Progress in development of liquid absorbent PCC technologies at CSIRO

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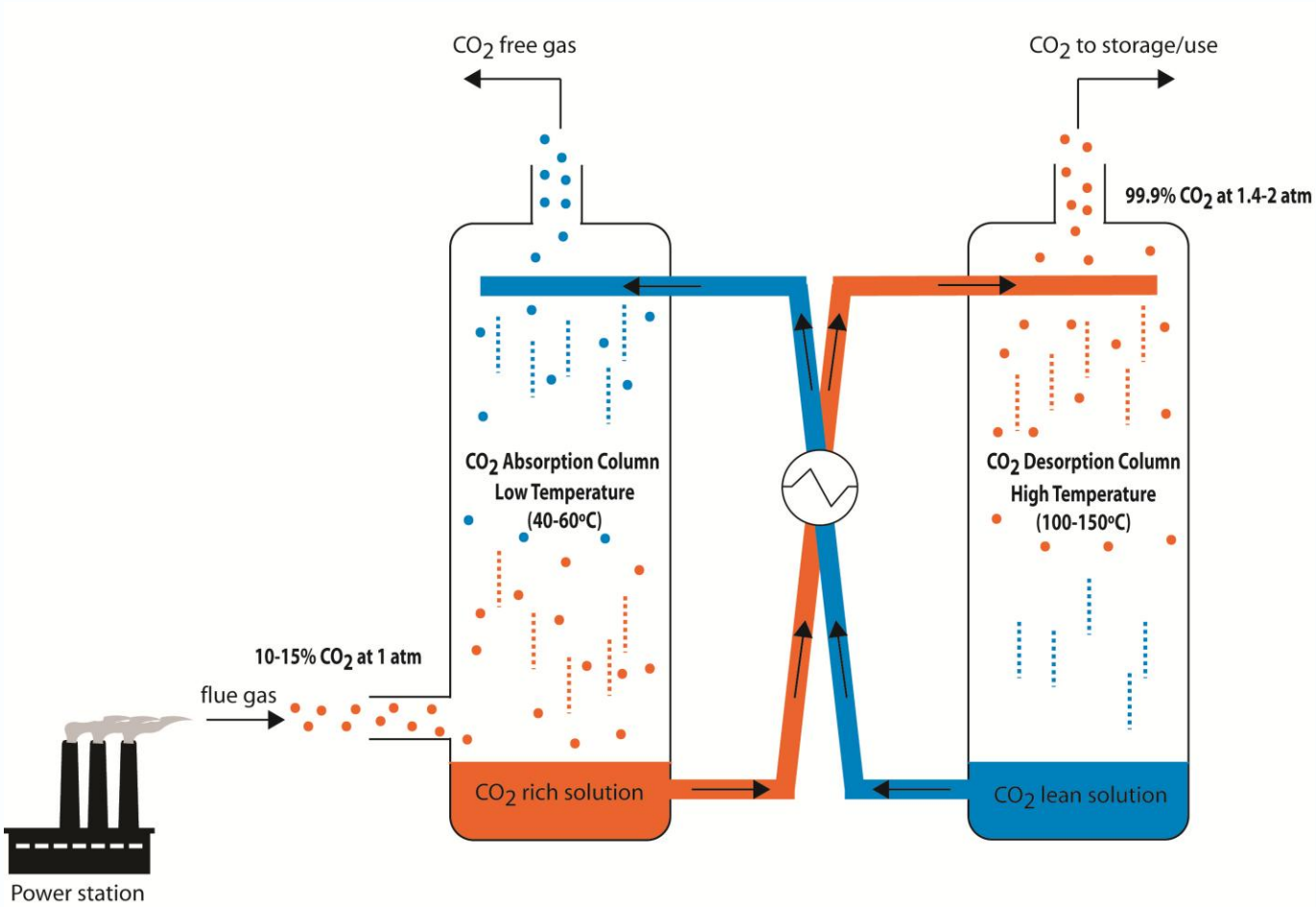
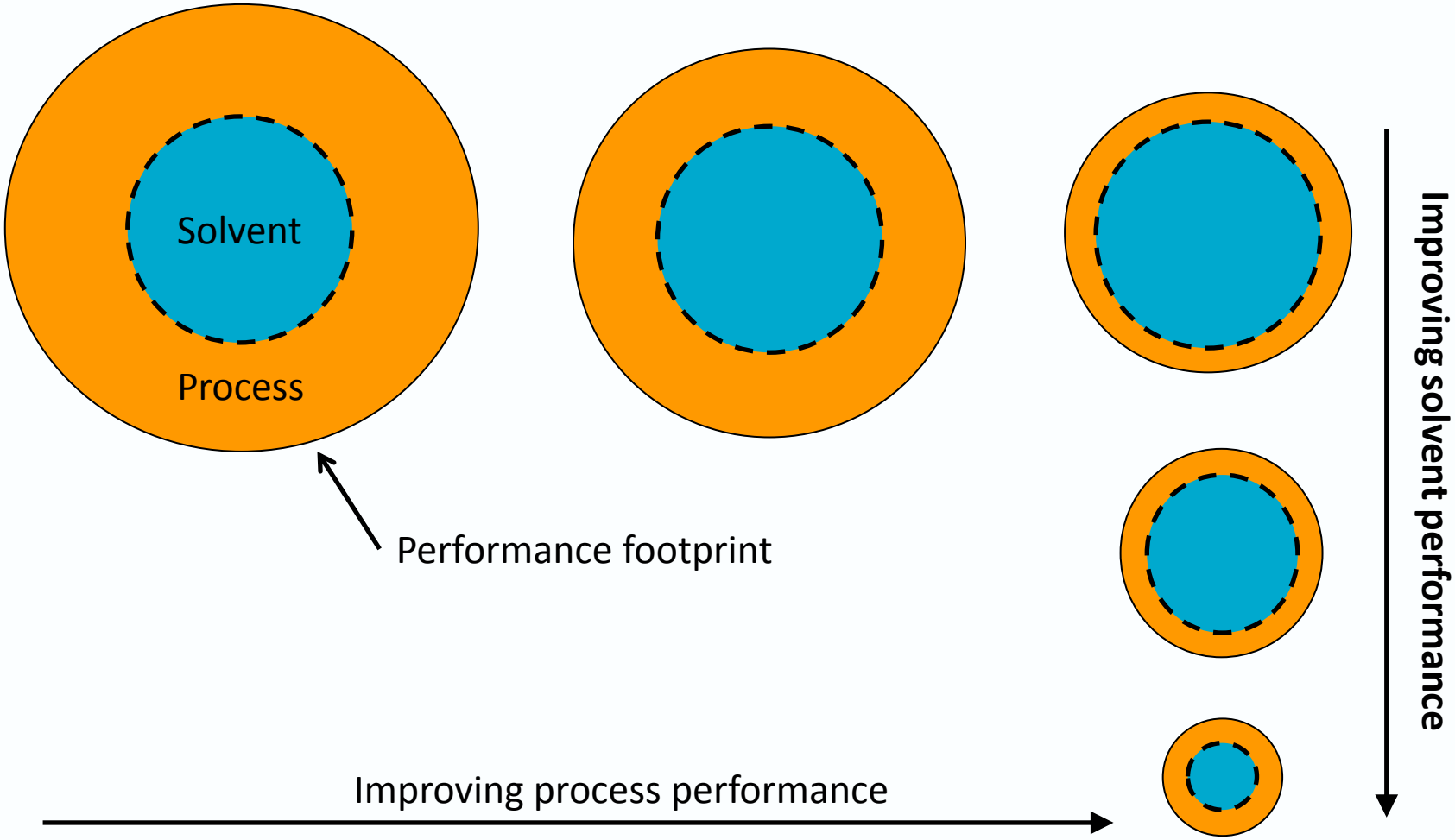
Post combustion CO_2 capture



Why do we care about the solvent?

The solvent defines the performance limits that can be achieved



The science challenges for solvent development

The flue gas environment is a challenging one for a solvent:

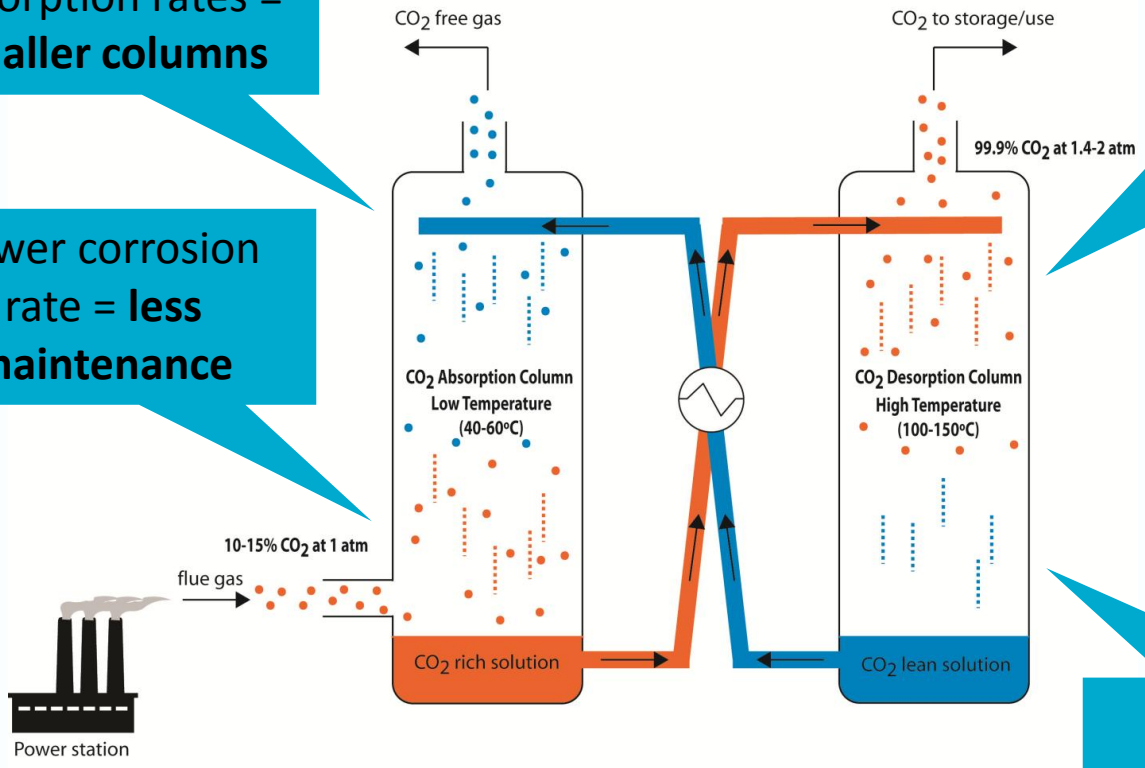
- CO_2 needs to be separated from a mixture of N_2, O_2, SO_x, NO_x and particulates
- As part of the process the solvent is continually heated and cooled (40-120°C)
- The solvent is in contact with steel

In the face of these challenges our goal is to develop solvents that deliver better performance in the following ways:

The goals for improved solvent performance

Faster CO_2 absorption rates = **smaller columns**

Lower corrosion rate = **less maintenance**

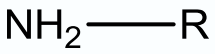


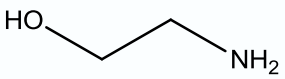
Lower rates of thermal and oxidative degradation = **longer solvent life**

Larger CO_2 cyclic capacity = **lower energy requirement**

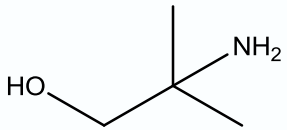
Types of solvents

Primary Amines



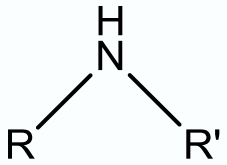


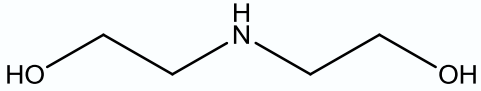
MonoEthanolAmine (MEA)



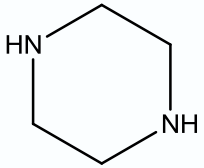
2-Amino-2-Methyl-1-Propanol (AMP)

Secondary Amines



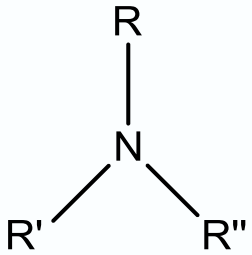


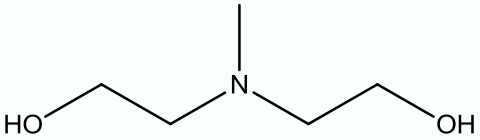
DiEthanolAmine (DEA)



PiperaZine (PZ)

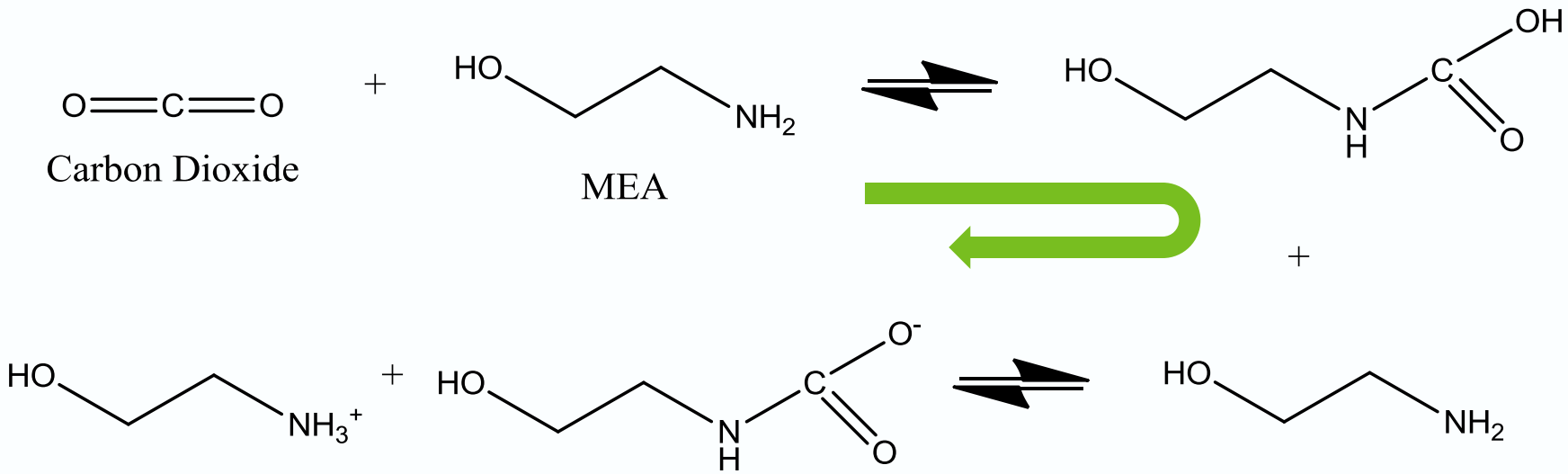
Tertiary Amines





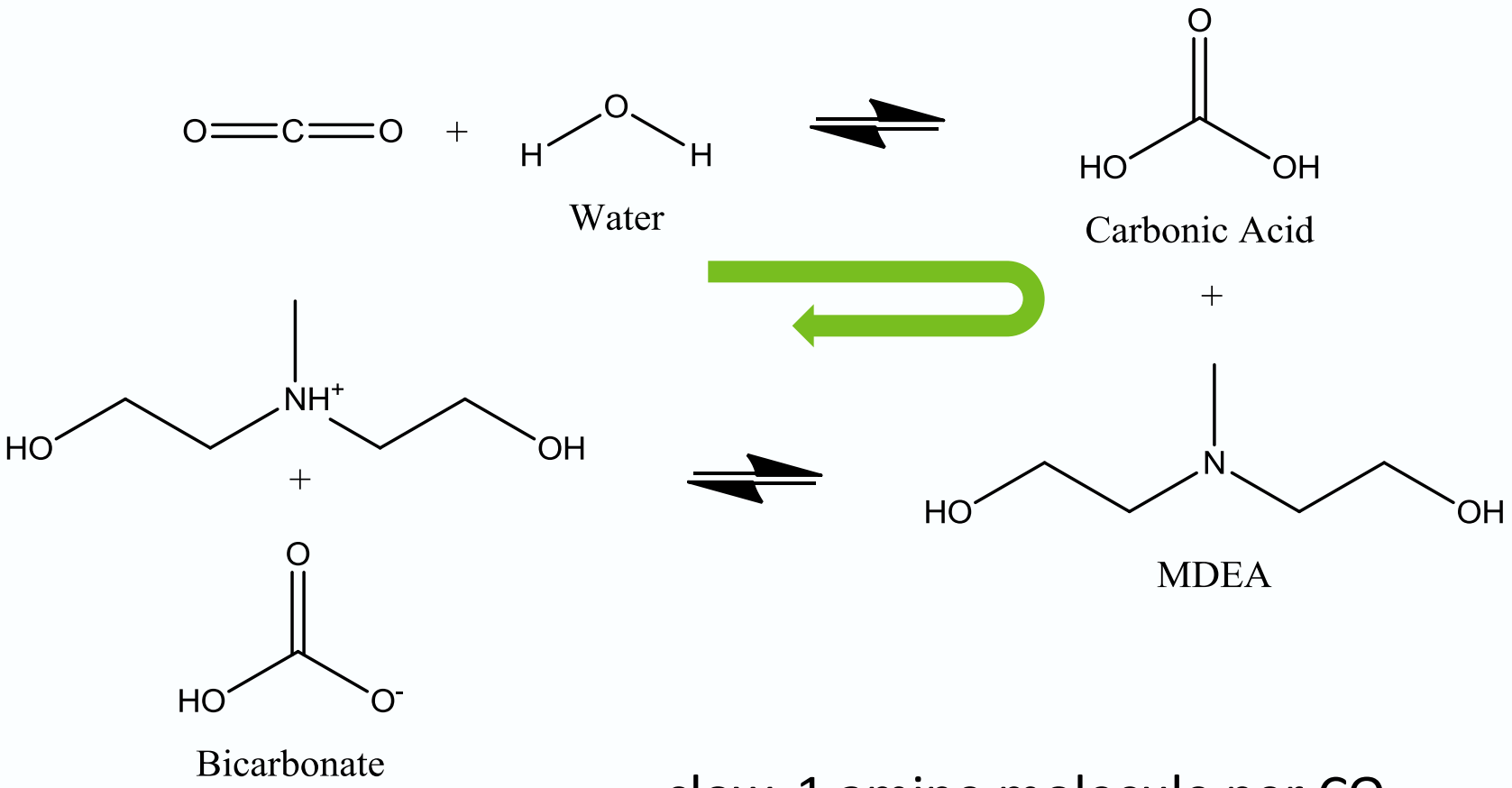
MethylDiEthanolAmine (MDEA)

Solvent chemistry – primary and secondary amines



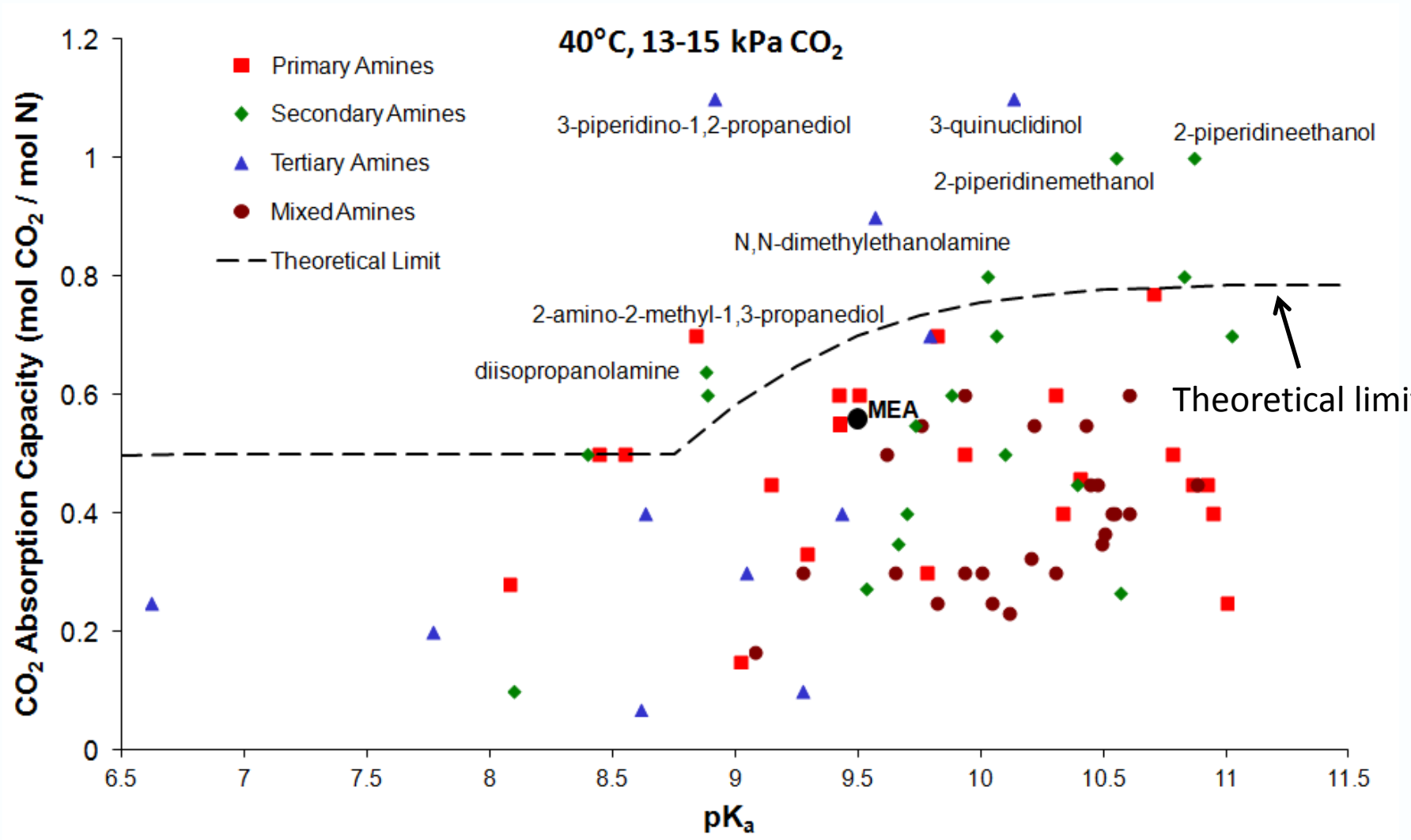
fast, 2 amine molecules per CO_2

Solvent chemistry – tertiary and hindered amines

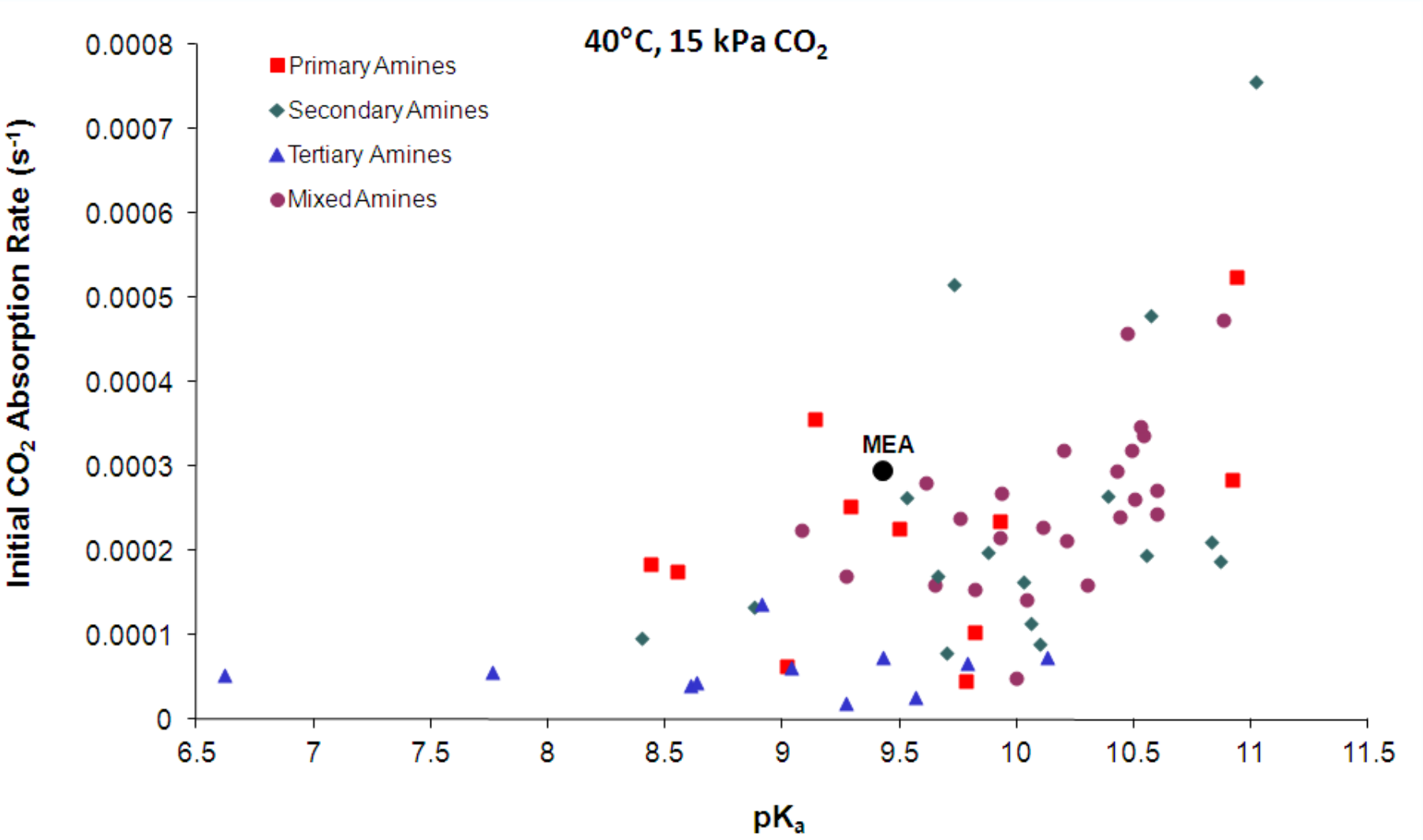


slow, 1 amine molecule per CO_2

Solvent screening – measuring CO_2 absorption capacity



Solvent screening – measuring initial CO_2 absorption rate



Screening study - outcome

Over 100 amines screened for CO_2 absorption capacity and initial absorption rate at a single set of conditions (40°C, 13-15 kPa CO_2)

A combination of model predictions and experimental results allowed identification of **7 amines that performed better than expected**

Results have been **patented and published**:

M. I. Attalla, G. D. Puxty, A. W. Allport, M. Bown, Q. Yang and R. C. Rowland, Carbon dioxide capturing process, involves contacting carbon dioxide containing gas stream with aqueous alkanolamine solution, where alkanolamine solution is selected from group consisting of Tricine and salts. WO2009121135-A1 (2009).

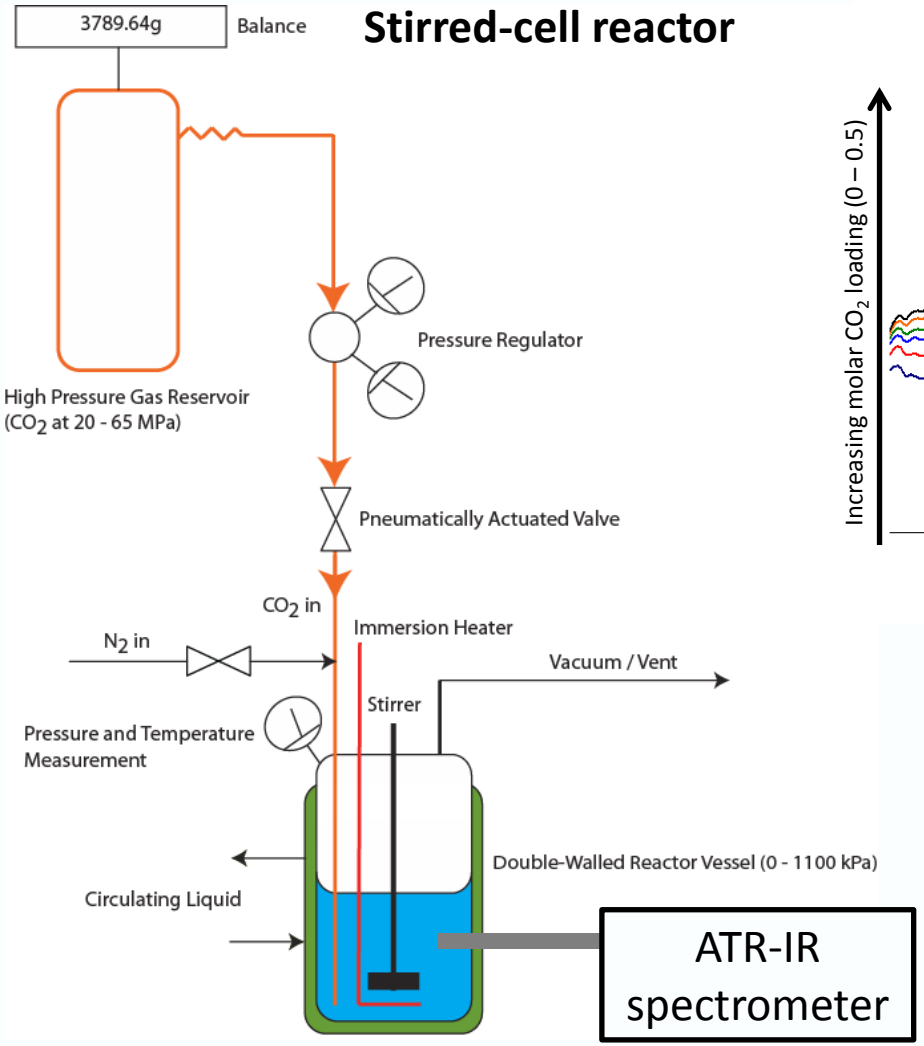
G. Puxty, R. Rowland, A. Allport, M. Attalla, Q. Yang, M. Bown, R. Burns and M. Maeder, Carbon dioxide post combustion capture: a novel screening study of the carbon dioxide absorption performance of 76 amines. *Environmental Science & Technology*, 43 (2009) 6427-6433.

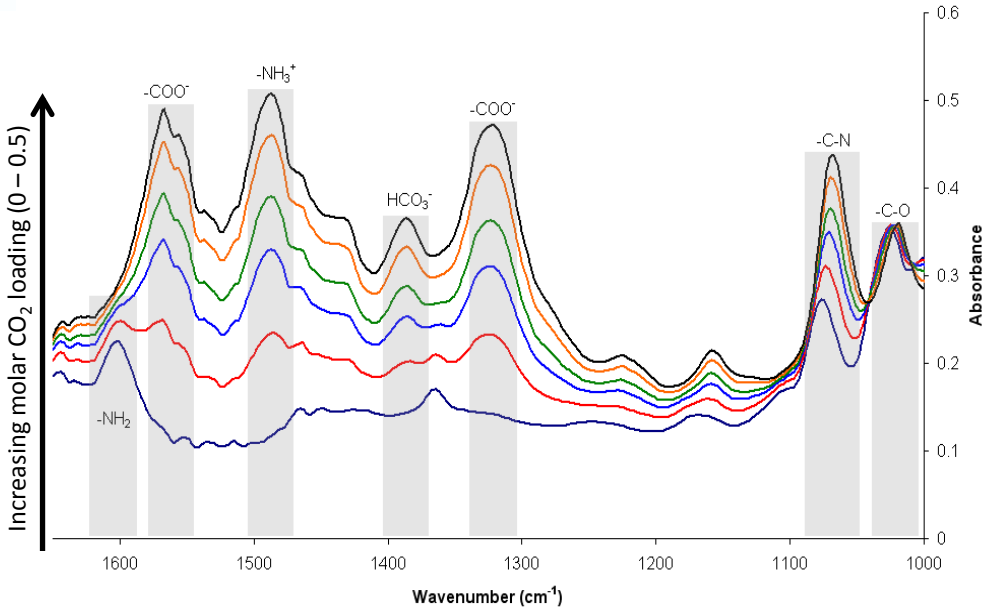
Detailed characterisation

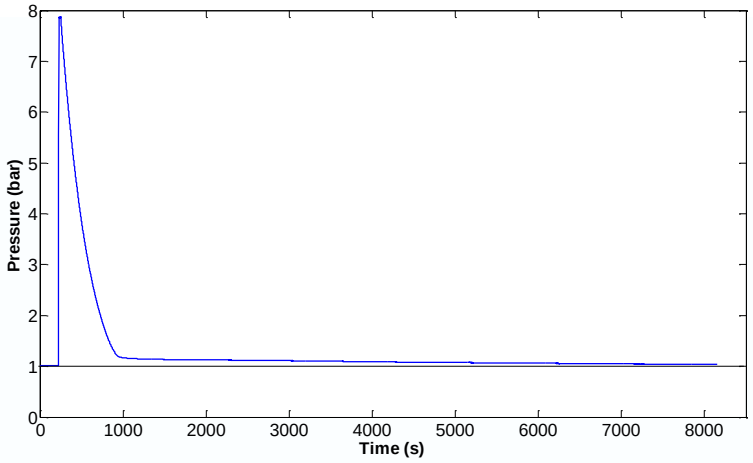
To understand the factors responsible for the performance of particular absorbents requires understanding of:

- CO_2 absorption capacity as a function of temperature and pressure
- CO_2 mass transfer as a function of temperature, pressure and loading
- Chemical reaction kinetics and thermodynamics
- Physical properties

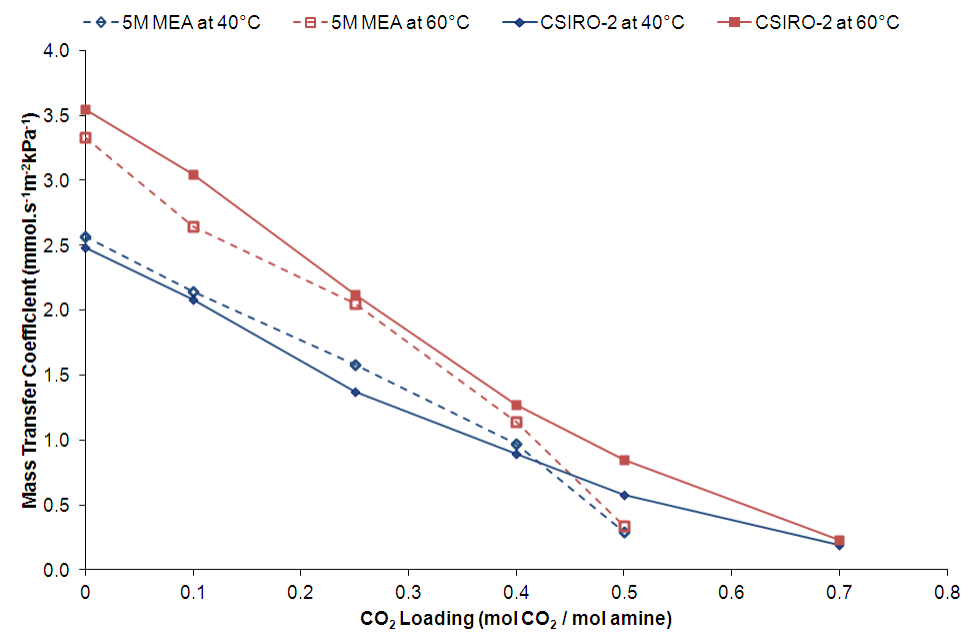
Detailed measurements of capacity





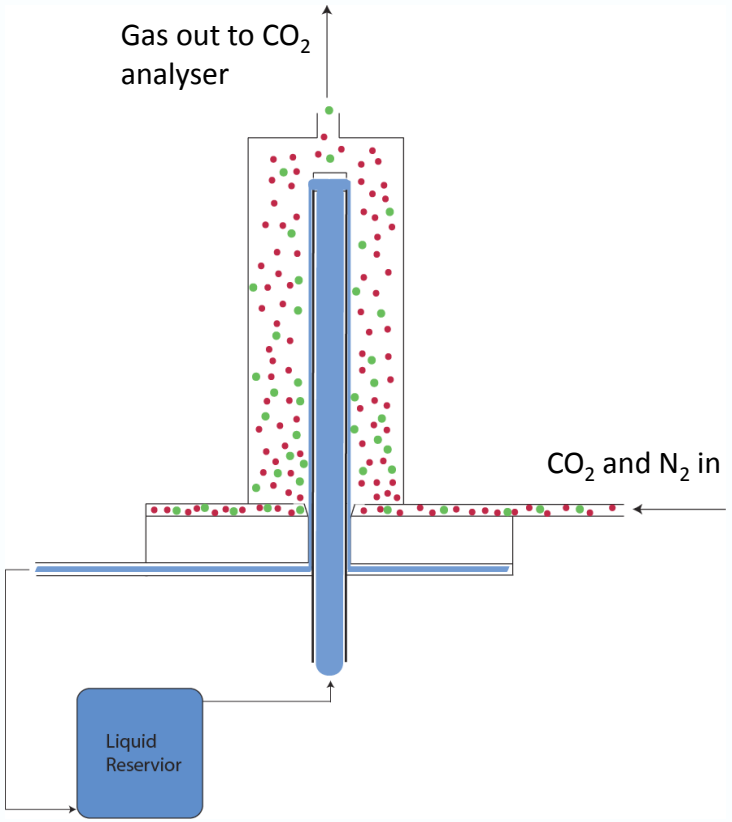


Detailed measurements of mass transfer



$$N_{CO2} = K_G(P_{CO2} - P^*_{CO2})$$

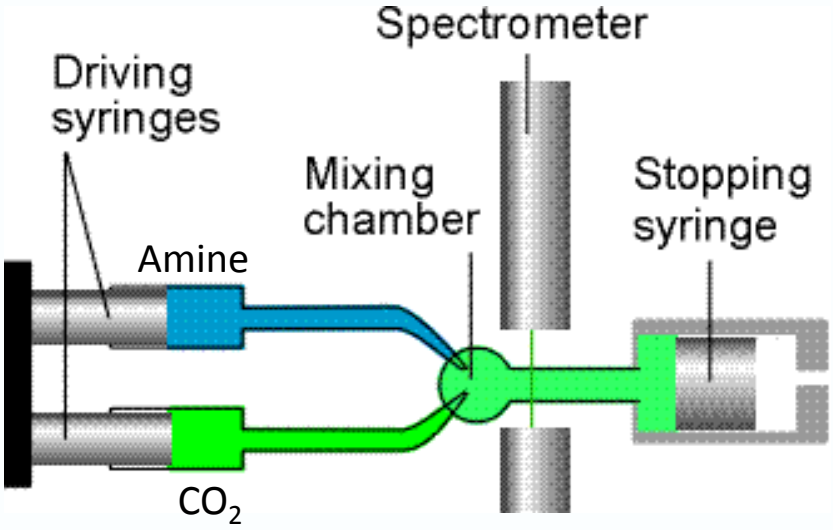
Wetted-wall reactor

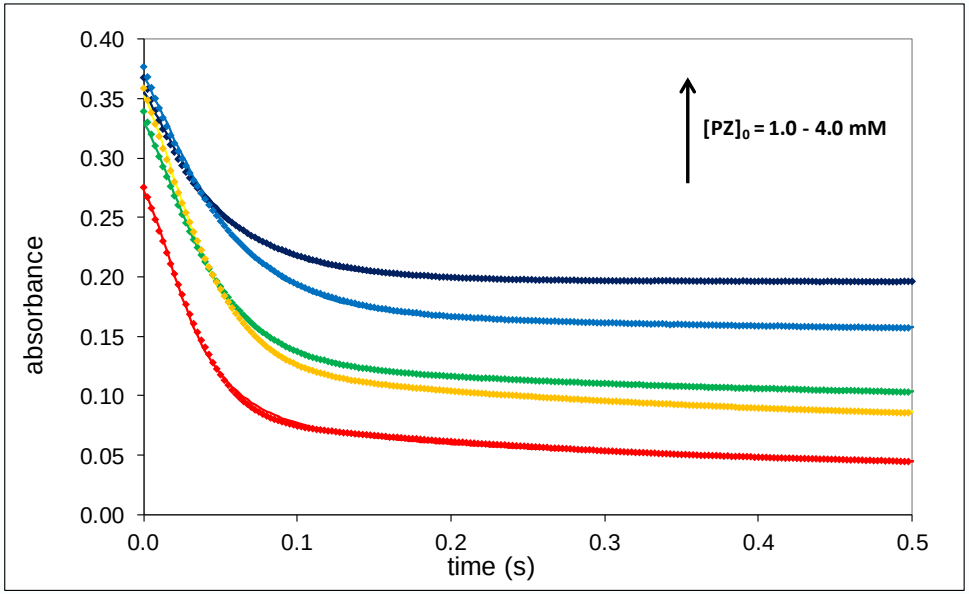


Chemical reaction kinetics and thermodynamics

Stopped-flow and UV-visible spectroscopy used to determine CO_2-amine reaction kinetics

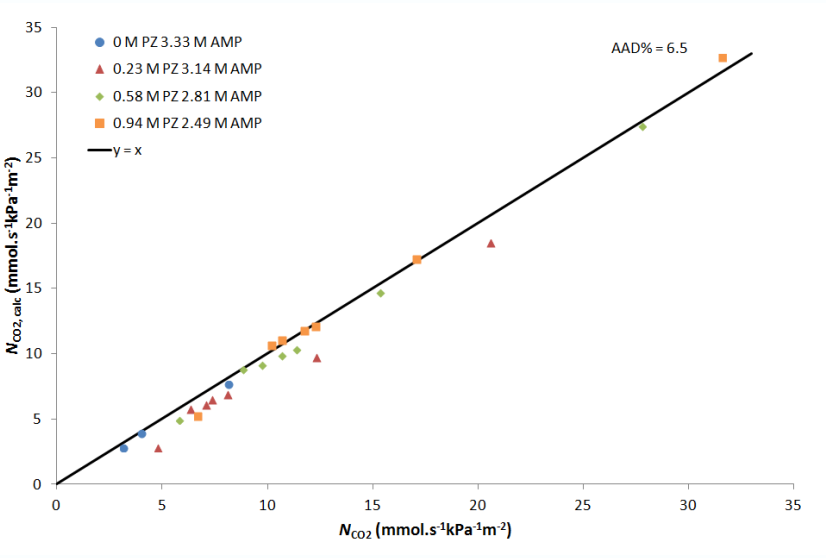
^{1}H-NMR used to determine CO_2-amine reaction equilibria

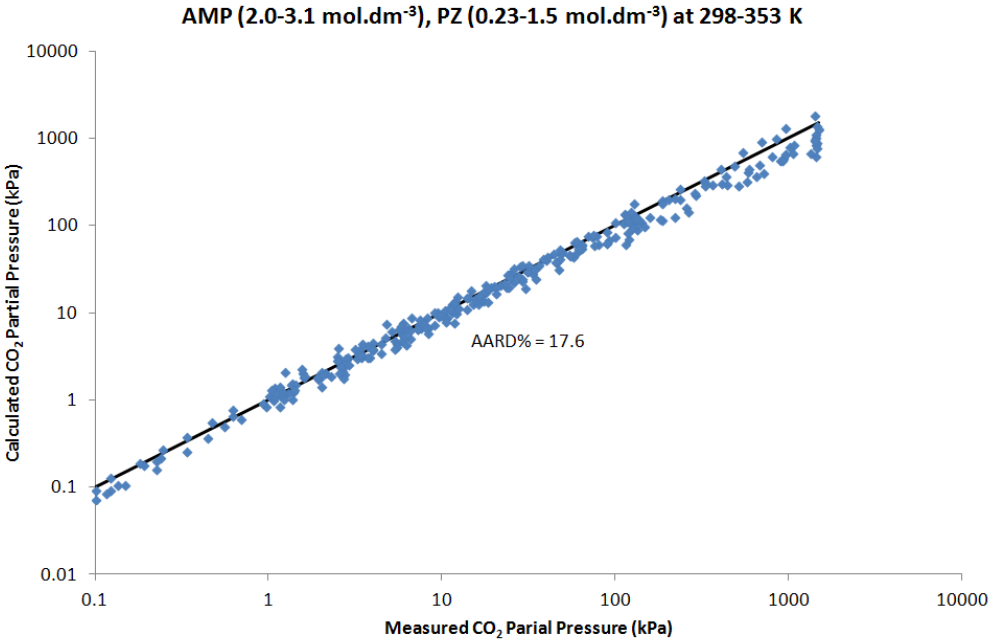




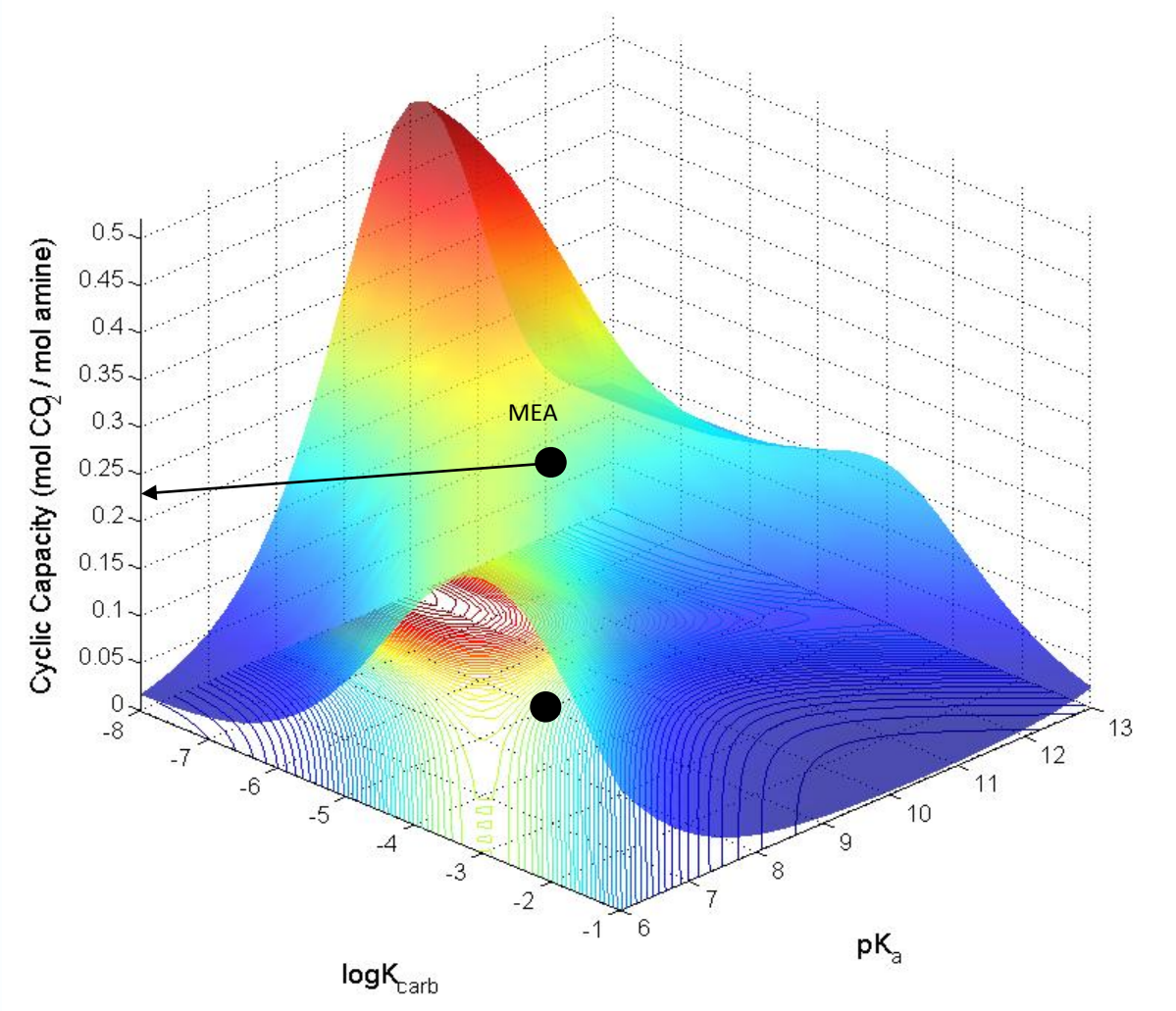
Modelling of chemical behaviour

Once the chemical and physical properties are known we can model absorption behaviour across a range of conditions including as mixtures





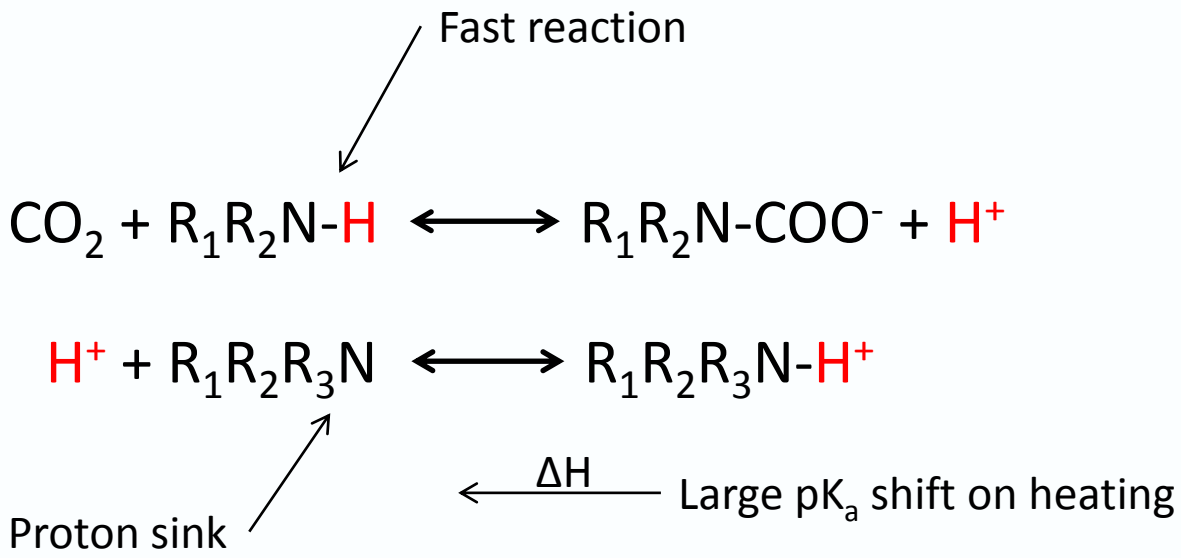
Modelling of chemical behaviour



What we learnt - Solvent formulation

No single *known* amine can deliver optimal performance due to a trade-off between absorption capacity and absorption rate

Detailed characterisation allows solvent formulations, or amine mixtures, to be designed that yield better performance than any single amine and tuned to the application



CSIRO solvent formulations

Four new CSIRO solvent formulations:

CSIRO-1 Designed to minimise the solvent regeneration energy requirement while maintaining reasonable absorption rates

CSIRO-2 Designed to maximise absorption rate while maintaining reasonable regeneration energy requirements

CSIRO-3 Designed to have increased absorption rates and better physical properties than CSIRO-1 while maintaining low regeneration energy requirements

CSIRO-4 Under development but will hopefully deliver increased absorption rates with a similar energy demand to CSIRO-3

Estimating solvent performance

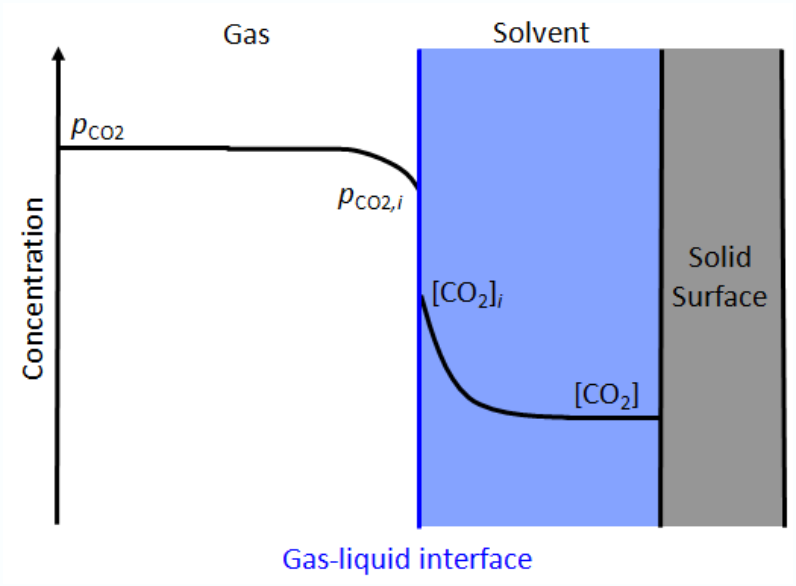
To allow a **fair comparison** solvent performance needs to be evaluated at optimal operating conditions

Estimate the **optimal energy requirement** using an equilibrium model:

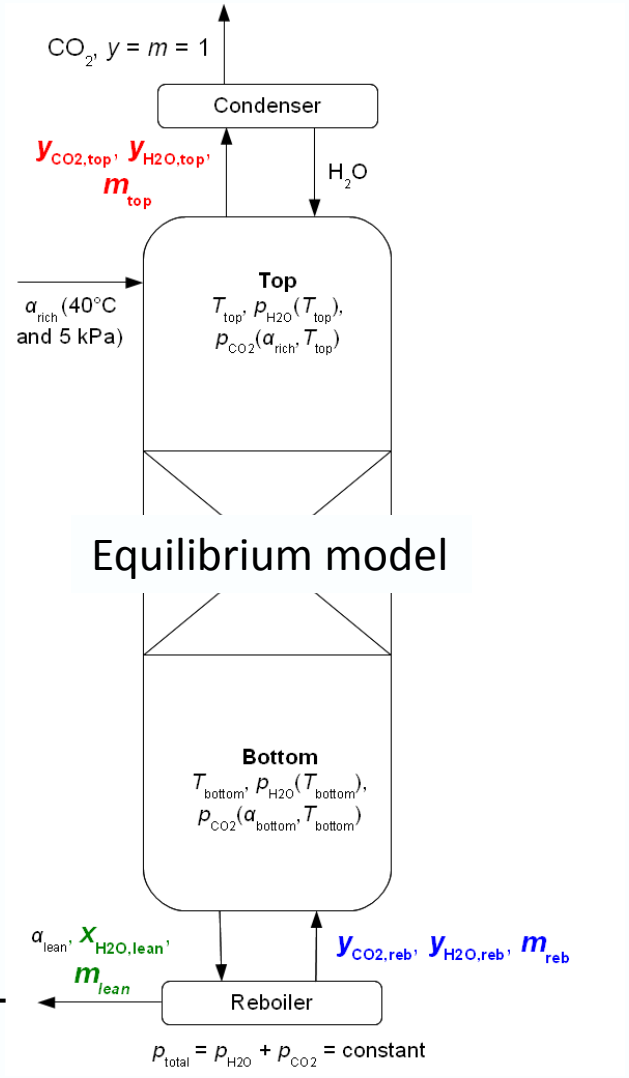
- Rich loading (α_{rich}) is fixed at 40°C for 5 kPa CO_2
- Optimise stripper bottom temperature and lean loading (α_{lean}) for minimum reboiler energy requirement (assume isobaric)

Estimate the **log mean mass transfer coefficient** for the absorber assuming 40°C and using α_{rich} and α_{lean} values from the stripper optimisation

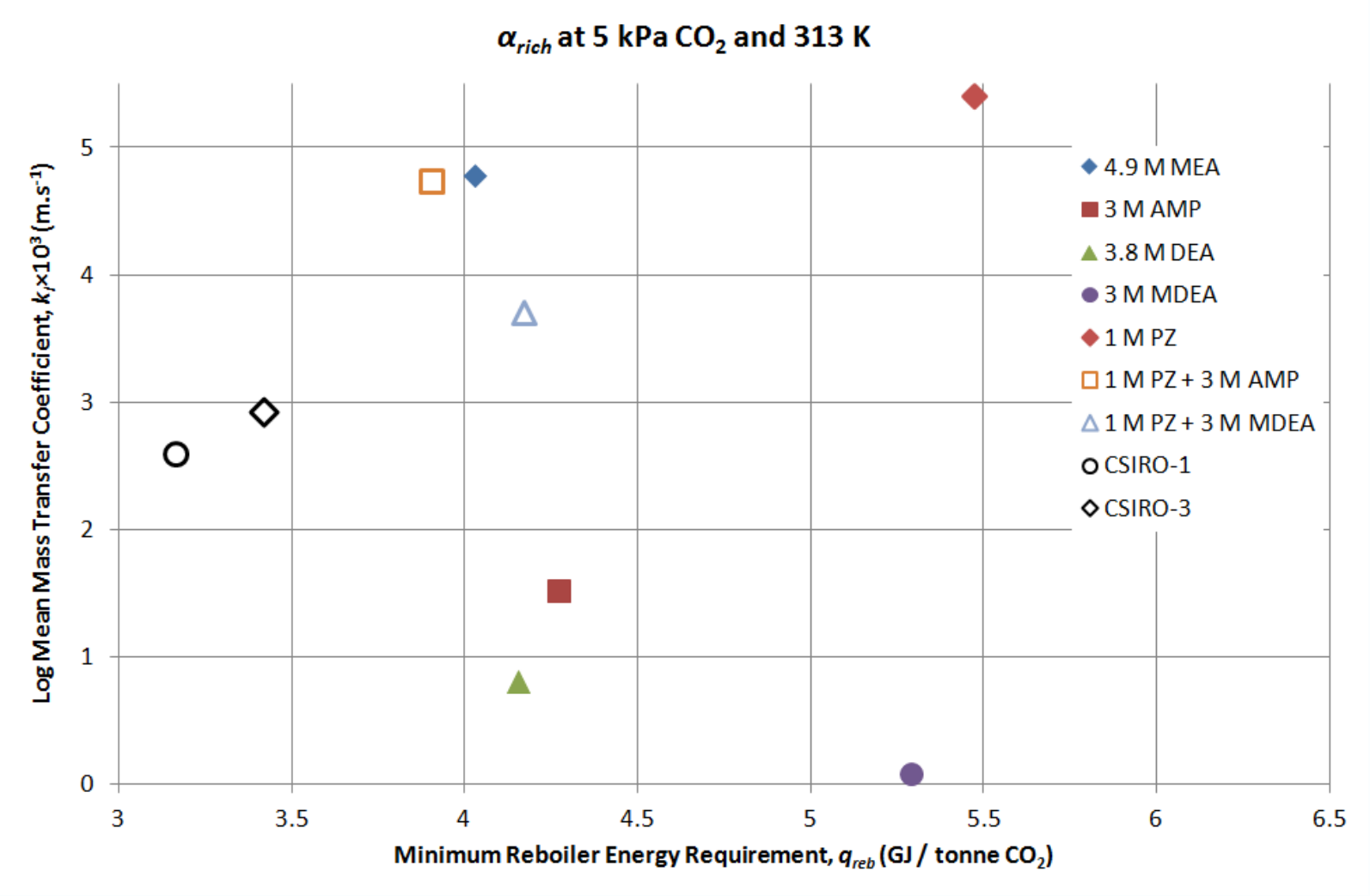
Estimating solvent performance



Dynamic model

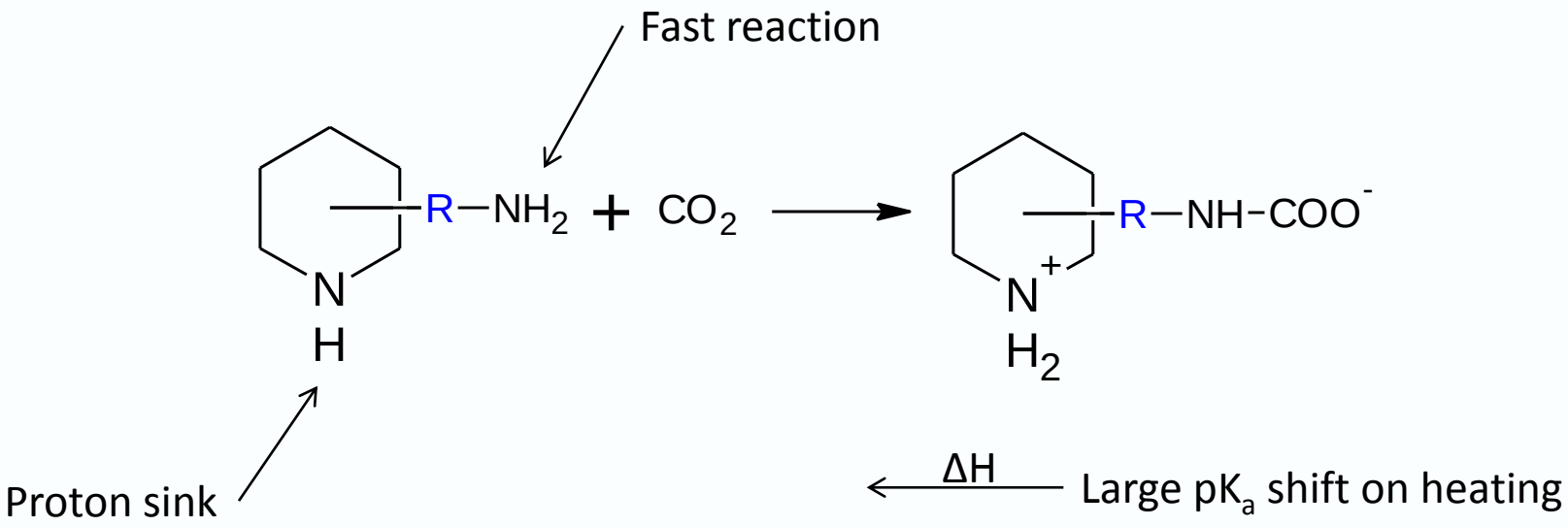


Estimating solvent performance



Molecular design of new amine molecules

The same design philosophy as for solvent formulations but in one molecule

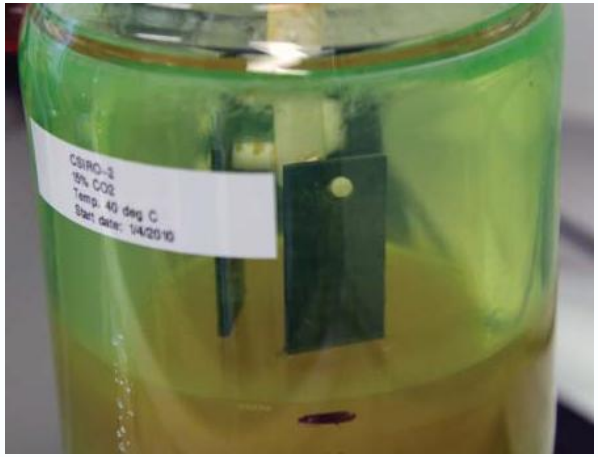


Corrosion – CSIRO-1 < CSIRO-2 = MEA

Corrosion studies were carried out according to ASTM G31-72

- Mild steel tokens were left in contact with solvents for 6-8 weeks at process relevant conditions
- Corrosion extent was determined by mass change

Solvent	Corrosion Rate (mm / yr)
5 M MEA	0.73
CSIRO-1	**0.54**
CSIRO-2	0.71



Less corrosion = less maintenance

Thermal degradation

- Samples were heated in closed stainless steel reactor vessels at 135°C for up to 8 weeks
- At regular intervals samples were collected and analysed for mass loss and degradation product formation
- Preliminary results indicate **CSIRO-1 and CSIRO-2 show greater thermal stability** than MEA

Greater thermal stability = longer solvent life

Summary

The screening study identified a **number of** candidate **amines with better** than expected **performance** forming the basis of a patent

Detailed characterisation and modelling has allows the development of **3 CSIRO solvent formulations** to-date with a 4th in the pipeline

A number of these are moving into pilot plant testing

There is still **scope for greater improvement** through a combination of experiment and modelling and this work is ongoing

The assessment and improvement of CSIRO solvents will lead to commercially valuable solvent options for industry in the near term

This work has been presented in **over 40 journal articles and conference publications**

Looking to the future

The application of our formulation design philosophies to the **design of new single molecules** will allow even better performance

Further enhancements will be achieved by **looking beyond amines** to:

- **Enzymes** such as carbonic anhydrase to enhance absorption rates
- **Ionic liquids** and their favourable physical properties for a clean and low energy process
- Moving towards a **light driven process** rather than a heat driven one that can utilise solar energy

The team behind this work

CSIRO CET

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Andrew Allport
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Craig Grimmond
Phil Jackson
Kelly Robinson

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Mat Ballard
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Thank you

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