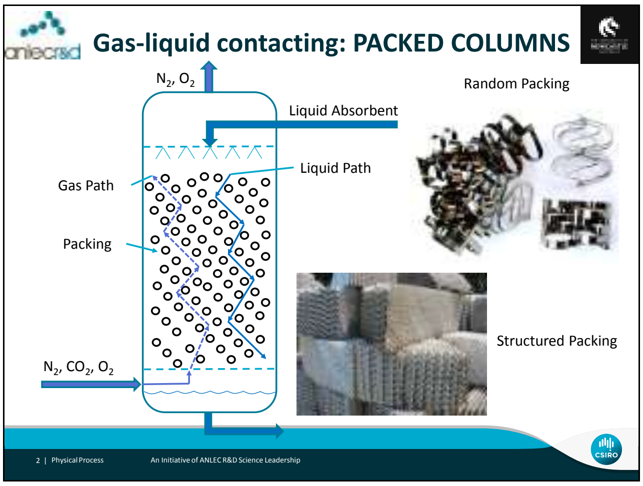
The physical process

- Gas-liquid contacting
- Mass transfer in packed columns
- CO_2 stripping

While much of what occurs during CO_2 capture is chemistry, much of it also involves physical processes. These processes are essentially governed by how the gas phase is contacted with the liquid phase. The most obvious thing to do would be to bubble the gas through the liquid. But when you are talking about millions of tonnes of gas per year, this may not be the best choice. In fact the method of choice is to use a packed column. Why this is the method of choice will be covered in this section.

Other important factors that come into play are the gas and liquid hydrodynamics, and how this influences the transfer of gas from the gas into the liquid phase. The rate of mass transfer of CO_2 into the liquid is a critical factor in the performance of a CO_2 capture process. This is governed by how the liquid and gas flow contact each other just as much as the reactions that occur.

Gas-liquid contacting: PACKED COLUMNS



Gas-liquid contacting: PACKED COLUMNS

N_2, O_2

Liquid Absorbent

Liquid Path

Gas Path

Packing

N_2, CO_2, O_2

Random Packing

Structured Packing

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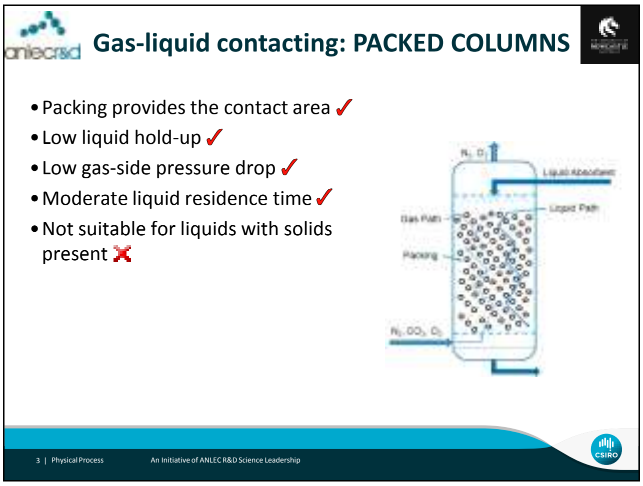
A packed column is basically a hollow vertical tube that is filled with a gas and liquid permeable packing. Liquid enters the column near the top and is sprayed over the packing. It flows down under the influence of gravity and is collected at the bottom of the column. A gas stream is introduced near the bottom of the column, above the liquid level and below the packing. The gas is driven up the column typically by a large fan and out the top.

Gas-liquid contacting: PACKED COLUMNS



Gas-liquid contacting: PACKED COLUMNS

- Packing provides the contact area ✓
- Low liquid hold-up ✓
- Low gas-side pressure drop ✓
- Moderate liquid residence time ✓
- Not suitable for liquids with solids present ✗

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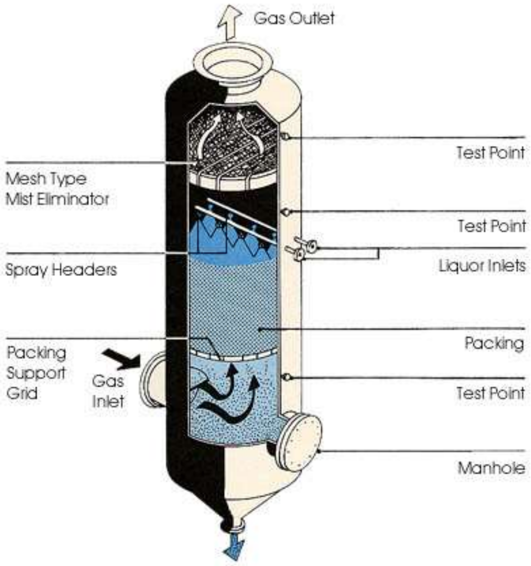
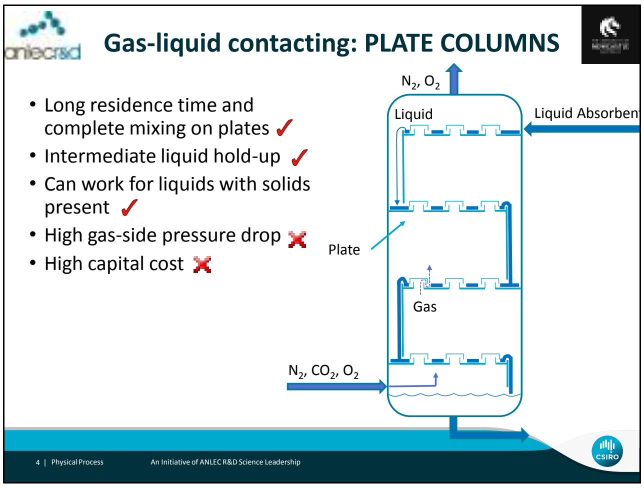
The gas and liquid are in what's called counter-current flow. That is, they flow in opposite directions. The job of the packing is to spread the liquid so that it flows as a thin film to increase the surface area of contact with the gas. As the gas and liquid flow past each other CO_2 is absorbed.

This is the preferred type of column for CO_2 absorption and desorption. The main reasons are they provide a large surface area of contact between the gas and liquid and there's little pressure drop across the column (in other words the gas moves freely). This is important when you consider the massive gas flows involved with CO_2 capture.



The insides of a packed column.

Gas-liquid contacting: PLATE COLUMNS



Gas-liquid contacting: PLATE COLUMNS

- Long residence time and complete mixing on plates ✓
- Intermediate liquid hold-up ✓
- Can work for liquids with solids present ✓
- High gas-side pressure drop ✗
- High capital cost ✗

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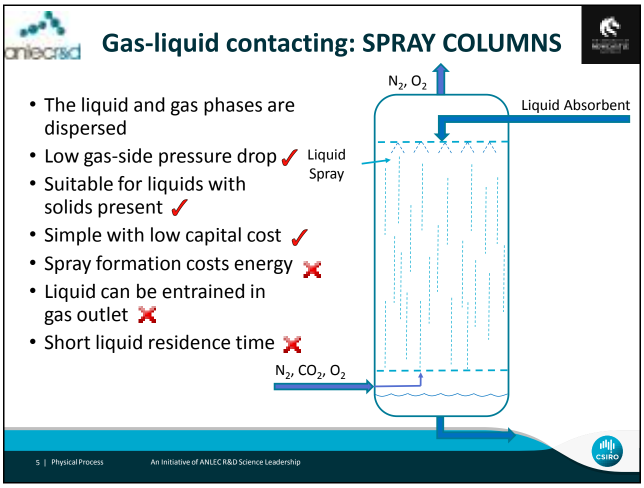
A plate column is also a hollow vertical tube but instead of packing it contains a series of platforms or plates. Again, liquid enters from the top of the column and flows downwards under gravity. The liquid flows from one plate to the next until it reaches the bottom. The gas enters the column above the liquid level and below the plates. The gas is driven up the column passing through holes in the plates that let the gas but not the liquid through. This is where mixing of the gas and liquid occurs as the gas bubbles through the flowing liquid.

A benefit of plate columns is that they can work even if solids are present. A major drawback that makes then unattractive for CO_2 capture from typical power stations is the large pressure drop. This pressure drop occurs because the gas must be forced through a relatively small number of orifices and through the liquid.

Gas-liquid contacting: SPRAY COLUMNS



Gas-liquid contacting: SPRAY COLUMNS

- The liquid and gas phases are dispersed
- Low gas-side pressure drop ✓
- Suitable for liquids with solids present ✓
- Simple with low capital cost ✓
- Spray formation costs energy ✗
- Liquid can be entrained in gas outlet ✗
- Short liquid residence time ✗

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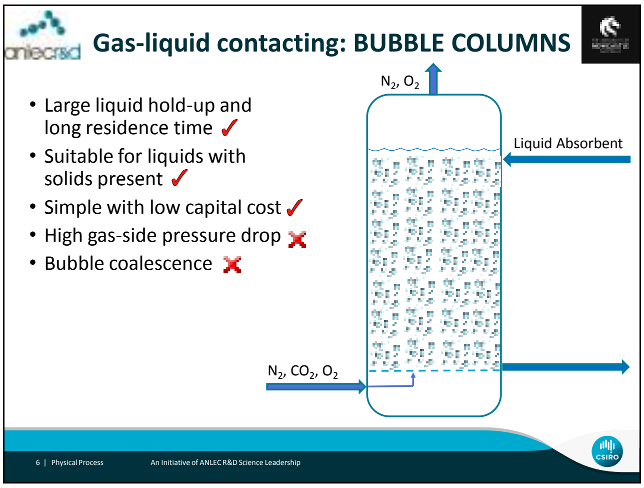
Spray columns have a very simple and low cost design. The liquid is sprayed as a fine mist from the top of the column. Gas enters at the bottom of the column and is driven upwards. The gas and liquid contact occurs as the gas and liquid move past each other.

This is a very simple and reliable design that can handle solids. The drawbacks are: formation of the spray is energy intensive; liquid is more easily entrained in the gas flow than in other columns; and the short liquid residence time means absorption must be very rapid for significant CO_2 removal to occur.

Gas-liquid contacting: BUBBLE COLUMNS



Gas-liquid contacting: BUBBLE COLUMNS

- Large liquid hold-up and long residence time ✓
- Suitable for liquids with solids present ✓
- Simple with low capital cost ✓
- High gas-side pressure drop ✗
- Bubble coalescence ✗

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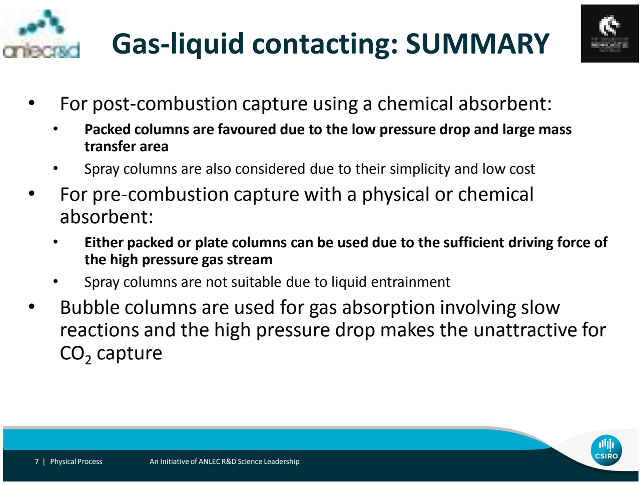
In a bubble column the column is filled with the liquid absorbent, which flows in at the top and out the bottom. The gas enters the column at the base and is sparged or bubbles through the liquid.

This is a very simple design so like a spray column it is very reliable and can also handle solids. The big drawback is pressure drop. Forcing a gas through a large column of liquid is very energy intensive. The long liquid residence time and good mixing caused by the bubbling means these columns are best suited to situations where absorption occurs slowly.

Gas-liquid contacting: SUMMARY



Gas-liquid contacting: SUMMARY

- For post-combustion capture using a chemical absorbent:
    - **Packed columns are favoured due to the low pressure drop and large mass transfer area**
    - Spray columns are also considered due to their simplicity and low cost
- For pre-combustion capture with a physical or chemical absorbent:
    - **Either packed or plate columns can be used due to the sufficient driving force of the high pressure gas stream**
    - Spray columns are not suitable due to liquid entrainment
- Bubble columns are used for gas absorption involving slow reactions and the high pressure drop makes the unattractive for CO_2 capture

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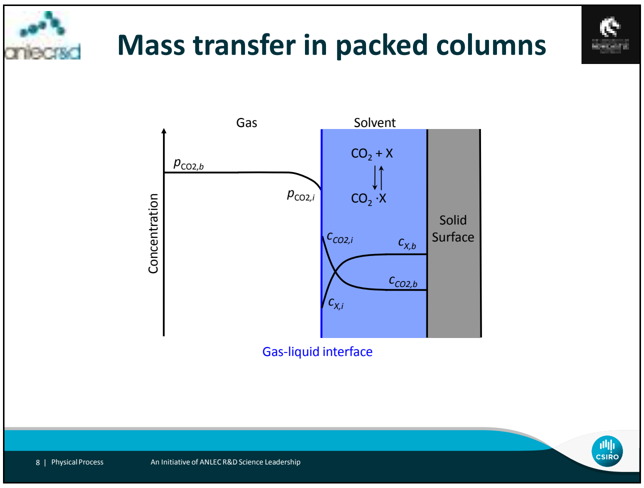
When all the benefits and drawbacks of each column are weighed up against the needs of doing CO_2 capture at coal or gas fired power stations packed columns are the winner. This mainly comes down to the combination of low pressure drop, large mass transfer area and moderate liquid residence times. Spray columns could also be considered but only for absorbent where absorption occurs very rapidly.

For higher pressure applications such as pre-combustion capture from a coal gasification plant, plate columns are also considered. The high pressure means pressure drop is less of an issue.

Bubble columns only find application where long liquid residence times are required. For example flue gas desulfurization systems where time must be allowed for oxidation of sulfite to sulfate.

Mass transfer in packed columns



Mass transfer in packed columns

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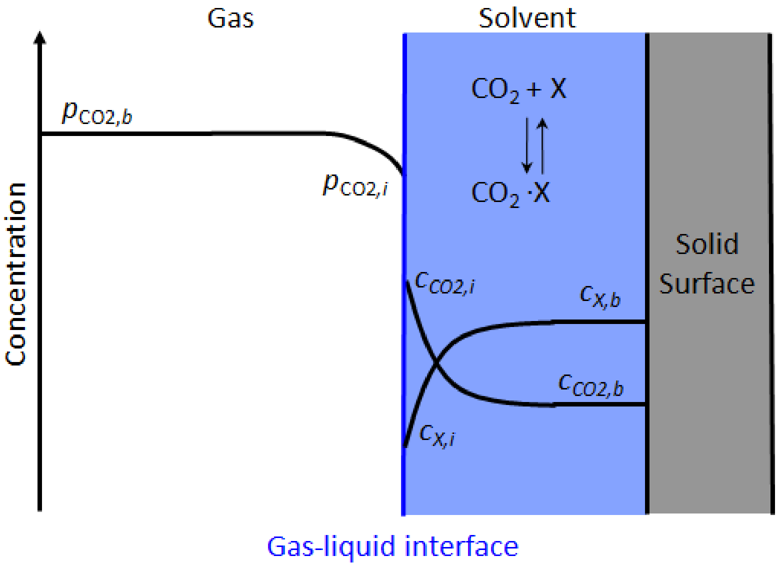
Since packed columns are the column of choice we will focus on mass transfer in this type of column. Mass transfer refers to the transfer of CO_2 from the gas to the liquid phase, or vice versa, and the various processes that control it.

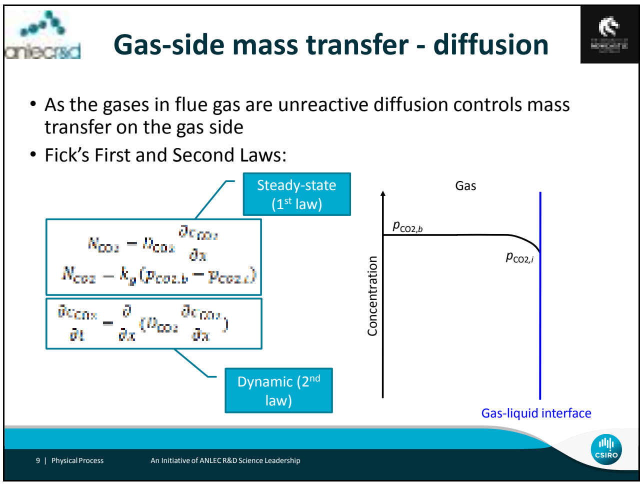
The most common way to describe mass transfer in a packed column is using what's called the two film model. This model separates what is occuring in the gas phase and the liquid phase. We have a liquid flowing down as a film over packing and a gas moving upwards in contact with the film. At the interface between the gas and liquid CO_2 gets dissolved. This depletes the gaseous CO_2 concentration at this point and more CO_2 diffuses to the interface. Once CO_2 is dissolved in the liquid it reacts with an amine (or any other component in the liquid reactive towards CO_2). This depletes the amine concentration at the gas-liquid interface and more amine diffuses to the interface.



A drawing of what is happening in the gas and liquid as mass transfer occurs.

The result of these processes of diffusion and reaction are profiles in concentration where away from the gas-liquid interface concentrations change slowly, and near the gas-liquid interface steep concentration gradients occur.

Gas-side mass transfer - diffusion



Gas-side mass transfer - diffusion

- As the gases in flue gas are unreactive diffusion controls mass transfer on the gas side
- Fick's First and Second Laws:

Steady-state (1st law)

$$N_{CO2} = D_{CO2}\frac{\partial c_{CO2}}{\partial x}$$
$$N_{CO2} = k_g(p_{CO2,b} - p_{CO2,i})$$

$$\frac{\partial c_{CO2}}{\partial t} = \frac{\partial}{\partial x}(D_{CO2}\frac{\partial c_{CO2}}{\partial x})$$

Dynamic (2nd law)

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No reactions are occurring in the gas phase. The transport of CO_2 from the bulk of the gas to the gas-liquid interface is governed by diffusion. It is driven by the concentration gradient that exists as CO_2 gets absorbed at the gas-liquid interface.

At steady-state, where no net changes in the conditions such as concentration or temperature are occurring with time, Fick's 1st law describes mass transfer.

$$N_{\mathrm{CO2}} = D_{\mathrm{CO2}}\frac{\partial c_{\mathrm{CO2}}}{\partial x}$$

$$N_{CO2} = k_g(p_{CO2,b} - p_{CO2,i})$$

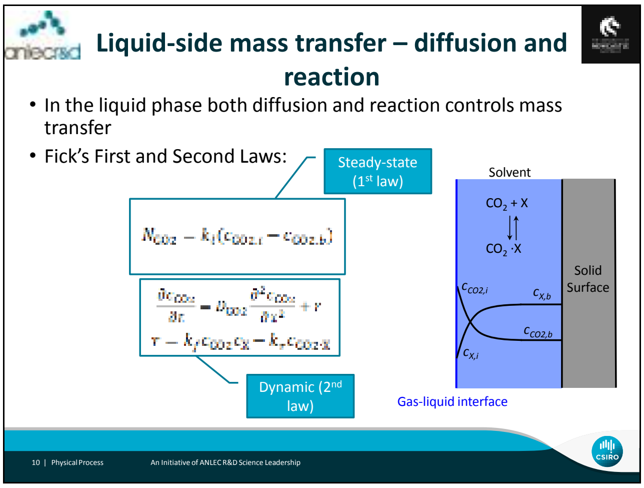
The first equation is the flux (N_{CO2}, mol.m^{-2}.s^{-2}) as a function of the diffusion coefficient D_{CO2} and rate of change in CO_2 concentration. The second is written in terms of the gas-side mass transfer coefficient k_g. The difference in CO_2 partial pressure between the bulk gas and at the gas-liquid interface is called the driving force.

If things are dynamic and changes are occurring as a function of time Fick's 2nd law is required.

$$\frac{\partial c_{\mathrm{CO2}}}{\partial t} = \frac{\partial}{\partial x}(D_{\mathrm{CO2}}\frac{\partial c_{\mathrm{CO2}}}{\partial x})$$

This can be derived from Fick's 1st law by applying conservation of mass.

Liquid-side mass transfer – diffusion and reaction



Liquid-side mass transfer – diffusion and reaction

- In the liquid phase both diffusion and reaction controls mass transfer
- Fick's First and Second Laws:

Steady-state (1st law)

$$N_{CO2} = k_l(c_{CO2,i} - c_{CO2,b})$$

$$\frac{\partial c_{CO2}}{\partial t} = D_{CO2}\frac{\partial^2 c_{CO2}}{\partial x^2} + r$$

$$r = k_f c_{CO2} c_X - k_r c_{CO2 \cdot X}$$

Dynamic (2nd law)

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When CO_2 is absorbed into a reactive liquid the flux is controlled by both diffusion of CO_2 and reactants as well as the rates of chemical reaction and the reaction equilibrium. If reactants are in large excess and can be assumed steady-state, a similar equation to that used on the gas-side can be applied.

$$N_{\mathrm{CO2}} = k_l(c_{\mathrm{CO2},i} - c_{\mathrm{CO2},b})$$

In this case k_l is called the liquid side mass transfer coefficient. It lumps together the effects of diffusion and chemical reaction of CO_2. The driving force is now the difference in CO_2 concentration between the gas-liquid interface and the liquid bulk.

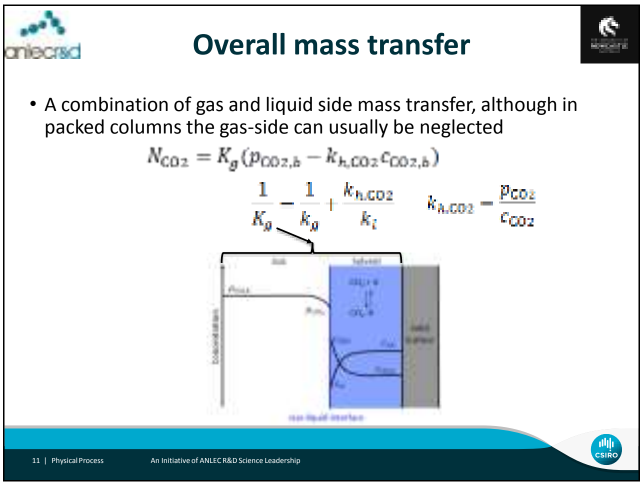
If the reactions are fast or the reactants are not in excess this steady-state equation cannot be used. In this case an extended form of Fick's Second Law is required.

$$\frac{\partial c_{\mathrm{CO2}}}{\partial t} = D_{\mathrm{CO2}}\frac{\partial^2 c_{\mathrm{CO2}}}{\partial x^2} + r$$

$$r = k_f c_{\mathrm{CO2}} c_{\mathrm{X}} - k_r c_{\mathrm{CO2 \cdot X}}$$

The additional term r is the rate of chemical reaction of CO_2.

Overall mass transfer



Overall mass transfer

- A combination of gas and liquid side mass transfer, although in packed columns the gas-side can usually be neglected

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

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{k_{h,\mathrm{CO2}}}{k_l} \qquad k_{h,\mathrm{CO2}} = \frac{p_{\mathrm{CO2}}}{c_{\mathrm{CO2}}}$$

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As we have seen mass transfer can be broken down into what occurs in the gas phase and what occurs in the liquid phase. The net CO_2 mass transfer from the bulk gas to the bulk liquid is the combination of these two processes. For the steady-state case this can be described by the driving force between the bulk gas and bulk liquid and an overall mass transfer coefficient K_g.

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

The term $k_{h,\mathrm{CO2}}c_{\mathrm{CO2},b}$ is the CO_2 partial pressure that the liquid bulk CO_2 concentration corresponds to calculated using the Henry constant $k_{h,\mathrm{CO2}}$.

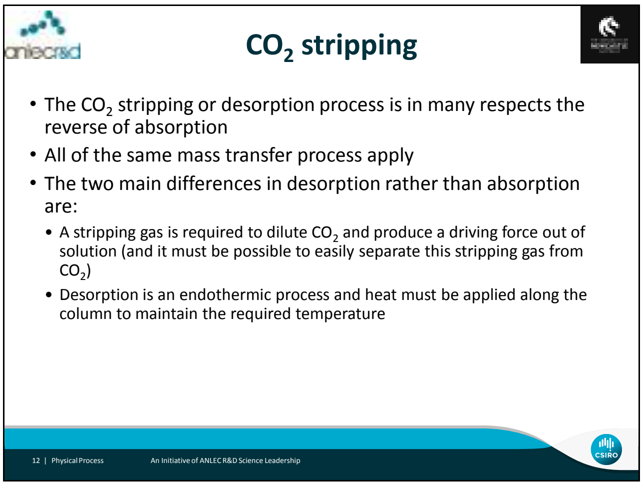
$$k_{h,\mathrm{CO2}} = \frac{p_{\mathrm{CO2}}}{c_{\mathrm{CO2}}}$$

The two film model treats the gas and liquid phases like resistances in series. The overall mass transfer coefficient can be calculated from the inverse of the gas and liquid side mass transfer coefficients.

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{k_{h,\mathrm{CO2}}}{k_l}$$

The dynamic case is more complex and won’t be covered here.

CO_2 stripping



CO_2 stripping

- The CO_2 stripping or desorption process is in many respects the reverse of absorption
- All of the same mass transfer process apply
- The two main differences in desorption rather than absorption are:
  - A stripping gas is required to dilute CO_2 and produce a driving force out of solution (and it must be possible to easily separate this stripping gas from CO_2)
  - Desorption is an endothermic process and heat must be applied along the column to maintain the required temperature

The CO_2 stripping process is carried out in a packed column similar to that used for absorption. There are two main differences, the columns are typically smaller because mass transfer is faster, and heat is required.

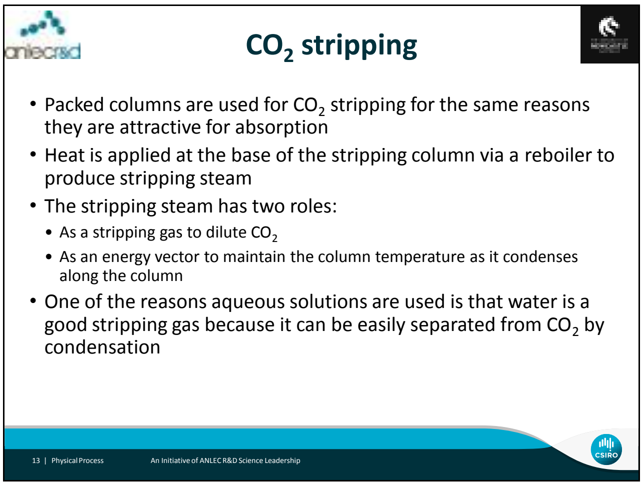
From a chemical and mass transfer point of view CO_2 stripping, or desorption, is the reverse of the absorption process. Heat is required to shift the chemical equilibria to favour CO_2 release. To drive desorption two things are required:

1) Dilution of CO_2 to produce a driving force out of the absorbent

2) The application of heat along the column to maintain the desorption temperature as desorption is endothermic

This is not as easy as you might think. The stripping gas to dilute CO_2 has to be easily separable from CO_2, otherwise you are back where you started! Also heating a column is a challenging task.

CO_2 stripping



CO_2 stripping

- Packed columns are used for CO_2 stripping for the same reasons they are attractive for absorption
- Heat is applied at the base of the stripping column via a reboiler to produce stripping steam
- The stripping steam has two roles:
  - As a stripping gas to dilute CO_2
  - As an energy vector to maintain the column temperature as it condenses along the column
- One of the reasons aqueous solutions are used is that water is a good stripping gas because it can be easily separated from CO_2 by condensation

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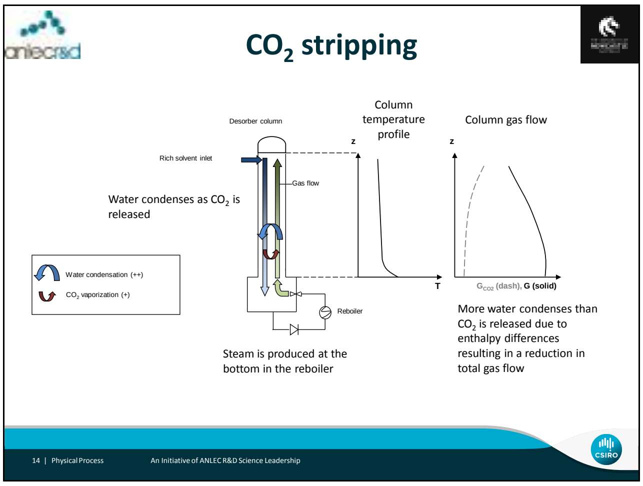
As mentioned, stripping is done in a packed column. The reasons are the same as for the absorber, low pressure drop, high surface area and moderate liquid residence time. Heat is applied at the base of the column using a reboiler. Reboilers are heaters that extract some or all of the solvent flow and heat it to produce steam.

This steam produced at the base of the column has two roles. One is that it acts as the dilution gas. As the steam moves up the column it dilutes the CO_2 to maintain the driving force for desorption. Its second job is as an energy vector. As CO_2 is released from the absorbent it cools as desorption is endothermic. This cooling leads to condensation of water vapour. The heat of condensation helps maintain the temperature required for desorption along the length of the column.

One of the major reasons aqueous solutions are used for CO_2 capture is so water can be used as the stripping gas. One of its attractive features is that water vapour can be easily separated from CO_2 by condensation.

CO_2 stripping



CO_2 stripping

Desorber column

Column temperature profile

Column gas flow

Rich solvent inlet

Gas flow

Water condenses as CO_2 is released

Water condensation (++)

CO_2 vaporization (+)

Reboiler

z

T

G_{CO2} (dash), **G (solid)**

Steam is produced at the bottom in the reboiler

More water condenses than CO_2 is released due to enthalpy differences resulting in a reduction in total gas flow

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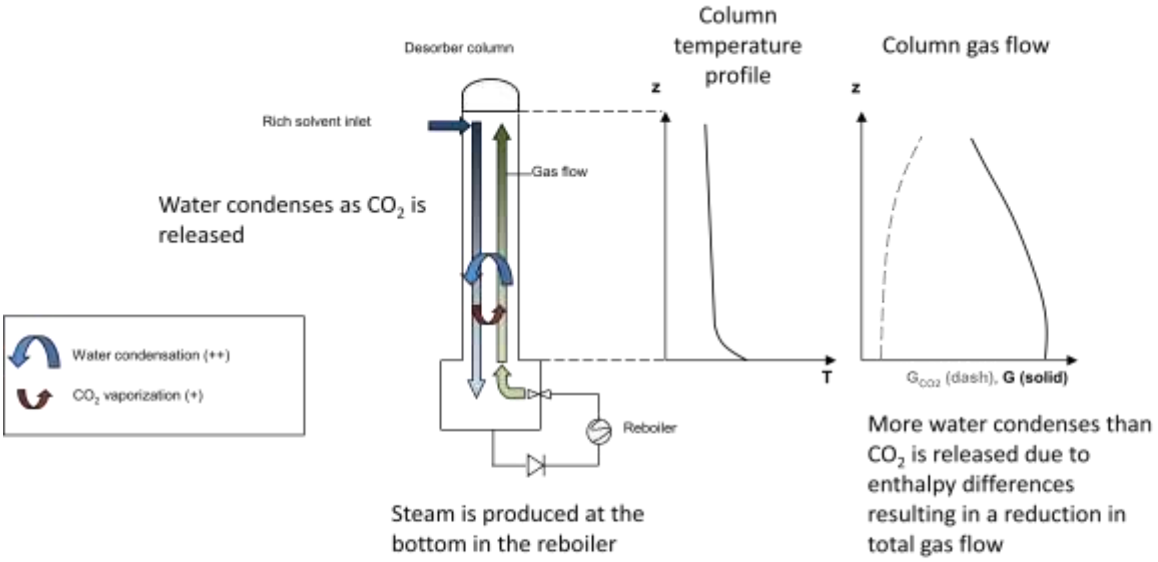
This diagram summarises what happens in a column during CO_2 desorption. In the column the liquid flow is represented in blue and the gas flow in green. Steam is produced in the column base by the reboiler. The CO_2 loaded solvent enters the column at the top. As the steam moves up the column it dilutes any CO_2 produced and condenses as the solvent cools.

At the top of the column the gas is mostly CO_2 with some residual water vapour. At the base of the column the gas is mostly water vapour as the CO_2 has desorbed along the column. When a stripper is operating optimally just enough steam is produced to result in only a small amount of residual water vapour at the top of the column.



What is happening in the desorber (stripper) column as CO_2 is released and water condenses.