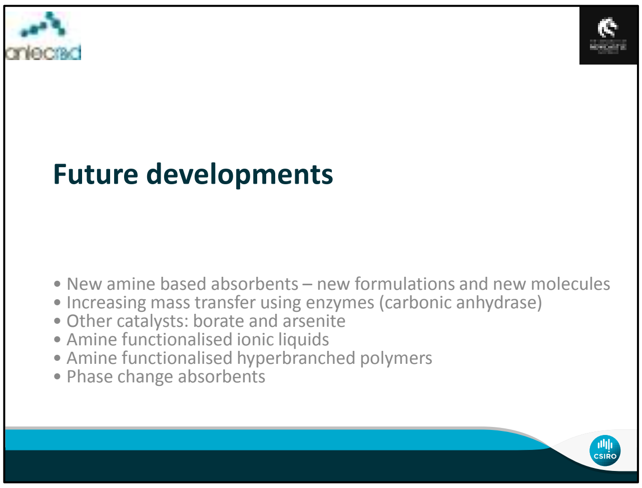
Future developments in chemical reactive absorbents



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.

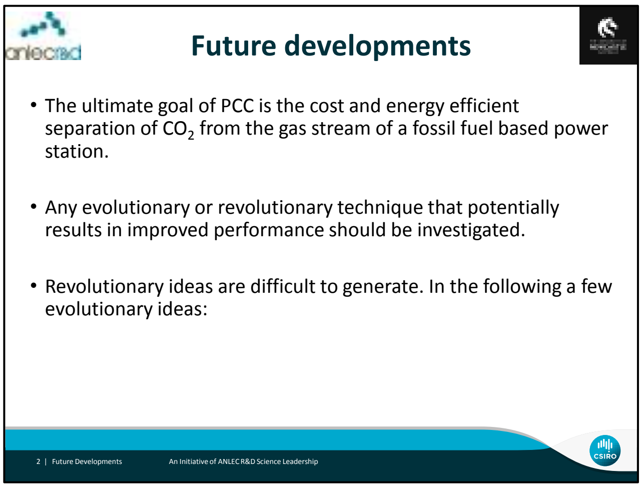
Enzymes can catalyse the reactions of dissolved CO_2 and indirectly accelerate mass transfer. There are inorganic catalysts such as borate and arsenite and of course there are enzymes such as carbonic anhydrase which are extremely efficient catalysts under the right conditions.

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:

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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.

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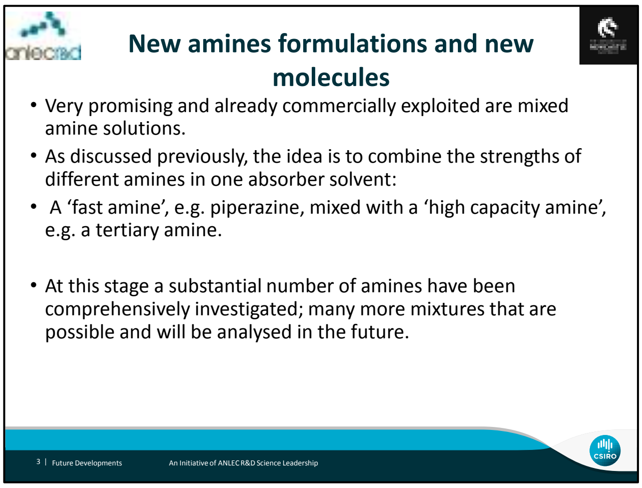

New amines formulations and new molecules

- 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.

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New amine based absorbents – new formulations and new molecules

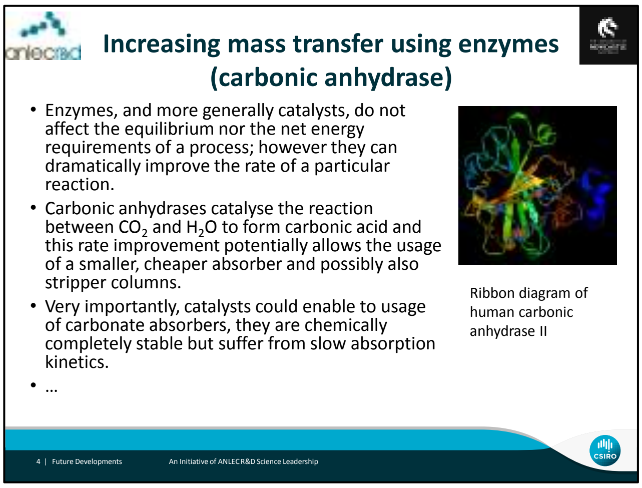
Reactive, i.e. carbamate forming amines have significant advantages (the reactions with CO_2 are very fast) as well as significant disadvantages (two amine molecules are required for the absorption of one molecule of CO_2).

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

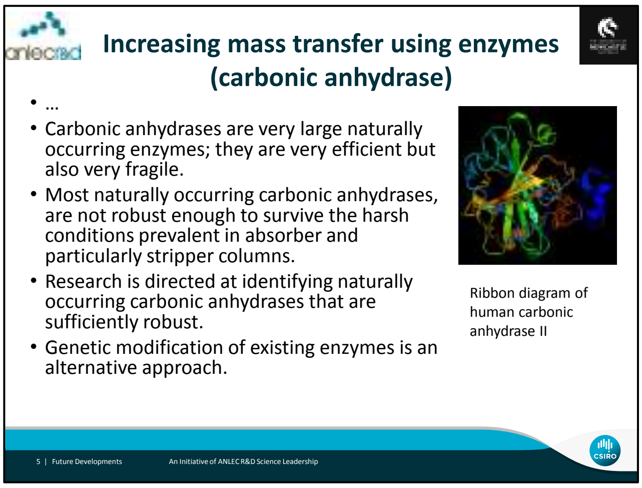
Increasing mass transfer using enzymes (carbonic anhydrase)

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?



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

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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.

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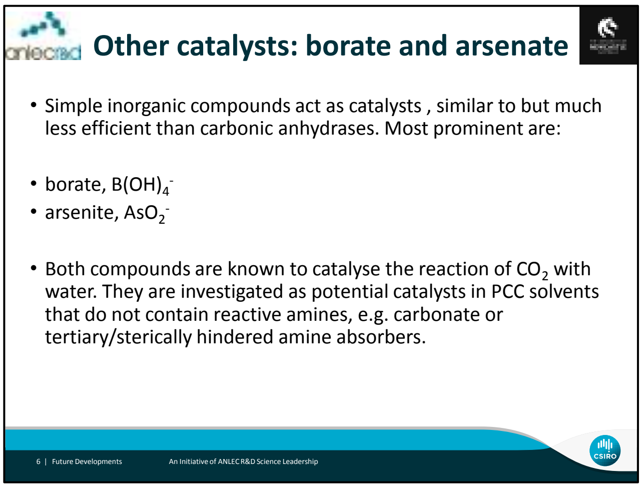

Other catalysts: borate and arsenate

- 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.

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.

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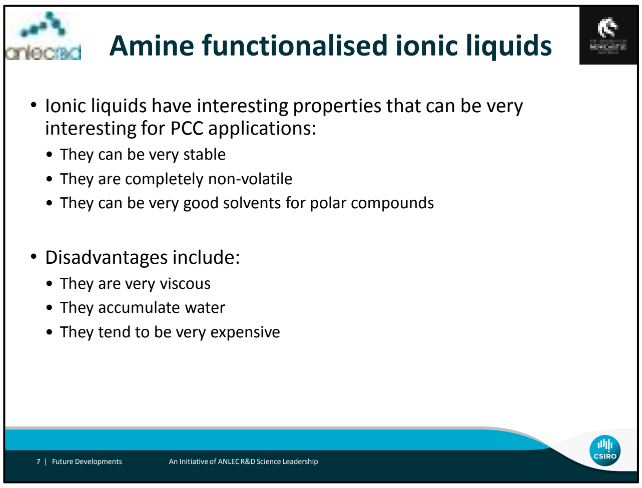

Amine functionalised ionic liquids

- 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

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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.

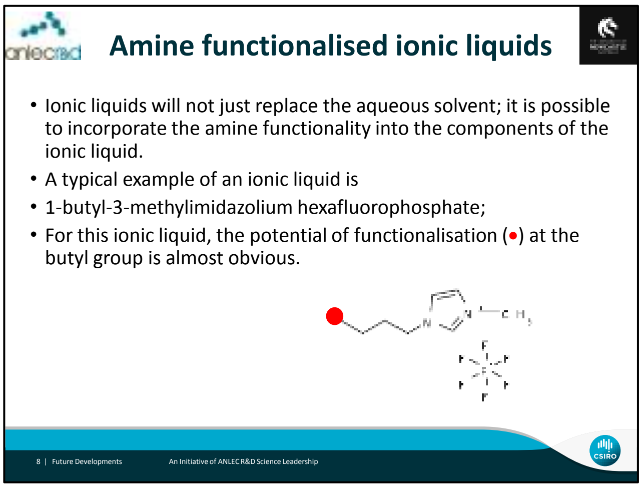
Ionic liquids have very interesting properties, some of them very attractive for PCC applications.

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.

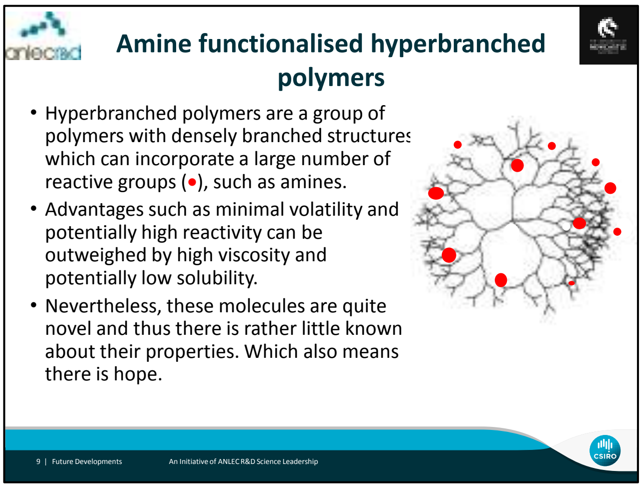
Amine functionalised ionic liquids

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.

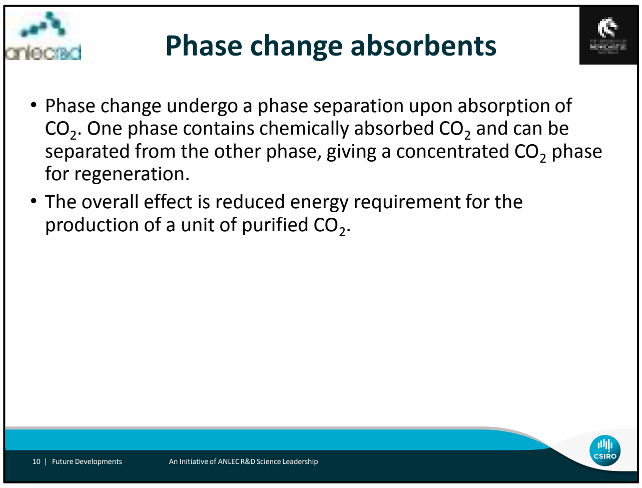
Amine functionalised hyperbranched polymers

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.