Document 13

From: Feron, Paul (DET, Newcastle)
To: "Boon, Ann"
Cc: Wright, John (DET, Newcastle); Brockway, David (DET, Newcastle); Smitham, Jim (DET, Newcastle); Briggs, Cameron (ET F/ship, North Ryde); Narasimhan, Anjana (DET, Newcastle); McGregor, James (DET, Newcastle); Attalla, Moetaz (DET, Newcastle); Cottrell, Aaron (DET, Newcastle)
Subject: PCC China Progress report A
Date: Tuesday, 3 June 2008 2:54:04 PM
Attachments: [S22] DELETION
TPRI CSIRO PCC TRAINING MATERIAL.pdf

Dear Ann,

Find enclosed our first progress report on APP PCC-China project. The two attachments to this progress report relate to:
- The design specifications as provided by CSIRO (NPCC pilot plant design)
- The PCC theoretical training package as delivered to the Chinese visitors (TPRI CSIRO PCC Training Material).
Also for this project we will supply the financial detalils at the end of this week.
I am looking forward to receiving your feedback on this report.

Best regards,

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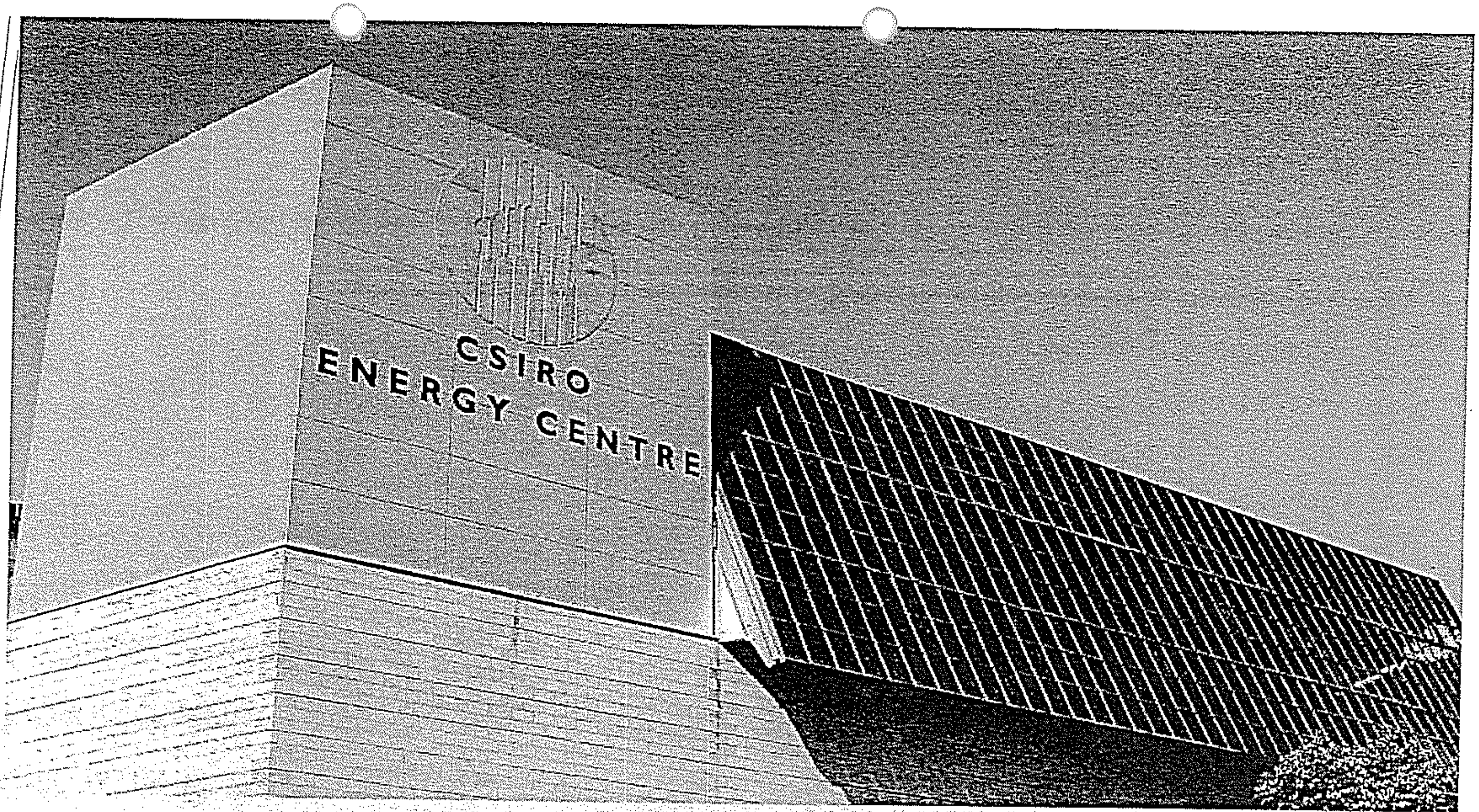

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Post-combustion CO_2 capture at CSIRO

Presentation to TPRI/China Huaneng
5 May 2008

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- Present at the meeting from CSIRO
- Moetaz Attalla
- Paul Feron
- Graeme Puxty
- Rob Rowland
- Andrew Allport
- Phil Jackson
- Kelly Robinson

Day Schedule

10:00 – 12:30: Presentations

12:30 – 13:30: Lunch (in boardroom)

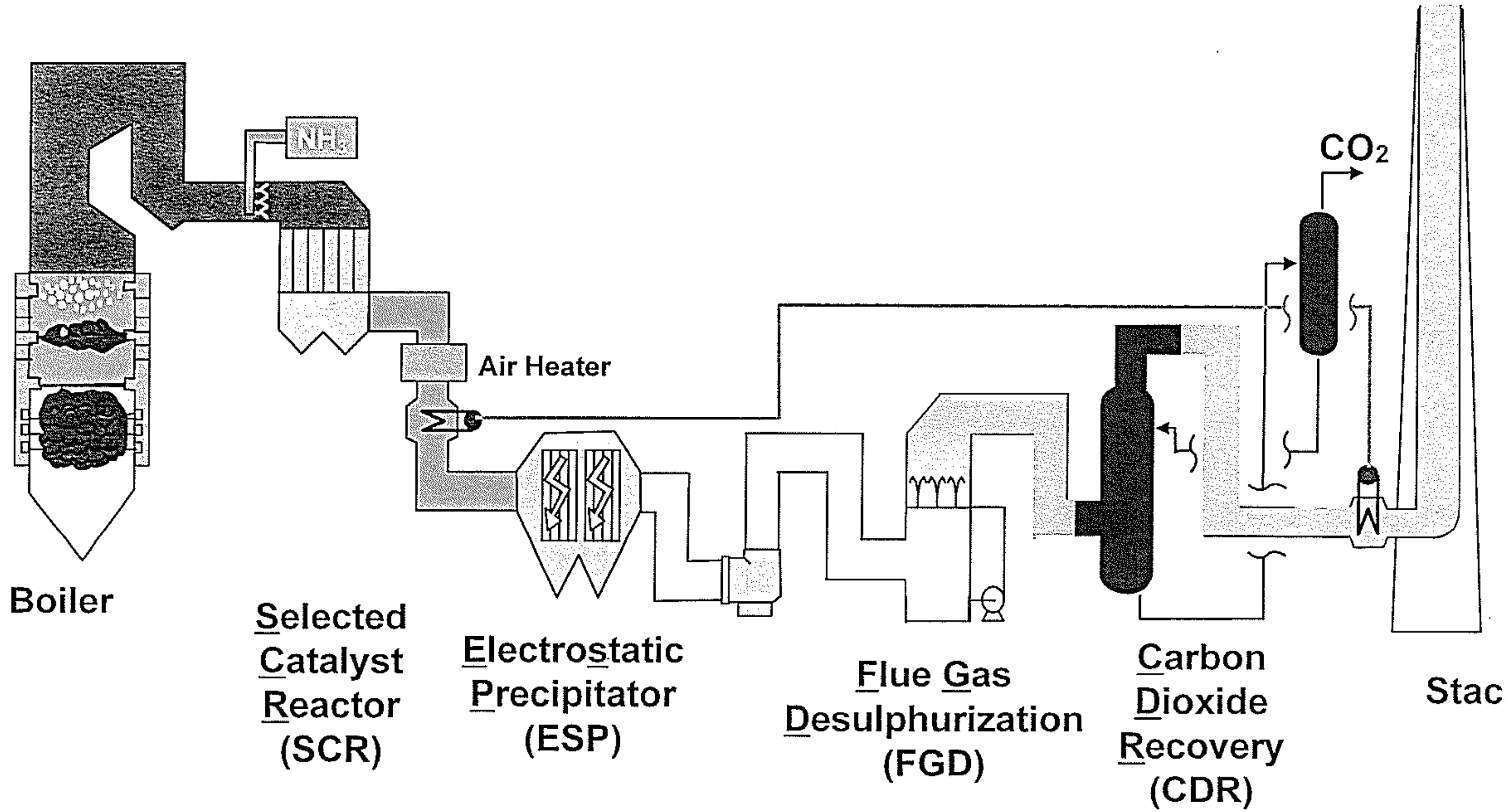
13:30 – 14:00: Lab Tour

14:00 – 14:30: Site Tour

Programme Overview

1. Introduction and overview of CSIRO's PCC project
2. Overview of the novel solvents research program and modelling
3. Absorption kinetics measurements of solvent systems for CO_2 capture
4. Oxidative degradation of CO_2 capture solvents
5. Laboratory scale CO_2 absorption/desorption apparatus

Post-combustion CO_2 capture (PCC)
CO_2-removal from coal fired power station



Source: Mitsubhishi Heavy Industries

Why prefer PCC?

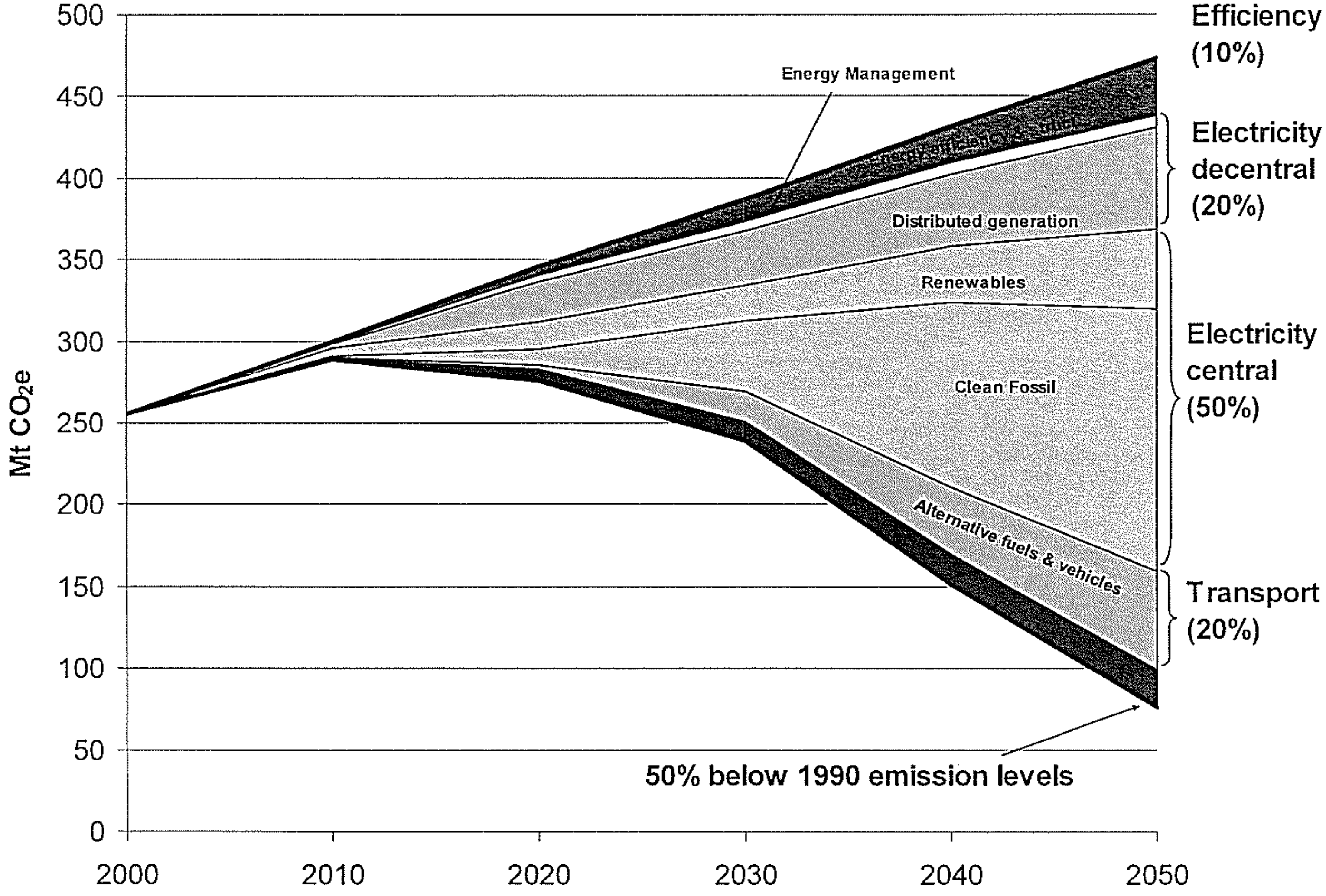
- Low technology risk
- Flexible operation, in tune with market requirements
- Ability to adopt technology improvements, providing pathway toward zero-emissions
- For new and retrofit applications, preventing stranded assets

PCC application in 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
- Flue gas temperature
  - Black coal: 120 °C
  - Brown coal: 180 °C
- Cooling water: 1.5-3.0 m^3/MWh

Data used from CCSD – technology assessment report 62

Emission reduction pathway for Australia



Source: Energy Futures, Paul Graham, CSIRO

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Known issues with PCC in coal fired power stations

- High cost: around $40-60/t CO_2 avoided
- Electricity cost increase from $30/MWh to $50/MWh for an 85% reduction in GHG
- Loss of generation efficiency around 20-30% to capture 90% of CO_2
- Not demonstrated in integrated power plants scale
- Sensitive to O_2, SOx and other flue gas constituents
- Large increase in cooling water requirement

PCC programme at CSIRO

Integrated PCC R&D Programme

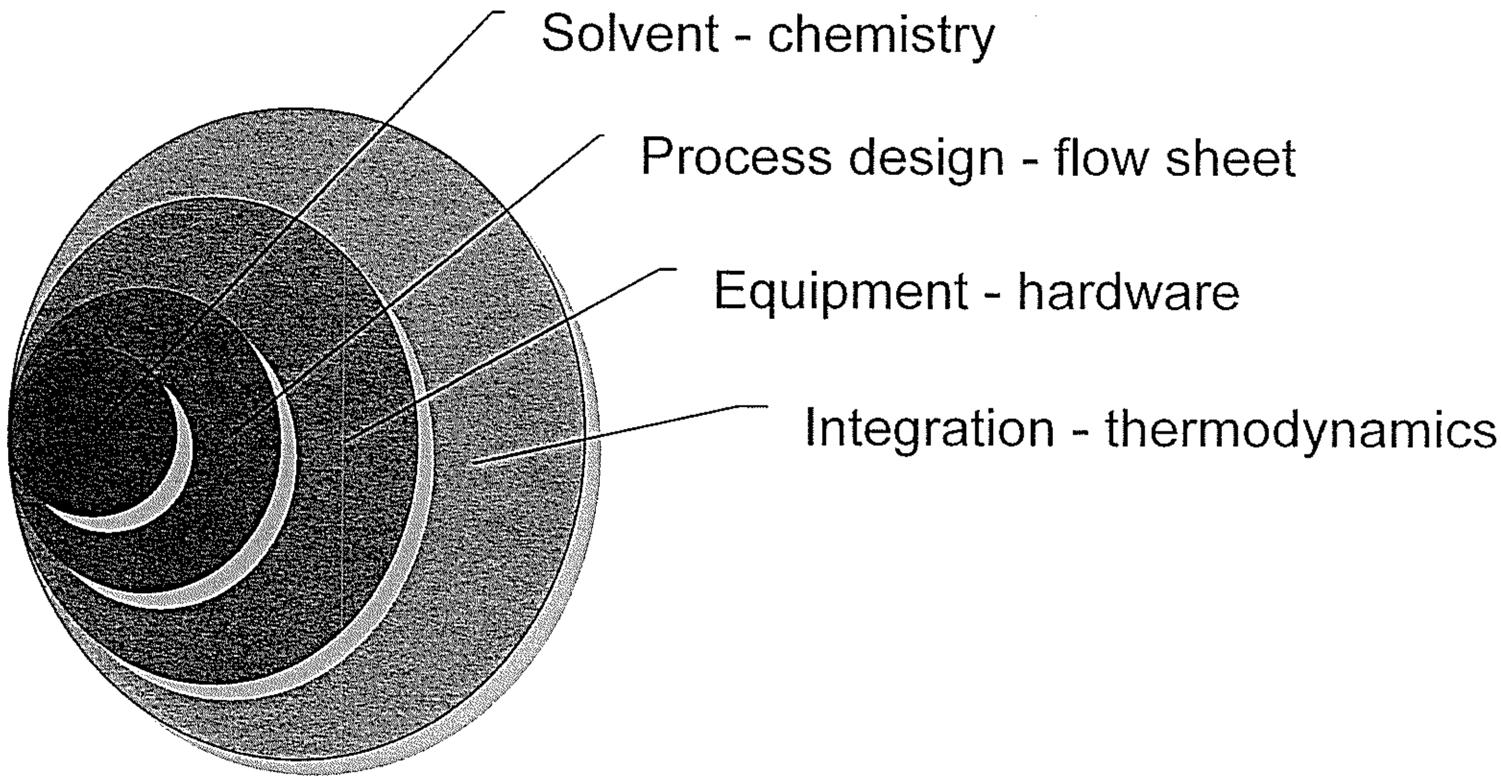
Pilot plant programme (Learning by doing)

- Hands-on experience for future operators
- Identification of operational issues and requirements
- Testing of existing and new technologies under real conditions

Lab research programme (Learning by searching)

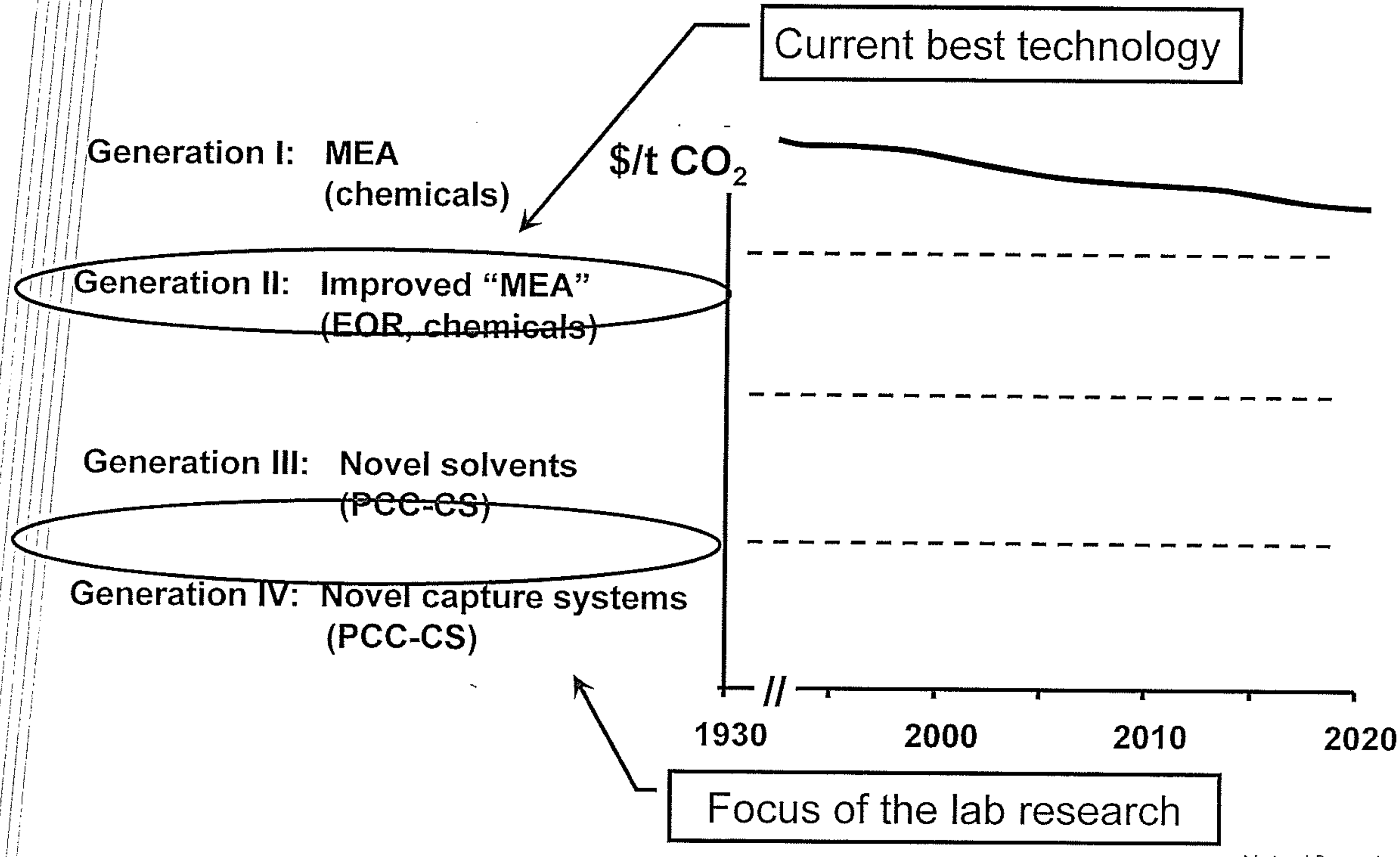
- Support to pilot plant operation and interpretation of results
- Develop novel solvents and solvent systems which result in lower costs for capture
- Addressing Australian specifics (flue gases, water)

Lab Research: Solvent system development



A holistic approach is essential!

Development Pathway for PCC



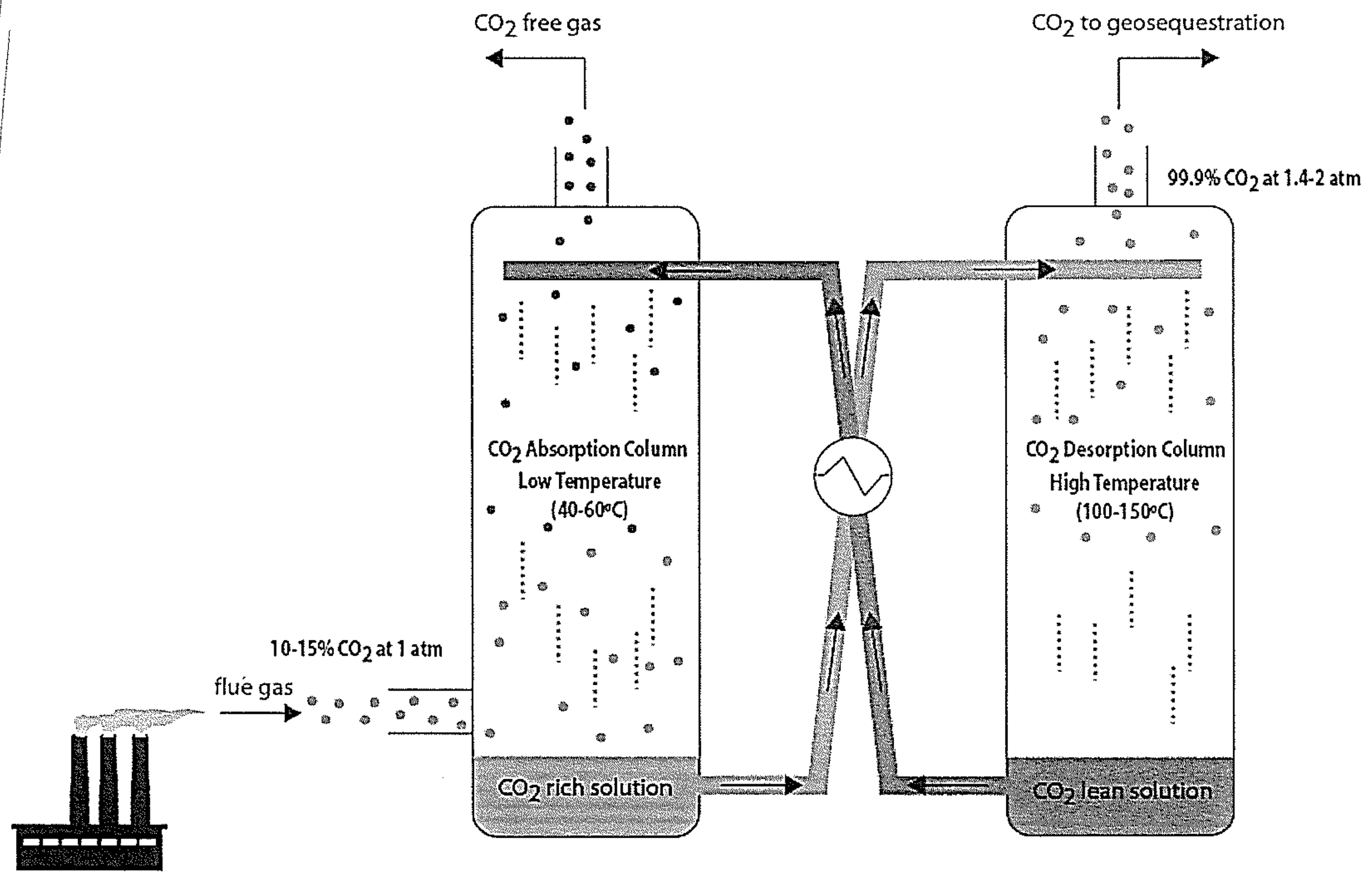
Post Combustion Capture (PCC) of CO_2 Research Program

Novel Solvent Development

PCC Options

- A range of physical and chemical methods exist to separate CO_2 from other gases
- Physical separation
  - Physical separation based on selectivity and a driving force
  - Membrane separation or adsorption
  - Zeolites, metal-organic frameworks, etc
  - Development needed to improve selectivity and performance at low pressure and low CO_2 concentration
- *Reactive chemical absorption*
  - Absorption into a liquid followed by chemical reaction
  - Amine or carbonate systems
  - Works well at low pressure and low CO_2 concentration
  - A mature technology
  - Development needed to improve performance at power station scale and flue gas conditions

PCC using Reactive Chemical Absorption



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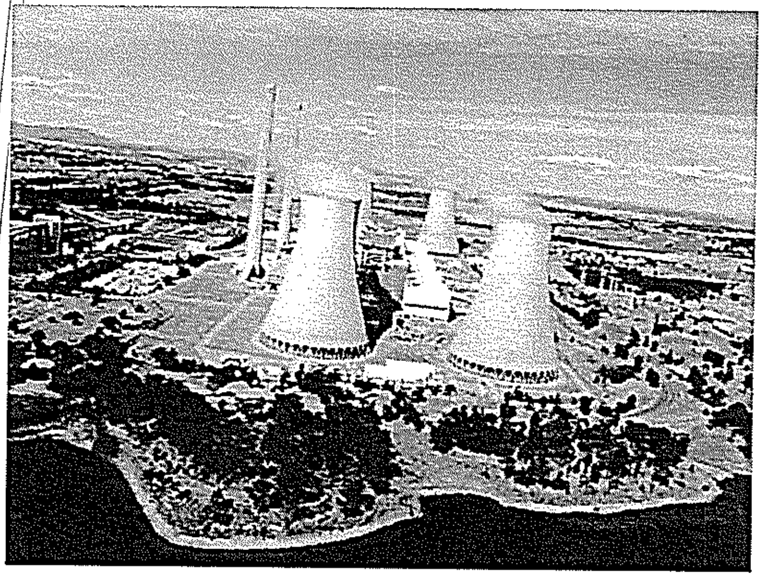
PCC Solvent Challenges



Typical Australian Power Station, 4×660 MW

- Increase CO_2 loading and cyclic capacity
- Increase the rate of absorption/desorption
- Decrease stripping energy requirement

- Resistance to oxidation
- Resistance to thermal degradation
- Impact of SO_x, NO_x and fly ash
- Corrosion
- Toxicity

The Novel Solvents Research Program

Generation I
Traditional capture solvents –
MEA, K_2CO_3/promoter, ...

Generation II
Modern capture solvents –
MDEA/PZ, AMP/PZ, ...

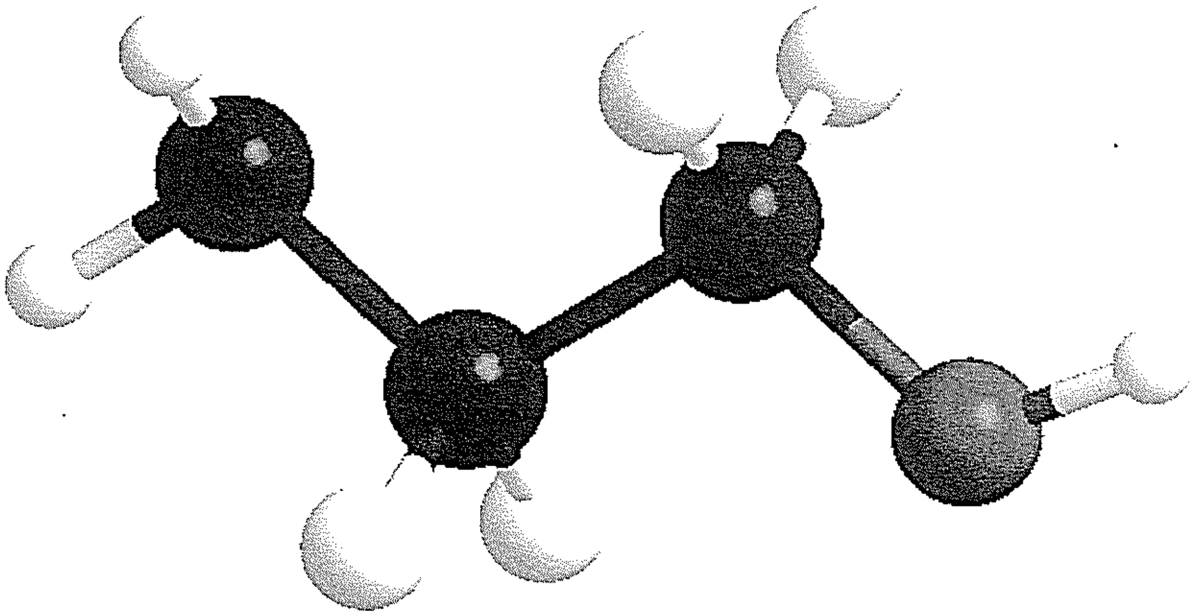
Generation III
Novel aqueous solvents –
novel amines, promoters, ...

Generation IV
Novel solvent systems –
ionic liquids, enzymes, ...

Alkanolamine Properties

Monoethanolamine (MEA)

Short carbon chain:
simple, reduces cost of amine

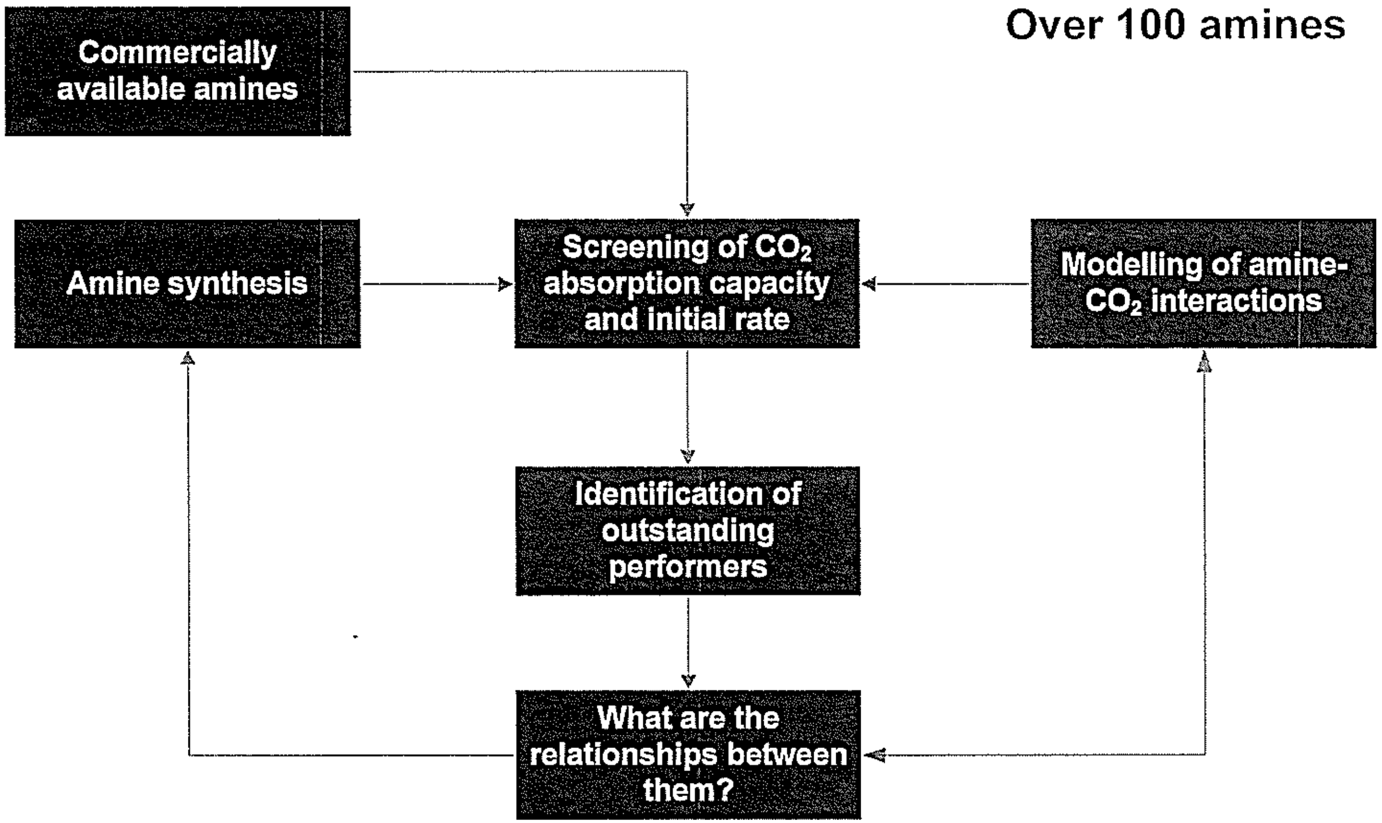


Nitrogen:
basic func
reacts witl
other acid
acts as a Brønsted base

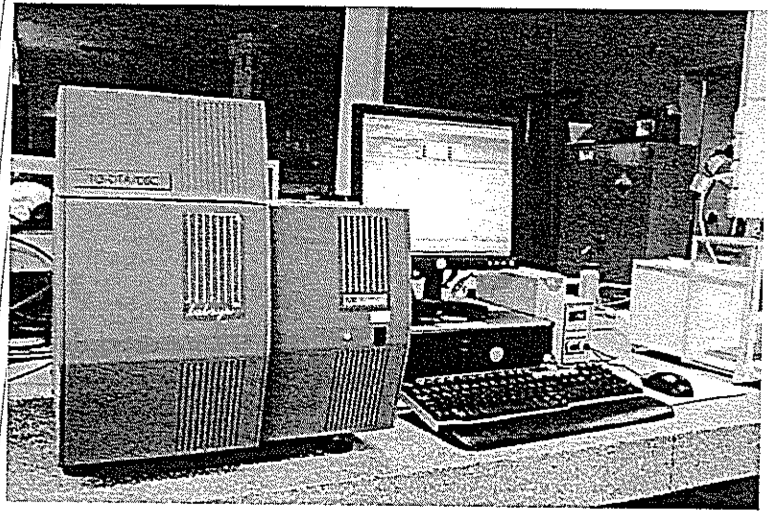
reduces volatility
increases solubility

Screening Study and Modelling

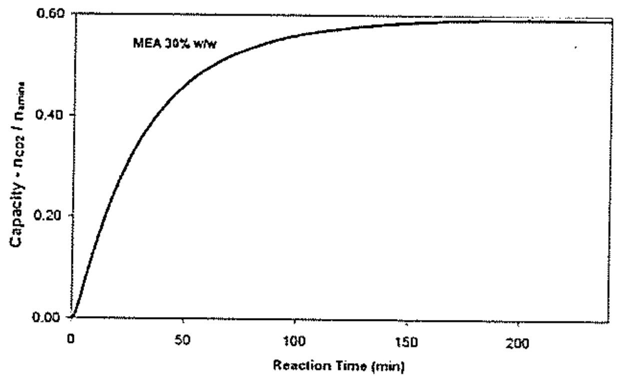
Over 100 amines



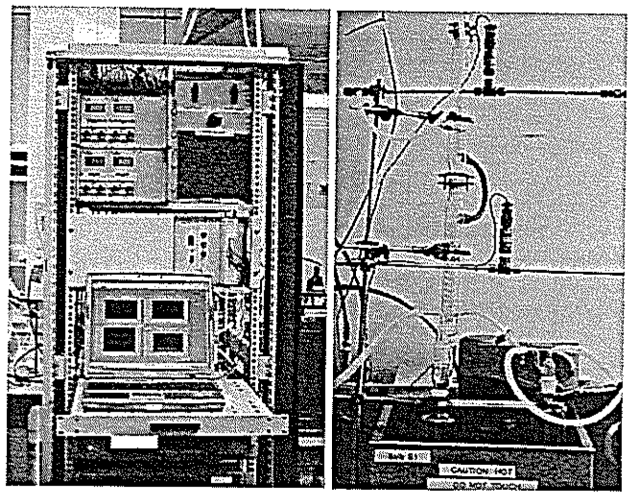
Screening of Capacity and Initial Rate



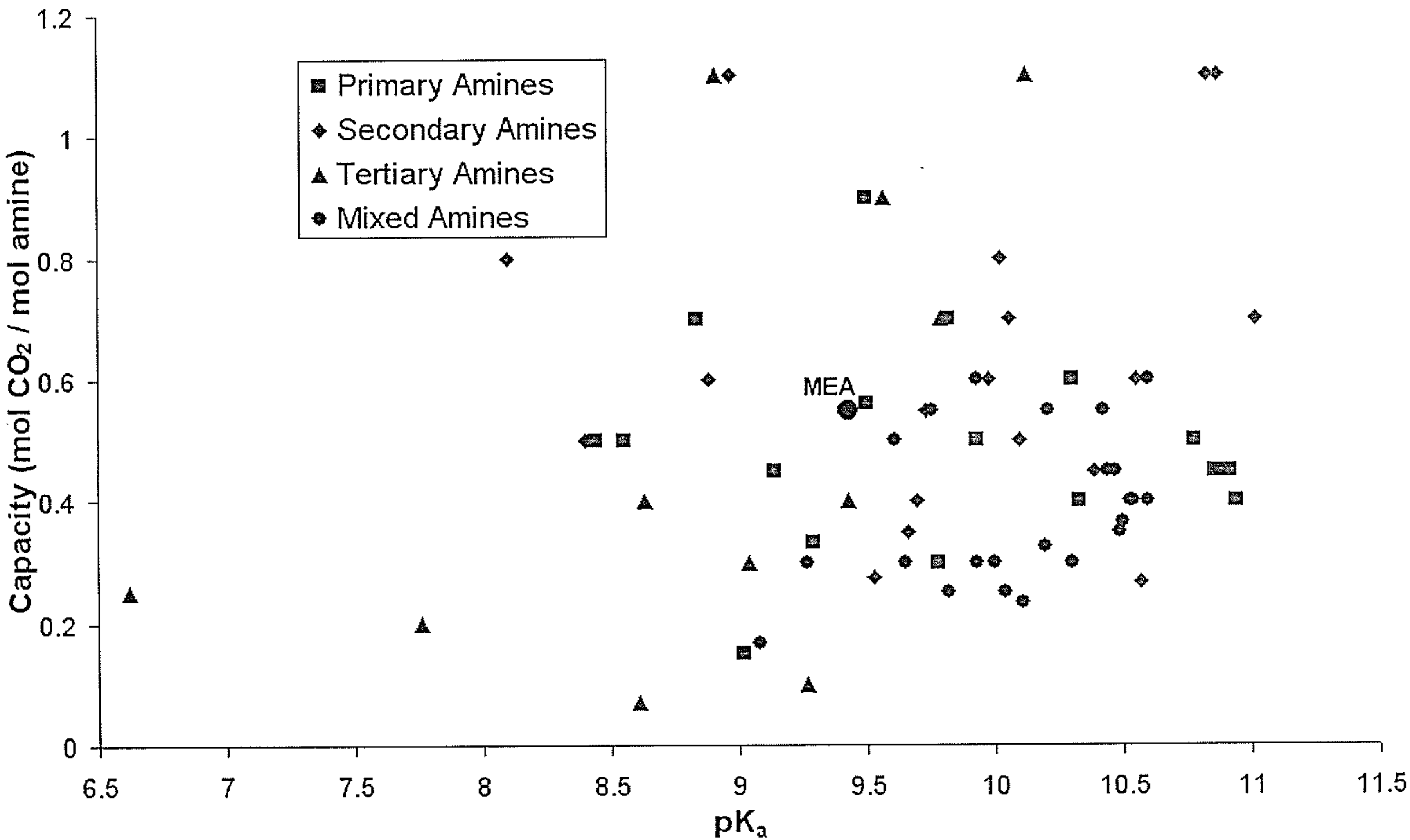
Gravimetric method used to measure CO_2 absorption and initial absorption rate on µL scale



Traditional absorption method used on the mL scale



Capacity vs pK_a



NB: For polyamines the capacity has been normalised to the number of amine functional groups.
Conditions: 40°C, 13% CO_2, 87% N_2 and atmospheric pressure.

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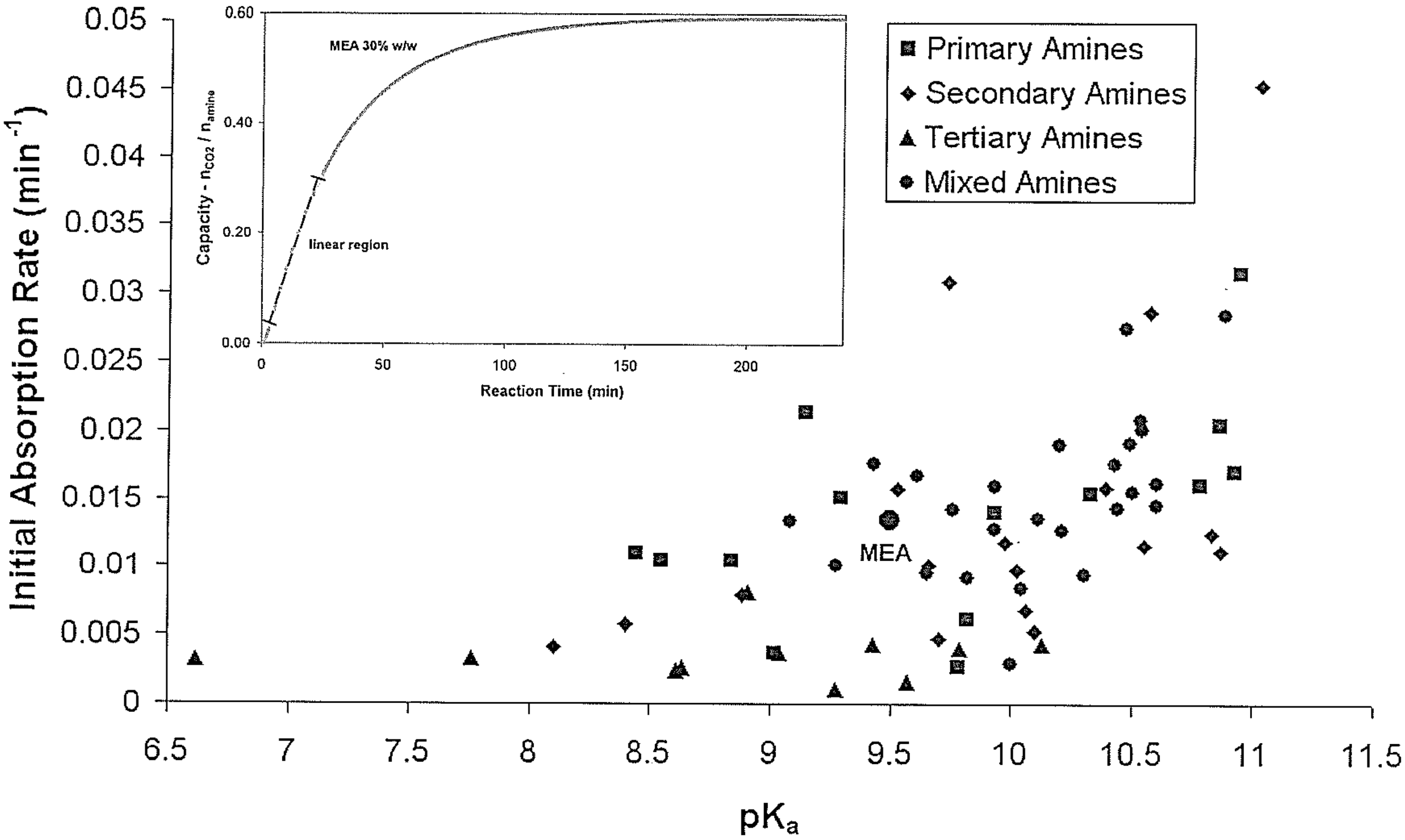
Initial Rate vs pK_a



Conditions: 40°C, 13% CO_2, 87% N_2 and atmospheric pressure.

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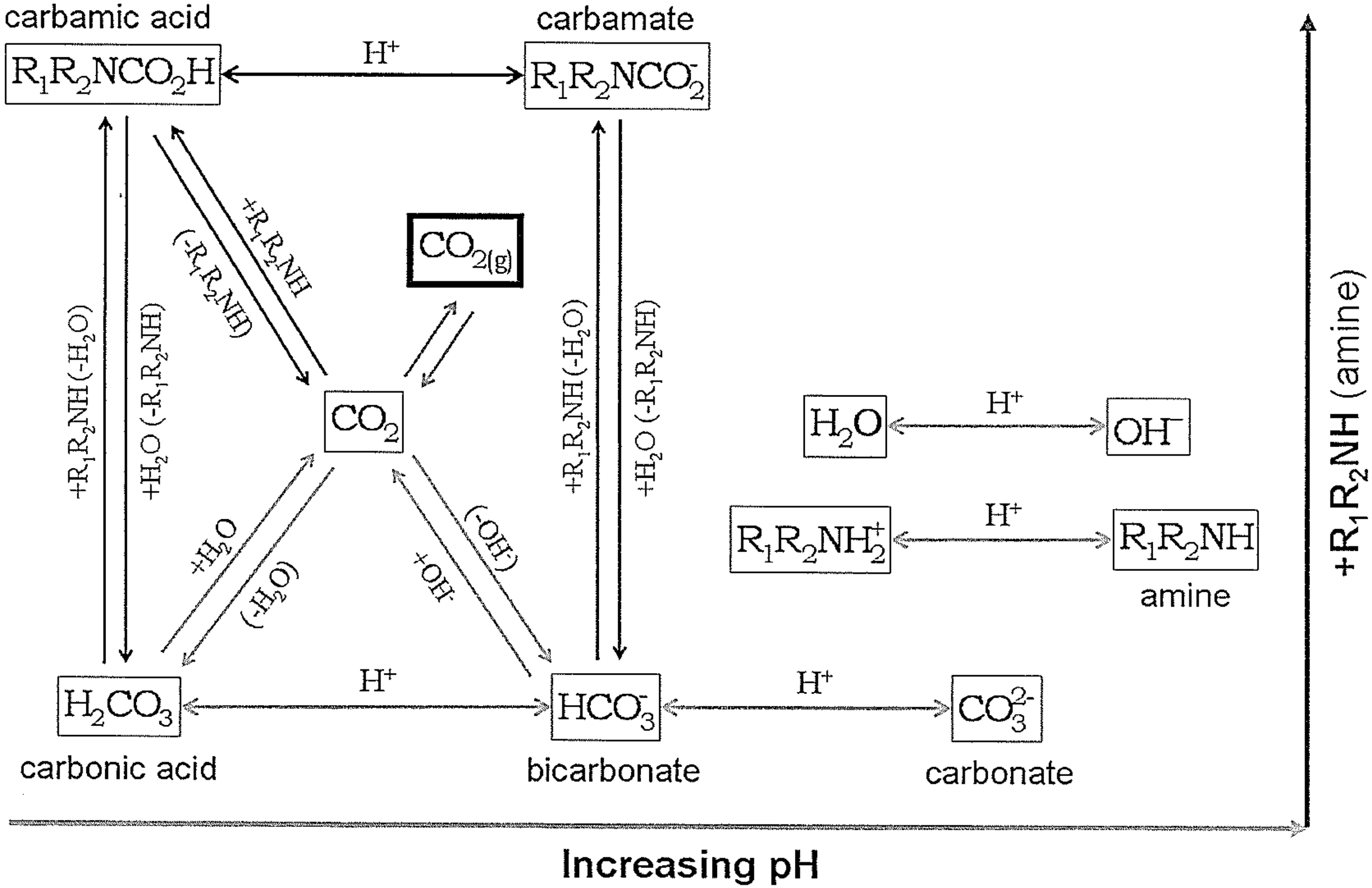
Modelling CO_2-Amine Interactions



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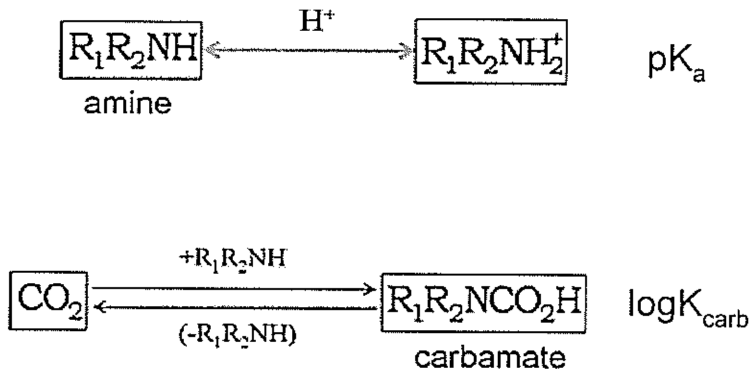
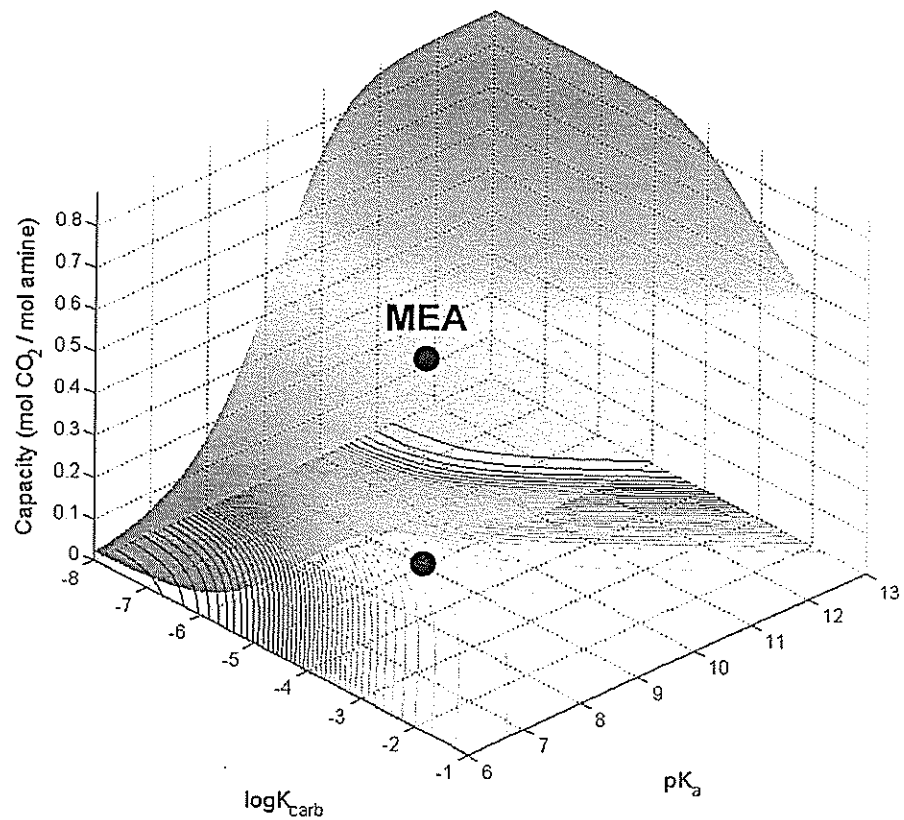
CO_2 Capture Performance - Capacity



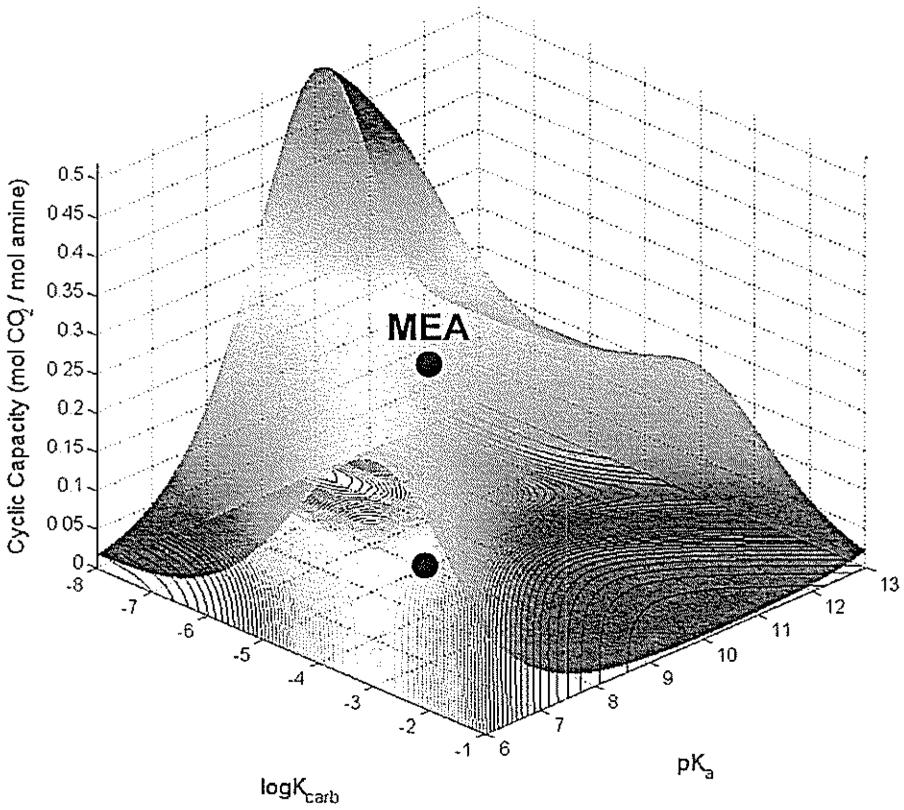
Capacity
moles of CO_2 / moles of amine @ 40°C



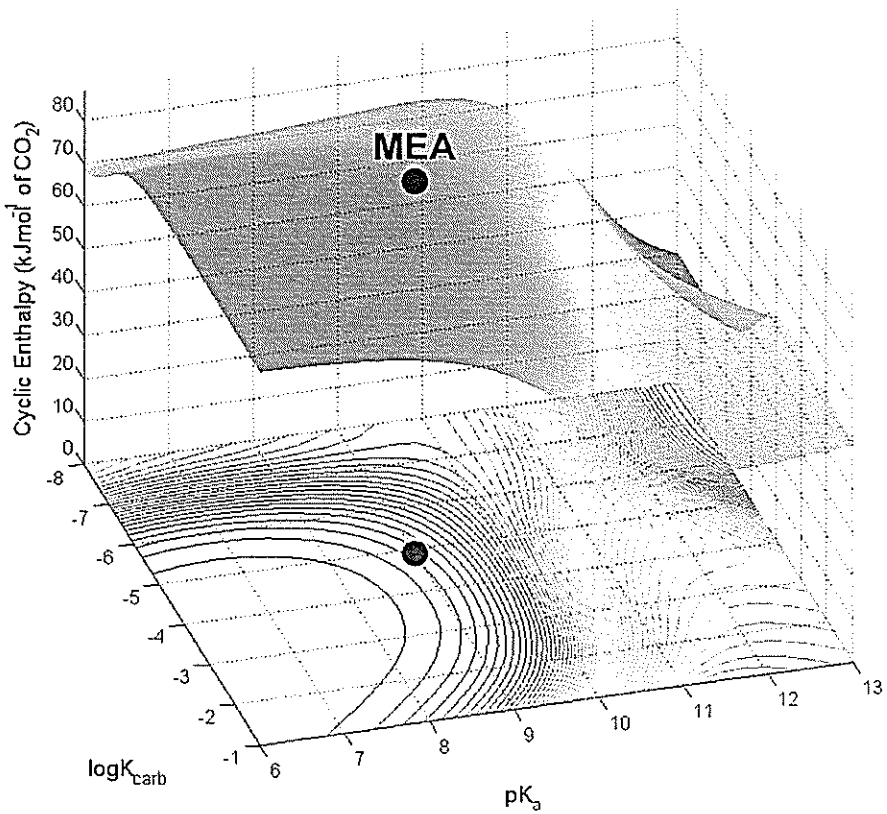
CO_2 Capture Performance – Cyclic Capacity and Cyclic Enthalpy

Cyclic capacity

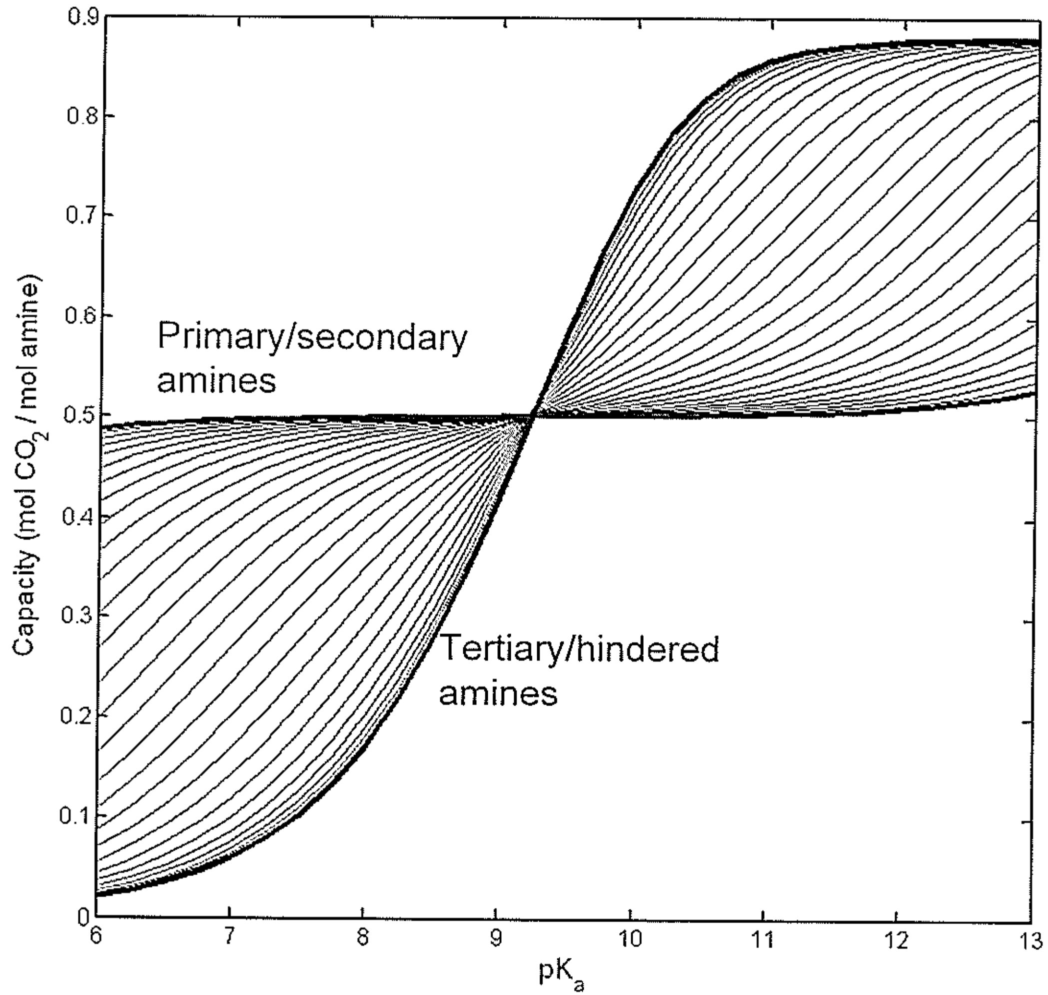
n_{CO2}/n_{amine} @ 40°C - n_{CO2}/n_{amine} @ 100°C



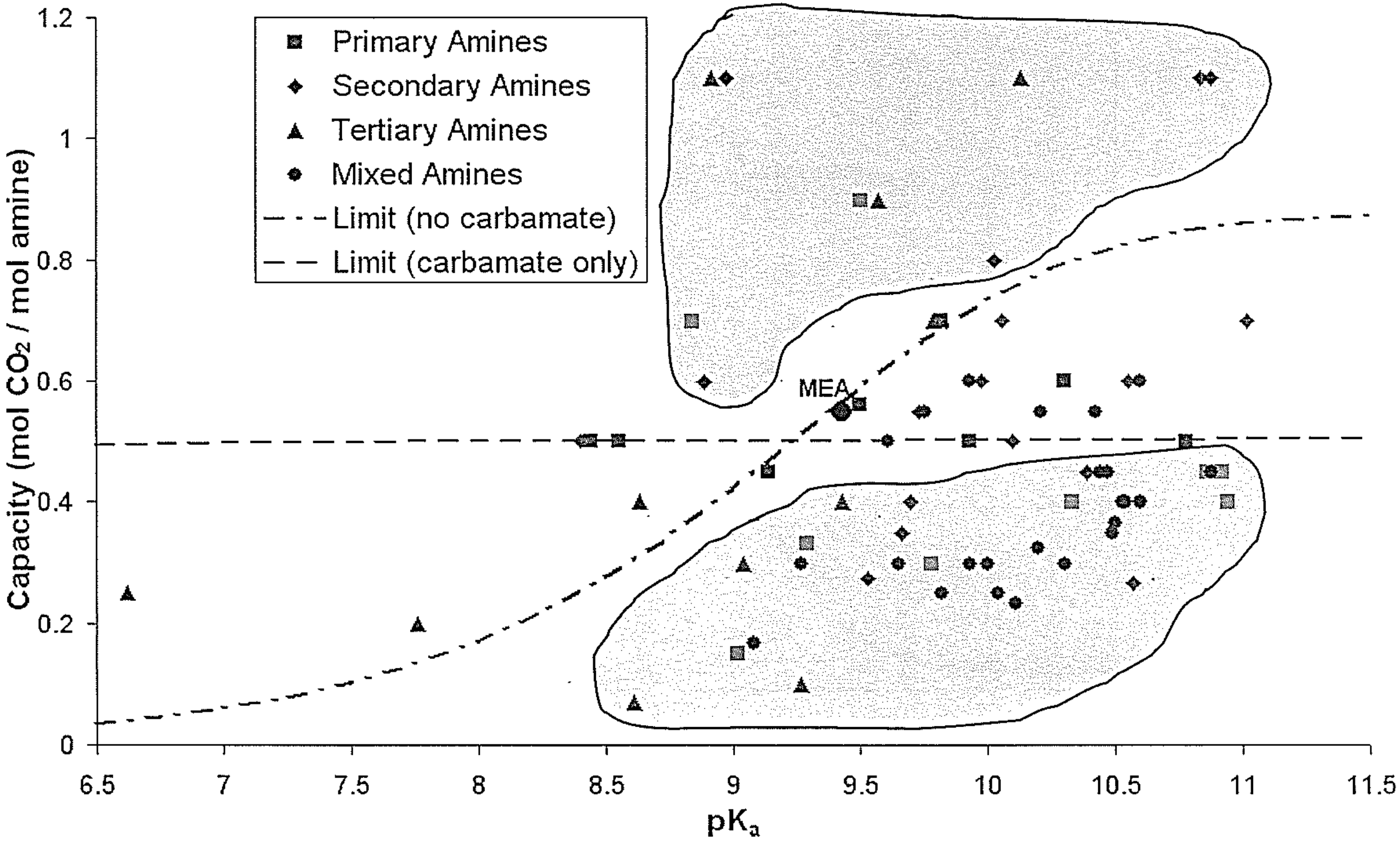
Energy required to release CO_2



Theoretical Capacity vs pK_a



Modelling + Screening

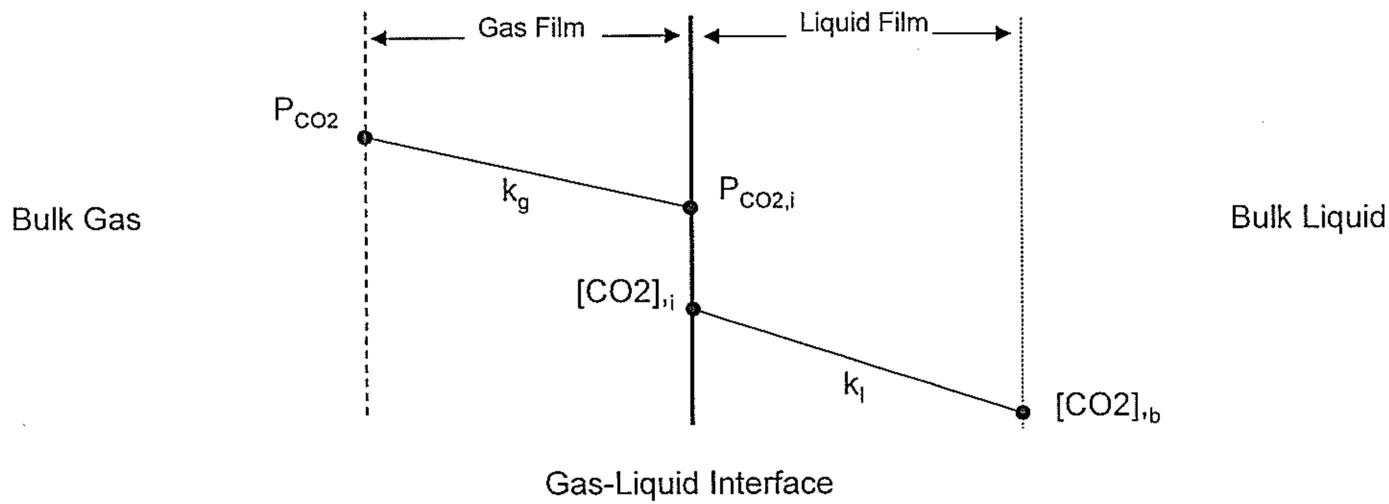


NB: For polyamines the capacity has been normalised to the number of amine functional groups.
Conditions: 40°C, 13% CO_2, 87% N_2 and atmospheric pressure.

- Absorption Kinetics of Solvent Systems for CO2 Capture

What are these Absorption Kinetic Measurements?

- They are the study of the gas-liquid interaction between gaseous CO2 and a carbon capture solvent.



- k_g = mass transfer coefficient in the gas film
- k_l = mass transfer coefficient in the liquid film

Why study the kinetics?

- The kinetics of a CO_2 solvent system have a large influence on the design of a PCC plant.
  - The faster the kinetics of the CO_2 absorption the smaller the absorber.

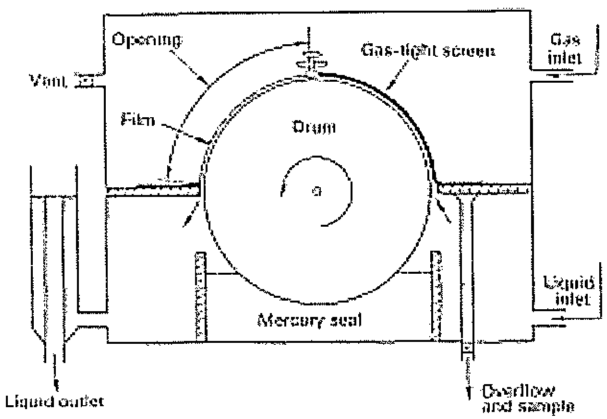
- We can directly measure the flux rate at which CO_2 is absorbed by a solvent (flux rate = amount of CO_2 absorbed per unit area of contact).

This allows;

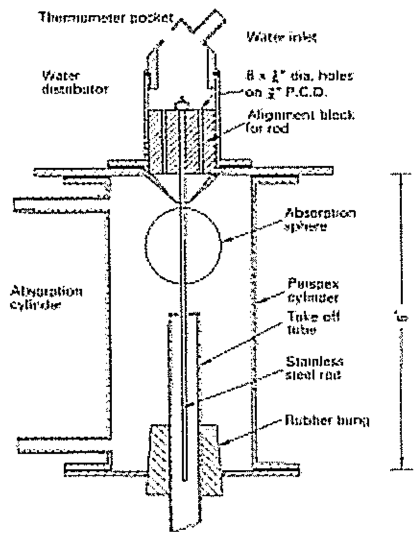
- the calculation of mass transfer coefficients, in particular k_l.
- the determination of whether a solvent system is controlled by diffusion or reaction kinetics.

How do we study these Gas-Liquid Interactions?

- There are several types of gas-liquid contactors that have been used to study these interaction. These include;
  - the rotating drum (Danckwerts & Kennedy, 1954)
  - the wetted sphere (Davidson & Cullen, 1957)
  - the laminar jet (Toor & Raimondi, 1959)
  - the wetted wall column (Roberts & Danckwerts, 1962)



Rotating Drum



Wetted Sphere

Laminar Jet

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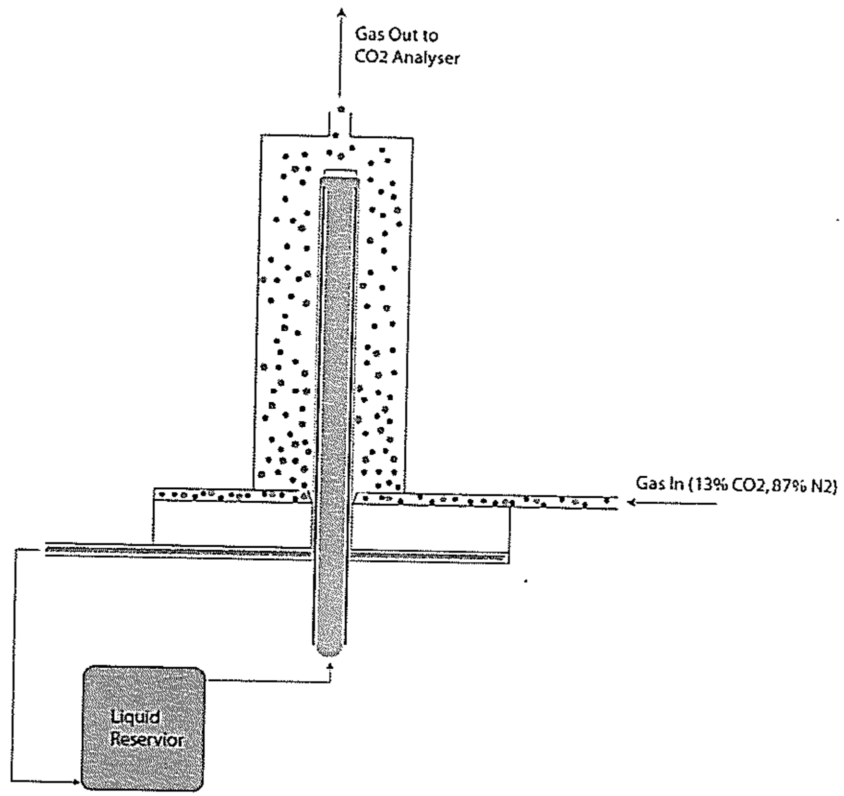
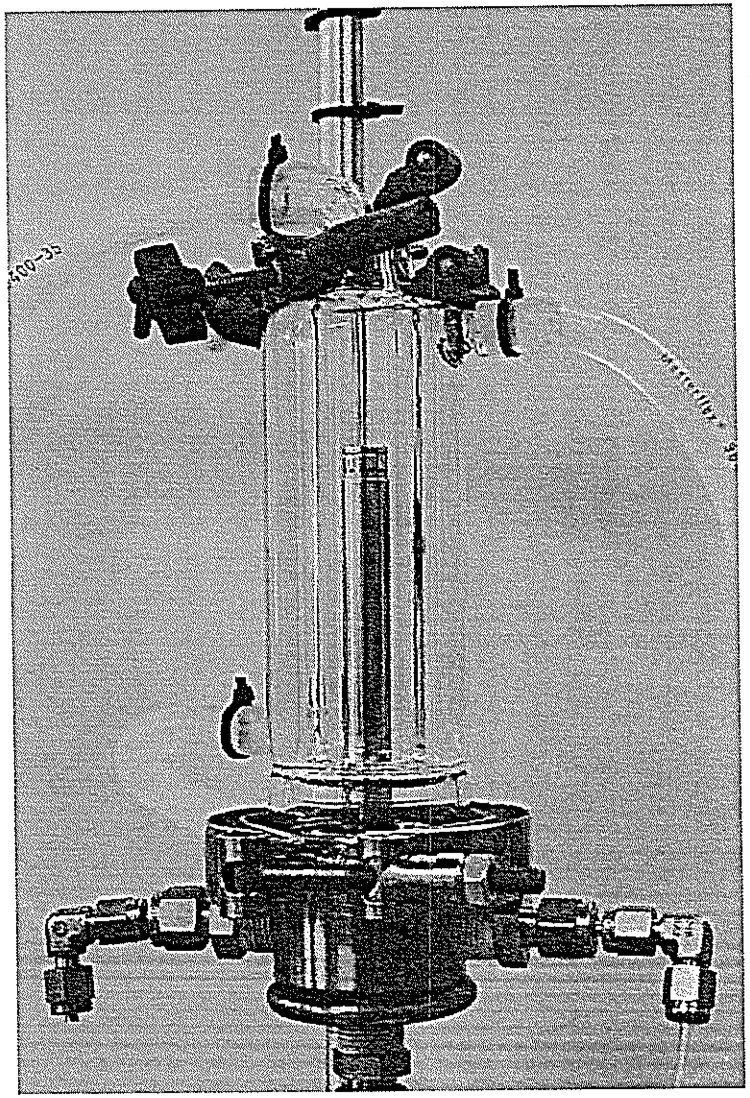
The Wetted Wall Column

- The wetted wall column is the most suitable gas-liquid contactor for our kinetic studies.
- This is due to the gas-liquid contact time (~0.5s) being suitable for the simulation of a packed absorption column.



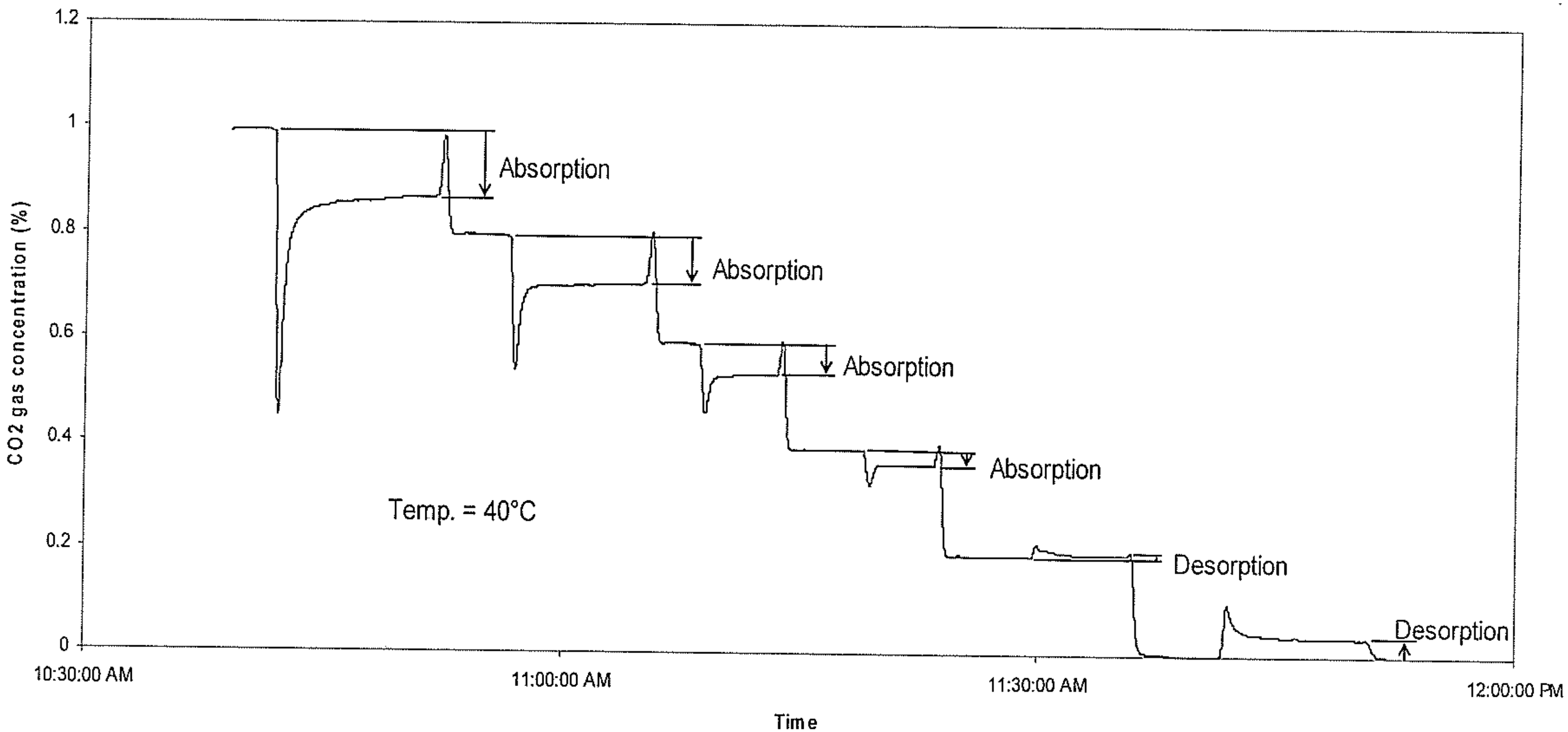
The Wetted-Wall Column



- Liquid and gas flow counter-currently
- The liquid is a thin film to mimic contacting in a packed column
- Direct measurement of CO_2 absorption flux into film

A Typical Experiment

WWC Run 30% MEA Loading ~0.45 mol/mol



- A Liquid Film Mass Transfer coefficient (k_l) can be calculated from the above results.

- Degradation

Why worry about solvent oxidation or degradation?

- 200-400 L of 30 wt % capture amine solution will be used in the PCC pilot plant to be deployed to Loy Yang (400 MW)
- The Loy Yang PCC pilot plant is designed to capture 1-5 kilotonnes of CO_2/p.a.
- Bayswater p.f. power station (2.6 GW) produces 31 tonnes/min CO_2 or 16.2 Mtonnes p.a.
- Degradation of the capture solution (whether it is thermal, carbamate-induced polymerisation, or oxidative) *reduces solution performance*
- This manifests as:
  - reduced capture capacity
  - increased corrosion (through solution viscosity)
  - increased foaming

Unchecked degradation

- In acid gas "sweetening" applications, an amine capture solution is considered "spent" when there is still 80 % active amine
- The solution either needs "base charging" or wholesale replacement
- Certain carbamates are carcinogens, and -in general- amines are good metal chelates

SPENT SOLUTIONS CANNOT BE RELEASED TO THE ENVIRONMENT

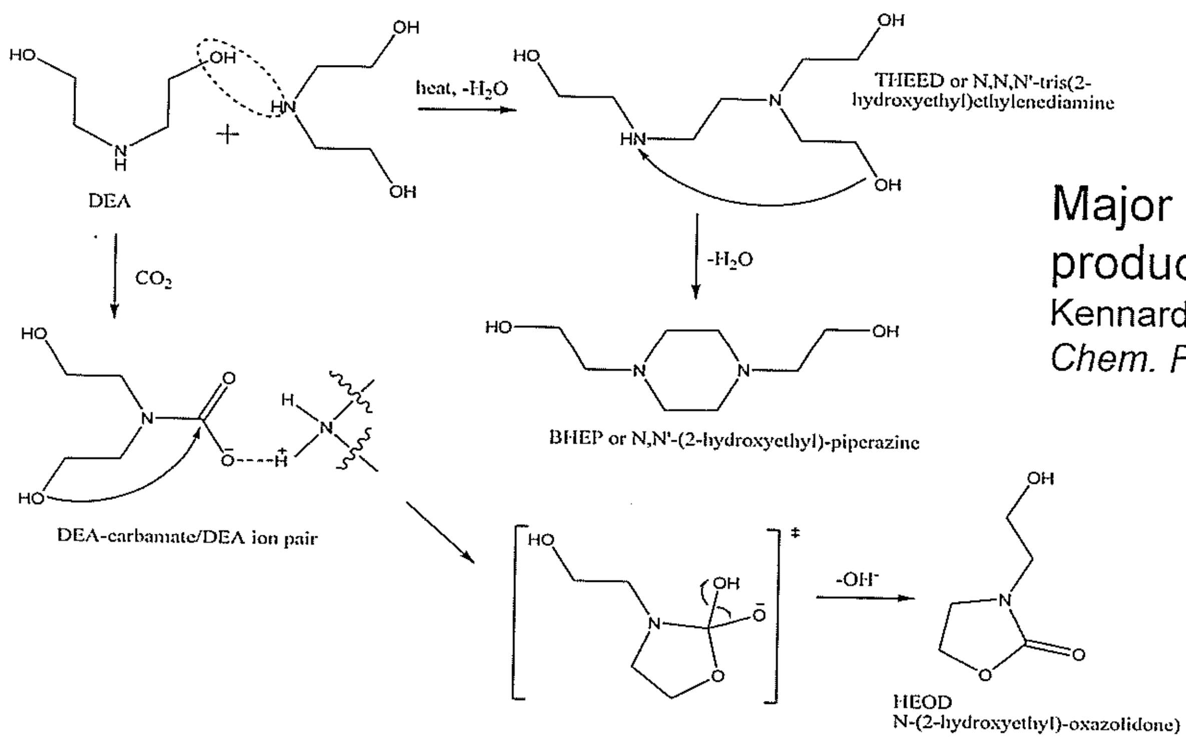
- Disposal is usually by incineration or sequestration with large associated solvent replacement costs
- 'Charging' usually involves online injection of OH^- to regenerate the amine solution
- Some degradation problems can be solved by building the PCC plant from stainless steel:

MEPS world steel prices, August 2007, US$/tonne:

Steel type	Product	Cost
carbon	merchant bar	650
st.st. 304	drawn bar	6663
st.st. 316	drawn bar	9916

Understanding is the key to controlling amine degradation

- Thermal degradation shouldn't be a significant problem in PCC plants (typical flue gas temperatures are ~ 100 °C, stripping temperatures are ~ 120 °C)
- If it is a problem……..hotspots on the stripper side
- What could you expect to see?



Major DEA degradation products

Kennard, Meisen. *Ind. Eng. Chem. Fundam.* **1985**, *24*, 129.

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Understanding is the key to controlling amine degradation

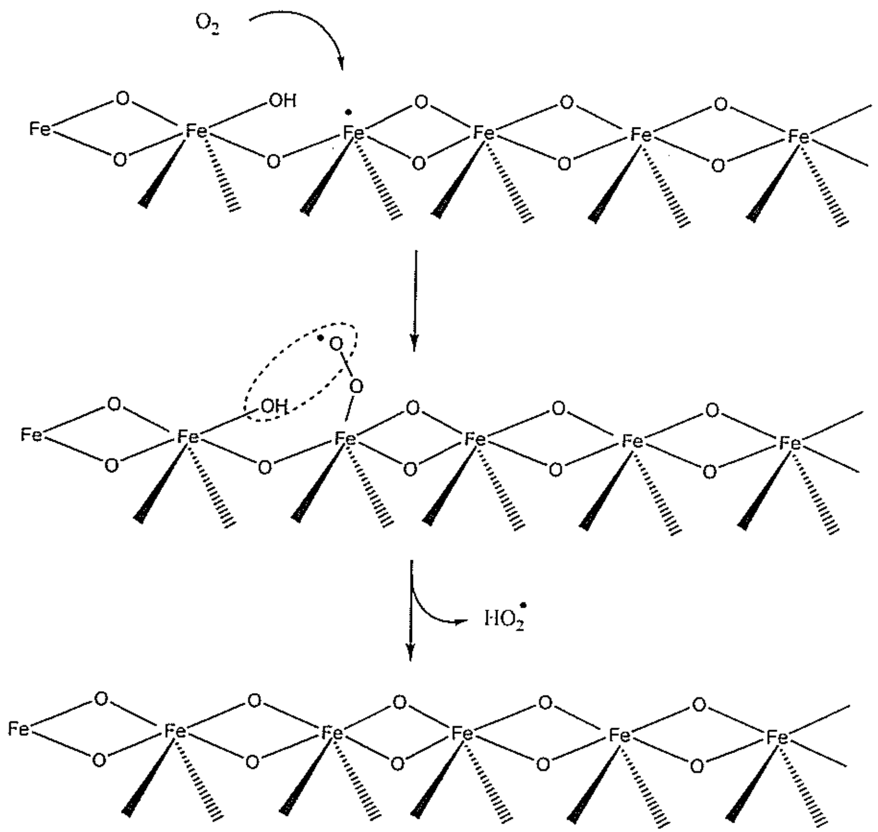
- Amine-alcohol chemistry should dominate
- The Loy Yang pilot plant will probably use 30 wt % MEA
- MEA thermal degradation products should include hydroxyethylethylenediamine, oxazolidone and piperazine - piperazine is actually used as a promotor for some CO_2 capture solvents
- Polymeric MEA-degradation products will contribute to solution viscosity eg $HO\text{-}[C_2H_4NH]_n\text{-}H$
- Carbamate-induced polymerisation will produce similar degradation products
- The rate of carbamate-induced degradation is faster (demonstrated by: Kennard and Meisen. *Ind. Eng. Chem. Fundam.* 1985, *24*, 129)
- The by-product is either bicarbonate or $OH^- + CO_2$
- Thermal- and carbamate- induced degradation products are either amines or alkanolamines → can capture CO_2 (efficiency reduction not as marked)
- Main drawbacks of non-oxidative degradation are:
  1. **increased solution viscosity**
  2. **less efficient capture amines (regeneration is more energy intensive or not possible)**

Understanding is the key to controlling amine degradation

- Reclaimers are used on the stripper side to trap these high boiling point products

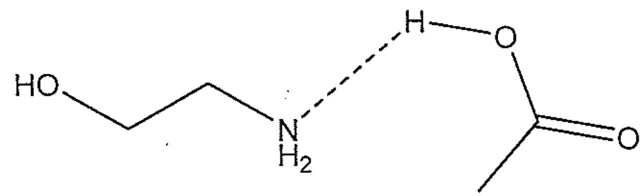
Oxidative Degradation

- Proceeds by a radical mechanism involving oxygen, as outlined by Rochelle (slightly modified by the presenter)
- HO_2 radical is the most plausible culprit, its formation catalysed by solubilised or surface-bound Fe or other transition metal
- Radicals attack the alkanolamine solvent by abstracting H-atoms (α-, β-H)
- This is supported by results published for lab temperature (270-300 K) ethanol oxidation: Meier, Grotheer, Rieckert, Just. *Ber. Bunsengenes. Physik. Chem.* 1985, *89*, 325.

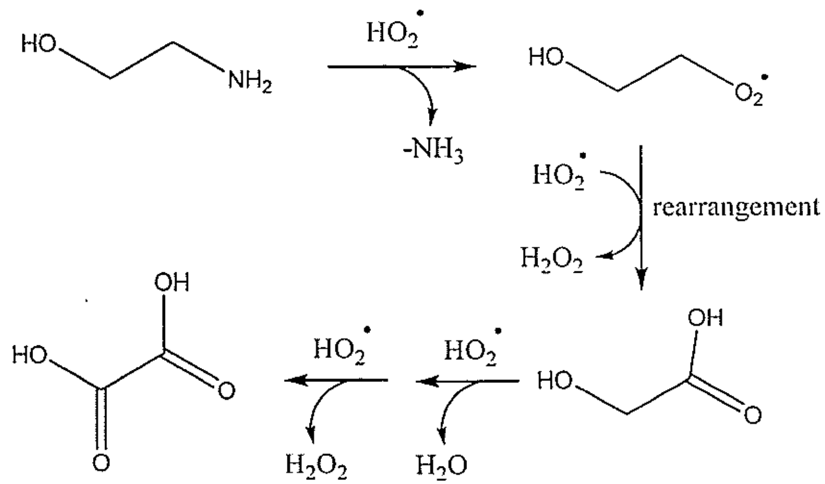


Oxidative degradation

- The major oxidative degradation products are NH_3 and organic acids
- The organic acids form heat-stable salts (industry jargon)



- HSS' lower the capture solution pH, reduce capture efficiency and increase corrosion by increasing viscosity (particularly in carbon steel plants)
- Oxalic acid or oxalate is the biggest corrosion offender (it is a good chelator of Fe^{3+})
- There is also an energy cost

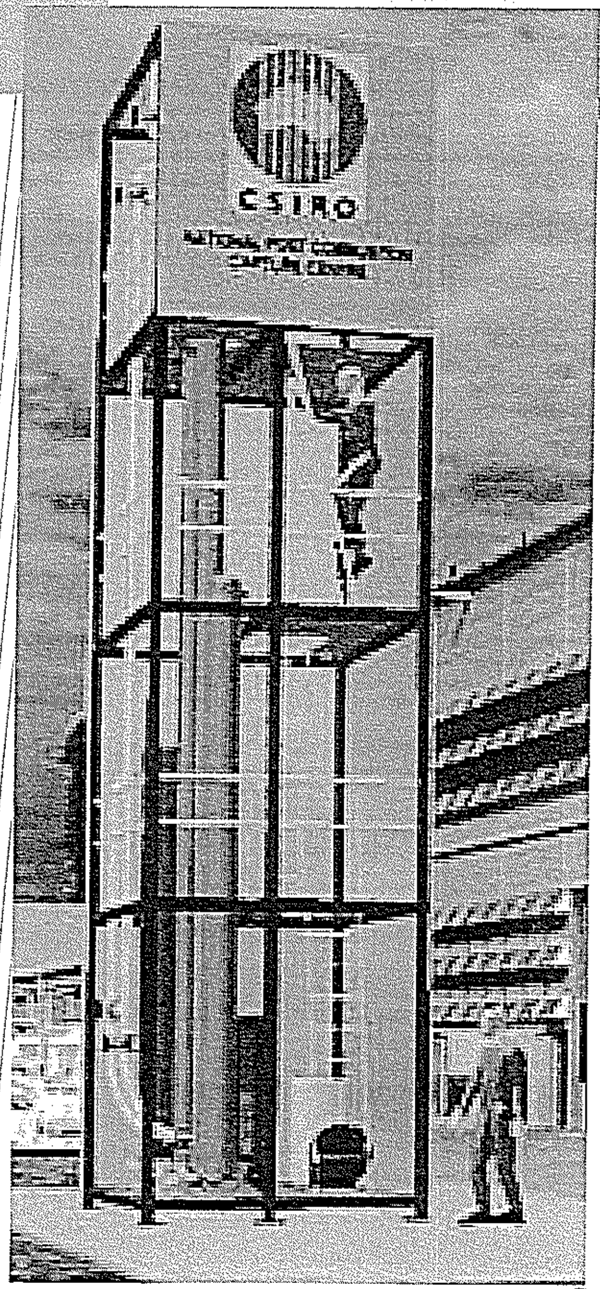


Monitoring for Oxidative degradation

- Ion chromatography (Dowex 50W-X8) can be used to monitor evolution of heat-stable salts
- Cationic iron (a corrosion product) can be monitored colourimetrically (UV-vis spectroscopy, 395 nm using a suitable chelating agent)
- Weight loss in corrosion coupons (pre-weighed and polished metal tokens) can also be used to monitor solution degeneration
- Questions?

- Lab Scale Absorber Stripper

OBJECTIVE



1. **Simulate** the principle process behind an amine based pilot-plant for the removal of CO2 from flue gas at a laboratory scale

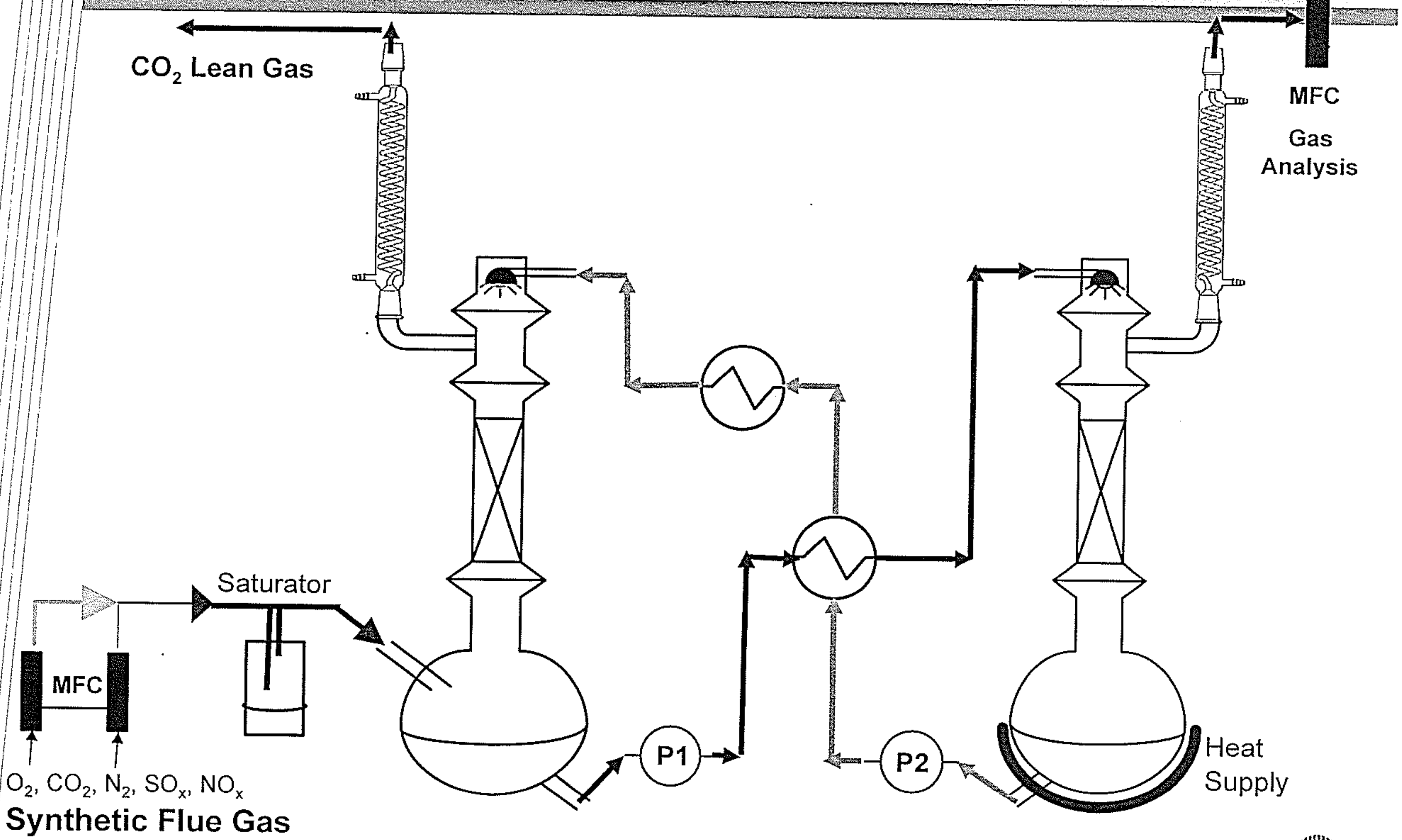
- Step by step progression to large scale implementation

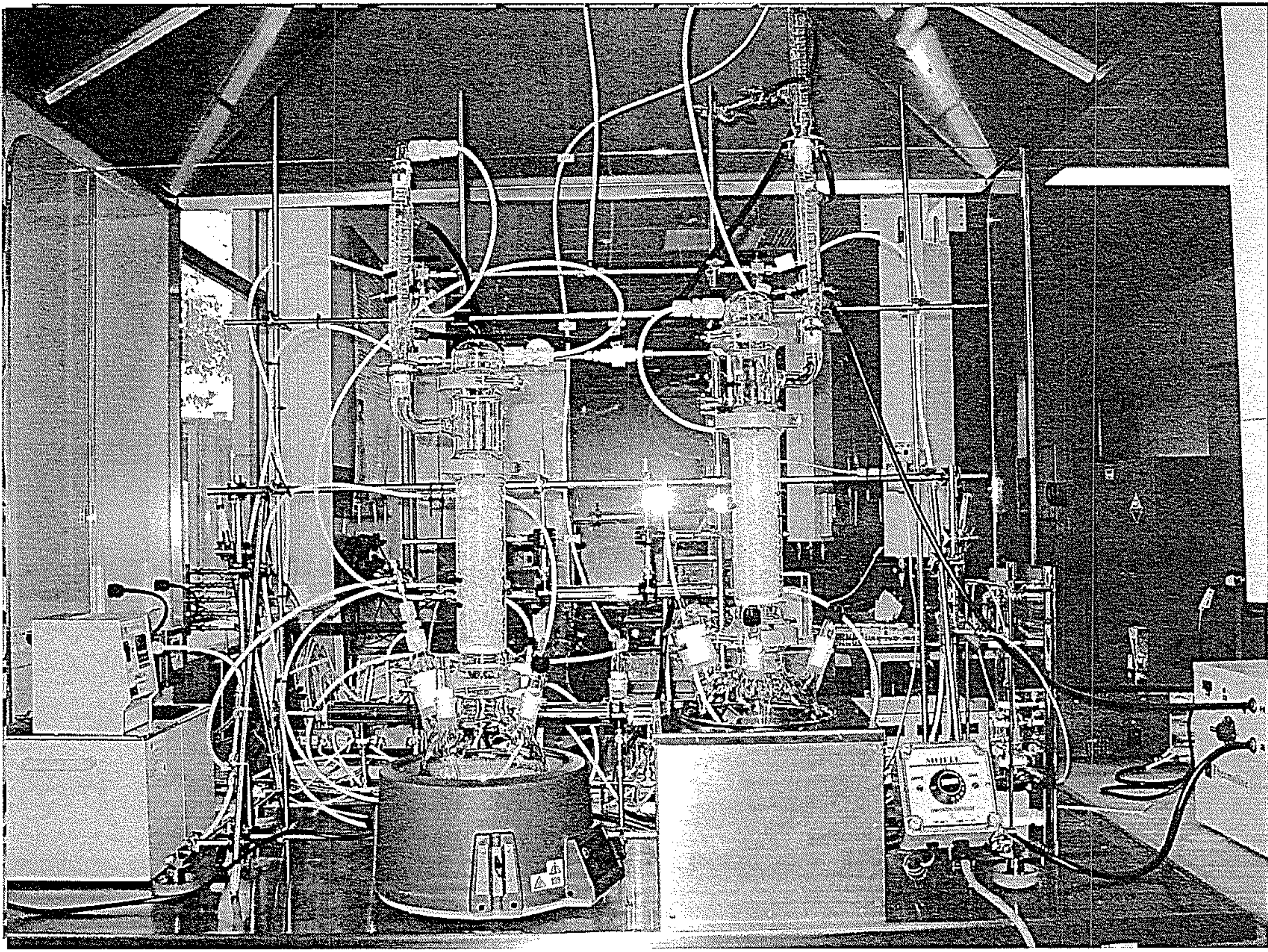
OBJECTIVE

2. To Design it in such a way that it offers:

- Flexibility with respect to gas composition and the gases that can be used
- Measurement and control capabilities
  - Gas and Liquid Flow Rates- CO_2 in and out
  - Temperature
  - System Pressure
  - Energy Consumption
- Feedback systems (Fluid Control, Heat input etc)
- Sampling Ease- analysis solvent by-product

Basic Design





Conclusion

Status

- The initial design has been modified significantly
- Modifications have been made to parts of the apparatus to comply with OHS&E
- Up to to putting everything together.............

Acknowledgements

Moetaz Attalla

Phil Jackson

Graham Puxty

Andrew Allport

Rob Rowland

The CSIRO Team

The Team

CSIRO

Energy Transformed

NATIONAL RESEARCH FLAGSHIPS

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Rob Rowland
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Molecular & Health Technologies:
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