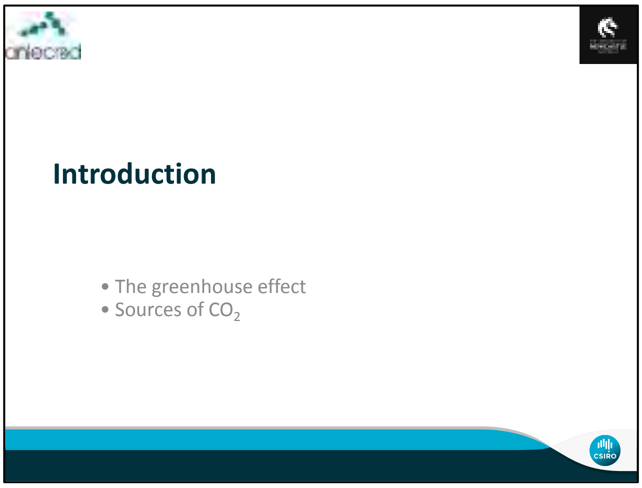
The greenhouse effect



Introduction

- The greenhouse effect
- Sources of CO_2

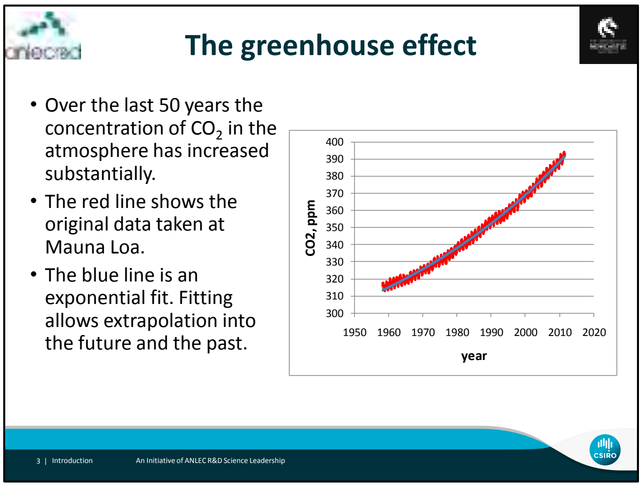
Introduction

It is an undisputable fact that the carbon dioxide concentration in the atmosphere is increasing, see next page for the evidence.

There are of course many sources of the CO_2 in the atmosphere, they include volcanoes, decaying organic matter (leaves in autumn), exchange with dissolved CO_2 in the oceans, the combustion of fossil fuel, and of course many other minor contributions. There are also sinks for the CO_2 in the atmosphere, most prominent the growing organic matter (trees) and exchange with the oceans. All these processes are connected in a *very big* equilibrium. This equilibrium has been reasonably constant over the last few thousand years and significant changes only occurred over much longer time spans. However, in very recent times the concentration started to increase significantly and much more abruptly than in the past.

The *almost* universally accepted reason is the increased combustion of fossil fuel since the beginning of industrialisation. As we will see in the next few slides this is clearly a very likely interpretation of the observations.

The greenhouse effect



The greenhouse effect

- Over the last 50 years the concentration of CO_2 in the atmosphere has increased substantially.
- The red line shows the original data taken at Mauna Loa.
- The blue line is an exponential fit. Fitting allows extrapolation into the future and the past.

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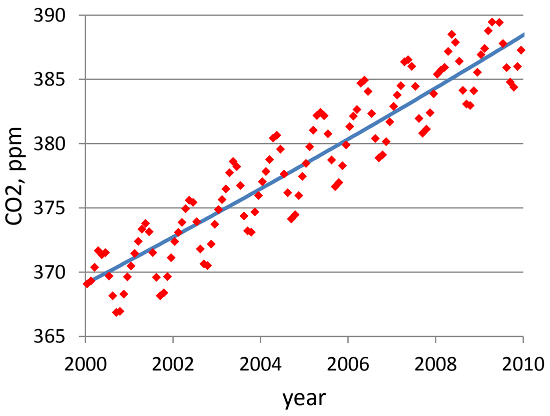
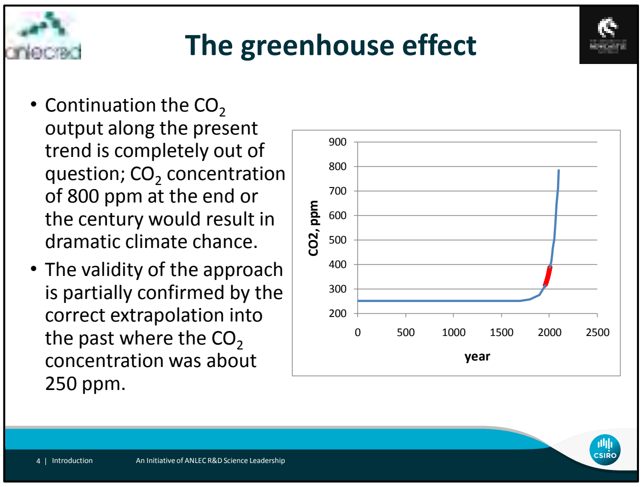
The concentration of CO_2 in the atmosphere over the last 50 years

The graph above shows the measured concentration of CO_2 in the atmosphere over the last 50 years. The increase is substantial in relative terms, approximately 25% over that time span.

Very importantly, the increase is not linear but approximately exponential. The blue line is an exponential fit of the concentration curve. Exponential growth is possible over short time periods, it *cannot* be maintained over long periods of time, in modern parlance, it is not sustainable. (Interestingly, it appears that economists still believe in sustainable growth.)



The figure displays an enlarged view of the last 10 years, featuring the monthly averages. The ups-and-downs are due to the seasonal decay and growth of plants resulting in maximal CO_2 concentration during winter and minimal atmospheric concentration during summer. The figure shows the large swings due to natural causes and on top the continuous increase due to anthropogenic release of additional CO_2.



The greenhouse effect

- Continuation the CO_2 output along the present trend is completely out of question; CO_2 concentration of 800 ppm at the end or the century would result in dramatic climate chance.
- The validity of the approach is partially confirmed by the correct extrapolation into the past where the CO_2 concentration was about 250 ppm.

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Extrapolation of the CO_2 concentration into the future

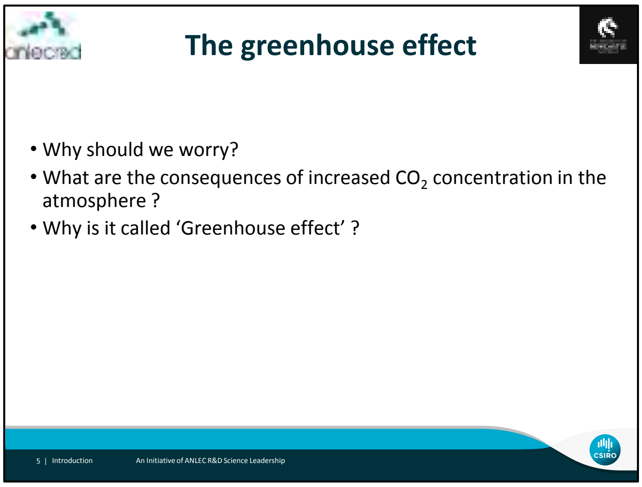
Fitting an appropriate function to the measured CO_2 data allows extrapolation into the future as well as the past. This has been done in the PowerPoint page above, the red markers are the measured data, and the blue line is the extrapolation into the past and the future.

The value for the extrapolation into the past can be compared with the actual history; it coincides well with a CO_2 concentration of about 250ppm. This gives some limited validity to the approach.

The extrapolation into the future, of course, is only valid if nothing changes in the underlying processes. The predicted values of approximately 800ppm by 2100 makes it absolutely clear that something rather dramatic will happen. Either humanity manages to reduce the CO_2 output significantly or the climate will be completely different.

The first option might be very expensive but it is clearly the preferred one not only because it is certainly much cheaper as well.

The greenhouse effect



The greenhouse effect

- Why should we worry?
- What are the consequences of increased CO_2 concentration in the atmosphere ?
- Why is it called ‘Greenhouse effect’ ?

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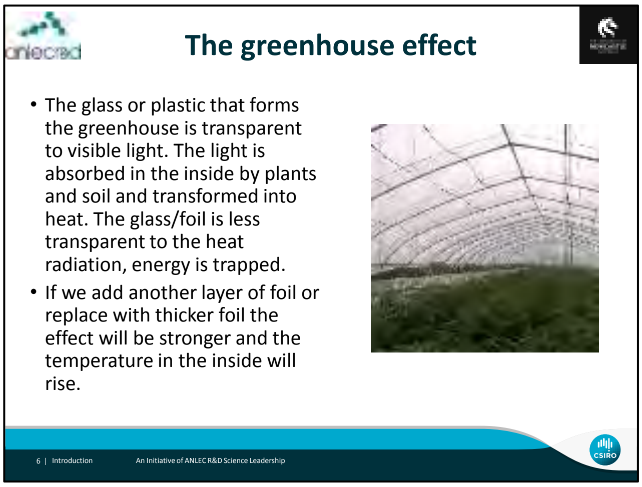
Increasing CO_2 concentration in the atmosphere

The concentration of carbon dioxide, or CO_2, in the atmosphere is increasing substantially and is predicted to increase much more in the not too far future. The absolute concentration of CO_2 in the atmosphere is small with only 300-400ppm which translates to 0.3-0.4%; clearly CO_2 is a minor gas. On top of that, as prominent ‘sceptics’ hasten to point out, CO_2 is odourless and colourless and at these very low concentrations it is absolutely non-toxic. It appears that there is clearly no point in worrying about the ‘slight’ increase?

However, in spite of the above, increasing concentrations of CO_2 will, indisputably, result in higher temperatures on the planet (what is not 100% clear, and disputable, is how much that increase is expected to be).

CO_2 and water and many other gases are so-called greenhouse gases; they act like a greenhouse, keeping the surface of the planet at the temperature it has. A simple observation supports this: on a bright sunny day on top of a mountain, say Mt Kosciusko, it is much cooler than lower down in a valley or at the beach, even if one is closer to the sun and thus might expect rather higher temperature. The atmosphere acts like a blanket, keeping things under it warm. If we make the blanket more efficient, it will get warmer. For good reasons we do not talk about the blanket effect, rather of the greenhouse effect.

The greenhouse effect



The greenhouse effect

- The glass or plastic that forms the greenhouse is transparent to visible light. The light is absorbed in the inside by plants and soil and transformed into heat. The glass/foil is less transparent to the heat radiation, energy is trapped.
- If we add another layer of foil or replace with thicker foil the effect will be stronger and the temperature in the inside will rise.

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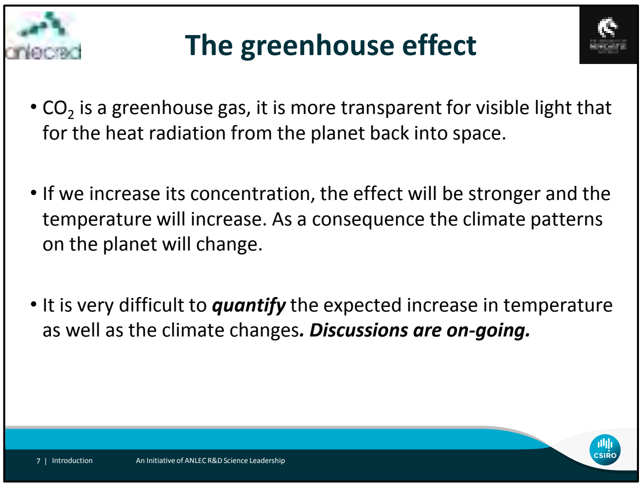
The Greenhouse

The expression ‘greenhouse effect’ is very appropriate, the principle is essentially the same as with a real greenhouse.

- The plastic or glass sheet of a greenhouse is transparent to the white light emitted by the sun. (The white light constitutes the largest fraction of the energy of sun light).
- The transmitted light is absorbed by the surface, the soil, and the plants in the greenhouse.
- The absorbed light energy is transformed into heat energy, thus the surface gets warmer.
- The warm surface radiates back energy in the shape of infrared radiation. Some of that radiation is absorbed by the plastic of the greenhouse and remains inside the greenhouse. This is why it is warmer inside.
- If we increase the thickness of plastic of the greenhouse, the back-radiation is reduced while the absorption is not affected, the balance is changed and the temperature will rise.
- Imagine the following: A gardener installing a thicker sheet of plastic on his greenhouse and the temperature in his greenhouse increases. Along comes a ‘sceptic’ and assigns this increase of temperature to sunspots.

The greenhouse effect



The greenhouse effect

- CO_2 is a greenhouse gas, it is more transparent for visible light that for the heat radiation from the planet back into space.
- If we increase its concentration, the effect will be stronger and the temperature will increase. As a consequence the climate patterns on the planet will change.
- It is very difficult to ***quantify*** the expected increase in temperature as well as the climate changes***. Discussions are on-going.***

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The Greenhouse Effect

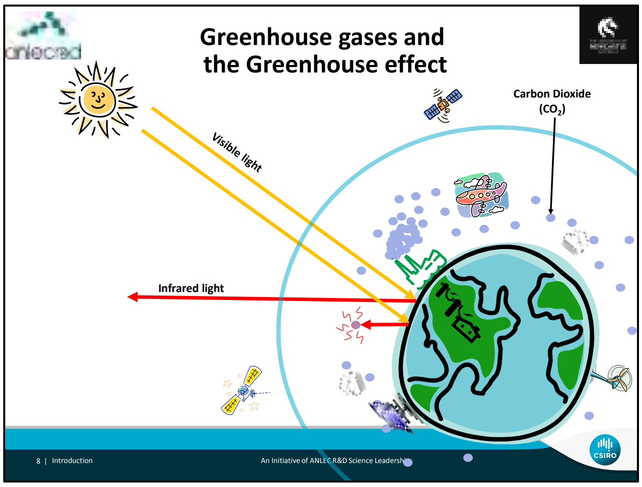
All gases in the atmosphere act to different degrees as greenhouse gases, similar to the plastic sheet of the real greenhouse.

Why do we concentrate on CO_2 as a greenhouse gas? Water for example is a very powerful greenhouse gas and nobody seems to worry about it. The reason is that water does not accumulate it is continuously removed as rain, overall the composition of the atmosphere is very constant. It is mainly the concentration of CO_2 that increases with time; see the graph on page 2. As we have seen this increase results in a better greenhouse or warmer temperature and subsequently significant changes in climate.

The weather is an extremely complex process. As we all know it is very difficult to predict the weather for more than a few days in advance. It is obviously much more difficult to predict the long term consequences of the greenhouse effect.

Should we stop worrying about and acting against greenhouse gas emissions and global warming because we cannot precisely predict the climate changes for any part of the planet?

The greenhouse effect



Greenhouse gases and the Greenhouse effect

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The Greenhouse Effect

The slide is a schematic diagram of the planet, its atmosphere and its interaction with solar radiation.

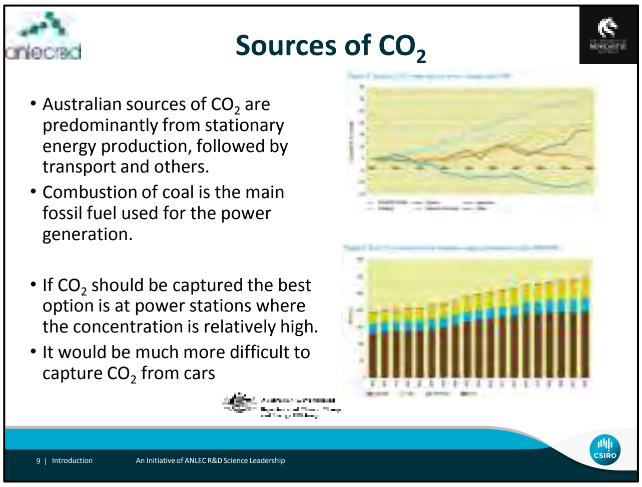
The atmosphere is very transparent for visible light (yellow in the Figure) which reaches the surface of the planet unhindered. The light is absorbed and transformed into heat. We can feel that by exposing a hand to the sunlight on a cold day.

The warm surface of the planet re-emits infrared light (red in the Figure). The atmosphere absorbs some of this infrared light and thus keeps us warm. More infrared light is absorbed for increasing concentration of CO_2, thus keeping us warmer. Enormous amounts of energy are passing through the atmosphere every day and the amount of extra absorbed infrared light is actually very small, but sufficient to change the climate.

An additional remark: the atmosphere forms a much thinner layer that suggested in the Figure above. The Troposphere (the lowest part of the atmosphere where we live and where the weather happens) is a about 10km thick. On a globe of 30cm diameter it would be about 0.2mm or 2-3 times the thickness of human hair.

The earth’s atmosphere is a thin film and needs to be looked after carefully.

The greenhouse effect



Sources of CO_2

- Australian sources of CO_2 are predominantly from stationary energy production, followed by transport and others.
- Combustion of coal is the main fossil fuel used for the power generation.
- If CO_2 should be captured the best option is at power stations where the concentration is relatively high.
- It would be much more difficult to capture CO_2 from cars

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Sources of CO_2 in the atmosphere

In order to reduce the CO_2 output we need to identify the large producers of CO_2 and also find out the output can be reduced best.

Energy production and transport are major sources of CO_2 in Australia. Using less energy and cycling instead of driving would be very efficient ways for the reduction of the CO_2 output but unfortunately they both are not very likely options.

Capturing the CO_2 with subsequent sequestering is another, maybe, more realistic option. This is much easier at a stationary and large source of CO_2 and thus coal fired power stations are the most prominent candidates for CO_2 capture.

Post-combustion CO_2 capture (PCC)

Graeme Puxty, CSIRO Energy Technology
Marcel Maeder, University of Newcastle

Introduction

- The greenhouse effect
- Sources of CO_2

The greenhouse effect

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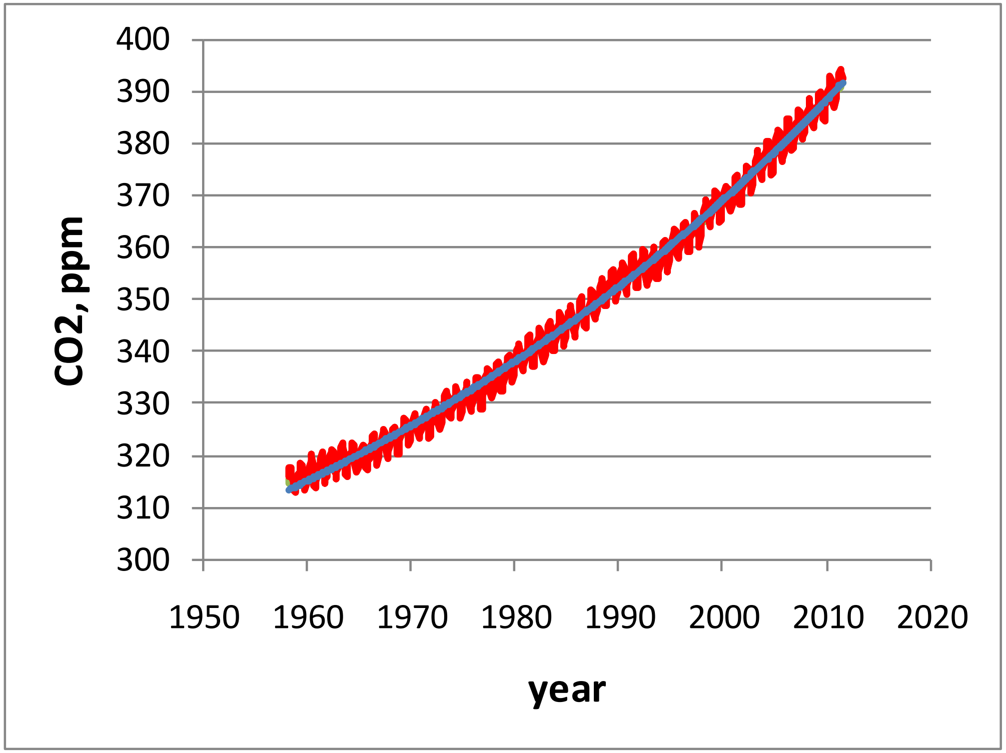

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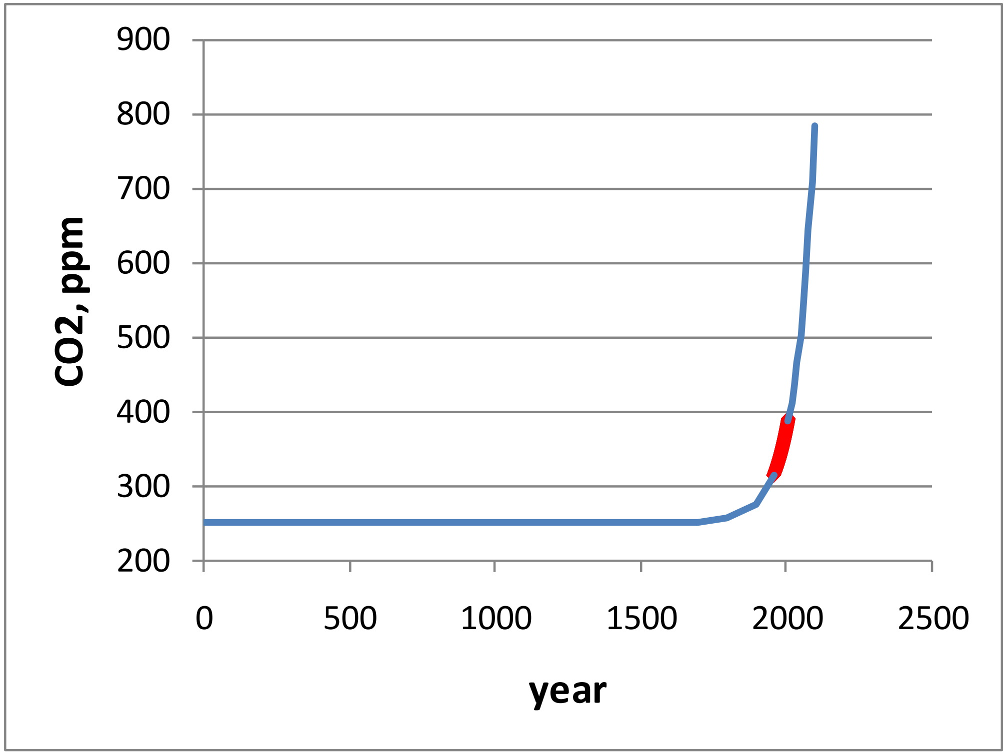

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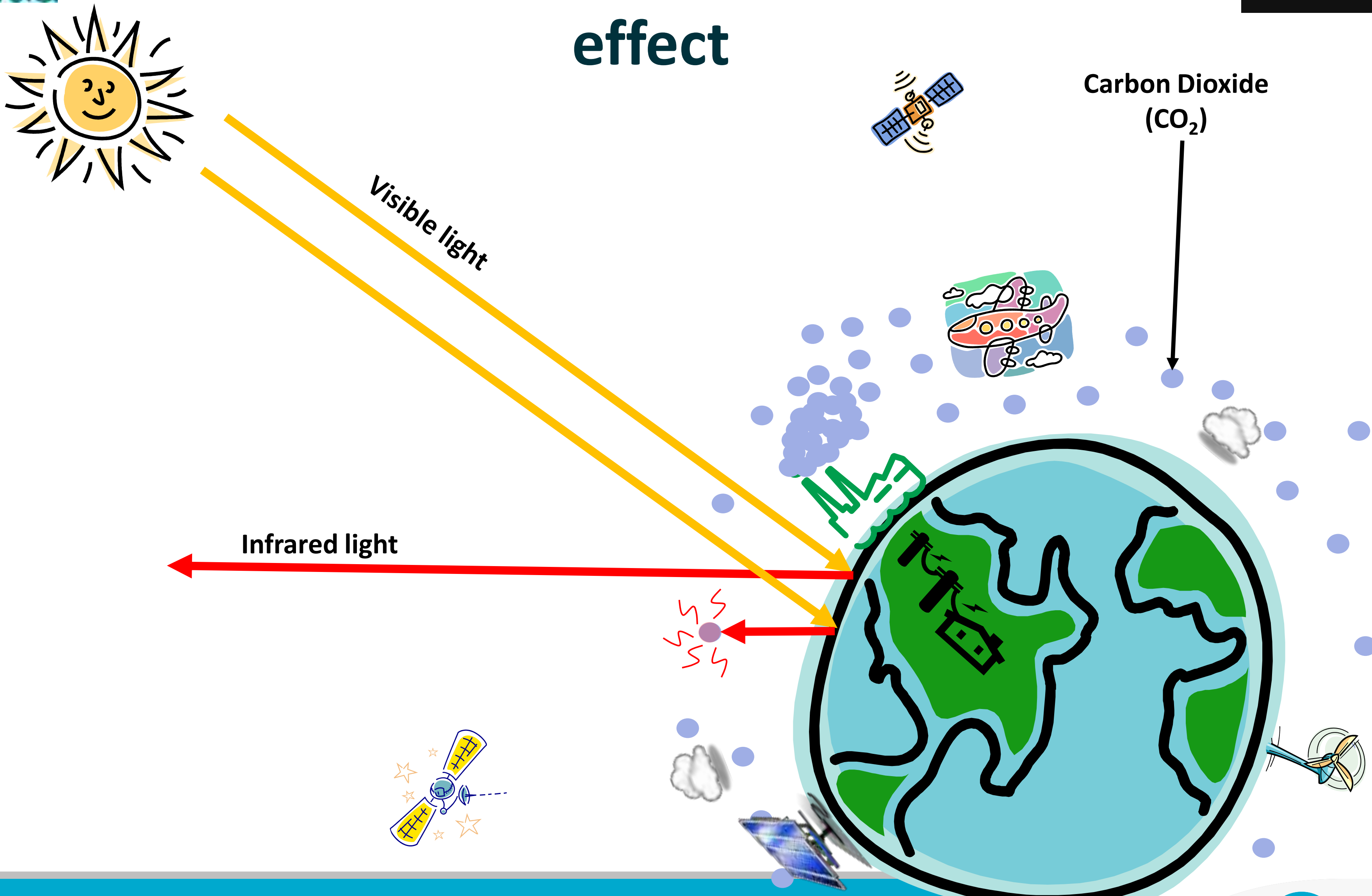
Greenhouse gases and the greenhouse effect



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- Combustion of coal is the main fossil fuel used for the power generation.

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- It would be much more difficult to capture CO_2 from cars

Figure 5: Trends in CO_2-e emissions by sector – change since 1990

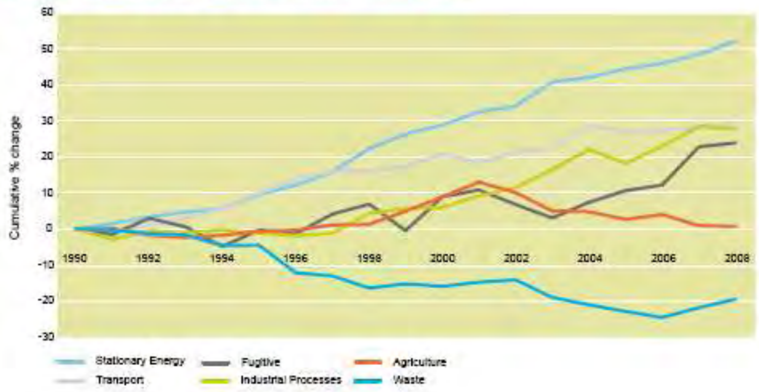
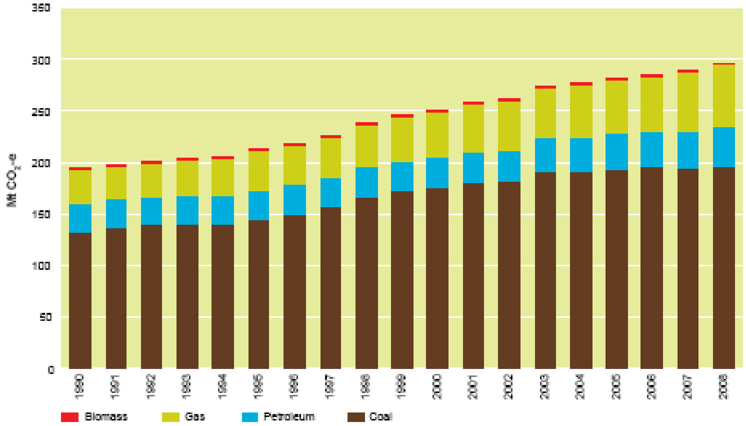


Figure 6: Total CO_2-e emissions from stationary energy combustion by fuel, 1990–2008

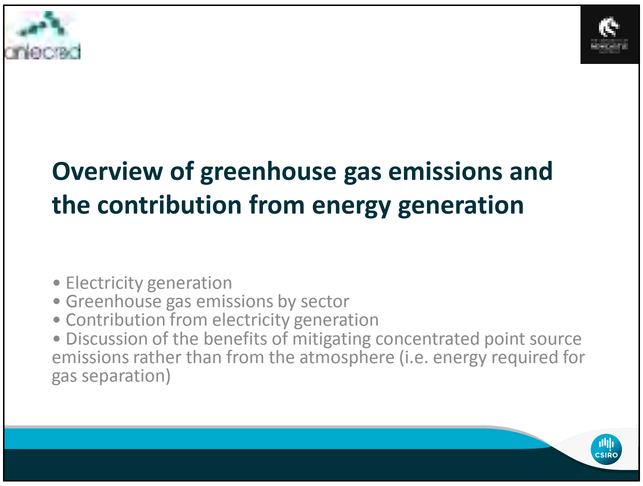


Australian Government
Department of Climate Change and Energy Efficiency

Acknowledgements

The authors wish to acknowledge financial assistance provided through Australian National Low Emissions Coal Research and Development (ANLEC R&D). ANLEC R&D is supported by Australian Coal Association Low Emissions Technology Limited and the Australian Government through the Clean Energy Initiative.

Overview of GHG emissions from energy generation



Overview of greenhouse gas emissions and the contribution from energy generation

- Electricity generation
- Greenhouse gas emissions by sector
- Contribution from electricity generation
- Discussion of the benefits of mitigating concentrated point source emissions rather than from the atmosphere (i.e. energy required for gas separation)

Greenhouse gas (GHG) emissions are ubiquitous with energy generation. Since the industrial revolution combustion of fossil fuels to produce heat has been the main energy source in use throughout the world. In the past this heat was converted to mechanical energy in the form of steam engines and the like. Today it is the conversion of heat to mechanical energy and then electrical energy that dominates.

Whether you use coal, oil or gas the combustion equation is essentially the same:

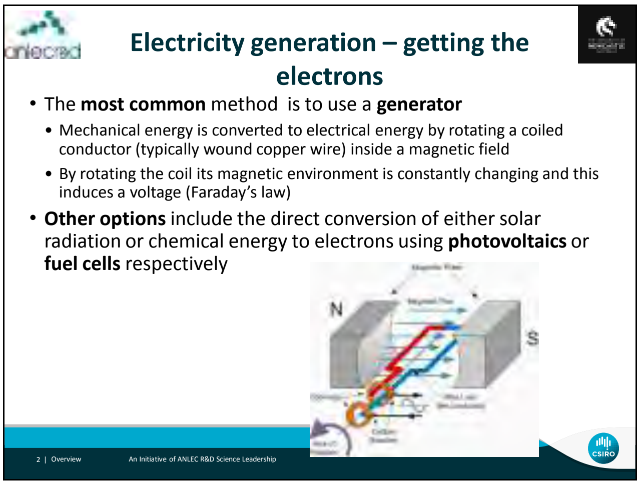
$$\mathrm{C}_x\mathrm{H}_y + \left(x + \frac{y}{4}\right)\mathrm{O}_2 \rightarrow x\mathrm{CO}_2 + \left(\frac{y}{2}\right)\mathrm{H}_2\mathrm{O} + \mathrm{heat}$$

and results in production of the GHG CO_2.

While CO_2 is not the worst GHG in terms of having the greatest ability to retain heat in the atmosphere per molecule (that award goes to sulfur hexafluoride), its presence at relatively large concentration makes it the most important.

The biggest source of CO_2 globally is from large scale electricity generation. Perversely, this large scale generation will have benefits in terms of capturing CO_2 emissions. It requires far less energy to capture from a large scale source with concentrated CO_2 emissions than from small or dilute sources or the atmosphere.

Electricity generation – getting the electrons



Electricity generation – getting the electrons

- The **most common** method is to use a **generator**
  - Mechanical energy is converted to electrical energy by rotating a coiled conductor (typically wound copper wire) inside a magnetic field
  - By rotating the coil its magnetic environment is constantly changing and this induces a voltage (Faraday's law)
- **Other options** include the direct conversion of either solar radiation or chemical energy to electrons using **photovoltaics** or **fuel cells** respectively

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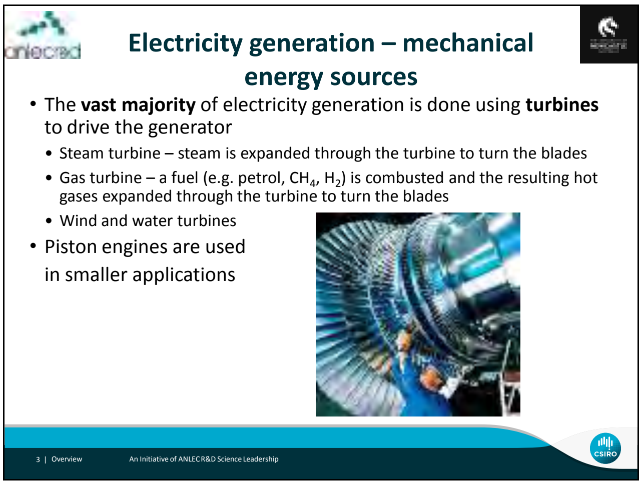
Generators

We are probably all familiar with an electric motor – a copper coil on an axle surrounded by magnets. When you apply a voltage to the coil a magnetic field is induced, and repulsion and attraction between the magnetic field of the coil and the outer magnets leads to rotation of the coil and axle. If you mechanically rotate the coil in a magnetic field the reverse occurs, and a current is produced in the coil (Faraday's law). This is the principle electrical generators use including small ones you can wind manually to charge batteries, wind turbines, to the largest power stations.

Today new classes of electrical generators exist that convert either solar radiation or chemical energy directly into electricity. Photovoltaics or solar cells rely on using solar radiation to give electrons an energy boost and set them free from a molecule such as silicon, resulting in an electric current (the photovoltaic effect). Fuel cells carry out the conversion of chemical energy into electricity via redox (reduction-oxidation) reactions. You have probably heard of hydrogen fuel cells, but there are fuel cells based on other materials as well, even coal!

Electricity generation – mechanical energy sources



Electricity generation – mechanical energy sources

- The **vast majority** of electricity generation is done using **turbines** to drive the generator
  - Steam turbine – steam is expanded through the turbine to turn the blades
  - Gas turbine – a fuel (e.g. petrol, CH_4, H_2) is combusted and the resulting hot gases expanded through the turbine to turn the blades
  - Wind and water turbines
- Piston engines are used in smaller applications

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Turbines

The most common source of mechanical energy to turn the axle and coil of an electricity generator is a turbine. Turbines consist of a blades attached to an axle, much like a fan. A gas or liquid passing over the blades applies a force to them and causes the blades and axle to rotate.

Steam turbines

Steam turbines are typically used in large-scale base load power stations. Water is heated by burning coal, oil or gas to produce high pressure steam and the steam is expanded through the turbines to turn the blades.

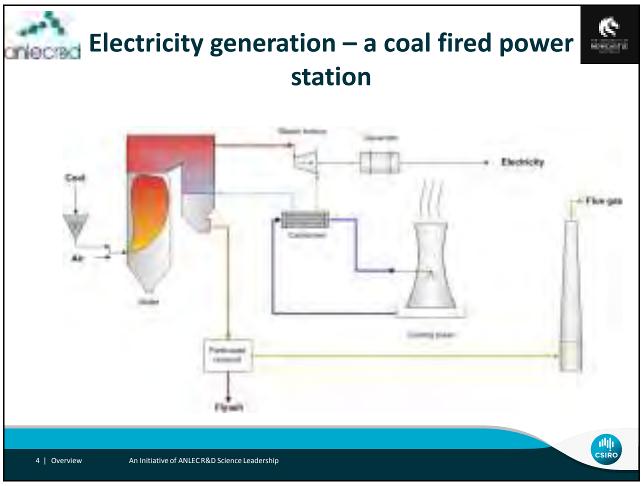
Gas turbines

Gas turbines are usually found in smaller power stations. They are often used as peaking plants (to provide additional electricity during peak demand periods) because they can be more easily turned on/off/up/down. They work by burning a gas such as methane or hydrogen in a combustion chamber. This produces hot gases under pressure that are expanded through the turbine blades.

Other turbines

Flowing water can also be used to turn turbines such as in hydroelectricity plants. Wind is used to turn the blades of a turbine for wind power. Solar thermal energy may also be used to heat water to make steam or heat air to produce hot gas to drive a turbine.

Electricity generation – a coal fired power station



Electricity generation – a coal fired power station

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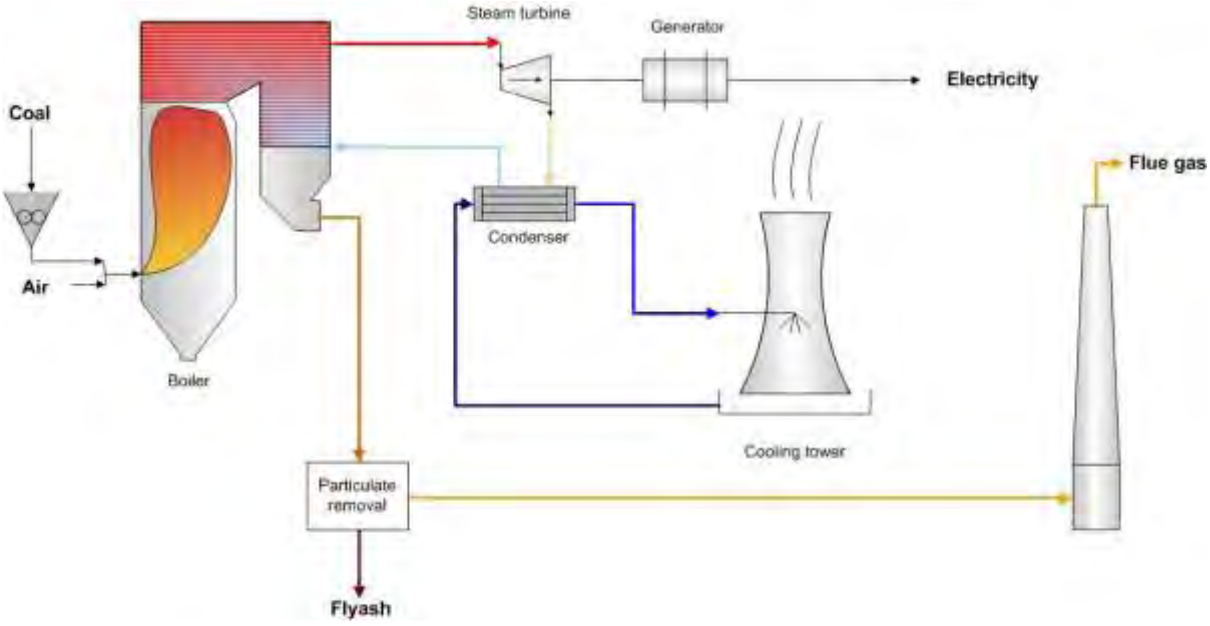
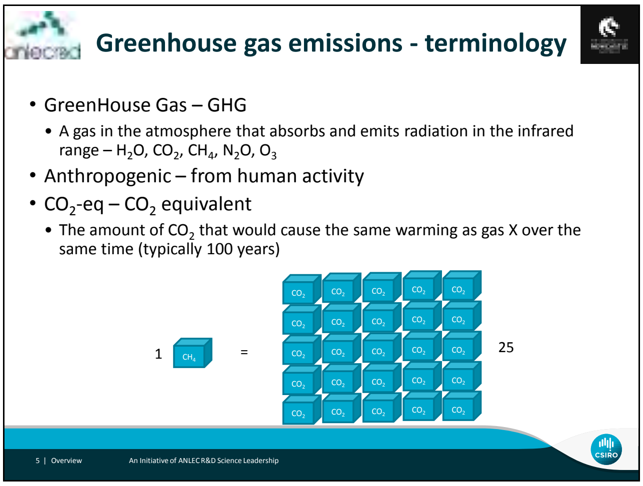
Coal fired power stations are the most common type of power station in use the world over and generate most of our electricity (80% in Australia and about 45% globally). They work by burning coal in a furnace. Water is passed into the furnace in pipes and the water is heated to produce high pressure steam. The steam is then expanded through a turbine to turn the blades, which in turn turns the axle and coil of an electricity generator. Once the steam has passed through the turbine it is cooled and condensed back to water before being returned to the furnace. Because the coal is burned in air the resulting flue gas is about 80% N_2, 15% CO_2 and 5% O_2. Other gases such as sulfur and nitrogen oxides are present in small amounts as are some particulates containing heavy metals.



Greenhouse gas emissions - terminology



Greenhouse gas emissions - terminology

- GreenHouse Gas – GHG
  - A gas in the atmosphere that absorbs and emits radiation in the infrared range – H_2O, CO_2, CH_4, N_2O, O_3
- Anthropogenic – from human activity
- CO_2-eq – CO_2 equivalent
  - The amount of CO_2 that would cause the same warming as gas X over the same time (typically 100 years)

5 | Overview

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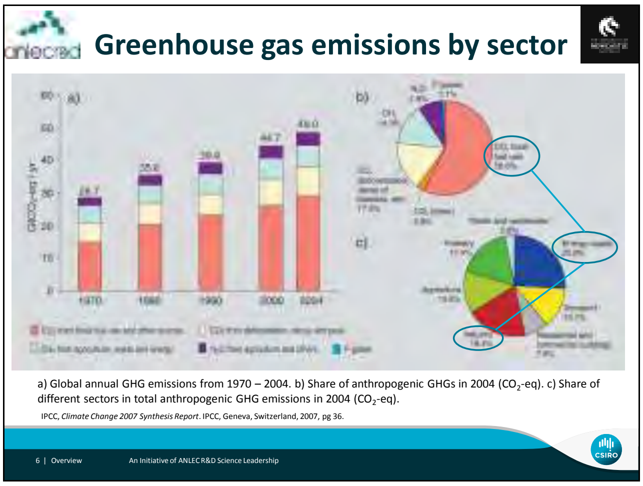
There are is some common jargon and abbreviations used when discussing greenhouse gases. The ones we will be using are given below.

GreenHouse Gas (GHG): A gas in the atmosphere that absorbs and emits radiation in the thermal infrared region. The name stems from the fact that these gases act to trap heat in the atmosphere much like a greenhouse traps heat. The most common GHG's are H_2O, CO_2, CH_4, N_2O and O_3.

Anthropogenic: This word refers to anything that is caused via human activity. It is used to distinguish the proportion of CO_2 and other GHG's whose emission is from human activity rather than natural environmental sources.

CO_2-equivalent (CO_2-eq): CO_2-eq is a measure of the warming potential of a GHG relative to CO_2. Specifically, it is the amount of CO_2 that would cause the same warming as gas X over the same time period (typically 100 years is used). For example the CO_2-eq value for CH_4 is 25. That means over 100 years 25 CO_2 molecules produce the same amount of warming as 1 CH_4 molecule.

Greenhouse gas emissions by sector



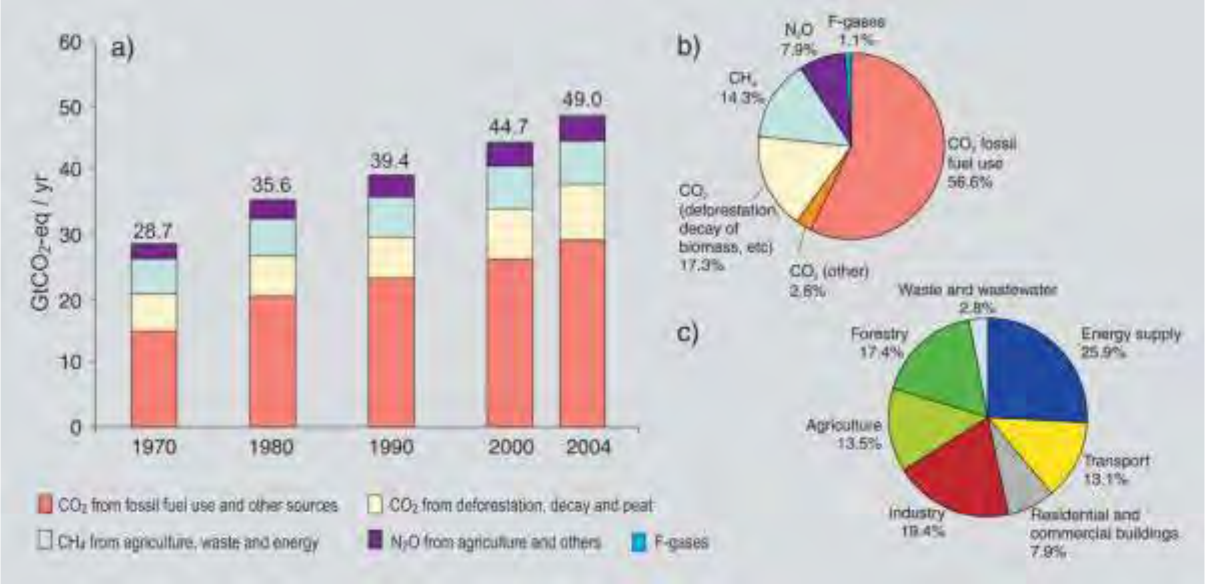
Greenhouse gas emissions by sector

a) Global annual GHG emissions from 1970 – 2004. b) Share of anthropogenic GHGs in 2004 (CO_2-eq). c) Share of different sectors in total anthropogenic GHG emissions in 2004 (CO_2-eq).

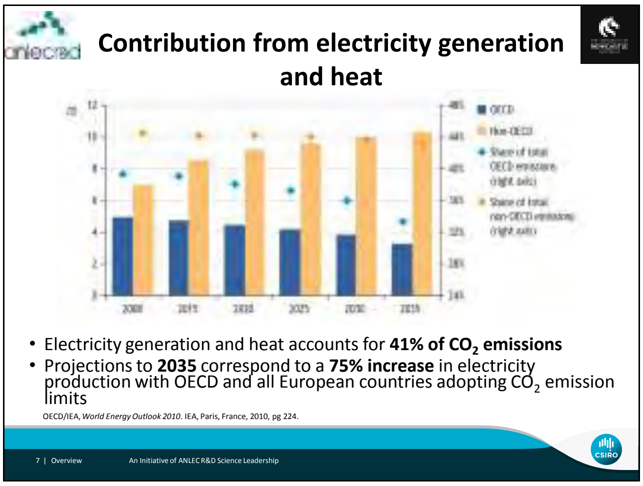
IPCC, *Climate Change 2007 Synthesis Report*. IPCC, Geneva, Switzerland, 2007, pg 36.

It is important to understand the sources of anthropogenic GHG emissions when thinking about the best way to reduce them. The figure below from the IPCC shows emissions for 2004. Chart a) is the total emissions of the main GHG's and chart b) is the share each gas represents of total emissions. Chart c) shows these emissions come from many different sectors in modern economies including transport (cars, trucks, planes, etc), the construction of buildings, industries like steel and cement manufacturing and the production of agricultural and forestry products. But the biggest single sector is energy supply. The second biggest source is industry. The CO_2 released by the burning of fossil fuels to provide heat and electricity for residential and industrial use accounts for almost half of global GHG emissions.

These sources are all possible targets for carbon dioxide capture and storage!



Contribution from electricity generation and heat



Contribution from electricity generation and heat

- Electricity generation and heat accounts for **41% of CO_2 emissions**
- Projections to **2035** correspond to a **75% increase** in electricity production with OECD and all European countries adopting CO_2 emission limits

OECD/IEA, *World Energy Outlook 2010*. IEA, Paris, France, 2010, pg 224.

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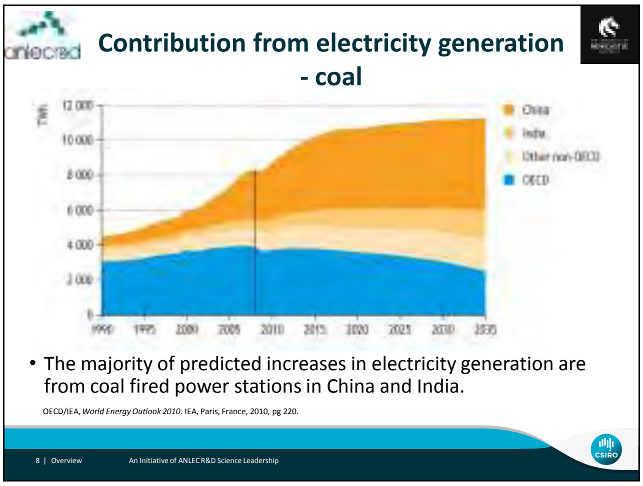
CO_2 accounts for 76.7% of total GHG emission as CO_2-eq. Since this value is in CO_2-eq the differing warming potential of the other gases has been taken into account. According to the International Energy Agency (IEA), in 2009 28 999 million tonnes of CO_2 was emitted. Of that 41% was for the generation of electricity and heat.

The reason electricity and heat are lumped together is because in many places around the world waste heat from electricity generation is used for district heating, in what are called combined heat and power plants. Also in colder climates large boilers burning fossil fuels are used just for heating.

The IEA has done projections of the likely increase in electricity demand with rising population and increased electricity use in developing countries. They predict a 75% increase in electricity production by 2035. To maintain CO_2 emissions from electricity and heat near current levels would require all OECD and European countries to adopt emission limits. Since fossil fuels are likely to still be the biggest source of energy to meet this demand carbon capture and storage will have a major role to play.

Contribution from electricity generation - coal



Contribution from electricity generation - coal

- The majority of predicted increases in electricity generation are from coal fired power stations in China and India.

OECD/IEA, *World Energy Outlook 2010*. IEA, Paris, France, 2010, pg 220.

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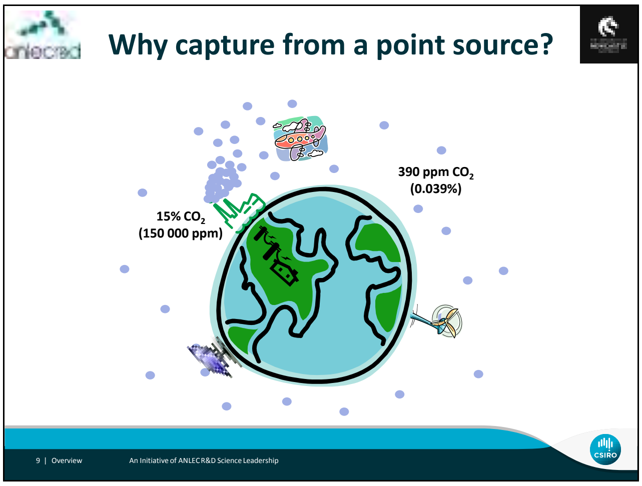
As mentioned electricity generation is predicted to have increased by 75% in 2035. The majority of this increase is from coal fired power stations in China and India. The reason is predominantly an economic one. Building power stations is a large investment as they typically cost $1 billion+ depending on their size. More than anything, it is this predicted increase in coal fired power stations that makes it crucial to have technology available that can reduce their CO_2 emissions.

Why capture from a point source?



Why capture from a point source?

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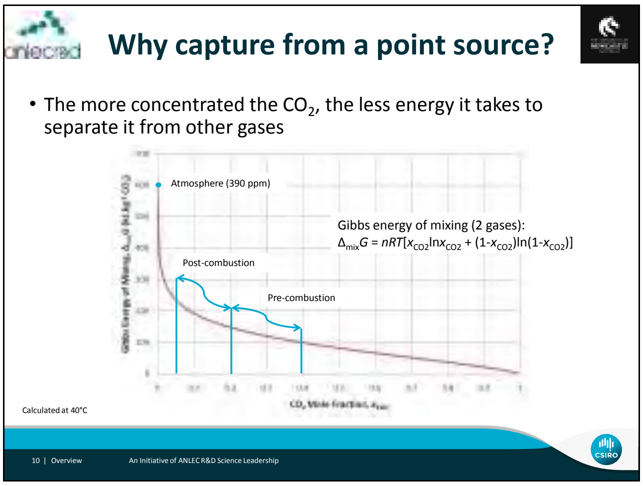
A point source is a power station, steel smelter, etc, where large amounts of CO_2 are being emitted in one place. For example the gas that goes up the chimney at a coal fired power station is 15% CO_2 (that is 150 000 ppm). Carbon capture and storage is focused on capturing CO_2 from these types of sources, but why? In principle it’s possible to capture CO_2 directly from the air rather than from a power station chimney. This would have the advantage of being able to be done anywhere meaning you could easily locate your capture plant near good CO_2 sequestration sites.

It comes down to concentration. The concentration of CO_2 in air is only 0.039% (390 ppm) and this low concentration means you have to put a lot more energy in to capture the same amount of CO_2.

Why capture from a point source?



Why capture from a point source?

- The more concentrated the CO_2, the less energy it takes to separate it from other gases

Calculated at 40°C

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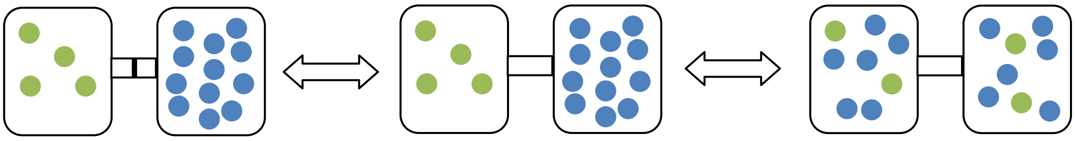
So why do you need less energy to separate CO_2 from a concentrated point source than the air? It's simple thermodynamics! The minimum amount of energy you need to separate 2 gases is the change in the Gibbs energy when they are mixed. Consider the illustration below where we have 4 molecules of a green gas and 12 molecules of a blue gas separated by a valve. We open the valve and let the gases mix. If the Gibbs energy of mixing is $\Delta_{mix}G$ Joules per molecule (we have 16 molecules) then for the green gas we get an energy of mixing of $16\times\Delta_{mix}G$ / 4 (Joules / molecules green gas) and for the blue gas $16\times\Delta_{mix}G$ / 12 (Joules / molecules blue gas). So the more concentrated the CO_2 source the less energy we need per molecule of CO_2 to do the separation.



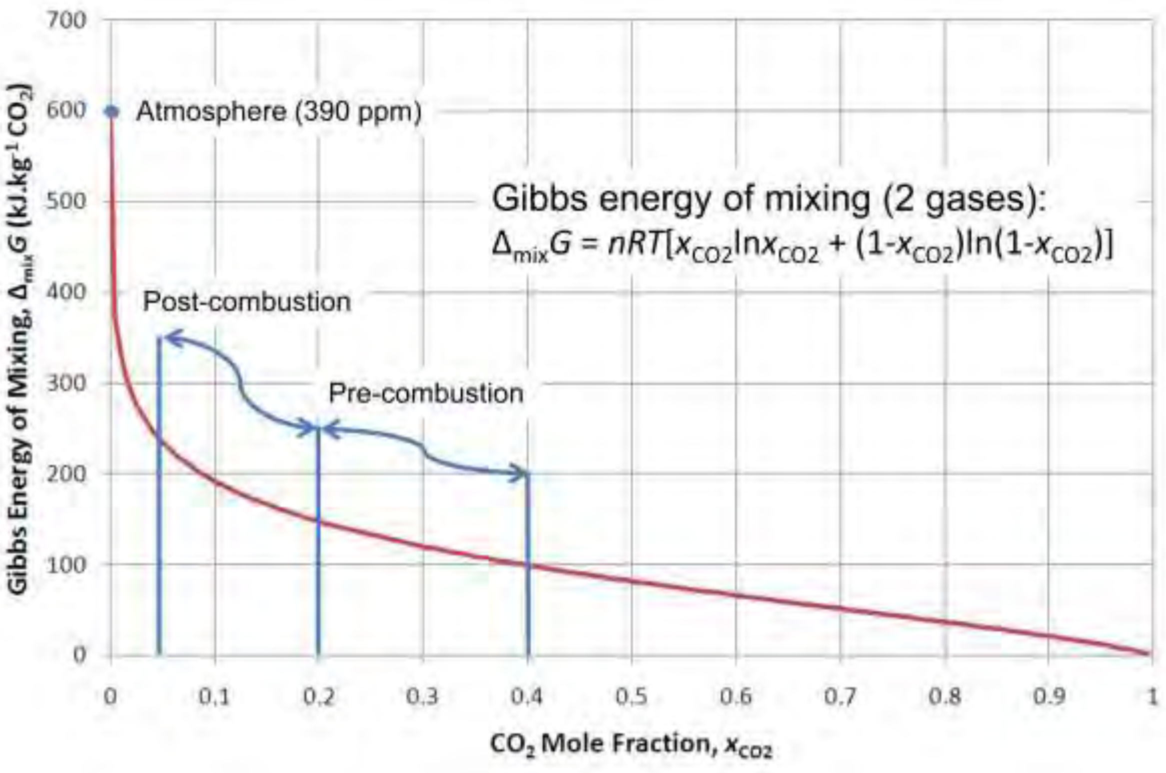
2 gases in separate containers with a valve in-between

open the valve and let them mix

now they are mixed

The chart below is the Gibbs energy of mixing in kJ per kg of CO_2 for two gases as a function of the CO_2 mole fraction in mixture. The value at 390 ppm is more than 3x greater the value at 15% CO_2 (a mole fraction of 0.15).

Why capture from a point source?

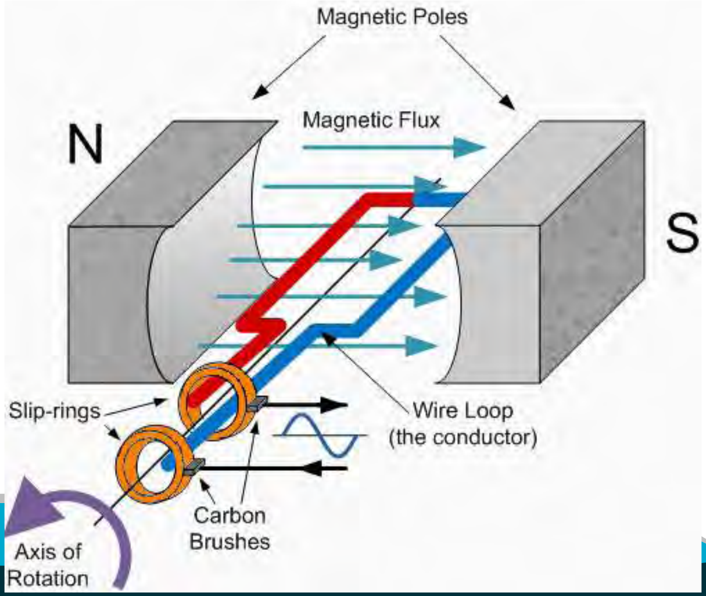


Overview of greenhouse gas emissions and the contribution from energy generation

- Electricity generation
- Greenhouse gas emissions by sector
- Contribution from electricity generation
- Discussion of the benefits of mitigating concentrated point source emissions rather than from the atmosphere (i.e. energy required for gas separation)

Electricity generation – getting the electrons

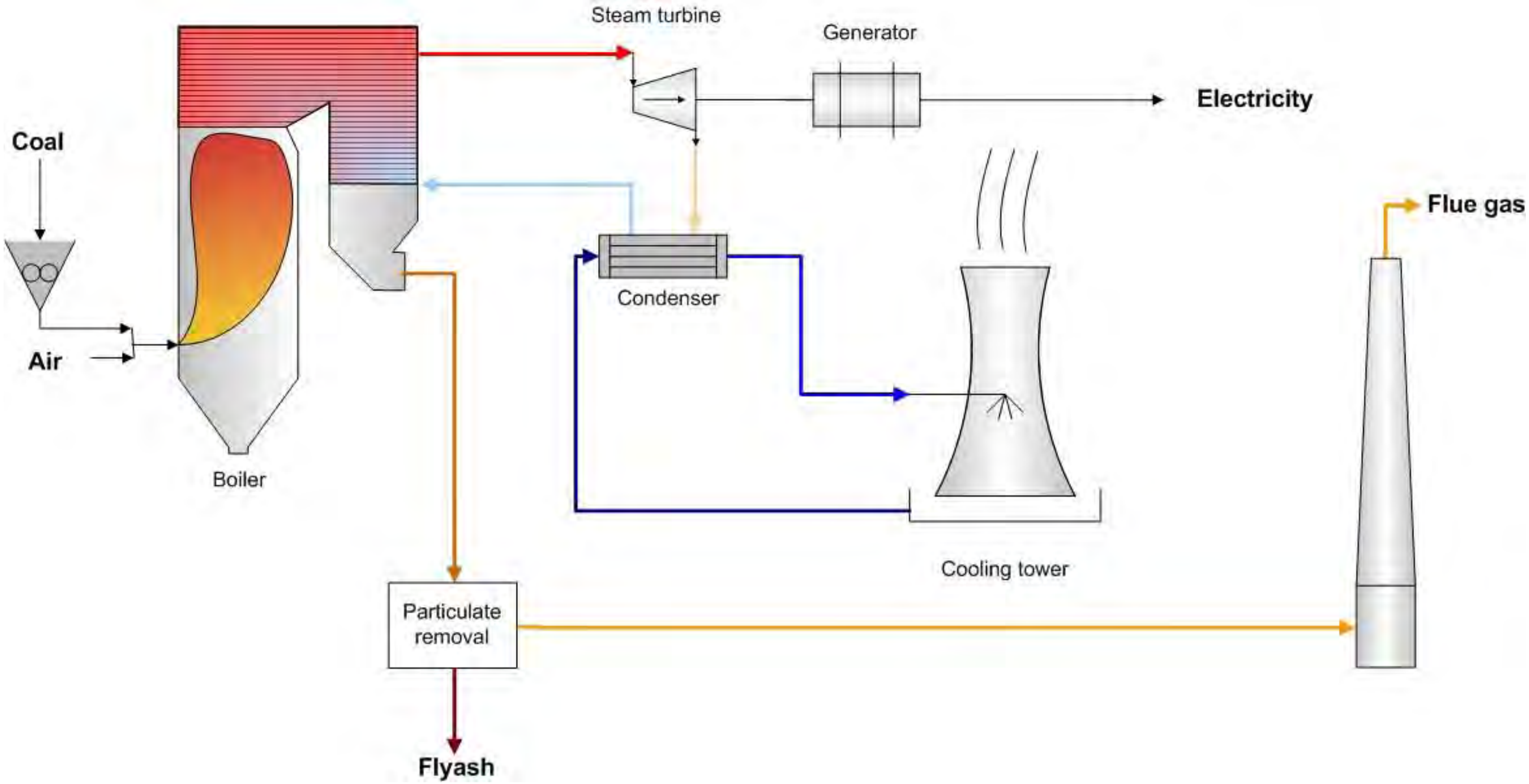
- The **most common** method is to use a **generator**
    - Mechanical energy is converted to electrical energy by rotating a coiled conductor (typically wound copper wire) inside a magnetic field
    - By rotating the coil its magnetic environment is constantly changing and this induces a voltage (Faraday's law)
- **Other options** include the direct conversion of either solar radiation or chemical energy to electrons using **photovoltaics** or **fuel cells** respectively



Electricity generation – mechanical energy sources

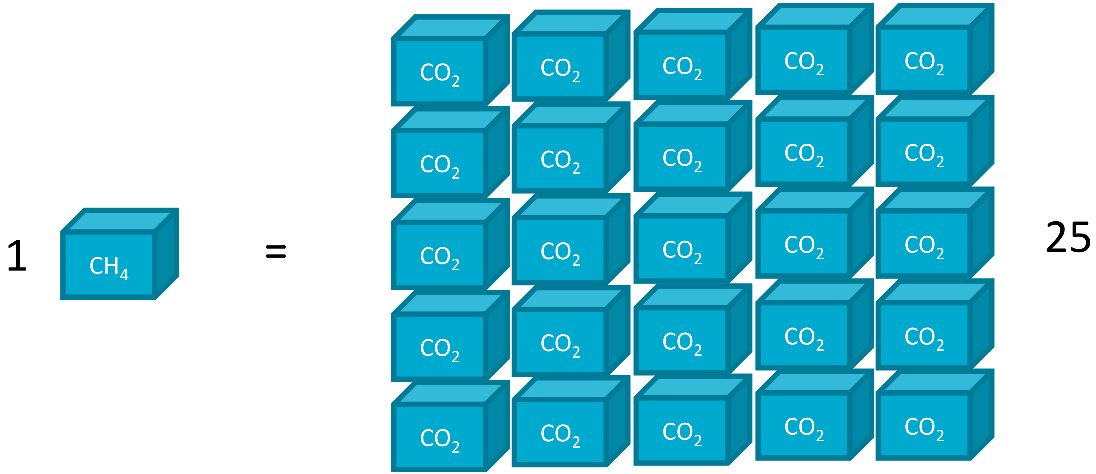
- The **vast majority** of electricity generation is done using **turbines** to drive the generator
  - Steam turbine – steam is expanded through the turbine to turn the blades
  - Gas turbine – a fuel (e.g. petrol, CH_4, H_2) is combusted and the resulting hot gases expanded through the turbine to turn the blades
  - Wind and water turbines
- Piston engines are used in smaller applications

Electricity generation – a typical Australian coal fired power station

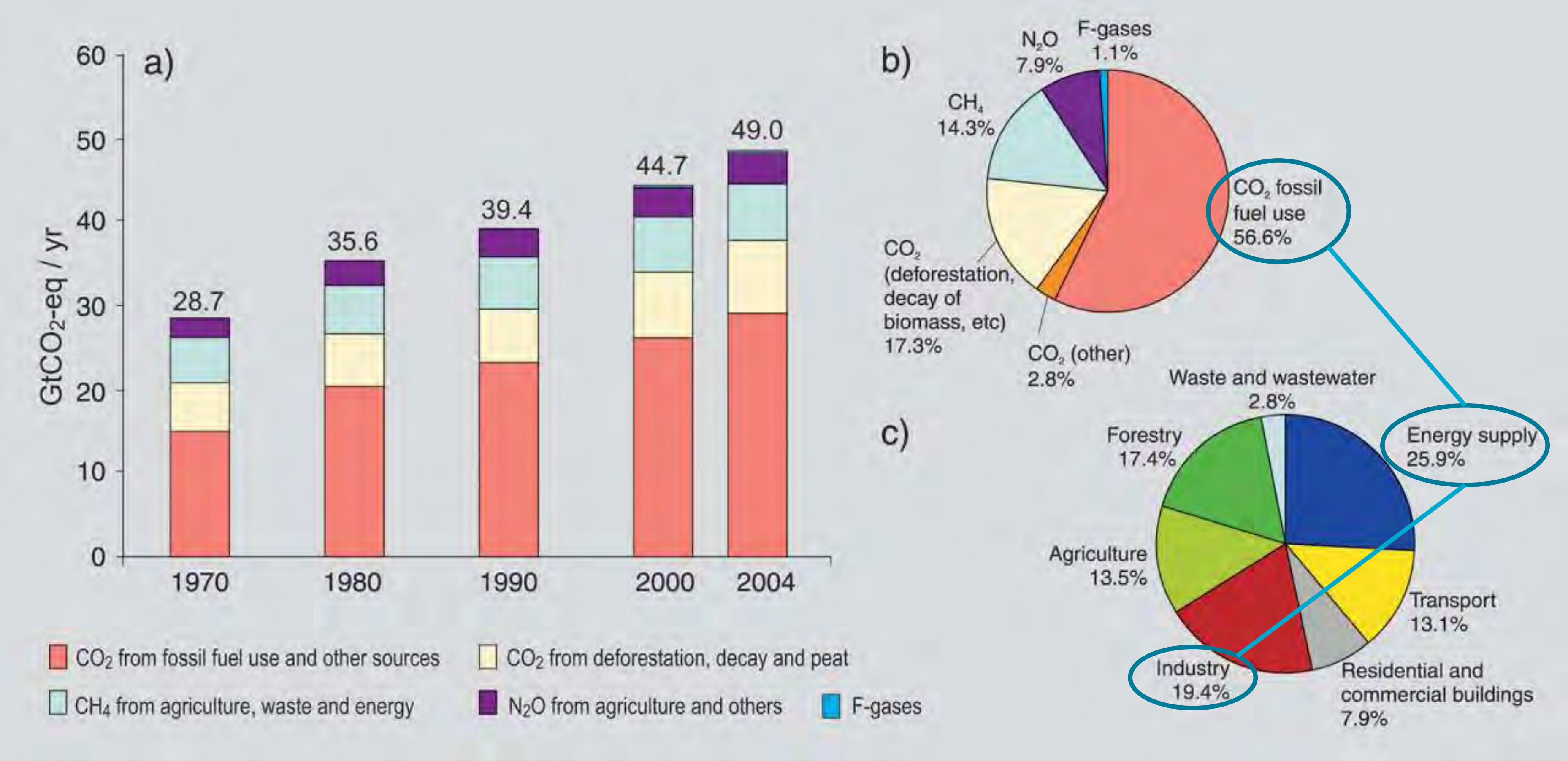


Greenhouse gas emissions - terminology

- GreenHouse Gas – GHG
  - A gas in the atmosphere that absorbs and emits radiation in the infrared range – H_2O, CO_2, CH_4, N_2O, O_3
- Anthropogenic – from human activity
- CO_2-eq – CO_2 equivalent
  - The amount of CO_2 that would cause the same warming as gas X over the same time (typically 100 years)



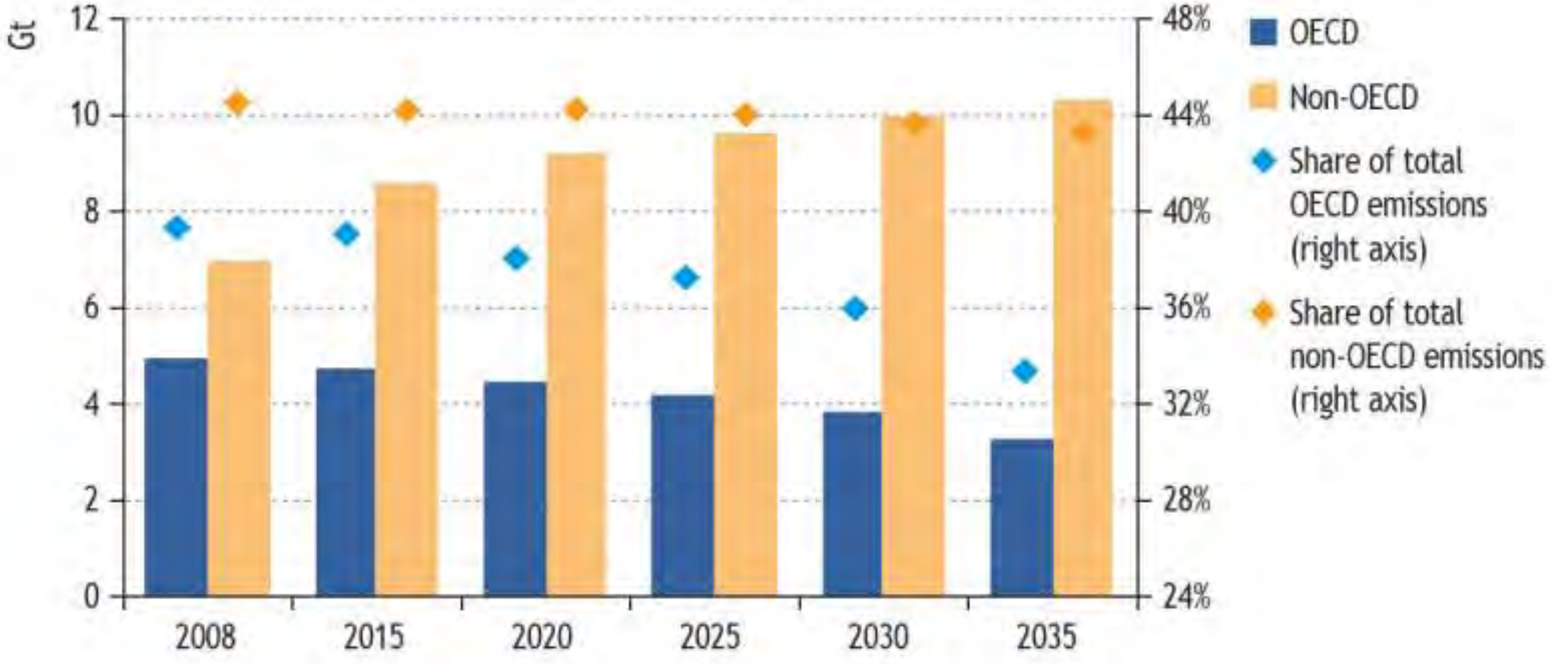
Greenhouse gas emissions by sector



a) Global annual GHG emissions from 1970 – 2004. b) Share of anthropogenic GHGs in 2004 (CO_2-eq). c) Share of different sectors in total anthropogenic GHG emissions in 2004 (CO_2-eq).

IPCC, *Climate Change 2007 Synthesis Report*. IPCC, Geneva, Switzerland, 2007, pg 36.

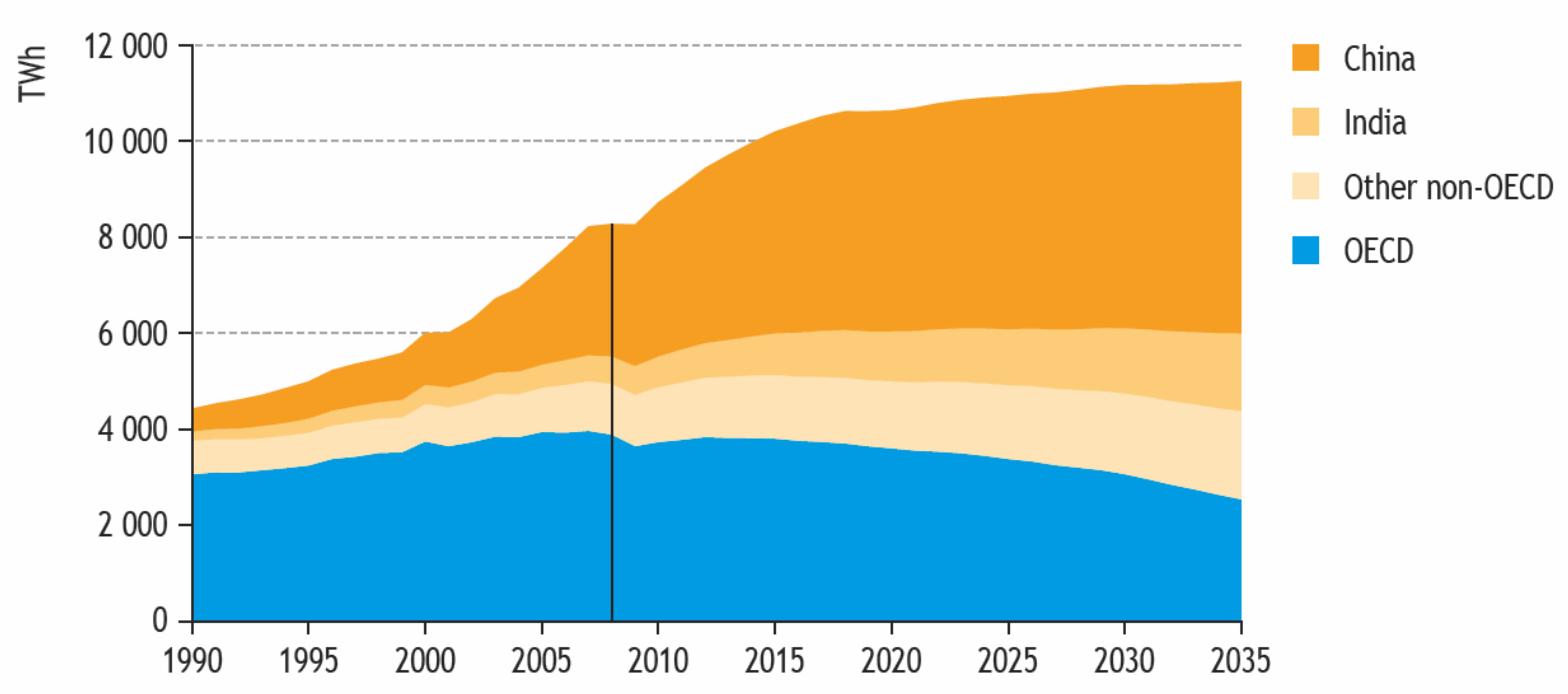
Contribution from electricity generation and heat



- Electricity generation and heat accounts for **41% of CO_2 emissions**
- Projections to **2035** correspond to a **75% increase** in electricity production with OECD and all European countries adopting CO_2 emission limits

OECD/IEA, *World Energy Outlook 2010*. IEA, Paris, France, 2010, pg 224.

Contribution from electricity generation - coal



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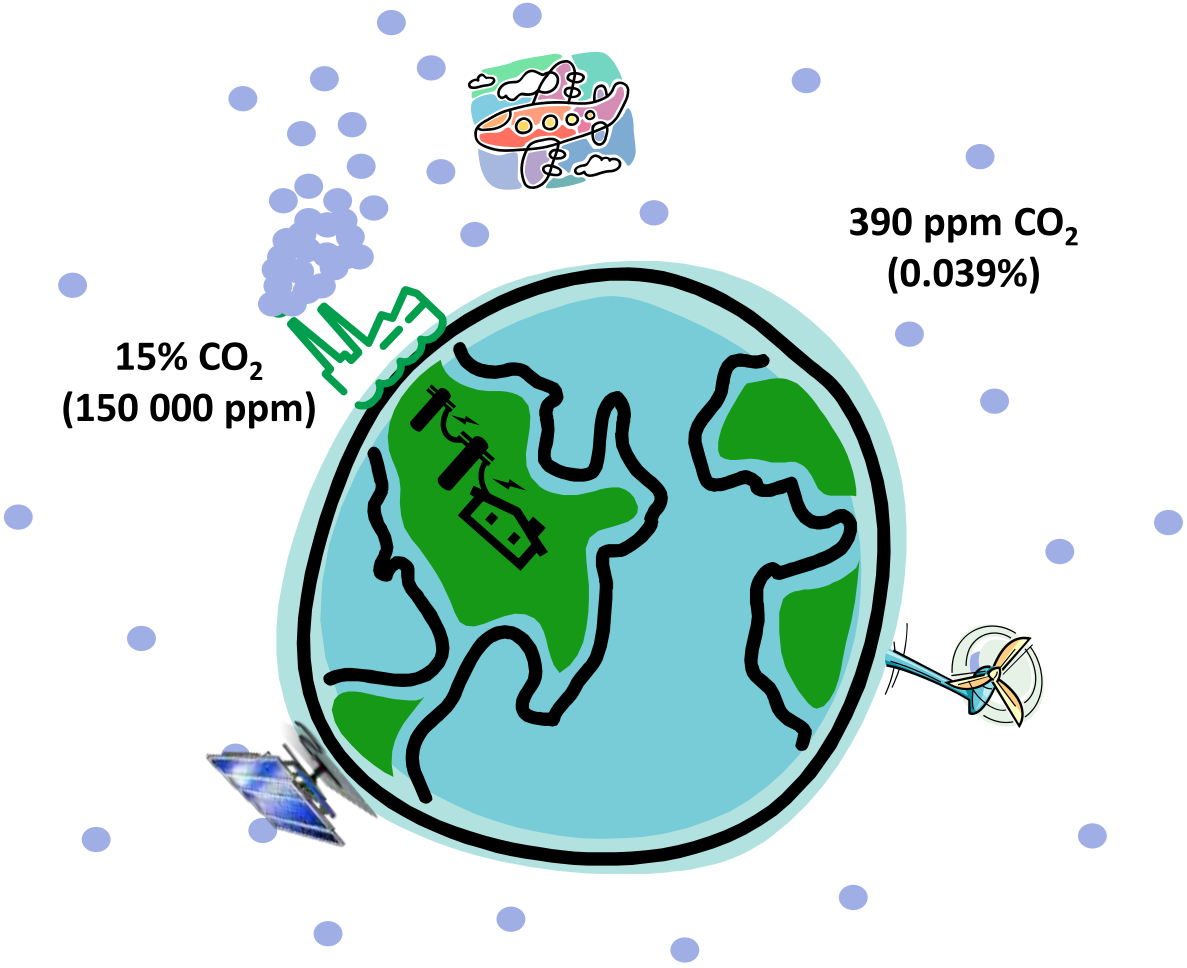

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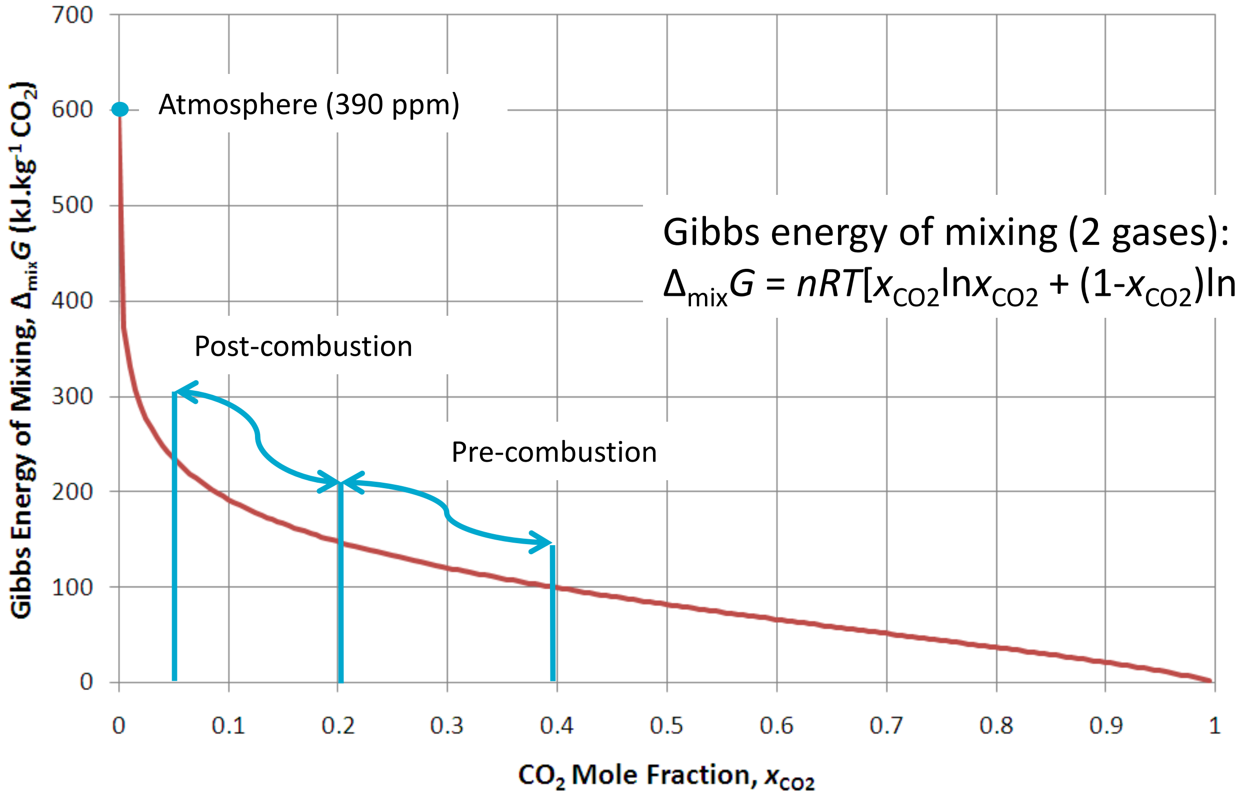

Gibbs energy of mixing (2 gases):

$$\Delta_{mix}G = nRT[x_{CO2}\ln x_{CO2} + (1-x_{CO2})\ln(1-x_{CO2})]$$

Calculated at 40°C

Acknowledgements

The authors wish to acknowledge financial assistance provided through Australian National Low Emissions Coal Research and Development (ANLEC R&D). ANLEC R&D is supported by Australian Coal Association Low Emissions Technology Limited and the Australian Government through the Clean Energy Initiative.

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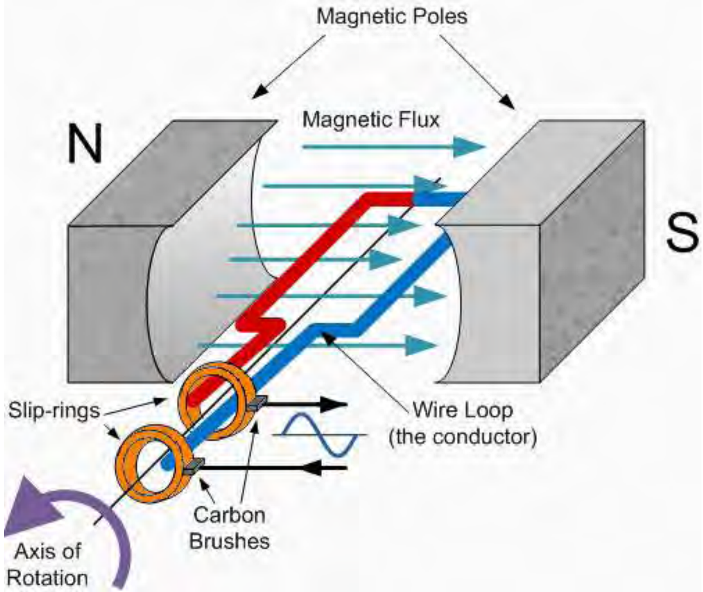

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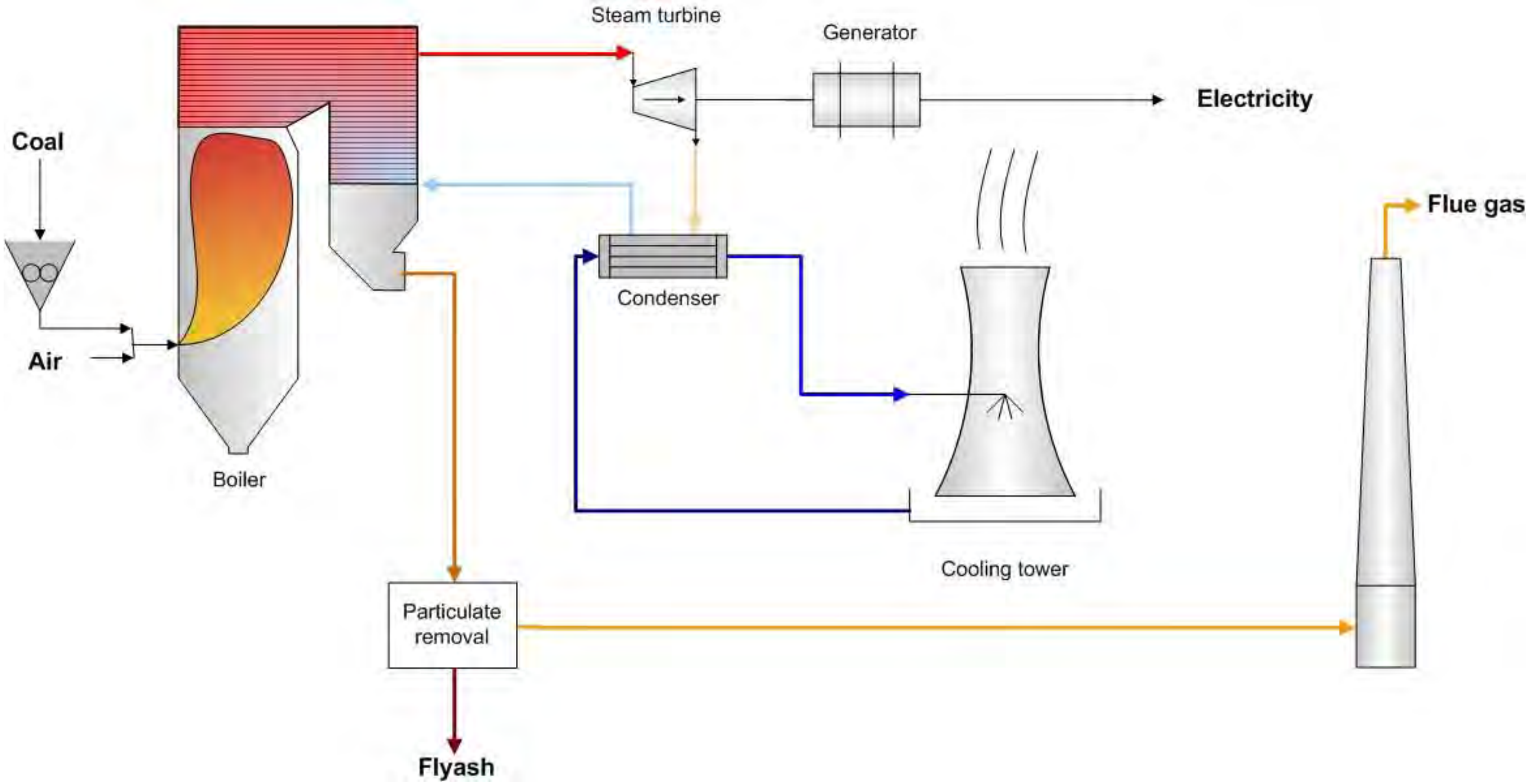

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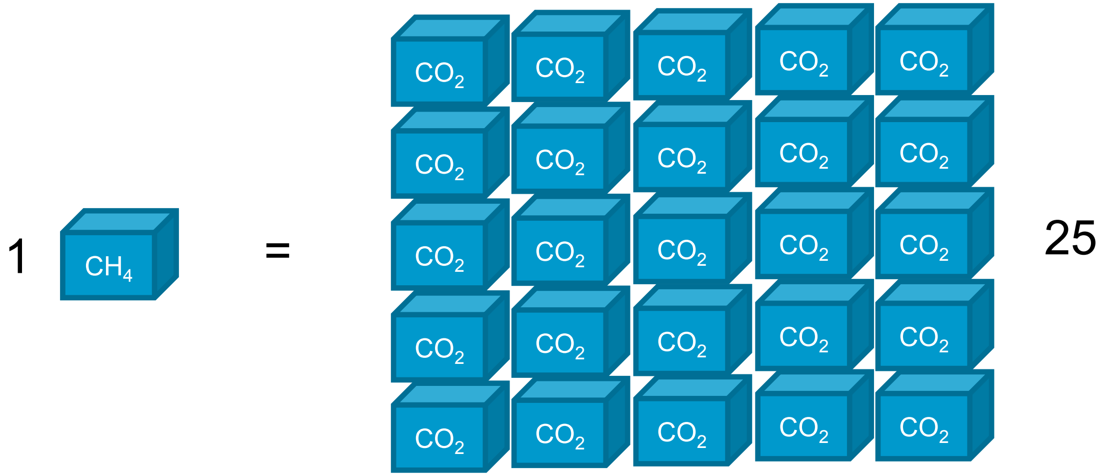

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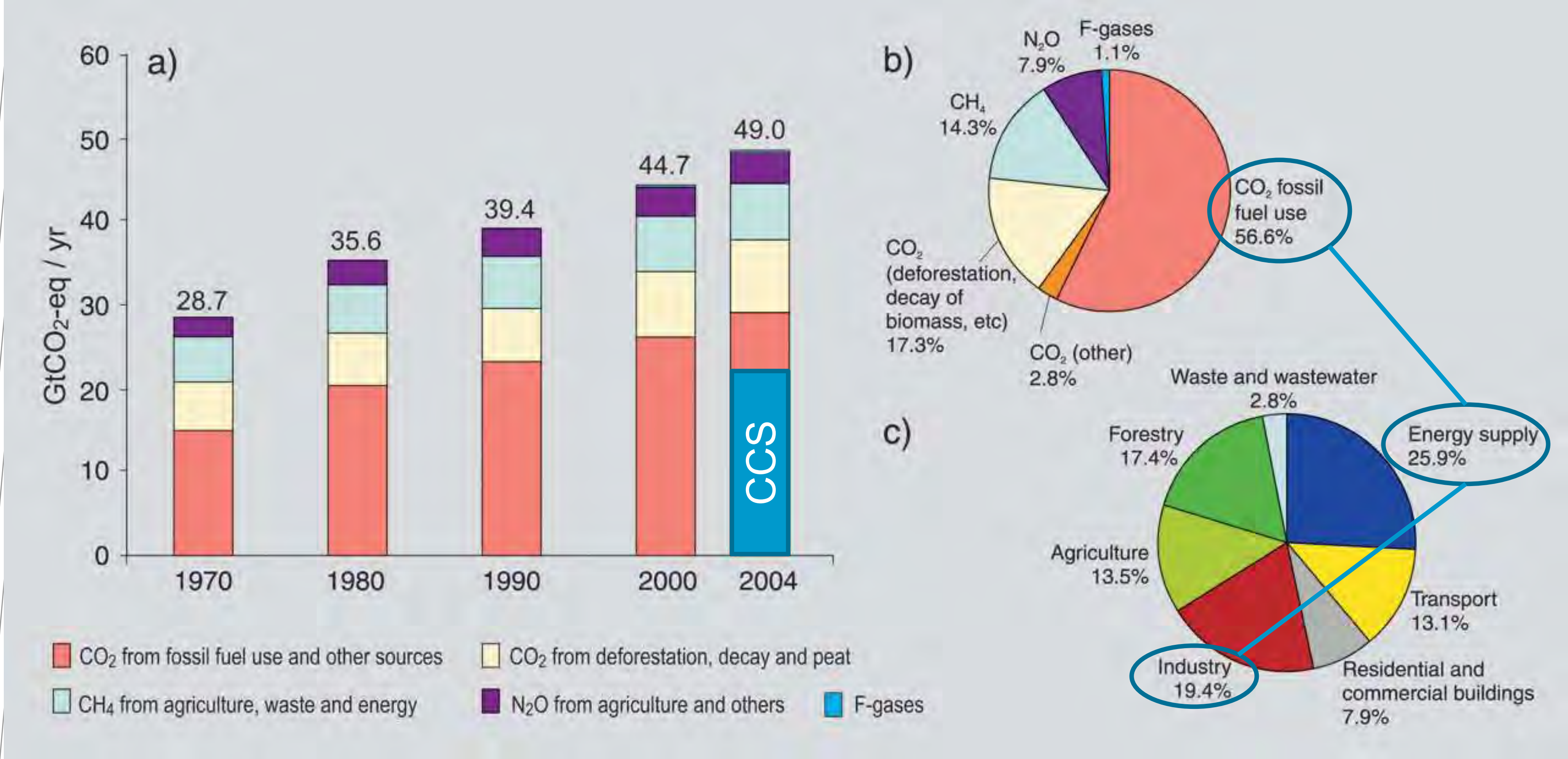

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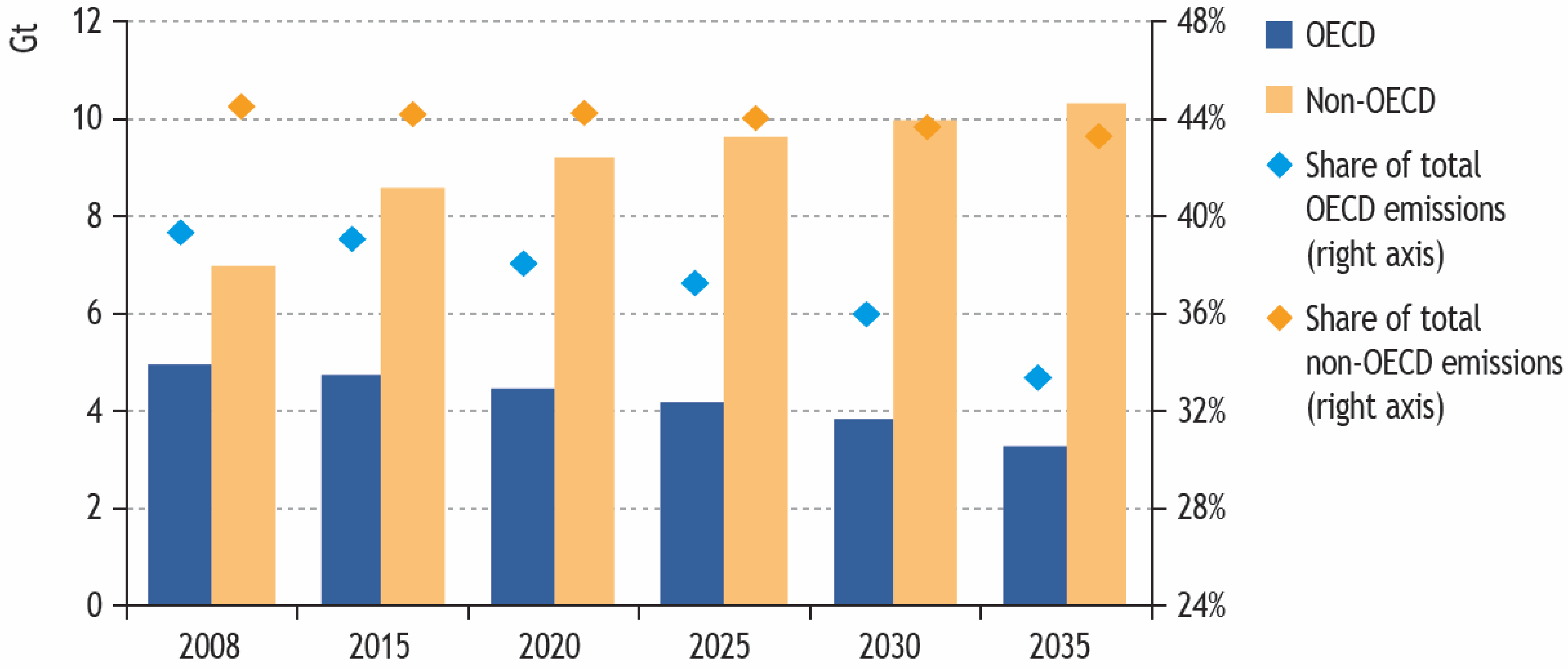

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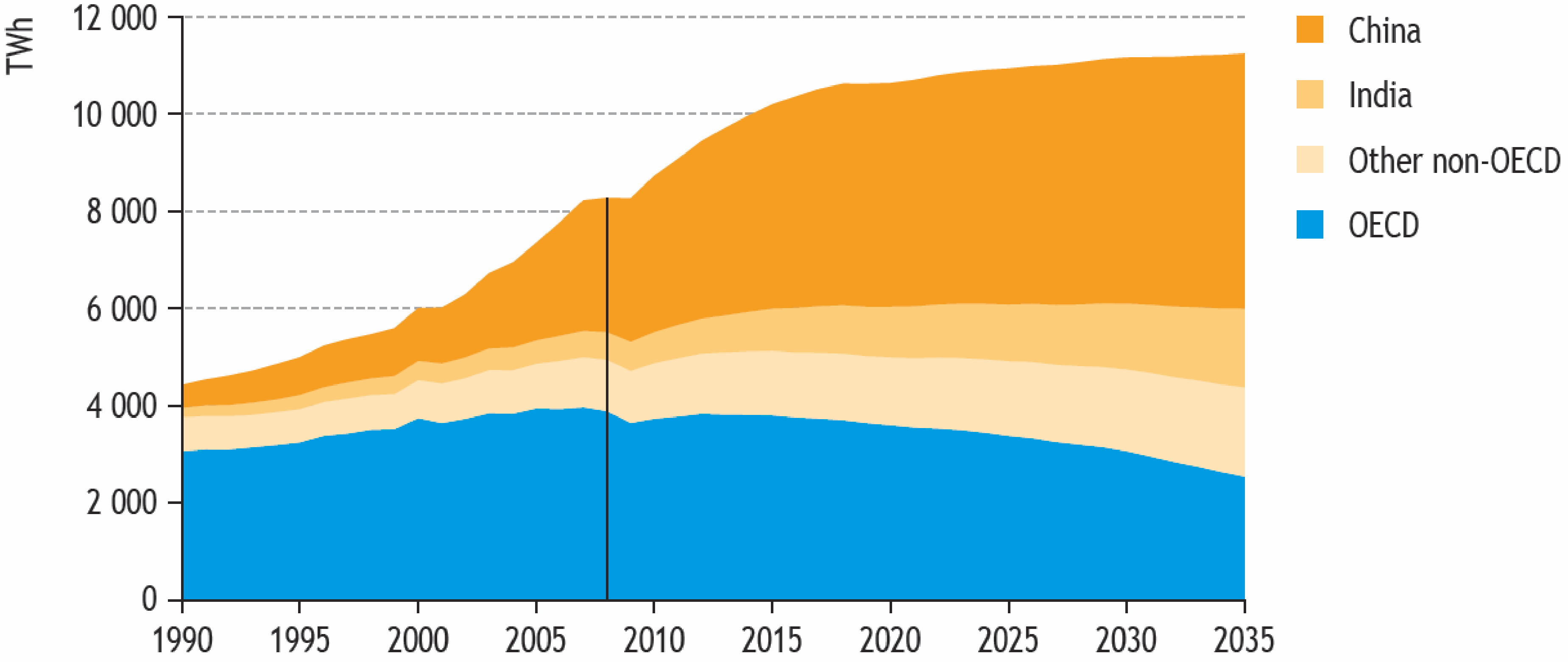

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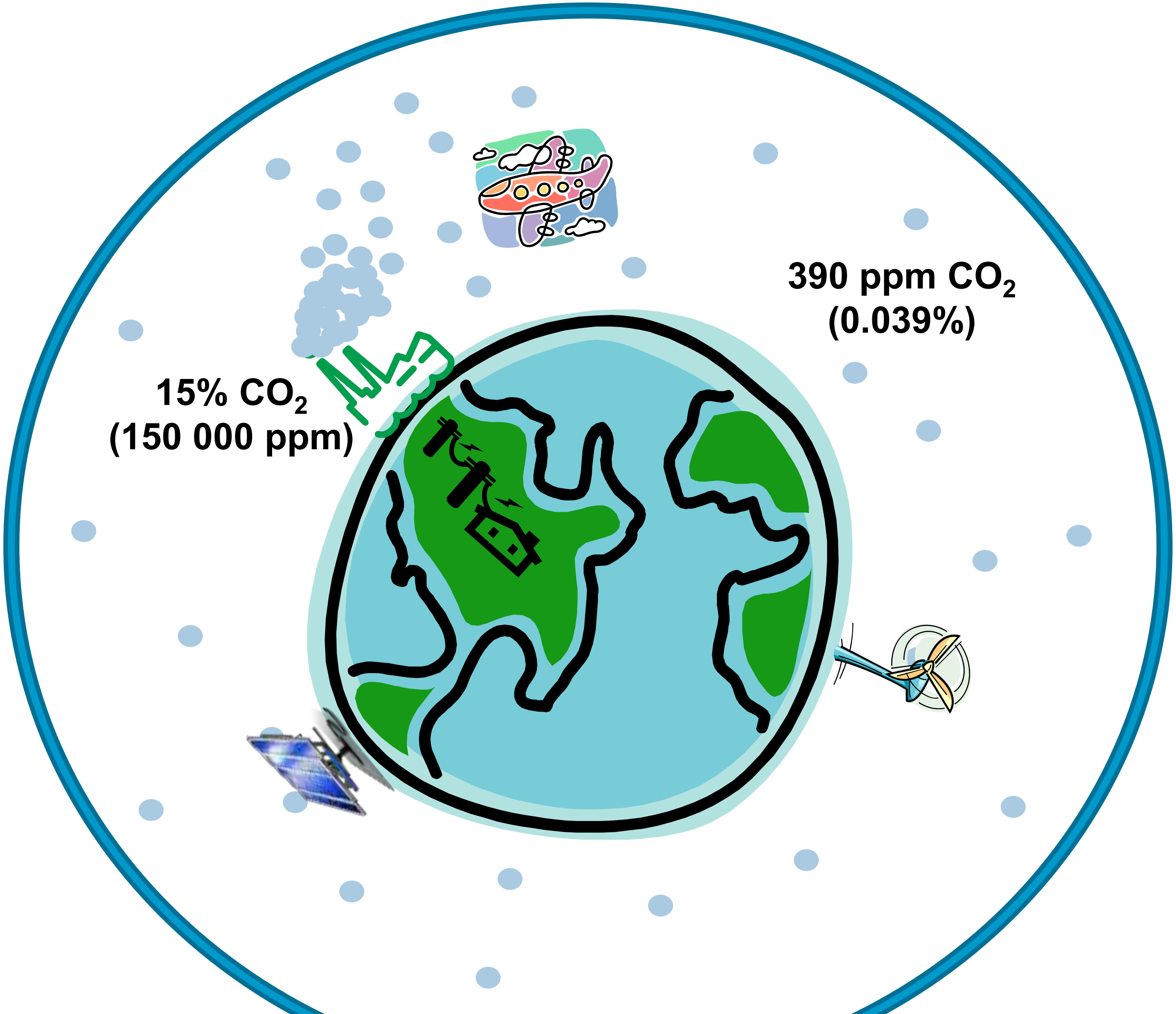

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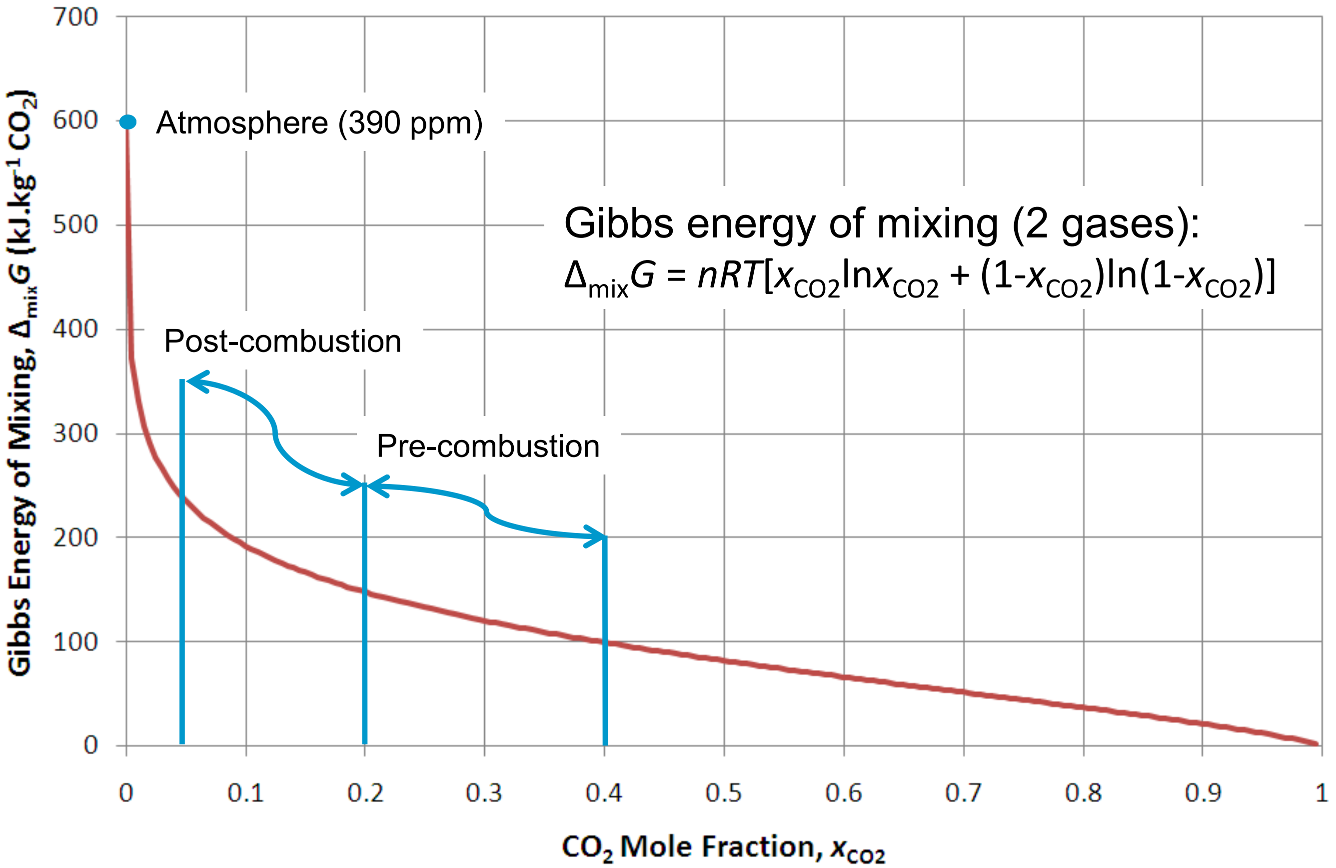

Gibbs energy of mixing (2 gases):

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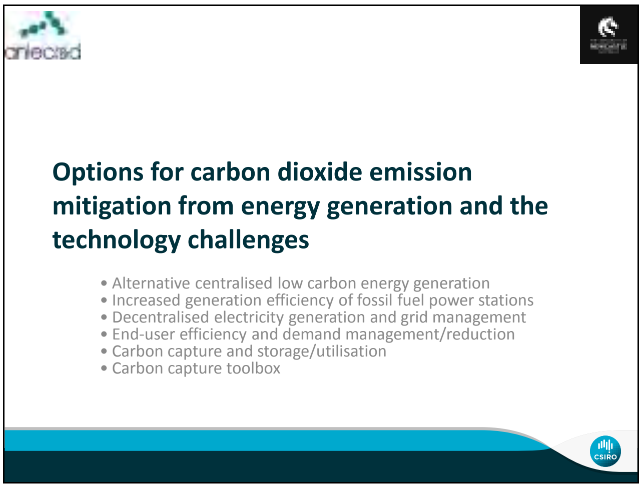
Calculated at 40°C

Options for CO_2 emission mitigation from energy generation and the technology challenges



Options for carbon dioxide emission mitigation from energy generation and the technology challenges

- Alternative centralised low carbon energy generation
- Increased generation efficiency of fossil fuel power stations
- Decentralised electricity generation and grid management
- End-user efficiency and demand management/reduction
- Carbon capture and storage/utilisation
- Carbon capture toolbox

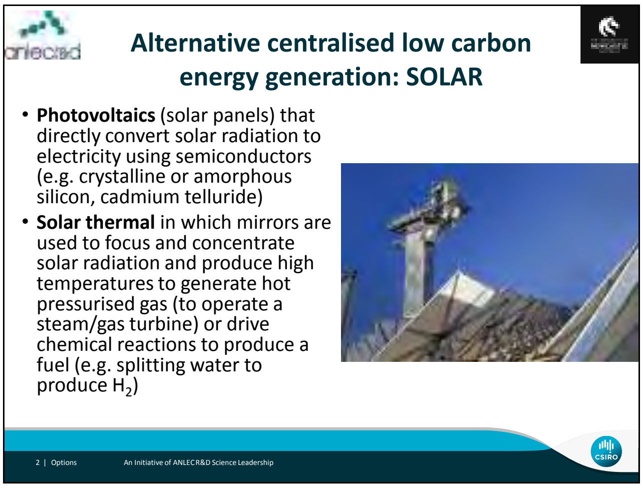
There are a whole host of ways that the CO_2 emissions from energy generation can be reduced. In terms of large scale centralised electricity generation there are renewable energy options like solar, wind and hot rocks. You can also improve the efficiency of fossil fuel power stations by using gas instead of coal or increased steam temperatures.

But, are large power plants often hundreds of kilometres from where the electricity is used the best way to do it? What about decentralised electricity generation where each household or community generates its own electricity and shares any extra with its neighbours?

And of course there is the question of demand. The fastest way to reduce CO_2 emissions is to use less electricity. This means finding ways to improve the efficiency of electricity use and intelligent methods to manage demand.

There will be no single solution to reducing CO_2 emissions, and large scale fossil fuel based power stations are here to stay for some time yet. That means we need to do something about their emissions, and this is why carbon capture and storage (CCS) is important. But CCS incorporates a number of technology options, and we need to consider the pros and cons of each to match the best CCS technology to the different types of fossil fuel power station (coal, oil, gas, …).

Alternative centralised low carbon energy generation: SOLAR



Alternative centralised low carbon energy generation: SOLAR

- **Photovoltaics** (solar panels) that directly convert solar radiation to electricity using semiconductors (e.g. crystalline or amorphous silicon, cadmium telluride)
- **Solar thermal** in which mirrors are used to focus and concentrate solar radiation and produce high temperatures to generate hot pressurised gas (to operate a steam/gas turbine) or drive chemical reactions to produce a fuel (e.g. splitting water to produce H_2)

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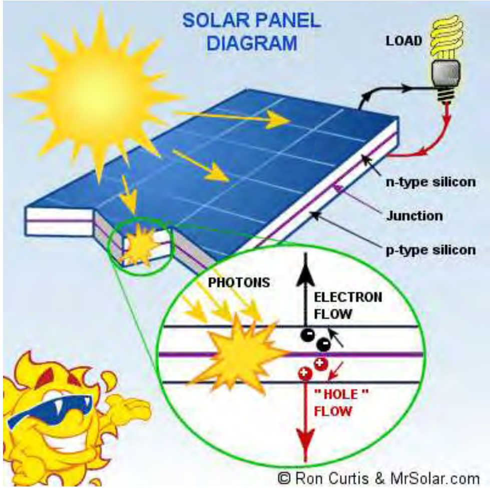
Photovoltaics

There are two flavours of solar electricity. The most common are photovoltaics. These are the typical solar panels you see on house roofs, but for centralised electricity generation they are arranged into large arrays called solar farms. They convert solar radiation to electricity by the photovoltaic effect. A p-n junction semiconductor (e.g. silicon or cadmium telluride) is attached between two electrodes. When photons strike the semiconductor electrons become excited and flow between the electrodes.

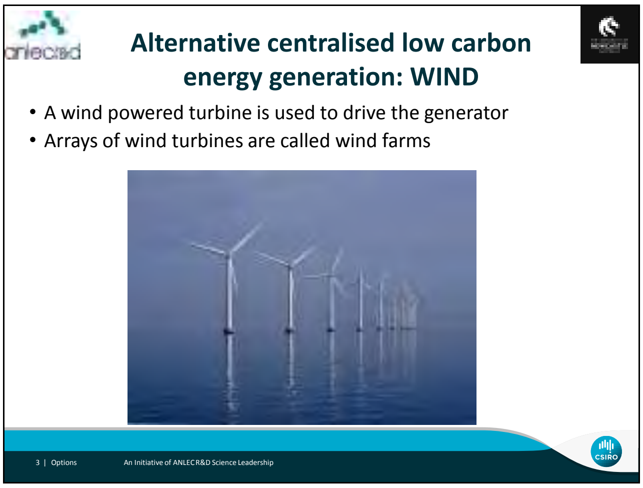


Solar thermal

Solar thermal is more straightforward. Mirrors are used to focus and concentrate solar radiation to produce heat. That heat is used either to produce steam and drive a turbine, or produce hot gas to drive a turbine. The heat might also be used in a chemical process to convert water or methane into hydrogen, which can then be combusted in a turbine.

The PS20 20 MW solar thermal power ststaion in Spain.

Alternative centralised low carbon energy generation: WIND



Alternative centralised low carbon energy generation: WIND

- A wind powered turbine is used to drive the generator
- Arrays of wind turbines are called wind farms

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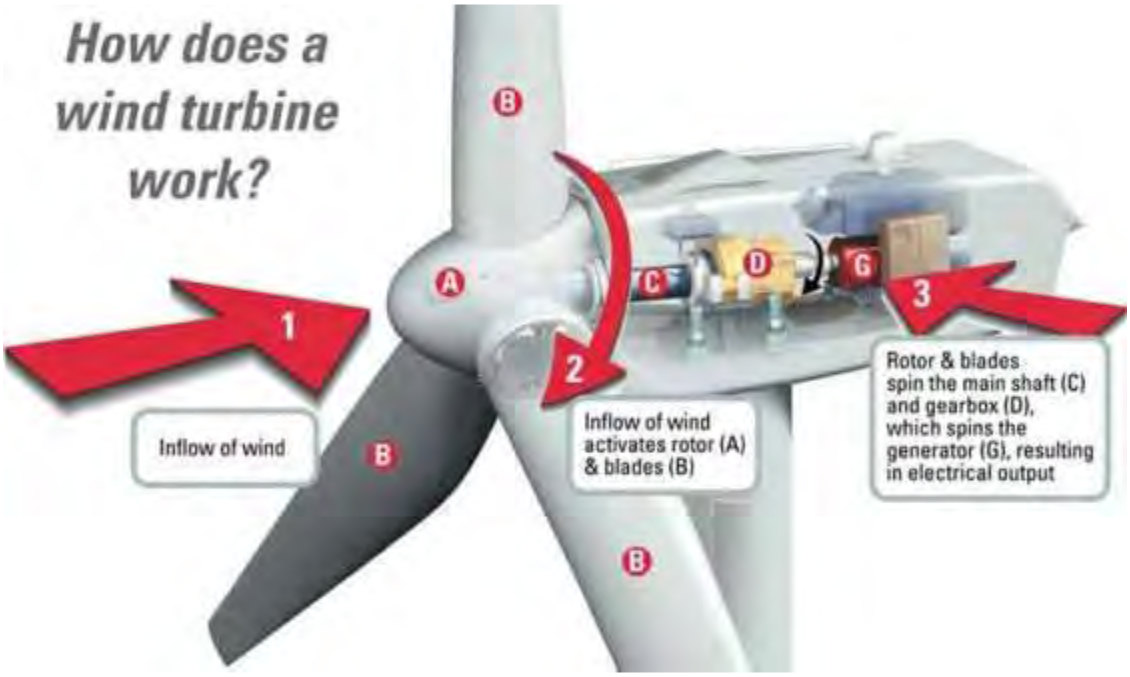
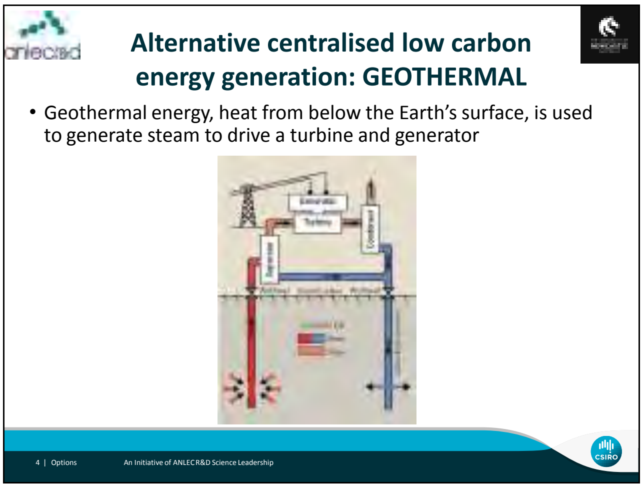
The use of wind to turn a turbine dates back centuries in the form of windmills. Originally the rotation was used to mill grain. In modern wind turbines the rotation turns the axle of a generator to produce electricity. Centralised electricity generation using wind turbines is achieved by having many turbines arranged in a wind farm.



Currently (as of 2012) the largest wind farm in the world, the Alta Wind Energy Centre, is in California. It has an installed capacity of 1020 MW from 390 turbines. But it is Denmark that generates the largest proportion of its electricity using wind – 26% in 2011.

Alternative centralised low carbon energy generation: GEOTHERMAL



Alternative centralised low carbon energy generation: GEOTHERMAL

- Geothermal energy, heat from below the Earth’s surface, is used to generate steam to drive a turbine and generator

4 | Options

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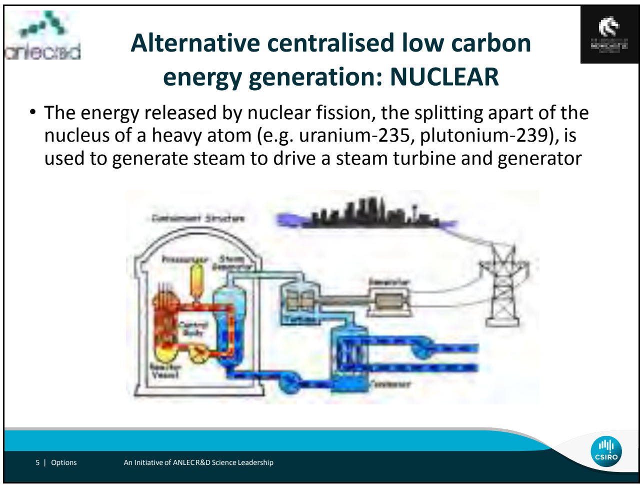
Geothermal electricity generation relies on “hot rocks” under the earth’s surface. Radioactive decay occurring in the earth’s core produces heat and this heat moves to the earth’s surface. At depths of several kilometres or more temperatures are high enough to generate steam for electricity generation. In some places with particular types of geology such as Iceland, there is geothermal activity close to the surface. These locations are the most attractive for geothermal power as bores need only be drilled to shallow depths.

The Nesjavellir Geothermal Power Station near Reykjavik in Iceland.

Steam is produced either by drilling bores in locations where water is already present, or by pumping water down into the hot subsurface to produce steam. The steam is returned to the surface to drive a steam turbine, condensed, and then pumped back underground.

Alternative centralised low carbon energy generation: NUCLEAR



Alternative centralised low carbon energy generation: NUCLEAR

- The energy released by nuclear fission, the splitting apart of the nucleus of a heavy atom (e.g. uranium-235, plutonium-239), is used to generate steam to drive a steam turbine and generator

Recently nuclear power has fallen out of favour due to heighten safety concerns from recent accidents and issues around waste disposal. But it is still a low CO_2 emission source of power that is used extensively, providing about 15% of electricity globally.

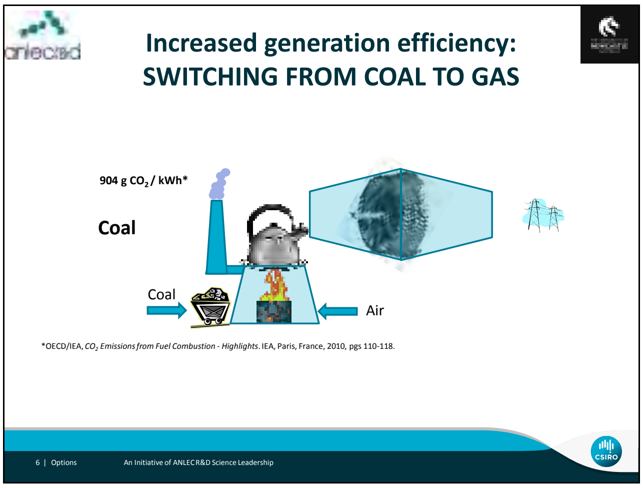
In a nuclear power station steam from heating water is used to drive a turbine in the same way as a typical fossil fuel power station. The difference is the heat is produced by nuclear reactions rather than combustion. When some atoms are hit by a neutron ($^{1}_{0}n$) they split or undergo fission and large amounts of energy are released. Typically the isotopes uranium-235 ($^{235}_{92}U$) and plutonium-239 are used as the fuel for nuclear power reactors. A neutron source such as californium-252 is also required to start the nuclear reaction.

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{142}_{58}Ba + ^{91}_{38}Kr + 3^{1}_{0}n + energy$$

In the above reaction fission also produces more neutrons which in turn results in more fission. This is a nuclear chain reaction, which occurs when a critical mass of nuclear fuel is present. Because of this chain reaction some of the neutrons produced must be absorbed or slowed down to avoid a runaway reaction, otherwise known as a nuclear bomb!

The atoms resulting from fission are still radioactive, which is why disposal of used nuclear fuel is a challenge.

Increased generation efficiency: SWITCHING FROM COAL TO GAS



Increased generation efficiency:
SWITCHING FROM COAL TO GAS

904 g CO_2 / kWh*

Coal

Coal

Air

*OECD/IEA, *CO_2 Emissions from Fuel Combustion - Highlights*. IEA, Paris, France, 2010, pgs 110-118.

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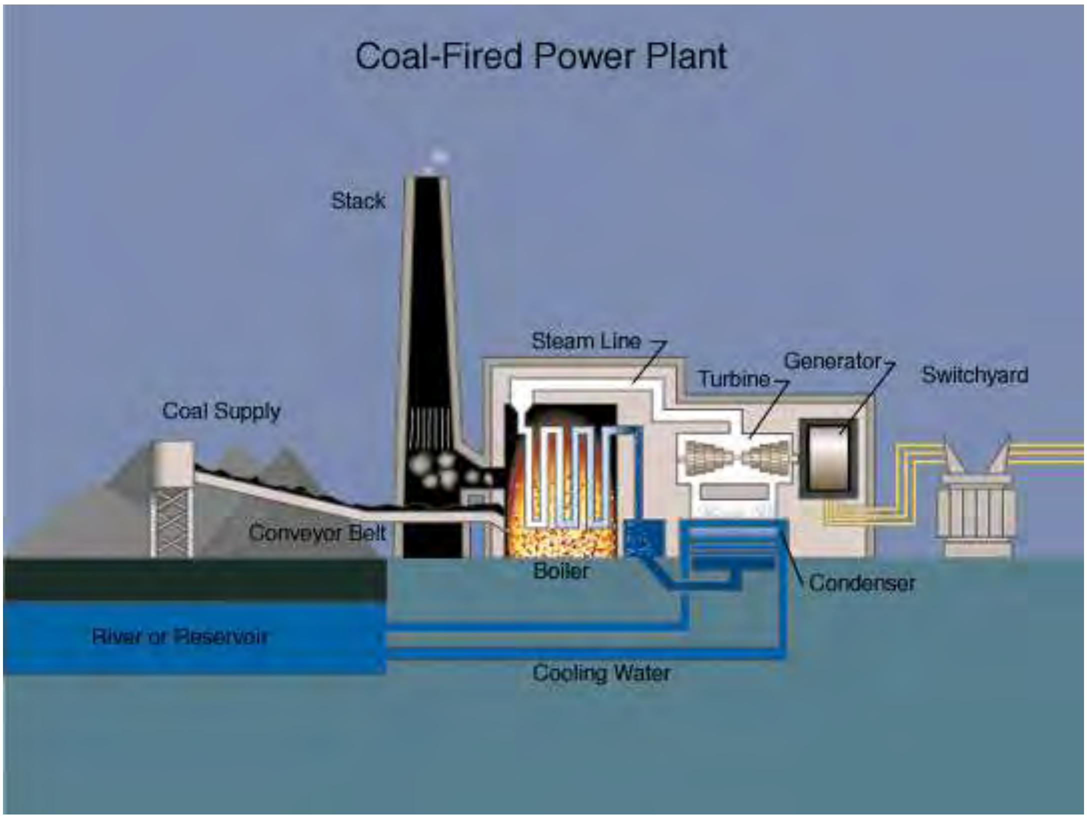
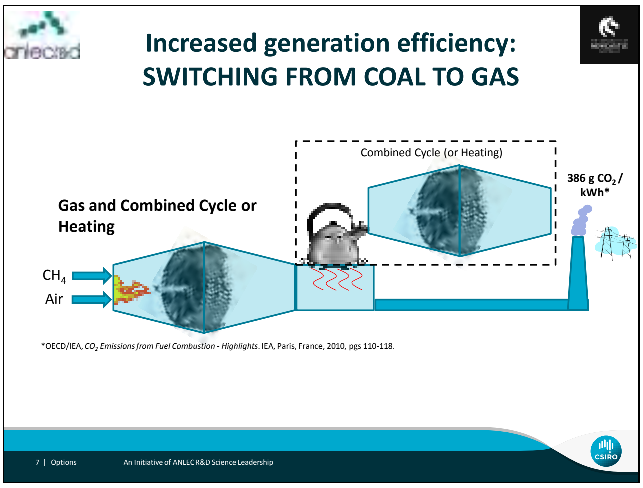
A typical black coal fired power station emits 904 g of CO_2 per kWh of electricity produced. This is because considerable energy is wasted via the process of heating water to produce steam followed by condensation of the vapour after it has passed through the turbines. The coal combustion is only indirectly driving the turbine.



A coal fired power station.

Increased generation efficiency:
SWITCHING FROM COAL TO GAS



Increased generation efficiency:
SWITCHING FROM COAL TO GAS

Combined Cycle (or Heating)

386 g CO_2 / kWh*

Gas and Combined Cycle or Heating

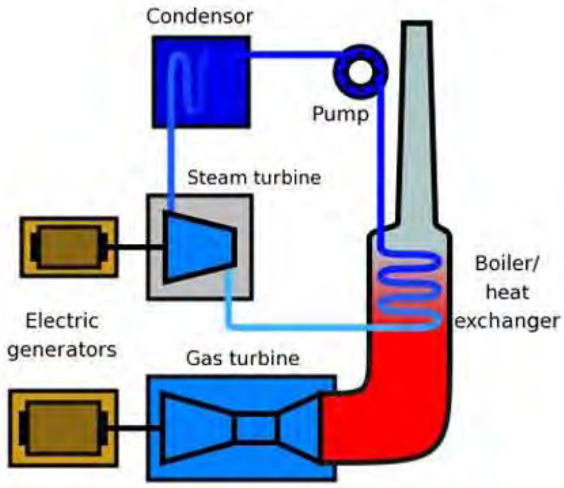
CH_4

Air

*OECD/IEA, *CO_2 Emissions from Fuel Combustion - Highlights*. IEA, Paris, France, 2010, pgs 110-118.

Alternatively using a gas turbine fuelled by methane results in emissions of 386 g CO_2 per kWh of electricity. The major reasons are the combustion gases can directly drive a turbine and the turbine exhaust gases are hot enough to produce steam. This steam can then be used to produce electricity using a steam turbine or for other heating, such as peoples' homes. It is this direct use of the combustion gases use of the waste heat from the gas turbine that makes the process more efficient. If a gas turbine is combined with a steam turbine it is called a combined cycle power station. If a gas turbine is combined with heating it is called a combined heat and power station.

Gas turbines have other advantages too. They can be more easily turned up or down to match production of electricity with demand.



A combined cycle gas power station.

Increased generation efficiency:
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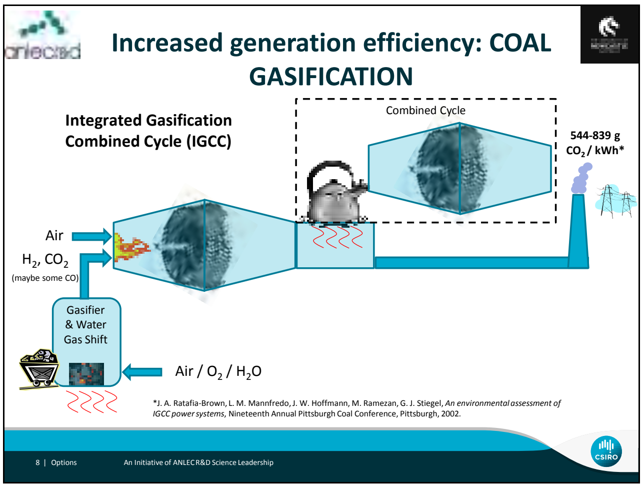

Increased generation efficiency: COAL GASIFICATION

Integrated Gasification Combined Cycle (IGCC)

Combined Cycle

544-839 g CO_2 / kWh*

Air

H_2, CO_2

(maybe some CO)

Gasifier & Water Gas Shift

Air / O_2 / H_2O

*J. A. Ratafia-Brown, L. M. Mannfredo, J. W. Hoffmann, M. Ramezan, G. J. Stiegel, *An environmental assessment of IGCC power systems*, Nineteenth Annual Pittsburgh Coal Conference, Pittsburgh, 2002.

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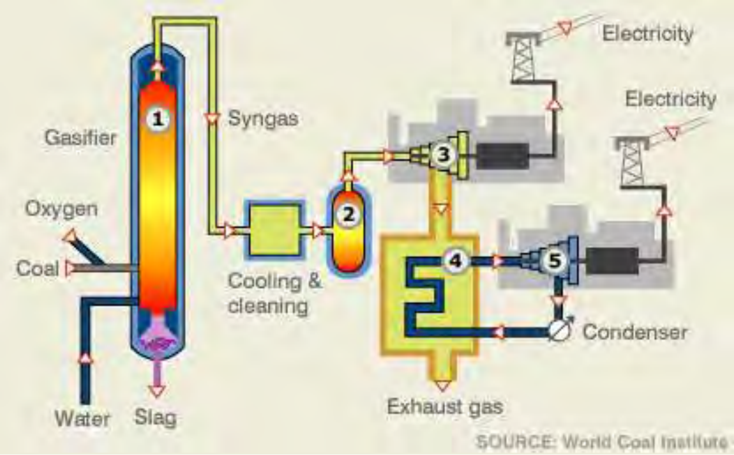
As we saw already electricity can be generated more energy efficiently using a gas turbine. But what if you want to use coal with a gas turbine? This is possible via the process of coal gasification. If coal is heated in the presence of steam and a restricted oxygen supply the coal is oxidised and hydrogen is formed:

$$3C\ (\text{coal}) + O_2 + H_2O \xrightarrow{heat} H_2 + 3CO$$

Syngas, the mixture of H_2 and CO, can be used as a fuel directly. Alternatively the H_2 content of syngas can be increased using the water gas shift reaction:

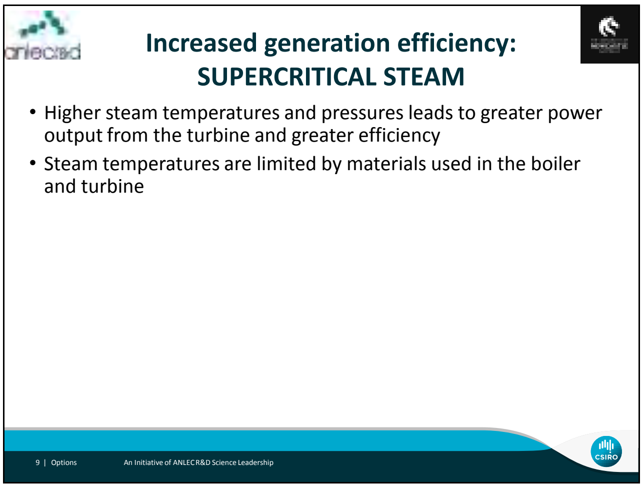
$$CO + H_2O \xrightarrow{heat} H_2 + CO_2$$



An integrated gasification combined cycle (IGCC) power station.

Gas turbines using syngas are commercially available, but turbines able to use pure H_2 are still being developed. Once the gasification process is complete the electricity and heat generation process is the same as that seen previously for a gas turbine.

Increased generation efficiency: SUPERCRITICAL STEAM



Increased generation efficiency: SUPERCRITICAL STEAM

- Higher steam temperatures and pressures leads to greater power output from the turbine and greater efficiency
- Steam temperatures are limited by materials used in the boiler and turbine

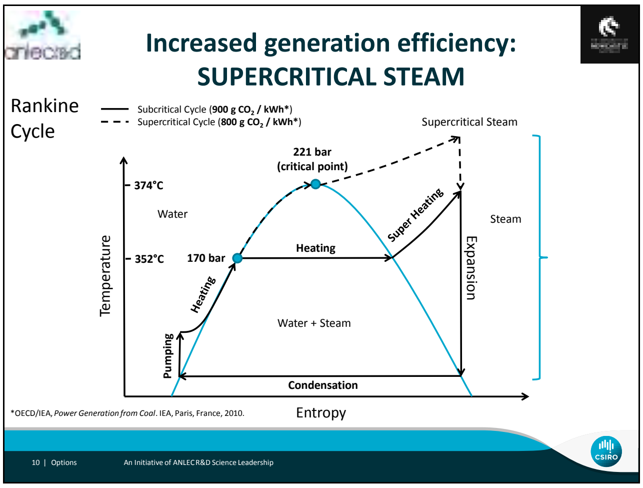
9 | Options   An Initiative of ANLEC R&D Science Leadership

The efficiency of a coal fired power station can be increased by increasing the temperature of the steam used to drive the turbines. The higher the steam temperature, the greater the amount of energy that can be extracted from it during expansion.

The steam temperature in a power station is limited by the materials used in the boiler and turbine. In the past it was necessary to keep the steam temperature and pressure below the critical point. This is called a subcritical steam power station. Above the critical point the steam becomes super critical and is an excellent solvent.

Modern materials mean it is now possible to operate at supercritical steam temperature and pressure. These are supercritical steam power stations and they are about 11% more efficient in terms of CO_2 emissions per kWh of electricity.

Increased generation efficiency: SUPERCRITICAL STEAM



Increased generation efficiency: SUPERCRITICAL STEAM

Rankine Cycle

*OECD/IEA, *Power Generation from Coal*. IEA, Paris, France, 2010.

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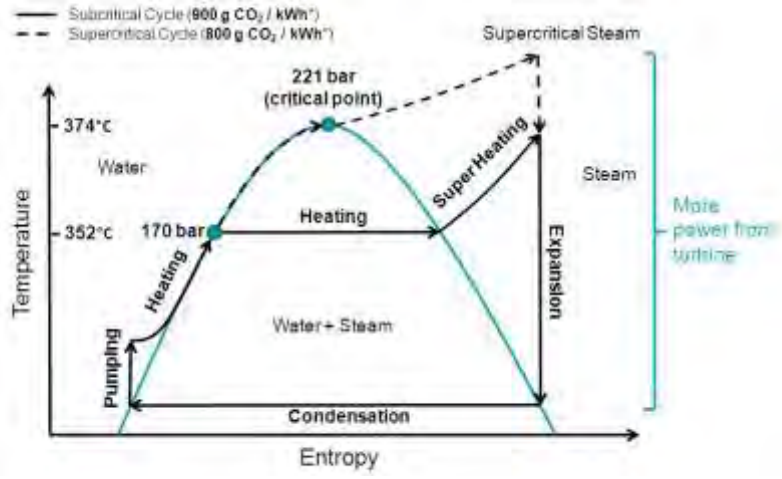
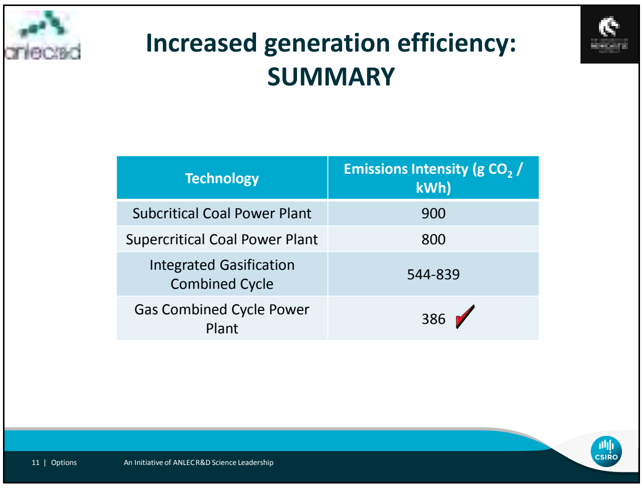
This temperature-entropy diagram shows the subcritical and supercritical steam cycles. The area under the blue curve is where both water and steam are present, to the left is water only and to the right steam. Above the critical point only the single supercritical phase is present.

Following the arrows for the subcritical cycle and starting at the bottom left: 1) water is heated by pumping; 2) further heating is then done in the boiler to 352°C and 170 bar; 3) heating is continued from this point at constant temperature (the heat energy goes into vaporisation); 4) the steam produced leaves the boiler and is superheated to ensure there are no water droplets; 5) the steam is expanded through the turbine, condensed and returned to 1.



The only difference for the supercritical cycle is that the heating in the boiler with increasing temperature and pressure is continued to the critical point.

Increased generation efficiency: SUMMARY



Increased generation efficiency:
SUMMARY

Technology	Emissions Intensity (g CO_2 / kWh)
Subcritical Coal Power Plant	900
Supercritical Coal Power Plant	800
Integrated Gasification Combined Cycle	544-839
Gas Combined Cycle Power Plant	386 ✓

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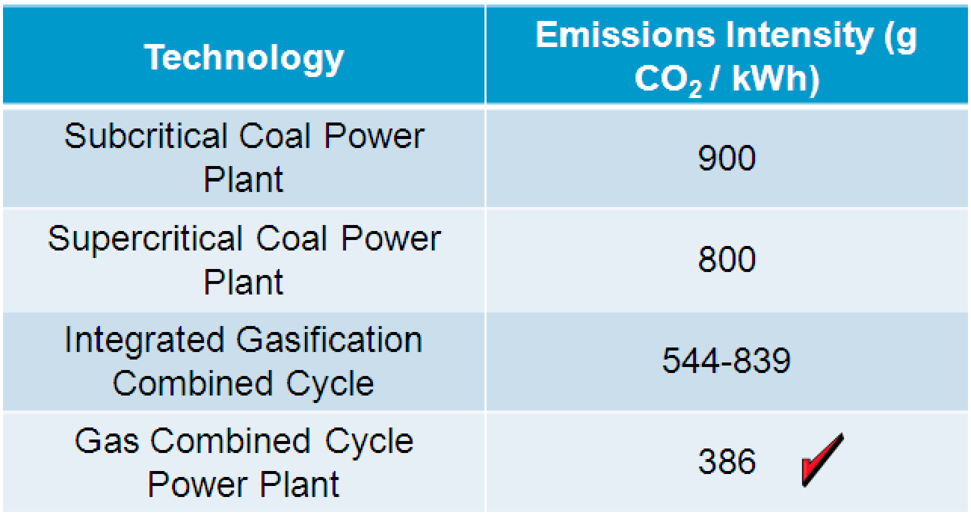
In terms of the CO_2 emissions intensity of fossil fuel electricity generation the clear winner is a combined cycle gas power station at 386 g CO_2 per kWh of electricity. Next is a combined cycle coal gasification plant followed by supercritical and subcritical steam coal fired power stations.

You might be wondering why oil doesn’t feature here? Oil is not really used for large scale electricity generation. It is typically only used to generate electricity in isolated areas that are not grid connected. Furthermore, areas that are not grid connected are becoming less common meaning oil will disappear as a fuel for electricity generation in the near future.



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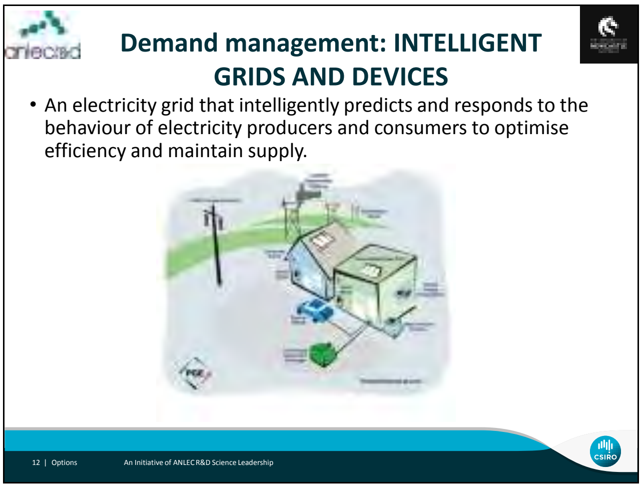
Demand management/reduction: INTELLIGENT GRIDS AND DEVICES



Demand management: INTELLIGENT GRIDS AND DEVICES

- An electricity grid that intelligently predicts and responds to the behaviour of electricity producers and consumers to optimise efficiency and maintain supply.

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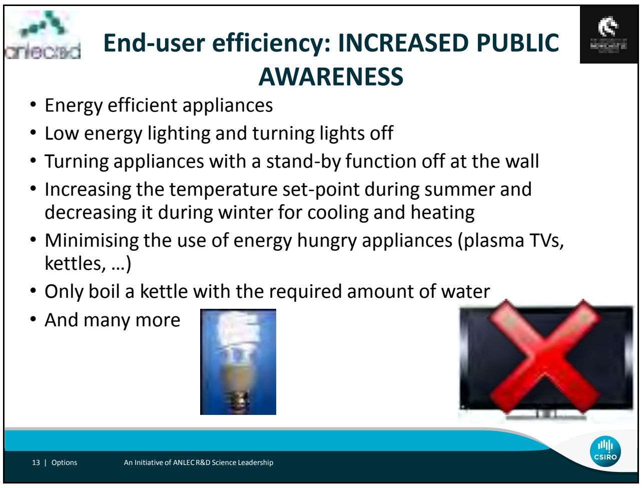
Electricity demand goes through peaks and troughs during the day and night and depending on the weather conditions. Power stations attempt to match their electricity production to demand, but this is difficult particularly for coal fired power stations which are slow to respond. Because of this there is often an excess of electricity produced to ensure enough is available for the next peak. Also as renewable electricity generation is introduced electricity supply is likely to fluctuate from location to location depending upon how sunny/windy it is.

This is where an intelligent electricity grid and intelligent devices come in. To reduce the peaks and troughs the devices in the grid measure supply and demand, and communicate with appliances such as air conditioners and refrigerators. These devices turn on/off in response to supply and demand to maintain a balanced electricity load across the grid. Sophisticated algorithms are used to control the devices in such a way that consumers don't see any significant loss in performance.

Price of electricity and electricity demand profiles for NSW during a week in April 2012.

End-user efficiency: INCREASED PUBLIC AWARENESS



End-user efficiency: INCREASED PUBLIC AWARENESS

- Energy efficient appliances
- Low energy lighting and turning lights off
- Turning appliances with a stand-by function off at the wall
- Increasing the temperature set-point during summer and decreasing it during winter for cooling and heating
- Minimising the use of energy hungry appliances (plasma TVs, kettles, …)
- Only boil a kettle with the required amount of water
- And many more

13 | Options

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An important and conceptually easy way to reduce electricity demand is to educate the general public about how to use electrical devices efficiently. This sounds easy but any social scientist will tell you that changing habitual behaviour is difficult.

In terms of buying devices energy rating stickers allow users to see how energy efficient they are. A lot of people don't realise for example that plasma TV's consume more electricity than old CRT technology.

In terms of behaviour there are a lot of habits people can get into that can significantly reduce electricity demand:

- Turn off lights when you leave a room
- Turn appliances off at the wall when not in use
- Only cool/heat rooms you are using
- Get used to being a little cooler/warmer and set the temperature accordingly (a degree or two makes a big difference in energy consumption)
- Only wash with a full load of clothes
- Only boil enough water in the kettle for what you are using
- And many more …

Carbon capture and storage/utilisation: THE CCS CHAIN

Carbon capture and storage/utilisation:
THE CCS CHAIN

14 | Options

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CAPTURE → TRANSPORT → STORAGE/UTILISATION

Capture

The first step in carbon capture and storage (CCS) is capture. This step involves separating CO_2 from other gases to produce captured pure CO_2. Typically this is done at an emissions point source (e.g. a power station), because as we have seen, it is more efficient to capture CO_2 when it is concentrated. But, CO_2 capture from air is also an option.

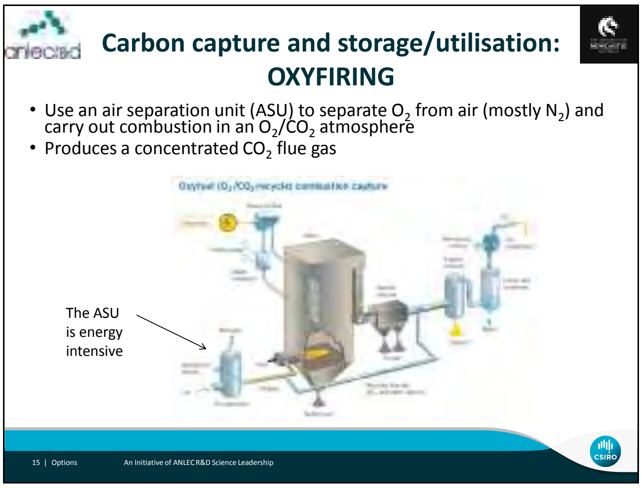
Transport

Once CO_2 has been captured we need to get it to the place where it will be stored or used. This is often some distance away. To transport CO_2 it is compressed until it becomes a liquid or supercritical gas (~130-150 bar). Once compressed is has the density of a liquid (the volume is reduced about ~400x) and it can be easily pumped through pipelines. In the US there are thousands of kilometres of CO_2 pipelines that have been used for enhanced oil recovery (pumping CO_2 into oil reservoirs to force more oil out) for decades.

Storage/Utilisation

The majority of CO_2 captured using CCS will end up stored by pumping into either deep saline aquifers of depleted gas reservoirs. Deep saline aquifers are at depths of 800 m or greater and are regions of porous rock impregnated with saline water. Suitable aquifers have an impermeable cap rock, and when pumped into the aquifer CO_2 dissolves forming a dense liquid that migrates downward.

Carbon capture and storage/utilisation: OXYFIRING



Carbon capture and storage/utilisation: OXYFIRING

- Use an air separation unit (ASU) to separate O_2 from air (mostly N_2) and carry out combustion in an O_2/CO_2 atmosphere
- Produces a concentrated CO_2 flue gas

The ASU is energy intensive

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Oxyfiring is also called denitrogenation. It is where in a step prior to combustion, oxygen is separated from air. This is done in an air separation unit which typically uses cryogenic distillation to separate O_2 from air. The O_2 is then combined with CO_2 and combustion is carried out in an O_2/CO_2 atmosphere. This results in a flue gas that is mostly CO_2 eliminating the post combustion separation step.

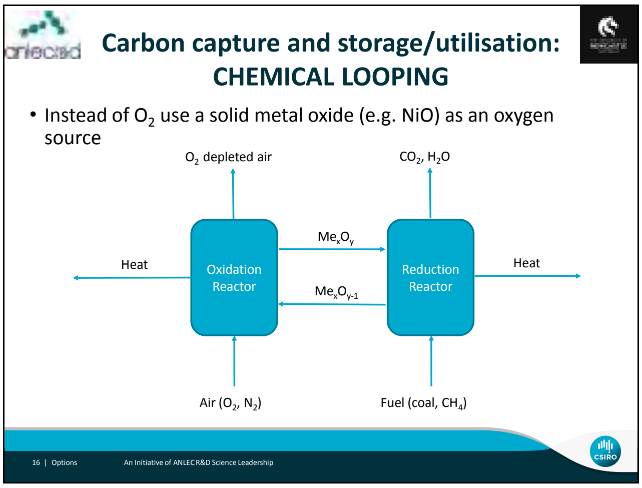
While the CO_2 separation step is eliminated, the air separation unit requires a large amount of energy. It relies on cooling air to below its boiling point and then raising the temperature to distil off O_2. Also post combustion gas clean-up is still required to remove any SO_x, particulates, water and other contaminants prior to CO_2 compression and transport.

The Callide A power station in Queensland.

In Queensland this oxyfiring process is being demonstrated at the Callide A power station: http://www.callideoxyfuel.com/

This is a 30 megawatt demonstration and includes CO_2 compression, transport and storage.

Carbon capture and storage/utilisation: CHEMICAL LOOPING



Carbon capture and storage/utilisation: CHEMICAL LOOPING

- Instead of O_2 use a solid metal oxide (e.g. NiO) as an oxygen source

16 | Options

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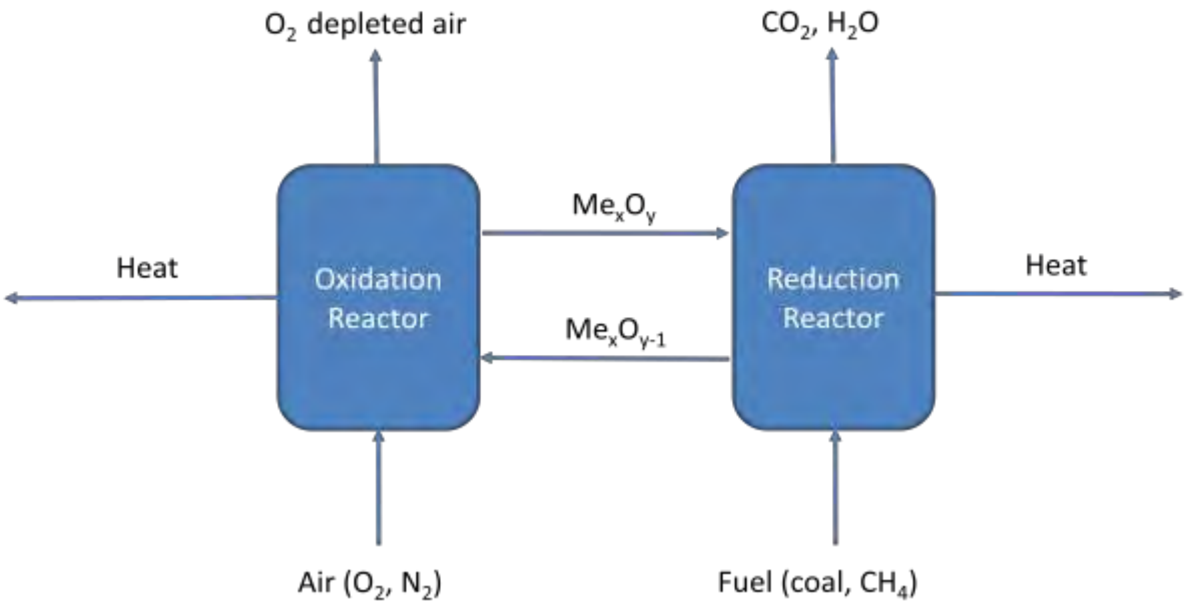
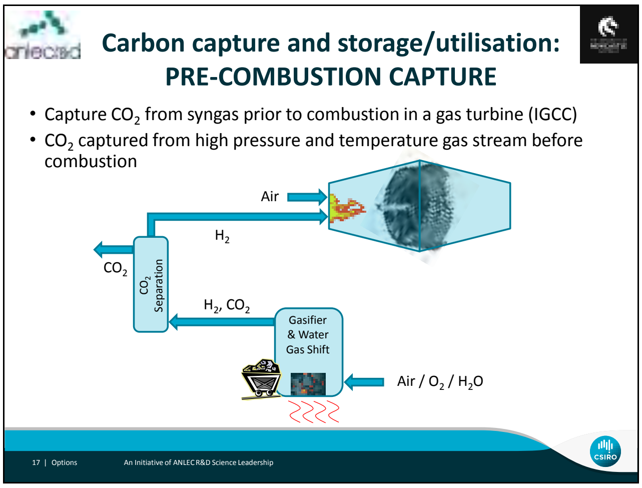
Chemical looping is a combustion process where an oxidant other than O_2 is used for the combustion process. Typically the oxidant is a metal oxide such as NiO. In a reduction reactor the solid metal oxide is contacted with a fuel such as coal or methane. The combustion process produces heat which is used for electricity generation. The flue gas consists only of CO_2 and water. The water can be easily separated and the CO_2 compressed for transport and storage. The reduced metal oxide then goes to an oxidation reactor where, upon exposure to O_2 it is oxidised ready for reuse. Oxidation also produces useful heat.

This technology is still at the research stage. With a number of challenges around the kinetics, and degradation of metal oxide still being addressed.



The chemical looping process.

Carbon capture and storage/utilisation: PRE-COMBUSTION CAPTURE



Carbon capture and storage/utilisation: PRE-COMBUSTION CAPTURE

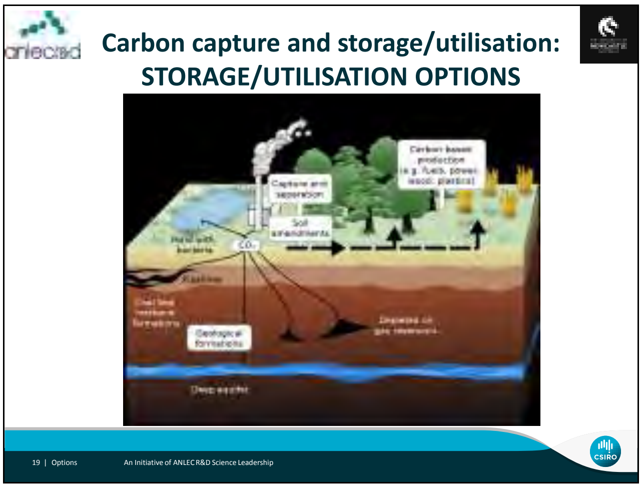
- Capture CO_2 from syngas prior to combustion in a gas turbine (IGCC)
- CO_2 captured from high pressure and temperature gas stream before combustion

17 | Options An Initiative of ANLEC R&D Science Leadership

We have already seen how the coal gasification works. By heating coal at high pressure in the presence of O_2 and applying the water gas shift reaction syngas is produced. Syngas is a mixture of H_2 and CO_2 and possibly some CO. This can be combusted in a turbine as is. An alternative to reduce CO_2 emissions is to carry out CO_2 capture to remove the CO_2 from the syngas prior to combustion.

Syngas is at high pressure and this, combined with the fact that CO_2 is being separated from H_2, makes it a relatively easy separation task. Separation can be done using reactive chemical absorption, but physical adsorption using solids (e.g. solid carbonates) or liquids (e.g. glycol) is also an option due to the high pressure of the gas.

Carbon capture and storage/utilisation: STORAGE/UTILISATION OPTIONS



Carbon capture and storage/utilisation: STORAGE/UTILISATION OPTIONS

19 | Options

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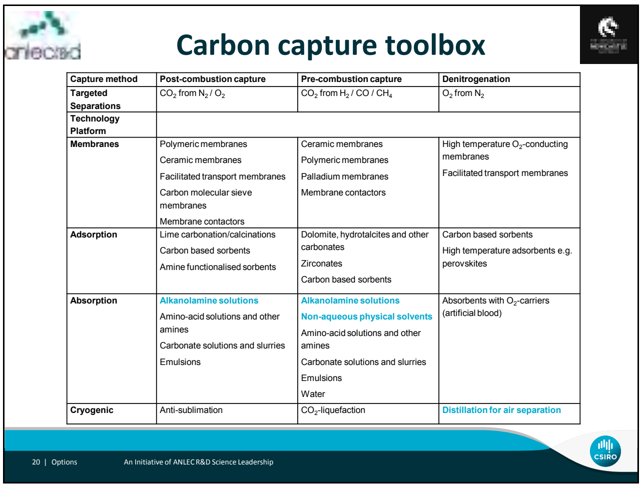
Once captured CO_2 is compressed into a liquid state. The question then remains about what should be done with it. CO_2 utilisation is an attractive option as it is putting a waste product to use. CO_2 can be used as a reagent in the synthesis of many carbon based materials such as plastics. It can also be used to synthesise liquid fuels such as methanol. However, for this type of utilisation to be viable it is critical that the synthesis process does not itself result in the production of more CO_2 than is used. Creating such low energy demand processes is an area of ongoing research. Another option is using CO_2 as a feedstock for the growth of algae. The algae can then be used to make biofuels.

Unfortunately utilisation will never be able to consume all the CO_2 captured if capture technology is rolled out at large scale. Storage will still be required. The bulk of CO_2 storage will occur by pumping captured CO_2 into depleted oil and gas reservoirs. This already occurs to some extent in storage studies and where CO_2 is used to force extra oil out of oil reservoirs. Another option is storage in deep saline aquifers. These are areas of porous rocks which contain mineral laden water, typically at depths of more than 1 km. Liquid CO_2 is pumped into these aquifers where it eventually dissolves in the water.

Carbon capture toolbox



Carbon capture toolbox

Capture method	Post-combustion capture	Pre-combustion capture	Denitrogenation
Targeted Separations	CO_2 from N_2 / O_2	CO_2 from H_2 / CO / CH_4	O_2 from N_2
Technology Platform			
Membranes	Polymeric membranes Ceramic membranes Facilitated transport membranes Carbon molecular sieve membranes Membrane contactors	Ceramic membranes Polymeric membranes Palladium membranes Membrane contactors	High temperature O_2-conducting membranes Facilitated transport membranes
Adsorption	Lime carbonation/calcinations Carbon based sorbents Amine functionalised sorbents	Dolomite, hydrotalcites and other carbonates Zirconates Carbon based sorbents	Carbon based sorbents High temperature adsorbents e.g. perovskites
Absorption	**Alkanolamine solutions** Amino-acid solutions and other amines Carbonate solutions and slurries Emulsions	**Alkanolamine solutions** **Non-aqueous physical solvents** Amino-acid solutions and other amines Carbonate solutions and slurries Emulsions Water	Absorbents with O_2-carriers (artificial blood)
Cryogenic	Anti-sublimation	CO_2-liquefaction	**Distillation for air separation**

20 | Options

An Initiative of ANLEC R&D Science Leadership

This is a table that lists the different electricity generation processes to which CO_2 capture could be applied as the columns. The rows are the capture technology options. The technologies that are most promising for each electricity generation process are highlighted in blue.

Capture method	Post-combustion capture	Pre-combustion capture	Denitrogenation
Targeted Separations	CO_2 from N_2 / O_2	CO_2 from H_2 / CO / CH_4	O_2 from N_2
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Options for carbon dioxide emission mitigation from energy generation and the technology challenges

- Alternative centralised low carbon energy generation
- Increased generation efficiency of fossil fuel power stations
- Decentralised electricity generation and grid management
- End-user efficiency and demand management/reduction
- Carbon capture and storage/utilisation
- Carbon capture toolbox

Alternative centralised low carbon energy generation: SOLAR

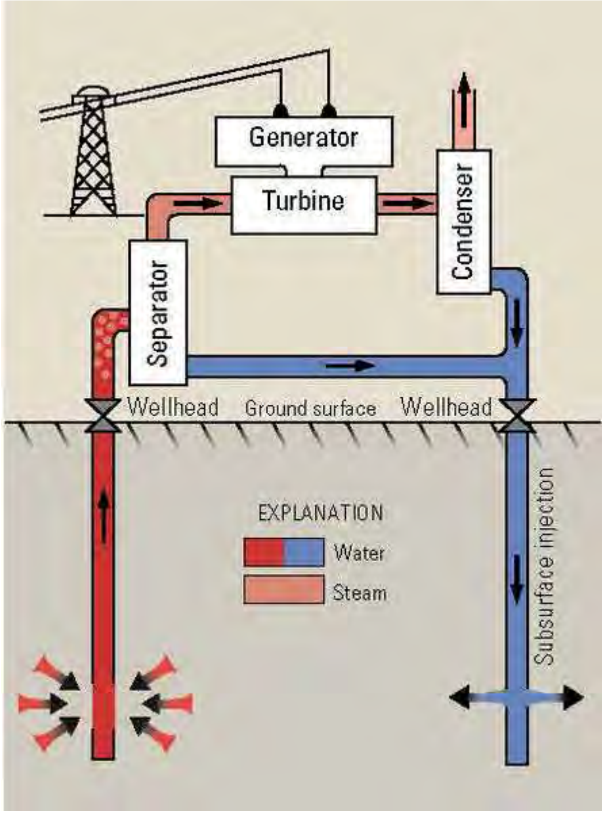
- **Photovoltaics** (solar panels) that directly convert solar radiation to electricity using semiconductors (e.g. crystalline or amorphous silicon, cadmium telluride)
- **Solar thermal** in which mirrors are used to focus and concentrate solar radiation and produce high temperatures to generate hot pressurised gas (to operate a steam/gas turbine) or drive chemical reactions to produce a fuel (e.g. splitting water to produce H_2)

Alternative centralised low carbon energy generation: WIND

- A wind powered turbine is used to drive the generator
- Arrays of wind turbines are called wind farms

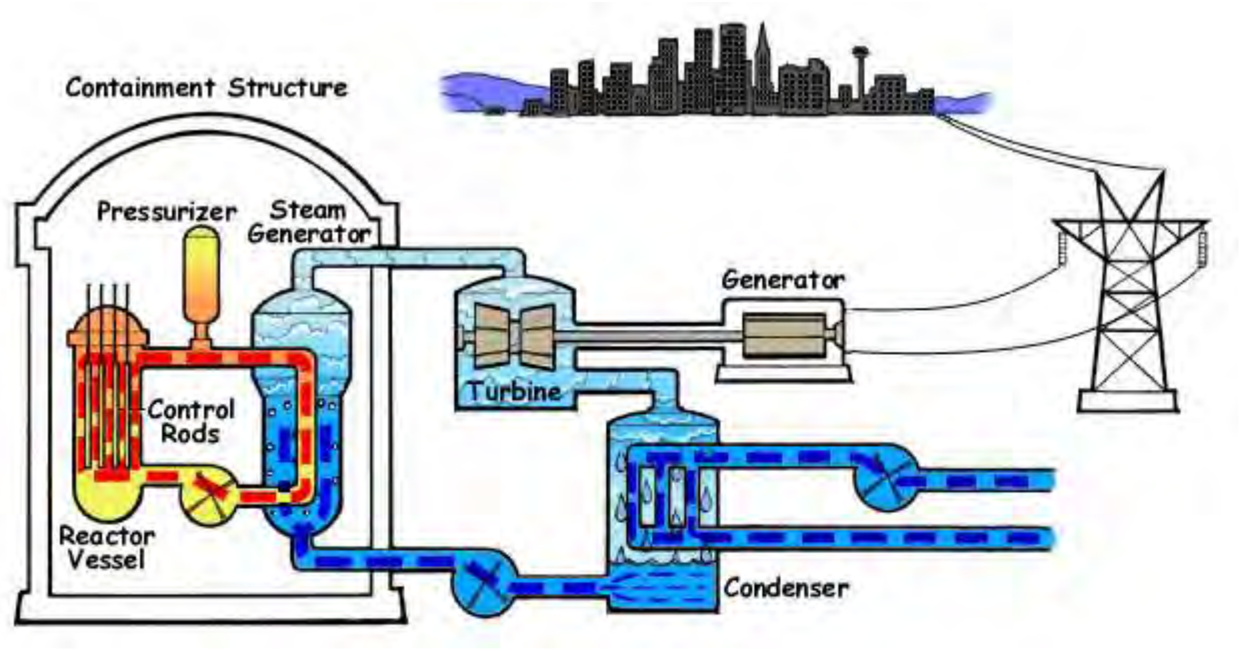
Alternative centralised low carbon energy generation: GEOTHERMAL

- Geothermal energy, heat from below the Earth's surface, is used to generate steam to drive a turbine and generator

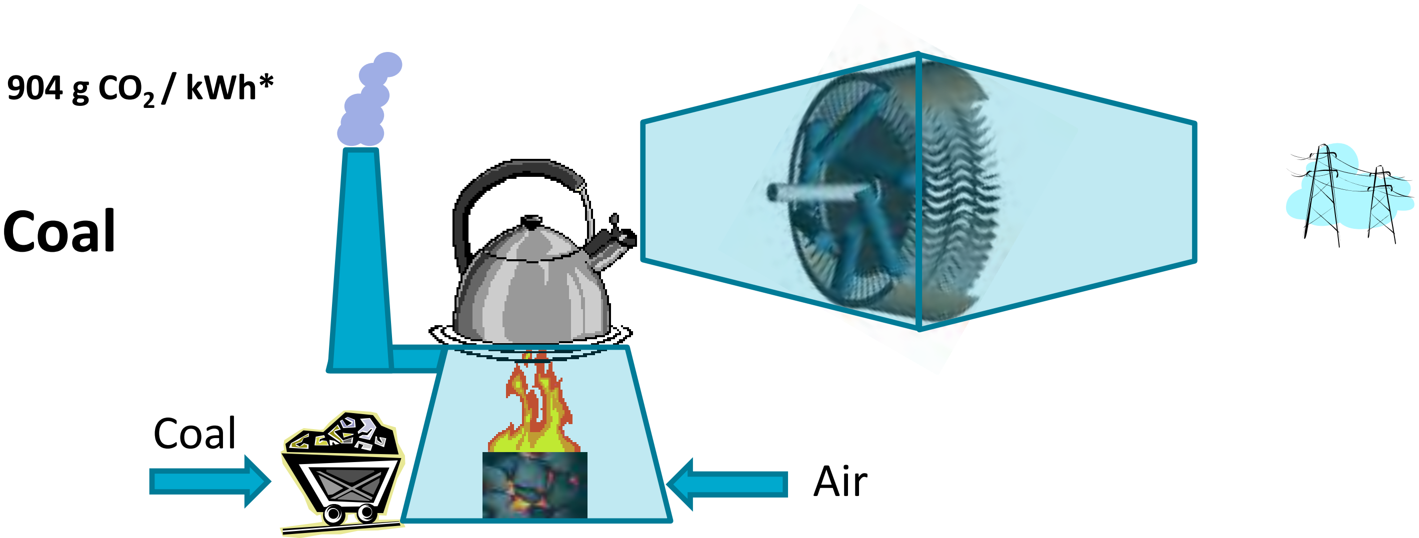


Alternative centralised low carbon energy generation: NUCLEAR

- The energy released by nuclear fission, the splitting apart of the nucleus of a heavy atom (e.g. uranium-235, plutonium-239), is used to generate steam to drive a steam turbine and generator

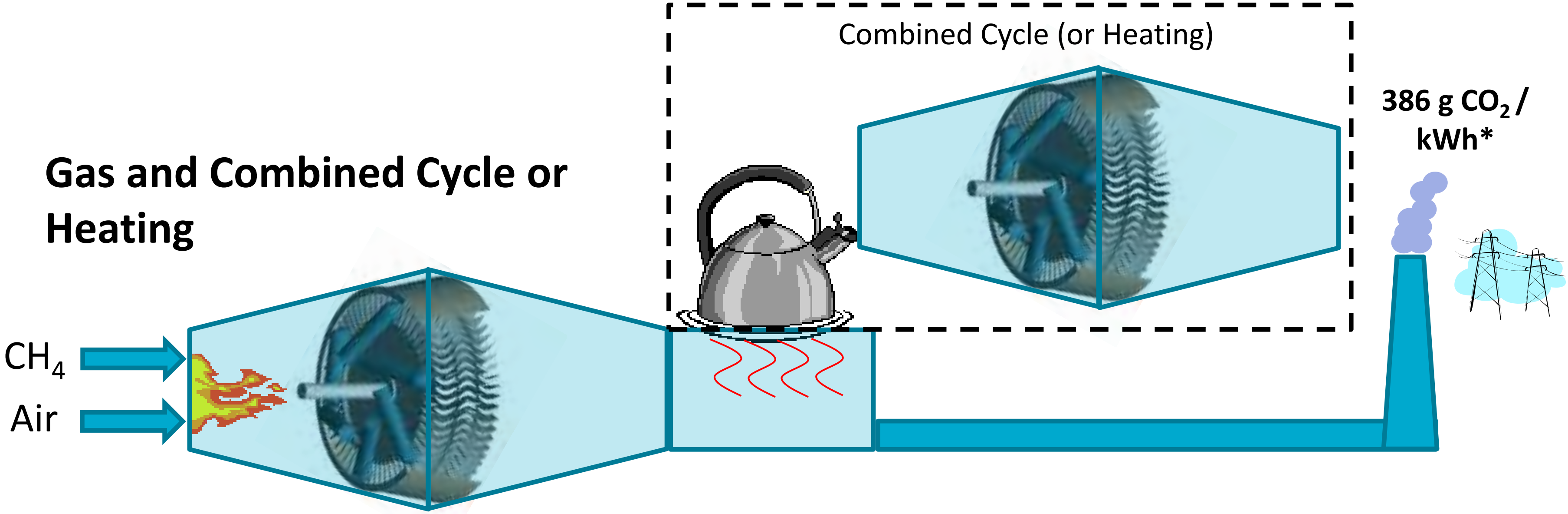


Increased generation efficiency:
SWITCHING FROM COAL TO GAS



*OECD/IEA, *CO_2 Emissions from Fuel Combustion - Highlights*. IEA, Paris, France, 2010, pgs 110-118.

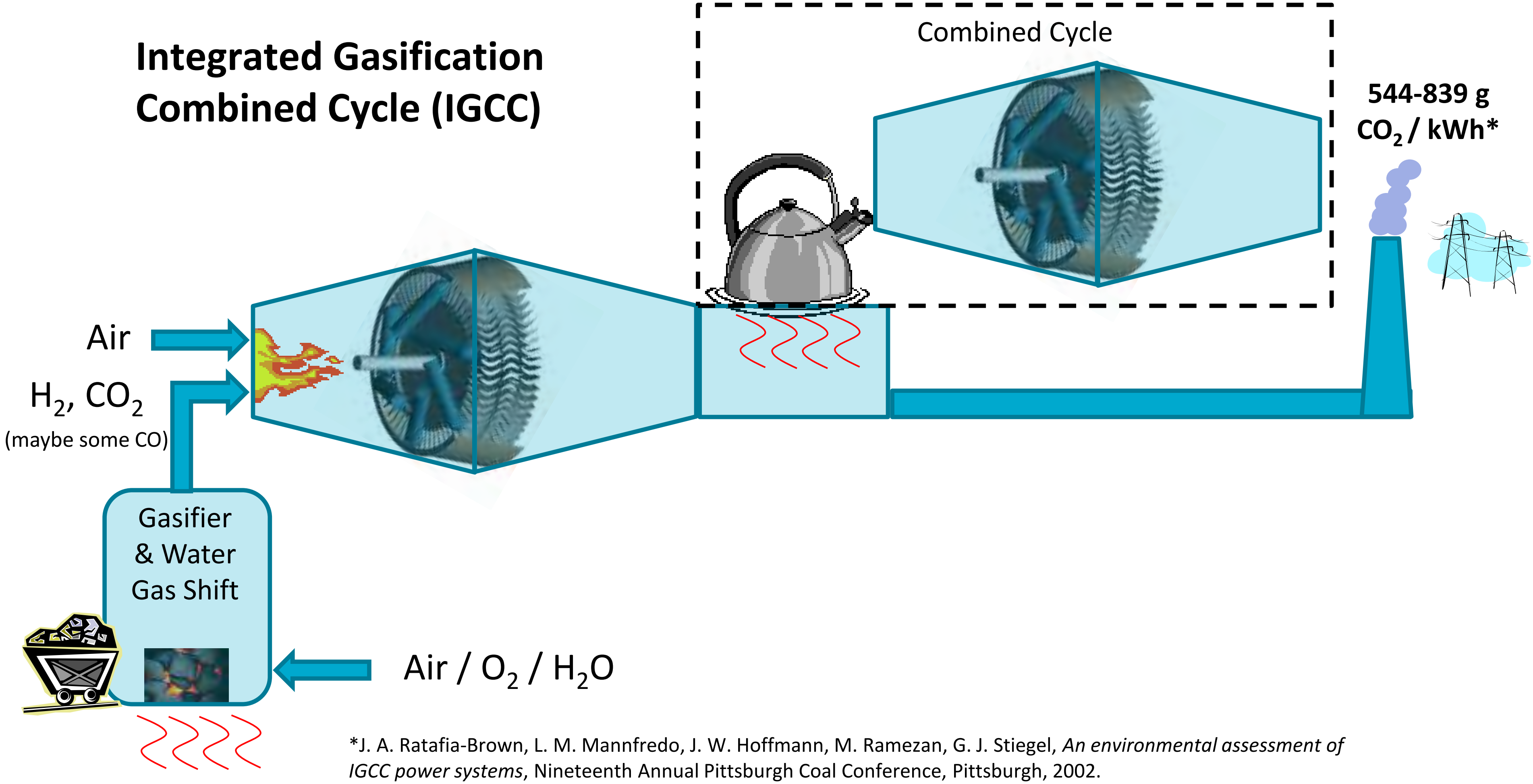
Increased generation efficiency: SWITCHING FROM COAL TO GAS



*OECD/IEA, *CO_2 Emissions from Fuel Combustion - Highlights*. IEA, Paris, France, 2010, pgs 110-118.

Increased generation efficiency: COAL GASIFICATION

Integrated Gasification Combined Cycle (IGCC)



*J. A. Ratafia-Brown, L. M. Mannfredo, J. W. Hoffmann, M. Ramezan, G. J. Stiegel, *An environmental assessment of IGCC power systems*, Nineteenth Annual Pittsburgh Coal Conference, Pittsburgh, 2002.

Increased generation efficiency: SUPERCRITICAL STEAM

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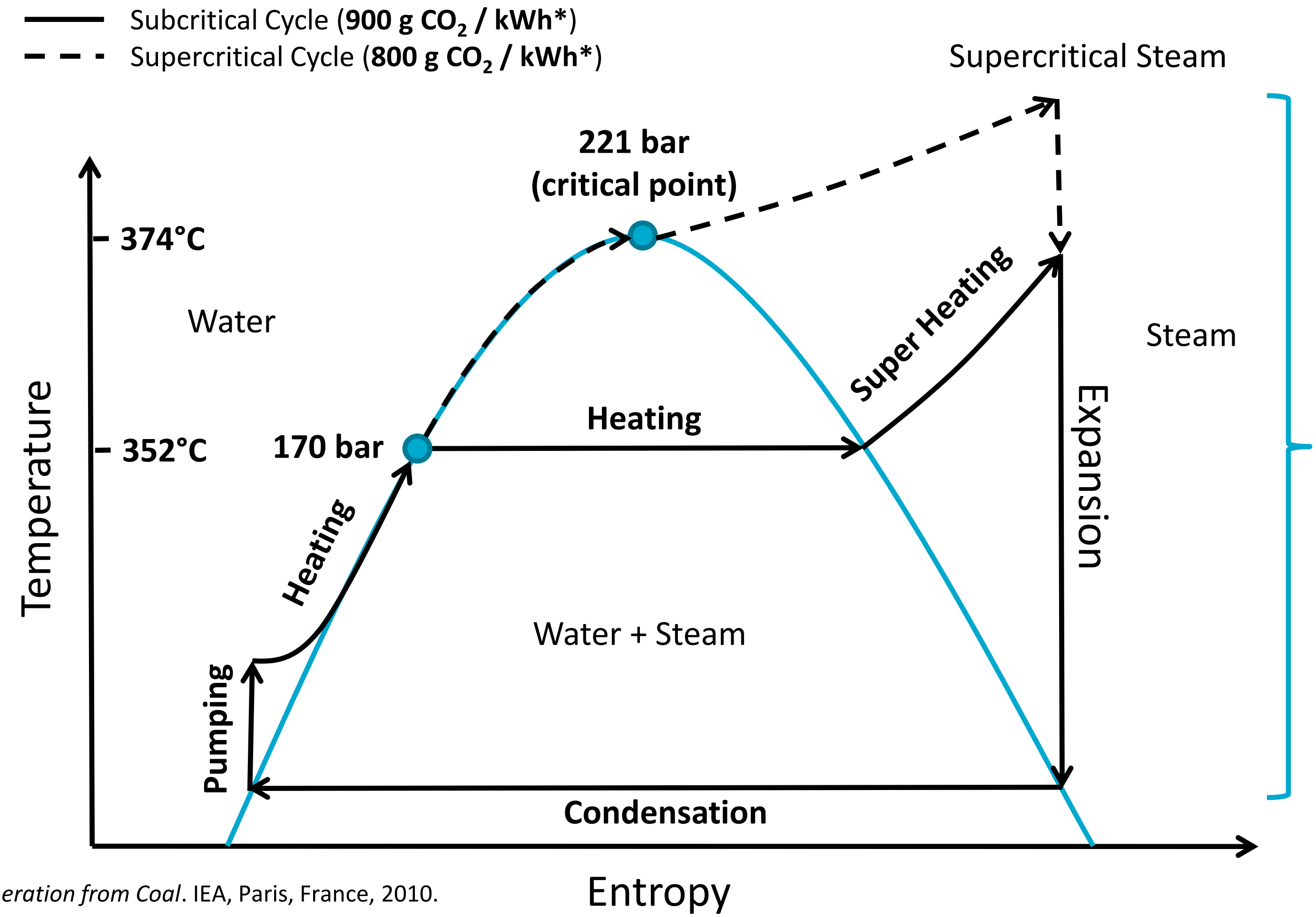
Increased generation efficiency: SUPERCRITICAL STEAM

Rankine Cycle



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Increased generation efficiency: SUMMARY

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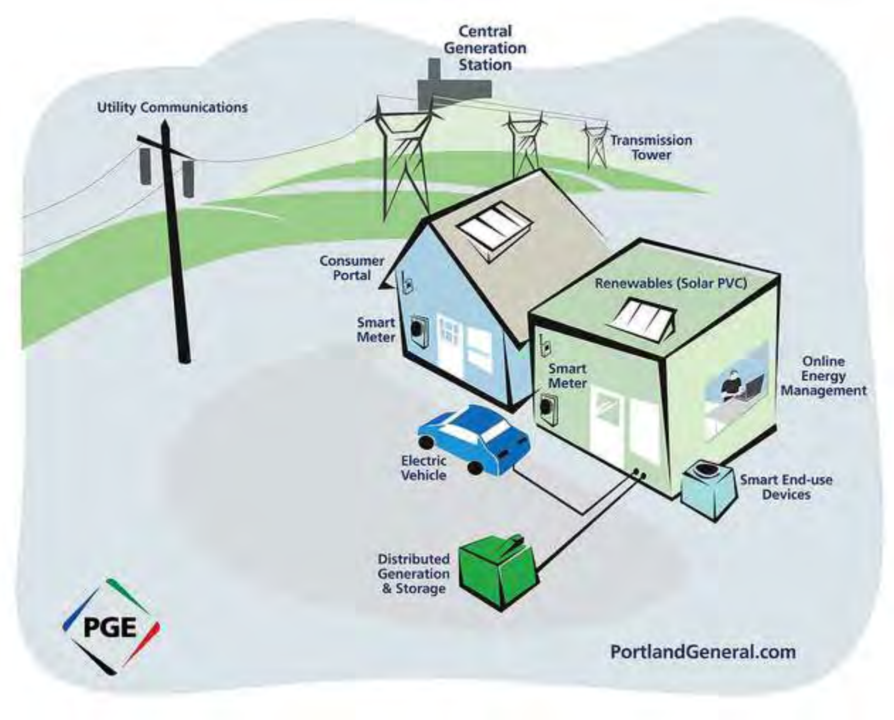

End-user efficiency: INCREASED PUBLIC AWARENESS

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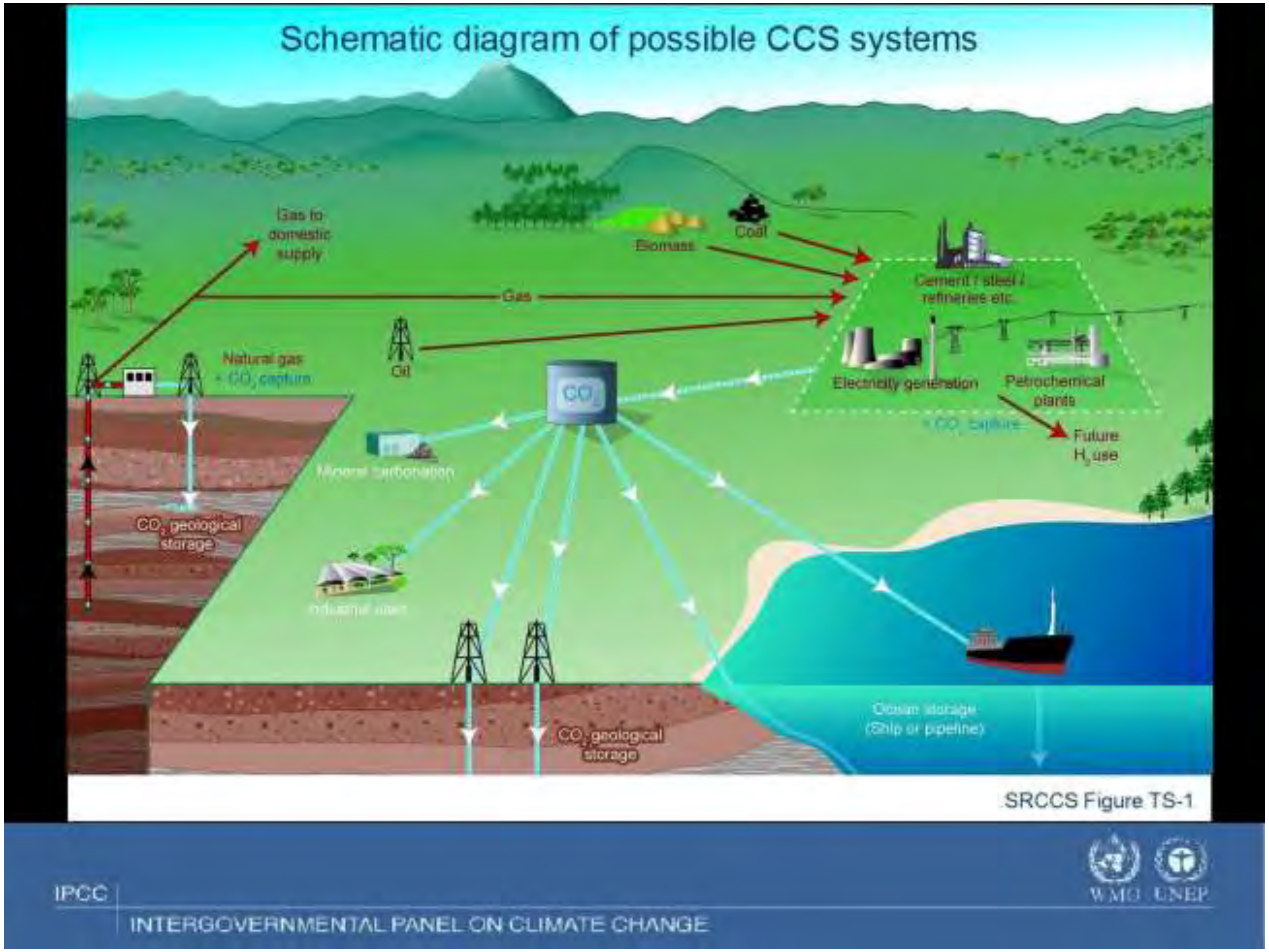
- And many more

Carbon capture and storage/utilisation: THE CCS CHAIN



Schematic diagram of possible CCS systems

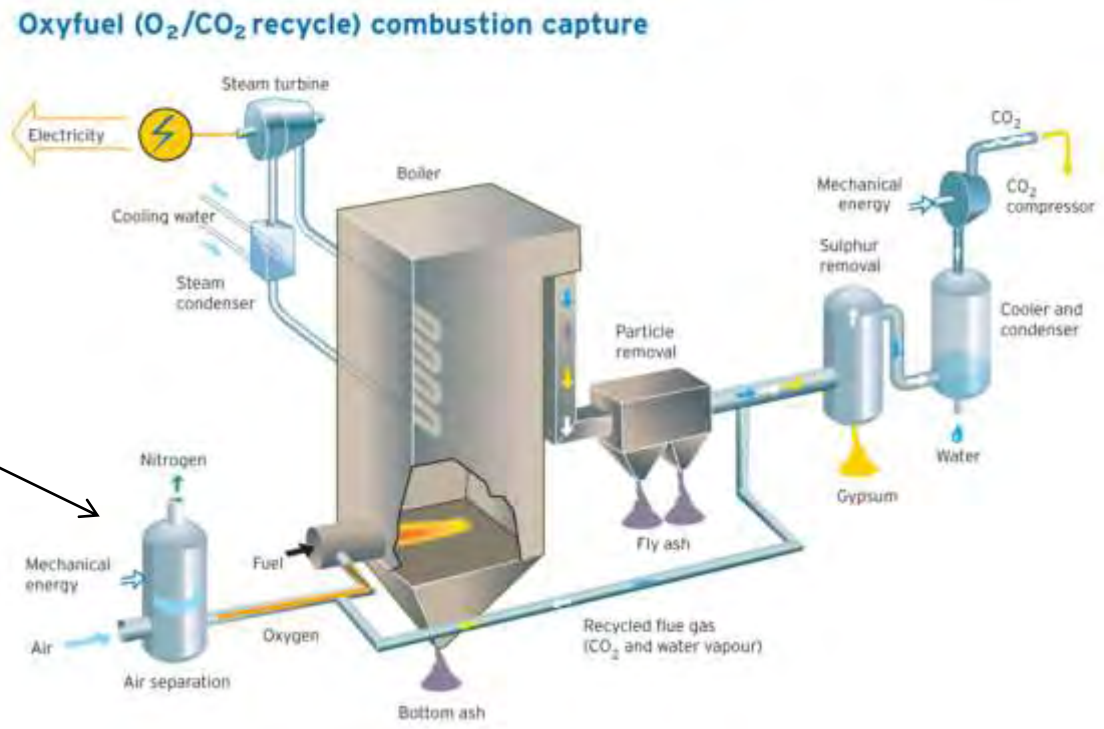
SRCCS Figure TS-1

IPCC

INTERGOVERNMENTAL PANEL ON CLIMATE CHANGE

Carbon capture and storage/utilisation: OXYFIRING

- Use an air separation unit (ASU) to separate O_2 from air (mostly N_2) and carry out combustion in an O_2/CO_2 atmosphere
- Produces a concentrated CO_2 flue gas



The ASU is energy intensive

Carbon capture and storage/utilisation: CHEMICAL LOOPING

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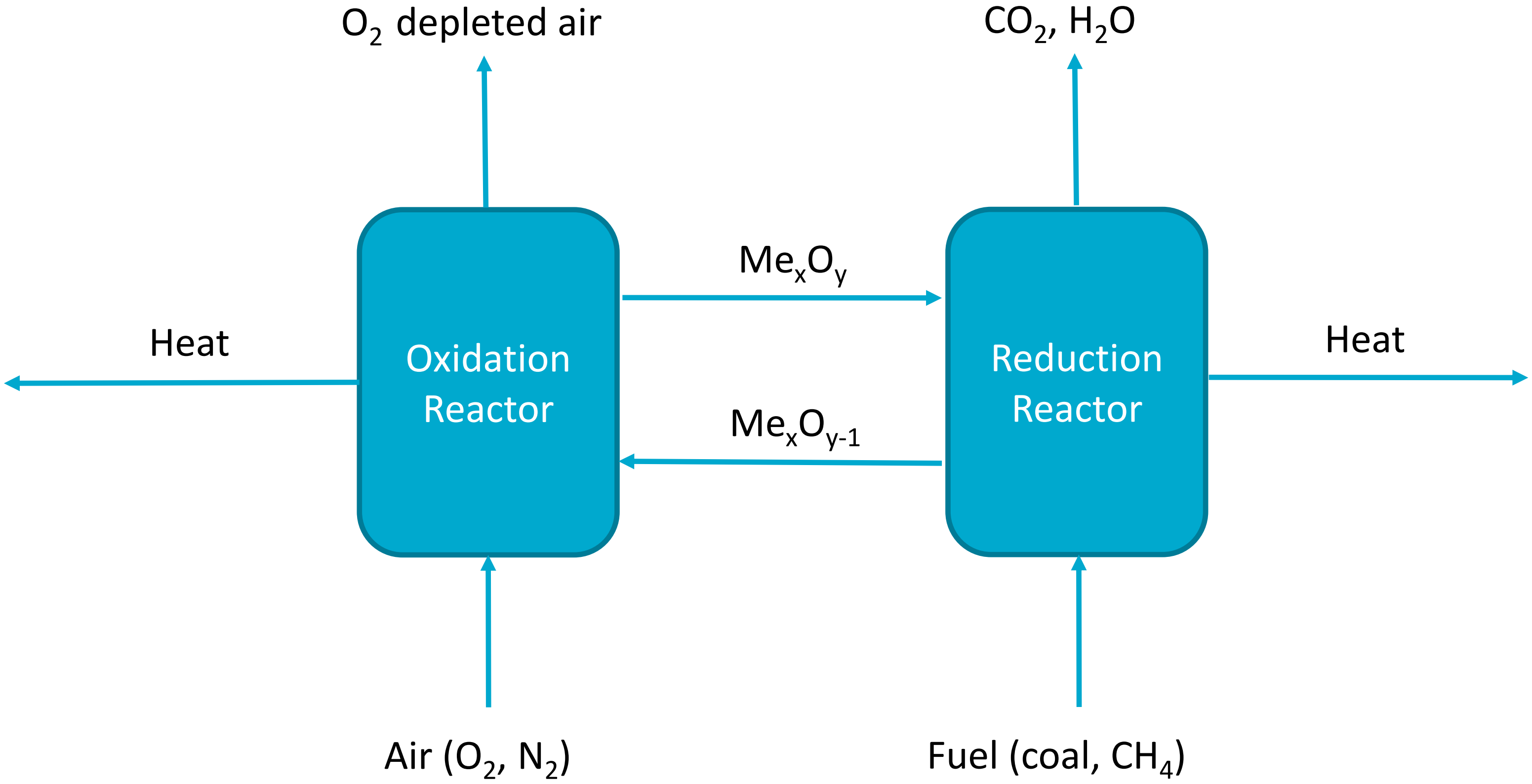

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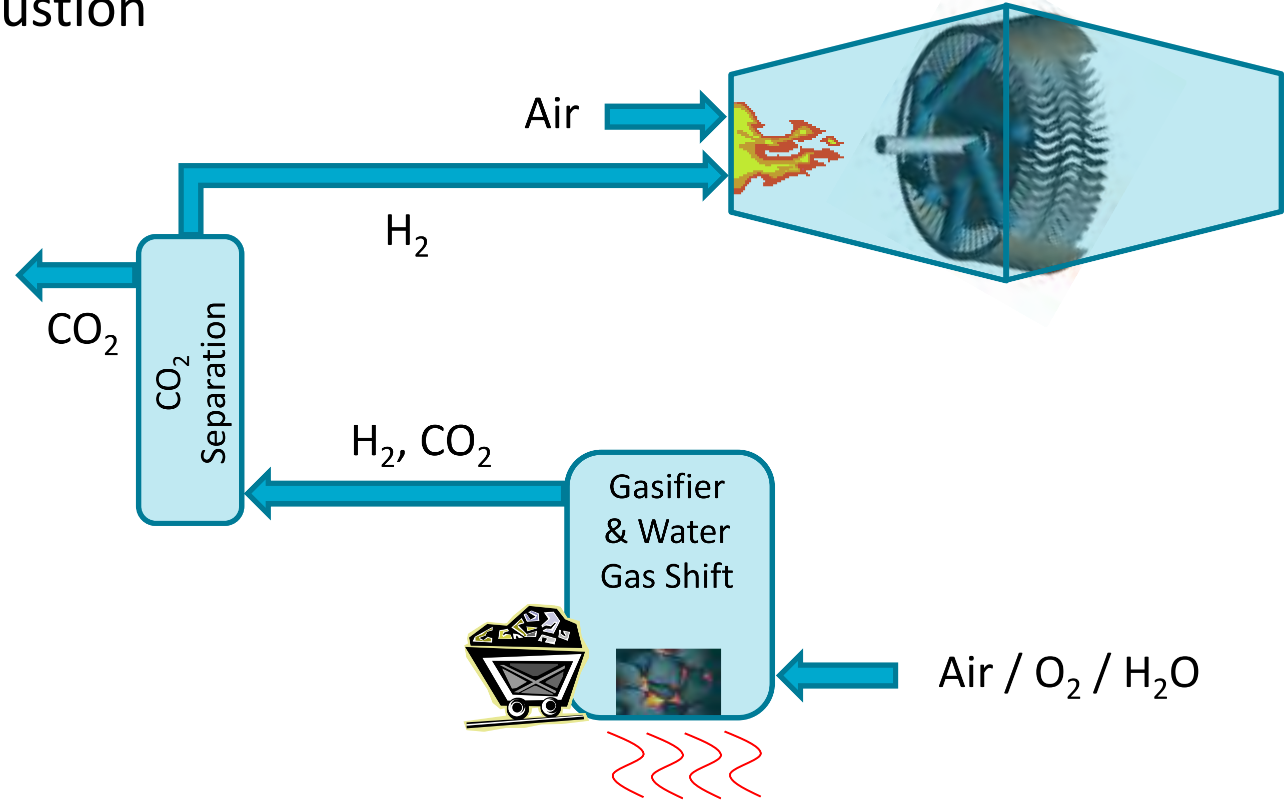
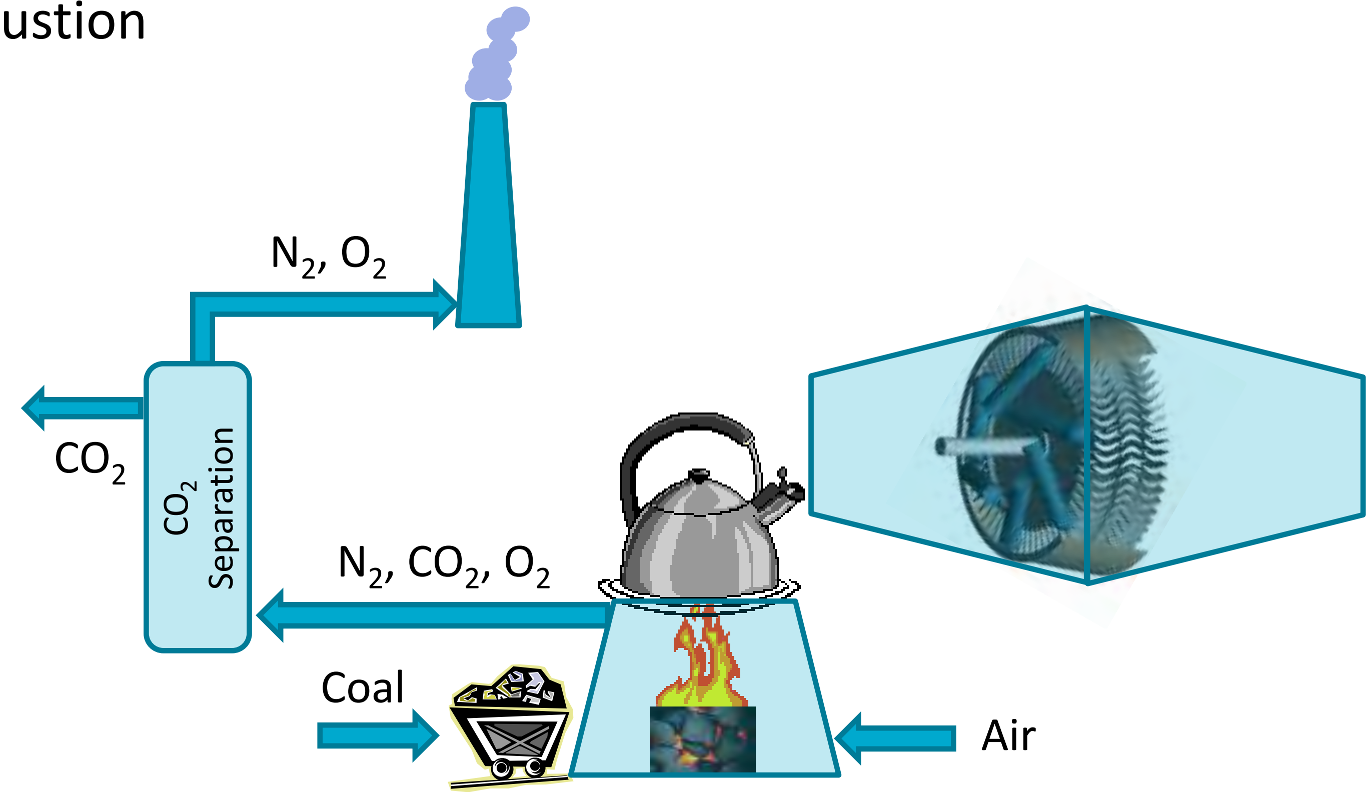
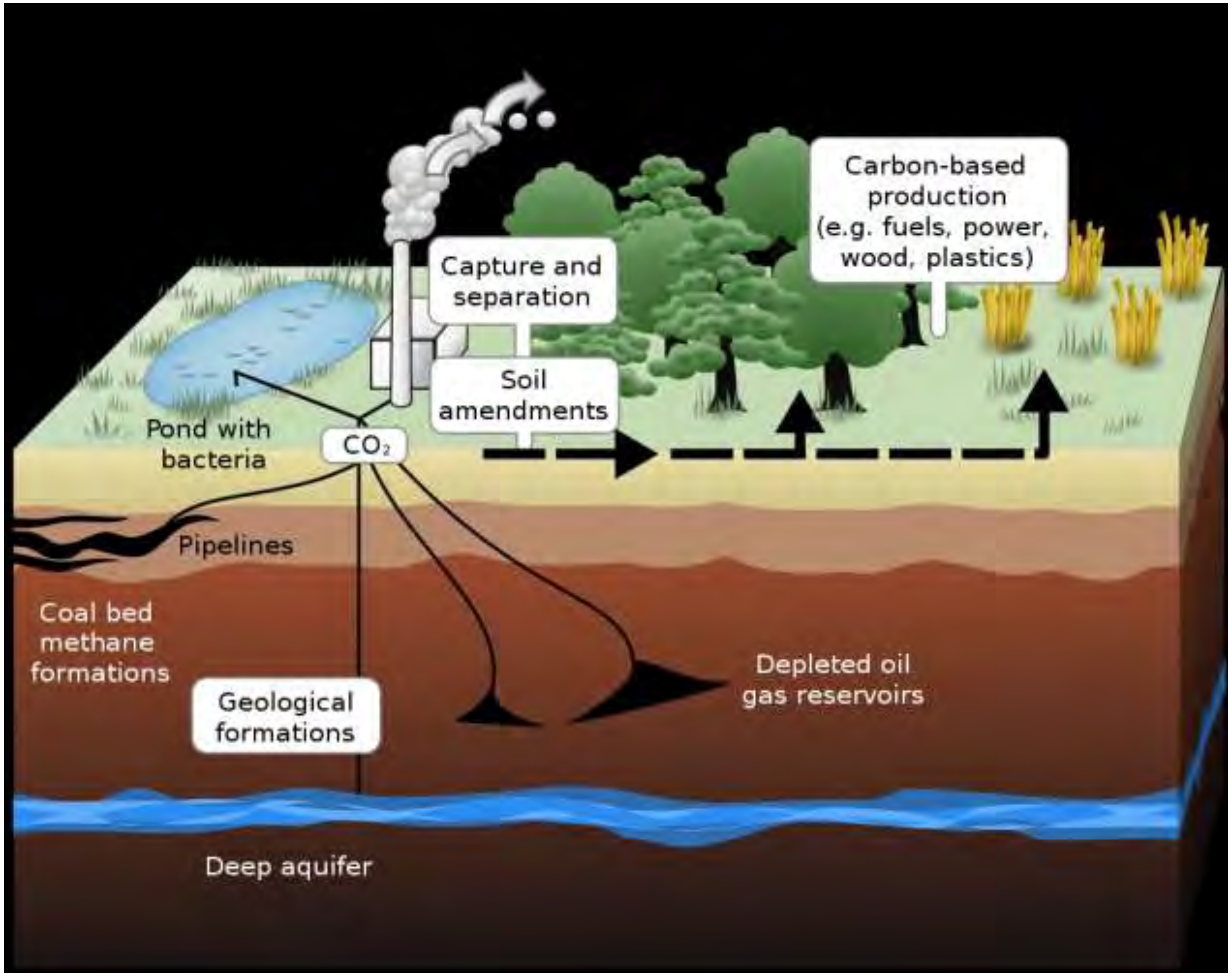


Carbon capture and storage/utilisation: POST-COMBUSTION CAPTURE

- Capture CO_2 from flue gas after combustion in a furnace / turbine
- CO_2 captured from low pressure and low temperature gas stream after combustion



Carbon capture and storage/utilisation: STORAGE/UTILISATION OPTIONS



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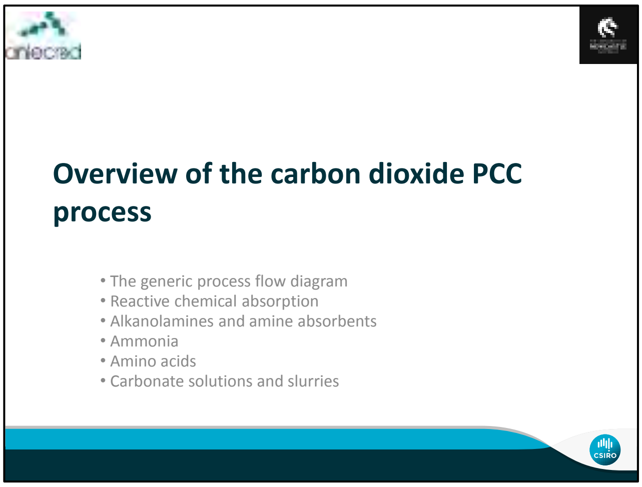
Acknowledgements

The authors wish to acknowledge financial assistance provided through Australian National Low Emissions Coal Research and Development (ANLEC R&D). ANLEC R&D is supported by Australian Coal Association Low Emissions Technology Limited and the Australian Government through the Clean Energy Initiative.

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

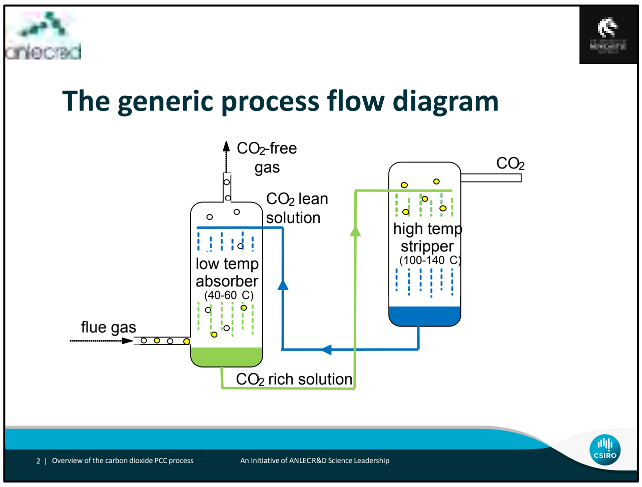
We start this section with a generic process flow diagram. It facilitates the understanding of the relatively simple process of cyclic and selective absorption of CO_2 from the flue gas stream of a power station. Included is an animation which further explains the process.

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

2 | Overview of the carbon dioxide PCC process

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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

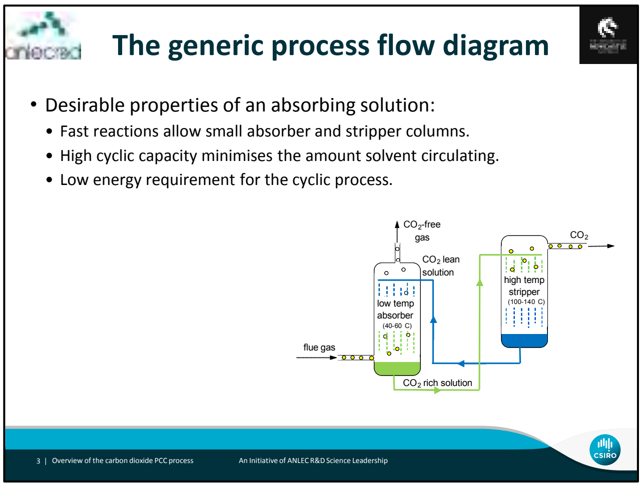
b) The gas mixture rises through the columns while the amine solution (blue) moves down. The counter current arrangement optimises the CO_2 uptake as the fresh amine solution interacts with the depleted gas at the top of the absorber.

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.

3 | Overview of the carbon dioxide PCC process

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The important features of the PCC process

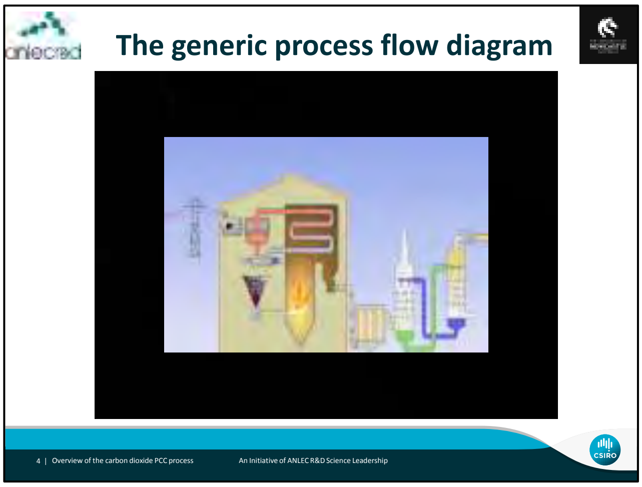
In the pursuit of improving PCC, there are two aspects that need attention:

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

4 | Overview of the carbon dioxide PCC process

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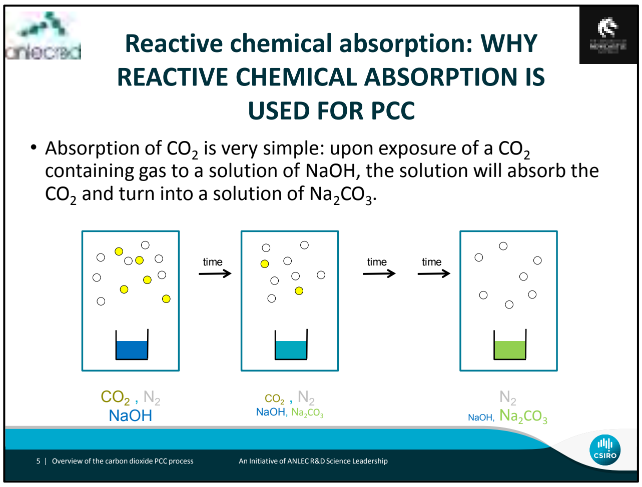
An animation of the PCC process

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.

Overview 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.

5 | Overview of the carbon dioxide PCC process

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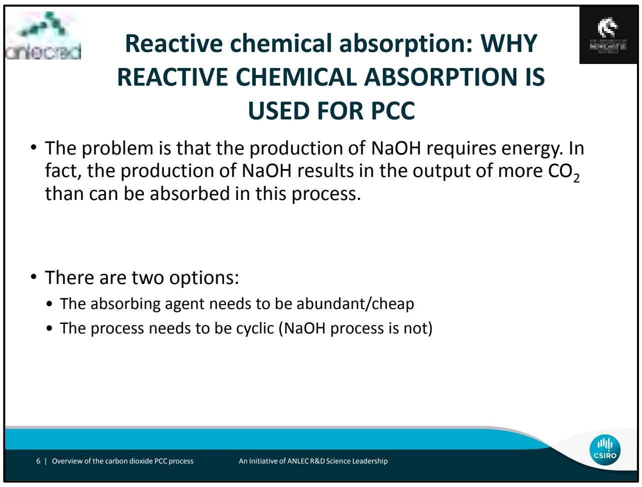
The basic principle of CO_2 absorption

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)

6 | Overview of the carbon dioxide PCC process

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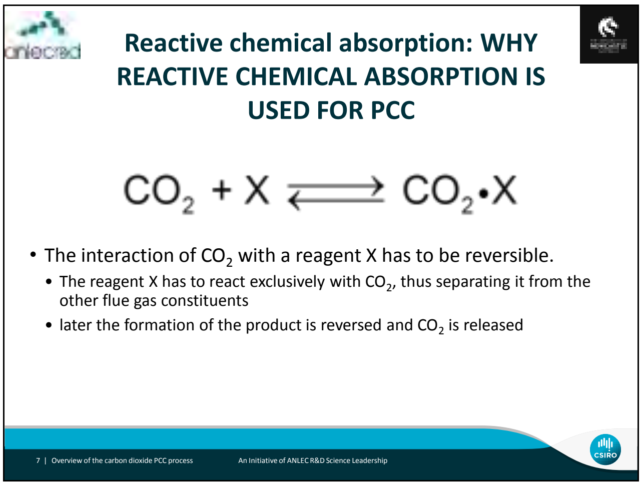
Absorption of CO_2 is easy, but not cheap

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

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

- 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

7 | Overview of the carbon dioxide PCC process

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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 $\rightleftharpoons$. 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.

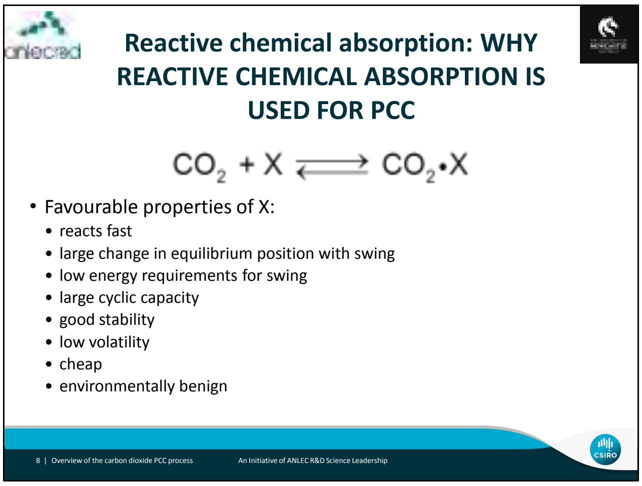
The position of the equilibrium has to be externally controllable. The most common such control parameter is the temperature. Generally, the lower the temperature the more the equilibrium lies to the right, on the side of the reaction product. Thus, at low temperature CO_2 is absorbed, at high temperature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

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

- 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

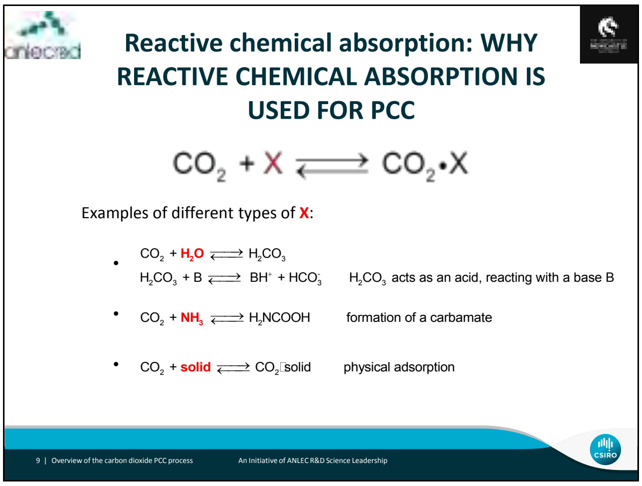
The ideal reagent reacts fast; the process requires less time and thus allows smaller absorber and desorber towers.

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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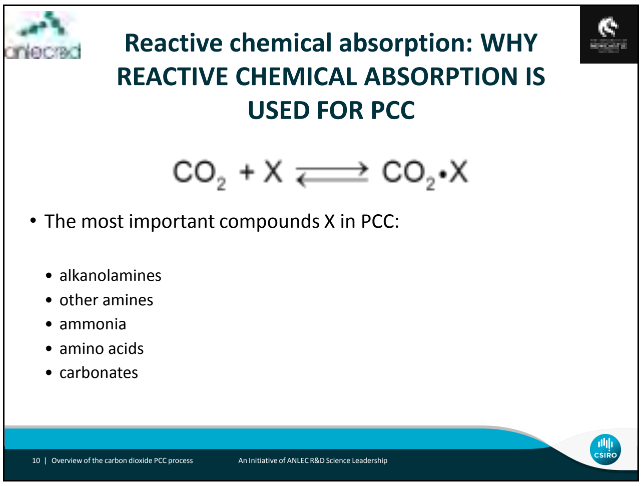
Examples of reactants X

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



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

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

- 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.

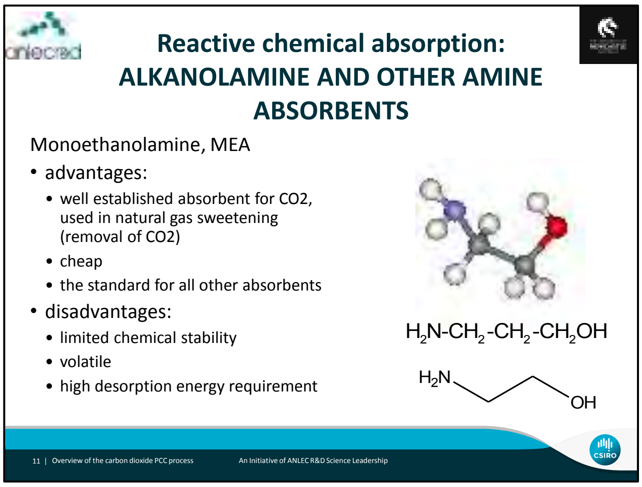
There is no need to restrict the playing to alkanolamines, to date many other amines have been tested; always in view of rate of reaction and ultimately energy requirement for the PCC process. There is almost no limit to the imagination of the chemist. Not to mention the possibility of using mixtures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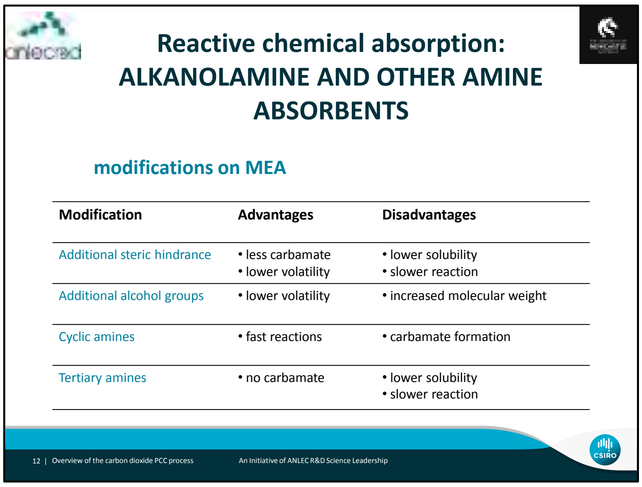
Monoethanolamine, MEA

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

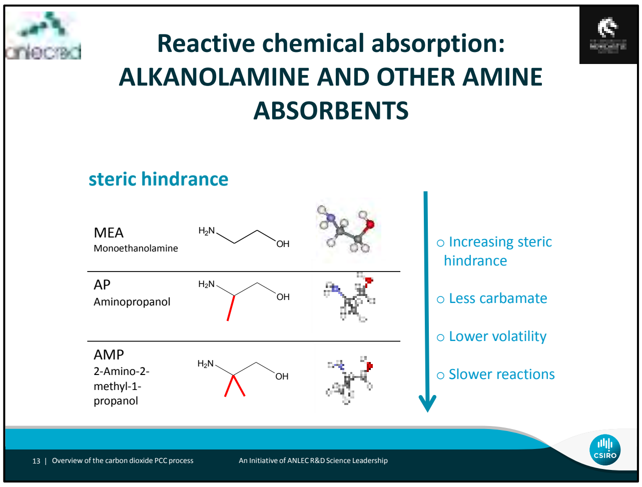
As mentioned before it is the chemist's enjoyment to 'play' with molecules, here in the sense of adjusting the structure in all sorts of ways with the goal of improving its properties.

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.



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

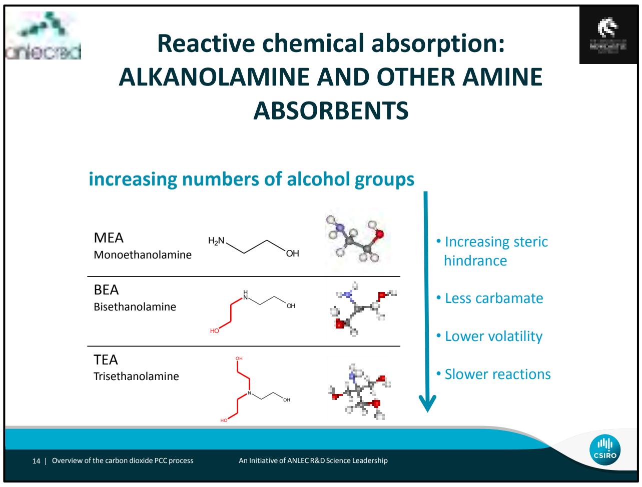
The easiest way to increase the steric hindrance around the amine is to replace a hydrogen on a neighbouring carbon with a methyl group(-CH_3). Chemists represent the methyl group with a short line, in the slide highlighted in red.

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

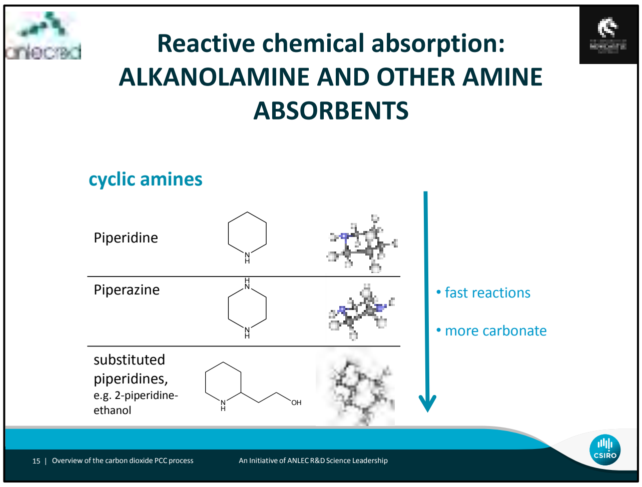
- Increasing steric hindrance
- Less carbamate
- Lower volatility
- Slower reactions

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.



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.

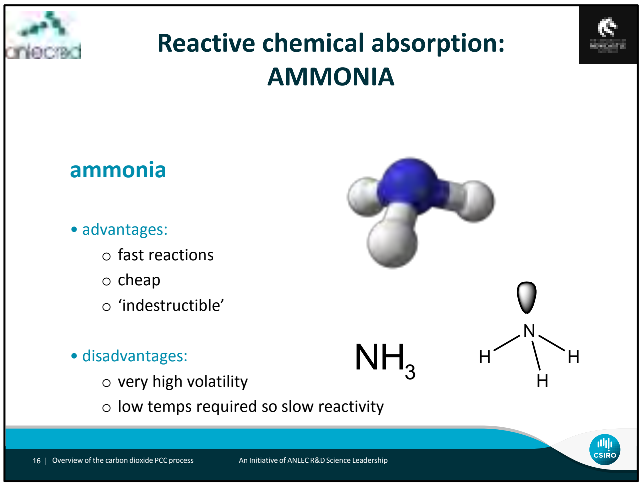
As the structure of the molecules indicate, the substituents on the amine nitrogen and 'bound back' exposing the nitrogen and rendering the reaction with CO_2 to form the carbamate very fast. Indeed the cyclic amines are amongst the fastest of all amines.

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.

Amines, MEA and substitutions



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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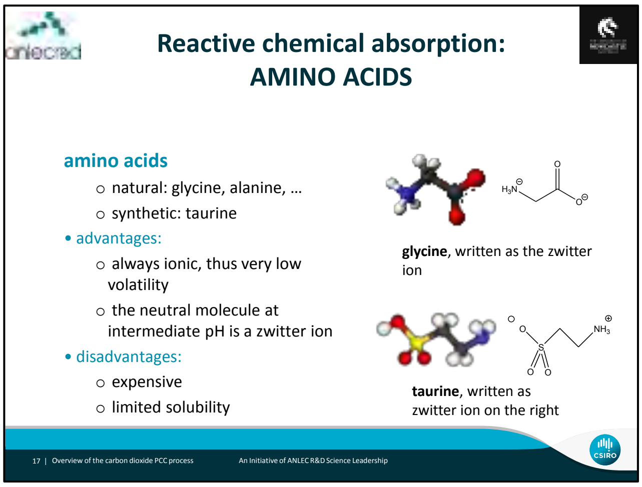
Ammonia

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.



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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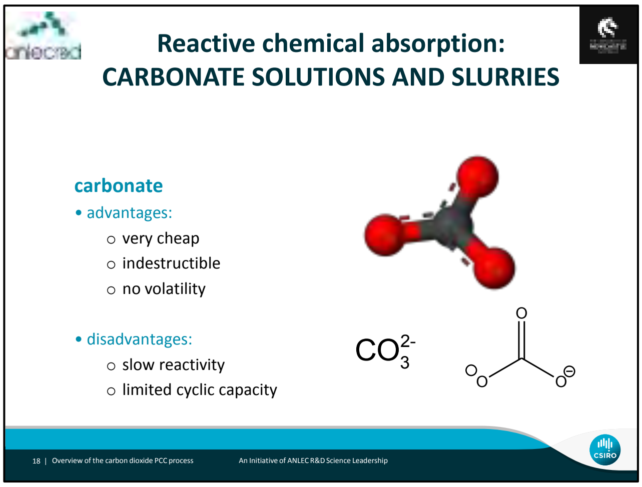
Amino Acids

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-}

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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.

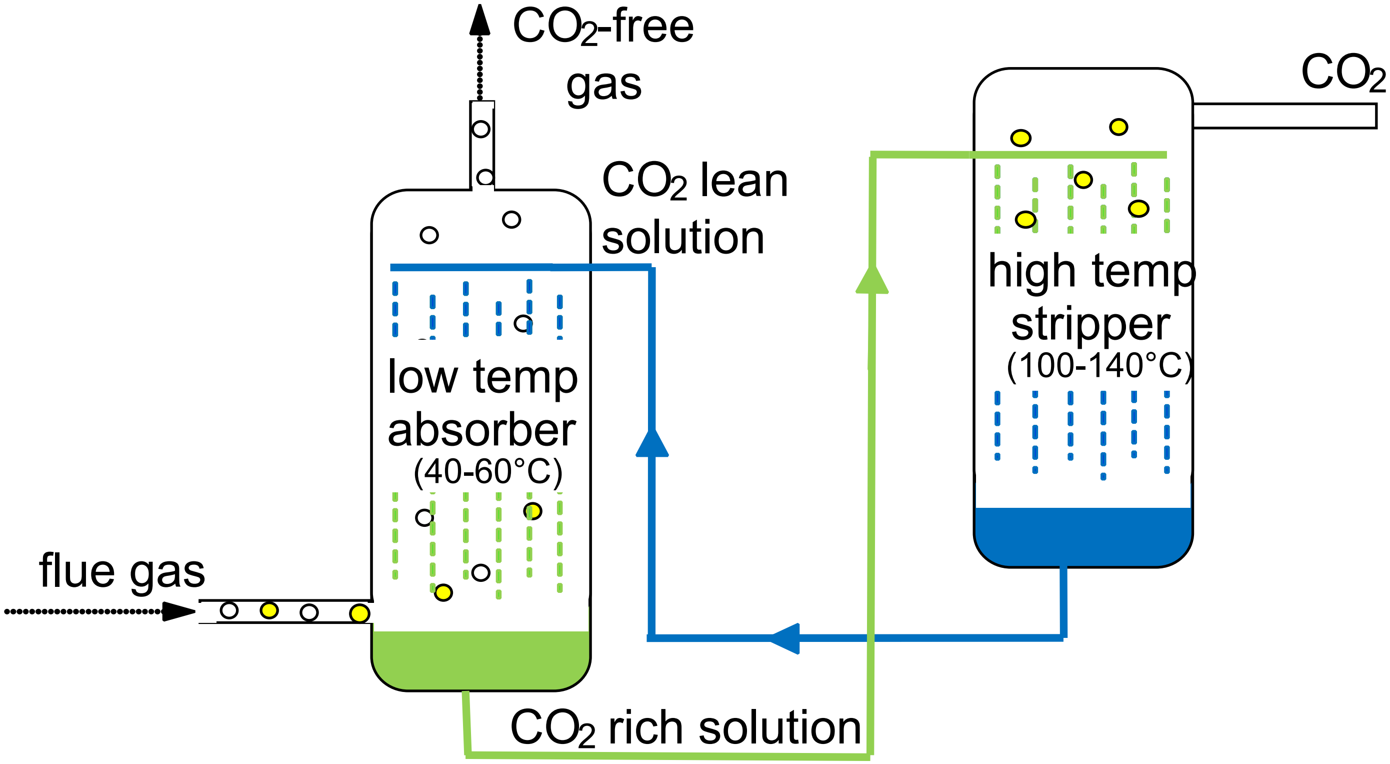
What is the problem? Not being an amine it cannot form the carbamate in a fast reaction and thus the absorption of CO_2 overall is relatively slow. Its cyclic capacity is also limited and thus a large amount of solution is required per unit of CO_2.

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.

Overview of the carbon dioxide PCC process

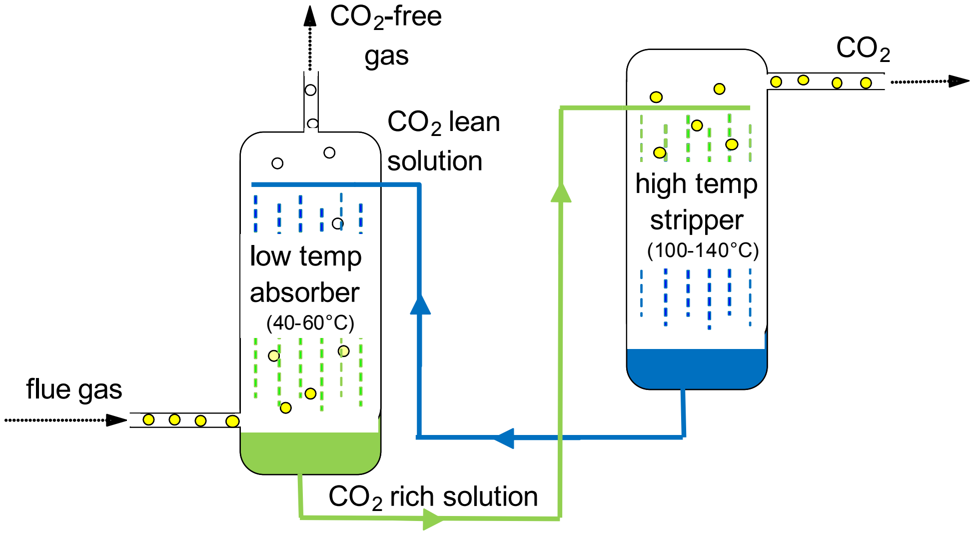
- The generic process flow diagram
- Reactive chemical absorption
- Alkanolamines and amine absorbents
- Ammonia
- Amino acids
- Carbonate solutions and slurries

The generic process flow diagram

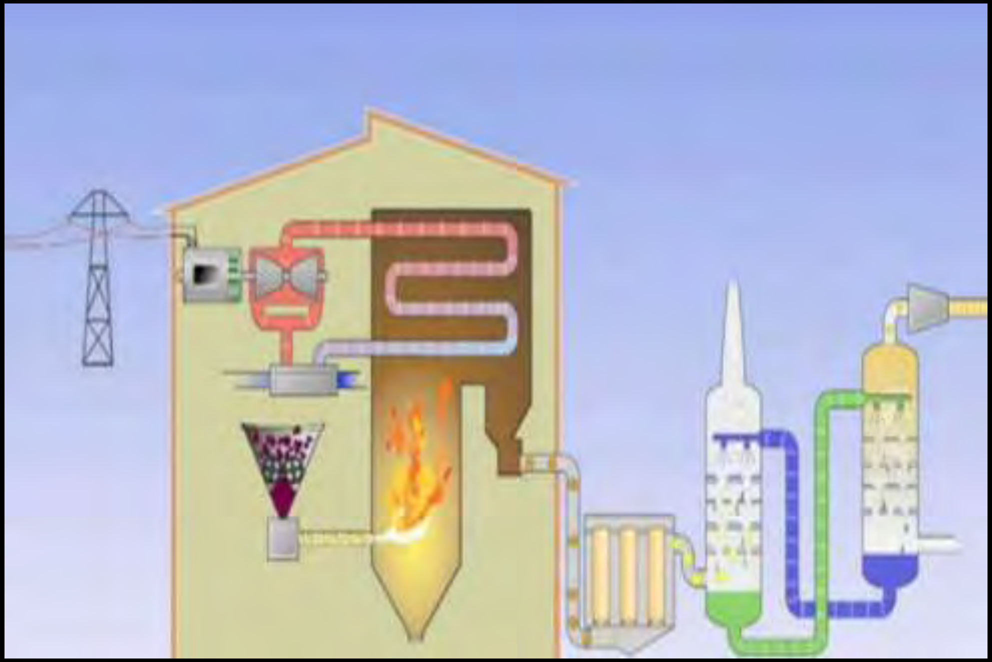


The generic process flow diagram

- 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

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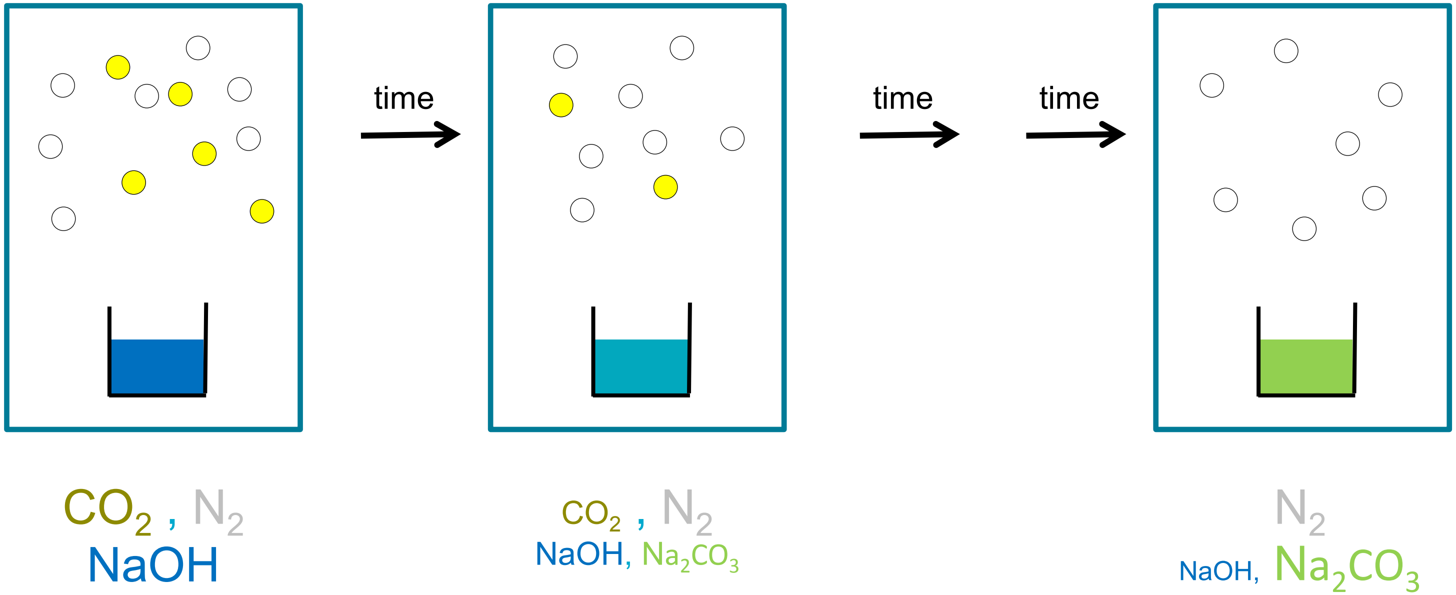

Reactive chemical absorption: WHY REACTIVE CHEMICAL ABSORPTION IS USED FOR PCC

- 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.

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

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

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

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- Favourable properties of X:
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  - good stability
  - low volatility
  - cheap
  - environmentally benign

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**:

- $CO_2 + \mathbf{H_2O} \rightleftharpoons H_2CO_3$

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

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

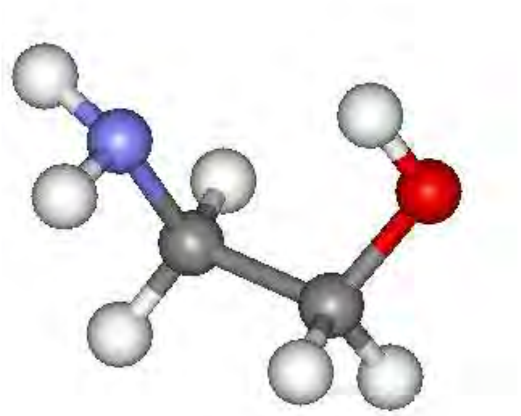
$$CO_2 + X \rightleftharpoons CO_2{\bullet}X$$

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

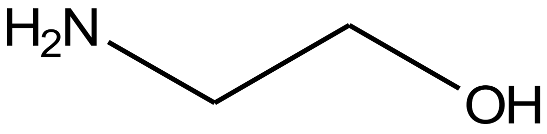
Reactive chemical absorption: ALKANOLAMINE AND OTHER AMINE ABSORBENTS

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

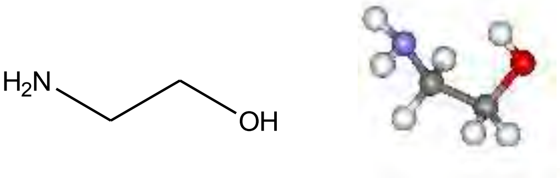
modifications on MEA

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

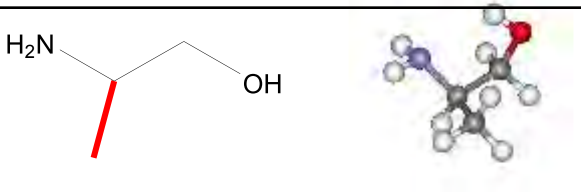
Reactive chemical absorption: ALKANOLAMINE AND OTHER AMINE ABSORBENTS

steric hindrance

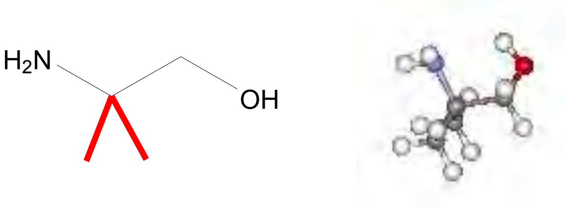
MEA
Monoethanolamine



AP
Aminopropanol



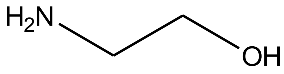
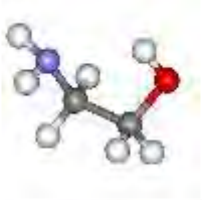
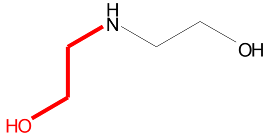
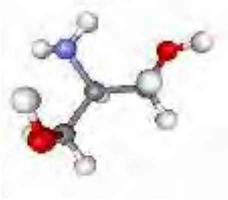
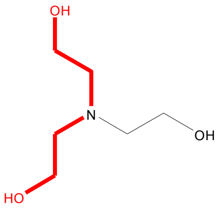
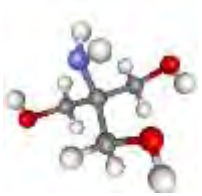
AMP
2-Amino-2-methyl-1-propanol



- 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		

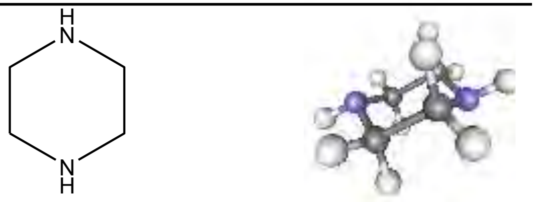
- Increasing steric hindrance
- Less carbamate
- Lower volatility
- Slower reactions

Reactive chemical absorption: ALKANOLAMINE AND OTHER AMINE ABSORBENTS

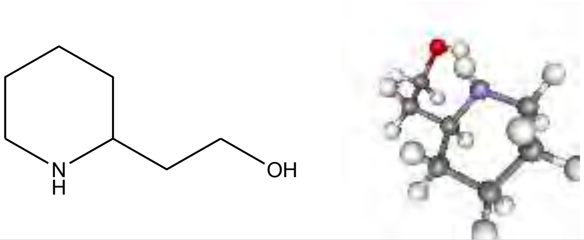
cyclic amines

Piperidine

Piperazine



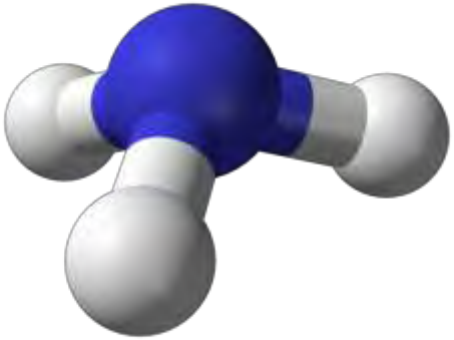
substituted piperidines,
e.g. 2-piperidine-ethanol



- fast reactions
- more carbonate

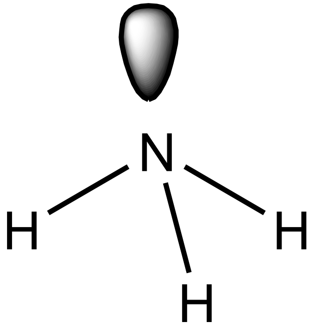
Reactive chemical absorption: AMMONIA

ammonia



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

NH_3

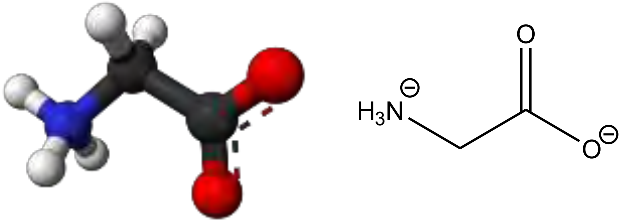


Reactive chemical absorption: AMINO ACIDS

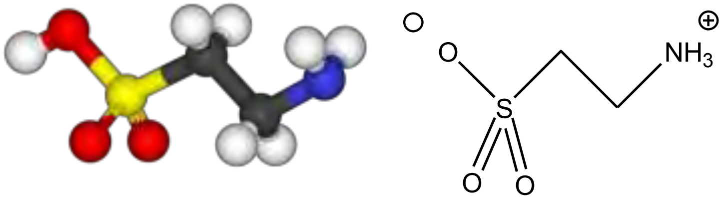
amino acids

- ○ 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

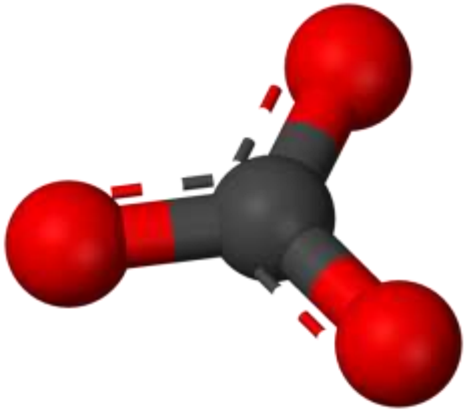


taurine, written as zwitter ion on the right

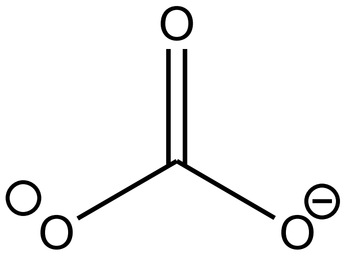
Reactive chemical absorption: CARBONATE SOLUTIONS AND SLURRIES

carbonate

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



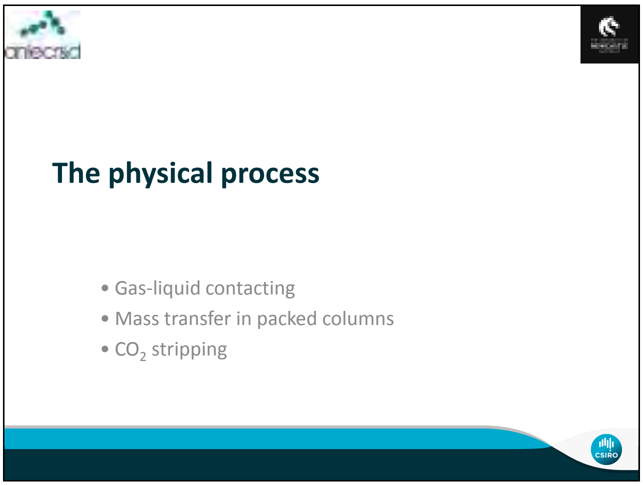
CO_3^{2-}



Acknowledgements

The authors wish to acknowledge financial assistance provided through Australian National Low Emissions Coal Research and Development (ANLEC R&D). ANLEC R&D is supported by Australian Coal Association Low Emissions Technology Limited and the Australian Government through the Clean Energy Initiative.

The physical process



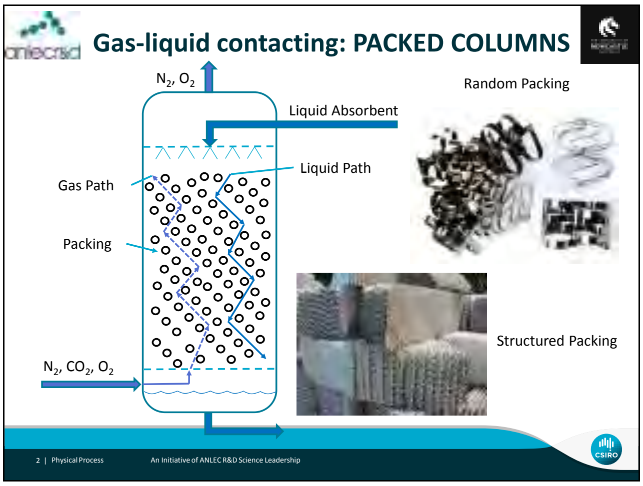
The physical process

- 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

Random Packing

Gas Path

Liquid Path

Packing

Structured Packing

N_2, CO_2, O_2

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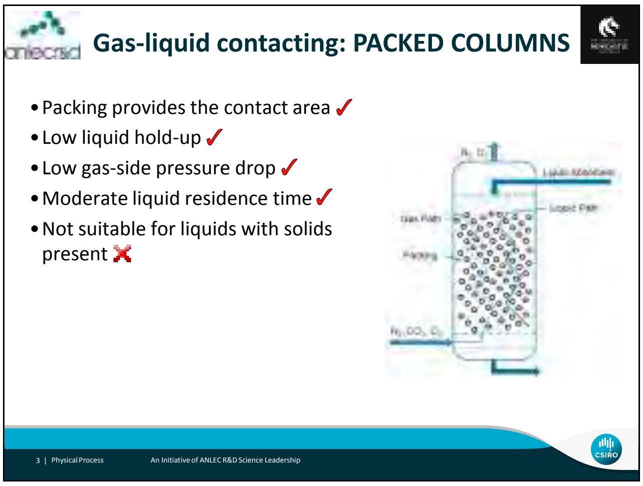
A packed column is basically a hollow vertical tube that is filled with a gas and liquid permeable packing. Liquid enters the column near the top and is sprayed over the packing. It flows down under the influence of gravity and is collected at the bottom of the column. A gas stream is introduced near 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

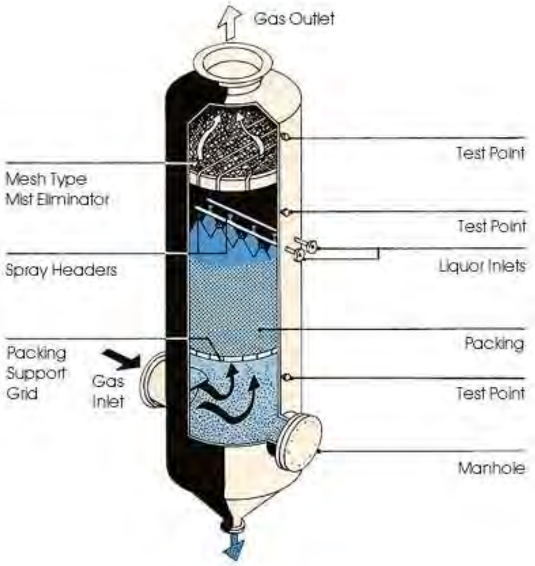


Gas-liquid contacting: PACKED COLUMNS

- 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 ✗

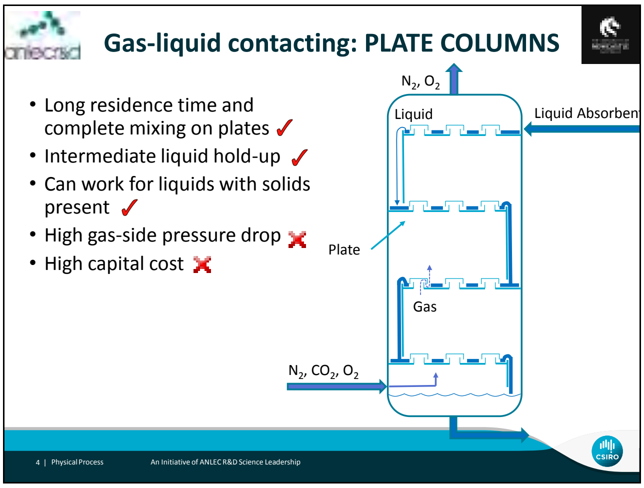
The gas and liquid are in what's called counter-current flow. That is, they flow in opposite directions. The job of the packing is to spread the liquid so that it flows as a thin film to increase the surface area of contact with the gas. As the gas and liquid flow past each other CO_2 is absorbed.

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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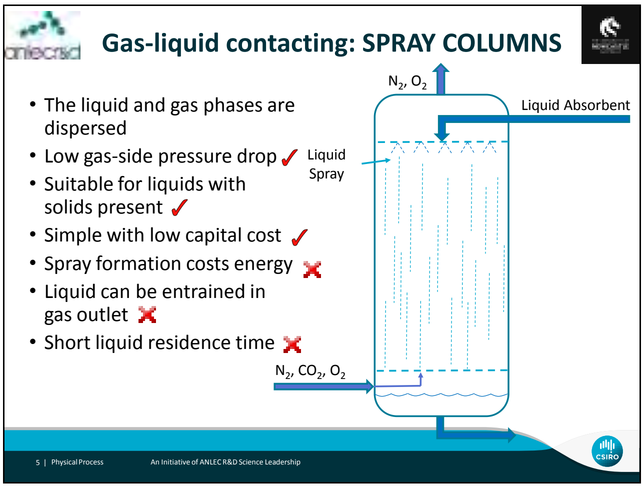
A plate column is also a hollow vertical tube but instead of packing it contains a series of platforms or plates. Again, liquid enters from the top of the column and flows downwards under gravity. The liquid flows from one plate to the next until it reaches the bottom. The gas enters the column above 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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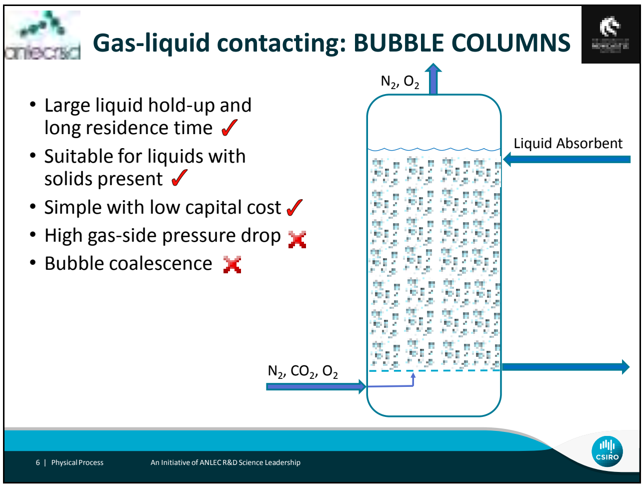
Spray columns have a very simple and low cost design. The liquid is sprayed as a fine mist from the top of the column. Gas enters at the bottom of the column and is driven upwards. The gas and liquid contact occurs as the gas and liquid move past each other.

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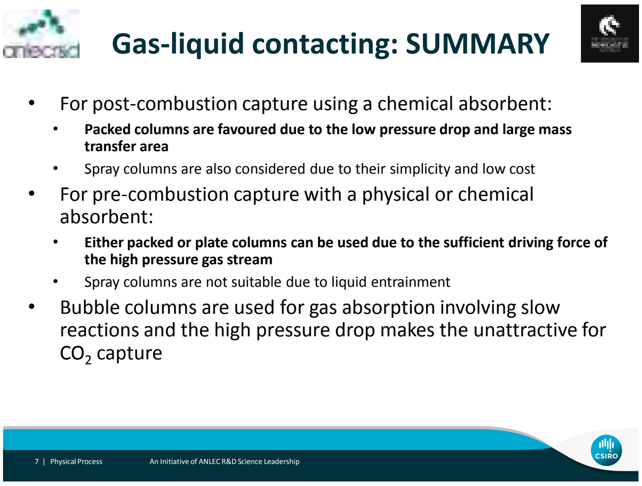
In a bubble column the column is filled with the liquid absorbent, which flows in at the top and out the bottom. The gas enters the column at the base and is sparged or bubbles through the liquid.

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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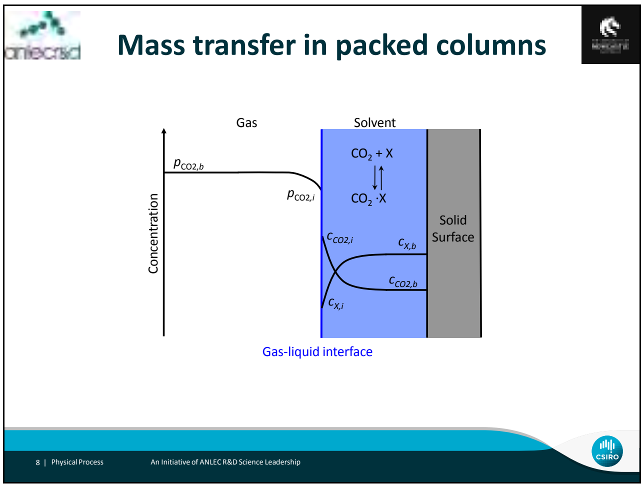
When all the benefits and drawbacks of each column are weighed up against the needs of doing CO_2 capture at coal or gas fired power stations packed columns are the winner. This mainly comes down to the combination of low pressure drop, large mass transfer area and moderate liquid residence times. Spray 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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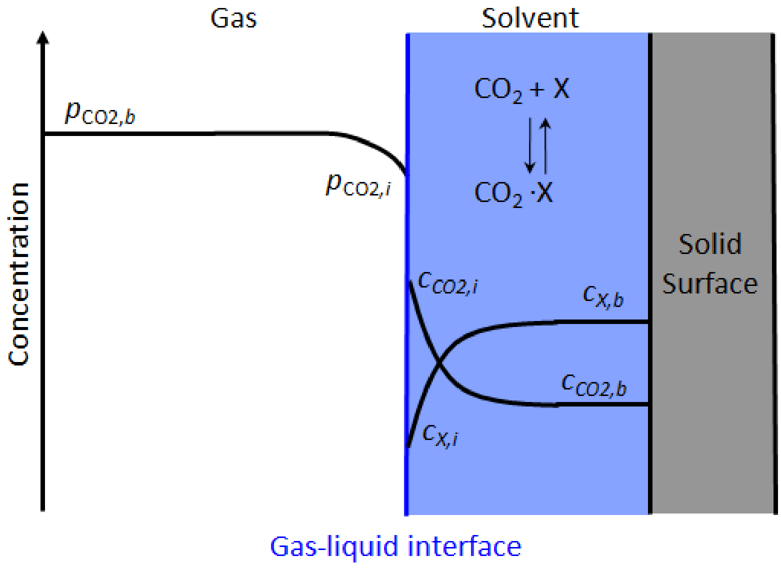
Since packed columns are the column of choice we will focus on mass transfer in this type of column. Mass transfer refers to the transfer of CO_2 from the gas to the liquid phase, or vice versa, and the various processes that control it.

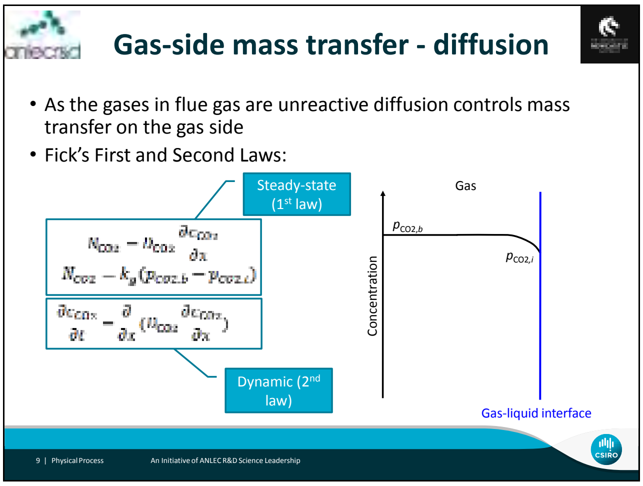
The most common way to describe mass transfer in a packed column is using what’s called the two film model. This model separates what is occuring in the gas phase and the liquid phase. We have a liquid flowing down as a film over packing and a gas moving upwards in contact with the film. At the interface 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.

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.



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

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 (1^{st} 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 (2^{nd} 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.

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

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

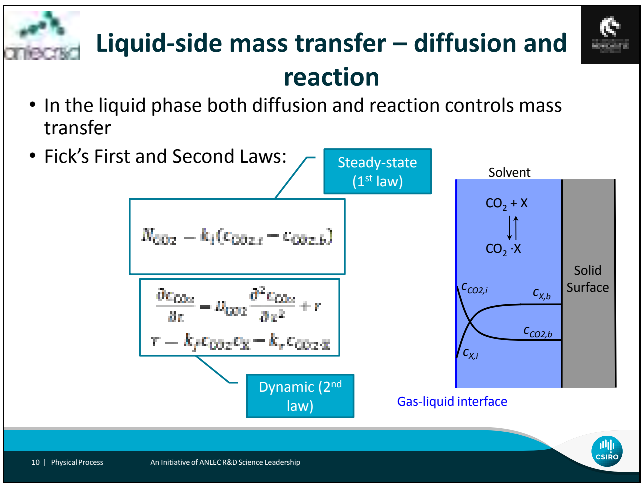
The first equation is the flux (N_{CO2}, mol.m^{-2}.s^{-2}) as a function of the diffusion coefficient D_{CO2} and rate of change in CO_2 concentration. The second is written in terms of the gas-side mass transfer coefficient k_g. The difference in CO_2 partial pressure between the bulk gas and at the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

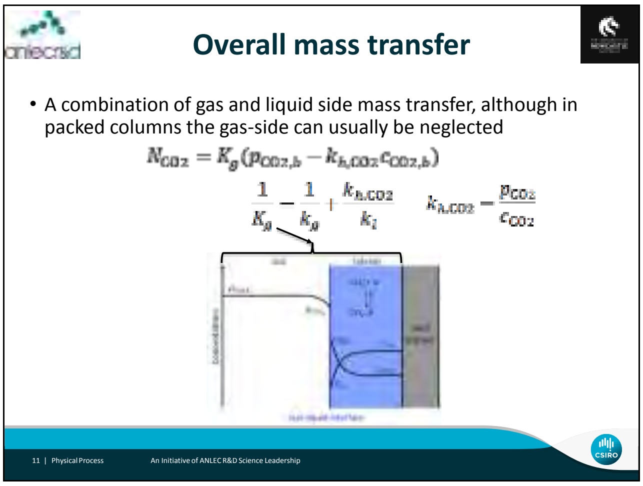
If the reactions are fast or the reactants are not in excess this steady-state equation cannot be used. In this case an extended form of Fick's Second Law is required.

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

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

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

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

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

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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.

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

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

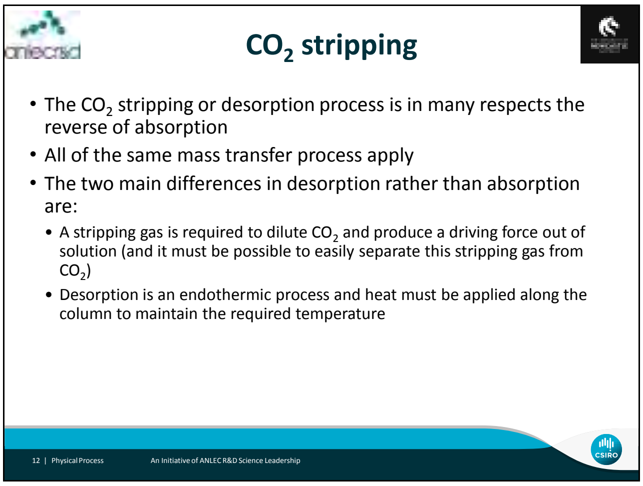
$$k_{h,CO2} = \frac{p_{CO2}}{c_{CO2}}$$

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.

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

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

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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.

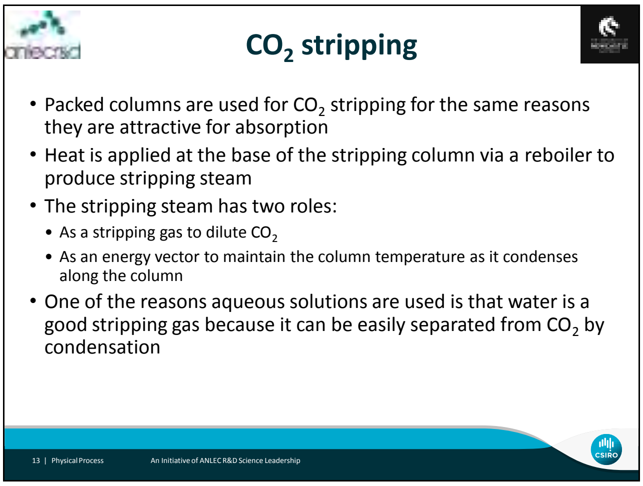
From a chemical and mass transfer point of view CO_2 stripping, or desorption, is the reverse of the absorption process. Heat is required to shift the chemical equilibria to favour CO_2 release. To drive desorption two things are required:

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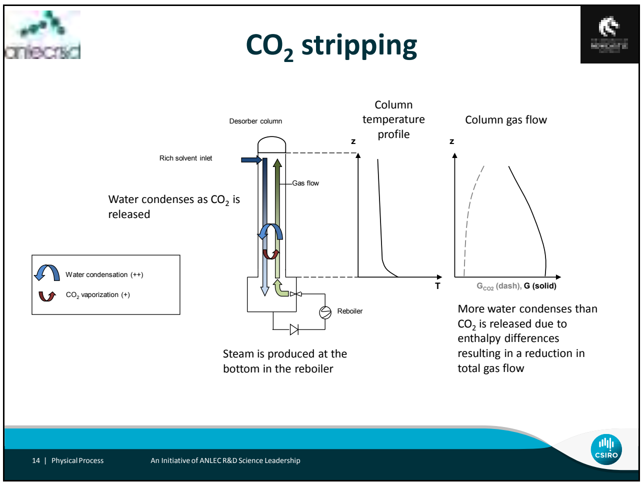
As mentioned, stripping is done in a packed column. The reasons are the same as for the absorber, low pressure drop, high surface area and moderate liquid residence time. Heat is applied at the base of the column using a reboiler. Reboilers are heaters that extract some or all of the solvent flow and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



anlecrd

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 (+)

z

T

z

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

Reboiler

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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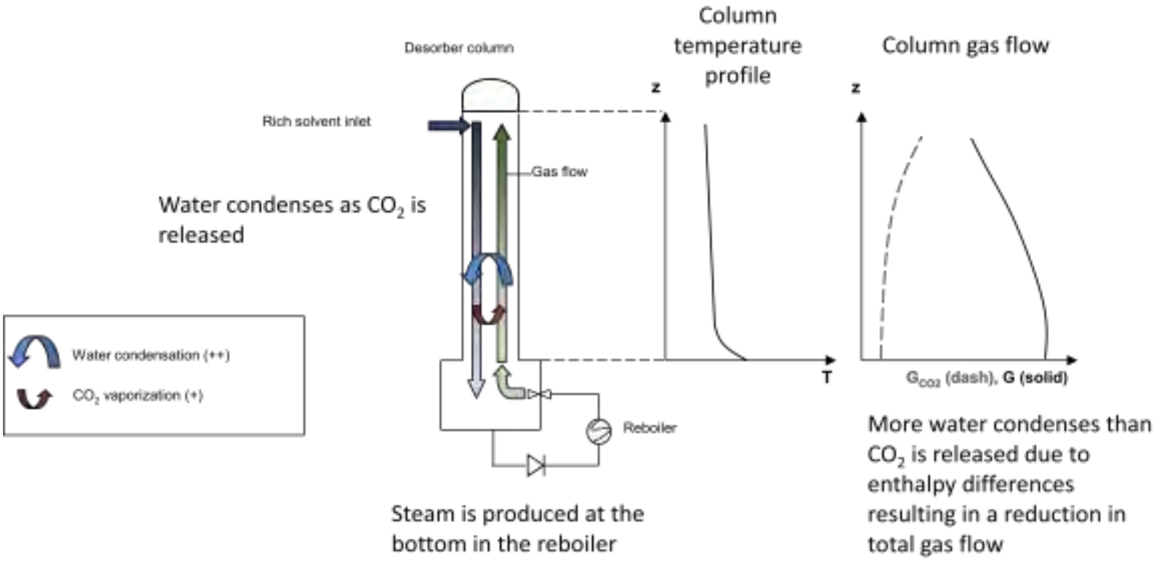
CSIRO

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.

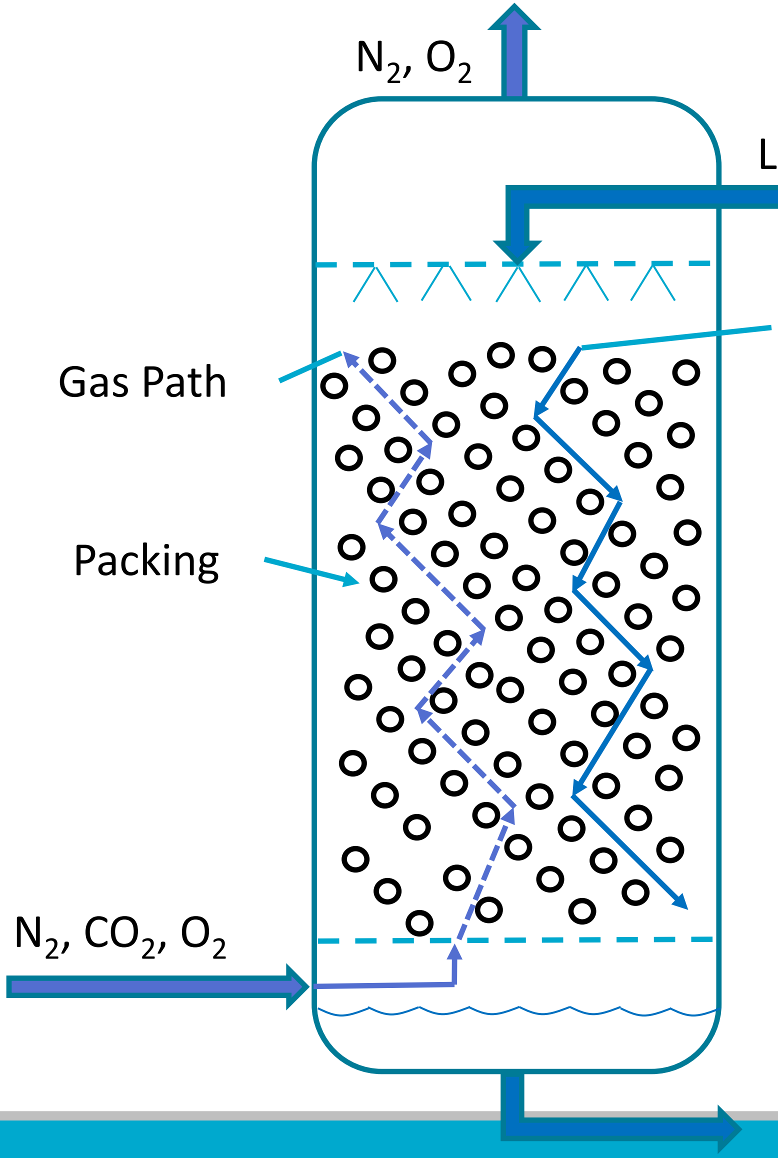


What is happening in the desorber (stripper) column as CO_2 is released and water condenses.

The physical process

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

Gas-liquid contacting: PACKED COLUMNS



N_2, O_2

Liquid Absorbent

Liquid Path

Gas Path

Packing

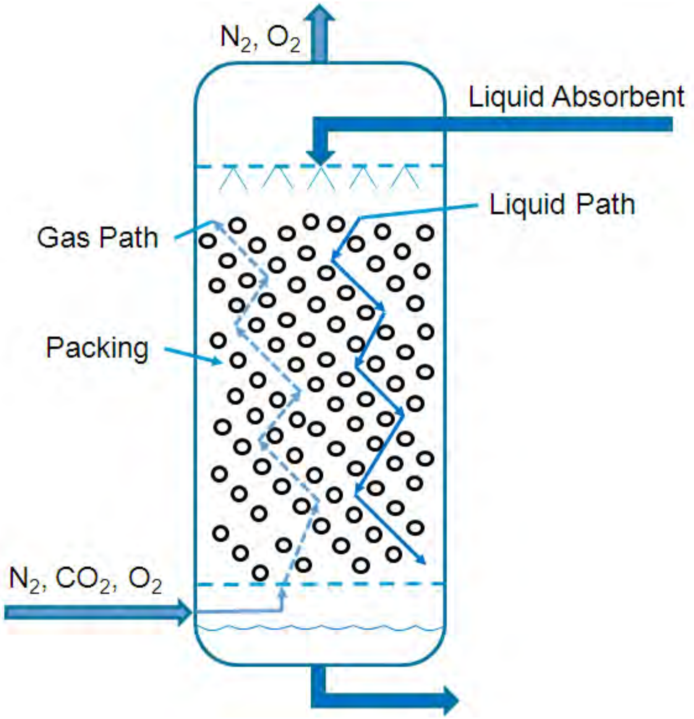
N_2, CO_2, O_2

Random Packing

Structured Packing

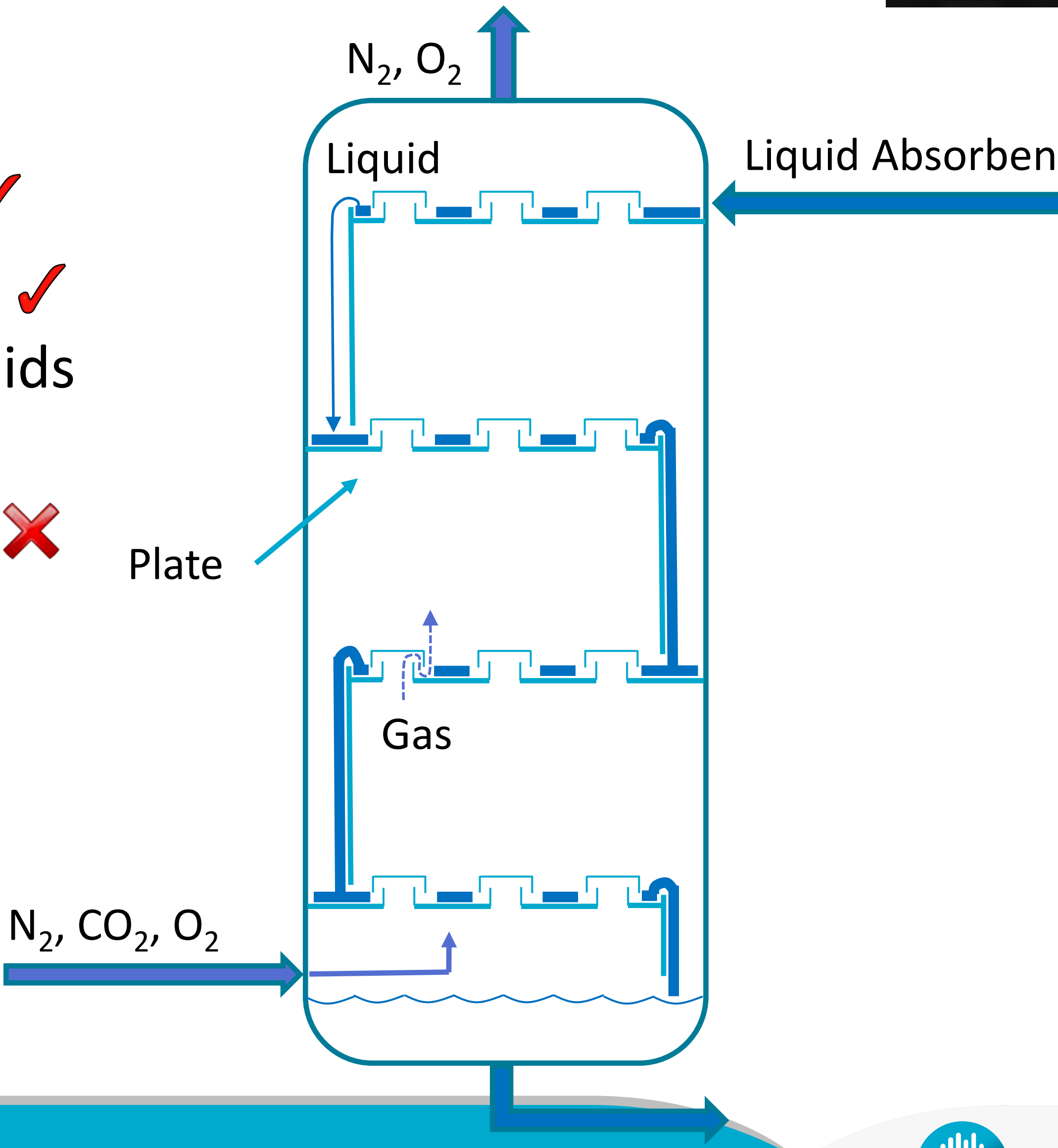
Gas-liquid contacting: PACKED COLUMNS

- 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 ✗



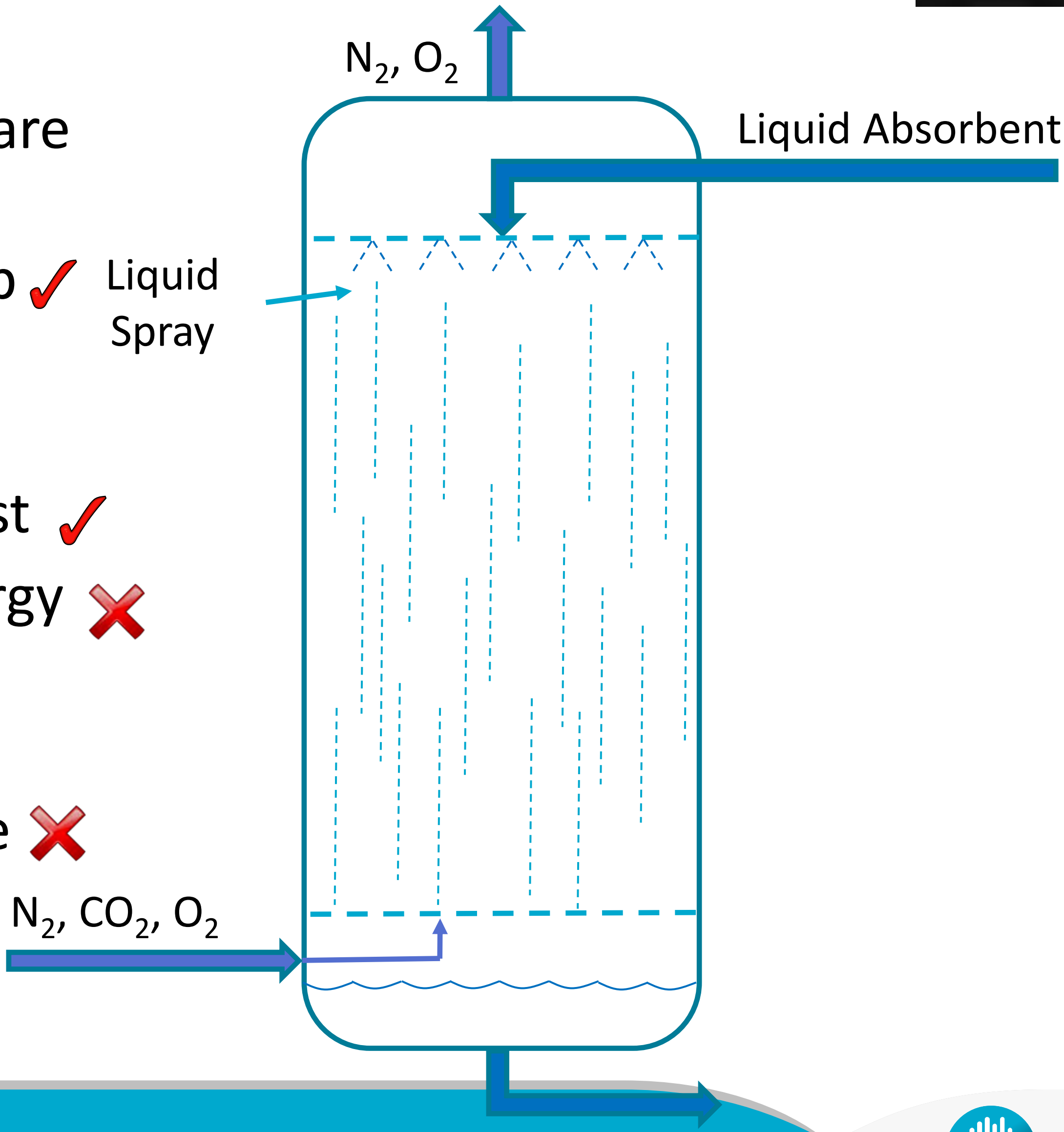
Gas-liquid contacting: PLATE COLUMNS

- 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 ✗



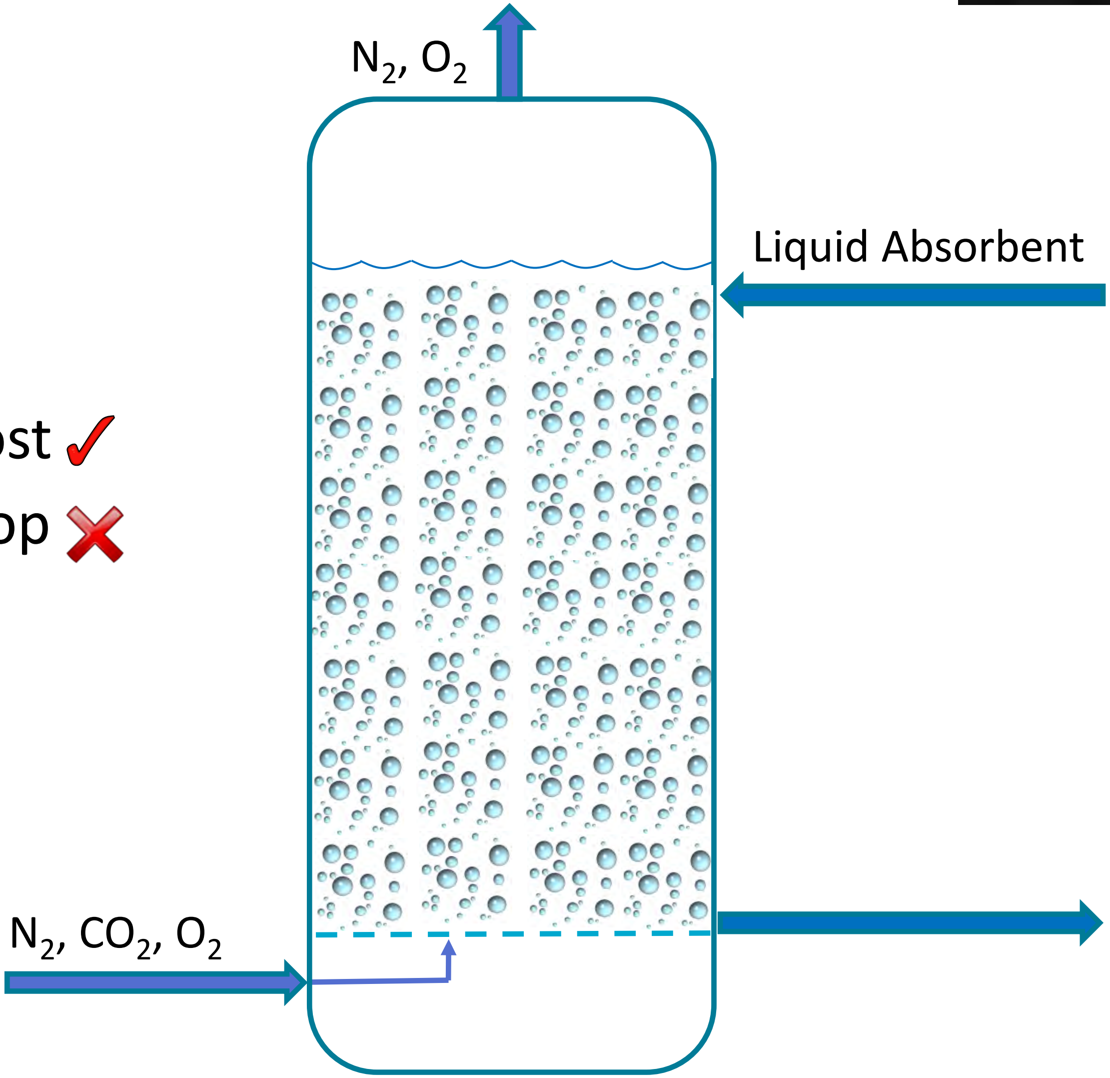
Gas-liquid contacting: SPRAY COLUMNS

- 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 ✗



Gas-liquid contacting: BUBBLE COLUMNS

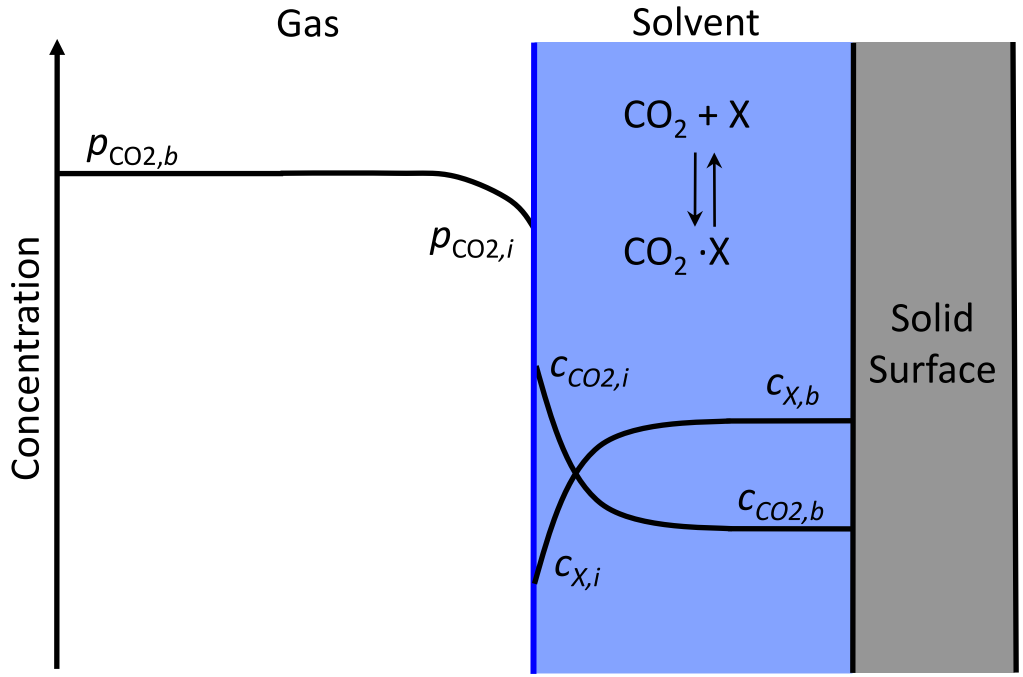
- Large liquid hold-up and long residence time ✓
- Suitable for liquids with solids present ✓
- Simple with low capital cost ✓
- High gas-side pressure drop ✗
- Bubble coalescence ✗



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

Mass transfer in packed columns



Gas-liquid interface

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:

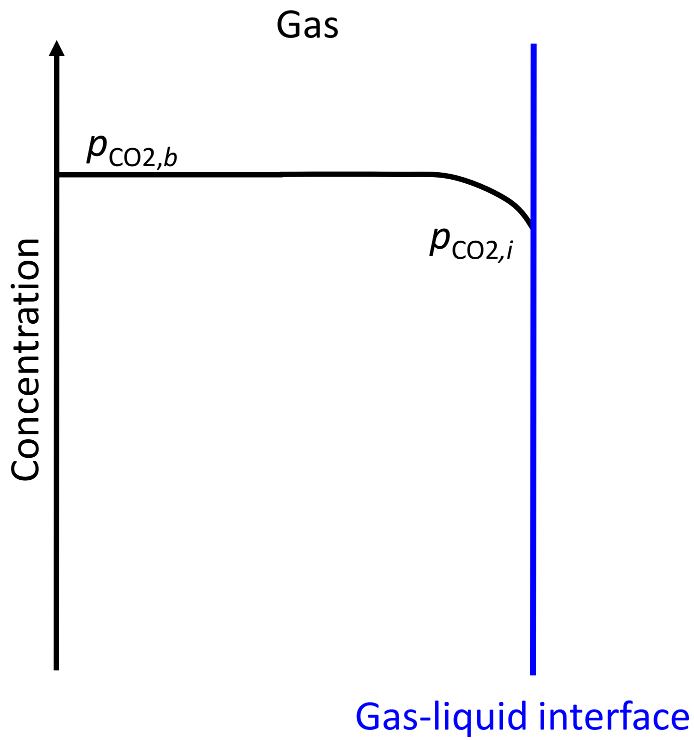
Steady-state (1st law)

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

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

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

Dynamic (2nd law)



Liquid-side mass transfer – diffusion and reaction

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

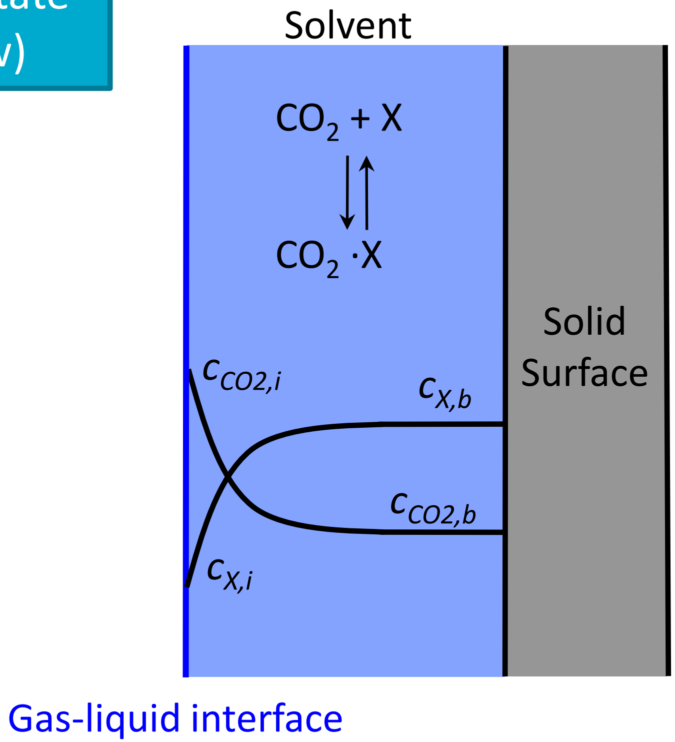
Steady-state (1st law)

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

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

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

Dynamic (2nd law)

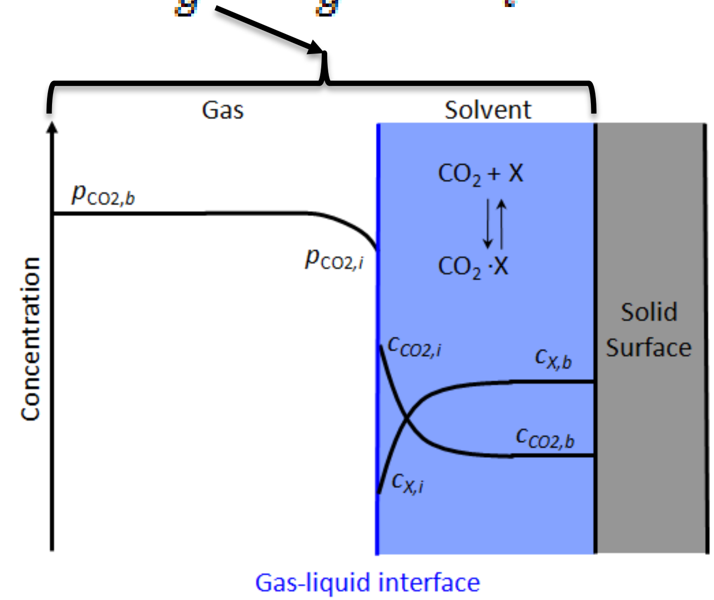


Overall mass transfer

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

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

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



CO_2 stripping

- The CO_2 stripping or desorption process is in many respects the reverse of absorption
- The absorbent is heated to shift the chemical equilibrium position more in favour of CO_2 release
- All of the same mass transfer process apply
- The two main differences in the operation of 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

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
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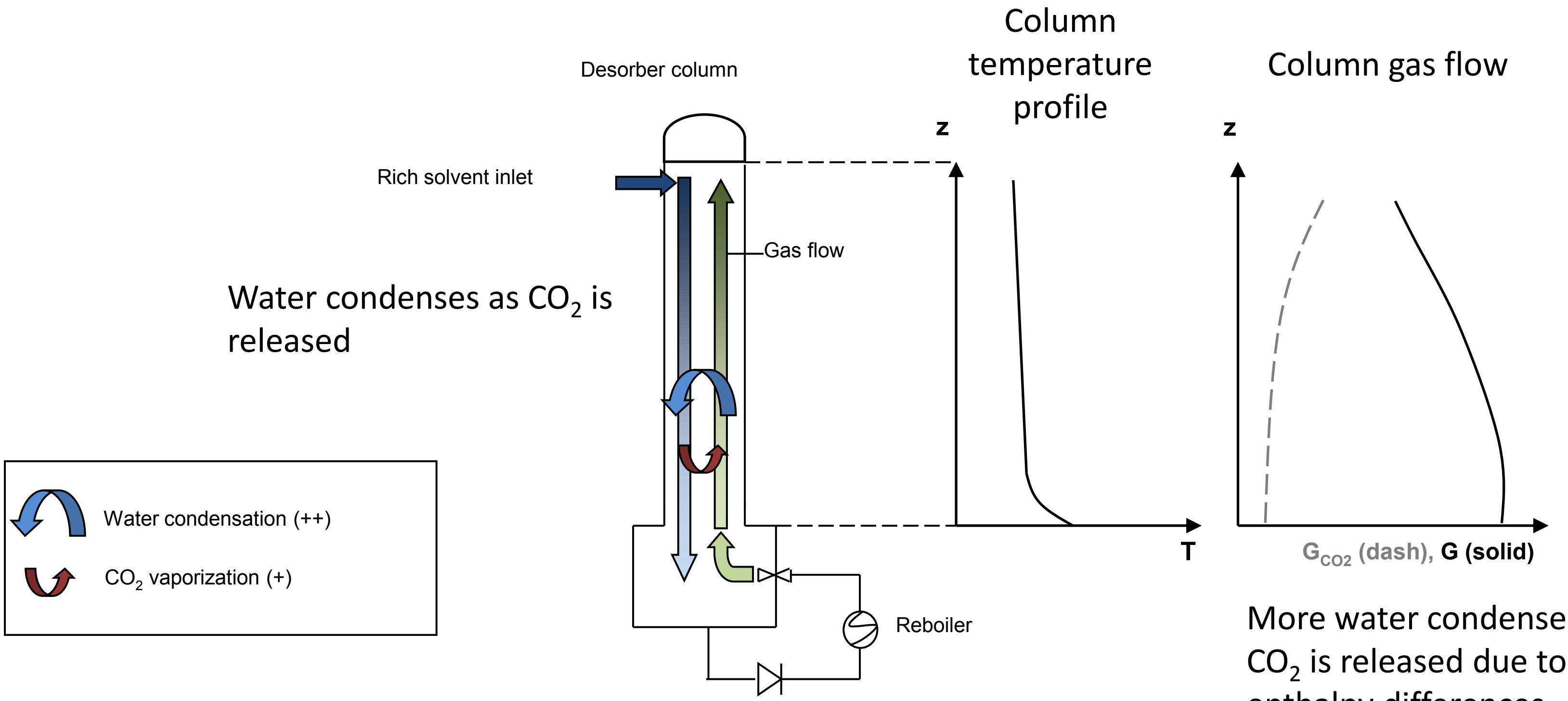
- One of the reasons aqueous solutions are used is that water is a good stripping gas because it can be easily separated from CO_2 by condensation

CO_2 stripping



Water condenses as CO_2 is released

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

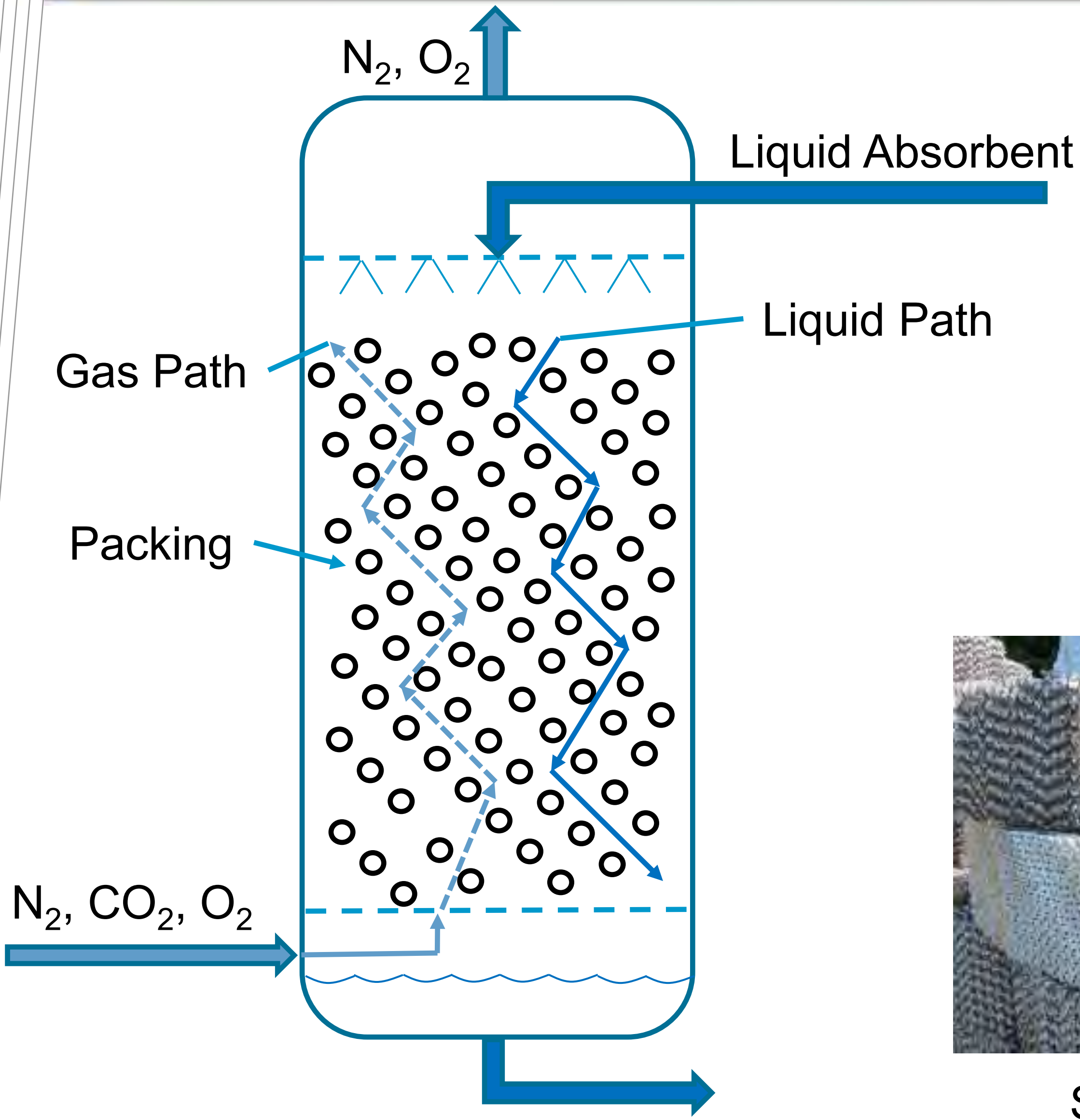
Acknowledgements

The authors wish to acknowledge financial assistance provided through Australian National Low Emissions Coal Research and Development (ANLEC R&D). ANLEC R&D is supported by Australian Coal Association Low Emissions Technology Limited and the Australian Government through the Clean Energy Initiative.

The physical process

- Gas-liquid contacting
- Mass transfer in packed columns

Gas-liquid contacting: PACKED COLUMNS

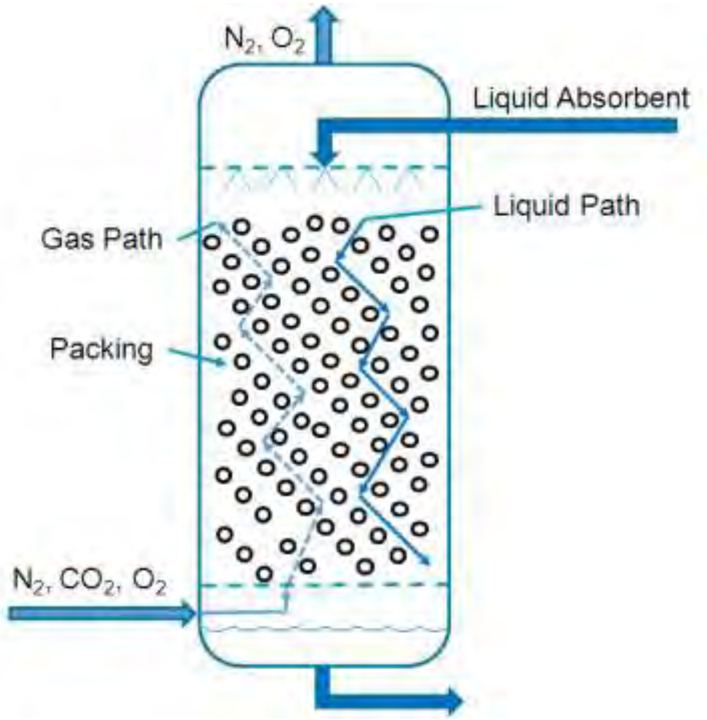


Random Packing

Structured Packing

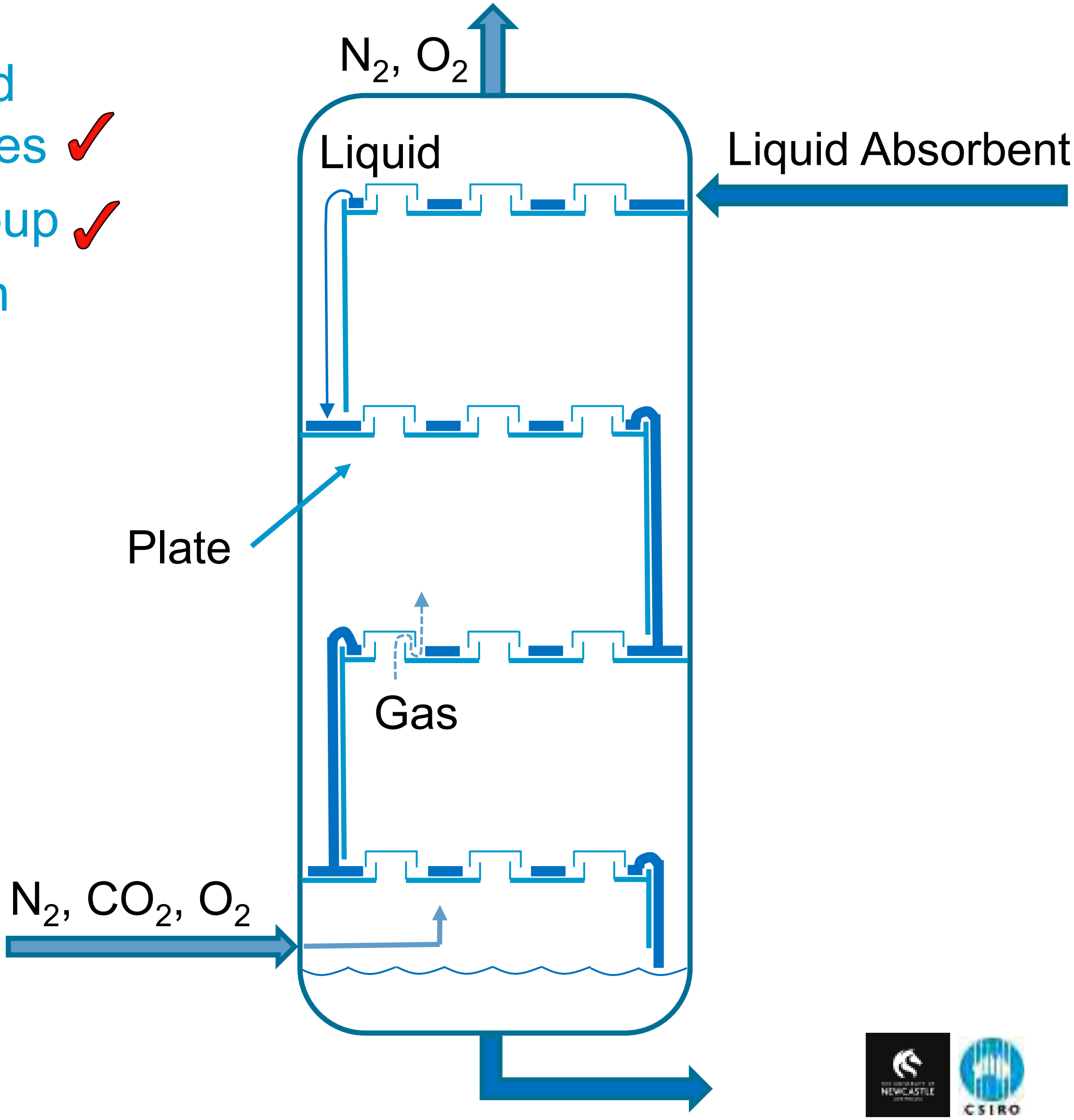
Gas-liquid contacting: PACKED COLUMNS

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



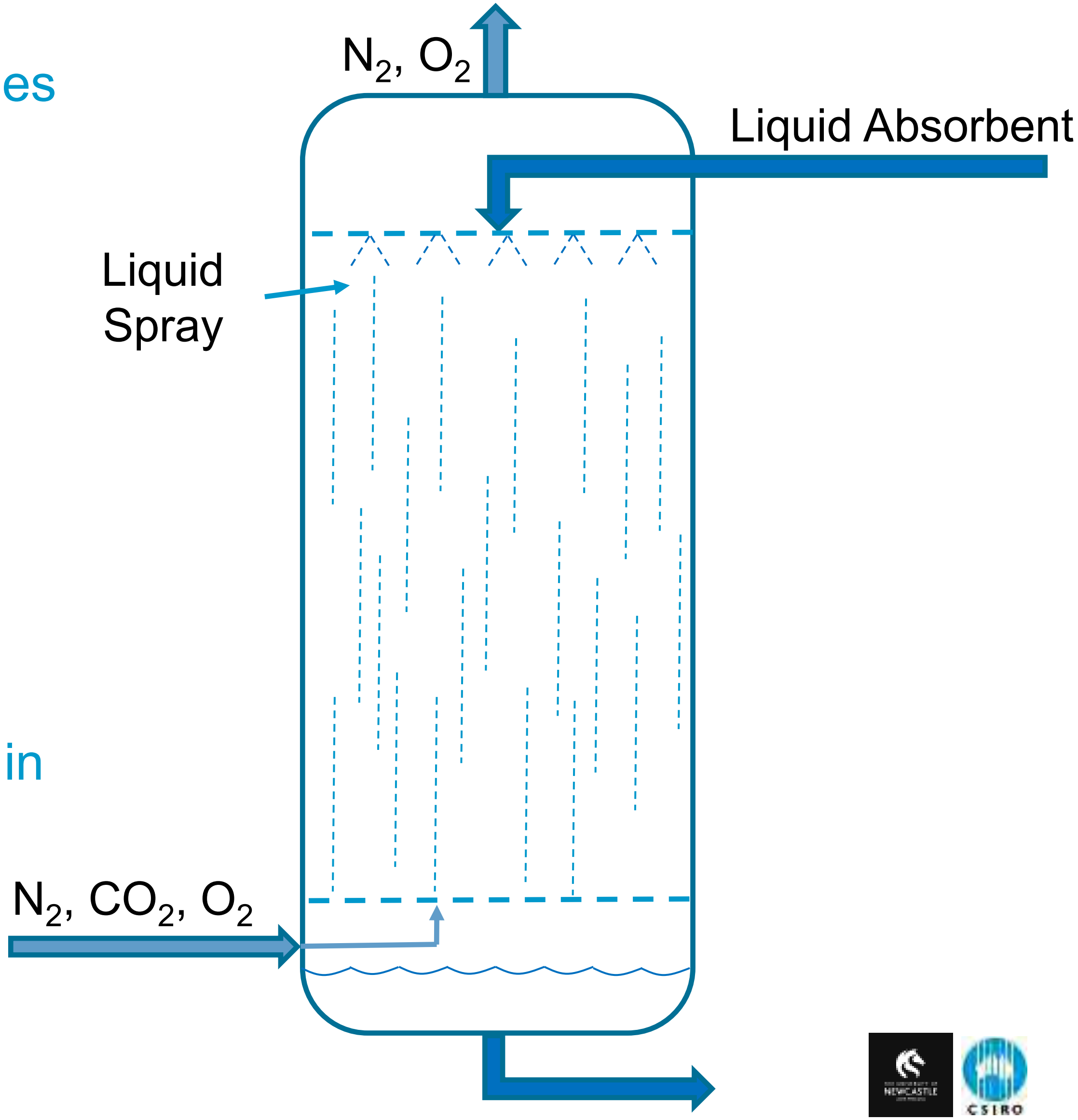
Gas-liquid contacting: PLATE COLUMNS

- 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 ✗



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 ✗



Gas-liquid contacting: BUBBLE COLUMNS

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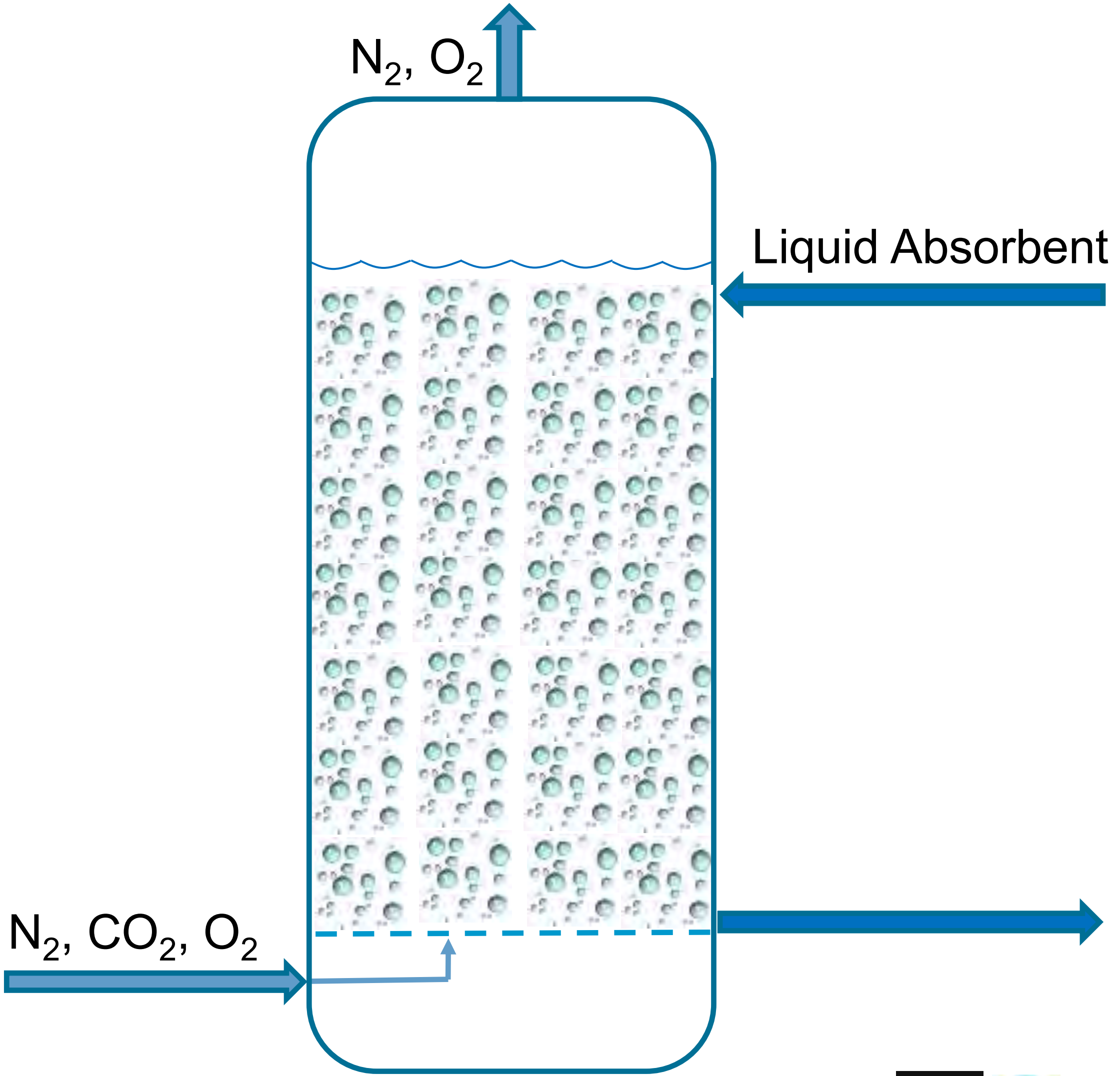
- High gas-side pressure drop ✗
- Bubble coalescence ✗



Gas-liquid contacting: SUMMARY

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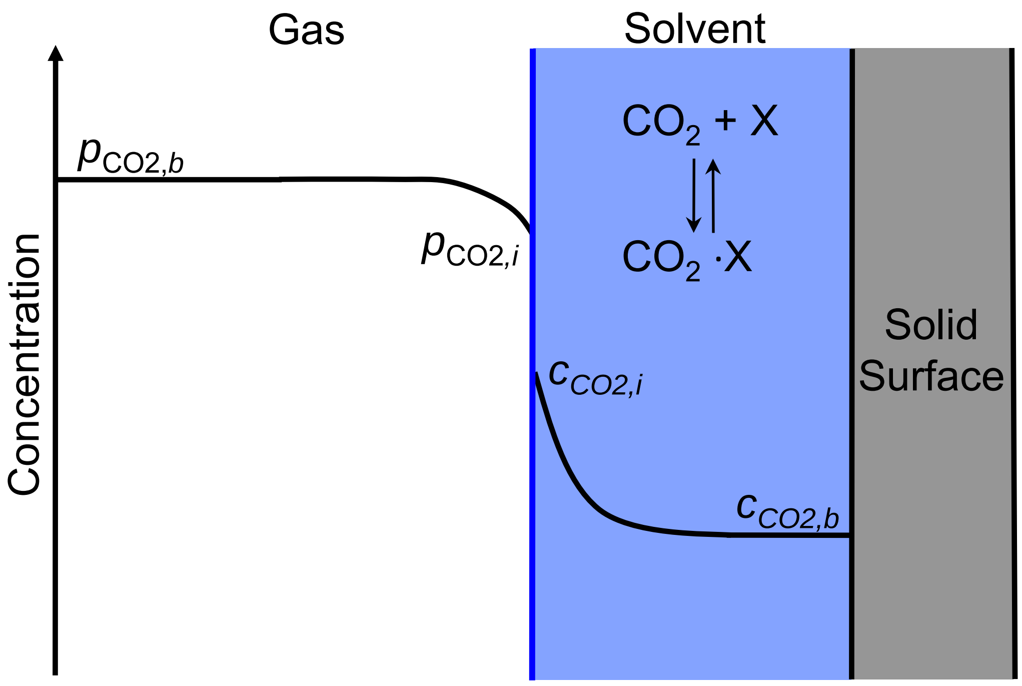
Mass transfer in packed columns



Gas-liquid interface

Mass transfer in packed columns: 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:

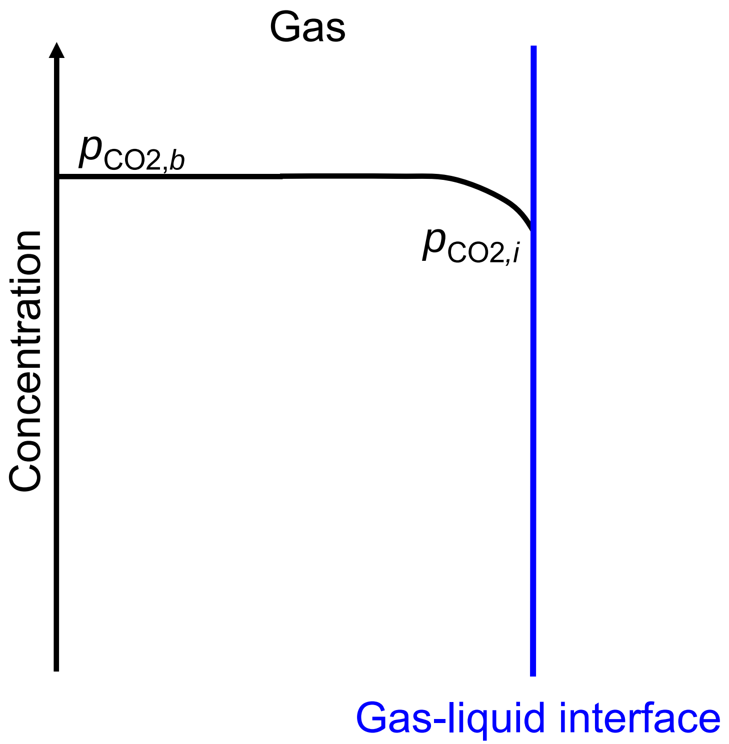
Steady-state (1st law)

$$N_{CO2} = D_{CO2} \frac{\partial p_{CO2}}{\partial x}$$

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

$$\frac{\partial p_{CO2}}{\partial t} = \frac{\partial}{\partial x}\left(D_{CO2} \frac{\partial p_{CO2}}{\partial x}\right) = D_{CO2} \frac{\partial^2 p_{CO2}}{\partial x^2}$$

Dynamic (2nd law)



Mass transfer in packed columns: 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)

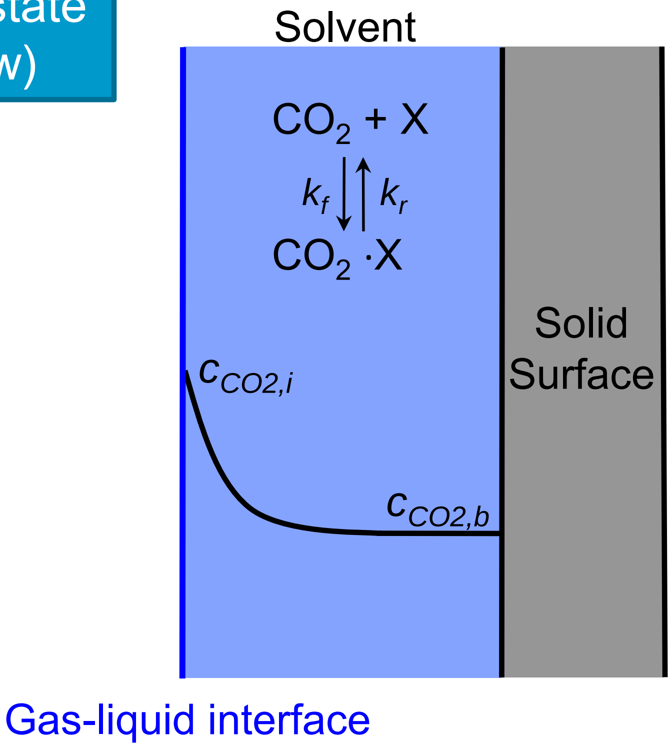
$$N_{CO2} = D_{CO2} \frac{\partial c_{CO2}}{\partial x}$$

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

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

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

Dynamic (2nd law)

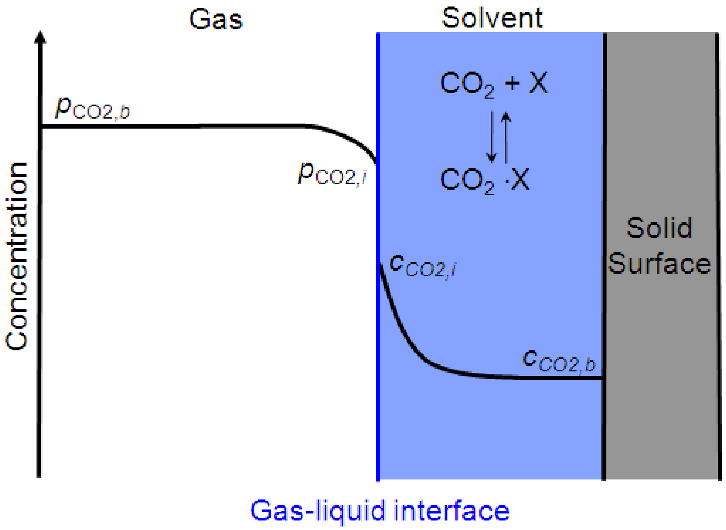


Mass transfer in packed columns: OVERALL MASS TRANSFER

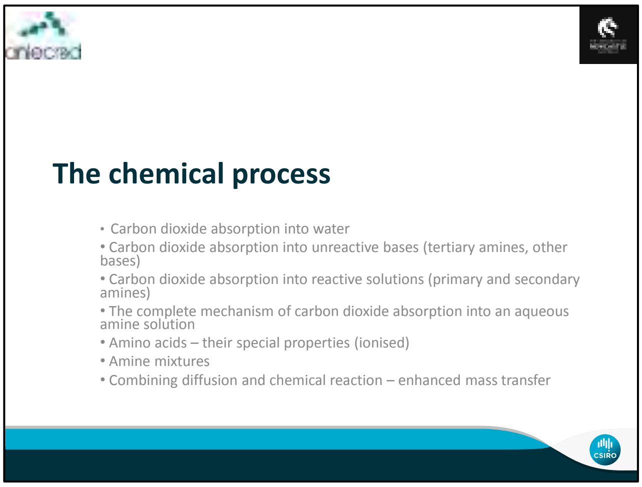
- A combination of gas and liquid side mass transfer, although in packed columns the gas-side can usually be neglected

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

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



The Chemical Process



The chemical process

- Carbon dioxide absorption into water
- Carbon dioxide absorption into unreactive bases (tertiary amines, other bases)
- Carbon dioxide absorption into reactive solutions (primary and secondary amines)
- The complete mechanism of carbon dioxide absorption into an aqueous amine solution
- Amino acids – their special properties (ionised)
- Amine mixtures
- Combining diffusion and chemical reaction – enhanced mass transfer

Overview of the chemical processes in PCC

There are several parallel processes that occur upon absorption of CO_2 into an aqueous amine solution

CO_2 is transferred from the gas phase into the solution; this is an essentially purely physical process and is to a large extent independent of the amine solution.

Once in solution CO_2 can react with water and hydroxide to form carbonic acid and bicarbonate. These are the only reactions with so-called unreactive bases, such as tertiary amines or carbonate.

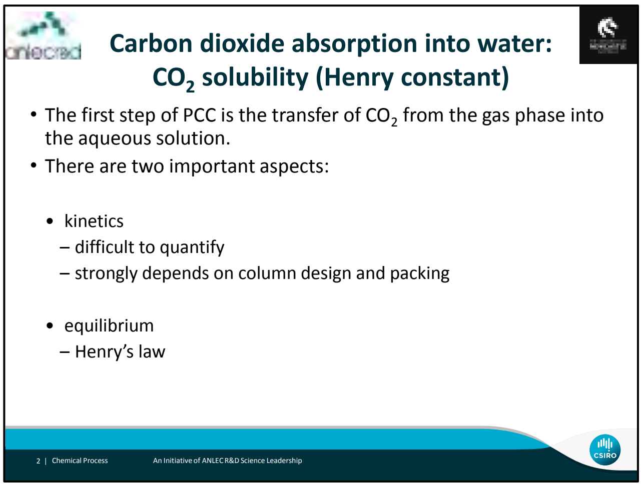
With reactive amines the formation of carbamates occurs parallel and is usually faster than the reactions with water and hydroxide.

Thus the overall reaction mechanism is complex with several reaction paths.

Special amines like di-amines are developed in order to improve the properties relevant for efficient PCC. Very interesting are solutions containing more two or more amine, thus combining the advantages of different amines.

In the end the overall process that includes physical absorption and chemical reactions in solution need to play together as fast and efficient as possible.

CO$_2$ absorption into aqueous solution



Carbon dioxide absorption into water:
CO$_2$ solubility (Henry constant)

- The first step of PCC is the transfer of CO$_2$ from the gas phase into the aqueous solution.
- There are two important aspects:

- kinetics
  - difficult to quantify
  - strongly depends on column design and packing

- equilibrium
  - Henry's law

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Solubility of CO$_2$ in aqueous solution, Henry's constant

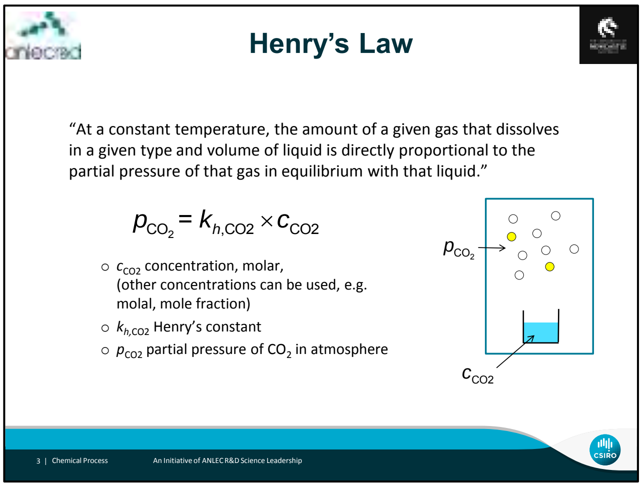
The very first step of the PCC process is the transfer of CO$_2$ from the gas into the aqueous solution.

There are two aspects that are important: the kinetics and the equilibrium.

The kinetics is difficult to quantify, it strongly depends on the viscosity of the solvent and on the physical shape of the interface surface between the gas and the solution. Column design and appropriate packing are most relevant in improving the kinetics of the process.

The equilibrium situation is much simpler; it is defined by Henry's law.

CO_2 absorption into aqueous solution



Henry's Law

"At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid."

$$p_{CO_2} = k_{h,CO2} \times c_{CO2}$$

- c_{CO2} concentration, molar, (other concentrations can be used, e.g. molal, mole fraction)
- $k_{h,CO2}$ Henry's constant
- p_{CO2} partial pressure of CO_2 in atmosphere

Henry's Law

"At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid."

It might be easier to understand the law if written as an equation

$$p_{CO_2} = k_{h,CO2} \times c_{CO2}$$

Where

p_{CO_2} is the partial pressure in the gas phase;

c_{CO2} is the concentration of CO_2 in the solution and

$k_{h,CO2}$ is Henry's constant

This equation represents the equilibrium, the relative concentrations reached after sufficient time. It is easy to reach equilibrium in a closed vessel, such as indicated in the figure; in a PCC absorber equilibrium is probably never really reached.

It is important to remember to use the correct units:

$$k_{h,pc} = \frac{p}{c} = 29.14 \frac{\text{L atm}}{\text{mol}}$$

$$k_{h,px} = \frac{p}{x} = 0.163 \times 10^4 \text{ atm}$$

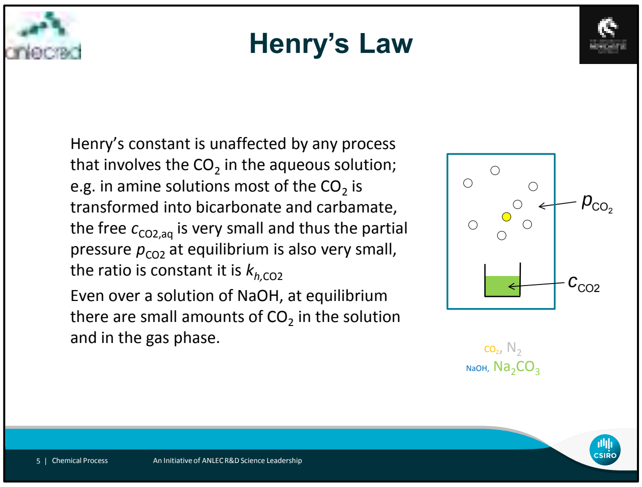
$$k_{h,cc} = \frac{c_{aq}}{c_{gas}} = 0.8317$$

p = partial pressure, in atm

c = concentration, in mol/L

x = mole fraction, dimensionless

CO_2 absorption into aqueous solution



Henry's Law

Henry's constant is unaffected by any process that involves the CO_2 in the aqueous solution; e.g. in amine solutions most of the CO_2 is transformed into bicarbonate and carbamate, the free $c_{CO2,aq}$ is very small and thus the partial pressure p_{CO2} at equilibrium is also very small, the ratio is constant it is $k_{h,CO2}$

Even over a solution of NaOH, at equilibrium there are small amounts of CO_2 in the solution and in the gas phase.

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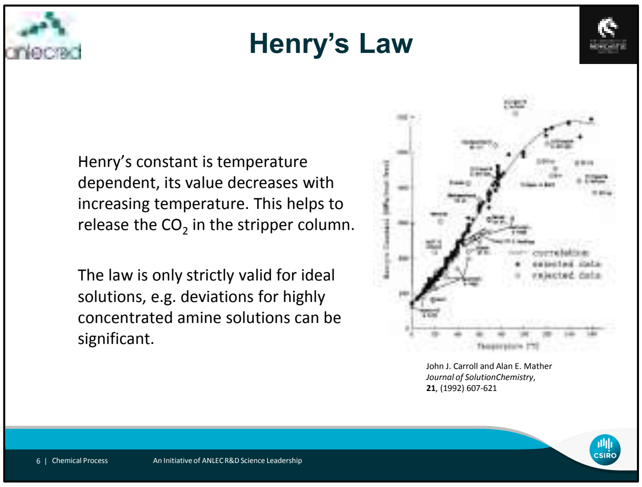
Henry's Law

It is important to realise that Henry's law only applies to the dissolved CO_2 in the liquid phase, not to all the products of the reactions of CO_2 that occur in solution.

In an amine solution most of the CO_2 will be converted into bicarbonate and carbamate, thus the concentration of free CO_2 is very small and as a consequence the partial pressure of CO_2 in the gas phase is also very small. In other words most of the CO_2 is absorbed.

However small the concentrations of CO_2 are in and over an amine solution, once equilibrium is reached the ratio of the two concentrations is the one given by Henry's constant.

CO_2 absorption into aqueous solution



Henry's Law

Henry's constant is temperature dependent, its value decreases with increasing temperature. This helps to release the CO_2 in the stripper column.

The law is only strictly valid for ideal solutions, e.g. deviations for highly concentrated amine solutions can be significant.

John J. Carroll and Alan E. Mather
Journal of SolutionChemistry,
21, (1992) 607-621

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Henry's Law

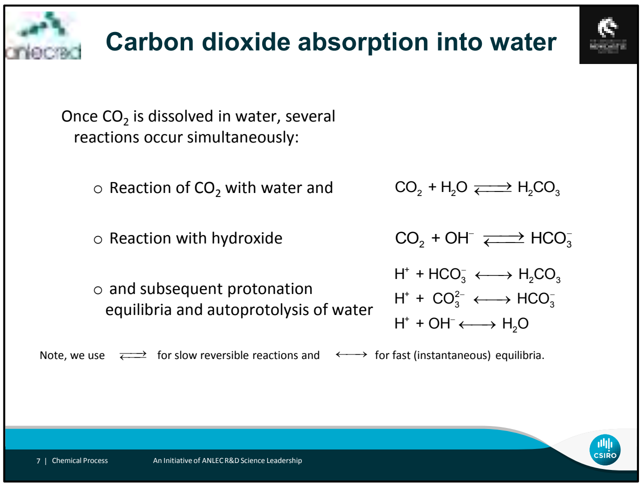
Henry's law describes the ideal case and is strictly valid only for ideal solutions, i.e. at very high dilution. Deviations can be significant for high concentrations, e.g. high concentrations of amine in PCC relevant situations.

Of course Henry's constant is also temperature dependent.

The graph displays published values for the constant as a function of temperature. Note here the partial pressure is expressed as MPa and the concentration in solution as mole fraction.

Most values seem to be consistent but there are also many outliers.

Reactions of CO_2 with H_2O and OH^-



Carbon dioxide absorption into water

Once CO_2 is dissolved in water, several reactions occur simultaneously:

- ○ Reaction of CO_2 with water and $CO_2 + H_2O \rightleftarrows H_2CO_3$
- ○ Reaction with hydroxide $CO_2 + OH^- \rightleftarrows HCO_3^-$
- ○ and subsequent protonation equilibria and autoprotolysis of water $H^+ + HCO_3^- \longleftrightarrow H_2CO_3$; $H^+ + CO_3^{2-} \longleftrightarrow HCO_3^-$; $H^+ + OH^- \longleftrightarrow H_2O$

Note, we use $\rightleftarrows$ for slow reversible reactions and $\longleftrightarrow$ for fast (instantaneous) equilibria.

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Reactions of CO_2 in basic aqueous solution

CO_2 reacts with water in a reversible reaction to form carbonic acid, H2CO3.

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$

CO_2 also reacts in a reversible reaction for from the bicarbonate ion, HCO_3^-.

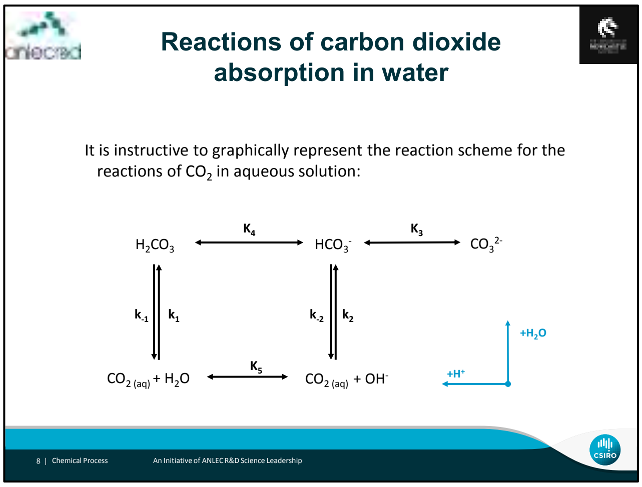
$$CO_2 + OH^- \rightleftarrows HCO_3^-$$

The rate constant for this second reaction is much higher. At high concentration of the hydroxide ions, high pH, the hydroxide path is faster, at low pH the water path is faster. At pH approximately 8.5 both paths are the same. Whatever the pH, both reactions occur simultaneously and only under extreme conditions can one be completely ignored.

In addition to these reactions there are three protonation equilibria. These protonation equilibria establish very fast, much faster that the reactions above, they can be considered instantaneous. (we use the $\longleftrightarrow$ for the protonation equilibria)

$$H^+ + HCO_3^- \longleftrightarrow H_2CO_3$$
$$H^+ + CO_3^{2-} \longleftrightarrow HCO_3^-$$
$$H^+ + OH^- \longleftrightarrow H_2O$$

Reactions of CO_2 with H_2O and OH^-



Reactions of carbon dioxide absorption in water

It is instructive to graphically represent the reaction scheme for the reactions of CO_2 in aqueous solution:

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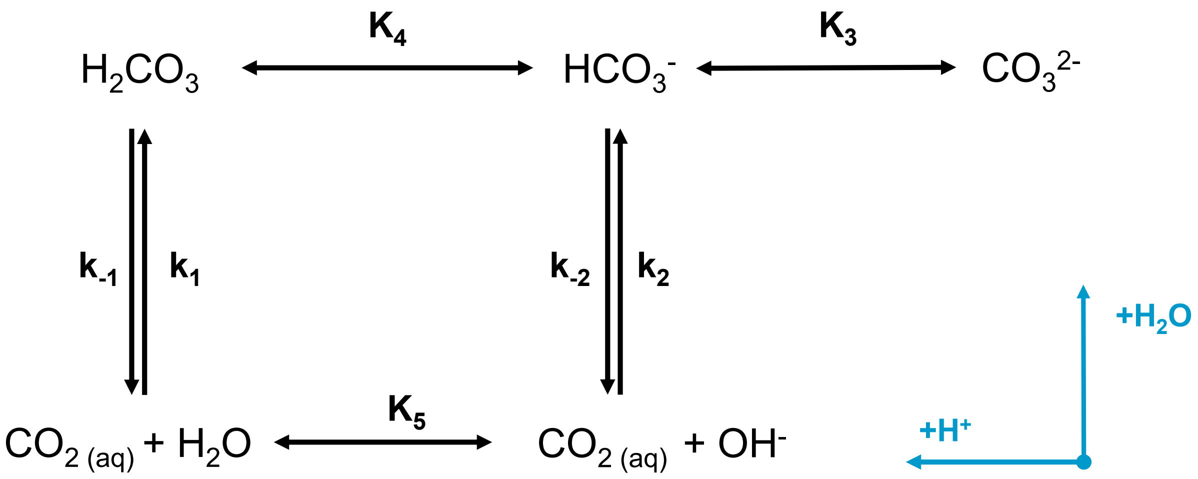
Reactions of CO_2 in basic aqueous solution

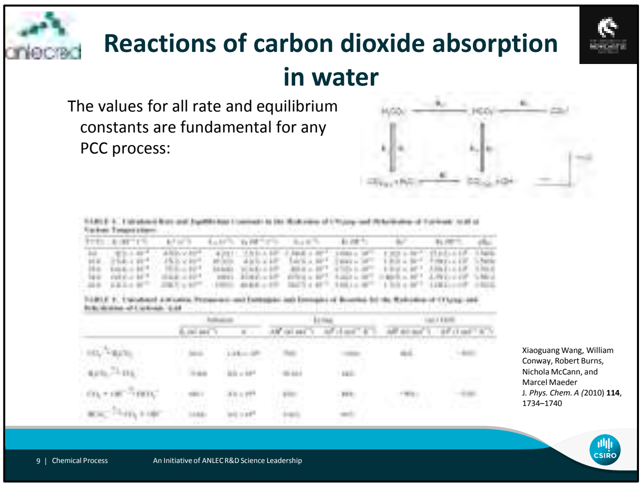
A diagram is probably best to represent the collection of reactions and equilibria that occur parallel in aqueous solution:



The vertical direction indicates reactions of CO_2 with water and hydroxide; the horizontal direction represents the protonation equilibria, the pH.

The diagram represents the interconnectedness of all processes.

Reactions of CO_2 with H_2O and OH^-



Reactions of carbon dioxide absorption in water

The values for all rate and equilibrium constants are fundamental for any PCC process:

Xiaoguang Wang, William Conway, Robert Burns, Nichola McCann, and Marcel Maeder
J. Phys. Chem. A (2010) **114**, 1734–1740

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Reactions of CO_2 in basic aqueous solution

Knowledge of the actual values for all rate and equilibrium constants allows complete quantitative understanding of all processes; this includes the time as well as the equilibrium behaviour.

Of course all constants are temperature dependent and this is quantitatively described by Arrhenius, Eyring and van't Hoff relationships:

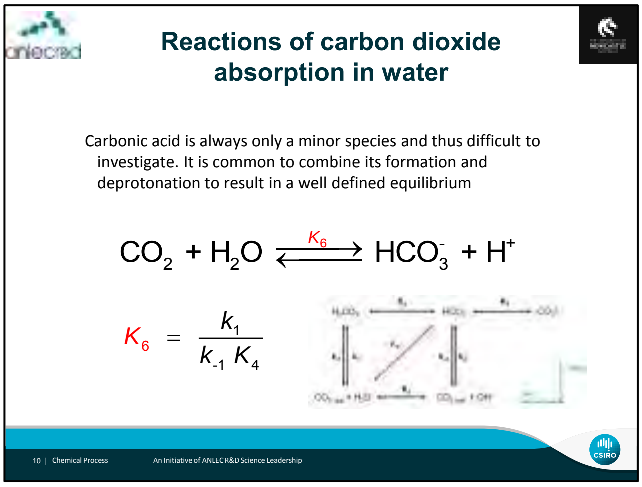
TABLE 1: Calculated Rate and Equilibrium Constants in the Hydration of CO_2(aq) and Dehydration of Carbonic Acid at Various Temperatures

T (°C)	k_1 (M^{-1} s^{-1})	k_1* (s^{-1})	k_{-1} (s^{-1})	k_2 (M^{-1} s^{-1})	k_{-2} (s^{-1})	K_1 (M^{-1})	K_1*	K_2 (M^{-1})	pK_{a2}
6.6	$8(2) \times 10^{-5}$	$4.5(9) \times 10^{-3}$	4.2(1)	$2.3(1) \times 10^{3}$	$1.54(4) \times 10^{-5}$	$1.9(4) \times 10^{-5}$	$1.1(2) \times 10^{-3}$	$15.1(1) \times 10^{7}$	3.54(9)
16.0	$2.7(4) \times 10^{-4}$	$15(2) \times 10^{-3}$	10.3(3)	$4.2(3) \times 10^{3}$	$5.6(3) \times 10^{-5}$	$2.6(4) \times 10^{-5}$	$1.5(3) \times 10^{-3}$	$7.59(1) \times 10^{7}$	3.59(8)
25.0	$6.6(4) \times 10^{-4}$	$37(2) \times 10^{-3}$	24.8(4)	$12.1(4) \times 10^{3}$	$40(1) \times 10^{-5}$	$2.7(2) \times 10^{-5}$	$1.5(1) \times 10^{-3}$	$3.02(1) \times 10^{7}$	3.70(3)
34.0	$2.0(1) \times 10^{-3}$	$112(4) \times 10^{-3}$	60(2)	$25.0(2) \times 10^{3}$	$107(1) \times 10^{-5}$	$3.4(2) \times 10^{-5}$	$1.86(5) \times 10^{-3}$	$2.35(1) \times 10^{7}$	3.58(1)
42.8	$4.2(1) \times 10^{-3}$	$236(7) \times 10^{-3}$	139(3)	$48.8(8) \times 10^{3}$	$381(7) \times 10^{-5}$	$3.0(1) \times 10^{-5}$	$1.7(1) \times 10^{-3}$	$1.28(1) \times 10^{7}$	3.52(2)

TABLE 2: Calculated Activation Parameters and Enthalpies and Entropies of Reaction for the Hydration of CO_2(aq) and Dehydration of Carbonic Acid

	Arrhenius		Eyring		van't Hoff	
	E_a (kJ mol^{-1})	A	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
$CO_2 \xrightarrow{k_1} H_2CO_3$	81(2)	$1.2(8) \times 10^{11}$	79(2)	−41(6)	10(2)	−55(7)
$H_2CO_3 \xrightarrow{k_{-1}} CO_2$	71.6(6)	$9(2) \times 10^{13}$	69.1(6)	14(2)		
$CO_2 + OH^- \xrightarrow{k_2} HCO_3^-$	64(1)	$2(1) \times 10^{14}$	62(1)	40(4)	−50(1)	−23(5)
$HCO_3^- \xrightarrow{k_{-2}} CO_2 + OH^-$	114(2)	$3(3) \times 10^{16}$	112(2)	63(7)		

Reactions of CO_2 with H_2O and OH^-



Reactions of carbon dioxide absorption in water

Carbonic acid is always only a minor species and thus difficult to investigate. It is common to combine its formation and deprotonation to result in a well defined equilibrium

$$CO_2 + H_2O \overset{K_6}{\rightleftarrows} HCO_3^- + H^+$$

$$K_6 = \frac{k_1}{k_{-1}\,K_4}$$

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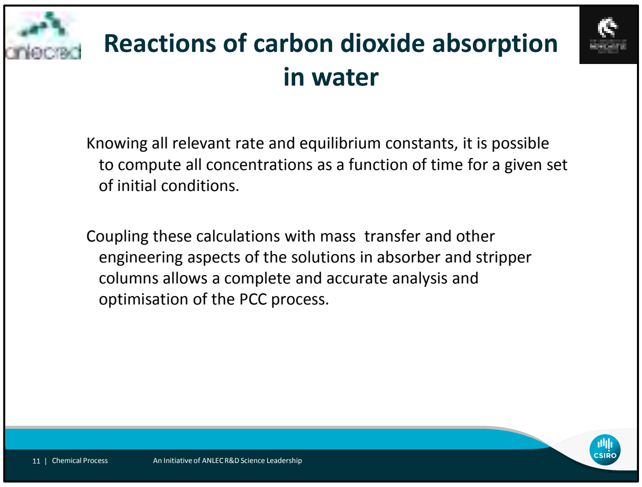
Reactions of CO_2 in basic aqueous solution

Carbonic acid, H_2CO_3, is always only a minor species in aqueous solution, even at low pH the main species is dissolved CO_2(aq), the ration is about 1:1000 at 25 °C.

For this reason it is common to take a ‘shortcut’ from CO_2 directly to the bicarbonate and define a combined equilibrium constant:

$$K_6 = \frac{k_1}{k_{-1}\,K_4}$$

Reactions of CO_2 with H_2O and OH^-



Reactions of carbon dioxide absorption in water

Knowing all relevant rate and equilibrium constants, it is possible to compute all concentrations as a function of time for a given set of initial conditions.

Coupling these calculations with mass transfer and other engineering aspects of the solutions in absorber and stripper columns allows a complete and accurate analysis and optimisation of the PCC process.

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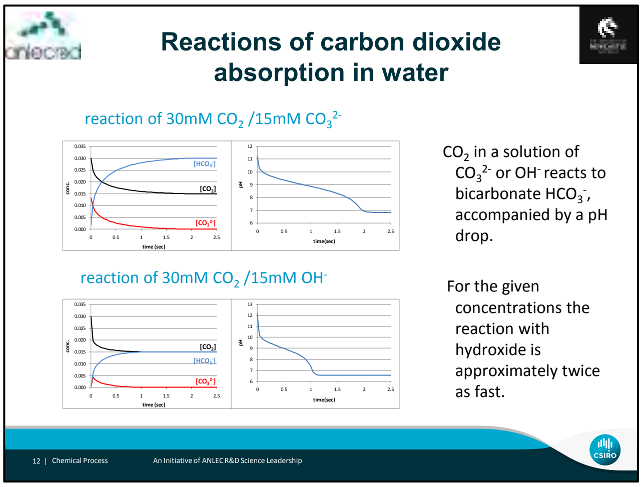
Reactions of CO_2 in basic aqueous solution

The reactions of CO_2 with water and hydroxide are of fundamental importance as they will occur in any PCC application based on aqueous solution. With non-reactive amines they are the only reactions, with reactive amines they occur parallel with the carbamate forming reactions.

The more detailed the knowledge about all aspects of the chemical reactions that occur during PCC processes, the more reliable the processes can be modelled and understood.

Maybe more importantly, the quantitative understanding of the PCC processes allow the rational development of improvements. It is the collaboration between scientists)who investigate the processes on a molecular/test tube level) and chemical engineers (who apply the chemistry in industrial size situations) that will result in the step-wise development of more efficient PCC processes.

Reactions of CO_2 with H_2O and OH^-



Reactions of carbon dioxide absorption in water

reaction of 30mM CO_2 /15mM CO_3^{2-}

reaction of 30mM CO_2 /15mM OH^-

CO_2 in a solution of CO_3^{2-} or OH^- reacts to bicarbonate HCO_3^-, accompanied by a pH drop.

For the given concentrations the reaction with hydroxide is approximately twice as fast.

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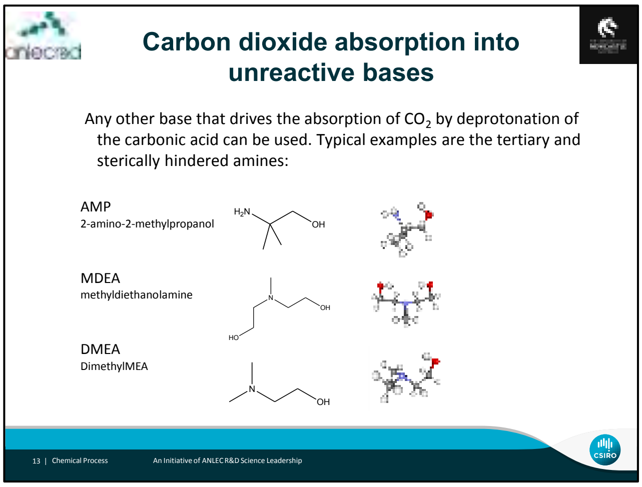
Reactions of CO_2 in basic aqueous solution

In this slide is an example of the insight that can be gained from modelling the relatively complex processes that CO_2 undergoes in basic solution.

The top panels represent the reaction of 30mM CO_2 in a 15mM CO_3^{2-} solution; the lower panels shows the processes with the replacement of 15mM CO_3^{2-} with 15mM OH^-. In both solutions 15 mM CO_2 is absorbed but the reaction is significantly faster for the OH^- solution.

The reaction is producing carbonic acid which immediately releases a proton and thus the pH drops during the reaction. This is shown in the right hand panels. For the CO_3^{2-} solution it takes about 2 sec for the final pH drop which indicates the exhaustion of the base; for the OH^- solution it takes only 1 sec.

Reactions of CO_2 with H_2O and OH^-



Carbon dioxide absorption into unreactive bases

Any other base that drives the absorption of CO_2 by deprotonation of the carbonic acid can be used. Typical examples are the tertiary and sterically hindered amines:

AMP
2-amino-2-methylpropanol

MDEA
methyldiethanolamine

DMEA
DimethylMEA

Tertiary amines

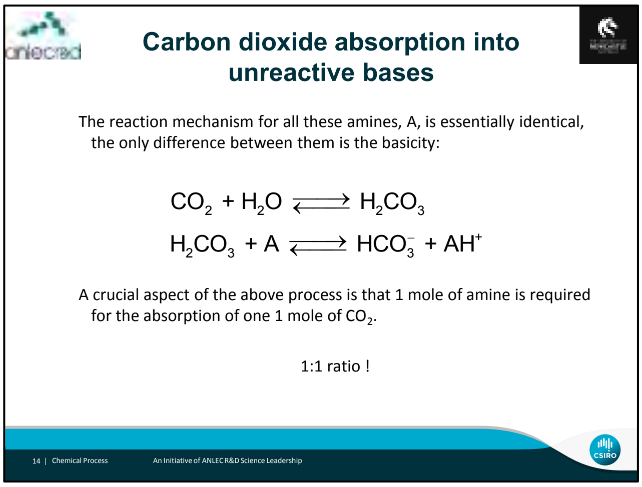
Instead of carbonate or hydroxide, any other base can potentially be used. Organic amines are the most prominent alternatives.

We have to distinguish between so-called reactive and unreactive bases. Reactivity refers to the formation of carbamates which will be discussed in a moment.

Most unreactive bases are tertiary amines as they cannot form the carbamate and their only relevant property is the basicity, the ability to react with a proton. The most prominent members for PCC are MDEA (methyldiethanolamine) and DMEA (dimethylMEA).

An alternative to tertiary amines sterically hindered secondary and primary amines such as AMP (2-amino-2-methylpropanol) also do not react directly with CO_2. While here carbamates could theoretically form, they do not as there is not enough space around the amine group for the incoming CO_2.

Reactions of CO_2 with H_2O and OH^-



Carbon dioxide absorption into unreactive bases

The reaction mechanism for all these amines, A, is essentially identical, the only difference between them is the basicity:

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$

$$H_2CO_3 + A \rightleftarrows HCO_3^- + AH^+$$

A crucial aspect of the above process is that 1 mole of amine is required for the absorption of one 1 mole of CO_2.

1:1 ratio !

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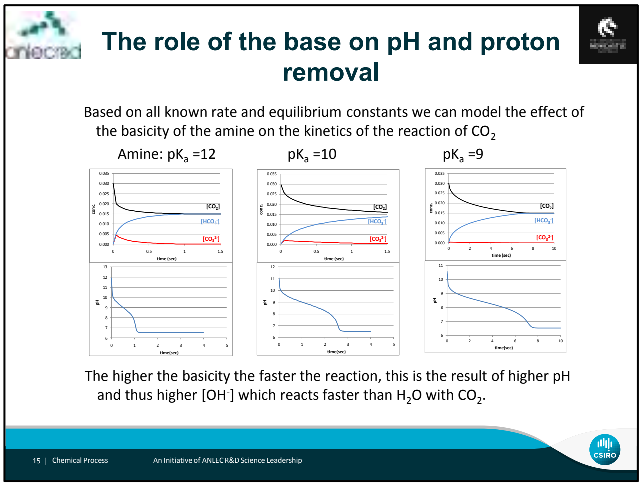
The role of the base

The only function of the non-reactive base A is to act as a Brønsted base and absorb a proton. The proton comes from a carbonic acid molecule which is contains a CO_2 molecule. In this way the reaction is pulled towards the products and as a result CO_2 is absorbed into the amine solution.

The only difference between such amines is the protonation constant or their basicities. They are often quantified as pK_a values.

An important aspect is that there is a net 1:1 interaction between a CO_2 and an amine molecule.

Reactions of CO_2 with H_2O and OH^-



The role of the base on pH and proton removal

Based on all known rate and equilibrium constants we can model the effect of the basicity of the amine on the kinetics of the reaction of CO_2

Amine: pK_a =12 pK_a =10 pK_a =9

The higher the basicity the faster the reaction, this is the result of higher pH and thus higher [OH^-] which reacts faster than H_2O with CO_2.

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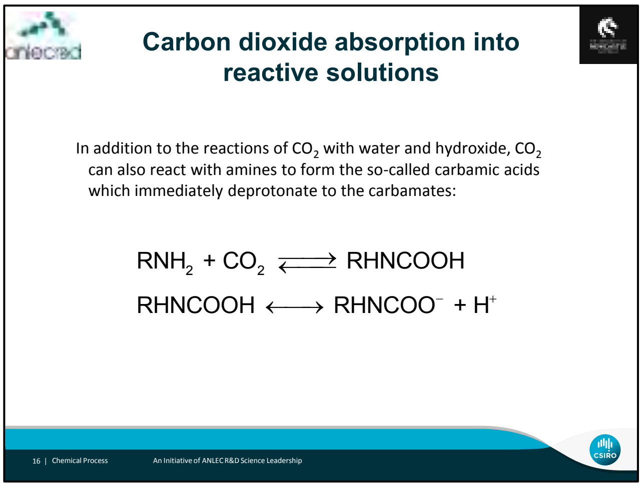
The effect of the basicity of the amine

Even if these non-reactive amines do not directly interact with CO_2, they indirectly influence the reaction via the pH of the solution. More basic amines with create a higher pH of the solution which increases the hydroxide concentration and this in turn accelerates the reaction of CO_2 to form the bicarbonate as the hydroxide ion reacts faster than water.

This is illustrated in the slide. It shows the concentration profiles of CO_2, HCO_3^- and CO_3^{2-} as a function of time for three fictional tertiary amines with pK_a values of 12, 10 and 9. The initial concentrations are $[A]_0$=0.015 M and $[CO_2]_0$=0.03 M; thus an excess of CO_2.

For the most basic amine it takes about 1 sec for the reaction to reach the final equilibrium, this is best indicated by the drop of pH; for the second amine it takes some 2.5 sec and for the third amine it takes more than 5 sec.

Reactive amines that form carbamates



Carbon dioxide absorption into reactive solutions

In addition to the reactions of CO_2 with water and hydroxide, CO_2 can also react with amines to form the so-called carbamic acids which immediately deprotonate to the carbamates:

$$RNH_2 + CO_2 \rightleftarrows RHNCOOH$$

$$RHNCOOH \longleftrightarrow RHNCOO^{-} + H^{+}$$

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CO_2 reactions with amines to form carbamates

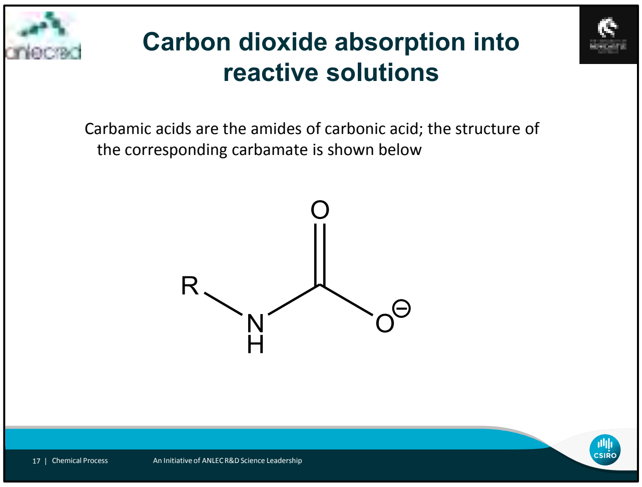
Parallel to the reactions of CO_2 with water and hydroxide to form carbonic acid and bicarbonate, CO_2 reacts with some amines to form the carbamic acid. This is a fast and reversible reaction defined by a forward and back rate constant:

Equation

The initially formed carbamic acid has a protonation constant of around logK=7, thus at pH values relevant for PCC which are around 9, the carbamic acid is deprotonated to form the much more stable carbamate.

equation

Reactive amines that form carbamates



Carbon dioxide absorption into reactive solutions

Carbamic acids are the amides of carbonic acid; the structure of the corresponding carbamate is shown below

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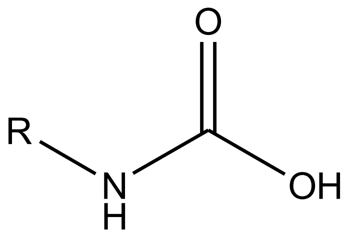
The carbamate

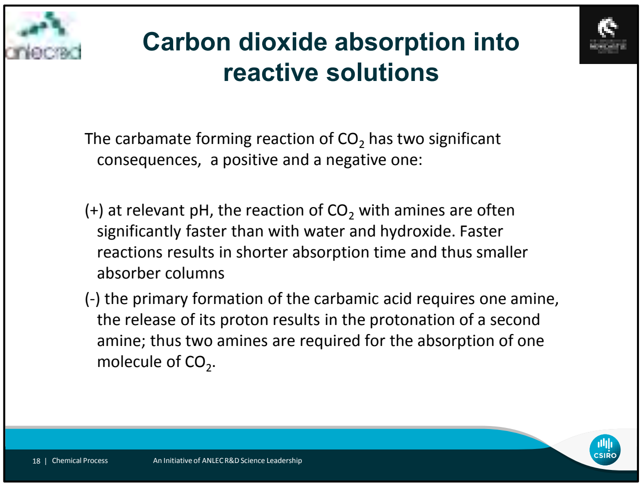
Carbamic acids are the mono-amides of carbonic acids. (The di-amides are called ureas, they are much more stable than the carbamic acids, they do not form under PCC conditions.)

The structure of carbamic acid is shown in the figure. Carbamic acid is often shown as a zwitter ion with the OH proton moved to the amine nitrogen. This is not correct, amides are very weak bases and are not protonated under normal circumstances.



The carbamate, deprotonated carbamic acid, features the carboxylate group with a negative charge ($-COO^-$). Under PCC conditions, pH, only the carbamate exists to any significant amount.

Reactive amines that form carbamates



Carbon dioxide absorption into reactive solutions

The carbamate forming reaction of CO_2 has two significant consequences, a positive and a negative one:

(+) at relevant pH, the reaction of CO_2 with amines are often significantly faster than with water and hydroxide. Faster reactions results in shorter absorption time and thus smaller absorber columns

(-) the primary formation of the carbamic acid requires one amine, the release of its proton results in the protonation of a second amine; thus two amines are required for the absorption of one molecule of CO_2.

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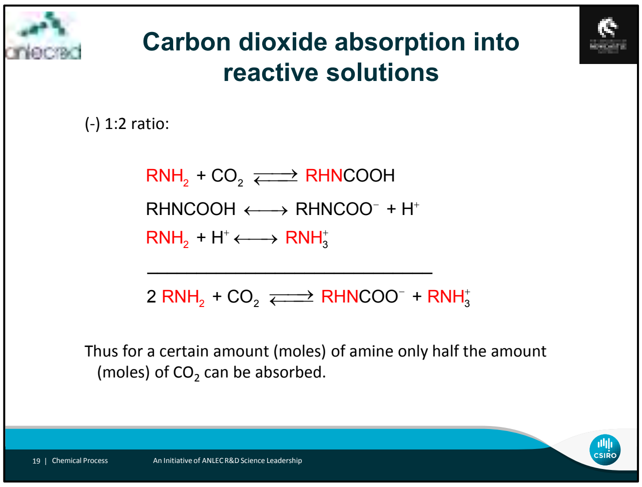
The relevance of the formation of the carbamate

The reaction of CO_2 with amines to form the carbamic acid is usually much faster than the reactions with water and hydroxide. This is a significant advantage as faster reactions results in faster absorption of CO_2 and eventually allows the usage of a shorter absorber column. The savings in capital expenditure is significant and steal is not getting cheaper. Thus the formation of carbamates is an **advantage**.

The **disadvantage** is the release of a proton by the carbamic acid; under PCC conditions it is picked up by an amine. Thus two amine molecules are required for each molecule of absorbed CO_2; one for the formation of the carbamic acid and one for the reaction with the released proton. Overall only half as much CO_2 can be absorbed compared with amines that do not form carbamates. For most amines both processes, carbamate formation and reaction of CO_2 with water/hydroxide occur simultaneously and the ratio never reaches 1:2.

Reactive amines that form carbamates



Carbon dioxide absorption into reactive solutions

(-) 1:2 ratio:

$$RNH_2 + CO_2 \rightleftarrows RHNCOOH$$

$$RHNCOOH \longleftrightarrow RHNCOO^- + H^+$$

$$RNH_2 + H^+ \longleftrightarrow RNH_3^+$$

$$2\,RNH_2 + CO_2 \rightleftarrows RHNCOO^- + RNH_3^+$$

Thus for a certain amount (moles) of amine only half the amount (moles) of CO_2 can be absorbed.

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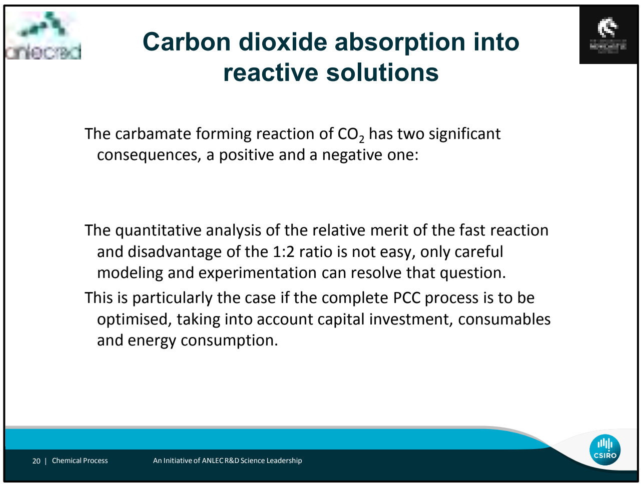
The chemical equations

The formation of the carbamates in aqueous solution under conditions relevant for PCC is a rather complex process which can be divided into the individual steps:

- The first step is the reaction of CO_2 with the amine to form carbamic acid
- The carbamic acid can undergo deprotonation, it is in equilibrium with the carbamate and a proton. The pH in PCC is usually high enough so the equilibrium is far on the carbamate side.
- The proton is picked up by an additional amine.
- The overall reaction is indicated under the line, it clearly shows the 1:2 ratio, per one CO_2 molecule two amine molecules are required.

Reactive amines that form carbamates



Carbon dioxide absorption into reactive solutions

The carbamate forming reaction of CO_2 has two significant consequences, a positive and a negative one:

The quantitative analysis of the relative merit of the fast reaction and disadvantage of the 1:2 ratio is not easy, only careful modeling and experimentation can resolve that question.

This is particularly the case if the complete PCC process is to be optimised, taking into account capital investment, consumables and energy consumption.

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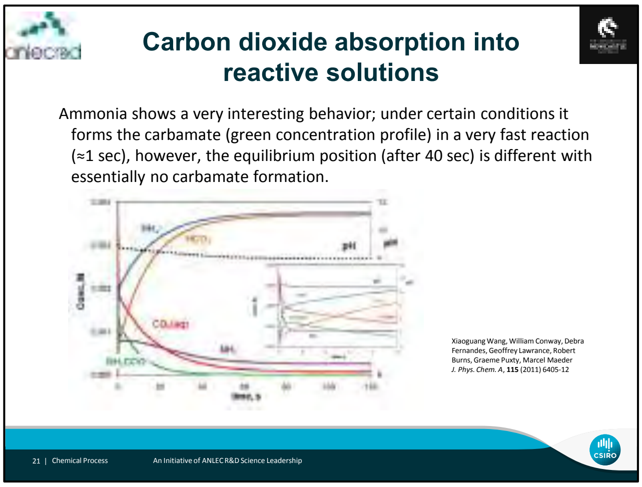
Summary advantages and disadvantages of carbamate formation

As carbamate formation has two opposite effects, it is not easy to assess the overall advantage for the PCC process. Faster reactions results in reduced size of the absorber, the unfavourable 1:2 ratio results in reduced CO_2 uptake per volume of amine solution.

Carful modelling of all facets of the process is crucial, this includes very different aspects such as capital investment in the construction of the plant, running costs in terms of consumables (most amines tend to decompose) and very importantly in terms of energy consumption which includes a variety of components such as the pumping of solutions and the heating of the CO_2 rich amine solution in the stripper.

Reactive amines that form carbamates



Carbon dioxide absorption into reactive solutions

Ammonia shows a very interesting behavior; under certain conditions it forms the carbamate (green concentration profile) in a very fast reaction (≈1 sec), however, the equilibrium position (after 40 sec) is different with essentially no carbamate formation.

Xiaoguang Wang, William Conway, Debra Fernandes, Geoffrey Lawrance, Robert Burns, Graeme Puxty, Marcel Maeder
J. Phys. Chem. A, **115** (2011) 6405-12

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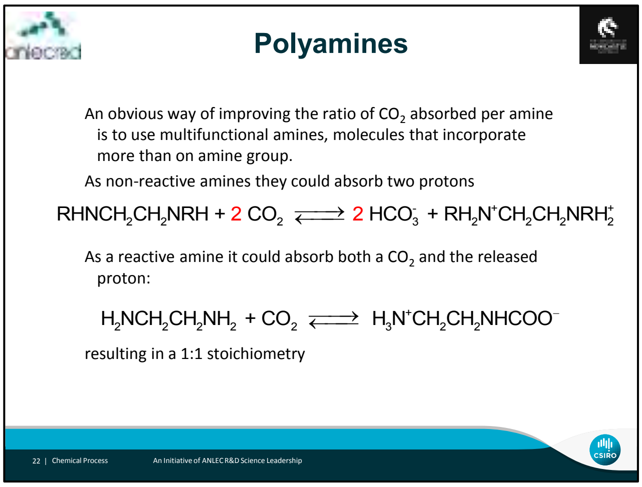
Ammonia forms a transient carbamate

Ammonia is featuring a surprising behaviour with respect to carbamate formation.

As we have seen carbamate formation is advantageous from the kinetic point of view but disadvantageous because of the unfavourable 1:2 ratio. Under certain conditions ammonia reacts to form carbamate without the disadvantage. Consider the concentration profiles in the slide, they represent the concentration changes during the reaction of 3.8 mM CO_2 in 4.0 mM ammonia: within about 1 sec some 40% of the total CO_2 reacts to form the carbamate. This reaction results in a pH-drop from about 10 to 9. Under such conditions the carbamate is less stable and slowly decomposes almost completely within 1 min.

While the conditions for the above calculations are not relevant for PCC, this example demonstrates that carful modelling of complex reactions can result in the detection and identification of interesting behaviours.



Polyamines

An obvious way of improving the ratio of CO_2 absorbed per amine is to use multifunctional amines, molecules that incorporate more than on amine group.

As non-reactive amines they could absorb two protons

$$RHNCH_2CH_2NRH + 2\ CO_2 \rightleftarrows 2\ HCO_3^- + RH_2N^+CH_2CH_2NRH_2^+$$

As a reactive amine it could absorb both a CO_2 and the released proton:

$$H_2NCH_2CH_2NH_2 + CO_2 \rightleftarrows H_3N^+CH_2CH_2NHCOO^-$$

resulting in a 1:1 stoichiometry

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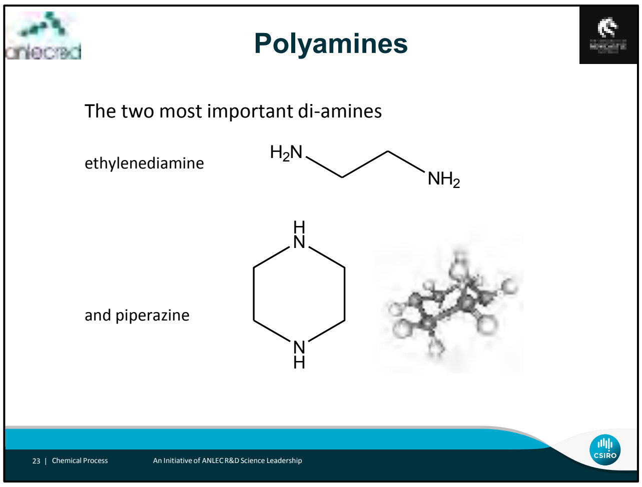
Di-amines to improve the CO_2:amine ratio

Under relevant conditions two amines are required to absorb one molecule of CO_2. One amine to form the carbamate the other to absorb a proton that is released in the carbamate formation.

An obvious way dealing with that problem is to use di-amines, compounds that contain two amine groups. One amine group is forming the carbamate while the other is absorbing the proton; this results in a desirable 1:1 stoichiometry.

On paper this looks great, however there are many additional aspects that need to be taken into account: solubility, stability, price, etc. No doubt more diamines are promising and their investigation is being pursued in many laboratories.

Reactive amines that form carbamates



Polyamines

The two most important di-amines

ethylenediamine

and piperazine

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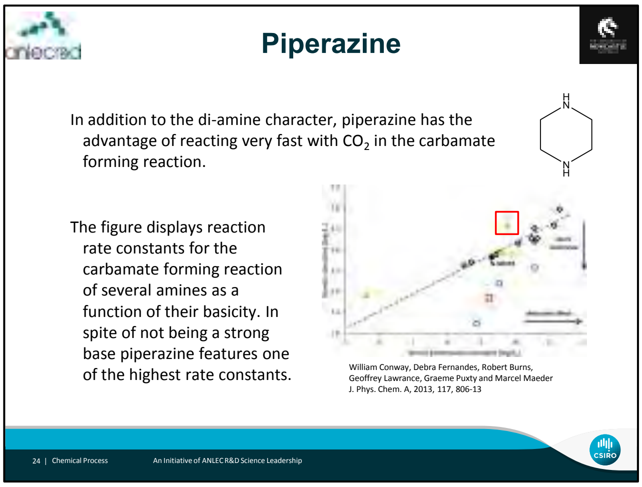
Ethylene-diamine and piperazine

The most prominent diamines are ethylene-diamine and piperazine. Ethylene-diamine is a relative of MEA, a linear molecule with primary amine groups at both ends.

A very well investigated molecule is piperazine. It is a six-membered ring with two secondary amines in trans position. The carbamate forming reaction is very fast and thus the molecule is promising. Detailed investigation of the complete reaction mechanism is much more difficult as the di-carbamate also forms. The existence of several protonation equilibria at the carbamate groups make life even more difficult.

There is little doubt that piperazine will be tested much more.

Reactive amines that form carbamates



Piperazine

In addition to the di-amine character, piperazine has the advantage of reacting very fast with CO_2 in the carbamate forming reaction.

The figure displays reaction rate constants for the carbamate forming reaction of several amines as a function of their basicity. In spite of not being a strong base piperazine features one of the highest rate constants.

William Conway, Debra Fernandes, Robert Burns, Geoffrey Lawrance, Graeme Puxty and Marcel Maeder
J. Phys. Chem. A, 2013, 117, 806-13

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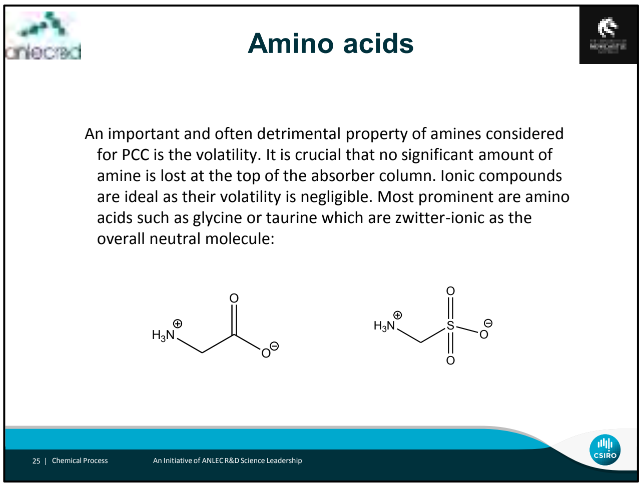
Piperazine

Piperazine is an interesting diamine for several reasons; most prominent is its surprisingly fast reaction with CO_2 to form the carbamate.

The graph in the powerpoint slide is a plot that attempts at relating the rate constant for carbamate formation to the basicity of several amines. For most investigated amines there is a rather straightforward linear relationship indicated by the dotted line. Several amines are under the line and most of these observations can be understood as steric effects, the CO_2 molecule is much larger than the proton and thus needs more free space around the amine nitrogen, if it is not available the rate is slower.

Piperazine is above the line and thus reacts faster than expected. Presently no reason can be given for this interesting observation.

Reactive amines that form carbamates



Amino acids

An important and often detrimental property of amines considered for PCC is the volatility. It is crucial that no significant amount of amine is lost at the top of the absorber column. Ionic compounds are ideal as their volatility is negligible. Most prominent are amino acids such as glycine or taurine which are zwitter-ionic as the overall neutral molecule:

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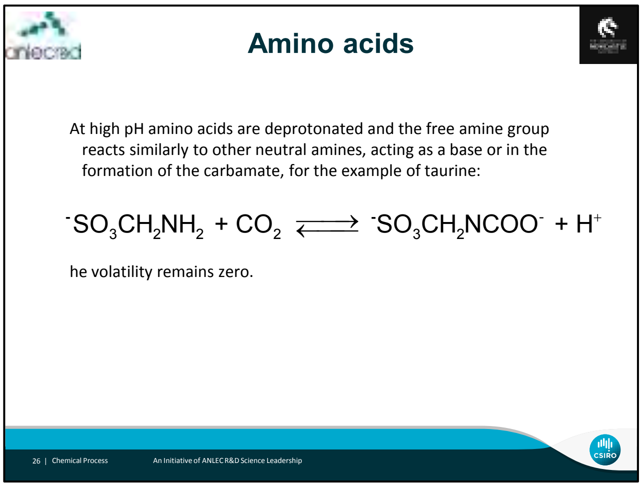
Non-volatile amino acids

A major problem with most amines is their volatility. The stripper operates at elevated temperatures (around 120-140°C) and at these temperatures most amines have a substantial vapour pressure, they will evaporate and need to be separated from the CO_2. Ammonia, of course, is the worst of them all.

Amino-acids feature the distinctive property of being charged at all pH values: at high pH the amine and the carboxylate are deprotonated and thus the charge is -1; at low pH both groups are protonated and the charge is +1. At intermediate pH values the proton is attached to the amine and not the carboxylate group and thus the molecule is a zwitter ion. While overall it is neutral, the zwitter-ion character results in a very low volatility.

As expected several research groups investigate amino acids for their PCC potential.

Reactive amines that form carbamates



Amino acids

At high pH amino acids are deprotonated and the free amine group reacts similarly to other neutral amines, acting as a base or in the formation of the carbamate, for the example of taurine:

$$^{-}SO_3CH_2NH_2 + CO_2 \rightleftarrows {}^{-}SO_3CH_2NCOO^{-} + H^{+}$$

he volatility remains zero.

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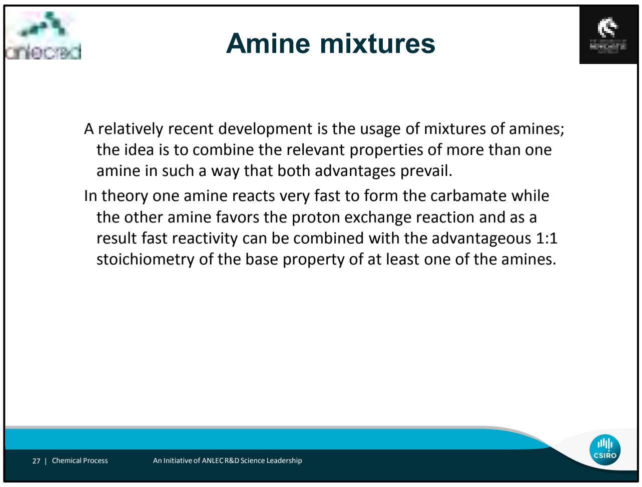
Taurine

Taurine is an unusual amino acid as the acid group is a sulfonic rather than a carboxylic acid; but taurine is still a naturally occurring amino acid with similar properties as the usual ones, in particular the property of being charged at any pH and thus being non-volatile. One interesting property is its relatively low second protonation constant of about 9.



Amine mixtures

A relatively recent development is the usage of mixtures of amines; the idea is to combine the relevant properties of more than one amine in such a way that both advantages prevail.

In theory one amine reacts very fast to form the carbamate while the other amine favors the proton exchange reaction and as a result fast reactivity can be combined with the advantageous 1:1 stoichiometry of the base property of at least one of the amines.

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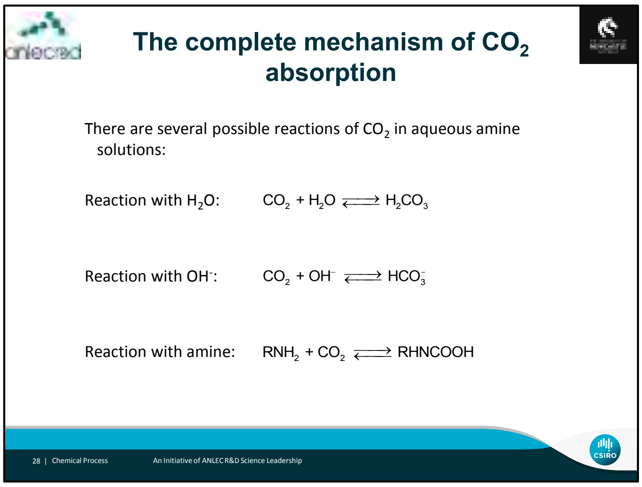
Mixtures of amines

The perfect amine encompasses so many properties that it is unlikely that it amine actually exists. An obvious option towards that goal is to combine different properties in on molecule which will have different substituents, each one with a preferable property; the diamines discussed earlier are just one example. The resulting molecule will be large, expensive and most likely not sufficiently soluble.

Probably a more promising and realistic approach is the employ a mixture of different molecules in the absorbing solutions, each one with a particularly useful property. An approach that is pursued by many research groups. Presently the best investigated idea is the combine a non-reactive amine that absorbs in a 1:1 ratio, with a fast, reactive amine such as piperazine.

As there is an infinity of such mixtures and mixture ratios it will not be possible to investigate their properties experimentally, either in the laboratory or the pilot plant. Well founded computational approaches are clearly preferable.

Reactive amines that form carbamates



The complete mechanism of CO_2 absorption

There are several possible reactions of CO_2 in aqueous amine solutions:

Reaction with H_2O: $CO_2 + H_2O \rightleftarrows H_2CO_3$

Reaction with OH^-: $CO_2 + OH^- \rightleftarrows HCO_3^-$

Reaction with amine: $RNH_2 + CO_2 \rightleftarrows RHNCOOH$

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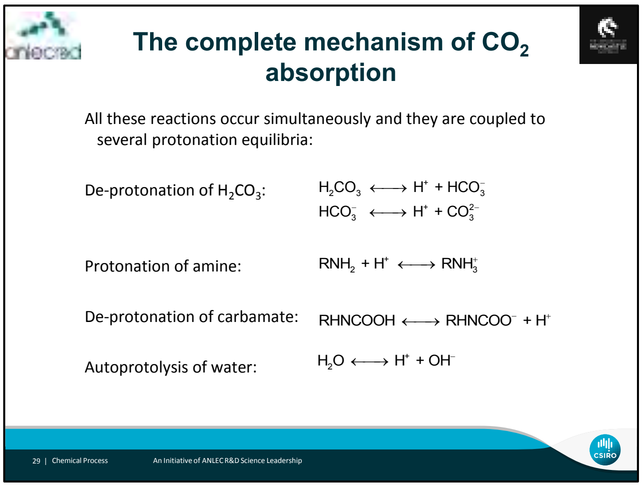
Amines that form carbamates

Most amines form the respective carbamate. As we have seen this reaction has positive and negative effects on the relevant properties of PCC.

One clear effect is that the additional reactions will add to the complexity of the chemistry of the process of CO_2 uptake in PCC. CO_2 has now three different reaction partners, all three reactions resulting in the uptake of dissolved CO_2. All three processes will occur parallel and it is the relative concentrations of the reaction partners that define the overall rate: the concentration of water is approximately constant and thus this path is fixed (pseudo-first order reaction); the hydroxy path is of course strongly pH dependent and the carbamate formation is dependent on the amine concentration. In addition the amine concentration will also influence the pH and thus the actual quantitative understanding requires substantial and detailed knowledge of all reactions involved.

Reactive amines that form carbamates



The complete mechanism of CO_2 absorption

All these reactions occur simultaneously and they are coupled to several protonation equilibria:

De-protonation of H_2CO_3: $H_2CO_3 \longleftrightarrow H^+ + HCO_3^-$

$HCO_3^- \longleftrightarrow H^+ + CO_3^{2-}$

Protonation of amine: $RNH_2 + H^+ \longleftrightarrow RNH_3^+$

De-protonation of carbamate: $RHNCOOH \longleftrightarrow RHNCOO^- + H^+$

Autoprotolysis of water: $H_2O \longleftrightarrow H^+ + OH^-$

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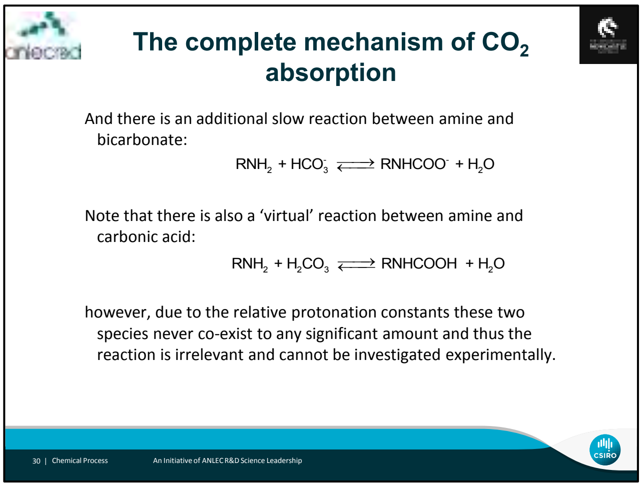
Carbamate formation and pH

There are several protonation equilibria that all play and change during the reaction of CO_2 in amine solutions.

The protonation equilibria of carbonate and bicarbonate, of the amine and the autoprotolysis of water are always active, also with non-carbamate forming amines. The carbamate adds another protonation equilibrium. The initial product of the reaction of CO_2 with the amine is the carbamic acid, however, under PCC conditions the acid is immediately deprotonated. The pK_a values of most known carbamates are between 7 and 8, substantially lower than the pH of a typical PCC solution, thus the carbamic acid exists only in very small concentrations.



The complete mechanism of CO_2 absorption

And there is an additional slow reaction between amine and bicarbonate:

$$RNH_2 + HCO_3^- \rightleftarrows RNHCOO^- + H_2O$$

Note that there is also a ‘virtual’ reaction between amine and carbonic acid:

$$RNH_2 + H_2CO_3 \rightleftarrows RNHCOOH + H_2O$$

however, due to the relative protonation constants these two species never co-exist to any significant amount and thus the reaction is irrelevant and cannot be investigated experimentally.

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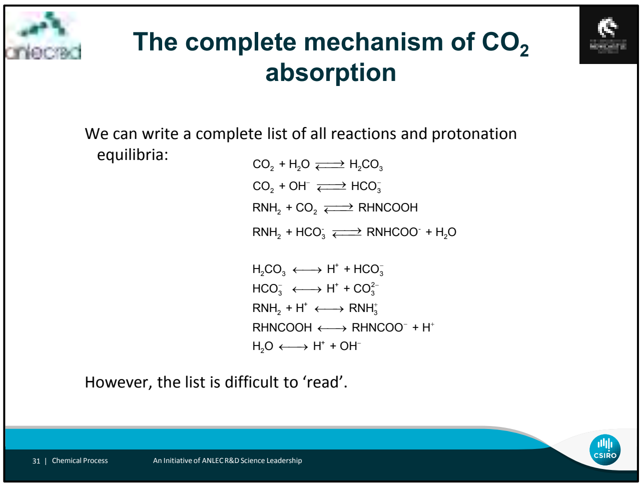
Carbamate formation with bicarbonate

Carbamate formation relevant for PCC is via the path just described, CO_2 reacting reversibly with the amine to form initially carbamic acid which is immediately deprotonated.

Amines react also reversibly with the bicarbonate ion, HCO_3^-, in a much slower reaction to form the carbamate directly.

While this reaction is not relevant for carbamate formation it is important for its decomposition. If the only path for carbamate decomposition is via the carbamic acid, the carbamate would be increasingly more stable at increasing pH, essentially without a limit. The bicarbonate path provides the direct decomposition of the carbamate. The rate for that reaction is much slower than for the carbamic acid.

Reactive amines that form carbamates



The complete mechanism of CO_2 absorption

We can write a complete list of all reactions and protonation equilibria:

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$
$$CO_2 + OH^- \rightleftarrows HCO_3^-$$
$$RNH_2 + CO_2 \rightleftarrows RHNCOOH$$
$$RNH_2 + HCO_3^- \rightleftarrows RNHCOO^- + H_2O$$

$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^-$$
$$HCO_3^- \longleftrightarrow H^+ + CO_3^{2-}$$
$$RNH_2 + H^+ \longleftrightarrow RNH_3^+$$
$$RHNCOOH \longleftrightarrow RHNCOO^- + H^+$$
$$H_2O \longleftrightarrow H^+ + OH^-$$

However, the list is difficult to ‘read’.

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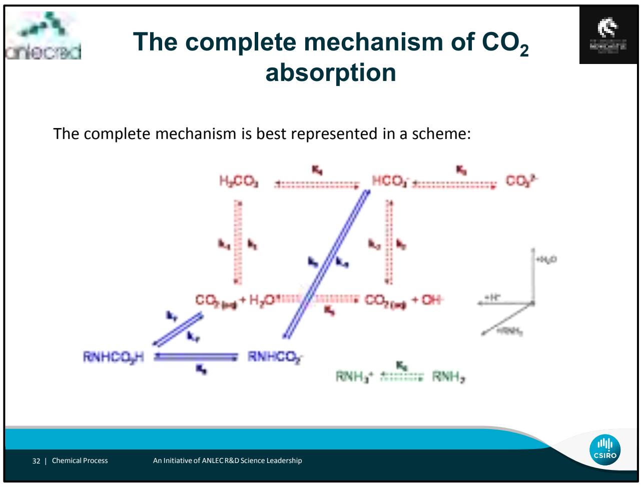
The complete reaction scheme for reactive amines

It is straightforward to collect all the individual reactions that can occur in aqueous amine solutions in the presence of dissolved CO_2.

There are four reversible reactions and five instantaneous protonation equilibria. The protonation equilibria are quantitatively described by five equilibrium constants; four of them are known the amine protonation constant if unknown can be determined easily, the only unknown equilibrium constant it the carbamate protonation constant. Two of the reversible reactions are also known, the remaining two reversible carbamate formation reactions need to be determined for each amine. Altogether after the determination of the four rate constants plus the one protonation constant, any amine is completely defined. This of course only at the particular temperature, if all temperature dependences are known, everything is known and the reactions can be completely modelled under all conditions, at least as long as activity coefficients are be estimated to a reasonable level.

Reactive amines that form carbamates



The complete mechanism of CO_2 absorption

The complete mechanism is best represented in a scheme:

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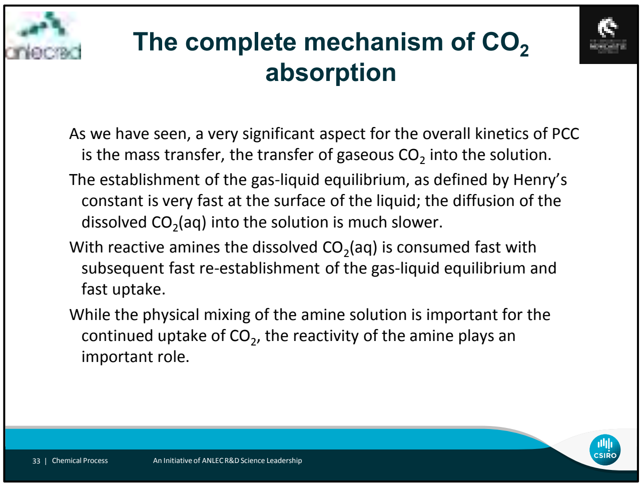
The complete reaction mechanism, graphically

It is possible to represent the complete reaction mechanism graphically. This is attempted in the slide above:

- In red we have the interactions of CO_2 in aqueous solution in the absence of amines
- In green the protonation equilibrium of the amine
- In blue the reactions relevant for carbamate formation and dissociation
- The pH is indicated in the right-left direction with high pH to the right
- The reactions with water/hydroxide are indicated in the up-down direction
- In the forward/backward direction we have the reactions of the CO_3/carbonate group with the amine



The complete mechanism of CO_2 absorption

As we have seen, a very significant aspect for the overall kinetics of PCC is the mass transfer, the transfer of gaseous CO_2 into the solution.

The establishment of the gas-liquid equilibrium, as defined by Henry's constant is very fast at the surface of the liquid; the diffusion of the dissolved $CO_2(aq)$ into the solution is much slower.

With reactive amines the dissolved $CO_2(aq)$ is consumed fast with subsequent fast re-establishment of the gas-liquid equilibrium and fast uptake.

While the physical mixing of the amine solution is important for the continued uptake of CO_2, the reactivity of the amine plays an important role.

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Inclusion of mass transfer

The reactions of CO2 in aqueous amine solution are complex but manageable. It is important not to forget that the first step in the process is the transfer of the gaseous CO_2 into the amine solution. This mass transfer only occurs at the surface of the liquid and is largely independent of the liquid phase. However, as soon as the CO_2 is dissolved it will start the diffusion into the liquid phase and on the way it will undergo all the reactions that are available. This complete process is supported by the constant physical mixing of the solution as it travels down the absorber column. Of course the reverse is happening in the stripper column where a certain amount of the absorbed CO_2 is released back into the gas phase.

The computation of the chemical processes coupled to diffusion and physical mixing is exceedingly complex and has been tackled only recently

The chemical process

- Carbon dioxide absorption into water
- Carbon dioxide absorption into unreactive bases (tertiary amines, other bases)
- Carbon dioxide absorption into reactive solutions (primary and secondary amines)
- The complete mechanism of carbon dioxide absorption into an aqueous amine solution
- Amino acids – their special properties (ionised)
- Amine mixtures
- Combining diffusion and chemical reaction – enhanced mass transfer

Carbon dioxide absorption into water: CO_2 solubility (Henry constant)

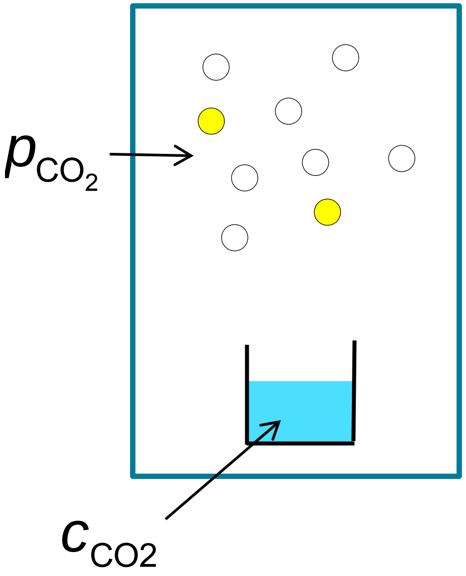
- The first step of PCC is the transfer of CO_2 from the gas phase into the aqueous solution.
- There are two important aspects:
  - kinetics
    - difficult to quantify
    - strongly depends on column design and packing
  - equilibrium
    - Henry's law

Henry's Law

"At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid."

$$p_{CO_2} = k_{h,\mathrm{CO2}} \times c_{\mathrm{CO2}}$$

- c_{CO2} concentration, molar, (other concentrations can be used, e.g. molal, mole fraction)
- $k_{h,\mathrm{CO2}}$ Henry's constant
- p_{CO2} partial pressure of CO_2 in atmosphere



Henry's Law

It is important to use the correct version/units for the equation !

A few examples:

$$k_{h,pc} = \frac{p}{c} = 29.14\ \frac{\text{L atm}}{\text{mol}}$$

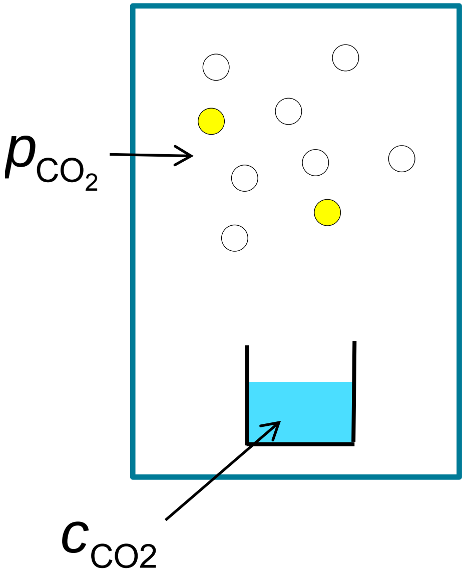
$$k_{h,px} = \frac{p}{x} = 0.163 \times 10^{4}\ \text{atm}$$

$$k_{h,cc} = \frac{c_{aq}}{c_{gas}} = 0.8317$$

p = partial pressure, in atm

c = concentration, in mol/L

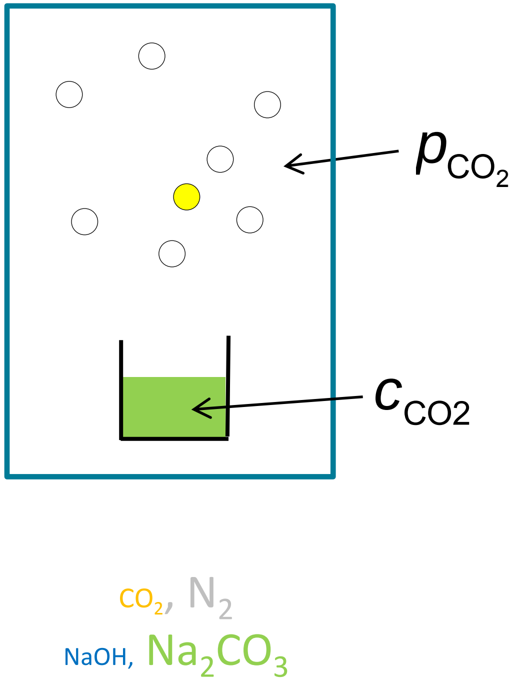
x = mole fraction, dimensionless



Henry's Law

Henry's constant is unaffected by any process that involves the CO_2 in the aqueous solution; e.g. in amine solutions most of the CO_2 is transformed into bicarbonate and carbamate, the free $c_{CO2,aq}$ is very small and thus the partial pressure p_{CO2} at equilibrium is also very small, the ratio is constant it is $k_{h,CO2}$

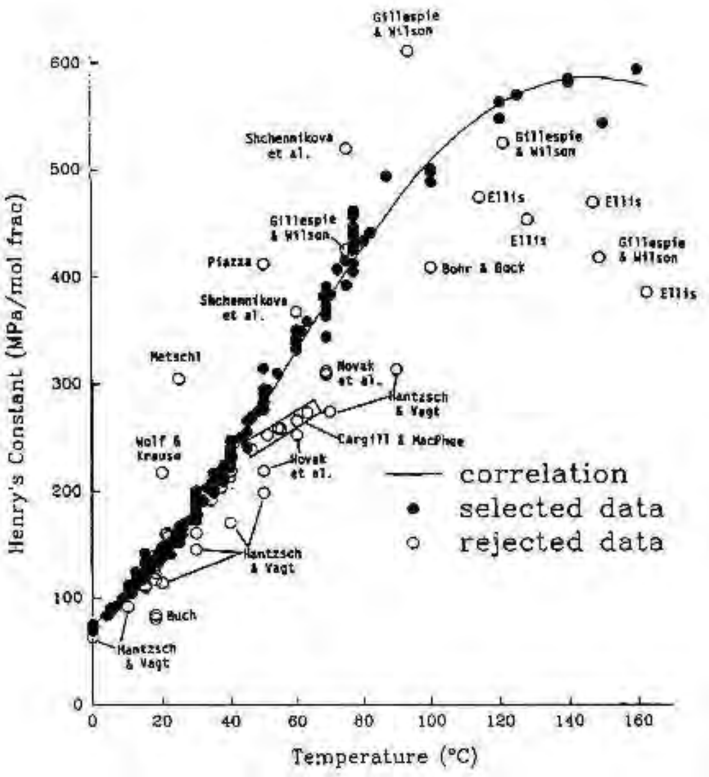
Even over a solution of NaOH, at equilibrium there are small amounts of CO_2 in the solution and in the gas phase.



Henry's Law

Henry's constant is temperature dependent, its value decreases with increasing temperature. This helps to release the CO_2 in the stripper column.

The law is only strictly valid for ideal solutions, e.g. deviations for highly concentrated amine solutions can be significant.



John J. Carroll and Alan E. Mather
Journal of SolutionChemistry,
21, (1992) 607-621

Carbon dioxide absorption into water

Once CO_2 is dissolved in water, several reactions occur simultaneously:

- ○ Reaction of CO_2 with water and $CO_2 + H_2O \rightleftharpoons H_2CO_3$
- ○ Reaction with hydroxide $CO_2 + OH^- \rightleftharpoons HCO_3^-$
- ○ and subsequent protonation equilibria and autoprotolysis of water

$$H^+ + HCO_3^- \longleftrightarrow H_2CO_3$$

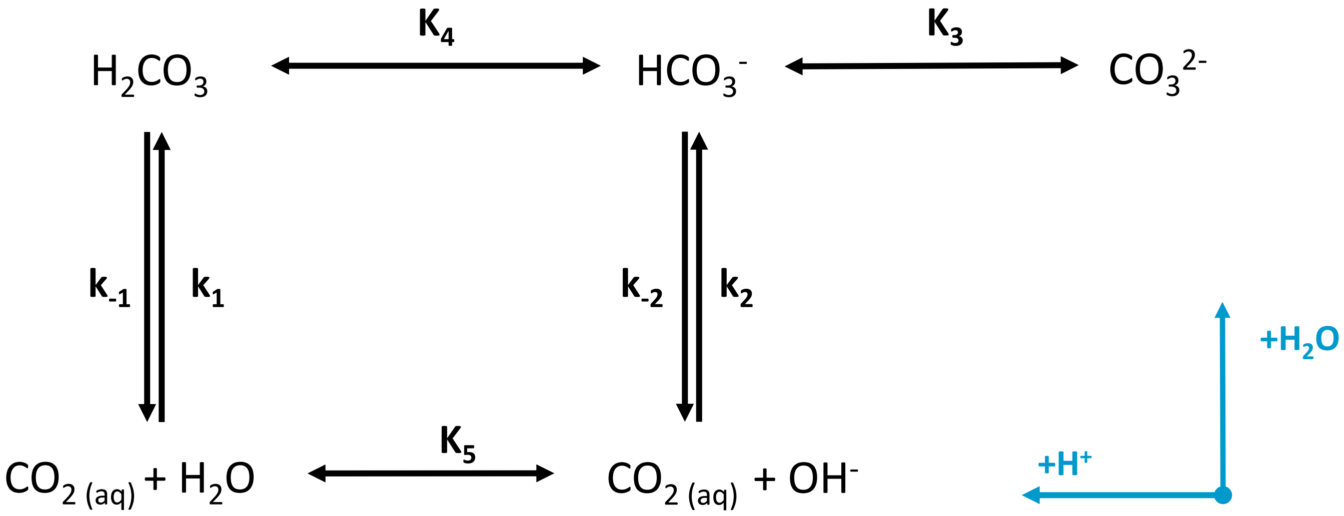
$$H^+ + CO_3^{2-} \longleftrightarrow HCO_3^-$$

$$H^+ + OH^- \longleftrightarrow H_2O$$

Note, we use $\rightleftharpoons$ for slow reversible reactions and $\longleftrightarrow$ for fast (instantaneous) equilibria.

Reactions of carbon dioxide absorption in water

It is instructive to graphically represent the reaction scheme for the reactions of CO_2 in aqueous solution:



H_2CO_3 $\xleftrightarrow{K_4}$ HCO_3^- $\xleftrightarrow{K_3}$ CO_3^{2-}

k_{-1} k_1

k_{-2} k_2

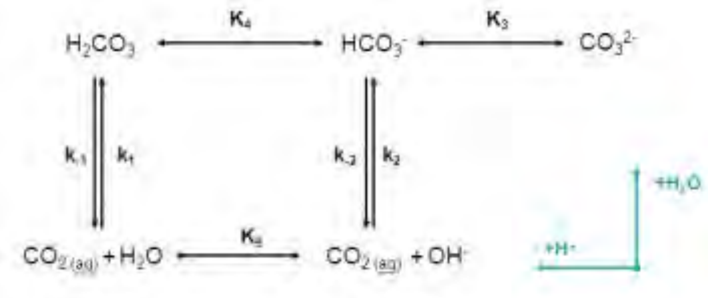
$CO_{2\,(aq)} + H_2O$ $\xleftrightarrow{K_5}$ $CO_{2\,(aq)} + OH^-$

$+H_2O$

$+H^+$

Reactions of carbon dioxide absorption in water

The values for all rate and equilibrium constants are fundamental for any PCC process:



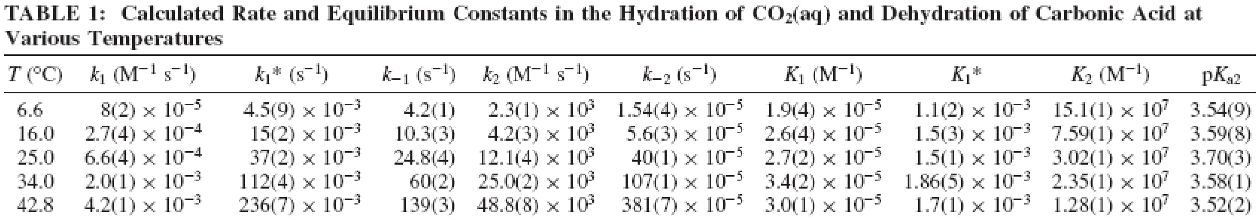


TABLE 1: Calculated Rate and Equilibrium Constants in the Hydration of CO_2(aq) and Dehydration of Carbonic Acid at Various Temperatures

T (°C)	k_1 ($M^{-1}\ s^{-1}$)	k_1^* (s^{-1})	k_{-1} (s^{-1})	k_2 ($M^{-1}\ s^{-1}$)	k_{-2} (s^{-1})	K_1 (M^{-1})	K_1^*	K_2 (M^{-1})	pK_{a2}
6.6	$8(2) \times 10^{-5}$	$4.5(9) \times 10^{-3}$	4.2(1)	$2.3(1) \times 10^3$	$1.54(4) \times 10^{-5}$	$1.9(4) \times 10^{-5}$	$1.1(2) \times 10^{-3}$	$15.1(1) \times 10^7$	3.54(9)
16.0	$2.7(4) \times 10^{-4}$	$15(2) \times 10^{-3}$	10.3(3)	$4.2(3) \times 10^3$	$5.6(3) \times 10^{-5}$	$2.6(4) \times 10^{-5}$	$1.5(3) \times 10^{-3}$	$7.59(1) \times 10^7$	3.59(8)
25.0	$6.6(4) \times 10^{-4}$	$37(2) \times 10^{-3}$	24.8(4)	$12.1(4) \times 10^3$	$40(1) \times 10^{-5}$	$2.7(2) \times 10^{-5}$	$1.5(1) \times 10^{-3}$	$3.02(1) \times 10^7$	3.70(3)
34.0	$2.0(1) \times 10^{-3}$	$112(4) \times 10^{-3}$	60(2)	$25.0(2) \times 10^3$	$107(1) \times 10^{-5}$	$3.4(2) \times 10^{-5}$	$1.86(5) \times 10^{-3}$	$2.35(1) \times 10^7$	3.58(1)
42.8	$4.2(1) \times 10^{-3}$	$236(7) \times 10^{-3}$	139(3)	$48.8(8) \times 10^3$	$381(7) \times 10^{-5}$	$3.0(1) \times 10^{-5}$	$1.7(1) \times 10^{-3}$	$1.28(1) \times 10^7$	3.52(2)

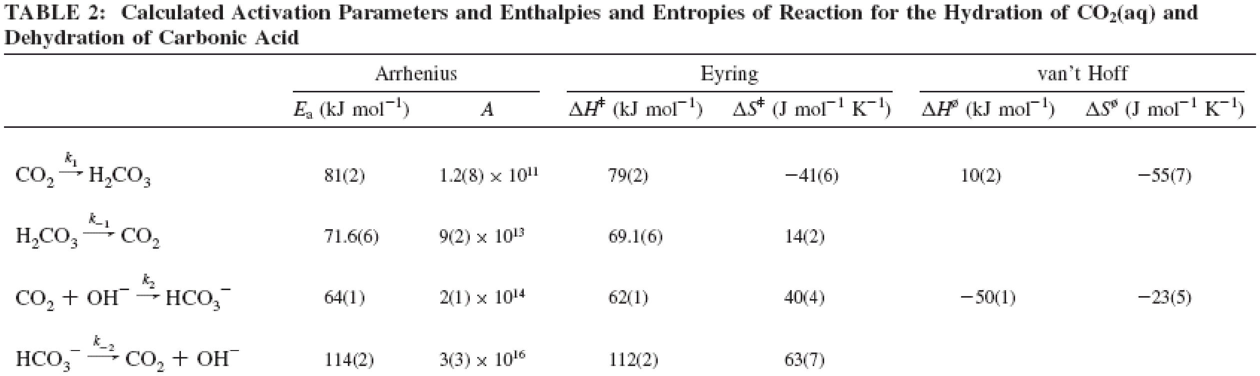


TABLE 2: Calculated Activation Parameters and Enthalpies and Entropies of Reaction for the Hydration of CO_2(aq) and Dehydration of Carbonic Acid

	Arrhenius		Eyring		van't Hoff	
	E_a (kJ mol^{-1})	A	$\Delta H^‡$ (kJ mol^{-1})	$\Delta S^‡$ (J mol^{-1} K^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
$CO_2 \xrightarrow{k_1} H_2CO_3$	81(2)	$1.2(8) \times 10^{11}$	79(2)	−41(6)	10(2)	−55(7)
$H_2CO_3 \xrightarrow{k_{-1}} CO_2$	71.6(6)	$9(2) \times 10^{13}$	69.1(6)	14(2)		
$CO_2 + OH^- \xrightarrow{k_2} HCO_3^-$	64(1)	$2(1) \times 10^{14}$	62(1)	40(4)	−50(1)	−23(5)
$HCO_3^- \xrightarrow{k_{-2}} CO_2 + OH^-$	114(2)	$3(3) \times 10^{16}$	112(2)	63(7)		

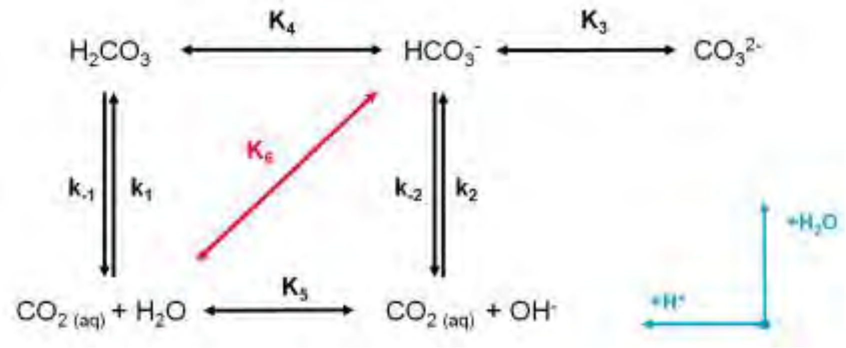
Xiaoguang Wang, William Conway, Robert Burns, Nichola McCann, and Marcel Maeder
J. *Phys. Chem. A* (2010) **114**, 1734–1740

Reactions of carbon dioxide absorption in water

Carbonic acid is always only a minor species and thus difficult to investigate. It is common to combine its formation and deprotonation to result in a well defined equilibrium

$$CO_2 + H_2O \underset{}{\overset{K_6}{\rightleftharpoons}} HCO_3^- + H^+$$

$$K_6 = \frac{k_1}{k_{-1} K_4}$$



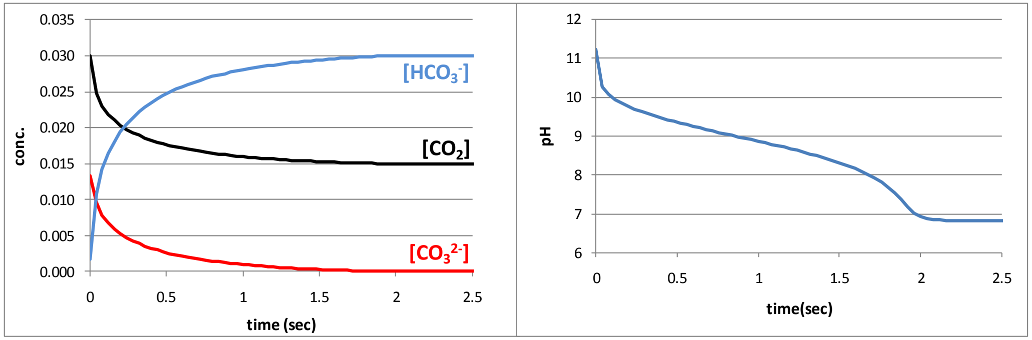
Reactions of carbon dioxide absorption in water

Knowing all relevant rate and equilibrium constants, it is possible to compute all concentrations as a function of time for a given set of initial conditions.

Coupling these calculations with mass transfer and other engineering aspects of the solutions in absorber and stripper columns allows a complete and accurate analysis and optimisation of the PCC process.

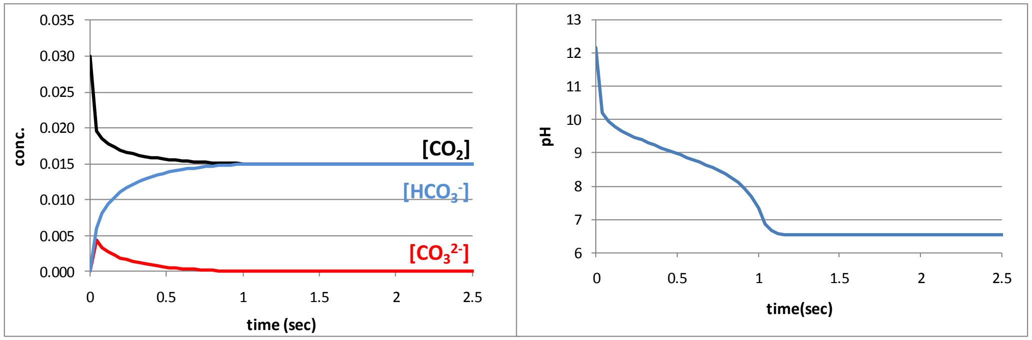
Reactions of carbon dioxide absorption in water

reaction of 30mM CO_2 /15mM CO_3^{2-}



CO_2 in a solution of CO_3^{2-} or OH^- reacts to bicarbonate HCO_3^-, accompanied by a pH drop.

reaction of 30mM CO_2 /15mM OH^-



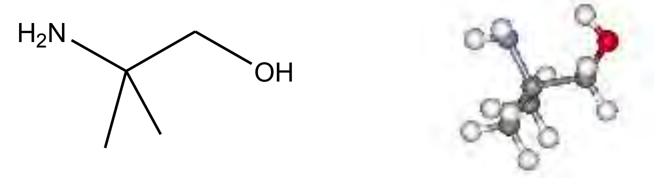
For the given concentrations the reaction with hydroxide is approximately twice as fast.

Carbon dioxide absorption into unreactive bases

Any other base that drives the absorption of CO_2 by deprotonation of the carbonic acid can be used. Typical examples are the tertiary and sterically hindered amines:

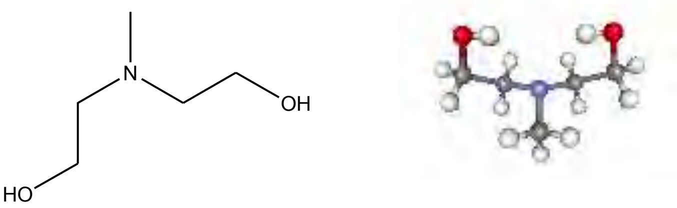
AMP

2-amino-2-methylpropanol



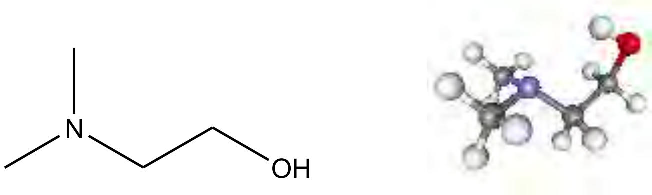
MDEA

methyldiethanolamine



DMEA

DimethylMEA



Carbon dioxide absorption into unreactive bases

The reaction mechanism for all these amines, A, is essentially identical, the only difference between them is the basicity:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$H_2CO_3 + A \rightleftharpoons HCO_3^- + AH^+$$

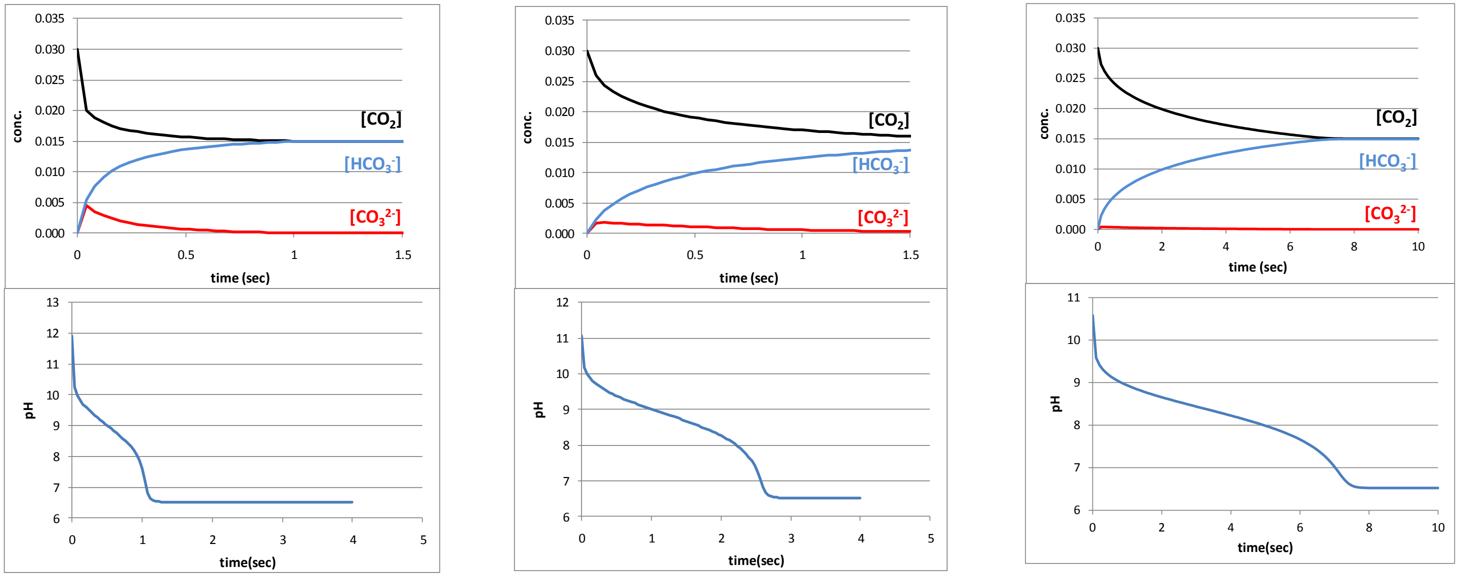
A crucial aspect of the above process is that 1 mole of amine is required for the absorption of one 1 mole of CO_2.

1:1 ratio !

The role of the base on pH and proton removal

Based on all known rate and equilibrium constants we can model the effect of the basicity of the amine on the kinetics of the reaction of CO_2

Amine: $pK_a = 12$ $pK_a = 10$ $pK_a = 9$



The higher the basicity the faster the reaction, this is the result of higher pH and thus higher [OH^-] which reacts faster than H_2O with CO_2.

Carbon dioxide absorption into reactive solutions

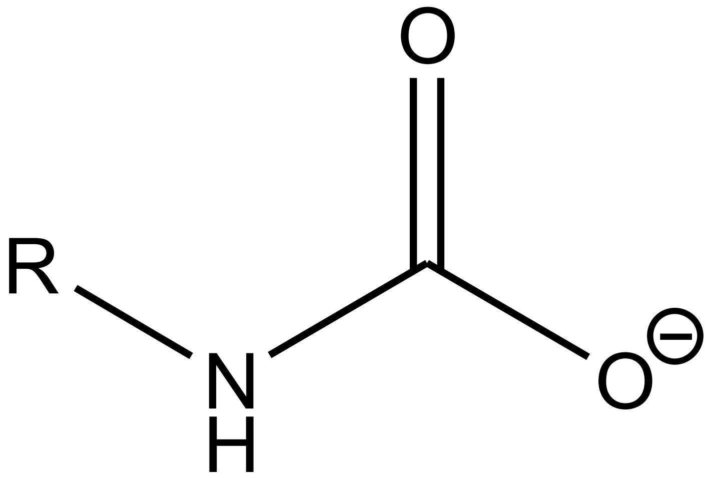
In addition to the reactions of CO_2 with water and hydroxide, CO_2 can also react with amines to form the so-called carbamic acids which immediately deprotonate to the carbamates:

$$RNH_2 + CO_2 \rightleftarrows RHNCOOH$$

$$RHNCOOH \longleftrightarrow RHNCOO^- + H^+$$

Carbon dioxide absorption into reactive solutions

Carbamic acids are the amides of carbonic acid; the structure of the corresponding carbamate is shown below



Carbon dioxide absorption into reactive solutions

The carbamate forming reaction of CO_2 has two significant consequences, a positive and a negative one:

(+) at relevant pH, the reaction of CO_2 with amines are often significantly faster than with water and hydroxide. Faster reactions results in shorter absorption time and thus smaller absorber columns

(-) the primary formation of the carbamic acid requires one amine, the release of its proton results in the protonation of a second amine; thus two amines are required for the absorption of one molecule of CO_2.

Carbon dioxide absorption into reactive solutions

(-) 1:2 ratio:

$$RNH_2 + CO_2 \rightleftarrows RHNCOOH$$

$$RHNCOOH \longleftrightarrow RHNCOO^- + H^+$$

$$RNH_2 + H^+ \longleftrightarrow RNH_3^+$$

$$2\,RNH_2 + CO_2 \rightleftarrows RHNCOO^- + RNH_3^+$$

Thus for a certain amount (moles) of amine only half the amount (moles) of CO_2 can be absorbed.

Carbon dioxide absorption into reactive solutions

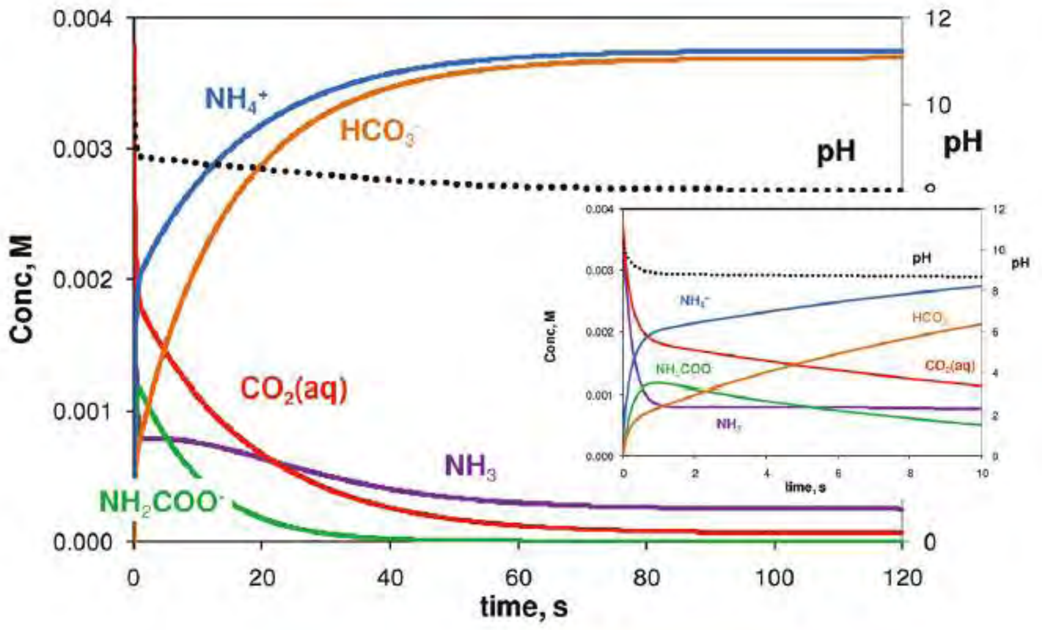
The carbamate forming reaction of CO_2 has two significant consequences, a positive and a negative one:

The quantitative analysis of the relative merit of the fast reaction and disadvantage of the 1:2 ratio is not easy, only careful modeling and experimentation can resolve that question.

This is particularly the case if the complete PCC process is to be optimised, taking into account capital investment, consumables and energy consumption.

Carbon dioxide absorption into reactive solutions

Ammonia shows a very interesting behavior; under certain conditions it forms the carbamate (green concentration profile) in a very fast reaction (≈1 sec), however, the equilibrium position (after 40 sec) is different with essentially no carbamate formation.



Xiaoguang Wang, William Conway, Debra Fernandes, Geoffrey Lawrance, Robert Burns, Graeme Puxty, Marcel Maeder
J. Phys. Chem. A, **115** (2011) 6405-12

Polyamines

An obvious way of improving the ratio of CO_2 absorbed per amine is to use multifunctional amines, molecules that incorporate more than on amine group.

As non-reactive amines they could absorb two protons

$$RHNCH_2CH_2NRH + 2\ CO_2 \rightleftarrows 2\ HCO_3^- + RH_2N^+CH_2CH_2NRH_2^+$$

As a reactive amine it could absorb both a CO_2 and the released proton:

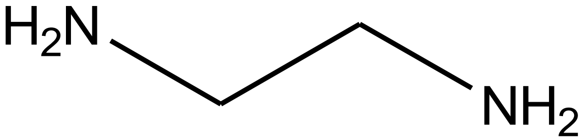
$$H_2NCH_2CH_2NH_2 + CO_2 \rightleftarrows H_3N^+CH_2CH_2NHCOO^-$$

resulting in a 1:1 stoichiometry

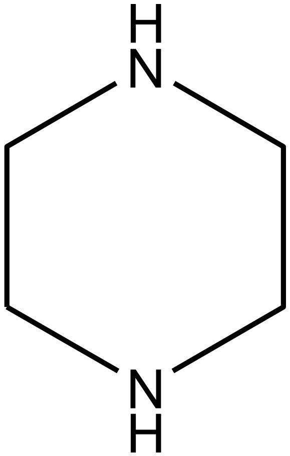
Polyamines

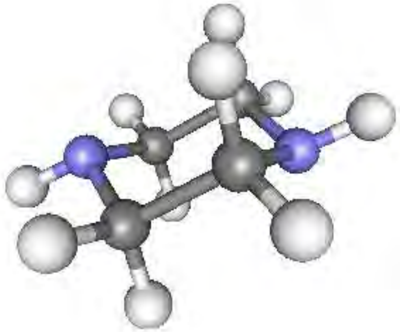
The two most important di-amines

ethylenediamine

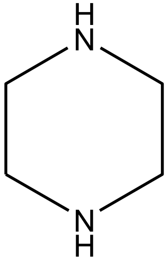


and piperazine



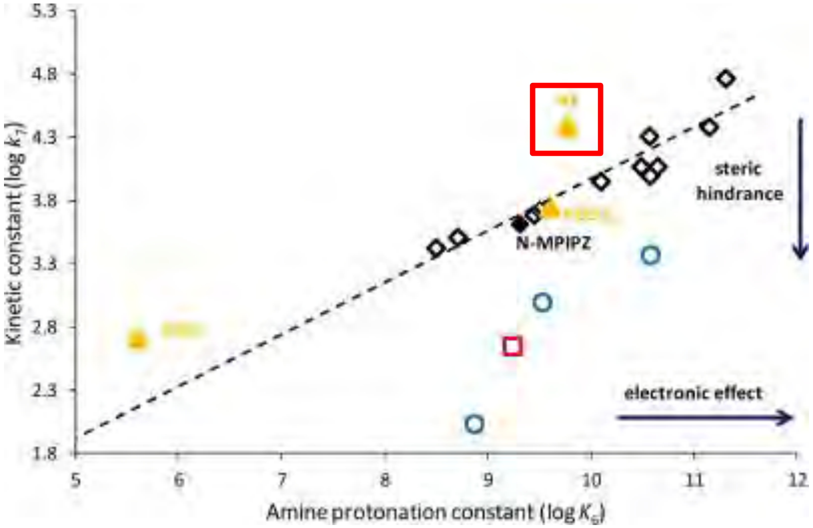


Piperazine



In addition to the di-amine character, piperazine has the advantage of reacting very fast with CO_2 in the carbamate forming reaction.

The figure displays reaction rate constants for the carbamate forming reaction of several amines as a function of their basicity. In spite of not being a strong base piperazine features one of the highest rate constants.



William Conway, Debra Fernandes, Robert Burns, Geoffrey Lawrance, Graeme Puxty and Marcel Maeder J. Phys. Chem. A, 2013, 117, 806-13

Amino acids

An important and often detrimental property of amines considered for PCC is the volatility. It is crucial that no significant amount of amine is lost at the top of the absorber column. Ionic compounds are ideal as their volatility is negligible. Most prominent are amino acids such as glycine or taurine which are zwitter-ionic as the overall neutral molecule:

Amino acids

At high pH amino acids are deprotonated and the free amine group reacts similarly to other neutral amines, acting as a base or in the formation of the carbamate, for the example of taurine:

$$^{-}SO_3CH_2NH_2 + CO_2 \rightleftarrows {}^{-}SO_3CH_2NCOO^{-} + H^{+}$$

The volatility remains zero.

Amine mixtures

A relatively recent development is the usage of mixtures of amines; the idea is to combine the relevant properties of more than one amine in such a way that both advantages prevail.

In theory one amine reacts very fast to form the carbamate while the other amine favors the proton exchange reaction and as a result fast reactivity can be combined with the advantageous 1:1 stoichiometry of the base property of at least one of the amines.

The complete mechanism of CO_2 absorption

There are several possible reactions of CO_2 in aqueous amine solutions:

Reaction with H_2O: $CO_2 + H_2O \rightleftarrows H_2CO_3$

Reaction with OH^-: $CO_2 + OH^- \rightleftarrows HCO_3^-$

Reaction with amine: $RNH_2 + CO_2 \rightleftarrows RHNCOOH$

The complete mechanism of CO_2 absorption

All these reactions occur simultaneously and they are coupled to several protonation equilibria:

De-protonation of H_2CO_3:

$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \longleftrightarrow H^+ + CO_3^{2-}$$

Protonation of amine:

$$RNH_2 + H^+ \longleftrightarrow RNH_3^+$$

De-protonation of carbamate:

$$RHNCOOH \longleftrightarrow RHNCOO^- + H^+$$

Autoprotolysis of water:

$$H_2O \longleftrightarrow H^+ + OH^-$$

The complete mechanism of CO_2 absorption

And there is an additional slow reaction between amine and bicarbonate:

$$RNH_2 + HCO_3^- \rightleftharpoons RNHCOO^- + H_2O$$

Note that there is also a ‘virtual’ reaction between amine and carbonic acid:

$$RNH_2 + H_2CO_3 \rightleftharpoons RNHCOOH + H_2O$$

however, due to the relative protonation constants these two species never co-exist to any significant amount and thus the reaction is irrelevant and cannot be investigated experimentally.

The complete mechanism of CO_2 absorption

We can write a complete list of all reactions and protonation equilibria:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^-$$

$$RNH_2 + CO_2 \rightleftharpoons RHNCOOH$$

$$RNH_2 + HCO_3^- \rightleftharpoons RNHCOO^- + H_2O$$

$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \longleftrightarrow H^+ + CO_3^{2-}$$

$$RNH_2 + H^+ \longleftrightarrow RNH_3^+$$

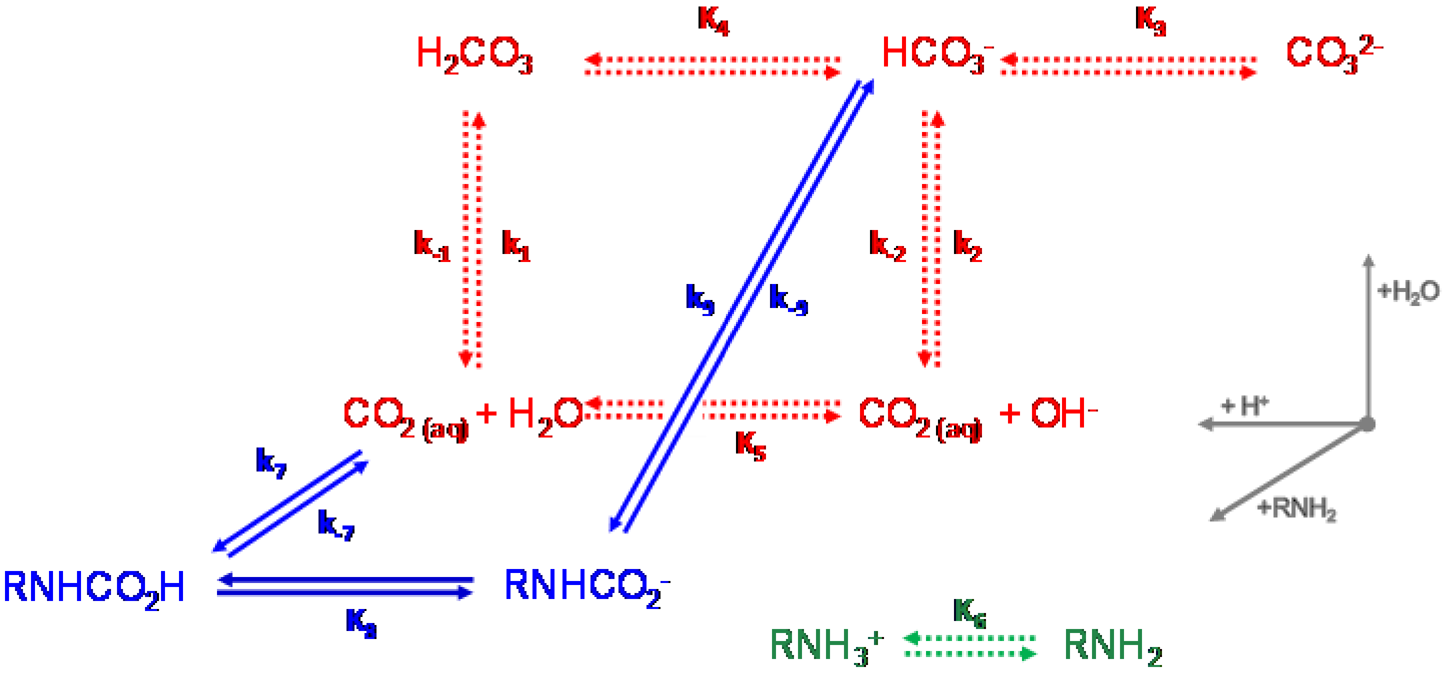
$$RHNCOOH \longleftrightarrow RHNCOO^- + H^+$$

$$H_2O \longleftrightarrow H^+ + OH^-$$

However, the list is difficult to ‘read’.

The complete mechanism of CO_2 absorption

The complete mechanism is best represented in a scheme:



The complete mechanism of CO_2 absorption

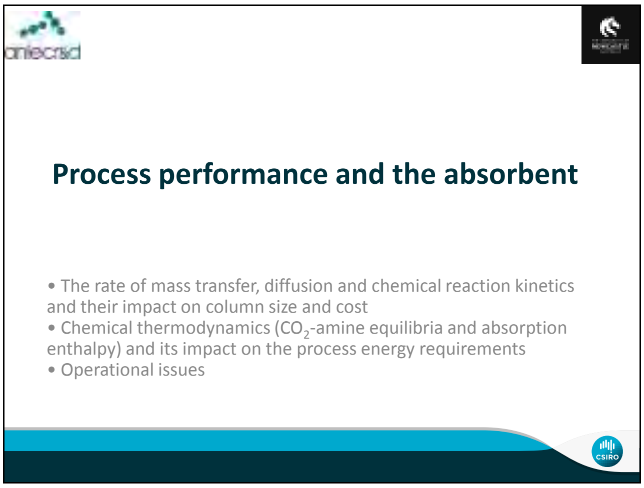
As we have seen, a very significant aspect for the overall kinetics of PCC is the mass transfer, the transfer of gaseous CO_2 into the solution.

The establishment of the gas-liquid equilibrium, as defined by Henry's constant is very fast at the surface of the liquid; the diffusion of the dissolved $CO_2(aq)$ into the solution is much slower.

With reactive amines the dissolved $CO_2(aq)$ is consumed fast with subsequent fast re-establishment of the gas-liquid equilibrium and fast uptake.

While the physical mixing of the amine solution is important for the continued uptake of CO_2, the reactivity of the amine plays an important role.

Process performance and the absorbent



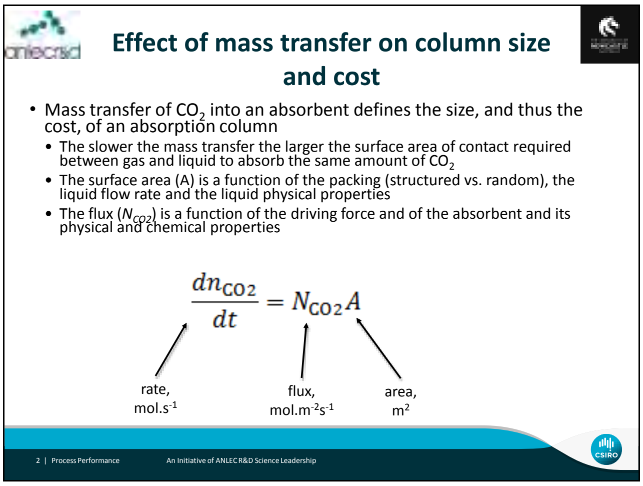
Process performance and the absorbent

- 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

2 | Process Performance

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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.

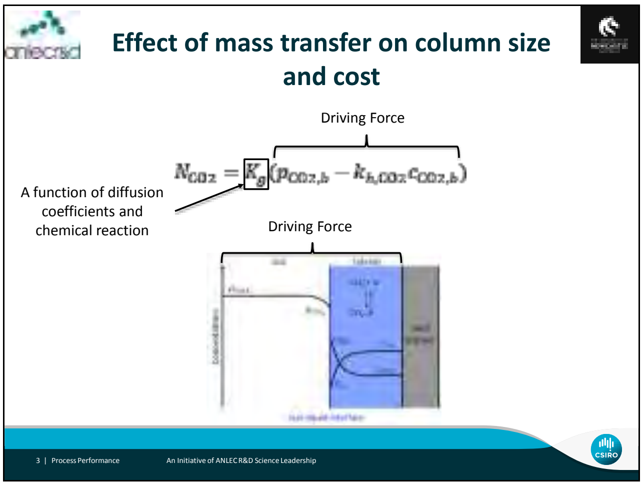
The rate at which CO_2 can be absorbed is governed by the mass transfer properties (the absorption flux, N_{CO2}) and the surface area of contact between the gas and liquid A.

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

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

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

A function of diffusion coefficients and chemical reaction

Driving Force

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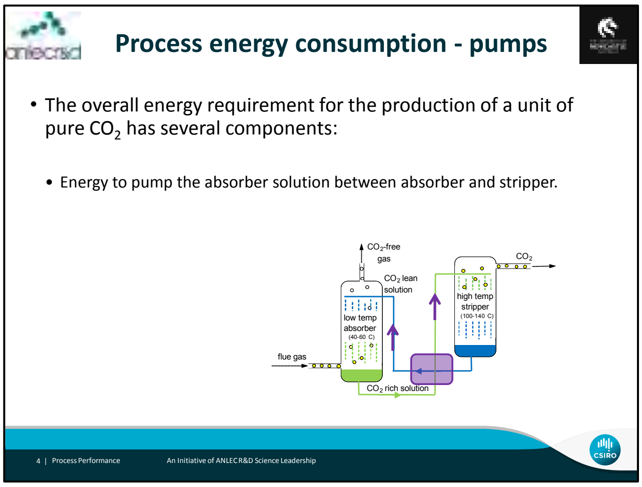
If the steady-state example is considered from section 5, the flux of CO_2 from the gas to the liquid, N_{CO2} (mol.m^2.s^{-1}), can be described by the equation below.

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

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 $k_{h,\mathrm{CO2}}$ which defines the solubility of CO_2.

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

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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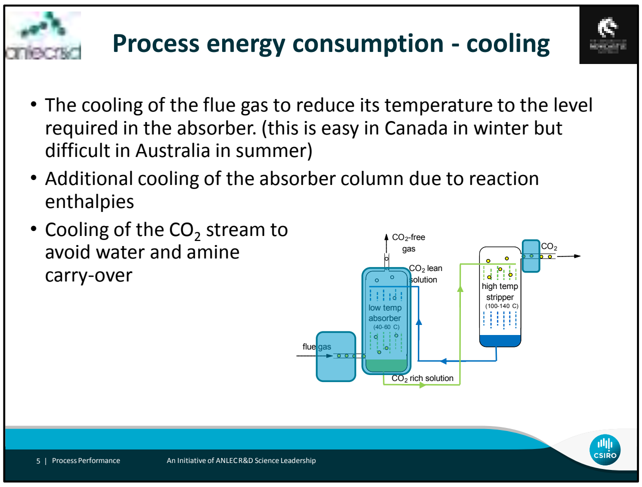
Pumping

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

5 | Process Performance

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Cooling

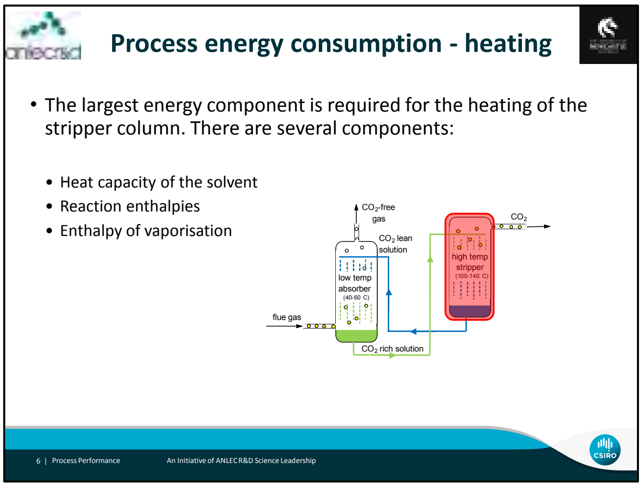
The flue gases coming from the powerstation are hot and need to be cooled before they are injected into the absorber column in order to react with the amine solution. In winter in the north of Canada this is much easier than on a hot summer day in Australia, and in Australia even water for such a purpose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

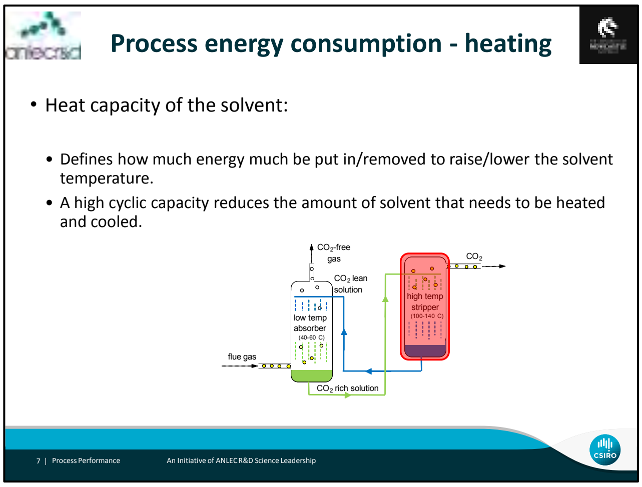
Heating

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

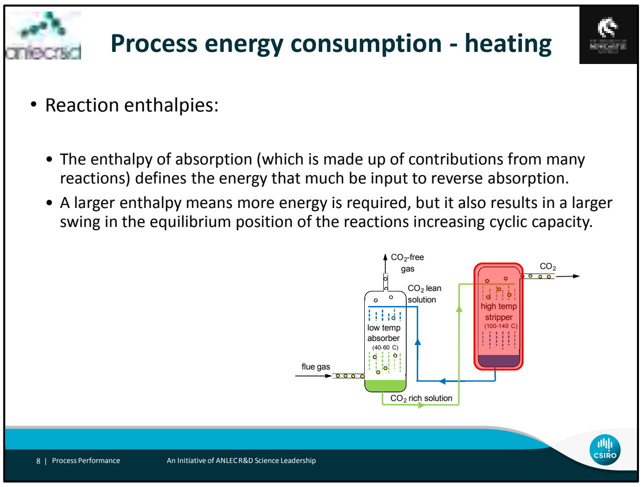
- Heat capacity of the solvent:
  - Defines how much energy much be put in/removed to raise/lower the solvent temperature.
  - A high cyclic capacity reduces the amount of solvent that needs to be heated and cooled.

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

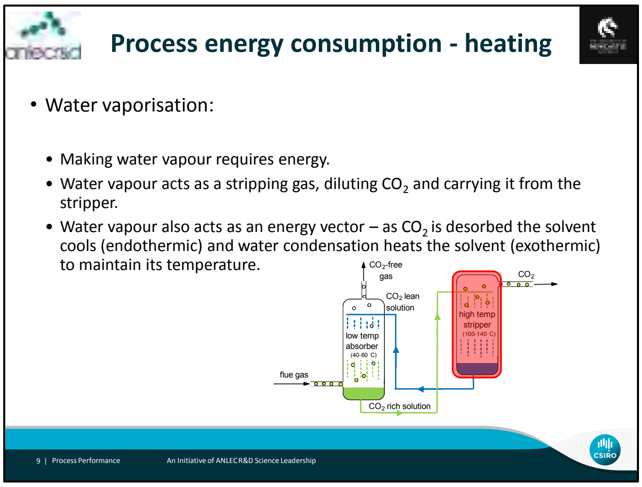
- Reaction enthalpies:
  - The enthalpy of absorption (which is made up of contributions from many reactions) defines the energy that much be input to reverse absorption.
  - A larger enthalpy means more energy is required, but it also results in a larger swing in the equilibrium position of the reactions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



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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.

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CSIRO

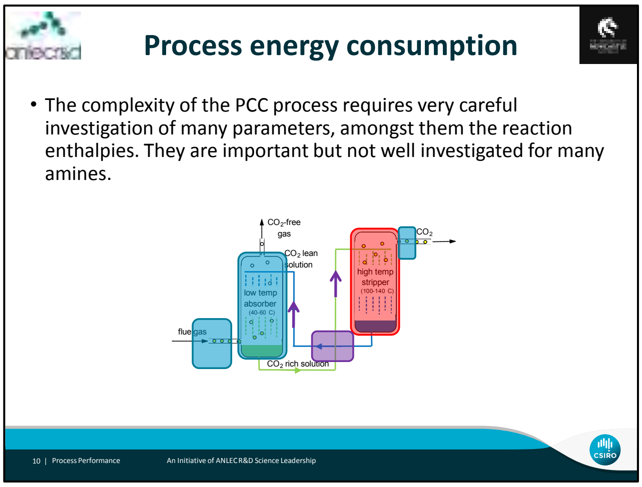
Heating

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.

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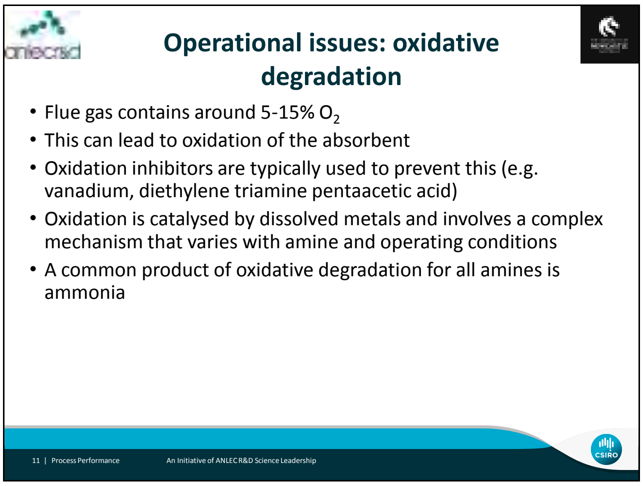
Overall energy consumption

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

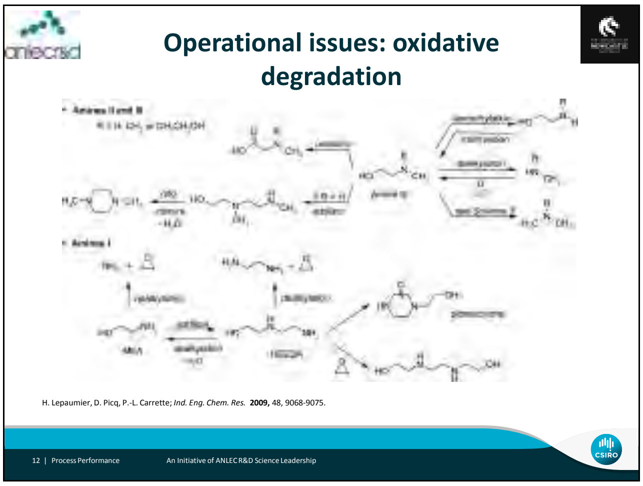
The original CO_2 capture process was developed for CO_2 from oxygen free environments. For example from natural gas or from a mixture with H_2 as part of ammonia synthesis. Power station flue gas contains between 5-15% residual O_2 following combustion. For susceptible absorbents like amines this leads 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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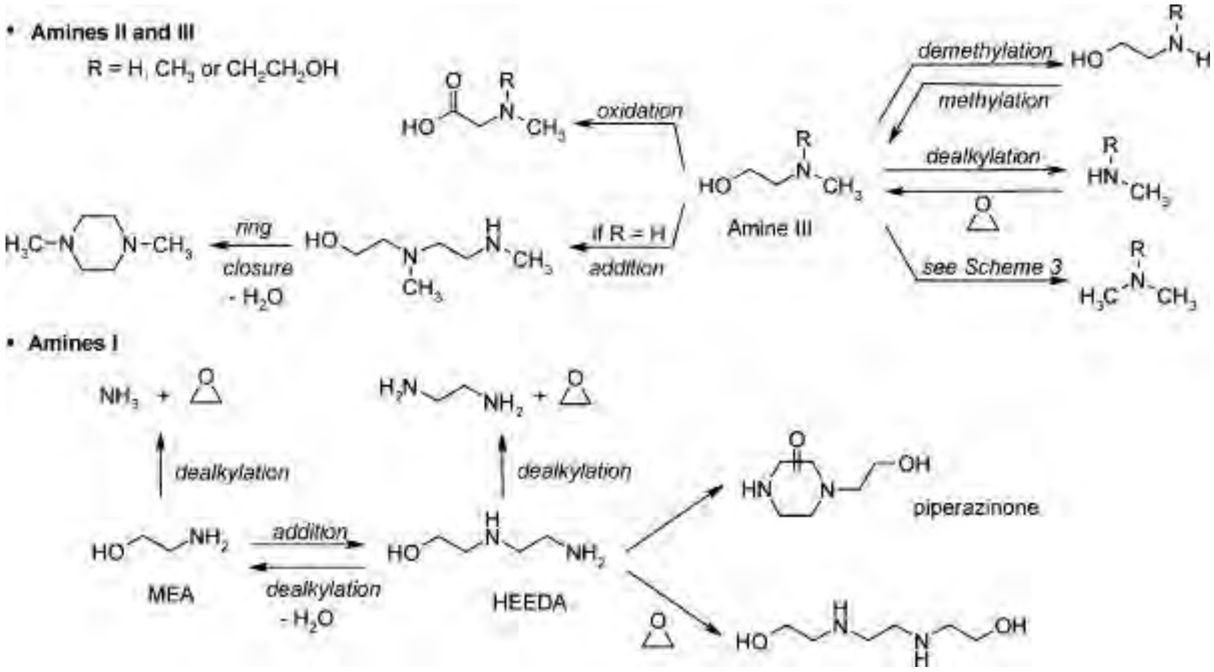
There are many different chemical pathways taken by oxidative degradation. It depends upon the amine structure and the conditions. These scheme summarises the different pathways for primary (I), secondary (II) and tertiary (III) amines.



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

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

$$\frac{dn_{CO_2}}{dt} = N_{CO_2} A$$

rate, mol.s^{-1}

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

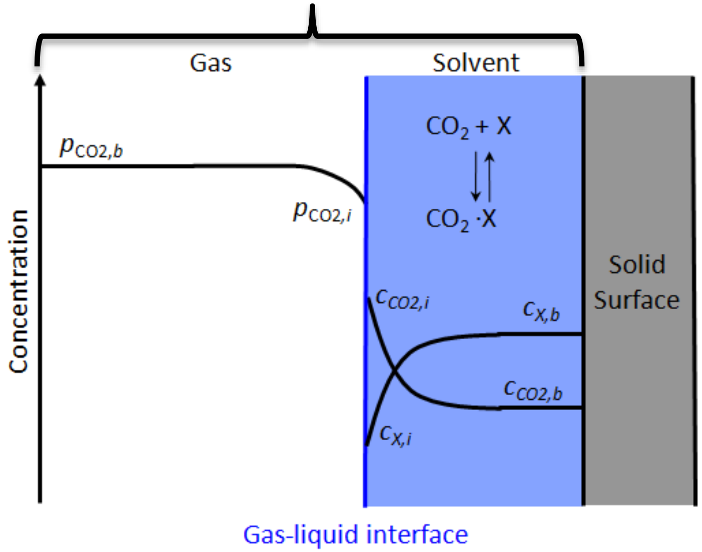
area, m^2

Effect of mass transfer on column size and cost

$$N_{CO2} = \boxed{K_g}\overbrace{(p_{CO2,b} - k_{h,CO2}c_{CO2,b})}^{\text{Driving Force}}$$

A function of diffusion coefficients and chemical reaction

Driving Force



Process energy consumption - pumps

- The overall energy requirement for the production of a unit of pure CO_2 has several components:
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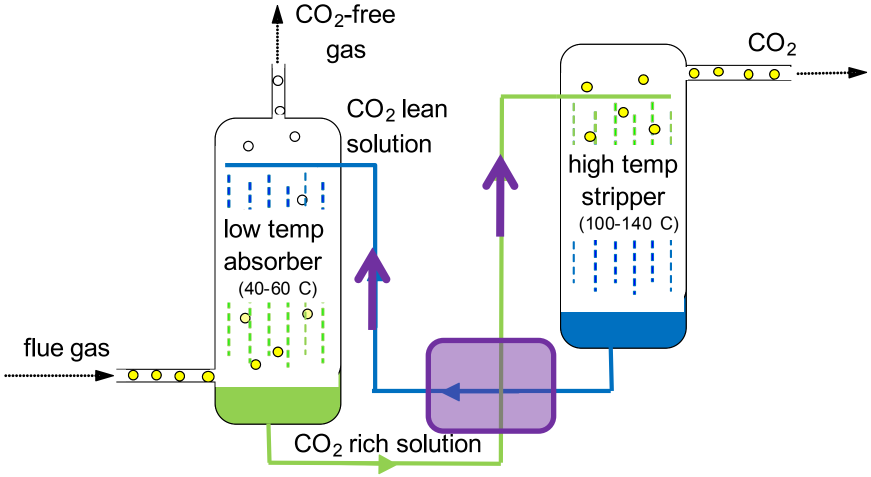

Process energy consumption - cooling

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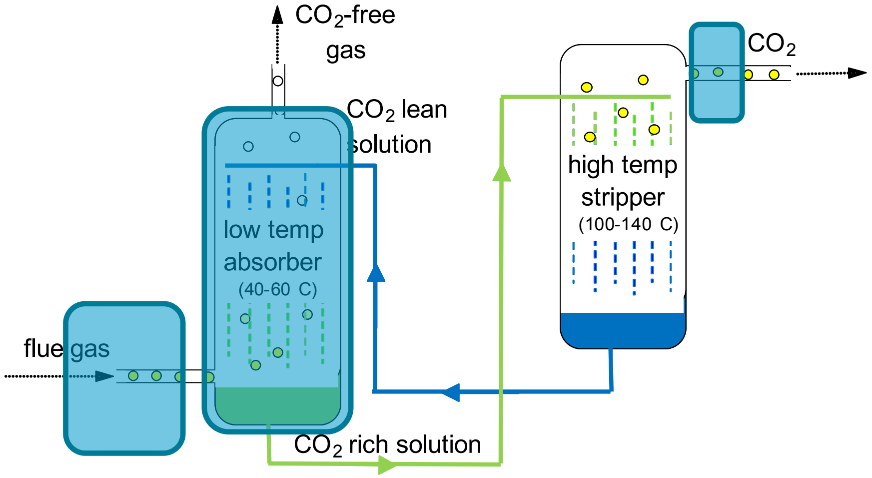
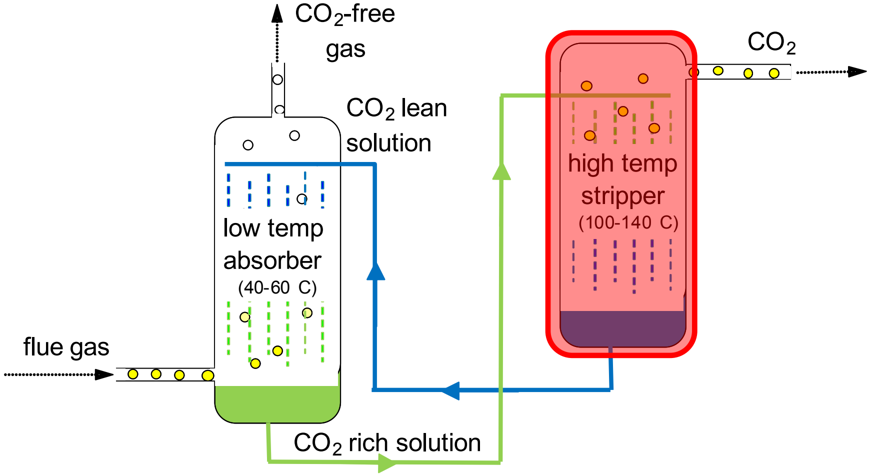
- Cooling of the CO_2 stream to avoid water and amine carry-over



Process energy consumption - heating

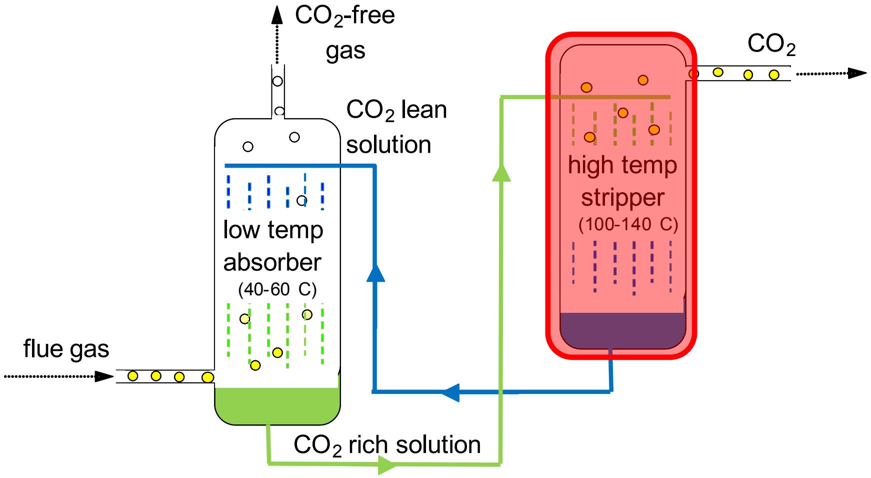
- The largest energy component is required for the heating of the stripper column. There are several components:

  - Heat capacity of the solvent
  - Reaction enthalpies
  - Enthalpy of vaporisation



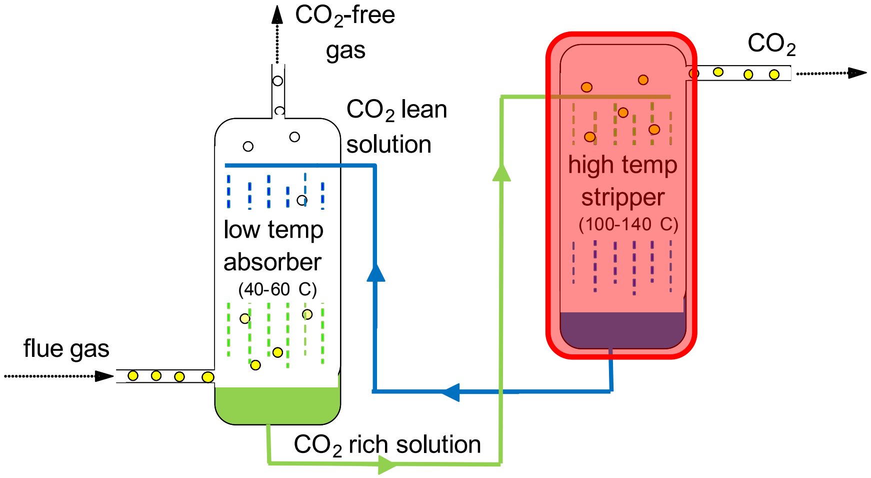
Process energy consumption - heating

- 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.



Process energy consumption - heating

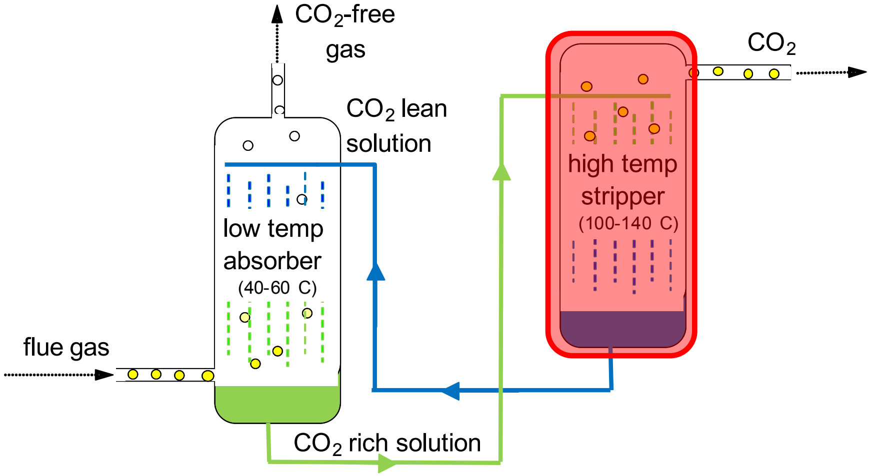
- Reaction enthalpies:
  - The enthalpy of absorption (which is made up of contributions from many reactions) defines the energy that much be input to reverse absorption.
  - A larger enthalpy means more energy is required, but it also results in a larger swing in the equilibrium position of the reactions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



Process energy consumption - heating

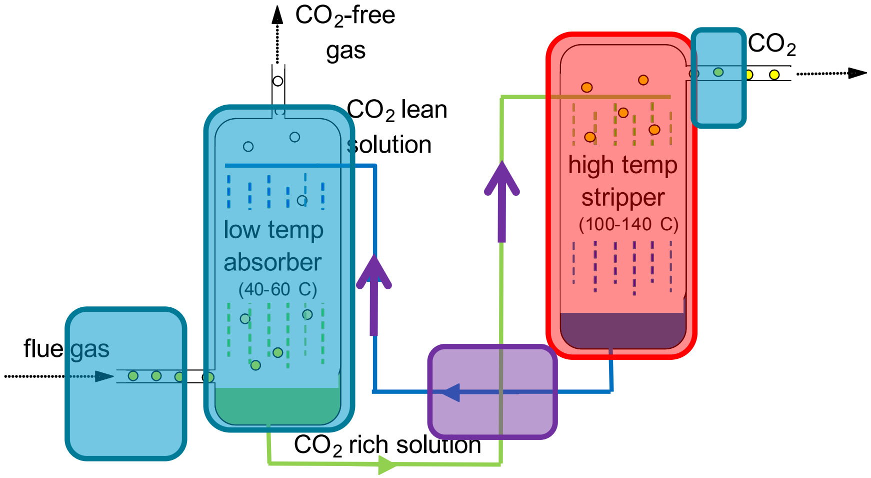
- Water vaporisation:

  - 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.



Process energy consumption

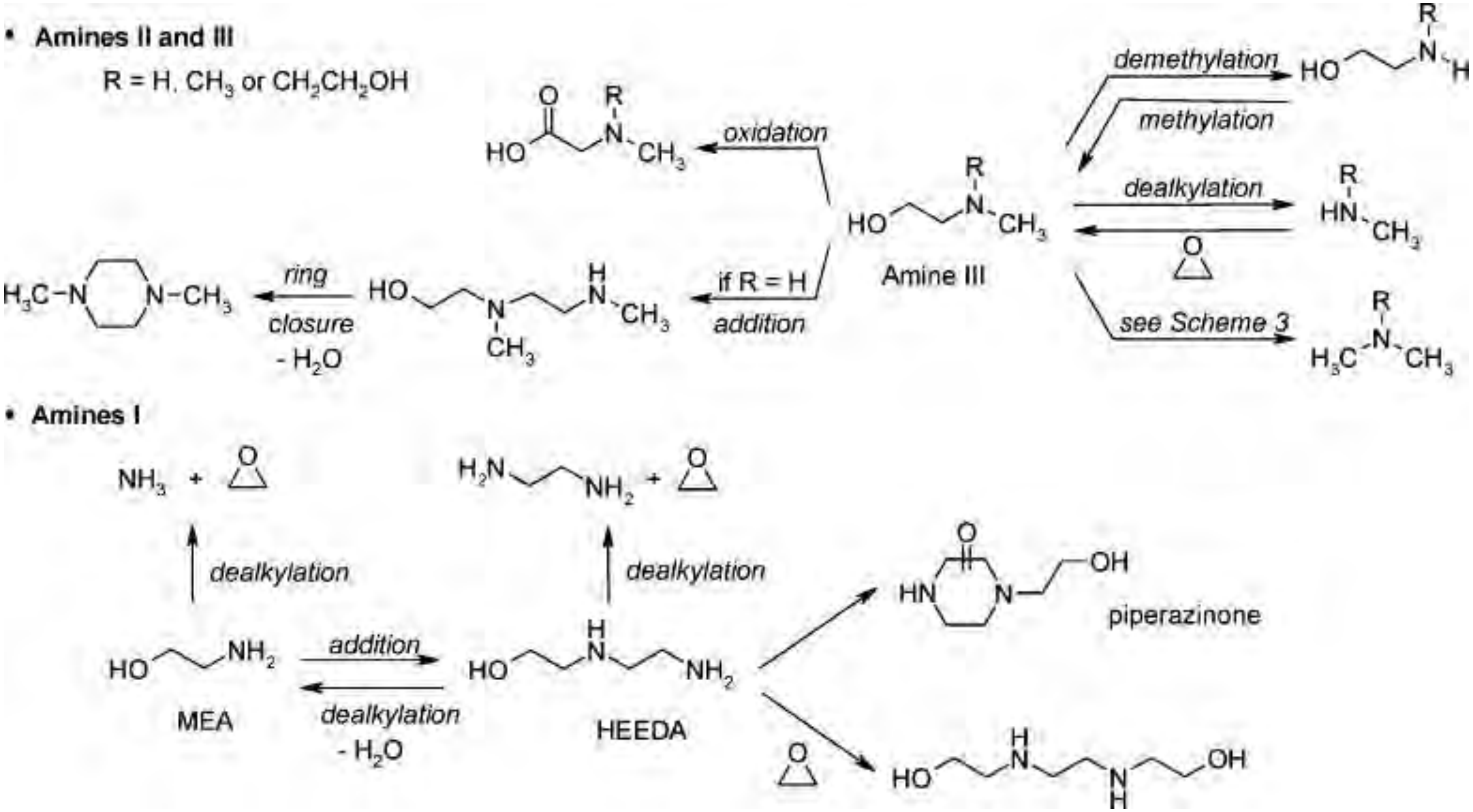
- The complexity of the PCC process requires very careful investigation of many parameters, amongst them the reaction enthalpies. They are important but not well investigated for many amines.



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

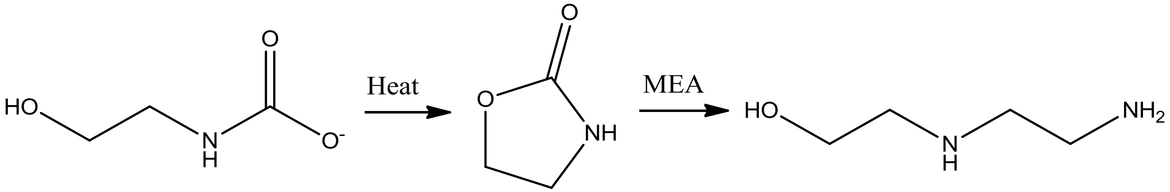
Operational issues: oxidative degradation



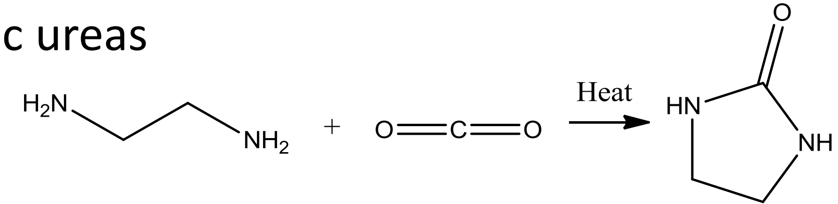
H. Lepaumier, D. Picq, P.-L. Carrette; *Ind. Eng. Chem. Res.* **2009,** 48, 9068-9075.

Operational issues: thermal degradation

- Thermal degradation limits the temperature that can be used for desorption
- Tertiary and cyclic amines are typically most resistant to thermal degradation
- The thermal degradation mechanism varies depending upon amine structure:
  - Primary and secondary alkanolamines undergo cyclic polymerisation of the carbamate



  - Primary and secondary diamines form cyclic ureas

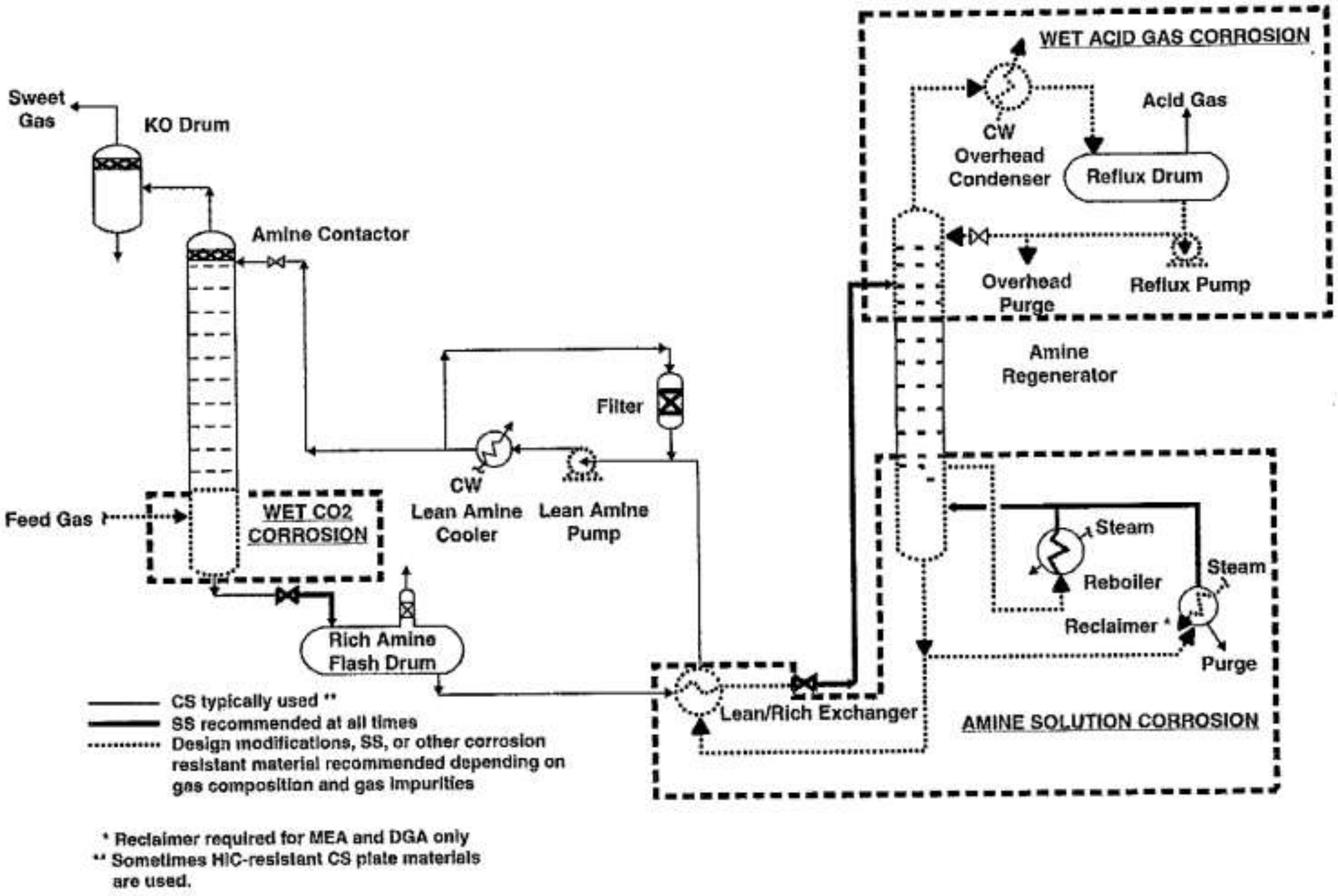


  - Tertiary amines undergo arm-switching and elimination reactions to form other secondary and tertiary amines
  - Cyclic amines undergo ring opening

Operational issues: corrosion

- Corrosion in PCC plants is caused either by wet acid gas (that is a saturated CO_2 containing gas stream) or amine solution
- Wet acid gas corrosion typically occurs near the flue gas inlet and at the top of the desorber
- Amine solutions are only corrosive when they contain some CO_2 and at elevated temperature
- Amine corrosion occurs on the hot side of the lean-rich absorbent heat exchanger, the bottom of the desorber and the reboiler

Operational issues: corrosion



——— CS typically used **

▬▬▬ SS recommended at all times

⋯⋯⋯ Design modifications, SS, or other corrosion resistant material recommended depending on gas composition and gas impurities

* Reclaimer required for MEA and DGA only

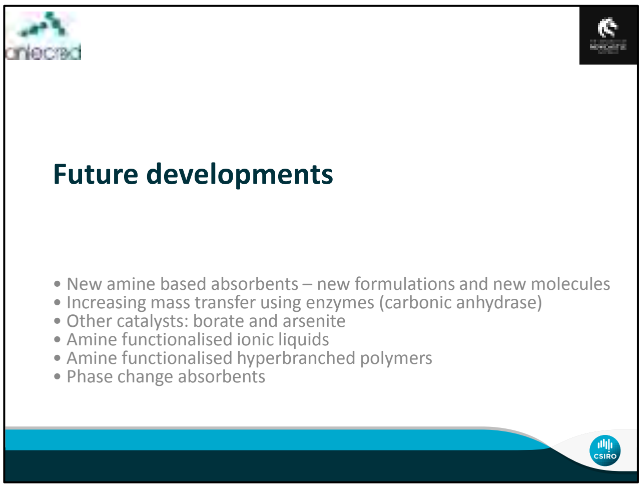
** Sometimes HIC-resistant CS plate materials are used.

Figure 3-1 from A. L. Kohl and R. B. Nielson, *Gas Purification (5th Ed.)*, Gulf Professional Publishing, Houston (1997).

Acknowledgements

The authors wish to acknowledge financial assistance provided through Australian National Low Emissions Coal Research and Development (ANLEC R&D). ANLEC R&D is supported by Australian Coal Association Low Emissions Technology Limited and the Australian Government through the Clean Energy Initiative.

Future developments in chemical reactive absorbents



Future developments

- New amine based absorbents – new formulations and new molecules
- Increasing mass transfer using enzymes (carbonic anhydrase)
- Other catalysts: borate and arsenite
- Amine functionalised ionic liquids
- Amine functionalised hyperbranched polymers
- Phase change absorbents

Future developments in chemical reactive absorbents

Presently, there are several well developed PCC processes, however, all suffer from high cost and that includes captial expenditure as well as high running cost/energy requirements.

Any development that reduces any of the above is most welcome.

An immediately obvious option si the find new amines or mixtures of amines that feature significnat improvements with respect to the standard MEA.

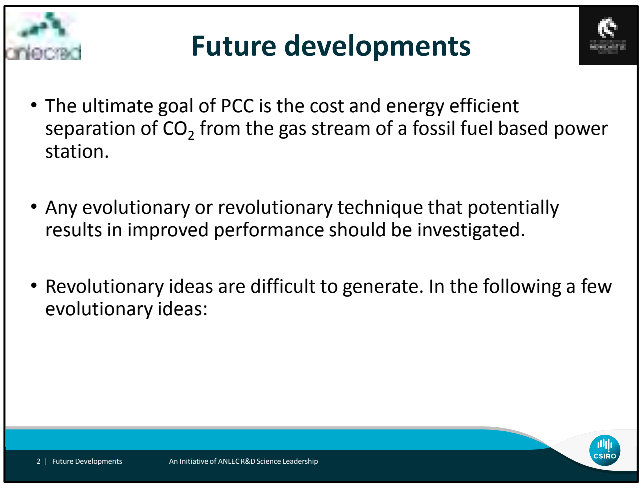
Enzymes can catalyse the reactions of dissolved CO_2 and indirectly accelerate mass transfer. There are inorganic catalysts such as borate and arsenite and of course there are enzymes such as carbonic anhydrase which are extremely efficient catalysts under the right conditions.

Ionic liquids have highly exceptional and potentially useful characteristics, modification for PCC purposes are presently investigated in several laboratories.

Another group of molecules with unique properties are hyperbranched macromelecules they can also be functionalised for PCC applications.

Future developments in chemical reactive absorbents

Phase change absorbents rely on precipitation of important molecules of the PCC process with poentially very interesting desorption advantages.



Future developments

- The ultimate goal of PCC is the cost and energy efficient separation of CO_2 from the gas stream of a fossil fuel based power station.
- Any evolutionary or revolutionary technique that potentially results in improved performance should be investigated.
- Revolutionary ideas are difficult to generate. In the following a few evolutionary ideas:

2 | Future Developments

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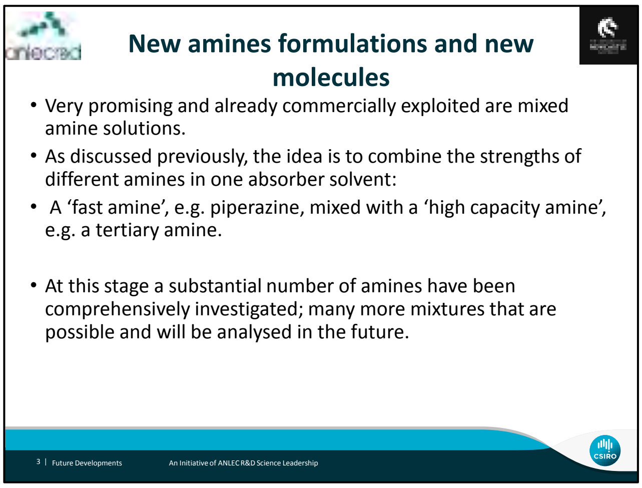
Future developments in chemical reactive absorbents

PCC is a well developed and established technique, it has been applied in natural gas cleaning for many decades. Many researchers and engineers have been working on improving the process and thus we cannot expect many simple and revolutionary solutions.

It is more likely that several gradual improvements will result in significant reduction in cost and energy requirement. Gradual improvements are most likely based on the adaptations of known materials with interesting properties to accommodate the requirements for PCC.

Future developments in chemical reactive absorbents



New amines formulations and new molecules

- Very promising and already commercially exploited are mixed amine solutions.
- As discussed previously, the idea is to combine the strengths of different amines in one absorber solvent:
- A 'fast amine', e.g. piperazine, mixed with a 'high capacity amine', e.g. a tertiary amine.

- At this stage a substantial number of amines have been comprehensively investigated; many more mixtures that are possible and will be analysed in the future.

3 | Future Developments An Initiative of ANLEC R&D Science Leadership

New amine based absorbents – new formulations and new molecules

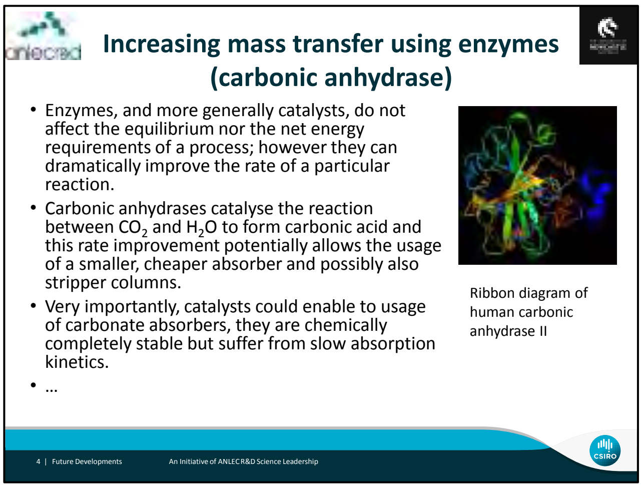
Reactive, i.e. carbamate forming amines have significant advantages (the reactions with CO_2 are very fast) as well as significant disadvantages (two amine molecules are required for the absorption of one molecule of CO_2).

It is attractive to try and develop solvents which feature the strength and avoiding the weaknes of the traditional reactive amines.

One pathway is to develop di-amines where one of the amine groups reacts fast to form the carbamate while the other acts as a base for the released proton, altogether resultsing in a 1:1 reaction between di-amine and CO_2.

Another option is to use mixed amine solutions, where one amine reacts very fast while the other acts as a proton sponge. This approch is very promising as there is almost no limit to the possibilites for the formulation of mixed amine solvents.

Future developments in chemical reactive absorbents



Increasing mass transfer using enzymes (carbonic anhydrase)

- Enzymes, and more generally catalysts, do not affect the equilibrium nor the net energy requirements of a process; however they can dramatically improve the rate of a particular reaction.
- Carbonic anhydrases catalyse the reaction between CO_2 and H_2O to form carbonic acid and this rate improvement potentially allows the usage of a smaller, cheaper absorber and possibly also stripper columns.
- Very importantly, catalysts could enable to usage of carbonate absorbers, they are chemically completely stable but suffer from slow absorption kinetics.
- …

Ribbon diagram of human carbonic anhydrase II

4 | Future Developments

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Increasing mass transfer using enzymes (carbonic anhydrase)

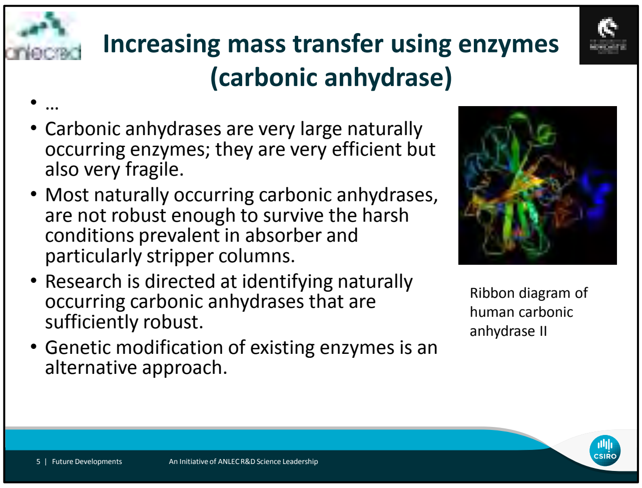
To a larte extent the sum over all reactions of a dissolved CO_2 molucules in the amine solution defines the mass transfer and thus the size of the absorber column. The reactions include the reaction with water, hydroxide and with the amine.

Tertiary, non-reactive amines as well as non-amine based absorbers, such as carbonate, suffer from the significant disadvantage of not including the fast carbamate forming reaction.

The reaction of CO_2 with water is much slower, however, this is exactly the reaction that is very efficiently catalysed by the natural enzyme carbonic anhydrase. Suddenly, the reaction of CO_2 with water is fast and this allows to use of non-reactive amines or carbonate as absorber solutions. The advantage of the 1:1 ratio of these absorbers is now combined with fast reactions and thus small absorber columns.

Are natural enzymes the solution?

Future developments in chemical reactive absorbents



Increasing mass transfer using enzymes (carbonic anhydrase)

- …
- Carbonic anhydrases are very large naturally occurring enzymes; they are very efficient but also very fragile.
- Most naturally occurring carbonic anhydrases, are not robust enough to survive the harsh conditions prevalent in absorber and particularly stripper columns.
- Research is directed at identifying naturally occurring carbonic anhydrases that are sufficiently robust.
- Genetic modification of existing enzymes is an alternative approach.

Ribbon diagram of human carbonic anhydrase II

5 | Future Developments An Initiative of ANLEC R&D Science Leadership

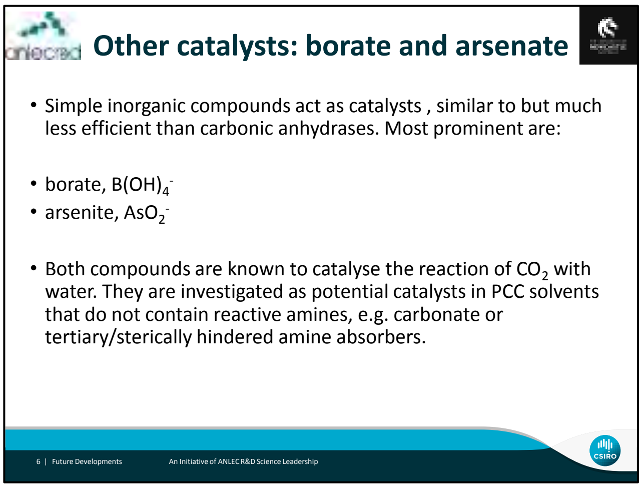
Increasing mass transfer using enzymes (carbonic anhydrase)

Carbonic anhydrase is an extremely efficient enzyme; it is also a very large molecule and thus it is also very fragile. The tremendous efficiency is actually only achieved under very closely defined conditions, of course these are also the conditions of optimal stabiltiy. These conditions exist in the living cell where the catalytic activity is taking place and thes conditions are clearly not met in the PCC process, certainly not in the stripper column under elevated temperatures. The pH values encountered in PCC are well outside the natural range in the living cell.

Modification of existing enzymes in an attempt to increase their temperature and pH range are being researched but it will be difficult to improve on nature. Maintaining the catalytic efficiency while manipulating these enzymes is a difficult task.

Another option is to explore carbonic anhydrases in organisms which live under extreme conditions of temperature and pH.

Future developments in chemical reactive absorbents



Other catalysts: borate and arsenate

- Simple inorganic compounds act as catalysts , similar to but much less efficient than carbonic anhydrases. Most prominent are:

- borate, $B(OH)_4^-$
- arsenite, AsO_2^-

- Both compounds are known to catalyse the reaction of CO_2 with water. They are investigated as potential catalysts in PCC solvents that do not contain reactive amines, e.g. carbonate or tertiary/sterically hindered amine absorbers.

6 | Future Developments

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Other catalysts: borate and arsenite

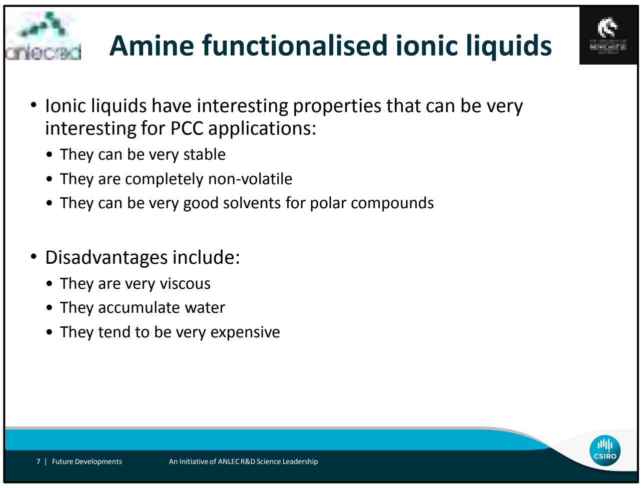
The delicate nature of enzymes are huge obstacle for their usage in PCC.

Inorganic molecules are known to catalyse the reaction between water and carbon dioxide, the most prominent ones are borate, $B(OH)_4^-$, and arsenite, ASO_2^-.

The catalytic activity of these inorganic compounds is many orders or magnitute smaller than those of the natural enzymes. However, they are potentially much more stable, potentially they are indistructable.

Clearly more research is required with the aim of finding more active but still stable inorganic catalysts.

Future developments in chemical reactive absorbents



Amine functionalised ionic liquids

- Ionic liquids have interesting properties that can be very interesting for PCC applications:
  - They can be very stable
  - They are completely non-volatile
  - They can be very good solvents for polar compounds

- Disadvantages include:
  - They are very viscous
  - They accumulate water
  - They tend to be very expensive

7 | Future Developments An Initiative of ANLEC R&D Science Leadership

Ionic liquids

A relatively recent interesting new class of solvents are the ionic liquids. Ionic liquids are salts, combinations of cations and anions, with a low melting point, most of them are liquid at room temperature.

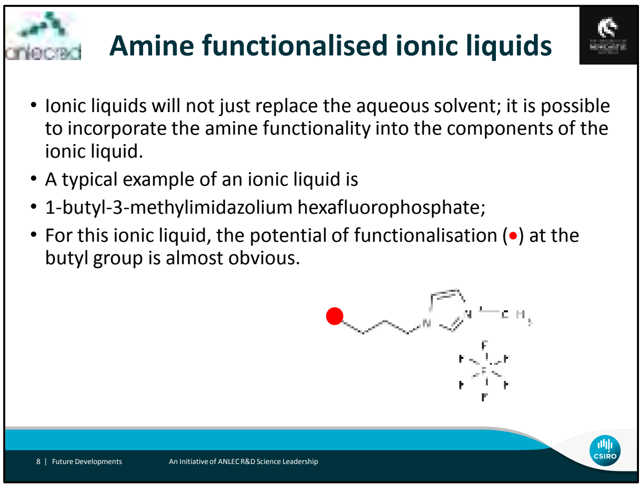
Ionic liquids have very interesting properties, some of them very attractive for PCC applications.

Being made up of ions, they are completely non-volatile and they can be extremely good solvents for polar compounds. Many of them are surprisingly heat stable, they do not decompose at quite high temperatures.

Of course there are also disadvantages: they are usually very viscous and also very expensive. However, the most important problem is the water content of the flue gas. It immediately is absorbed into the ionic liquid, transforming the ionic liquid into a salt solution with the loss of many of the favourable properties.

Most ionic liquids will not react with CO_2 other than just physically dissolving it. Additions of amine or other bases is still required.

Future developments in chemical reactive absorbents



Amine functionalised ionic liquids

- Ionic liquids will not just replace the aqueous solvent; it is possible to incorporate the amine functionality into the components of the ionic liquid.
- A typical example of an ionic liquid is
- 1-butyl-3-methylimidazolium hexafluorophosphate;
- For this ionic liquid, the potential of functionalisation (●) at the butyl group is almost obvious.

8 | Future Developments   An Initiative of ANLEC R&D Science Leadership

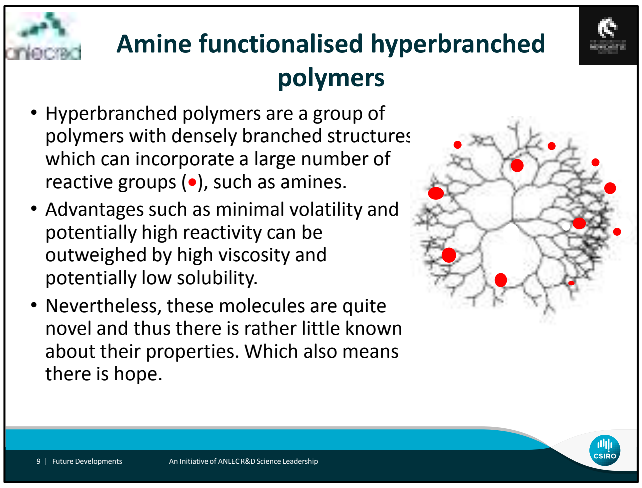
Amine functionalised ionic liquids

An interesting potential enhancement of ionic liquids is to incorporate the amine functionality into the actual components of the ionic liquid. As there are many known ionic liquids and their number is rapidly growing there is an almost unlimited number of possible modifications.

One example is given in the slide. An important ionic liquid is 1-butyl-3-methylimidazolium hexafluorophosphate, BMIM PF_6. An obvious modification could occur at the end of the butyl group, it is indicated as a red circle. It could be a primary amine or any other amine containing group.

It is unlikely that the modification will significantly change the ionic liquid property of the now salt; but presently there is no convincing experimental evidence for or against modified ionic liquids.

Future developments in chemical reactive absorbents



Amine functionalised hyperbranched polymers

- Hyperbranched polymers are a group of polymers with densely branched structures which can incorporate a large number of reactive groups (●), such as amines.
- Advantages such as minimal volatility and potentially high reactivity can be outweighed by high viscosity and potentially low solubility.
- Nevertheless, these molecules are quite novel and thus there is rather little known about their properties. Which also means there is hope.

9 | Future Developments

An Initiative of ANLEC R&D Science Leadership

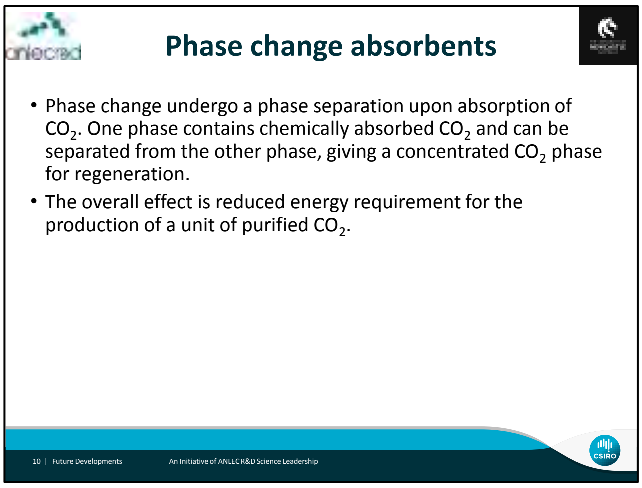
Amine functionalised hyperbranched polymers

Another family of attractive but little known molecules for PCC applications are amine functionalised hyperbranched polymers. Most polymers are linear or they are sparsely branched or bridged. Hyperbranched polymers are polymers with a high degree of branching, the slide indicates the general structure of such polymers, they are approximately spherical but still only loosely filled.

There is a lot of room for the incorporation of reactive groups such as amines. In the slide they are again indicated by red circles.

Similar to functionalised ionic liquids, these polymers will be non-volatile, have the potential of high reactivity but will feature high viscosity and potentially low solubility. And, also similar to ionic liquids, these molecules are novel, they are not yet well investigated and there is a lot of room for surprises.

Future developments in chemical reactive absorbents



Phase change absorbents

- Phase change undergo a phase separation upon absorption of CO_2. One phase contains chemically absorbed CO_2 and can be separated from the other phase, giving a concentrated CO_2 phase for regeneration.
- The overall effect is reduced energy requirement for the production of a unit of purified CO_2.

Phase change absorbants

Imagine a reagent that reversibly reacts with CO_2 but where the reaction product precipitates. Instead of pumping the CO_2 loaded solvent into the stripper for heating and CO_2 release, the precipitate could be physically separated and heated for CO_2 release. This could substantially reduce the energy requirement for the stripping process as the actual amount of compound is greatly reduced. Only the precipitate rather than the process solution which contains a substantial amount of water needs to be heated.

While the handling of heterogeneous mixtures is generally much more complex than the pumping of homogeneous solutions, filtration is a well understood process in chemical engineering and overall such a process could significantly improve the energy requirement of PCC.

Future developments

- New amine based absorbents – new formulations and new molecules
- Increasing mass transfer using enzymes (carbonic anhydrase)
- Other catalysts: borate and arsenite
- Amine functionalised ionic liquids
- Amine functionalised hyperbranched polymers
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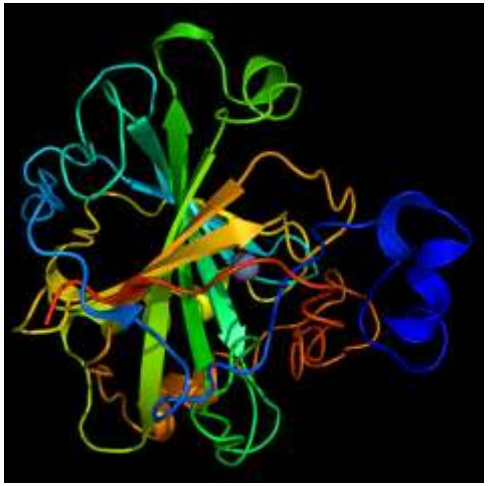

Ribbon diagram of human carbonic anhydrase II

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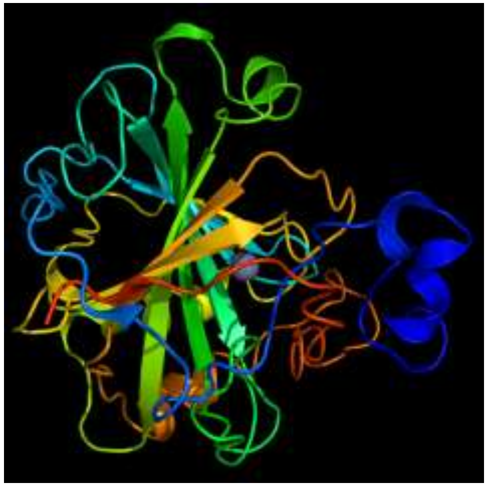

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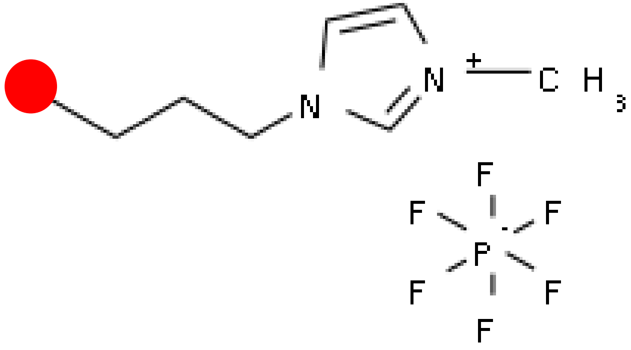

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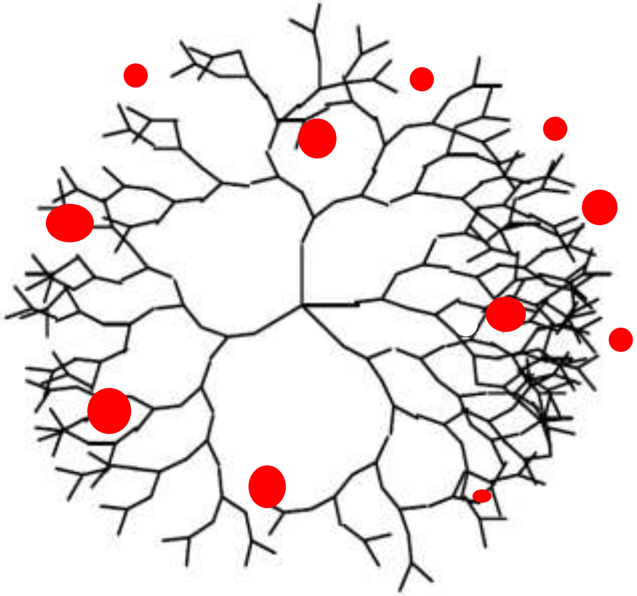

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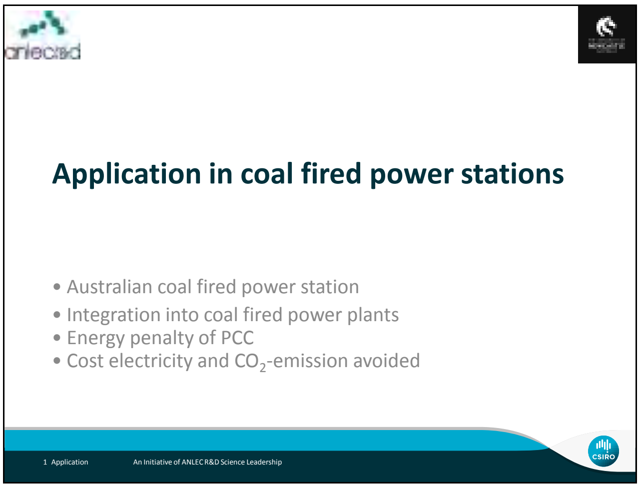
Application in coal fired power stations



Application in coal fired power stations

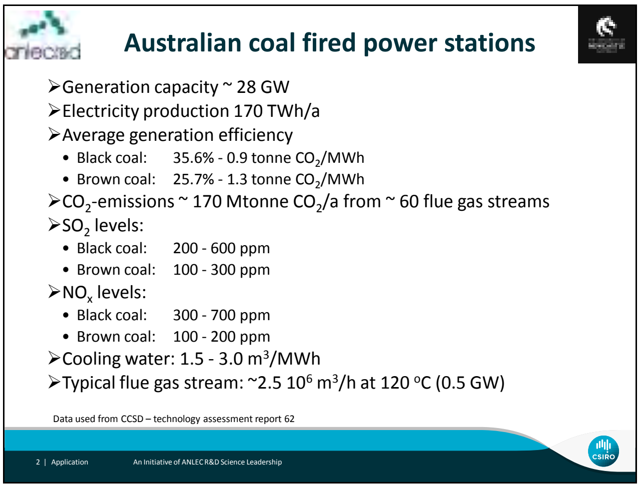
- Australian coal fired power station
- Integration into coal fired power plants
- Energy penalty of PCC
- Cost electricity and CO_2-emission avoided

1 Application An Initiative of ANLEC R&D Science Leadership

This section represents a brief foray into some of the practical considerations and the consequences of doing CO_2 capture in a coal fired power station. The focus will be on Australian coal fired power stations.

There are different ways you can integrate a capture plant into a power station. Do you use steam produced from electrical heating or extract it from the power station steam cycle? Does the station have flue gas desulfurization? If no what sort of pre-treatment of the flue gas is required? What is the energy penalty in terms of electricity output of operating the capture plant? What effect will capture have on the price of electricity and how much CO_2 will you avoid releasing into the atmosphere?

Australian coal fired power stations



Australian coal fired power stations

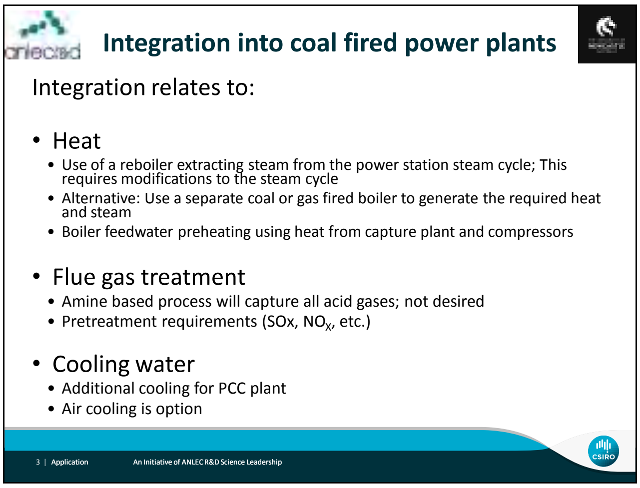
- Generation capacity ~ 28 GW
- Electricity production 170 TWh/a
- Average generation efficiency
  - Black coal: 35.6% - 0.9 tonne CO_2/MWh
  - Brown coal: 25.7% - 1.3 tonne CO_2/MWh
- CO_2-emissions ~ 170 Mtonne CO_2/a from ~ 60 flue gas streams
- SO_2 levels:
  - Black coal: 200 - 600 ppm
  - Brown coal: 100 - 300 ppm
- NO_x levels:
  - Black coal: 300 - 700 ppm
  - Brown coal: 100 - 200 ppm
- Cooling water: 1.5 - 3.0 m^3/MWh
- Typical flue gas stream: ~2.5 10^6 m^3/h at 120 °C (0.5 GW)

Data used from CCSD – technology assessment report 62

2 | Application An Initiative of ANLEC R&D Science Leadership

75% of the Australian electricity demand is generated on black and brown coal fired power stations. The CO_2 emissions from brown coal fired power stations are significantly higher because of the lower efficiency, resulting from the high moisture content of brown coal. The levels of sulphur- and nitrogen-oxides are important because they will react with the alkaline solutions used for PCC. Cooling water requirement is also important as there are limitations in its availability in Australia. Cooling water is not necessary in an air-cooled power plant.

Integration into coal fired power plants



Integration into coal fired power plants

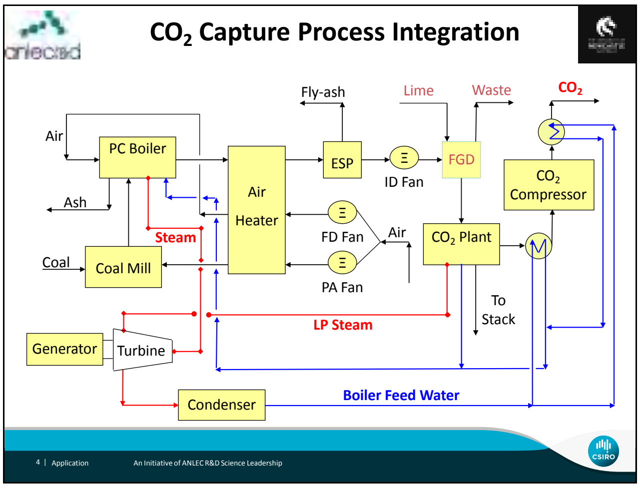
Integration relates to:

- Heat
  - Use of a reboiler extracting steam from the power station steam cycle; This requires modifications to the steam cycle
  - Alternative: Use a separate coal or gas fired boiler to generate the required heat and steam
  - Boiler feedwater preheating using heat from capture plant and compressors
- Flue gas treatment
  - Amine based process will capture all acid gases; not desired
  - Pretreatment requirements (SOx, NO_X, etc.)
- Cooling water
  - Additional cooling for PCC plant
  - Air cooling is option

3 | Application An Initiative of ANLEC R&D Science Leadership

This slide mentions the interfaces between a capture plant and power station. The capture process requires energy in particular heat to increase the temperature of the solvent which then releases the captured CO_2. Part of this heat can be reused in the power plant at lower temperature levels. Compression of CO_2 will also generate heat (*feel the valve of your bike pump when you inflate the tyre*) and this heat can be used the power plant. The other important consideration for integration into a power station is flue gas pre-treatment. If the power station has flue gas desulfurization and NO_x removal minimal pre-treatment will be required. However, if these processes are not present a pre-treatment column (typically a packed column containing a weakly caustic solvent) will be required to reduce the concentration of these contaminants passing into the capture process as well as to cool the flue gas to the absorption temperature. The capture plant will also require some cooling and this will need to be minimised. Air cooling in the capture plant might be preferred as this does not require more cooling water.

CO₂ capture process integration



CO$_2$ Capture Process Integration

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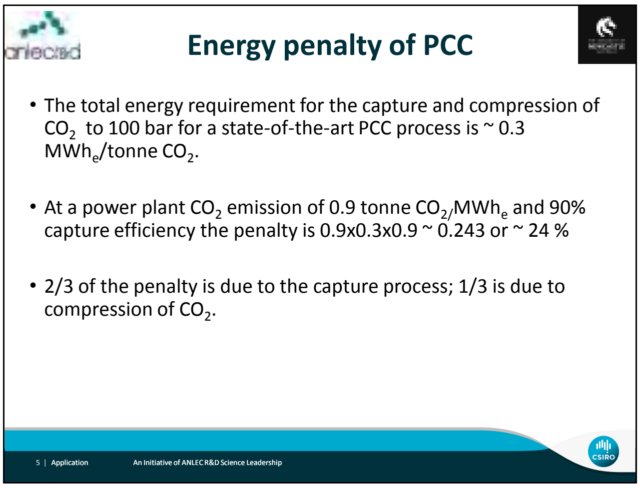
The figure shows how a capture plant could be integrated into a power station. In this case the flue gas pre-treatment would consist of an electro-static precipitator (ESP) and flue gas desulphurisation (FGD) in addition to flue gas cooling. Low pressure (LP) steam is used to regenerate the solvent and the condensate is returned to the pulverised coal (PC) fired boiler. This steam is then not available to generate electricity.

Improvement potential in energy performance

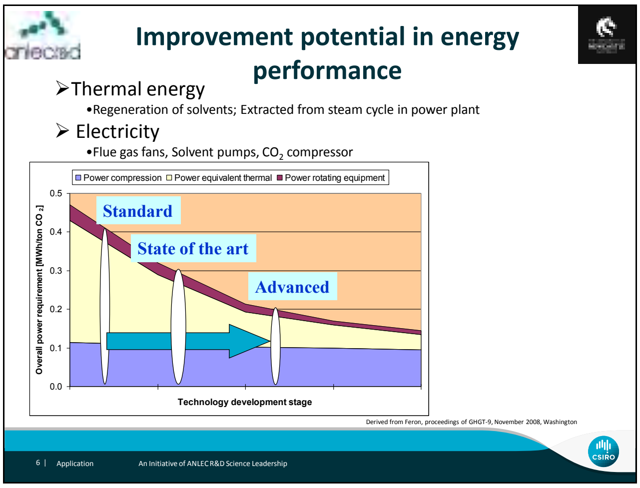


Energy penalty of PCC

- The total energy requirement for the capture and compression of CO_2 to 100 bar for a state-of-the-art PCC process is ~ 0.3 MWh_e/tonne CO_2.
- At a power plant CO_2 emission of 0.9 tonne CO_2/MWh_e and 90% capture efficiency the penalty is 0.9x0.3x0.9 ~ 0.243 or ~ 24 %
- 2/3 of the penalty is due to the capture process; 1/3 is due to compression of CO_2.

As you would expect CO_2 capture does not come free. The energy demand in a CO_2 capture plant comes to a large extent from the heat required to produce the steam for CO_2 stripping. Taking steam from the steam cycle and/or electricity reduces the power station’s electricity output. Also pumps, fans and the compressors will use electricity from the power station. Typically the aim is to capture a significant amount of the emissions of a power station, i.e. 90 %. For a state-of-the-art CO_2 capture process a typical energy requirement is ~0.3 MWh/CO_2 captured. This represents about 24% of the output of a coal fired power station.

Improvement potential in energy performance



Improvement potential in energy performance

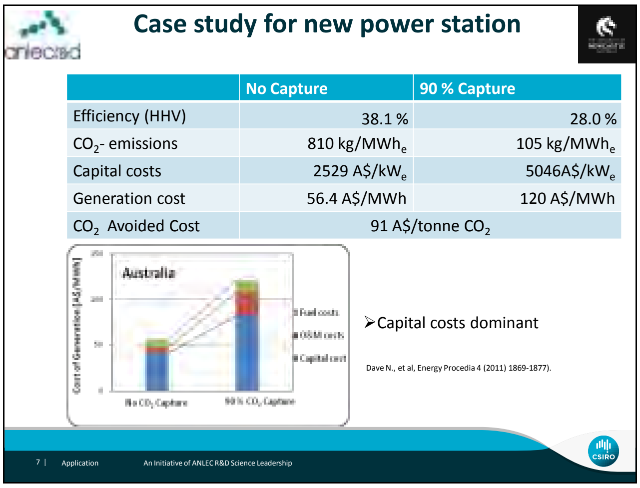
- Thermal energy
  - Regeneration of solvents; Extracted from steam cycle in power plant
- Electricity
  - Flue gas fans, Solvent pumps, CO_2 compressor

Derived from Feron, proceedings of GHGT-9, November 2008, Washington

6 | Application An Initiative of ANLEC R&D Science Leadership

This slide indicates that there is considerable improvement potential in the energy performance of the PCC process. Over the past two decades the energy requirement has come down from ~0.4 MWh/tonne CO_2 to ~0.3 MWh/tonne CO_2. In particular the thermal energy requirement has been reduced. Further reduction to ~0.2 MWh/tonne CO_2 appear possible. One has to bear in mind that the theoretical minimum is ~0.1 MWh/tonne CO_2.

Case study for new power station



Case study for new power station

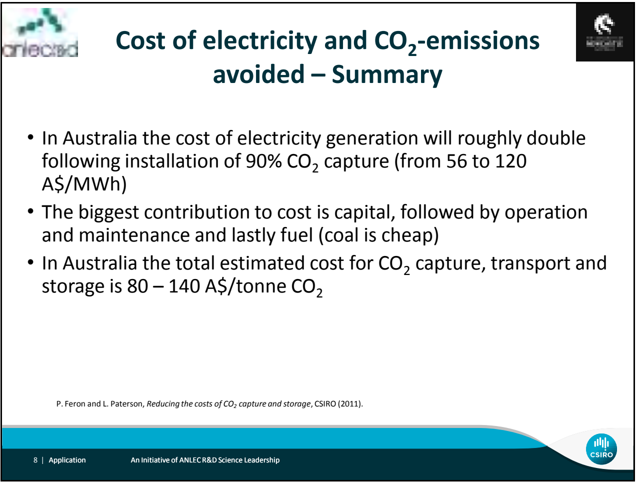
	No Capture	90 % Capture
Efficiency (HHV)	38.1 %	28.0 %
CO_2- emissions	810 kg/MWh_e	105 kg/MWh_e
Capital costs	2529 A$/$kW_e$	5046A$/$kW_e$
Generation cost	56.4 A$/MWh	120 A$/MWh
CO_2 Avoided Cost	91 A$/tonne CO_2	

- Capital costs dominant

Dave N., et al, Energy Procedia 4 (2011) 1869-1877).

This slide gives relevant data for the power plant efficiency, CO_2 emissions, capital costs, generation cost and CO_2-avoided cost for a new power station, in the situation without capture and with 90% CO_2 capture. Although the emissions are significantly reduce the increase in the capital cost and electricity generation cost is significant.

Cost of electricity and CO_2-emissions avoided – Summary



Cost of electricity and CO_2-emissions avoided – Summary

- In Australia the cost of electricity generation will roughly double following installation of 90% CO_2 capture (from 56 to 120 A$/MWh)
- The biggest contribution to cost is capital, followed by operation and maintenance and lastly fuel (coal is cheap)
- In Australia the total estimated cost for CO_2 capture, transport and storage is 80 – 140 A$/tonne CO_2

P. Feron and L. Paterson, *Reducing the costs of CO_2 capture and storage*, CSIRO (2011).

8 | Application An Initiative of ANLEC R&D Science Leadership

It has been estimated that in Australia 90% CO_2 capture will double the cost of electricity generation. This is not as bad as it sounds as the cost of generation is only part of the cost of the final price paid by electricity consumers. The biggest contribution to cost is the capital cost to build the capture plant. Second is the energy required for capture plant operation and the loss of electricity output, followed by maintenance and lastly fuel. In Australia the predicted cost for capture, transport and storage is in the range 80 – 140 $/tonne CO_2.

Application in coal fired power stations

- Australian coal fired power station
- Integration into coal fired power plants
- Energy penalty of PCC
- Cost electricity and CO_2-emission avoided

Australian coal fired power stations

- Generation capacity ~ 28 GW
- Electricity production 170 TWh/a
- Average generation efficiency
  - Black coal: 35.6% - 0.9 tonne CO_2/MWh
  - Brown coal: 25.7% - 1.3 tonne CO_2/MWh
- CO_2-emissions ~ 170 Mtonne CO_2/a from ~ 60 flue gas streams
- SO_2 levels:
  - Black coal: 200 - 600 ppm
  - Brown coal: 100 - 300 ppm
- NO_x levels:
  - Black coal: 300 - 700 ppm
  - Brown coal: 100 - 200 ppm
- Cooling water: 1.5 - 3.0 m^3/MWh
- Typical flue gas stream: ~2.5 10^6 m^3/h at 120 ^oC (0.5 GW)

Data used from CCSD – technology assessment report 62

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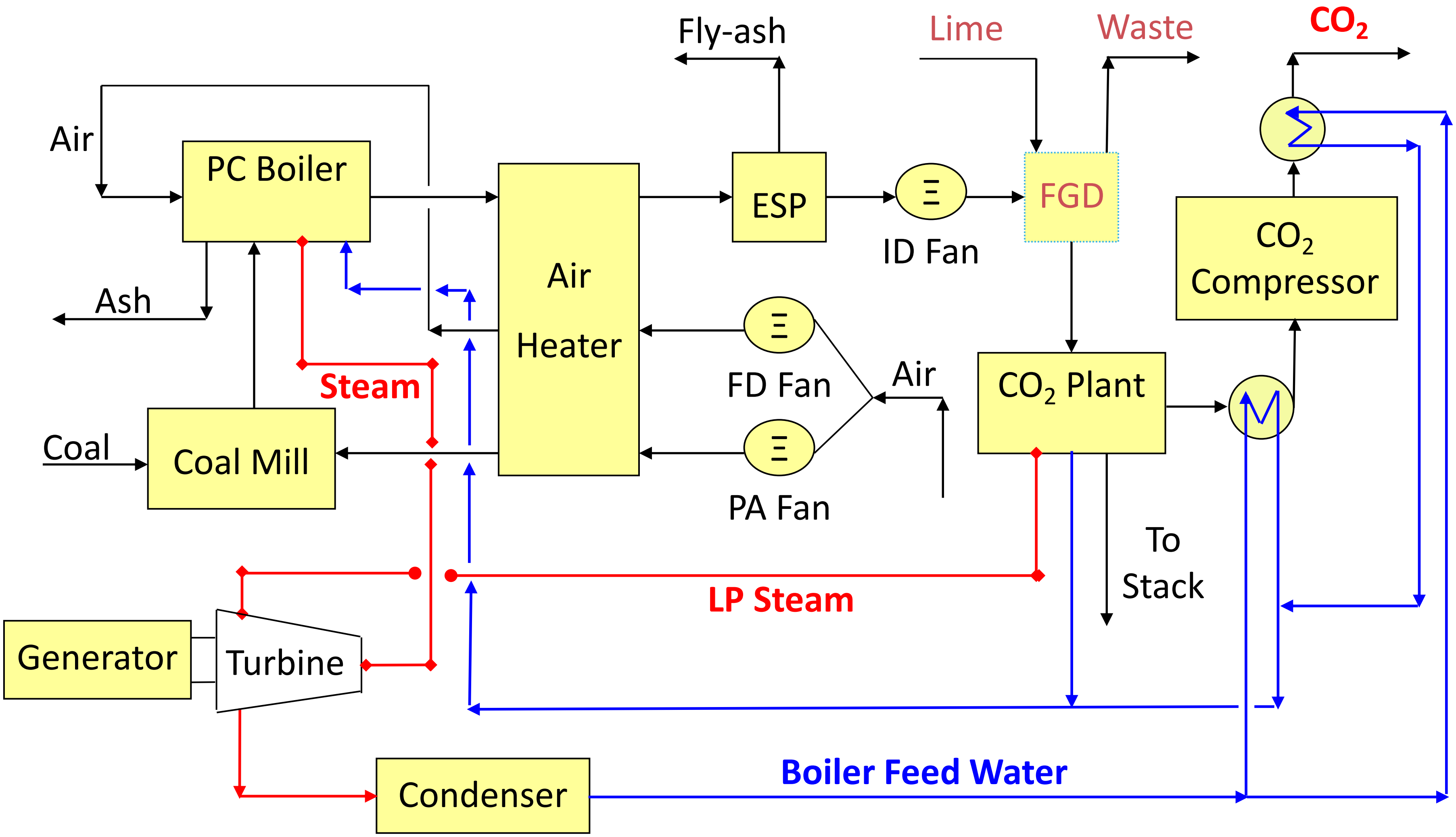
CO_2 Capture Process Integration



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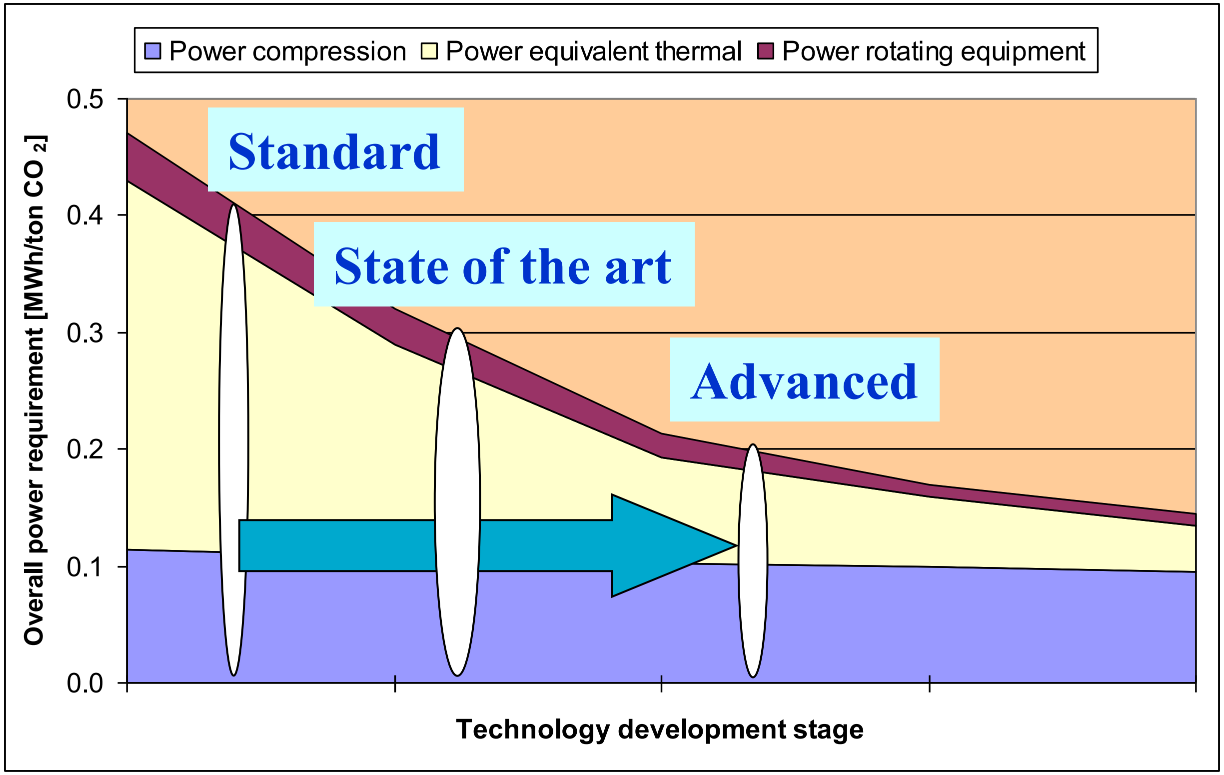

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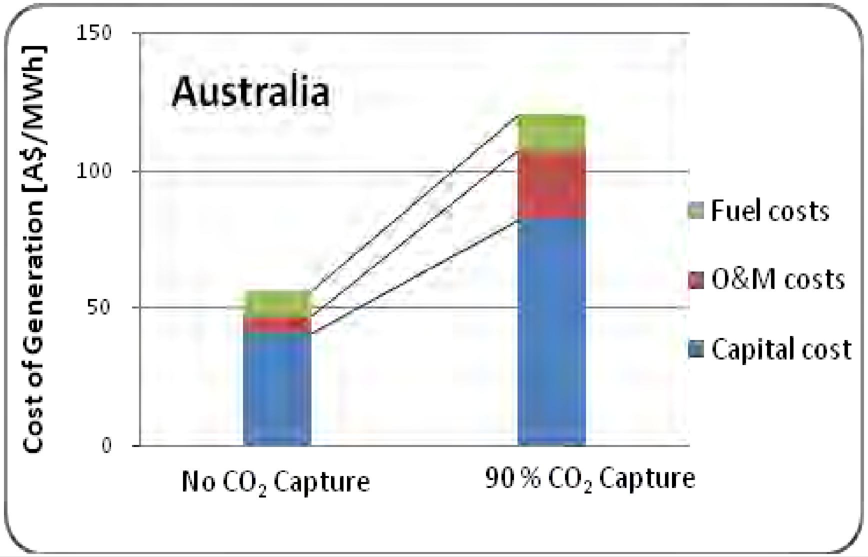

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Acknowledgements

The authors wish to acknowledge financial assistance provided through Australian National Low Emissions Coal Research and Development (ANLEC R&D). ANLEC R&D is supported by Australian Coal Association Low Emissions Technology Limited and the Australian Government through the Clean Energy Initiative.