Solvent Development for CO₂ Absorption Process

Dr. Prachi Singh, IEAGHG R&D Programme, M.Sc. CCS, The University of Edinburgh, 14:00, 23rd March 2012,
Outline

- Introduction
  - Myself
  - IEAGHG R&D programme

- CO₂ Capture Technology

- Amine Based Solvents:
  - Structure Activity Relationships: Basicity, Absorption and Regeneration
  - Degradation Problem
  - Foaming Issue
Introduction
Myself

- **Project Officer**, Post Combustion capture, IEAGHG
- **Post Doc.**, Reactive Distillation, 2011, Institute of Sustainable Process Technology, The Netherlands
- **PhD**, 2010, Shell (2 year) / University of Twente, The Netherlands
  
  Thesis: Amine Based Solvent for CO₂ Absorption process
  ‘From Molecular Structure to Process’
- **M.Sc.** Chemical Engineering, 2004, University of Amsterdam, The Netherlands
IEA GREENHOUSE GAS R&D PROGRAMME
IEA Greenhouse Gas R&D Programme

- A collaborative international research programme founded in 1991

- **Aim:** Provide members with definitive information on the role that technology can play in reducing greenhouse gas emissions

- **Scope:** All greenhouse gases, all fossil fuels and comparative assessments of technology options.

- **Focus:** On CCS in recent years
IEA Greenhouse Gas R&D Programme

- Producing information that is:
  - Objective, trustworthy, independent
  - Policy relevant but NOT policy prescriptive
  - Reviewed by external Expert Reviewers
  - Subject to review of policy implications by Members

- IEAGHG is an IEA Implementing Agreement in which the participants contribute to a common fund to finance the activities.
Members and Sponsors

BG GROUP
CEZ GROUP
Chevron
en
Shell
Total
EPRI
ExxonMobil
Schlumberger
Doosan Babcock
EnBW
E.ON
Masdar Carbon
B&W
Enel
GLOBAL CCS INSTITUTE
JGC
RWE
Statoil
What IEAGHG does

- Technical evaluations of mitigation options
  ✓ Comparative analyses with standardised baseline

- Assist international co-operation
  ✓ International research networks

- Assist technology implementation
  ✓ Near market research
  ✓ GCCSI

- Disseminate information
Specific Focus on CCS

- **Power Sector**
  - Coal, Natural Gas and Biomass

- **Industrial sectors**
  - Gas production
  - Oil Refining & Petrochemicals
  - Cement sector
  - Iron & Steel Industry

- **Cross cutting issues**
  - Policy/Regulations
  - Health & Safety
  - Transport & System Infrastructure
Global Policy Context

- National/Corporate policy setting
- National/Corporate research programmes
- Implementation actions

- International Policy Setting

Logos and icons representing various organizations and initiatives related to global policy context, including IEA, Carbon Sequestration Leadership Forum, CIAB Clean Coal Centre, and other international partners.
$\text{CO}_2$ Capture Technology
Challenges for CCS

- Large Scale Demonstration
- Reducing CO\textsubscript{2} Capture Cost
- Reducing Energy Penalty
- Building Infrastructure
- Safe CO\textsubscript{2} Storage
- Non-technological Issues
- Environmental Impact
CO₂ Capture Options

Postcombustion (PC)

Coal → Power & Heat → CO₂ Separation
Coal → Air → Power & Heat

Precombustion (IGCC)

Coal → Gasification → Shift, Gas Cleanup + CO₂ Separation → Power & Heat
Air/O₂ → Steam

Oxyfuel Combustion

Coal → Power & Heat
Air → Air Separation → N₂ → Power & Heat
Air → O₂

CO₂ Compression and Dehydration

Ref: EPRI 2007
Post Combustion Capture

- Makeup Water
- Sweet gas
- Condenser
- Acid gas
- Reflux drum
- Reboiler
- Condensate
- Stream

40-50°C 1 bar
40-50°C 1 bar
120°C 1.5 bar

Absorber
40-50°C 1 bar
12% CO₂
5% O₂
7% H₂O
H₂S, SO₂,
HCl, NO

Regenerator
120°C 1.5 bar
Lean amine
Rich amine
Lean amine
Reflux
Pump

Top Tray
Bottom Tray
Top Tray
Bottom Tray

Rich amine
Lean amine
Amine based absorbents: Alkanolamine

- **Primary**: One of the three hydrogen bonds of nitrogen atom is replaced by functional group.

- **Secondary**: In Secondary amine two of the three hydrogen bonds of nitrogen atom is replaced by functional group and for tertiary amine will be three functional groups at nitrogen atom.

- **Tertiary**: One or Two functional groups present by side chain substitution at 1\textsuperscript{st} carbon to nitrogen atom creates steric hindrance.

**Sterically Hindered**
Main reaction with CO₂ and Primary & Secondary amine

Acid Base Temperature Dependent Reversible Reaction

\[ 2R_2NH + CO_2 \rightleftharpoons R_2NCOO^- + R_2NH_2^+ \]

In Termolecular mechanism for carbamate formation, it is single step reaction in which the bonding between amine and CO₂ and proton transfer takes place simultaneously. Here, B is a base molecule, which may be a hydroxyl ion, water or an amine-functionality.
Main reaction with CO$_2$ and Primary & Secondary amine

Acid Base Temperature Dependent Reversible Reaction

The carbamate formed undergo hydrolysis forming a bicarbonate species. The degree of hydrolysis of the carbamate species depends on several factors, such as its chemical stability, which is strongly influenced by the temperature. Carbamate formation equilibrium constant showed a nonlinear relationship with the pKa (basicity) of the solvent, which suggests that factors other than basicity play a role in the formation and breakdown of carbamate.

\[
\begin{align*}
R_2NCOO^- + H_2O & \rightleftharpoons HCO_3^- + R_2NH \\
\text{Hydrolysis} & \\
HCO_3^- & \rightleftharpoons CO_3^- + H^+
\end{align*}
\]
Main reaction with CO$_2$ and Primary & Secondary amine

$$2R_2NH + CO_2 \rightleftharpoons R_2NH_2^+ + R_2NCOO^-$$

Fast reaction

Low Temp.

Hydrolysis

$$R_2NCOO^- + H_2O \rightleftharpoons HCO_3^- + R_2NH$$

Bicarbonate

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

Very Slow

CO$_3^{2-}$

Carbamate

CO$_2$ remain in these form in liquid phase
Main reaction with CO$_2$ and Tertiary amine

Tertiary amines groups cannot react with CO$_2$ directly to form a carbamate, because these amines lack a free proton.

$$R_3N + CO_2 + H_2O \rightleftharpoons HCO_3^- + R_3NH^+$$

- Slow
- Bicarbonate

$$HCO_3^- \rightleftharpoons CO_3^- + H^+$$

- Very Slow
- Carbonate

- Tertiary alkanolamines act as a base and catalyse the hydration of CO$_2$, leading to the formation of bicarbonate.
- The tertiary alkanolamines react in equi-molar ratio with CO$_2$ and this confers to them a CO$_2$ loading capacity of 1 mole of CO$_2$/mole of amine.
## Commercially available solvents systems

<table>
<thead>
<tr>
<th>Process Concept</th>
<th>Example</th>
<th>Developers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional MEA</td>
<td>Econamine +</td>
<td>Fluor, ABB</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Chilled Ammonia</td>
<td>Alstom</td>
</tr>
<tr>
<td>Hindered Amines</td>
<td>KS-1, AMP, …</td>
<td>MHI, EXXON,</td>
</tr>
<tr>
<td>Tertiary Amines</td>
<td>MDEA</td>
<td>BASF, DOW</td>
</tr>
<tr>
<td>Amino Acid Salts</td>
<td>CORAL</td>
<td>TNO, Siemens, BASF</td>
</tr>
<tr>
<td>Piperazine</td>
<td></td>
<td>Uni Texas</td>
</tr>
<tr>
<td>HiCapt, DMX</td>
<td>Mixture</td>
<td>IFP</td>
</tr>
<tr>
<td>Integrated SO$_2$/CO$_2$</td>
<td>Amines</td>
<td>Cansolv/Shell</td>
</tr>
<tr>
<td>Amine</td>
<td></td>
<td>Aker Clean Carbon</td>
</tr>
<tr>
<td>Chemical solvents</td>
<td>DEAB, KoSol, Calcium based,</td>
<td>HTC, Uni Regina, KEPRI, NTNU, SINTEF, CSIRO, KEPRI, EnBW</td>
</tr>
</tbody>
</table>
Challenges in Post Combustion Capture

- Degradation
- Corrosion
- Heat stable salt
- Volatile organic comp.

CO₂ Absorption Capacity & Kinetics

Regeneration temperature
Reaction enthalpy

- Detailed Model development
- Process Integration

Absorbent & water → Scrubber Column
Energy → Power plant
Fossil fuel & air → Exhaust gas with CO₂

Cleaned exhaust gas → Heat exchanger

Cooling

CO₂ → Regenerator

Heating
Demand for New Absorbents

- Low Capacity
- High Regeneration Cost
- Low Absorption Rate
- Corrosion
- Heat Stable Salts Formation
- Degradation

Issues with Solvents
Solvent Development Criteria

- **Structural properties**
  - Carbon Chain length
  - Side chain
  - Different Functional group
  - Cyclic amine

- **Solubility in water**

- **Basicity (pKa)**

- **Environmental aspects**

- **Economically feasibility**
Amine Based Solvents
Basicity/ Dissociation Constant (pKa)

• Dissociation constants provide the basic strength of the amine-based absorbent at a specific temperature.

\[
R_2NH + H_2O \rightleftharpoons R_2NH_2^+ + OH^- \\
\]

\[
K_b = \frac{[R_2NH^+][OH^-]}{[R_2NH_2^+]} \\
\]

\[
pKa = -\log K_b \\
\]

• First indicator for the reactivity of various amine-based absorbents towards CO\textsubscript{2}
Carbon Chain Length: Alkanolamine (Primary)

Monoethanolamine (MEA)  \[ \text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{OH} \]

3-Amino-1-propanol  \[ \text{H}_2\text{N}-\text{CH}(\text{CH}_3)-\text{CH}_2\text{OH} \]

4-Amino-1-butanol  \[ \text{H}_2\text{N}-\text{CH}(\text{CH}_3)-\text{CH}_2\text{CH}_2\text{OH} \]

5-Amino-1-pentanol  \[ \text{H}_2\text{N}-\text{CH}(\text{CH}_3)-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \]

For Secondary and Tertiary amine molecule structure was kept same for all solvent molecules except amine group was changed to secondary and tertiary by alkyl group.
As OH group is electron withdrawing group result in lower electron density at the Nitrogen atom. Therefore increase in carbon chain length, reduces this effect and increase pKa.

Tertiary amine basicity reduced due to decrease in number of H₂ atom (in cation form) which is capable of forming hydrogen bond with water reducing the solvation in water. Means crowding of alkyl groups cover nitrogen atom from all sides and thus makes the approach and bonding by a proton relatively difficult which results the maximum steric strain in tertiary amines.

Carbon Chain Length: Alkylamine (Primary)

- Ethylamine: \( \text{CH}_3\text{-}\text{CH}_2\text{-NH}_2 \)
- Propylamine: \( \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-NH}_2 \)
- Butylamine: \( \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2 \)
- N-Pentylamine: \( \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2 \)
- Hexylamine: \( \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2 \)

For Secondary and Tertiary amine molecule structure was kept same for all solvent molecules except amine group was changed to secondary and tertiary by alkyl group.
In alkyl amine no effect is noticed with increase in carbon chain length. As in ammonia substituted by one alkyl group basicity changes from 9.3 to 10.6, this does not affect the size of alkyl group.

Similar reason for lower basicity in tertiary amine as for alkanolamine.
## Carbon Chain Length: Diamine (Primary)

<table>
<thead>
<tr>
<th>Diamine</th>
<th>Molecular Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylenediamine</td>
<td>( \text{H}_2\text{N} - \text{NH}_2 )</td>
</tr>
<tr>
<td>1,3-Diamino propane</td>
<td>( \text{H}_2\text{N} - \text{NH}_2 )</td>
</tr>
<tr>
<td>1,4-Diamino butane</td>
<td>( \text{H}_2\text{N} - \text{NH}_2 )</td>
</tr>
<tr>
<td>Hexadimethylenediamine</td>
<td>( \text{H}_2\text{N} - \text{NH}_2 )</td>
</tr>
<tr>
<td>1,7-Diaminoheptane</td>
<td>( \text{H}_2\text{N} - \text{NH}_2 )</td>
</tr>
</tbody>
</table>

For Secondary and Tertiary amine, molecule structure was kept same for all solvent molecules except only one amine group was changed to secondary and tertiary by alkyl group and second amine group was kept primary for all solvents.
Carbon Chain Length: Diamine

Due to intramolecular hydrogen bonding between NH+----N in mono-protonated amine the basicity is lower. e.g. in Ethyelendiamine (2 carbon chain length primary diamine), the basicity is reduced. Increase in carbon chain length reduces this effect and increase basicity.

Brønsted plot: pKα vs Kinetics

K₂ second order rate constant for carbamate formation reaction

\[
\ln k_2 \quad \text{vs} \quad \text{pKα}
\]

Amine based solvents at 303K (30°C)

- Monoethanolamine (MEA)
- Diethanolamine (DEA)
- HMDA
- Pz
- HMDA N,N'
- EDA
- DETA

Brønsted plot: pKa vs Kinetics

Different correlation for diamine based solvents

Amine based solvents at 303K (30°C)


Amine based solvents at 303K (30°C)
Brønsted plot: pKa vs Kinetics

Amine based solvents at 303K (30°C)

- HMDA
- HMDA N,N\(^*\)
- EDA
- DETA
- MEA
- DEA
- Pz
- Diethylenetriamine (DETA)
- Piperazine (Pz)

Brønsted plot: pKa vs Kinetics

Amine based solvents at 303K (30°C)

Amine molecular structural influence can be noticed in the Brønsted plot.

CO₂ Absorption and Regeneration

Absorption Experiment
- Temp. 30°C
- Pure CO₂
- Solvent Conc. mostly 2.5 mole/L

Regeneration Experiment
- Temp. 80°C
- Atmospheric Pressure
- N₂ gas used for stripping
- Solvent Conc. mostly 2.5 mole/L

Main focus of these experiments was to identify structural influence on various amine based solvents on their reactivity towards CO₂.
Carbon Chain Length: Alkanolamine

**Monoethanolamine (MEA)**

\[ \text{H}_2\text{N} - \text{OH} \]

**3-Amino-1-propanol**

\[ \text{H}_2\text{N} - \text{OH} \]

**4-Amino-1-butanol**

\[ \text{H}_2\text{N} - \text{OH} \]

**5-Amino-1-pentanol**

\[ \text{H}_2\text{N} - \text{OH} \]
Carbon Chain Length: Alkanolamine

CO₂ absorbed over time from absorption experiment

Amount of CO₂ regenerated from desorption experiment

Rich loading (mole CO₂ / mole amine)

Time (min)

Solvent Concentration: 2.5 moles/L

Carbon Chain Length: Alkanolamine

200 minute was found to be sufficient to reach equilibrium.

Rich loading (mole CO₂ / mole amine)

Time (min)

Solvent Concentration: 2.5 moles/L

Desorption Capacity [%]

Carbon Chain length Alkanolamine


Represents how much CO₂ is regenerated, 100% means complete CO₂ regeneration.
Carbon Chain Length: Alkanolamine

Increase in absorption capacity indicate lower carbamate stability also proven by quantum mechanical calculations.

Increase in carbon chain length reduce initial absorption rate.

Solvent Concentration: 2.5 moles/L

Carbon Chain Length: Alkanolamine

Rich loading (mole CO₂ / mole amine)

Time (min)
Solvent Concentration: 2.5 moles/L

Desorption Capacity [%]

Carbon Chain length Alkanolamine

MEA
3-Amino-1-propanol
4-Amino-1-butanol
5-Amino-1-pentanol

Increase in CO₂ desorption capacity upto 4 carbon chain

Carbon Chain Length: Alkylamine

- Ethylamine: \( \text{CH}_3\text{-}\text{NH}_2 \)
- Propylamine: \( \text{CH}_3\text{-}\text{-}\text{NH}_2 \)
- Butylamine: \( \text{CH}_3\text{-}\text{-}\text{NH}_2 \)
- N-Pentylamine: \( \text{CH}_3\text{-}\text{-}\text{-}\text{-}\text{NH}_2 \)
No clear trend is noticed, absorption capacity increase upto 3 carbon chain as basicity is also not affected.

Fast initial absorption rate for 5-Carbon chain length.

Carbon Chain Length: Alkylamine

Solvent Concentration: 2.5 moles/L

Carbon Chain Length: Diamine

- Ethylenediamine
- 1,3-Diamino propane
- 1,4-Diamino butane
- Hexa(dimethylene) diamine
- 1,7-Diaminoheptane
Carbon Chain Length: Diamine

Increase in carbon chain increase capacity as pka is also increased.

6-carbon chain shows fast initial absorption rate and capacity. This might very well be caused by a formation of a hydrogen bond between the amine groups in this absorbent, thus creating a ring shaped structure.

Solvent Concentration: 2.5 moles/L
Carbon Chain Length: Diamine

Rich loading (mole CO₂ / mole amine)

Time (min)

0 50 100 150 200

Regeneration capacity is slightly improved, due to lower regeneration temp. (80°C) more concrete explanation cannot be given at this stage

Desorption Capacity [%]

Carbon Chain length Diamine

1 2 3 4 6

Solvent Concentration: 2.5 moles/L

Steric Hindrance

Rotation around the N-COO\(^-\) bond is unrestricted in the carbamate species.

In sterically hindered amines, the rotation around the N-COO\(^-\) bond in the carbamate species is restricted. Makes carbamate much less stable.

Side Chain: Alkylamine

Butylamine

\[
\text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{NH}_2
\]

Sec-butylamine (α-carbon)

\[
\text{H}_3\text{C} \text{CH} \text{CH}_2 \text{CH}_3 \text{NH}_2
\]

Isobutylamine (β-carbon)

\[
\text{H}_3\text{C} \text{CH} \text{CH}_3 \text{CH}_2 \text{NH}_2
\]
Side Chain: Alkylamine

Slight increase in absorption capacity due to α-carbon substitution

Increase in initial absorption rate due to β-carbon substitution

Rich loading (mole CO₂ / mole amine)

Solvent Concentration: 2.5 moles/L

Side Chain: Alkylamine

Solvent Concentration: 2.5 moles/L


Increase in regeneration capacity due to reduced carbamate stability by steric hindrance.
Multiple amine group

Ethylenediamine

Diethylenetriamine

Triethylenetetramine
Multiple amine group

Increase in absorption capacity by increase in number of amine group

Increase in initial absorption rate with increase in amine group

Solvent Conc. 2.5 mole/L

Multiple amine group

Solvent Conc. 2.5 mole/L


Desorption capacity is also increased
Cyclic amine

Piperidine (Pd)

Piperazine (Pz)

Trans piperazine, 2,5-dimethyl (2,5 Pz)
Cyclic amine

Rich loading (mole CO₂ / mole amine)

Time (min)

No effect of absorption capacity

Piperidine has higher pKa of 11.24, reaches similar loading as that of Piperazine (pKa 9.7)

Piperazine reaches highest desorption capacity

Solvent Conc. 0.5 mole/L

Cyclic diamine: Different Functional Group

N-ethyl piperazine

2-(1-Piperazinyl)ethylamine

2-(1-Piperazinyl)ethanol
Cyclic diamine: Different Functional Group

Substitution with an amine and alkyl group in saturated diamines leads to comparable increase in initial CO₂ absorption rates.

Substitution with an amine increase capacity


Time (min) Solvent Conc. 1.0 mole/L
Cyclic diamine: Different Functional Group

Substitution with an amine showed higher desorption capacity still lower than that of non-substituted i.e. Piperazine

Amine Degradation

Oxidative Degradation

Makeup Water

Sweet gas

Condenser

( H₂S + CO₂ )

Acid gas

Reflux drum

Reflux

Condensate

Steam

Reboiler

Vapor

Liquid

Pump

Lean amine

Rich amine

Rich amine

Lean amine

Absorber

Top Tray

Bottom Tray

Regenerator

Top Tray

Bottom Tray

Sour gas

12% CO₂
5% O₂
7%H₂O
H₂S, SO₂, HCl, NO
Amine Degradation Issues

• Solvent Makeup Cost can be significant Operating Cost

• Environmental implications of amine waste disposal

• System performance including corrosion and foaming
Thermal Degradation

- Occurs in presence of CO₂

Occurs in stripper packing, stripper sump, reboiler, reclaiming system (if present) and may occur in piping leading from main cross heat exchanger of stripper

<table>
<thead>
<tr>
<th>Primary &amp; Secondary Carbamate Alkanolamine</th>
<th>Carbamate Polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tertiaryamine</td>
<td>Transalkylation</td>
</tr>
</tbody>
</table>

High molecular weight degradation products
Oligomers/polymers
Cyclic compounds
### Thermal Degradation: Maximum Stripper Temp.

<table>
<thead>
<tr>
<th>Amine</th>
<th>Estimated Stripper Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexamethylenediamine (HMDA)</td>
<td>170</td>
</tr>
<tr>
<td>Ethylenediamine (EDA)</td>
<td>150</td>
</tr>
<tr>
<td>Trans, 2,5 Dimethyl Piperazine (2,5 Pz)</td>
<td>120</td>
</tr>
<tr>
<td>Piperazine (Pz)</td>
<td>190</td>
</tr>
<tr>
<td>Piperidine (Pd)</td>
<td>180</td>
</tr>
<tr>
<td>2-Amino-2-Methyl-1-propanol (AMP)</td>
<td>150</td>
</tr>
<tr>
<td>Methyleneediethanolamine (MDEA)</td>
<td>160</td>
</tr>
<tr>
<td>Diethanolamine (DEA)</td>
<td>140</td>
</tr>
<tr>
<td>3-AminoPropanol (AMP)</td>
<td>140</td>
</tr>
<tr>
<td>Monoethanolamine (MEA)</td>
<td>130</td>
</tr>
<tr>
<td>Diethylenetriamine (DETA)</td>
<td>120</td>
</tr>
</tbody>
</table>

Based on 2% of initial amine per week loss.

Ref: Stephanie, 201, PhD Thesis
Thermal Degradation: Maximum Stripper Temp.

Based on 2% of initial amine per week loss

Hexamethylenediamine (HMDA)
Ethylenediamine (EDA)
Trans, 2,5 Dimethyl Piperazine (2,5 Pz)
Piperazine (Pz)
Piperidine (Pd)
2-Amino-2-Methyl-1-propanol (AMP)
Methylenediethanolamine (MDEA)
Diethanolamine (DEA)
3-AminoPropanol (AMP)
Monoethanolamine (MEA)
Diethylenetriamine (DETA)

Estimated Stripper Temp. (°C)

Ref: Stephanie, 201, PhD Thesis
Thermal Degradation: Maximum Stripper Temp.

Secondary amine DEA degradate above 120°C

- Hexamethylenediamine (HMDA)
- Ethylenediamine (EDA)
- Trans, 2,5 Dimethyl Piperazine (2,5 Pz)
- Piperazine (Pz)
- Piperidine (Pd)
- 2-Amino-2-Methyl-1-propanol (AMP)
- Methylenediethanolamine (MDEA)
- Diethanolamine (DEA)
- 3-AminoPropanol (AMP)
- Monoethanolamine (MEA)
- Diethylenetriamine (DETA)

Ref: Stephanie, 201, PhD Thesis
Thermal Degradation: Maximum Stripper Temp.

6-Carbon chain diamine (HMDA) has higher temp. as this cannot form cyclic degradation products

Hexamethylenediamine (HMDA)
Ethylenediamine (EDA)
Trans, 2,5 Dimethyl Piperazine (2,5 Pz)
Piperazine (Pz)
Piperidine (Pd)
2-Amino-2-Methyl-1-propanol (AMP)
Methylenediethanolamine (MDEA)
Diethanolamine (DEA)
3-AminoPropanol (AMP)
Monoethanolamine (MEA)
Diethylenetriamine (DETA)

Ref: Stephanie, 201, PhD Thesis
Thermal Degradation: Maximum Stripper Temp.

Cyclic diamine (Pd, Pz and 2,5Pz) has higher regeneration temp.

Hexamethylenediamine (HMDA)
Ethylenediamine (EDA)
Trans, 2,5 Dimethyl Piperazine (2,5 Pz)
Piperazine (Pz)
Piperidine (Pd)
2-Amino-2-Methyl-1-propanol (AMP)
Methylenediethanolamine (MDEA)
Diethanolamine (DEA)
3-AminoPropanol (AMP)
Monoethanolamine (MEA)
Diethylenetriamine (DETA)

Ref: Stephanie, 201, PhD Thesis
Oxidative Degradation

- Occurs in presence of $O_2$

Degradation products, which can act as chelating agents which can cause iron concentrations as high as 160 ppm. These metals are catalytically active and promote oxidative degradation when they come in contact with oxygen.

Radical Reaction

Metal Catalyzed e.g. Iron

Occurs in liquid-holdup in absorber bottom, temp. bulge due to heat of absorption in the middle / top of absorber

Oxidized fragments of the solvent

Organic Acids
Amide
Aldehyde
Alcohols
Ammonia ($NH_3$)
Nitrosamines
Oxidative Degradation

Oxidative degradation Experiment at 80°C with 50% O₂ + 50% CO₂ and solvent concentration of 2.5 mole/L.

Alkalinity is a measure of solution capacity to react with acid.

- 2-Amino-2-Methyl-1-propanol (AMP)
- Methylene diethanolamine (MDEA)
- Triethanolamine (TEA)
- Diethanolamine (DEA)
- Monoethanolamine (MEA)

Loss of Alkalinity%

Issues with Foaming in Amines

- Solvent Loss
- Premature Flooding
- Reduction in plant throughput
- Off-specification of products
- High Solvent Carryover to downstream plants

Causes:

- High Gas Velocity
- Sludge deposit on gas contractor
- Process contaminants

Foaming Occurs during start-ups and operating plant
## Parameters affecting Foaming

<table>
<thead>
<tr>
<th>Process Parameters</th>
<th>Physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flow rate</td>
<td>Gas density</td>
</tr>
<tr>
<td>Solvent Volume</td>
<td>Liquid density</td>
</tr>
<tr>
<td>Solvent Concentration</td>
<td>Liquid viscosity</td>
</tr>
<tr>
<td>CO$_2$ Loading</td>
<td>Surface tension</td>
</tr>
<tr>
<td>Solvent Temperature</td>
<td></td>
</tr>
</tbody>
</table>
Foaming: Effect of Solvent Concentration

- Based on Monoethanolamine (MEA) solvent, test was done with N\textsubscript{2} gas flow
- Foaminess coefficient (min): Average Lifetime of Foam

Absorber Top → Temp. 40°C, CO\textsubscript{2} Loading: 0.2 mole CO\textsubscript{2} / mole amine
Absorber Bottom → Temp. 60°C, CO\textsubscript{2} Loading: 0.4 mole CO\textsubscript{2} / mole amine

Foaming: Effect of Solvent Concentration

- Based on Monoethanolamine (MEA) solvent, test was done with N₂ gas flow
- Foaminess coefficient (min): Average Lifetime of Foam

Increase in solvent concentration increase density and bulk viscosity. As foaminess first increases and then decreases with increase in solvent concentration is called creaming process when bulk viscosity plays important role in rising bubble. Such decrease is also caused by reduced foam stability by increase in surface viscosity.

Foaming: Effect of CO₂ loading

Increase in CO₂ loading decreases surface tension and solution density increases. This reduced surface tension promote foam formation.

At higher CO₂ loading solution viscosity increases and become more significant than surface tension and density, hence foaming is reduced.

MEA Concentration: 5 mol/L, N₂ Flow rate: 2.06 m³/m².h

Foaming: Density

MEA Concentration: 5 mol/L

Foaming: Viscosity

MEA Concentration: 5 mol/L

Foaming: Effect of Temperature

MEA Concentration: 5 mol/L, N₂ Flow rate: 2.06 m³/m²


Poor foam stability due to reduced bulk viscosity, and turbulent flow created by vigorous movement of molecule at an elevated temperature.
Foaming: Effect of Degradation products

<table>
<thead>
<tr>
<th>Degradation products</th>
<th>Avg. Foaminess Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.79</td>
</tr>
<tr>
<td>Ammonium Thiosulfate</td>
<td>0.97</td>
</tr>
<tr>
<td>Glycolic Acid</td>
<td>0.94</td>
</tr>
<tr>
<td>Sodium Sulphate, Malonic Acid</td>
<td>0.92 (each)</td>
</tr>
<tr>
<td>Oxalic Acid, Sodium Thiosulfate, Sodium Chloride</td>
<td>0.90 (each)</td>
</tr>
<tr>
<td>Sodium Thiosulfate, Bicine</td>
<td>0.85 (each)</td>
</tr>
<tr>
<td>Hydrochloric Acid, Formic Acid</td>
<td>0.83 (each)</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>0.82</td>
</tr>
<tr>
<td>Sulphuric Acid</td>
<td>0.77</td>
</tr>
</tbody>
</table>

Anionic surfactants formation in presence of sulfate, sulfonate and carboxylate, reduce surface tension and foaminess increases.

Foaming: Different Alkanolamine

MEA solution are easier to have creaming process due to lower solution viscosity.

CO₂ stripped out during experiment (from 0.4 mol/mol to 0.2 mol/mol) thus increase foaminess.

DEA and AMP don’t foam due to high bulk viscosity.

ASAP

Pilot Plant

Absorber height 150cm; packing height 145cm and 28 mm internal diameter

Regenerator height 150cm and packing height 130cm and 28mm diameter

Structured Packing

Experiment:
Absorber: 40C & 1.3 bar;
Regeneration: 124C & 2 Bar

## Energy Efficient Solvent Development

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CO₂ inlet Conc.</th>
<th>Flue gas flow rate</th>
<th>Solvent flow rate</th>
<th>CO₂ recovery</th>
<th>Cyclic loading</th>
<th>Energy requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vol%</td>
<td>nL/h</td>
<td>kg/h</td>
<td>%</td>
<td>mole CO₂/mole amine</td>
<td>MJ/kg CO₂</td>
</tr>
<tr>
<td><strong>MEA 31 wt%</strong>(*)</td>
<td>5</td>
<td>645</td>
<td>0.90</td>
<td>91</td>
<td>0.29</td>
<td>4.80</td>
</tr>
<tr>
<td><strong>AMP 30 wt% + Pz 5 wt%</strong>(*)</td>
<td>5</td>
<td>645</td>
<td>0.63</td>
<td>90</td>
<td>0.51</td>
<td>3.87</td>
</tr>
<tr>
<td><strong>New Solvent 51 wt%</strong></td>
<td>5</td>
<td>645</td>
<td>0.48</td>
<td>93</td>
<td>0.84</td>
<td>2.48</td>
</tr>
<tr>
<td><strong>AMP 26.74 wt% + HMDA 11.91 wt%</strong></td>
<td>5</td>
<td>645</td>
<td>0.63</td>
<td>91</td>
<td>0.44</td>
<td>3.62</td>
</tr>
<tr>
<td><strong>MEA 31 wt%</strong>(*)</td>
<td>10</td>
<td>400</td>
<td>0.91</td>
<td>89</td>
<td>0.34</td>
<td>4.33</td>
</tr>
<tr>
<td><strong>AMP 35.6 wt%</strong>(*)</td>
<td>10</td>
<td>400</td>
<td>1.07</td>
<td>90</td>
<td>0.37</td>
<td>3.91</td>
</tr>
<tr>
<td><strong>New Solvent 51 wt%</strong></td>
<td>10</td>
<td>400</td>
<td>0.57</td>
<td>89</td>
<td>0.80</td>
<td>2.26</td>
</tr>
<tr>
<td><strong>AMP 26.74 wt% + HMDA 1.91 wt%</strong></td>
<td>10</td>
<td>400</td>
<td>0.73</td>
<td>88</td>
<td>0.46</td>
<td>3.41</td>
</tr>
</tbody>
</table>

## Energy Efficient Solvent Development

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CO₂ inlet Conc.</th>
<th>Flue gas flow rate</th>
<th>Solvent flow rate</th>
<th>CO₂ recovery</th>
<th>Cyclic loading</th>
<th>Energy requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vol%</td>
<td>nL/h</td>
<td>kg/h</td>
<td>%</td>
<td>mole CO₂/mole amine</td>
<td>MJ/kg CO₂</td>
</tr>
<tr>
<td>MEA 31 wt%(*)</td>
<td>5</td>
<td>645</td>
<td>0.90</td>
<td>91</td>
<td>0.29</td>
<td>4.80</td>
</tr>
<tr>
<td>AMP 30 wt% + Pz 5 wt%(*)</td>
<td>5</td>
<td>645</td>
<td>0.63</td>
<td>90</td>
<td>0.51</td>
<td>3.87</td>
</tr>
<tr>
<td>New Solvent 51 wt%</td>
<td>5</td>
<td>645</td>
<td>0.48</td>
<td>93</td>
<td>0.84</td>
<td><strong>2.48</strong></td>
</tr>
<tr>
<td>AMP 26.74 wt% + HMDA 11.91 wt%</td>
<td>5</td>
<td>645</td>
<td>0.63</td>
<td>91</td>
<td>0.44</td>
<td>3.62</td>
</tr>
<tr>
<td>MEA 31 wt%(*)</td>
<td>10</td>
<td>400</td>
<td>0.91</td>
<td>89</td>
<td>0.34</td>
<td>4.33</td>
</tr>
<tr>
<td>AMP 35.6 wt%(*)</td>
<td>10</td>
<td>400</td>
<td>1.07</td>
<td>90</td>
<td>0.37</td>
<td>3.91</td>
</tr>
<tr>
<td>New Solvent 51 wt%</td>
<td>10</td>
<td>400</td>
<td>0.57</td>
<td>89</td>
<td>0.80</td>
<td><strong>2.26</strong></td>
</tr>
<tr>
<td>AMP 26.74 wt% + HMDA 1.91 wt%</td>
<td>10</td>
<td>400</td>
<td>0.73</td>
<td>88</td>
<td>0.46</td>
<td>3.41</td>
</tr>
</tbody>
</table>

Conclusions

• Solvent structure influence their CO$_2$ absorption characteristics

• Environmental issues in solvent development are as important as other solvent issues.

• All aspects should be taken into account for solvent development

• Process specific solvent is required to be developed
Post Combustion: Where to Focus

- Novel solvents: Higher capacity, lower reaction enthalpy, stable and cheaper
- Smart process concepts and heat integration
- Capture environmental impact
- Cheaper equipments (absorber > 45% of CAPEX)
- Membranes, adsorbents and other processes have the potential as 2\textsuperscript{nd}/3\textsuperscript{rd} generation

Source: Figueroa et al., 2008
My Selected Publications:

- Singh P., van Swaaij W. P. M., Brilman D. W. F., 2011, Kinetics study of carbon dioxide absorption in aqueous solutions of 1,6 Hexamethyldiamine (HMDA) and 1,6 Hexamethyldiamine, N,N’ di-methyl (HMDA, N,N’). Chemical Engineering Science, Vol 66 (20), pp 4521–4532


Thank you

E-mail: prachi.singh@ieachg.org
Website: www.ieachg.org

GHGT-11
Kyoto, Japan
www.ghgt.info
18th - 22nd Nov. 2012