Environmental Effects of Emissions from Amine-based CO₂ PCC Process

Merched Azzi, Sunil Sharma, Narendra Dave, Paul Feron, Moetaz Attalla, Martin Cope, Mohammed Abuzahra

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Objectives

Assess the benefits of the deployment of PCC plants in terms of their potential reductions related to atmospheric emissions by:

- Identifying the types and rate of emissions expected from the deployment of PCC processes using available information;
- Identifying the reduction technology that could be deployed to reduce selected emissions;
- Assessing the expected impact of these emissions on the environment;
- Clarifying how new scientific understanding can be communicated and integrated in the current environmental regulations.
CSIRO PCC Activities

- Process Modelling
- Solvent Chemistry/Development
- Three Pilot Plants
- Atmospheric Chemistry
- Air Quality Model

- Reactive & non-reactive Licensing & permitting
- Inputs to Air Quality Regulators

Plant Optimisation

CSIRO Presentation to IEA PCCC1 19th May 2011 Abu Dhabi
Main environmental challenges for PCC

How to identify and minimise volumes of harmful pollutants that may escape from the plant?

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Overview

• All solvents used for amine-based CO₂ capture degrade during the capture process by thermal, oxidation and both thermal-oxidation.

• The degradation products depend on the:
  • The type of solvent used
  • Process operational conditions
  • Temperature
  • Oxygen levels, NOₓ, SOₓ and other impurities
  • Types of additives used
Issues: Does the photo-oxidation of amines produce compounds with health/environmental concerns?

- What types of pollutants are being emitted or formed during subsequent atmospheric chemical reactions?
- What kind of experiments should be carried out to determine the photochemical lifetime of selected amines?
- How will new type of pollutants be identified and measured?
- What are the major removal processes for these pollutants?
Expected Degradation Products from MEA

• Volatile products: 
  NH₃, aldehydes, acetone, “methylamine, dimethylamine”, etc.

• Products with volatility close or less than that of the solvent: 
  Oxazolidine, HEED, HEI, HEIA etc.

• Non-volatile products: 
  formic acid, acetic acid, oxalic acid and heat stable salts HSS.

• Small quantities of N-nitroso ppb levels were reported from MEA. However, this N-nitroso production may be due to impurities in the used solvent.

• Other non volatile products can also be found in the reclaimer waste
## Selected MEA Degradation products

<table>
<thead>
<tr>
<th>Volatile MEA Products</th>
<th>Atmospheric chemistry</th>
<th>Non volatile</th>
<th>Atmospheric chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine</td>
<td>Photochemical reactions (PCR)</td>
<td>Formic acid</td>
<td>Atmospheric reactions</td>
</tr>
<tr>
<td>Ammonia</td>
<td>(PCR)</td>
<td>Acetic acid</td>
<td>Atmospheric reactions</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>(PCR)</td>
<td>Oxalic acid</td>
<td>Atmospheric reactions</td>
</tr>
<tr>
<td>acetaldehyde</td>
<td>(PCR)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>(PCR)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylamine</td>
<td>(PCR)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>diethylamine</td>
<td>(PCR)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-nitroso compounds</td>
<td>Atmospheric reactions</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Process Modelling
Coal fired/Natural Gas Power Plants
Characteristics of feed flue gas and CO$_2$ capture plant conditions used for the simulation

<table>
<thead>
<tr>
<th>Main operating conditions:</th>
<th>CFUS Power Plant</th>
<th>NGCC Power Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Rate (Tonnes/hr)</td>
<td>2973</td>
<td>4733</td>
</tr>
<tr>
<td>Temperature ($^\circ$C)</td>
<td>50</td>
<td>101</td>
</tr>
<tr>
<td>Pressure (kPa)</td>
<td>102.3</td>
<td>102.3</td>
</tr>
<tr>
<td>Composition:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_2$ (Mole %)</td>
<td>4.3</td>
<td>12.5</td>
</tr>
<tr>
<td>CO$_2$ (Mole %)</td>
<td>12.4</td>
<td>4</td>
</tr>
<tr>
<td>H$_2$O (Mole %)</td>
<td>12.2</td>
<td>7.8</td>
</tr>
<tr>
<td>N$_2$ (Mole %)</td>
<td>71.1</td>
<td>75.7</td>
</tr>
<tr>
<td>SO$_2$ (mg/m3)</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>NO$_x$ (mg/m3)</td>
<td>200</td>
<td>20</td>
</tr>
<tr>
<td>PCC plant conditions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absorber inlet temperature ($^\circ$C)</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Stripper bottom temperature ($^\circ$C)</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Lean amine solvent inlet temperature at absorber ($^\circ$C)</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>CO$_2$ loading with lean amine (mole/mole of MEA)</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>CO$_2$ capture efficiency (%v)</td>
<td>87.5</td>
<td>85</td>
</tr>
<tr>
<td>Demineralised and cooling water temperature ($^\circ$C)</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Maximum temperature of cooling water ($^\circ$C)</td>
<td>19</td>
<td>19</td>
</tr>
</tbody>
</table>
Tasks

• Evaluate the effect of process parameters on the formation and emission of potentially harmful compounds (amines, nitrosamines, alkylamines, nitramines, aldehydes)

  ➢ Flue gas composition, CO₂ loading, DCC treatment, absorber, water wash, demister, stripper, reclaimer/reboiler, metallurgy

• Prediction of degradation products of H&E relevance
• Emission estimates, vapour and droplet dominated emissions
CO2 Capture Process Simulations

• ASPEN Process Simulations

- Generic process flow-sheet
- ASPEN Equilibrium model for Absorber/Stripper (RADFRAC)
- ASPEN Amine Property Package (Electrolyte NRTL)
- Optimised operating conditions (Minimum Re-boiler Duty)
- Inclusion of Degradation Chemistry (Within ASPEN limits)
- Material and Energy balance
Modelling Challenges for predicting degradation products

- Plant Design, Operating and Maintenance practice
- Type of packing in the absorber and wash sections
- Hydrodynamics in the absorber and wash sections
- Type of demister before and after gas wash
- Impact of degradation products on solvent property
- Kinetics and Stoichiometry of degradation unclear

Modern plants may use structured packing in the absorber and the water wash section. Inter-cooling in the absorber will affect the vapour phase and droplet carryover.
Factors affecting the emission of degradation products

• The chemical properties of the solvent and additives

• The design of capture plant and the control technology used for the capture

• It appears that the proper design of an optimised water wash system will be capable to reduce most of the amines emissions and other non-volatile products. However, this system may not be efficient to capture N-nitroso compounds as well as other compounds such as NH3 and alkylamines.
Range of atmospheric emissions of MEA and its degradation products that leaves the water wash tower (Coal fired)

<table>
<thead>
<tr>
<th>Chemical Emissions</th>
<th>Minimum (mg/tonne)</th>
<th>Maximum (mg/tonne)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>0.86</td>
<td>0.86</td>
</tr>
<tr>
<td>NH3</td>
<td>1980</td>
<td>3600</td>
</tr>
<tr>
<td>DEA</td>
<td>-</td>
<td>0.14</td>
</tr>
<tr>
<td>FORMALDEHYDE</td>
<td>919</td>
<td>936</td>
</tr>
<tr>
<td>ACETALDEHYDE</td>
<td>978</td>
<td>990</td>
</tr>
<tr>
<td>ACETONE</td>
<td>1160</td>
<td>1200</td>
</tr>
<tr>
<td>METHYLMINE</td>
<td>745</td>
<td>764</td>
</tr>
<tr>
<td>ACETAMIDE</td>
<td>-</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Atmospheric Fate of major pollutants

- Chemical mechanism
- Windfields/dispersion
- Emission Inventory

Industry/pilot plant ➔ Transport ➔ Biogenics

Dry and wet deposition ➔ Impacts
- Human health
- Ecosystem health

AQMs
- 2-D Langrangian Model
- 3-D (CTM)

- What would be the impact of changing emissions profiles?
Atmospheric chemical reactions. The CSIRO smog chamber facility

The smog chamber is an 18 m$^3$ Teflon-lined enclosure with UV lamps at both ends to simulate sunlight.

The chamber is filled with clean air and dosed with NO$_x$ and VOC to simulate ozone and secondary organic aerosol formation in the atmosphere.

Dedicated instruments track the concentrations of:
- Ozone,
- NO$_x$
- Particles
- VOCs
Atmospheric Reaction Scheme for MEA

• In the atmosphere, MEA undergo complex chemical reactions with OH, O$_3$, NO$_3$ and HNO$_3$.

• A generic chemical reaction scheme was established using smog chamber data.

• These reactions were embedded into the 3-D CSIRO Chemical Transport Model (CTM) to calculate the GLCs of major pollutants.
GLCs of MEA
Emission Reduction Technology of Pollutants

- Scrubbing technology could be easily retrofitted into existing PCC plants.
- Droplets that are enriched with amine will reduce the efficiency of water wash system. A demister placed before the water wash section should be able to remove most of the droplets while the gas continues its pathway.
- Ultrafine droplets can be captured by Brownian demisters
- An optimised multi-stage water-wash system installed on top of the absorber outlet will be able to minimise solvent losses due to evaporation and droplet carryover.
- Acid-wash may be an option that should be investigated as well as an optimised UV system for the destruction of N-nitroso compounds.
• Identify the main waste streams from MEA PCC plants, and approximate emission quantities.
  • Gaseous and aerosols (to atmosphere)
  • Liquid and solid discharges
• Examine existing federal and state legislation that may apply to these plants
  • Ambient air quality guidelines
  • Occupational health and safety standards
• Are there gaps in legislation?
• What information will be necessary to conduct appropriate environmental impact assessments?
• Compliance issues:
  • Measurement techniques for components in waste streams
Legislative, Regulatory and Permitting Requirements of Amine PCC

- Criteria pollutants (Regulated by Agencies)
- Air Toxics
- Emerging pollutants
- Biodegradation, hydrolysis and photolysis in Water streams
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Contact Us
Phone: 1300 363 400 or +61 3 9545 2176
Email: enquiries@csiro.au  Web: www.csiro.au

Thank you