This document was created in response to a Freedom of Information request made to CSIRO.

FOI Number: FOI2011/65

Date: 4 July 2012


Document: Part 2 – Documents 16-34

For more information, please refer to CSIRO’s FOI disclosure log at www.csiro.au/FOILog
Hi John,

Cameron has asked me to send through some updated words on this. Please find them attached. As you can see, I've provided both a long and a short version to use depending on the medium/space etc.

Please let me know of your approval or of any changes.

Thanks in advance,

Lou
Louise Morrissey | Communication Manager | CSIRO | Energy Transformed Flagship & Division of Energy Technology
10 Murray Dwyer Circuit, Steel River Industrial Park, Mayfield West, NSW 2304
T +61 2 4960 6140 | F +61 2 4960 6054 | M 0419 168 940 | lou.morrissey@csiro.au | www.csiro.au

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To the extent permitted by law, CSIRO does not represent, warrant and/or guarantee the integrity of this communication has been maintained nor the communication is free of error, virus, interception or interference.
CSIRO and Tarong Energy’s PCC project

CSIRO’s Energy Transformed Flagship is working with Tarong Energy to undertake a research project into post-combustion capture (PCC) technologies in an effort to stem climate change.

Post-combustion capture (PCC) is a process that uses a liquid to capture carbon dioxide ($\text{CO}_2$) from power station flue gases and is a key technology that can potentially reduce carbon dioxide emissions from existing and future coal-fired power stations by more than 85 per cent.

Commencing in July 2008, the two-year project will see the design, construction and operation of a 1500 tonnes per annum PCC pilot plant at Tarong Power Station near Yarraman in south-east Queensland.

The Tarong trial will focus on assessing the performance of an amine-based PCC pilot plant that will be integrated into the existing coal-fired power station. CSIRO and Tarong Energy will each contribute $2.5 million to the project.

The installation of the PCC pilot plant at Tarong forms part of the Asia Pacific Partnership on Clean Development and Climate initiative (APP) and is an important part of the APP Flagship project focussed on developing world-class PCC laboratory and pilot projects.

The APP program for PCC also includes a pilot plant installation (based on ammonia) at Delta Electricity’s Munmorah power station on the NSW Central Coast and the establishment of a pilot plant at Gaobeidian Power Station in Beijing. The Australian Government is supporting this work through a $12 million grant.

Reducing emissions from coal-fired power stations is one of the key ways to help cut Australia’s greenhouse gas emissions. CSIRO is at the leading edge of developing PCC technologies that can be retrofitted to existing coal-fired power stations to help achieve this goal.

*If shorter blurb required:*

CSIRO and Tarong Energy are undertaking a two-year project to design, construct and operate a 1500 tonnes per annum post-combustion capture (PCC) pilot plant at Tarong Power Station in south-east Queensland. The trial will focus on assessing the performance of an amine-based PCC pilot plant that has the potential to reduce carbon dioxide emissions by more than 85 per cent – a major step in tackling climate change. CSIRO and Tarong Energy are each contributing $2.5 million to the project, and CSIRO’s involvement has been made possible through funding from the Australian Government as part of the Asia Pacific Partnership on Clean Development and Climate initiative.
Thanks Ann.

Steve - We're now looking at putting it out on Thursday, so there's a little more time. A slightly amended version is also attached.

Lou

---

From: Boon, Ann [mailto:Ann.Boon@ret.gov.au]
Sent: Friday, 25 July 2008 4:10 PM
To: Morrissey, Lou (ET F/ship, Newcastle)
Cc: Woolcott, Stephen
Subject: RE: Media release re China PCC project [SEC=UNCLASSIFIED]

Hi Lou,

We've had an internal restructure here so Steve Woolcott is now looking after both PCC projects.

He'll get back to you shortly on this.

Kind regards,
Ann

Ann Boon
Low Emissions Coal Policy Section
Resources Division
Ph: 61-2-6213 7408
Email: ann.boon@ret.gov.au

---

From: Lou.Morrissey@csiro.au [mailto:Lou.Morrissey@csiro.au]
Sent: Friday, 25 July 2008 12:23 PM
To: Boon, Ann
Subject: Media release re China PCC project

Hi Ann,

Hope all's well.

Please find attached a media release we're looking at distributing on Monday about the launch of the PCC plant in China. Please let me know if you have any questions on this or if you're happy with the content. David Brockway will be our spokesperson and has approved the release.

Lou
Louise Morrissey | Communication Manager | CSIRO | Energy Transformed Flagship & Division of Energy Technology
10 Murray Dwyer Circuit, Steel River Industrial Park, Mayfield West, NSW 2304
T +61 2 4980 6140 | F +61 2 4980 6054 | M 0419 168 940 | lou.morrissey@csiro.au | www.csiro.au

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******************************************************************************
31 July 2008
Ref 071 (Supplied by Corp. Comms)

**Media Release**

**Carbon capture milestone for CSIRO in China**

Just weeks out from the Olympics, the CSIRO and its Chinese partners have officially launched a post-combustion capture (PCC) research-pilot plant in Beijing that strips carbon dioxide from power station flue gases in an effort to stem climate change.

The project represents another first for the CSIRO PCC program - the first capture of carbon dioxide in China using a PCC technology pilot plant. It begins the process of applying the technology to Chinese conditions and evaluating its effectiveness.

Post-combustion capture (PCC) is a process that uses a liquid to capture carbon dioxide from power station flue gases and is a technology that can potentially reduce carbon dioxide emissions from existing and future coal-fired power stations by more than 85 per cent.

The post-combustion research pilot plant at the Huaneng Beijing Co-Generation Power Plant is designed to capture 3000 tonnes per annum of carbon dioxide.

CSIRO's partners in the Beijing pilot project are China's Huaneng Group and the Thermal Power Research Institute (TPRI).

Chief of CSIRO's Energy Technology Division, Dr David Brockway, said the project was part of a broad research-program to identify ways to significantly reduce greenhouse gas emissions from the energy sector.

"Given the world's reliance on coal, we need to find ways to make it a cleaner energy source. We're delighted to be working with our partners in China to help find solutions to this global challenge," Dr Brockway said.

"In a recent visit to China, the Prime Minister said that China was the largest consumer of coal in the world and Australia was the world's largest exporter of coal. As such, Australia and China should work together develop low emissions coal technologies."

The carbon capture project will focus on assessing the performance of an amine-based PCC research-pilot plant under Chinese conditions.

"It will allow PCC technology to be progressed in the Chinese energy sector which will have a much greater impact than operating in Australia alone," Dr Brockway said.

"The next steps in the research would be moving to a much larger demonstration phase, before then progressing to a full scale system."

The Australian Government is supporting PCC research through a $12 million grant, $4 million of which supports this work in China.

The installation of the PCC pilot plant in Beijing is a CSIRO Energy Transformed Flagship research project and forms part of the Asia Pacific Partnership on Clean Development and Climate initiative (APP). The APP program for PCC also includes a pilot plant installation at Delta Electricity's Munmorah power station on the NSW Central Coast, with an additional Queensland site currently under negotiation.

CSIRO is also undertaking PCC research outside the scope of the APP program with a $5.6 million project in the Latrobe Valley, which focuses on brown coal.

**National Research Flagships** [www.csiro.au/flagships]: CSIRO initiated the National Research Flagships to provide science-based solutions in response to Australia's major research challenges and opportunities. The nine Flagships form multidisciplinary teams with industry and the research community to deliver impact and benefits for Australia.

**Image available at:** (Link to be provided to Corporate Comms by Science Image Online)
Further Information:  (ALL text in 10pt Arial)
Dr David Brockway, Division of Energy Technology  Ph: 0418 543 985 / 02 4960 6048
david.brockway@csiro.au

Media Assistance:
Ms Lou Morrissey, Energy Transformed Flagship  Ph: 02 4960 6140 / 0419 168 940
lou morrissey@csiro.au

www.csiro.au

If you would like to be removed from this mailing list please contact CSIROMedia@csiro.au
Hi Lou

Sorry for not responding earlier. I have included some changes in tracking mode in the attached document. I am not sure if I need to but we agree to the release.

Regards
Stephen Woolcott
Manager
APP & Contract Management Section
APP Aluminium Task Force Secretariat
International, Resources Development
& Taxation Branch
Resources Division

Department of Resources, Energy and Tourism
Level 10, 10 Binara Street, Canberra City ACT 2601
GPO Box 1564, Canberra ACT 2601 Australia
PH: 61-2-6276 1890 Fax: 61-2-6213 6026
Email: Stephen.Woolcott@ret.gov.au
Internet: http://www.rei.gov.au
ABN 46 252 861 927

Hi Steve,

Did you have any changes to the release or am I right to send it through to our media unit ready for distribution?

Lou

From: Morrissey, Lou (ET F/ship, Newcastle)
Sent: Friday, 25 July 2008 4:15 PM
To: 'Boon, Ann'
Cc: Woolcott, Stephen
Subject: RE: Media release re China PCC project [SEC=UNCLASSIFIED]

Thanks Ann.

Steve - We’re now looking at putting it out on Thursday, so there’s a little more time. A slightly amended version is also attached.

Lou

From: Boon, Ann [mailto:Ann.Boon@ret.gov.au]
Media Release

31 July 2008
Ref 07/ ? (Supplied by Corp. Comms)

Carbon capture milestone for CSIRO in China

Just weeks out from the Olympics, the CSIRO and its Chinese partners have officially launched a post-combustion capture (PCC) research-pilot plant in Beijing that strips carbon dioxide from power station flue gases in an effort to stem climate change.

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Chief of CSIRO's Energy Technology Division, Dr David Brockway, said the project was part of a broad research program to identify ways to significantly reduce greenhouse gas emissions from the energy sector.

"Given the world's reliance on coal, we need to find ways to make it a cleaner energy source. We're delighted to be working with our partners in China to help find solutions to this global challenge," Dr Brockway said.

"In a recent visit to China, the Prime Minister Kevin Rudd said that China was the largest consumer of coal in the world and Australia was the world's largest exporter of coal. As such, Australia and China should work together to develop low emissions coal technologies."

The carbon capture PCC project will focus on assessing the performance of an amine-based PCC research-pilot plant under Chinese conditions.

"It will allow PCC technology to be progressed in the Chinese energy sector which will have a much greater impact than operating in Australia alone," Dr Brockway said.

"The next steps in the research would be moving to a much larger demonstration phase, before then progressing to a full scale system."

The Australian Government is supporting PCC research through a $42 million grant, $4 million of which supports this work in China.

The installation of the PCC pilot plant in Beijing is a CSIRO Energy Transformed Flagship research project and forms part of which receives funding from the Australian Government through the Asia Pacific Partnership on Clean Development and Climate initiative (APP). The APP program for PCC also includes a pilot plant installation at Delta Electricity's Munmorah power station on the NSW Central Coast, with an additional Queensland site currently under negotiation.

The Australian Government's APP support PCC research is $12 million, $4 million of which supports this work in China.

CSIRO is also undertaking PCC research outside the scope of the APP program with a $5.6 million project in the Latrobe Valley, which focuses on brown coal.
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Further Information: (ALL text in 10pt Arial)
Dr David Brockway, Division of Energy Technology
Ph: 0418 543 985 / 02 4960 6048
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Media Assistance:
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Ph: 02 4960 6140 / 0419 168 940
lou.morrissey@csiro.au

www.csiro.au

If you would like to be removed from this mailing list please contact CSIROMedia@csiro.au
Hi Stephen,

CSIRO and Tarong have signed the PCC agreement so we're ready to announce this project publicly.

Please find attached a draft media release for your review. Please let me know of your approval, or of any changes, and we will finalise ready for distribution (likely to be early/mid next week).

I understand that Tarong have also drafted a media release for the QLD Minister for Mines and Energy, Geoff Wilson, to release at the same time.

Kind regards,

Lou
Louise Morrissey | Communication Manager | CSIRO | Energy Transformed Flagship & Division of Energy Technology
10 Murray Dwyer Circuit, Steel River Industrial Park, Mayfield West, NSW 2304
T +61 2 4960 6140 | F +61 2 4960 6054 | M 0419 168 940 | lou.morrissey@csiro.au | www.csiro.au

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Pilot plant to help tackle climate change – a QLD first

In a first for Queensland, CSIRO and Tarong Energy today announced a $5 million joint pilot project to capture greenhouse gases.

The project will see the installation of a post-combustion capture (PCC) pilot plant at Tarong Power Station, 45km south of Kingaroy.

The pilot plant is designed to capture 1500 tonnes per annum of CO2 from the power station and is part of a broader research program to identify ways to reduce greenhouse gas emissions from the energy sector.

The two year project will start immediately, with the pilot plant expected to be operational by July 2009. This will allow 12 months to carry out further research activities associated with the technology.

Director of CSIRO’s Energy Transformed National Research Flagship, Dr John Wright, said low emission energy generation was a key research area for the Flagship.

“80 per cent of the energy consumed in Australia is generated from large, coal-fired power stations. It’s critical that we find ways to make coal a cleaner energy source and we’re pleased to be working with Tarong Energy to help find these solutions,” Dr Wright said.

“When coupled with CO2 sequestration, post-combustion capture, offers the potential for near zero emissions from coal-fired power stations.

“While this project won’t immediately reduce emissions, the information gathered from the research work will be used to further develop the technology for a commercial-scale application.”

Tarong Energy Chair, Graham Carpenter, said the Corporation is proud to be part of the CSIRO project which is the first of its type in Queensland.

“The project marks a significant milestone for Tarong Energy in its efforts to reduce its environmental footprint,” Mr Carpenter said.

“The Corporation is acutely aware of its environmental responsibilities and over the past few years we have introduced a number of initiatives to reduce our impact on the environment.

“We will work very closely with the CSIRO to deliver a successful project which may lead to similar technology being installed at coal-fired generators throughout Australia.”

In the PCC process the power station’s flue gas is passed through a chemical solution (sorbent) where 85-95% of the CO2 is captured. The CO2-rich sorbent is then treated to separate the CO2. The CO2 is then able to be compressed and cooled to form a liquid for pipeline transport to a sequestration site.
The Tarong trial will focus on assessing the performance of an amine-based PCC pilot plant that will be integrated into the existing coal-fired power station. CSIRO and Tarong Energy will each contribute $2.5 million to the project.

The PCC pilot plant at Tarong is an integral part of the PCC Flagship Project under the Asia Pacific Partnership on Clean Development and Climate (APP). This project involves trials at several power stations, including Tarong, a pilot plant installation (based on ammonia) at Delta Electricity’s Munmorah power station on the NSW Central Coast and the establishment of a pilot plant at Gaobeidian Power Station in Beijing. These trials are backed up by the development of a world-class PCC laboratory in Australia.

The work in Australia and China is making a leading contribution to the international development of technology that can be retrofitted to existing coal power stations to capture greenhouse gas emissions. CSIRO is operating at the leading edge in developing PCC technologies. The Australian Government is supporting this work by CSIRO through a $12 million grant.

CSIRO is also undertaking PCC research outside the scope of the APP program with a $5.6 million project in the Latrobe Valley, which focuses on brown coal.

National Research Flagships [www.csiro.au/flagships]: CSIRO initiated the National Research Flagships to provide science-based solutions in response to Australia’s major research challenges and opportunities. The nine Flagships form multidisciplinary teams with industry and the research community to deliver impact and benefits for Australia.
Hi Lou

A few minor changes and we agree to the release.

Regards
Stephen Woolcott
Manager
APP & Contract Management Section
APP Aluminium Task Force Secretariat
International, Resources Development
& Taxation Branch
 Resources Division

Department of Resources, Energy and Tourism
Level 10, 10 Binara Street, Canberra City ACT 2601
GPO Box 1564, Canberra ACT 2601 Australia
PH: 61-2-6276 1890  Fax: 61-2-6213 6026
Mob: 0420 962 726
Email: Stephen.Woolcott@ret.gov.au
Internet: http://www.ret.gov.au
ABN 46 252 861 927
Pilot plant to help tackle climate change – a QLD first

In a first for Queensland, CSIRO and Tarong Energy today announced a $5 million joint pilot project to capture greenhouse gases.

The project will see the installation of a post-combustion capture (PCC) pilot plant at Tarong Power Station, 45km south of Kingaroy.

The pilot plant is designed to capture 1500 tonnes per annum of CO2 from the power station and is part of a broader research program to identify ways to reduce greenhouse gas emissions from the energy sector.

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Director of CSIRO’s Energy Transformed National Research Flagship, Dr John Wright, said low emission energy generation was a key research area for the Flagship.

"80 per cent of the energy consumed in Australia is generated from large, coal-fired power stations. It’s critical that we find ways to make coal a cleaner energy source and we’re pleased to be working with Tarong Energy to help find these solutions," Dr Wright said.

"When coupled with CO2 sequestration, post-combustion capture, offers the potential for near zero emissions from coal-fired power stations.

"While this project won’t immediately reduce emissions, the information gathered from the research work will be used to further develop the technology for a commercial-scale application."

Tarong Energy Chair, Graham Carpenter, said the Corporation is proud to be part of the CSIRO project which is the first of its type in Queensland.

"The project marks a significant milestone for Tarong Energy in its efforts to reduce its environmental footprint," Mr Carpenter said.

"The Corporation is acutely aware of its environmental responsibilities and over the past few years we have introduced a number of initiatives to reduce our impact on the environment.

"We will work very closely with the CSIRO to deliver a successful project which may lead to similar technology being installed at coal-fired generators throughout Australia."

In the PCC process the power station’s flue gas is passed through a chemical solution (sorbent) where 85-95% of the CO2 is captured. The CO2-rich sorbent is then treated to separate the CO2. The CO2 is then able to be compressed and cooled to form a liquid for pipeline transport to a sequestration site.
The Tarong trial will focus on assessing the performance of an amine-based PCC pilot plant that will be integrated into the existing coal-fired power stations. CSIRO and Tarong Energy will each contribute $2.5 million to the project.

The PCC pilot plant at Tarong is an integral part of the Asia Pacific Partnership on Clean Development and Climate (APP) program’s PCC Flagship Project under the Asia Pacific Partnership on Clean Development and Climate (APP). This APP project involves trials at several power stations, including Tarong, a pilot plant installation (based on ammonia) at Delta Electricity’s Munmorah power station on the NSW Central Coast and the establishment of a pilot plant at Gaobeidian Power Station in Beijing. These trials are backed up by the development of a world-class PCC laboratory in Australia.

The work in Australia and China is making a leading contribution to the international development of technology that can be retrofitted to existing coal power stations to capture greenhouse gas emissions. CSIRO is operating at the leading edge in developing PCC technologies. The Australian Government is supporting this work by CSIRO through a $12 million grant under the APP.

CSIRO is also undertaking PCC research outside the scope of the APP program with a $5.6 million project in the Latrobe Valley, which focuses on brown coal.

National Research Flagships [www.csiro.au/flagships]: CSIRO initiated the National Research Flagships to provide science-based solutions in response to Australia’s major research challenges and opportunities. The nine Flagships form multidisciplinary teams with industry and the research community to deliver impact and benefits for Australia.
Dear Stephen,

It was good to catch up with you earlier this month on the ongoing PCC-projects supported through the Asia Pacific Partnership on Clean Development and Climate.

As part of these projects we are organising various annual workshops and meetings. The workshop organised by COAL21 on 6 August was the first one, within the PCC programme. As I mentioned during our meeting we are organising a second workshop on 16/17 October in Newcastle: first day a PCC Science & Technology Seminar and second day a visit to the pilot plant at Delta Electricity's power station at Lake Munmorah. This workshop will focus on the use of aqueous ammonia for CO2 capture and we will send you and your colleagues an invitation once we have the programme and speakers confirmed.

We have also been invited to participate in the China Energy and Environment Summit in December 2008 organised by the National Development and Reform Commission and I have included some background information on this event. This event could present us with the opportunity to highlight our R&D programme and activities in China and we are considering a sponsorship of a theme (PCC would be our suggestion and this would be the projected annual workshop) in this event. This would help us progressing towards the possibility of a second PCC pilot plant in China. Before we commit we would like to have your advice/opinion on this. It is an event that is likely to be supported by the EU as well and I wondered if we then should brand our support as a support from the Australian Government (through APP). Could you discuss this internally and give us some feedback? Let me know if your require further information on this.

Best regards,

Paul H.M. Feron
PCC Science Leader
CSIRO Energy Technology
10 Murray Dwyer Cct, Mayfield West
P.O. Box 330
Newcastle NSW 2300
Australia
Tel +61(0)2 4960 6022
Mob +61(0) 447688747

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From: Feron, Paul (DET, Newcastle)
Sent: Wednesday, 3 September 2008 1:04 PM
To: Woolcott, Stephen
Subject: Approval
Attachments: PCC IEA brief.doc

Dear Stephen,

I am seeking your approval for the submission of the enclosed 2-pager on our PCC programme, intended to be included in a publication of the International Energy Agency. It is based on existing information, so it should not present any surprises. I appreciate your comments at your earliest convenience. Thank you.

Best regards,

Paul H.M. Feron
PCC Science Leader
CSIRO Energy Technology
*Murray Dwyer Cct, Mayfield West
 ▽ Box 330
Newcastle NSW 2300
Australia
Tel +61(0)2 4960 6022
Mob +61(0) 447688747

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Post-combustion CO₂ Capture at CSIRO in Australia

Background and rationale

80% of Australia’s power generation is derived from coal (black and brown). Coal is relatively cheap and it is likely that baseload power will continue to be generated by coal-fired power stations over the next decades. The resulting CO₂-emissions can only be reduced by the introduction of post-combustion capture of CO₂ (PCC), followed by geological storage. The expected increases in the cost of electricity together with the reduction in power generation due to the capture process are important hurdles for commercial implementation of the technology. There is also a lack of operational experience in PCC with Australian flue gases, which undergo limited cleaning before they get emitted to the atmosphere. The Commonwealth Scientific and Industrial Research Organisation (CSIRO) in Australia has therefore established a comprehensive research and development programme for post-combustion CO₂ capture. This programme is supported by the Australian government through the Asia-Pacific-Partnership on Clean Development and Climate.

Post-combustion capture R&D program overview

The CSIRO PCC R&D program consists of two major parts:
1. a pilot plant program
   The pilot plant programme is meant to provide hands-on experience for future operators, to identify of operational issues and requirements and to enable the testing of existing and new technologies under real conditions.
2. a laboratory research program
   The laboratory reserach programme provides support to pilot plant operation and interpretation of results, aims to develop novel solvents and solvent systems which result in lower costs for capture and it will address Australian specific issues, such the flue gas contaminants and issues related to water shortage.

PCC Pilot plants

The CSIRO Energy Transformed Flagship and the CSIRO Division of Energy Technology have progressed PCC in Australia and China through the establishment of three pilot plants in 2008 and a fourth one in 2009.

The first pilot plant, part of the Latrobe Valley Post-Combustion Capture Project, was officially opened at the end of April 2008 in Victoria at Loy Yang Power Station and after a commissioning period started producing CO₂ one month later. It is now undergoing a series of 7 test campaigns due to be completed in 2009. Flue gases are coming from a lignite fired power station and the max. plant capacity is 1000 ton/a CO₂. Lignite is the basis for nearly all power generation in Victoria. This pilot plant is supported by Victorian Government through the ETIS programme.

The second pilot plant went into the commissioning stage in July 2008 at Delta Electricity’s power station at Lake Munmorah in NSW. Based on the use of aqueous ammonia, which has a high volatility, this pilot plant is more complex and is expected to start producing CO₂ in October 2008, planned to operate until mid 2010. Flue gases are coming from black coal firing and the max. plant capacity is 3000 ton/a CO₂.

Paul Feron – PCC Science Leader, CSIRO Energy Technology
paul.feron@csiro.au
Whereas the Australian PCC pilot plants are based on flue gases with limited emission controls, the third pilot plant in China is based on clean flue gases from coal firing. This pilot plant, operating at the site of the Huaneng Beijing Cogeneration plant was opened in July 2008 and produced CO₂ since then to a food-grade quality. The pilot plant was established by the China Huaneng Group and its subsidiary TPRI, with CSIRO providing technical and training input. The capacity is 3000 ton/a CO₂. A research programme running until the end of 2009 will be established.

The fourth pilot plant will be operating at the site of Tarong Energy in Queensland, with a planned start-up date of July 2009. The anticipated capacity is 1500 ton/a CO₂.

The Australian pilot plants are backed up by laboratory based research programme with the centre at Newcastle and hubs being developed in Melbourne and Brisbane to serve the local interests.

**PCC Laboratory**

The laboratory research programme consists of four integrated parts:

1. Solvent development focusing on new chemicals or chemical formulations for reversible binding of CO₂
2. Solvent process development involving the development of alternative processes, novel process flow sheets, inclusion of other separation processes such as adsorption to improve the solvent process performance
3. Equipment development aimed at reducing the equipment sizes and the physical footprint of capture technology and hence reducing investment costs
4. Optimal power plant integration to have minimal impact of the capture process on the power plant, including the usual of solar energy.

The overall programme organisation is summarised in the figure below.

![PCC-programme Diagram](image)

Paul Feron – PCC Science Leader, CSIRO Energy Technology
paul.feron@csiro.au
Hi Paul

RET approves the document but please note that I made some minor grammatical changes to the attached document and have asked a couple of questions which I would be interested in your response.

Regards
Stephen Woolcott
Manager
APP & Contract Management Section
APP Aluminium Task Force Secretariat
International, Resources Development
& Taxation Branch
Resources Division

Department of Resources, Energy and Tourism
Level 10, 10 Binara Street, Canberra City ACT 2601
GPO Box 1564, Canberra ACT 2601 Australia
PH: 61-2-6276 1890 Fax: 61-2-6213 6026
Mob: 0420 962 726
Email: Stephen.Woolcott@ret.gov.au
Internet: http://www.ret.gov.au
ABN 46 252 861 927

From: Paul.Feron@csiro.au [mailto:Paul.Feron@csiro.au]
Sent: Wednesday, 3 September 2008 1:04 PM
To: Woolcott, Stephen
Subject: Approval

Dear Stephen,

I am seeking your approval for the submission of the enclosed 2-pager on our PCC programme, intended to be included in a publication of the International Energy Agency. It is based on existing information, so it should not present any surprises. I appreciate your comments at your earliest convenience. Thank you.

Best regards,

Paul H.M. Feron
PCC Science Leader
CSIRO Energy Technology
10 Murray Dwyer Cct, Mayfield West
P.O. Box 330
Newcastle NSW 2300
Australia
Tel +61(0)2 4960 6022
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Post-combustion CO₂ Capture at CSIRO in Australia

Background and rationale

80% of Australia’s power generation is derived from coal (black and brown). Coal is relatively cheap and it is likely that baseload power will continue to be generated by coal-fired power stations over the next decades. The resulting CO₂-emissions can only be reduced if we adopt a comprehensive approach to commercial scale implementation and validation, by the introduction of post-combustion capture of CO₂ (PCC), followed by geological storage. The expected increases in the cost of electricity together with the reduction in power generation due to the capture process are important hurdles for commercial implementation of the technology. There is also a lack of operational experience in PCC with Australian flue gases, which undergo limited cleaning before they get emitted to the atmosphere. The Commonwealth Scientific and Industrial Research Organisation (CSIRO) in Australia has therefore established a comprehensive research and development programme for post-combustion CO₂ capture. This programme is supported by the Australian government through the Asia-Pacific-Partnership on Clean Development and Climate.

Post-combustion capture R&D programme overview

The CSIRO PCC R&D programme consists of two major parts:

1. a pilot plant programme
   The pilot plant programme is meant to provide hands-on experience for future operators, to identify operational issues and requirements and to enable the testing of existing and new technologies under real conditions.
2. a laboratory research programme
   The laboratory research programme provides support to pilot plant operation and interpretation of results, aims to develop novel solvents and solvent systems which result in lower costs for capture and it will address Australian specific issues, such as the flue gas contaminants and issues related to water shortage.

PCC Pilot plants

The CSIRO Energy Transformed Flagship and the CSIRO Division of Energy Technology have progressed PCC in Australia and China through the establishment of three pilot plants in 2008 and a fourth one in 2009.

The first pilot plant, part of the Latrobe Valley Post-Combustion Capture Project, was officially opened at the end of April 2008 in Victoria at Loy Yang Power Station and after a commissioning period started producing CO₂ one month later. It is now undergoing a series of 7 test campaigns due to be completed in 2009. Flue gases are coming from a lignite fired power station and the max. plant capacity is 1000 ton a CO₂. Not seen this before what does it mean? Lignite is the basis for nearly all power generation in Victoria. This pilot plant is supported by Victorian Government through the ETIS programme.

The second pilot plant went into the commissioning stage in July 2008 at Delta Electricity’s power station at Lake Munmorah in NSW. Based on the use of aqueous

Paul Feron – PCC Science Leader, CSIRO Energy Technology
paul.feron@csiro.au
ammonia, which has a high volatility, this pilot plant is more complex and is expected to start producing CO₂ in October 2008, planned to operate until mid 2010. Flue gases are coming from black coal firing and the max. plant capacity is 3000 ton/a CO₂.

Whereas the Australian PCC pilot plants are based on flue gases with limited emission controls, the third pilot plant in China is based on clean flue gases from coal firing. This pilot plant, operating at the site of the Huaneng Beijing Cogeneration plant was opened in July 2008 and produced CO₂ since then to a food-grade quality. The pilot plant was established by the China Huaneng Group and its subsidiary TPRI, with CSIRO providing technical and training input. The capacity is 3000 ton/a CO₂. A research programme running until the end of 2009 will be established.

The fourth pilot plant will be operating at the site of Tarong Energy in Queensland, with a planned start-up date of July 2009. The anticipated capacity is 1500 ton/a CO₂.

The Australian pilot plants are backed up by laboratory based research programme with the centre at Newcastle and hubs being developed in Melbourne and Brisbane to serve the local interests.

**PCC Laboratory**

The laboratory research programme consists of four integrated parts:

1. Solvent development focusing on new chemicals or chemical formulations for reversible binding of CO₂
2. Solvent process development involving the development of alternative processes, novel process flow sheets, inclusion of other separation processes such as adsorption to improve the solvent process performance
3. Equipment development aimed at reducing the equipment sizes and the physical footprint of capture technology and hence reducing investment costs
4. Optimal power plant integration to have minimal impact of the capture process on the power plant, including the usual of solar energy.

The overall programme organisation is summarised in the figure below.

![PCC-programme diagram]

Paul Feron – PCC Science Leader, CSIRO Energy Technology
paul.feron@csiro.au
Dear Stephen,

thanks for the approval and grammar changes. Regarding your questions:

- If power continues to be generated by coal over the next decades (because it is cheap) then I see no other way to reduce these on-going emissions than by using post-combustion capture and geological storage of CO2. If we decide not to use coal in the future (change to gas, more windpower, etc.) than that is a different situation. So I have started from the premise that we will have coal fired power generation, which is the reality. I appreciate that the PCC-technology is not commercially demonstrated yet, but you can order a full-scale capture plant today and have it delivered within three years. Unfortunately there is no mechanism which would pay for this plant and it would be expensive - the main reason for our PCC-research. I see larger uncertainties around CO2-storage as a lot of work still needs to be done. We need probably more Otway-like projects in Australia.

the plant capacities are given as ton CO2/a (1 ton = 1000 kg; a = per year) and a typical 600 MW powerplant would emit early 4 million ton CO2 per year.

I hope this goes some way towards answering your questions.

Best regards,

Paul Feron
Hi David,

As discussed, please find below some information about the Munmorah PCC Pilot Plant:

CSIRO’s Energy Transformed Flagship has been working with Delta Electricity to set up a PCC pilot plant at the Munmorah Power Station on the NSW Central Coast. The pilot plant is designed to capture 5000 tonnes per annum of CO₂ from the power station. The $5 million project is a joint initiative by Delta Electricity and the CSIRO, with CSIRO’s involvement supported by the Australian Government. The Munmorah trial will focus on assessing the performance of an ammonia-based PCC pilot plant. The Munmorah plant uses black coal. The trial is expected to take up to three years to complete.
[ends]

I have also attached the media release that was distributed by Minister Macdonald’s office at the time of the commissioning.

Lou
Louise Morrissey | Communication Manager | CSIRO | Energy Transformed Flagship & Division of Energy Technology
10 Murray Dwyer Circuit, Steel River Industrial Park, Mayfield West, NSW 2304
T +61 2 4960 6140 | F +61 2 4960 6054 | M 0419 168 940 | lori.morrissey@csiro.au
www.csiro.au

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In an Australian first, NSW Mineral Resources Minister Ian Macdonald will today commission the Lake Munmorah Pilot Carbon Capture plant, a research facility designed to capture about 3000 tonnes of carbon dioxide a year from the nearby power station.

Minister Macdonald said it is the first time the technology, developed on the State's Central Coast by Delta Electricity and the CSIRO, will be seen in action in Australia.

"This $5 million Post Combustion Capture pilot facility will capture greenhouse gas emissions from the Munmorah Power Station using ammonia absorption technology," Mr Macdonald said.

"This research scale pilot plant is designed to capture up to 3000 tonnes a year of carbon dioxide from the power station.

"A key benefit of this technology is that it can be used on new or existing power stations.

"With the Garnaut Report expected out later today, there is no better time to commission this facility."

Minister Macdonald said while the State Government strongly backed renewable energy sources, it also realised that active support for clean coal technologies, to complement renewable energy plans, was needed if we are to achieve significant reductions in carbon dioxide emissions.

"It is hoped this pilot project will provide the foundation for a large scale $150m post combustion capture and storage demonstration project in NSW planned for operation by 2013, capturing up to 100,000 tonnes of carbon dioxide each year," he said.

"This environmentally responsible Munmorah pilot plant is a first step in the process which will allow NSW to make further deep cuts in greenhouse gas emissions from electricity, while providing reliable base load supply to hardworking NSW families and businesses for the next three decades."

The NSW $100 million Clean Coal Fund, which is now in effect following the passing of the Clean Coal Administration Bill 2008 last week, will allow the funding of further research into clean coal technologies.

"The Lemma Government is committed to reducing greenhouse gas emissions in NSW, while continuing to maintain a strong and sustainable mining sector," Minister Macdonald said.

"The recent Owen Inquiry noted the need for coal-fired power to meet the State's base-load energy requirements beyond 2013 that is why clean coal technology is so important - we need to make our energy sources as clean and green as possible."
A range of capture technologies are under development internationally, although none are currently commercially available for coal fired generation.

"Although the greenhouse emission rate from coal fired generation technology is improving, to achieve deep emission cuts capture and sequestration of carbon dioxide emissions is necessary," Mr Macdonald said.

Further reading

Post-combustion capture of CO2 emissions from power stations (CSIRO)

Media contact: Jason Bartlett, 0438 209 281
Dear Stephen,

enclosed is a draft presentation containing some previously unpublished information from the Delta Electricity PCC pilot plant to be given by Jim Smitham at the Carbon Capture Showcase in Houston, Texas. The presentation describes our overall R&D programme. I am asking permission to release the Delta Electricity part of this presentation (Slide 16-21), as this contains new information. There are no IP-concerns from our side. Thank you very much.

Best regards,

Paul H.M. Feron
PCC Science Leader
SIRO Energy Technology
J Murray Dwyer Cct, Mayfield West
P.O. Box 330
Newcastle NSW 2300
Australia
Tel +61(0)2 4960 6022
Mob +61(0) 447688747

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Post-Combustion Capture (PCC) Pilot Plant Programs at CSIRO

Dr. Jim Bellmam
Deputy Director
21 October 2009

Chemical Capture Technologies

- Carbon dioxide capture is not a new technology.
- Applying carbon capture at power station scale, integrated with power production and at a cost that is affordable is new technology.
- Chemical processes are dominant at this stage because they are the incumbent technology, their principles are understood (although not as well as many believe) and they are closest in scale to power plant adoption.
- While storage sites for commercial scale storage are under investigation in Australia, there is an important role to play for pilot scale capture programs.

PCC Application in Australian Coal Fired Power Stations

- Generation capacity ~ 25 GW
- Electricity production 170 TWh/y
- Average generation efficiency HHV
  - Black coal: 35.6% - 0.9 tonne CO2/MWh
  - Brown coal: 25.7% - 1.3 tonne CO2/MWh
- CO2 emissions ~ 170 Mtone CO2/y from ~ 60 flue gas streams
- SO2 levels:
  - Black coal: 200 - 400 ppm
  - Brown coal: 100 - 300 ppm
- NOx levels:
  - Black coal: 300-700 ppm
  - Brown coal: 100-200 ppm
- Flue gas temperature:
  - Black coal: 120 °C
  - Brown coal: 160 °C
- Cooling water: 1.5-3.0 m³/MWh

Known issues with PCC

- High capital cost
- Electricity cost increased
- Loss of generation efficiency
- Not demonstrated at the scale of an integrated power plant
- Sensitive to O2, SOx and other flue gas constituents
- Large increase in cooling water requirement

Established Pilot Plants

- Liddell Valley Post Combustion Project
  - ETIE support
  - Loy Yang Power Station
  - Lignite
  - Amine based
  - No FGD/DeNOx

- CHINA HUANENG
  - APP support
  - Guodian Power Station
  - Black coal
  - Amine based
  - FGD/DeNOx installed

- APP support
  - Murmornah Power Station
  - Black coal
  - Ammonia based
  - No FGD/DeNOx

Geographic Distribution of Pilot PCC Plants
General scope of pilot plant experiments

- Technical and economical scale-up information about CO₂ capture plant based on operation on flue gas from brown and black coal combustion
- This includes determining the following interrelationships:
  - CO₂ capture energy consumption
  - CO₂ capture efficiency
  - Solvent CO₂ loading
  - Solvent and flue gas flow ratio
  - Regeneration temperature and pressure
  - Absorption temperature
  - Solvent consumption and degradation rates
  - Fouling and corrosion
  - Effectiveness of the conditioning stage
  - Reactant loss rate both to acid gas and to release with flue gas
  - System water consumption

General pilot plant design principles

- Use of two columns with a specified single column design CO₂ capacity at 85% removal
- Based on local flue gas composition (~ 8% CO₂)
- Based on the use of MEA or aqueous ammonia
- Operate with reboiler temperatures 100 - 150°C
- Operate with stripper pressures 1 - 10 bar
- Be able to determine thermal and electrical energy requirements of the pilot plant
- Be able to determine emissions to atmosphere and CO₂ product quality

Aims of Loy Yang Program

- To obtain practical experience of PCC with real flue gas from a lignite fired power plant
- To test the performance of PCC Loy Yang pilot plant under nominal conditions
- To assess the effect of operational parameters alteration on the performance of CO₂ absorption

Pilot Plant Gas Analysis

Gas analysis will be performed at 5 points throughout the pilot plants.

Diagram adapted from EMTC

Solvent Feed Tank
- Condenser
- Stripper
- Absorbers

- Pilot plant scale: 159 kgh
- Design CO₂ capture: 85%
- Solvent base: MEA 30%
- First capture: April 2008
Loy Yang Pilot Plant (150kg CO₂/hr)
Simplified Process Flow Diagram

Loy Yang Program
- Seven campaigns planned
- Program includes
  - Performance measurement,
  - Evaluation of novel solvents,
  - Technical and economic modelling of performance and integration of capture with power plant
- Completion late 2010

Munmorah PCC
Overview:
- CSIRO and Delta Electricity have been constructing a $3 million research scale Post Combustion Capture (PCC) pilot plant at the Munmorah Power Station
- The pilot plant is part of and is supported by the Asia Pacific Partnership on Clean Development and Climate (APP)
- The pilot plant is designed to capture up to 3,000 tonnes per annum of CO₂ from the power station, using aqueous ammonia as the chemical absorbent.
- The pilot plant is expected to be operational in October 2008 and the experimental program will take 2 years

Introduction to Aqueous Ammonia PCC
Overview
Advantages
- Low cost of solvent
- Does not degrade in the presence of oxygen
- High CO₂ loading capacity
- Less corrosive and damaging to the equipment than some amines
- Potential to remove multi-components (SOx, NOx and CO₂) simultaneously and produce value added products

Challenges
- Loss of ammonia
- Accommodating low temperature flue gas

Aqueous Ammonia PCC
Batch scale investigations (all at atmospheric pressure)

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Type of reactor</th>
<th>NH₃ Concentration (%)</th>
<th>Absorber Temp °C</th>
<th>Desorber Temp °C</th>
<th>Absorbys product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yan and Slade 1999</td>
<td>Semi-batch absorber</td>
<td>7-15%</td>
<td>10-40</td>
<td>Not applicable</td>
<td>Bisolvores</td>
</tr>
<tr>
<td>Doon et al. 2004</td>
<td>Semi batch</td>
<td>0.1-0.2%</td>
<td>25-50</td>
<td>Not applicable</td>
<td>Bisolvores</td>
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<tr>
<td>Yeoh et al. 2005</td>
<td>Semi batch absorber</td>
<td>7-14%</td>
<td>10-30</td>
<td>40-90</td>
<td>Bisolvores</td>
</tr>
<tr>
<td>Paskal, Yeoh, 2005</td>
<td>Continuous flow system</td>
<td>19.5-21%</td>
<td>10-30</td>
<td>75-81</td>
<td>Bisolvores</td>
</tr>
<tr>
<td>Kim et al. 2008</td>
<td>Semi batch absorber</td>
<td>7-17</td>
<td>18-60</td>
<td>Not applicable</td>
<td>Carbonic Carbonates</td>
</tr>
</tbody>
</table>
Aqueous Ammonia PCC

<table>
<thead>
<tr>
<th>Investigators</th>
<th>Location</th>
<th>Capacity</th>
<th>Start-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>Akslon and EPN</td>
<td>Wex Energet, Wisconson</td>
<td>16,000 ton CO2 year</td>
<td>March 2008</td>
</tr>
<tr>
<td>Akslon and EPN</td>
<td>Kärutton Power Plant, Sweden</td>
<td>5 MWh CO2 capture</td>
<td>2008</td>
</tr>
<tr>
<td>Akslon and EPN</td>
<td>Mongolian Refinery, Norway</td>
<td>80,000 ton CO2 year</td>
<td>2009-2010</td>
</tr>
<tr>
<td>Powenagen</td>
<td>First Energy's R.E.B. Burger plant, Ohio</td>
<td>50 ton CO2 per year</td>
<td>2008</td>
</tr>
<tr>
<td>Xeol of Kentucky</td>
<td>Center for Applied Energy Research</td>
<td>5-1MW CO2 capture</td>
<td>May 2008</td>
</tr>
<tr>
<td>Tonghua Uni</td>
<td>China</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>CSIRO and Delta Ener</td>
<td>Delta Ener, NSW</td>
<td>3,000 ton CO2 per year</td>
<td>October 2008</td>
</tr>
</tbody>
</table>

Munmorah PCC

- Flow gas
- Ammonia
- Water
- Heat Exchanger
- Knock-out drum
- Pump
- Blower
- Desorber
- Absorber
- Pre-treatment Column

Objective of Aqueous Ammonia Pilot Plant Program

- Gain an improved understanding of ammonia based capture system
- Develop and evaluate the process control logic and operation system
- Provide information for technological and economic analyses of the capture system
- Identify opportunities for thermal process integration or novel approaches to minimize the energy requirements and loss of ammonia
- Explore the potential of using aqueous ammonia solution to capture CO2 from coal fired power plants under Australian conditions

China – A developing nation

<table>
<thead>
<tr>
<th>Year</th>
<th>Total primary energy consumption (TJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005</td>
<td>110,000 Tj</td>
</tr>
<tr>
<td>2010</td>
<td>130,000 Tj</td>
</tr>
</tbody>
</table>

Asia Pacific Partnership – avenue for collaboration

- DRET provide funding under the APP Cleaner Fossil Energy Taskforce
- Objective to promote technology exchange between Australia and China
- Development and operation of pilot plant at Guodian Cogeneration plant in Beijing
- Partners:
  - China Huaheng Group
    - Invited and operator of PCC pilot plant
  - Thermal Power Research Institute
    - Chinese research provider for project – new in PCC area
  - Commonwealth Scientific and Industrial Research Organisation
    - Australian research provider – PCC expertise

Application of Chinese Pilot Plant

- DWE
- SCF
- ERP
- FGO
- CO2 capture
- Steam
- Power
- Capture inlet gas
  - CO2: 10% - 15%
  - CH4: 3% - 5%
  - 90%: 500 mg
  - Temp: 51°C - 53°C

Existing plant
Huaneng Pilot Plant

Pilot plant operation to date

- The first run was completed on 4th July
- 9th July – 31st July commissioning and successive operation
- Flow Rates tested: 1800-3200Nm3/h (75%-135%)
- CO2 in Exhaust Gas: 2%-4%
- Captured CO2: 59.5%, 350-600kg/h
- Currently undergoing experimental operation to determine optimum operating conditions

Political interest

From Australian Government

From Chinese Government

Conclusion

- The pilot plant programs have effectively engaged power station owners in PCC
- The planning and execution of the pilot plants has highlighted issues that the full scale plants will need to address with chemical engineering skills, operator training, reagent handling
- The pilot plant programs will enable the power station operators to make informed decisions when selecting companies for the demonstration scale and commercial scale PCC plants in the period 2010 to 2017

Our supporters

Australian Government
Department of Resources, Energy and Tourism

Victoria

TARONG ENERGY
Delta

CHINA HUANENG

TPRI: Thermal Power Research Institute

Our Team
Hi Paul

Apologies for taking a little while to get back to you. I have only two small suggested amendments and if too late these are not disasters.

On the slide titled "Asia Pacific Partnership - avenue for collection" the flag banner does not contain Canada (I have attached a complete flag banner in case you don't have one) and we refer to our department by the acronym RET not DRET.

Otherwise happy with the presentation.

Regards
Stephen Woolcott
Manager
APP & Contract Management Section
APP Aluminium Task Force Secretariat
International, Resources Development
& Taxation Branch
Resources Division

Department of Resources, Energy and Tourism
Level 10, 10 Binara Street, Canberra City ACT 2601
GPO Box 1564, Canberra ACT 2601 Australia
PH: 61-2-6276 1890 Fax: 61-2-6213 6026
Mob: 0420 962 726
Email: Stephen.Woolcott@ret.gov.au
tenet: http://www.ret.gov.au
ABN 46 252 861 927
Post-Combustion Capture (PCC) Pilot Plant Programs at CSIRO

Dr Jim Birdtham, Deputy Director, 21 October 2008

Chemical Capture Technologies

- Carbon dioxide capture is not a new technology.
- Applying carbon capture at power station scale, integrated with power production and at a cost that is affordable is new technology.
- Chemical processes are dominant at this stage because they are the incumbent technology, their principles are understood (although not as well as many believe) and they are closest in scale to power plant adoption.
- While storage sites for commercial scale storage are under investigation in Australia, there is an important role to play for pilot scale capture programs.

PCC Application in Australian Coal Fired Power Stations

- Generation capacity: 38.5 GW
- Electricity production: 170 TWh/a
- Average generation efficiency: 27.3%
- Steam CO₂ emissions: 175 Mt/a CO₂ from 60 flue gas streams
- SO₂ levels:
  - Black coal: 200 - 800 ppm
  - Brown coal: 100 - 300 ppm
- NOx levels:
  - Black coal: 300-700 ppm
  - Brown coal: 600-200 ppm
- Flue gas temperature:
  - Black coal: 120°C
  - Brown coal: 160°C
- Cooling water: 1.5-3.0 m³/MWh

Data used from CSIRO - biomass assessment report 02

Known issues with PCC

- High capture cost
- Electricity cost increased
- Loss of generation efficiency
- Not demonstrated at the scale of an integrated power plant
- Sensitive to O₂, SOx and other flue gas constituents
- Large increase in cooling water requirement

Geographic Distribution of Pilot PCC Plants

Established Pilot Plants

- Latrobe Valley Pilot Combustion Project
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  - Loy Yang Power Station
  - Lignite
  - Amine based
  - No FGD/DeNox

- CHINA HUANENG
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  - Guandebian Power Station
  - Black coal
  - Amine based
  - FGD/DeNox Installed

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Stripper
Absorbers
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- Solvent base : MEA 30%
- First capture : April 2008
Loy Yang Pilot Plant (150kg CO₂/hr)
Simplified Process Flow Diagram

% CO₂ captured

Loy Yang Program
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Bench scale investigations (all at atmospheric pressure)

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<th>Absorber Temp °C</th>
<th>Desorber Temp °C</th>
<th>Absorption product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yeh and Wee 1999</td>
<td>Semi batch absorber</td>
<td>7-75%</td>
<td>10-60</td>
<td>Not applicable</td>
<td>Bioamine</td>
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<tr>
<td>Duan et al 2004</td>
<td>Slurry loop</td>
<td>0.1-4.2%</td>
<td>25-65</td>
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<td>Bioamine</td>
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<tr>
<td>Yeh et al 2005</td>
<td>Semi batch absorber</td>
<td>7-14%</td>
<td>15-35</td>
<td>40-90</td>
<td>Bioamine, Carbonate</td>
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<tr>
<td>Park, Yeh et al 2005</td>
<td>Continuous miniplant</td>
<td>10-20%</td>
<td>15-35</td>
<td>77-83</td>
<td>Bioamine, Carbonate</td>
</tr>
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<td>Kim et al 2006</td>
<td>Semi batch absorber</td>
<td>7-17%</td>
<td>19-60</td>
<td>Not applicable</td>
<td>Carbonate, Carbonate, Bioamine</td>
</tr>
</tbody>
</table>
Aqueous Ammonia PCC

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Location</th>
<th>Capacity</th>
<th>Start-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avestras and EPRI</td>
<td>We Energies, Wisconsin</td>
<td>15,000 ton CO2/year</td>
<td>March 2006</td>
</tr>
<tr>
<td>Avestras and EPRI</td>
<td>Karlshamn Power Plant, Sweden</td>
<td>9.0 MW CO2 capture</td>
<td>2008</td>
</tr>
<tr>
<td>Avestras and EPRI</td>
<td>Montgali Power Plant, New York</td>
<td>80,000 ton CO2/year</td>
<td>2010-2011</td>
</tr>
<tr>
<td>Power Plant</td>
<td>FirstEnergy's R.E. Burger plant, Ohio</td>
<td>20 TCE/kWh</td>
<td>2008</td>
</tr>
<tr>
<td>University of Kentucky</td>
<td>Center for Applied Energy Research</td>
<td>0.1 MW CO2 reduction</td>
<td>May 2008</td>
</tr>
<tr>
<td>Tsinghua University</td>
<td>China</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>CSIRO and Delta Energy</td>
<td>Delta Energy, NSW</td>
<td>3,000 ton CO2/year</td>
<td>October 2008</td>
</tr>
</tbody>
</table>

Munmorah PCC

- Flue gas
- Ammonia
- Wash water
- Fluid Exchanger
- Knock out drum
- Pump
- Absorber
- Scrubber
- Reducer
- Ammonium tank
- Schematic of Munmorah Pilot Plant

Objectives of Aqueous Ammonia Pilot Plant Program

- Gain an improved understanding of ammonia-based capture system
- Develop and evaluate the process control logic and operation system
- Provide information for a technological and economic analysis of the capture system
- Identify opportunities for the integration of existing or novel processes to minimize the energy requirements and cost of capture
- Explore the potential of using aqueous ammonia solutions to capture CO2 from coal-fired power plants under Australian conditions

China – A developing nation

- Total primary energy consumption (PJ)

Asia Pacific Partnership – avenue for collaboration

- DRET provide funding under the APP Cleaner Fossil Energy Taskforce
- Objective to promote technology exchange between Australia and China
- Development and operation of pilot plant at Guangdong Cogeneration plant in Beijing

Application of Chinese Pilot Plant

- Boiler
- SCR
- ESP
- FGD
- Turbine
- Steam
- CO2 capture
- Power
- Capture inlet gas CO2: 10% - 15% 
  O2: 5% - 8% 
  NOx: 100ppm
  Temp.: 65°C - 95°C

- CO2 Geodome
Huaneng Pilot Plant

Pilot plant operation to date

- The first run was completed on 4th July
- 9th July – 31st July commissioning and successive operation
- Flow Rates tested: 1800–3200Nm³/h (75%-135%)
- CO₂ in Exhaust Gas: 2%-4%
- Captured CO₂: 90.5% , 350-600kg/h
- Currently undergoing experimental operation to determine optimum operating conditions

Political interest

From Australian Government

From Chinese Government

Conclusion

- The pilot plant programs have effectively engaged power station owners in PCC
- The planning and execution of the pilot plants has highlighted issues that the full scale plants will need to address with chemical engineering skills, operator training, reagent handling
- The pilot plant programs will enable the power station operators to make informed decisions when selecting companies for the demonstration scale and commercial scale PCC plants in the period 2010 to 2017

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TARONG ENERGY

Delta Energy

CHINA HUANENG

TPRI: Thermal Power Research Institute
From: Feron, Paul (DET, Newcastle)
Sent: Thursday, 13 November 2008 4:50 PM
To: 'Woolcott, Stephen'
Subject: GHGT-9 papers

Contacts: Stephen Woolcott

Dear Stephen,

We would like to ask you to review the enclosed papers which will be published after the Greenhouse Gas Technology Conference held in Washington and welcome any comments you might have. The publications relate to work funded through the APP PCC project. Thank you.

Best regards,

H.M. Feron
C Science Leader
CSIRO Energy Technology
10 Murray Dwyer Cct, Mayfield West
P.O. Box 330
Newcastle NSW 2300
Australia
Tel +61(0)2 4960 6022
Mob +61(0) 447688747

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Enzyme technologies for postcombustion CO₂ capture

Victoria S. Haritos *, Greg Dojchinov, Meihong Su

Energy Transformed Flagship, CSIRO Entomology, GPO Box 1700, Canberra, ACT 2601 Australia

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Abstract

Enzymes are catalysts of exquisite specificity and very rapid turnover rates. They catalyse reactions at room temperature which would otherwise require a driving force such as high temperatures or chemical catalysts. Several classes of enzyme are currently produced at industrial scale, and have advantages in being of low toxicity and biodegradable. Enzymes have shown excellent potential for use in postcombustion CO₂ capture both in the direct capture of CO₂ from flue gas streams and as a 'catalytic stripper' which regenerates amines and CO₂ for sequestration from stable carbamate complexes without high temperatures. We describe the advantages of enzymes in postcombustion capture and highlight rapid enzyme turnover, increased robustness, immobilization and greater CO₂ transfer efficiency as areas where improvement is needed for wider uptake of this technology.

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Keywords: Carbonic anhydrase; directed evolution; immobilization, turnover, carbamates

1. Introduction

International consensus among scientists has deemed that anthropogenic release of CO₂ is the major contributor to global warming of our planet and that emissions need to be reduced in order to prevent catastrophic climate change for many parts of the world [1]. In Australia, as in many other developed and developing countries, we are dependent on coal to provide relatively inexpensive electrical energy. CO₂ is the inevitable byproduct of carbon combustion in air and it comprises around ~13% of the postcombustion gas stream from power stations with the balance including nitrogen, oxygen, SOₓ, NOₓ and contaminants including mercury and ash. Effective removal of millions of tonnes of CO₂ from the postcombustion flue gas from power stations, and concentrating the gas for later storage, use or sequestration presents a huge challenge.

Enzymes can be used for CO₂ capture from fuel gas as an alternative to the current technology. This involves aqueous amine solutions such as monoethanolamine (MEA) to selectively remove CO₂ in an absorber unit, and the high energy requiring release of CO₂ in a separate stripper unit. Enzymes can catalyse very rapid reactions at room

* Corresponding author. Tel.: +61 2 6246 4245; fax: +61 2 6246 4000.
E-mail address: victoria.haritos@csiro.au.
temperature using relatively small quantities of protein. Biotechnology has provided the means to engineer enzymes to remain active in harsh environments of elevated temperatures, high alkalinity and in the presence of contaminants, and to produce large quantities of protein cost-effectively. Research and development into enzymes for CO₂ capture has lagged behind amine solvent capture but there have been some exciting developments in the area internationally that are now attracting substantial government and industry investment.

This paper aims to identify the advantages and challenges of the use of enzymes in postcombustion CO₂ capture, describe how the enzymatic capture system could work and what would be required for success, and describe the possible application opportunities.

2. The advantages of using enzymes

Enzymes are proteins that are folded in a specific manner that enables them to behave as a catalyst for reactions without the need for high energy inputs or chemical agents. The concept of using enzymes for removal of CO₂ from flue gas streams is a different approach in many respects from solvent based absorber and stripper systems but there are some definite advantages as outlined in Table 1.

Table 1. Advantages and disadvantages of enzymes compared with amines for postcombustion CO₂ capture and release

<table>
<thead>
<tr>
<th>Enzymes</th>
<th>Amines/Alkanolamines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low energy pathways</td>
<td>High energy requirement for carbamate stripping</td>
</tr>
<tr>
<td>Fast-rapid reactions</td>
<td>Carbamate-forming reactions generally fast;</td>
</tr>
<tr>
<td>Catalytic quantities required</td>
<td>bicarbonate-forming reactions generally slower</td>
</tr>
<tr>
<td>Evolvable for different conditions and harsh</td>
<td>Stoichiometric or greater quantities</td>
</tr>
<tr>
<td>environments like elevated temperatures, chemical contaminants</td>
<td>Select from among large variety for amines with low levels of reaction with SOx and NOx and volatility</td>
</tr>
<tr>
<td>Biodegradable and generally safe for easy disposal</td>
<td>May require special disposal</td>
</tr>
<tr>
<td>Large diversity of known reactions and enzymes available to select from</td>
<td>Large variety</td>
</tr>
<tr>
<td>Large scale production by fermentation</td>
<td>Production by chemical synthesis</td>
</tr>
<tr>
<td>Cost competitive and large scale production by fermentation</td>
<td>Production by chemical synthesis; scalable</td>
</tr>
<tr>
<td>Potentially inhibited by contaminants like SOx NOx</td>
<td>Degrade in presence of SOx, NOx and O₂</td>
</tr>
</tbody>
</table>
Enzymes do have special requirements for optimal activity. Most enzymes need some water for maximal catalytic activity; for some enzymes reactions there may be a requirement for excess water to catalyse reactions but for others including industrial enzymes like lipases and proteases function normally in non-aqueous solvents [2]. Enzymes generally operate best within a temperature range of 20 – 50°C although many have been isolated from extremophile organisms or evolved enzymes that can operate at temperatures close to 100°C. In general enzymes catalyse reactions maximally at solution pH of around two logs range around neutral pH but again there are many exceptions with enzymes operating optimally at pH >11 or extremes of acidic pH [3]. Enzyme activity can be inhibited by chemicals, usually analogs of the normal substrate but this can be circumvented by selection of an enzyme with a higher tolerance of the inhibitor, or by pre-removal of the inhibitor. Over extended operation time, oxidation and other chemical damage of enzymes will affect enzyme efficiency and ultimately, they will need replacement. The rate of replacement will depend on the inherent robustness of the enzyme and the conditions they are exposed to.

3. Proposed uses for enzyme technologies in postcombustion CO₂ capture

Discrete uses for enzymes in postcombustion capture and stripping are envisaged:

3.1. Direct absorption of CO₂ from flue gas streams by enzymes

In enzymatic postcombustion capture, enzyme is the primary CO₂ capture agent replacing solvent in the absorber stage of CO₂ capture. Due to the rapid turnover rate of enzymes and catalytic, not stoichiometric quantities that are required, there is potential to reduce the size of the absorber unit for capture CO₂ from the flue gas stream and hence reduce capital costs. Carbonic anhydrase has been tested in laboratory and in small pilot scale systems for the removal of CO₂ from flue gas streams [4, 5]. This enzyme is the main candidate for CO₂ absorption studies because it is one of the fastest enzymes known with turnover rates in the order of 10⁶ per second at 25°C albeit with moderately strong affinity for CO₂. These enzymes are responsible for removing CO₂ from the tissues in the human body (and other animals) and transporting them to the lungs. Plants also use carbonic anhydrase to aid the uptake of CO₂ which is fixed into carbohydrates during photosynthesis.

In this example of the use of enzymes in CO₂ capture, enzymes in either free or immobilized state are present in the absorbing unit and brought in close contact with the flue gas stream where they catalyzing the conversion of CO₂ to bicarbonate, thereby removing it from the gas stream. For example, enzyme could be immobilized onto solid supports such as nylon rings [6] immobilized at a membrane surface [5]. Carbozyme Inc has developed an enzyme-based hollow fibre membrane system to remove CO₂ from a flue gas and reportedly able to enrich it from a feed of 3-20% to 95-99% at high flux.

The hydration of CO₂ proceeds with a lowering of solution pH due to the formation of carbonic acid which spontaneously decays releasing a proton and bicarbonate as shown in Equation 1. Carbonic anhydrase speeds up the reaction 5-orders of magnitude in comparison to the background hydrolysis rate [7]. As the solution pH becomes more acidic with hydration of CO₂, carbonic anhydrase becomes less efficient as a catalyst. Therefore, a counter-ion or base is required to be added to maintain solution pH in the alkaline and operational region.

\[ \text{CO}_2 + \text{H}_2\text{O} + \text{carbonic anhydrase} \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{HCO}_3^- + \text{H}^+ \]  
Equation 1

3.2. Enzymes for the low energy stripping of CO₂ absorbed to solvents, especially MEA or from bicarbonate

Primary amines such as monoethanolamine (MEA) react rapidly with CO₂ and are therefore very useful for postcombustion CO₂ capture. However, as MEA forms a stable carbamate when it reacts with CO₂ (Equation 2) this complex requires large amounts of energy in the heat stripper to regenerate the amine from the carbamate: up to 4 MJ kg⁻¹ amine for a 30% amine solvent solution [8]. An enzyme-catalysed route to the release of CO₂ and
regeneration of amine from carbamate would reduce the energy costs by a considerable margin as enzymes generally operate at 20 – 50°C. A proposed enzymatic route would replace the energy-intensive steam stripping regeneration step and would proceed as shown in Equation 3.

\[
2 \text{HOCH}_{2}\text{CH}_{2}\text{NH}_{2} + \text{CO}_{2} \rightarrow \text{HOCH}_{2}\text{CH}_{2}\text{NCOO}^- \text{NH}_{3}\text{CH}_{2}\text{OH} \quad \text{Equation 2}
\]

\[
\text{HOCH}_{2}\text{CH}_{2}\text{NCOO}^- \text{NH}_{3}\text{CH}_{2}\text{CH}_{2}\text{OH} + \text{enzyme} \rightarrow 2 \text{HOCH}_{2}\text{CH}_{2}\text{NH}_{2} + \text{CO}_{2} \quad \text{Equation 3}
\]

In this example of the use of enzymes in CO₂ capture, MEA solvent capture operates as per normal and the CO₂-rich amine solution is pumped into a Catalytic Stripper rather than a Thermal Stripper. The alkanoamine decarboxylase enzyme that will regenerate the amine with the release of CO₂ gas is immobilised or confined such that carbamate-rich amine solution is contacted with the enzyme which acts on the carbamate, releasing amine back into the solution and gaseous CO₂ is released. CO₂-lean amine solution is then returned to the absorber. The main advantage to this system is the avoidance of the large amount of thermal energy required to regenerate amines from carbamates such as MEA-carbamate by replacing the thermal process with an enzymatic one which operates at room or slightly elevated temperatures.
4. Production and use of industrial enzymes

4.1. Global industrial enzyme market and segments

The global market for industrial enzymes was US$2.2 billion in 2005 and is predicted to grow steadily in the future as current industries expand and new demand grows especially in the bioenergy sector. The major industries that already employ enzymes in their processes include the pharmaceutical/fine chemical transformations, animal feed, starch processing to ethanol, waste treatment, diagnostics, biotechnology, food (flavours, fats, oils, protein hydrolysis, and beverages), textiles and leather processing, paper bleaching and detergent production. Cellulosic ethanol production, mineral leaching, pulp and paper processing and mill effluent treatment are further application areas where the requirement for enzymes are expected to grow. The industrial enzyme market is dominated by hydrolases (including cellulases), proteases, and lipases and the major enzyme companies include Novozymes, Genencor/Calando, DSM, BASF, Asahi, Degussa and Diversa (now Celulol). Many of the industrial enzymes in the food, detergent and pulp and paper industries are commodity products – produced in large amounts and competitive on price.

Production of enzymes is most commonly performed by microorganisms genetically engineered to overproduce the enzymes, in large fermentation cultures. Volumes for commodity enzyme production are at least 100,000 L per batch delivering 70 g organism per L. Several enzymes are marketed at the 1000 t production levels per annum. For industrial applications, the expressed enzymes undergo minimal purification and formulation steps. Ideally, the enzyme is spray dried and packaged such that the enzyme is stable at room temperature for an extended period.

4.2. Quantity of enzyme required for CO₂ capture

CO₂ solutions Inc has reported a running trial with a carbonic anhydrase absorbers on a municipal waste gas stream for at least 5 weeks continuously with no loss of activity. In the case of a coal-fired power station releasing 18 M t pa CO₂ or about 0.578 t per sec and depending on the catalytic turnover rate of the enzyme in the absorber unit, from a maximum of 10⁶ sec⁻¹ to a less optimal 10⁵ sec⁻¹, would require between 0.3 – 305 kg of enzyme and replaced at 5 weekly, or greater, intervals. As the turnover rate of the enzyme in the absorber conditions will make a big difference to the size of the unit required for CO₂ capture, the focus of research needs to be on achieving the fastest possible turnover rate for the enzyme.

5. Challenges for the use of enzymes in postcombustion CO₂ capture

Specific success criteria for enzymes and their environment in postcombustion capture process include:

- very robust in conditions of elevated flue gas temperature, shear forces
- rapid turnover rates (>10⁵ sec⁻¹), less enzyme required, smaller absorber unit
- has moderate to high affinity for CO₂
- does not require cofactors
- is modifiable to tolerate contaminants (e.g. >10 ppm SO₂) without sacrificing turnover
- be immobilised onto solid supports to increase longevity and aid replacement
- stable under the flue gas stream conditions for at least 40 d
- maintain solution pH in operational range
- absorber and stripper units designed specifically for enzyme processes
- be produced routinely and cheaply in large quantities through fermentation processes
- readily transported and stored in a dehydrated state.
This is a challenging set of criteria for enzymes to meet; some of the technologies available for addressing these are detailed below. As described in Section 3.1 human and bovine carbonic anhydrase II are the most commonly investigated enzymes for CO₂ capture. They are relatively small proteins (~25,000 Da), do not require cofactors for activity, have amongst the fastest turnover rates of any enzyme (~10⁶ sec⁻¹), are expressed at high level in the soluble fraction from bacterial cultures and easily purified [9]. The enzymes have been well studied due to their roles in mammalian CO₂ transport and maintenance of cellular pH.

5.1. Robust enzymes for elevated temperature and shear force conditions

Most enzymes function in the range 20 – 50°C and once the ambient temperature exceeds a threshold, proteins can undergo unfolding and then aggregation, which drastically reduces activity. In a similar manner, shear causes enzyme inactivation by altering protein structure which reduces activity. Carbonic anhydrase II is a relatively stable enzyme and tolerates temperatures of ~50°C for extended periods without denaturation however, enzyme engineering or ‘evolution’ can derive enzymes that are more stable and robust toward higher temperatures. Several approaches can be taken including computational design aided by crystal structure, sequence analysis and enzyme mechanism, in vitro/directed evolution which makes no assumptions about mechanism and relies on high throughput screening of mutants, or rationally guided evolution which is a combination of the other approaches. Carbonic anhydrase has been the subject of many successful enzyme engineering approaches and a selection of these are summarized in Table 2 although there is excellent potential for further ‘evolution’ of these enzymes for their application to postcombustion capture.

<table>
<thead>
<tr>
<th>Enzyme</th>
<th>Approach</th>
<th>New activity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>hCAII</td>
<td>Rational design - site specific mutagenesis</td>
<td>Esterase efficiency and specificity</td>
<td>[10]</td>
</tr>
<tr>
<td>hCAII</td>
<td>Directed evolution</td>
<td>Increased turnover of a promiscuous substrate</td>
<td>[11]</td>
</tr>
<tr>
<td>hCAI</td>
<td>Directed evolution</td>
<td>Thermal stability and ligand binding relationship using Thermofluor</td>
<td>[12]</td>
</tr>
<tr>
<td>BCAII</td>
<td>Data guided mutagenesis</td>
<td>Increased esterase activity on long acyl chains</td>
<td>[13]</td>
</tr>
</tbody>
</table>

5.2. Will enzymes tolerate flue gas contaminants sufficiently (where flue gas desulfurization not fitted)?

Carbonic anhydrase II does experience inhibition especially from monovalent anions as shown in Table 3 which has the effect of slowing the enzyme reaction. The inhibition constants in Table 3 suggest that NO₂⁻ and SO₂⁻ products entering the capture solution from flue gas and reacting to form nitrites or sulfites may cause inhibition of carbonic anhydrase in the absorber and reduce effectiveness although sulphate is well tolerated. A build up of bicarbonate may be problematic for enzyme activity.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Human carbonic anhydrase II</th>
<th>Bovine carbonic anhydrase II [14]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO₃⁻</td>
<td>85</td>
<td>26</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>35</td>
<td>48</td>
</tr>
<tr>
<td>HSO₃⁻</td>
<td>89</td>
<td>30</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>&gt;200</td>
<td></td>
</tr>
<tr>
<td>Cl⁻</td>
<td>190</td>
<td></td>
</tr>
</tbody>
</table>

Liu et al [15] investigated bovine carbonic anhydrase II for its ability to capture CO₂ from coal fired power plant flue gas and sequester the bicarbonate and acid products directly into brine solutions. While seawater was not
inhibitory to carbonic anhydrase, sulfate and nitrate were inhibitory at high concentrations (0.1 M and above). This suggests some removal of SO_4 and NO_3 from the flue gas or solvated anions in the capture solution may be required for optimal turnover of native carbonic anhydrase II.

5.3. Enzyme immobilization for greater stability and ease of handling

Industrial enzymes are routinely immobilized onto inert supports such as silica, resins, nylon and polyurethane for use in reactors. Immobilization often increases stability of enzymes and useful life as well as increasing their ease of handling, separation and recovery. As the shear forces are high in postcombustion capture of CO_2 and solvent (e.g. seawater, alkaline solutions) conditions may be harsh, the preferred approach for immobilization is covalent linkages in order to retain the maximal amount of enzyme in the absorber. Immobilization technology for enzymes is a growing field and a range of techniques have already been trialed with carbonic anhydrase as summarized in Table 4 although most of the applications were not in postcombustion capture. To date there has not been a report of a successful combination of increased stability, maintenance of enzyme activity and high enzyme loading for immobilization of carbonic anhydrase although this is a definite requirement for postcombustion capture.

<table>
<thead>
<tr>
<th>Immobilization strategy</th>
<th>Residual activity (Kcat/Km)</th>
<th>Stability</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalent linkers and polymer</td>
<td>98%</td>
<td>Unchanged from native</td>
<td>[16]</td>
</tr>
<tr>
<td>Sol-gel encapsulation</td>
<td>&lt;1%</td>
<td>74°C majority folded</td>
<td>[17]</td>
</tr>
<tr>
<td>Photocured polymer</td>
<td>7%</td>
<td>Dry 90 d r 45% loss</td>
<td>[18]</td>
</tr>
<tr>
<td>Palmityl methion globule</td>
<td>70% (at 60°C treatment)</td>
<td>45% native at 65°C</td>
<td>[19]</td>
</tr>
<tr>
<td>Chitosan-alginate beads</td>
<td>Not stated</td>
<td>Not stated</td>
<td>[20]</td>
</tr>
<tr>
<td>Nylon raschig rings</td>
<td>45 - 18%</td>
<td>Not stated</td>
<td>[6]</td>
</tr>
</tbody>
</table>

5.4. Maintain solution pH in operational range

For the specific use of carbonic anhydrase in postcombustion capture and to maintain optimal enzyme activity, solution pH requires management in the alkaline range due to production of acid during the hydration of CO_2. Maintenance of alkaline pH can be achieved in several ways such as by the use of a base or counterion which is introduced into the absorber at stoichiometric quantities, or through the use of brine or seawater as the solvent in the absorber [15]. Calcium and to a lesser extent magnesium ions in seawater can combine with bicarbonate and form stable salts. In this application, seawater or brine is the absorber solution used with carbonic anhydrase and once the bicarbonate absorption capacity has been reached, the solution is stored in salty aquifers or potentially, algal ponds. Alternatively a range of basic or buffered solutions can be used to maintain reaction pH in the alkaline regions.

5.5. Optimizing mass transfer between flue gas and enzyme

The efficiency of CO_2 transfer from flue gas to the solution that is bathing the enzyme is a critical issue for the future use of enzymes in postcombustion capture. Although carbonic anhydrase has a very fast turnover rate, it is limited by the diffusion rate of CO_2 so in order to take maximal advantage of the enzyme’s fast turnover, CO_2 needs to be delivered to the enzyme at the diffusion limited rate. Extensive networks of high surface area membranes have been proposed as a way of increasing the transfer efficiency [21, 22] but there is large scope for improvement in this field to improve utility of enzymes in CO_2 capture.

6. Conclusions

Enzymes have shown great potential for use in postcombustion CO_2 capture and have superior advantages in catalyzing very fast reactions at ambient conditions using small quantities, and their ability to be evolved to cope
with elevated temperature and shear conditions, and immobilized onto inert supports for greater longevity, stability and ease of use. However, there is great scope for further research aimed at the use of the enzymes in the specific conditions of CO2 capture and release and amine carbamate regeneration including improvement of the enzymes' robustness, maintenance of alkaline solution pH (in capture), immobilization that has high stability, enzyme loading and activity and optimizing mass transfer of CO2 into the capture solution.

7. Acknowledgements

This work was carried out within CSIRO's Energy Transformed Flagship Research Stream on Post-Combustion Capture and was supported by the Australian Government through the Asia Pacific Partnership on Clean Development and Climate.

8. Development and Climate.References

GHGT-9

The potential for improvement of the energy performance of pulverized coal fired power stations with post-combustion capture of carbon dioxide

Paul H.M. Feron*

CSIRO Energy Technology, P.O. Box 330, Newcastle, NSW 2260, Australia

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Abstract

The application of post-combustion capture processes in coal fired power stations can result in large reductions of the CO₂ emissions, but the consequential decrease in generation efficiency is an important draw-back. The leading PCC technology is based on an absorption process and the energy performance of this process is analysed. The analysis shows that the potential for improvement of the energy performance is quite large. In conclusion it is demonstrated that further development of the capture technology and the power plant technology can lead to generation efficiencies for power plants with 90% CO₂ capture which are equivalent to the current efficiencies without CO₂ capture, i.e. 0.4 (HHV).

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Keywords: post-combustion capture; power station; coal; absorption processes

1. Introduction

Capture and geological storage of CO₂ (CCS) is now widely recognised as an option that could contribute significantly to the prevention of greenhouse gas emissions. Globally coal fired power stations are emitting approximately 8 Gton CO₂ per annum from 2000 sources [1]. The typical lifetime of a coal fired power plant is more than 25 years. This means that once in place the power station will be emitting CO₂ for a long period. Only post-combustion capture (PCC) can effectively address the emissions of the existing power stations, often referred to as “locked-in carbon”. Other capture options can only be implemented in new power plants which will result in a more limited impact of CCS on the reduction of CO₂ emissions. It is often suggested that the potential for technology improvements is limited for a post-combustion CO₂ capture process. The underlying assumption is that this process is commercially available and that it is therefore fully developed. However, it must be emphasised that PCC has not been demonstrated on a full-scale power plant with optimal integration, nor has it been optimised. The objective of this contribution is to explore the potential for improvement in the energy performance of a coal fired
power plant with post-combustion CO₂-capture based on an analysis of energy flows in both the capture process as well as the power plant.

2. Post-combustion capture of CO₂ (PCC)

In a conventional coal-fired power station the fuel is mixed with air and burnt. The heat generated is used to generate steam at high pressure and power is produced by the expansion of steam through turbines. The flue gas undergoes a number of treatment steps, e.g. particulate removal and removal of nitrogen- and sulphur oxides before it is discharged to the atmosphere through the stack. The CO₂ concentration in the flue gas is typically around 12%. Flue gases are normally at atmospheric pressure but the temperatures might be between 45 °C and 120 °C, depending on the extent and type of contaminant removal. The general post-combustion process scheme is shown in Figure 1.

Power plants with post-combustion CO₂ capture involve two main process steps: an energy conversion step, during which power is produced, followed by a CO₂ separation process in which a concentrated stream of CO₂ is produced.

The separation task is to remove CO₂ from a mixture of mainly nitrogen and oxygen, but also the impact of flue gas impurities (SO₂, NOₓ, particulates) needs to be taken into account. The post-combustion CO₂ capture process can be thought of as an add-on to a power plant and is similar to other flue gas treatment which might already be in place. This makes it the capture process which is the easiest to implement in existing power stations.

3. Absorption processes for post-combustion CO₂ capture

Although several different processes are currently under development for the separation of CO₂ from flue gases, absorption processes using aqueous solutions of chemical absorbents are the leading technology. The typical flow sheet of CO₂ recovery using chemical absorbents is shown in Figure 2.

After cooling the flue gas, it is brought into contact with the chemical absorbent in the absorber. A blower is required to pump the gas through the absorber. At temperatures typically between 40 and 60 °C CO₂ is then bound by the chemical absorbent in the absorber. After passing through the absorber the flue gas undergoes a water wash section to balance water in the system and to remove any droplets or vapour carried over and then leaves the absorber. The “rich” absorbent solution, which contains the chemically bound CO₂ is then pumped to the top of a stripper, via a heat exchanger. The regeneration of the chemical absorbent is carried out in the stripper at elevated temperatures (100 – 140 °C) and pressures between 1 and 2 bar(a). Heat is supplied to the reboiler to maintain the regeneration conditions. This leads to a thermal energy penalty as a result of heating up the solution, providing the required desorption heat for removing the chemically bound CO₂ and for steam production which acts as a stripping gas. Steam is recovered in the condenser and fed back to the stripper, whereas the CO₂ product gas leaves the condenser. The CO₂-product is a relatively pure (> 99%) product, with water vapour being the main other component. Due to the selective nature of the chemical absorption process, the concentration of inert gases is low. The “lean” absorbent solution, containing far less CO₂ is then pumped back to the absorber via the lean-rich heat exchanger and a cooler to bring it down to the absorber temperature level. CO₂ removal is typically around 90%.
4. The thermal energy requirement in chemical absorption processes

Various novel chemical absorbents are being investigated, with the object of achieving a reduced energy use for solvent regeneration. This has the following contributions:

- The energy required to break the bond between CO₂ and the active component in the solvent
  Reducing this energy requirement can be achieved by using amines with a lower binding energy for CO₂. This has to be balanced with the reaction rates, which might be lower. This will then lead to a larger absorber.
- The heat required for the bringing the solvent up to the reboiler temperature
  A solvent with a high cyclic loading will lead to a lower heat requirement, as there is less solvent to heat up.
- The evaporation enthalpy for the stripping steam which leaves the stripper together with the CO₂
  The amount of water vapour leaving the stripper is controlled by the operating conditions of the stripper and the type of solvent.

Taking a historical perspective, it must be realised that the absorption process based on MEA has been patented in the 1930’s and used for removal of acid gases from industrial gas streams. Operational issues related to corrosion have resulted in the development of alternative amines with a better performance. The development of corrosion inhibitors has resulted in renewed applications for CO₂ removal from flue gases in the 1980’s, where the product CO₂ would be used for enhanced oil recovery. One may call these technologies first generation capture technologies (G1). More recently, the interest in post-combustion capture processes for reduction of CO₂ emissions has resulted in further process improvements and development of alternatives. These processes are either based on further improvements in MEA-based processes through e.g., use of intercooling in the absorber and use of a split-flow system [2] or novel chemical absorbents [3]. These can be called second generation capture technologies (G2), where the CO₂-removal process is heat-integrated with a power plant. However, as it will be demonstrated further on, there is scope for further improvement in the overall process efficiency, leading to third and fourth generation technologies (G3, G4). The technological performance of the various capture technologies can be measured by the energy performance of the absorption process and the energy performance of the power plant with integrated CO₂ capture.

In Table 1 the heat of absorption of CO₂ for different absorbents, based on data from the literature, is given.

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>Heat of reaction/absorption [GJ/ton CO₂]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA – H₂O</td>
<td>1.92</td>
<td>[4]</td>
</tr>
<tr>
<td>DGA – H₂O</td>
<td>1.91</td>
<td>[4]</td>
</tr>
<tr>
<td>DIPA – H₂O</td>
<td>1.67</td>
<td>[4]</td>
</tr>
<tr>
<td>DEA – H₂O</td>
<td>1.63</td>
<td>[4]</td>
</tr>
<tr>
<td>AMP – H₂O</td>
<td>1.52</td>
<td>Derived from [5] at 313 K</td>
</tr>
<tr>
<td>MDEA – H₂O</td>
<td>1.34</td>
<td>[4]</td>
</tr>
<tr>
<td>TEA – H₂O</td>
<td>1.08</td>
<td>[4]</td>
</tr>
<tr>
<td>K₂CO₃ – H₂O</td>
<td>0.64</td>
<td>[4]</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.39</td>
<td>Clausius-Clapeyron fit to CO₂ solubility data</td>
</tr>
<tr>
<td>N-Methyl-Pyrollon</td>
<td>0.37</td>
<td>[6]</td>
</tr>
<tr>
<td>Propylene Carbonate</td>
<td>0.36</td>
<td>[6]</td>
</tr>
<tr>
<td>Sulfolane</td>
<td>0.28</td>
<td>[6]</td>
</tr>
</tbody>
</table>

Table 1 shows that the commonly used MEA is the chemical absorbent with the highest binding energy. Physical solvents like propylene carbonate have a binding energy which is less than 20% of the value for MEA. There seems to be quite some potential for improvement of lowering this contribution to the energy required for releasing the CO₂ from the chemical absorbent. The value for the binding energy for chemical absorbent is determined by the overall reaction path which includes [7]:

- Hydration of CO₂ in the solution, which for water is around 25% of the binding energy in case of MEA (~ 20 kJ/mol CO₂)
Carbamate formation depending on the amine which is around 15% of the binding energy in case of MEA (~ 10 kJ/mol CO₂)

Protonation of the amine which contributes around 60% of the binding energy in case of MEA (~ 50 kJ/mol CO₂)

The summation of these contributions results in an overall binding energy of around 80 kJ/mol CO₂ (1.82 GJ/tonne CO₂), which is slightly lower than the value given in Table 1 (1.92 GJ/tonne CO₂ for MEA) and this is the representative value for a first generation solvent (G1).

The typical reaction paths for mono-amines are shown to be:

- Primary amines: CO₂ + 2R₂NH → R₂NH₂ + R₂NH⁺
- Secondary amines: CO₂ + 2R₂NH → R₂N⁺ + R₂NH₂

In these cases CO₂ reacts with the amine to form a carbamate and a protonated amine, limiting the theoretical capacity to 0.5 mol CO₂/mol amine. A second reaction path without the formation of a carbamate, is the following:

- Tertiary amines: CO₂ + R₃RN + H₂O → R₃RN⁺ + HCO₃⁻
- Sterically hindered primary or secondary amine: CO₂ + R₂NH₂/R₂NH + H₂O → R₂NH⁺/R₂NH₂ + HCO₃⁻

In these cases CO₂ reacts with the amine to form a bicarbonate and protonated amine, allowing a theoretical capacity of 1 mol CO₂/mol amine.

As shown above the contribution of the protonation step on the overall binding energy is quite dominant. The enthalpy changes associated with the protonation can be derived from the temperature dependence of the pKₐ [10]. Current developments have already resulted in the development of sterically hindered amines for post-combustion capture of CO₂ [3]. Through the avoidance of carbamate formation the binding energy is reduced by 10 kJ/mol CO₂ to 70 kJ/mol CO₂ (1.59 GJ/tonne CO₂). Further reductions through the identification of amines with lower enthalpy requirement for the protonation [8] might result in a further reduction of 15 kJ/mol CO₂ to 55 kJ/mol CO₂ (1.25 GJ/tonne CO₂) in a third generation chemical absorbent (G3). In Table 2 the enthalpy for protonation of several commercial chemical absorbents is given [9].

<table>
<thead>
<tr>
<th>Chemical absorbents</th>
<th>Heat of protonation [GJ/tonne CO₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>1.15</td>
</tr>
<tr>
<td>DEA</td>
<td>0.96</td>
</tr>
<tr>
<td>AMP</td>
<td>1.13</td>
</tr>
<tr>
<td>MDEA</td>
<td>0.79</td>
</tr>
<tr>
<td>DIPA</td>
<td>0.97</td>
</tr>
<tr>
<td>DGA</td>
<td>1.14</td>
</tr>
<tr>
<td>Piperazine</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Fourth generation chemical absorbents (G4) might then involve chemical absorbents making use of bicarbonate formation, which is shown to have the lowest binding energy of any chemical absorbent. Examples of such solvents are aqueous solutions of ammonia or potassium carbonate.

Next the contribution of the absorbent heating up in the stripper is analysed. For a G1 chemical absorbent the flow requirement is 20 m³/tonne CO₂ [10], a typical heat capacity of 4 MJ/(m³K) and an approach temperature of 15 K the contribution to the overall energy requirement is 1.20 GJ/tonne CO₂. At first it appears that this can be decreased quite simply by reducing the lean/rich heat exchanger approach temperature to 10 K. In addition it is clear that a switch from a primary amine to a sterically hindered amine (G2), doubling the molar capacity of the chemical absorbent, would also bring benefits. By combining these two approaches the contribution can be reduced by 2/3 to 0.4 GJ/tonne CO₂, which is a large improvement over a G1 absorbent. Further progress is still possible through reduction of the approach temperature to 5 K and a 20% reduction in the solvent flow rate associated with the G3 absorbent technology, resulting in a contribution of chemical absorbent heating of 0.16 GJ/tonne CO₂. G4 absorbent technology assumes a further halving of the absorbent flow rate, which might be achieved through the use of an aqueous ammonia solution [11]. Also the heat exchanger approach temperature is further reduced, by incorporating the heat exchanger partly in the stripper section. Such flow sheet alterations have been suggested in [12] providing
for a more efficient regeneration process. Approach temperatures as low as 3 K are deemed possible and have been realised in seawater desalination equipment. Other engineering approaches to reduce the overall energy requirement are split-flow [12] and intercooling. Intercooling results in a higher loading of the solvent by limiting the increase in temperature in the absorber [2, 13].

Finally the contribution of the evaporation enthalpy required for the generation of stripping steam was assessed. The stripping steam generated in the stripper bottom is needed to provide a high enough driving force for CO₂ desorption. It also provides the heat requirement of the overall stripper and releases this heat upon condensation in the stripper column. However, the CO₂ will leave the top of the stripping still saturated with water vapour and the heat of condensation will be lost in the cooling water. The condensate is returned to the stripper and the reflux ratio, expressed as ton H₂O/ton CO₂, for a G1 absorbent is typically 0.7. The reflux ratio can be reduced by the use of chemical absorbents which exhibit a higher CO₂-partial pressure at a given loading and temperature, leading to an increase in the CO₂/H₂O ratio in the gas stream exiting the stripper. An example is the KSI chemical absorbent developed by Mitsubishi Heavy Industries [3]. For such a G2 chemical absorbent the reflux ratio might be reduced to 0.6. Further lowering of the reflux ratio is achievable by the use of an integrated heat exchanger in the stripper, which allows recovery of the evaporation enthalpy inside the regeneration process [14, 15], leading to a G3 solvent process with a reflux ratio equal to 0.4. Finally, this might be further reduced to 0.1 in G4, which is achievable by non-aqueous chemical absorbents, based on e.g. ionic liquids.

The improvement potential in the three contributions to the thermal regeneration energy requirement can now be combined to provide the overall results. This is shown in Table 3.

Table 3: Synthesis results for the thermal energy requirement for regeneration of chemical absorbents

<table>
<thead>
<tr>
<th>Absorption process development status</th>
<th>G1</th>
<th>G2</th>
<th>G3</th>
<th>G4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding energy</td>
<td>80</td>
<td>70</td>
<td>55</td>
<td>30</td>
</tr>
<tr>
<td>HTX approach</td>
<td>15</td>
<td>10</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Solvent flow</td>
<td>20</td>
<td>10</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Reflux ratio</td>
<td>0.7</td>
<td>0.6</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Thermal energy</td>
<td>4.56</td>
<td>3.31</td>
<td>2.29</td>
<td>0.95</td>
</tr>
<tr>
<td>Contribution CO₂ binding</td>
<td>1.82</td>
<td>1.59</td>
<td>1.25</td>
<td>0.68</td>
</tr>
<tr>
<td>Contribution solvent heating</td>
<td>1.20</td>
<td>0.40</td>
<td>0.16</td>
<td>0.05</td>
</tr>
<tr>
<td>Contribution steam stripping</td>
<td>1.54</td>
<td>1.32</td>
<td>0.88</td>
<td>0.22</td>
</tr>
</tbody>
</table>

For G1 chemical absorption technology the thermal energy requirement is higher compared to results from recent analyses executed for a 30% MEA solution [10]. It presents the status of commercially available processes in the 80/90's of the last century. The binding energy typically amounts to 40% of the energy requirement, whereas liquid absorbent heating and the overhead steam contribute around 25% and 35%. Going from G1 towards a G2 technology the overall thermal energy requirement is reduced by 27%, which is achieved predominantly by the increased CO₂-loading of the solvent and a closer temperature approach in the heat exchanger. The thermal energy requirement for regeneration is somewhat higher than e.g. the thermal energy requirement for MHI's KS-1 solvent [3]. Next going from a G2 technology towards a G3 technology the thermal energy requirement is reduced by an additional 22% compared to G1 technology. A typical example of G3 technology is the precipitating absorbent technology [15], which results in high absorbent loadings enabling an easier regeneration and incorporates a heat integrated stripper. Finally, going from a G3 to a G4 technology an additional reduction of 29% in the thermal energy requirement compared to G1 technology is projected. A typical example of a G4 technology is aqueous ammonia [16]. Overall the potential for improvement of the thermal energy requirement for chemical absorbent is nearly 80%.

5. Power requirement of the capture process

The power requirement in the absorption process is in general determined by:
- The power needed for the blower to guide the flue gases through the absorber
  This is determined by the volumetric flow rate, the pressure drop over the absorption column and the percentage removal of CO₂.
- The power needed for the solvent pumps
  This is determined by the achievable solvent loading in the absorption process and the level of solvent regeneration, combined into the cyclic loading.
- The power needed for the compression process
  This is determined by the thermodynamic properties of CO₂ and the number of stages.

Table 4 gives an overview of the expected technology improvements for G1 to G4 technologies. Here it is assumed that the scope for improvements in the efficiency of compression technologies is limited. However, through the use of lower pressure drop absorber packing materials and solvent with higher absorption rates, it is expected that the power for rotating equipment can be reduced significantly.

<table>
<thead>
<tr>
<th>Process development status</th>
<th>G1</th>
<th>G2</th>
<th>G3</th>
<th>G4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power rotating equipment</td>
<td>MWh/ton CO₂</td>
<td>0.040</td>
<td>0.030</td>
<td>0.020</td>
</tr>
<tr>
<td>Power compression</td>
<td>MWh/ton CO₂</td>
<td>0.114</td>
<td>0.108</td>
<td>0.102</td>
</tr>
<tr>
<td>Power total</td>
<td>MWh/ton CO₂</td>
<td>0.154</td>
<td>0.138</td>
<td>0.122</td>
</tr>
</tbody>
</table>

6. Efficiency improvement of conventional coal fired power plants

The generation efficiency of pulverised coal fired power plants continues to be improved as a result of the progression towards higher steam pressures and temperatures [17]. This requires the development of new and stronger materials for use in piping and tubing in the boiler, including their manufacturing methods. The generation efficiency, however, is also influenced by the temperature of the cooling water, the air to fuel ratio, the allowable stack gas temperature and the use of reheated steam in the steam cycle [18]. In addition, the definition of the heating value of the fuel - higher heating value HHV (USA, Australia) versus lower heating value (Europe) - affects the numerical efficiency value. The efficiencies are therefore also influenced by the local conditions and conventions. The average generation efficiency for coal fired power stations in Australia is currently 0.35 (based on the HHV). In this study it is assumed that the efficiency will undergo an improvement from 0.35 (G1) to 0.5 (G4). The latter efficiency is not unlike the highest efficiency mentioned in [19], translated to the Australian conditions and conventions, i.e. higher cooling water temperatures and the use of the HHV definition. The two intermediate points have been chosen somewhat arbitrarily but it is assumed it will get increasingly difficult to obtain further efficiency improvements. Table 5 shows the efficiency development path for different generations of power plant technology.

<table>
<thead>
<tr>
<th>Status power plant technology</th>
<th>G1</th>
<th>G2</th>
<th>G3</th>
<th>G4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efficiency</td>
<td>0.35</td>
<td>0.41</td>
<td>0.46</td>
<td>0.50</td>
</tr>
<tr>
<td>CO₂-emission</td>
<td>[ton CO₂/MWh]</td>
<td>0.928</td>
<td>0.792</td>
<td>0.706</td>
</tr>
</tbody>
</table>

Table 5 shows that by jumping from G1 power plant technology to G4 power plant technology CO₂-emissions are reduced by 30%. Although this is sizeable emission reduction on its own, the reduction by CO₂ capture and storage would be much higher.

7. Integration of post-combustion capture plant with the power plant

The absorption liquids are regenerated by raising the temperature, upon which CO₂ evolves from the solution. The heat can be supplied by an external heat source, but because of the low temperature levels (typically 120 °C) it is more efficient to derive the heat from the power plant by the extraction of steam from the steam cycle. The capture plant can be considered to be a cogeneration plant with the capture process being the heat recipient. The steam is
typically extracted at the cross-over between the intermediate and low pressure steam turbine. The extracted steam condenses in the reboiler to provide the heat for the regeneration process, but then it is not used to generate electricity and hence leads to a reduction in the power output. The loss in output of the power plant can be determined by a detailed integration study of the capture process with the power plant. Such a study would also entail the use of waste heat for the preheating of boiler feed water in detail. For the purpose of the present explorative assessment a much simpler analysis, which can be used for the future power plants with a higher efficiency and hence different steam and water flow rates, is followed. A convenient way of assessing the impact of the steam extraction on the power plant output is the use of a power equivalent factor (PeF) which relates the steam needed for the reboiler duty to the power output reduction. In [20] this factor is given graphically as a function of steam temperature and pressure for a natural gas fired combined cycle. In [21] the impact of the steam extraction is analysed in further detail and a general description for the power equivalent factor is given which takes into account both the reduction in power output and the use of the reboiler condensate for feedwater preheating. A significant portion of the heat requirement of the solvent process is, however, still recoverable as it leaves the regenerator as steam and its heat of condensation can be used, but because of the large amounts its re-use in the power station might be limited. The power equivalent factor has been estimated, for the different technology generations, assuming that the thermal energy re-use will increase if the thermal energy requirement of the absorption process will decrease. However the power equivalent factor is assumed to level out at 0.15. The results of the analysis are shown in Table 6.

| Table 6: Results of thermal integration of absorption process with power plant |
|---------------------------------------|-----|-----|-----|-----|
| Status power plant technology         |     | G 1 | G 2 | G 3 | G 4 |
| Efficiency                            | [-] | 0.35| 0.41| 0.46| 0.50|
| Thermal energy                        | GJ/ton CO₂ | 4.56| 3.31| 2.29| 0.95|
| Power equivalent factor               | [-] | 0.25| 0.20| 0.15| 0.15|
| Equivalent power requirement          | MWh/ton CO₂ | 0.317| 0.184| 0.095| 0.040|

8. Synthesis of analysis results and conclusions

The results of the thermal analysis of the absorption process and its integration into the power plant can now be combined to provide the overall assessment of the improvement potential. The synthesis results are given in Table 7, which draws on Tables 3, 4, 5 and 6, assuming 90% CO₂ capture.

| Table 7: Synthesis results from overall analysis of energy performance |
|-----------------------------------------------|-----|-----|-----|-----|
| Status PCC technology                        |     | G 1 | G 2 | G 3 | G 4 |
| Efficiency (no capture)                      | [-] | 0.35| 0.41| 0.46| 0.50|
| CO₂-emission (no capture)                    | ton CO₂/MWh | 0.928| 0.792| 0.706| 0.650|
| Thermal energy absorption process            | GJ/ton CO₂ | 4.56| 3.31| 2.29| 0.95|
| Equivalent power requirement of solvent regeneration process | MWh/ton CO₂ | 0.317| 0.184| 0.095| 0.040|
| Power requirement of capture process and compression | MWh/ton CO₂ | 0.154| 0.138| 0.122| 0.105|
| Overall power loss due to capture           | MWh/ton CO₂ | 0.471| 0.322| 0.217| 0.145|
| Efficiency (with 90% CO₂ capture)           | [-] | 0.212| 0.316| 0.397| 0.458|
| CO₂-emission (with 90% CO₂ capture)         | ton CO₂/MWh | 0.153| 0.103| 0.082| 0.071|
| Increase in coal use due to capture         | [%] | 65  | 30  | 16  | 9   |

The results presented in Table 7 give an indication of the large potential for improvement of the post-combustion CO₂ capture process. Going from a G1 to a G4 technology leads to a 70% reduction in the overall power loss due to the CO₂ capture process. Further development of both the absorption process technology and the conventional
power plant technology have the potential to achieve generation efficiencies for coal fired power plants with post-combustion capture equivalent to current technologies (G2) without CO2 capture. The required performance is typically slightly better than a G3 power plant with PCC technology, which achieves an overall generation efficiency of ~0.40 with 90% CO2-capture.

9. Acknowledgments

This work was carried out within CSIRO's Energy Transformed Flagship Research stream on Post-Combustion Capture and was supported by the Australian Government through the Asia Pacific Partnership on Clean Development and Climate.

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In situ Fourier Transform-Infrared (FT-IR) analysis of carbon dioxide absorption and desorption in amine solutions

P. Jackson, K. Robinson, G. Puxty and M. Attalla*

Energy Transformed Flagship, CSIRO Energy Technology, Newcastle, Australia

Abstract

The chemical reactions involved in CO\textsubscript{2} absorption and desorption by chemical absorbents such as aqueous amines are being investigated and modelled to identify and make potential improvements in efficiency. Recent advances in FT-IR spectroscopy have allowed for convenient and rapid analysis of chemical species to be carried out in an aqueous environment. This paper presents the findings of an investigation of carbon dioxide absorption and desorption into/from amine solutions. The amines investigated, including primary capture solvents (eg. MEA) as well as promoters (eg. MDEA), have been selected to demonstrate that both carbamate and carbonate formation can be monitored using this technique. New insights into a much applied but little understood industrial chemical process have been revealed.

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Key word: carbon dioxide, amine, absorption, desorption, FT-IR

1. Introduction

The reduction of greenhouse gas emissions from anthropogenic activities such as power generation is proving to be a real and immediate challenge to Australia and other developed and developing nations worldwide. A potential solution to greenhouse gas emissions from fossil-fuelled combustion sources has emerged in recent years in the form of CO\textsubscript{2} capture and sequestration. The technologies and systems used for capture and sequestration of CO\textsubscript{2} have been used in the chemical- and oil and gas industries for decades. Although none of the capture
technologies have been specifically developed for application in coal fired power generation, they are based on various chemical and physical processes that could be implemented at the end of a fossil fuelled combustion source. These capture methods vary from (i) absorption with amine based solvents to (ii) adsorption on substrates, (iii) separation with CO₂ selective membranes, and (iv) cryogenic separation methods. Of these technologies, the most mature and widely implemented in industry is absorption with an aqueous amine based absorbent.

The chemical reactions involved in CO₂ absorption and desorption by chemical absorbents such as aqueous amines are being investigated and modelled to identify and make potential improvements in efficiency. Recent advances in FT-IR spectroscopy now allow for the convenient and rapid analysis of chemical species to be carried out in an aqueous environment. The present paper reveals the findings of an investigation of carbon dioxide absorption into amine and ammonia solutions. The reactions between CO₂ and amines were followed in situ using an attenuated total reflectance (ATR) probe head optically coupled to the FT-IR spectrometer. The chemical species formed in the reaction were identified using the IR absorption of characteristic functional groups. The results are presented for a range of amines including the more established solvents monoethanolamine (MEA) and methyldiethanolamine (MDEA). This technique has revealed new insights into a much applied but little understood industrial chemical process.

2. Experimental

A schematic diagram of the experimental apparatus is presented in Figure 1. Briefly, a mixture of N₂ (>99.99% purity, BOC Australia, 1.48 L/min) and CO₂ (99.5% purity, BOC Australia, 222 mL/min), the precise composition of which was set using mass-flow controllers (EL-FLOW, Bronkhurst), was first passed through a mixing chamber and subsequently through a pre-humidifier to limit evaporation from the reaction solution. The temperature of the reaction solution was maintained at 40°C using a water bath (Techne Instruments). The gas flow was then entrained into an unstirred reaction mixture, and the CO₂-depleted gas stream passed to a calibrated IR gas analysis unit (VS-3000, Horiba). The depletion of the CO₂ content of the gas stream was used to evaluate the capture performance of selected amines independently of the ATR-FTIR measurements.

The water bath temperature (monitored using a calibrated K-type thermocouple), system pressure and CO₂ content of the gas stream, were logged using a dedicated PC running the software Labview v.7 interfaced to a SCXI-1000 DAQ unit (National Instruments).

During these experiments, a composite zinc selenide and diamond ATR crystal, mounted on the end of a 36 cm (C-276) Hastelloy® probe and attached to either:

(i) a one-piece, flexible chalcogenide optic fibre conduit, or

(ii) a multi-piece elbowed and internally-mirrored conduit

was immersed in situ in the reaction solution and interfaced to a ReactIRiC10 Fourier-Transform Infrared (FT-IR) spectrometer (Mettler-Toledo). The IR system was controlled by a dedicated PC running the software icIR v2 (Mettler-Toledo). A typical scan range was 3000 – 700 cm⁻¹. A drawback of the ATR diamond-tipped probe is the diamond absorption in the region 1960-2250 cm⁻¹. Fortunately, alternatives to vibrational bands falling in this region lie beyond this wavenumber range.
Figure 1 Gas absorption rig interfaced with an FT-IR probe and spectrometer

Ab initio geometry optimisations and harmonic frequency calculations were performed at the B3LYP/6-31G(d,p) level using the GAMESS software suite \(^1\) on a PC with a dual-core processor running Windows XP. Harmonic frequencies are useful guides for assigning vibration modes to spectra, but the exclusion of anharmonic effects and solvent corrections in the calculations leads to large differences between the experimental solution phase and calculated gas phase values. Nonetheless, the 3-parameter hybrid DFT method, which mixes in the exact Hartree-Fock exchange with gradient-corrected DFT exchange and correlation, usually yields a good approximation to the PES in the vicinity of the energy minimum which is critical for the energy derivatives used to evaluate vibrational
frequencies. High quality results are often achieved at a low computational cost with a prudent choice of exchange-correlation quadrature grid (in this case 248,832 points per atom).

3. Results and Discussion

3.1. Base-catalysed CO₂ capture: OH⁻ + CO₂

Figure 2 is a partial temporal profile of the reaction between CO₂ (222 mL/min) and 50 ml 0.489 M NaOH solution (standardised against potassium phthalate solution). The figure legend (right) indicates time elapsed between introduction of gas to the reaction vessel, and spectral acquisition. The peak at 1638 cm⁻¹ (6.09 μm) is assigned as an overtone of the broad O-H stretch at 3368 cm⁻¹ (2.96 μm). Both peaks are evident in pure water spectra and in subsequent spectra acquired for aqueous amine systems, but neither peak was observed by Falk and Miller in their study of the CO₂/water system [2].

The smaller peak between 1400-1300 cm⁻¹ not only increases with time, but appears to shift in frequency during the course of the reaction (1389 cm⁻¹ at t = 00:02:12 to 1362 cm⁻¹ at t = 01:19:12). According to IR correlation charts, C-OH stretches appear in this region of the IR spectrum. This is consistent with the assignments by Falk and Miller [2] of 1385 cm⁻¹ for CO₃²⁻, and 1360 cm⁻¹ for HCO₃⁻. As the CO₂ loading of the reaction solution increases, the pH of the same solution decreases from a high to intermediate basic value (pH ~ 13 down to ~ 9). This shifts the equilibrium in the CO₃²⁻/HCO₃⁻ system towards HCO₃⁻, for which the C-OH stretch has a lower wavenumber than the C-O stretch of CO₃²⁻. According to DFT calculations, the vibrational mode of bicarbonate being monitored corresponds to an O-C-O symmetric stretch (1193 cm⁻¹). A more intense asymmetric O-C-O IR stretching mode is predicted to lie at 1719 cm⁻¹, however it is probably swamped by the O-H overtone at 1638 cm⁻¹. As a result of the diamond absorption, monitoring dissolved CO₂ in solution (2343 cm⁻¹) [2] is also impossible.

![Figure 2 IR spectra recorded at different time intervals (legend, right) during the reaction of 50 ml of 0.489 M NaOH and a gas stream of 1.702 L/min containing 13.04 % CO₂.](image-url)
3.2. Industry standard: MEA + CO₂

MEA (monoethanolamine, or simply ethanolamine, see Figure 3) is a small organic molecule possessing both an hydroxyl group (-OH, red + 1 white) and an amine group (-NH₂, blue + 2 white). These groups are at opposite ends of the molecule, helping to confer the unique properties (high solubility and reactivity with aqueous CO₂) that make MEA the industry standard for CO₂ capture/removal from industrial gas streams [3]. Like most primary amines, MEA reacts with CO₂ to form a stable carbamate, and the concentration of CO₂ present in the reaction solution as “carbonate” (hereafter collectively referred to as both HCO₃⁻ and CO₃²⁻) should remain relatively low for the duration of solution loading.

![Figure 3](image-url)  IR spectrum of pure MEA, and (inset) a ball-and-stick model of MEA [4]. The white atoms = hydrogen, black = carbon, blue = nitrogen, red = oxygen. See Table 1 for peak assignments.

The peaks labelled 1-4 in the IR spectrum of pure MEA (Figure 3) are of lesser utility for monitoring CO₂ capture kinetics in an aqueous solution of MEA, due to the broad O-H IR absorption feature of water. However, there are a number of peaks in the region 2000-900 cm⁻¹ that can be used to monitor evolution of CO₂/MEA reaction products. The surface plot in Figure 4 suggests at least 6 major peaks, and up to 5 minor peaks, could be used to derive rate constants for the CO₂/MEA reaction, as their temporal variation is clear in the figure.

At times close to t = 0, peaks due to MEA and water should dominate the IR spectra. Peaks 5, 7-10, labelled in Figure 5, are within 5 cm⁻¹ of the values measured for pure MEA. As the reaction progresses (CO₂ loading increases), all of these peaks either:

(i) disappear, or
(ii) shift in frequency.
Table 1 IR peak assignments for pure MEA

<table>
<thead>
<tr>
<th>Peak</th>
<th>Frequency (cm(^{-1}))</th>
<th>Assignment</th>
<th>B3LYP/6-31G(d,p) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2</td>
<td>3355, 3293</td>
<td>O-H, N-H</td>
<td>3644; 3612, 3508</td>
</tr>
<tr>
<td>3, 4</td>
<td>2927, 2864</td>
<td>C=H</td>
<td>3036, 2995, 2959, 2948</td>
</tr>
<tr>
<td>5</td>
<td>1601</td>
<td>H(_2)C-NH(_2)</td>
<td>1672 (H-N-H scissor)</td>
</tr>
<tr>
<td>6, 7*</td>
<td>1461, 1355</td>
<td>H(_2)C-OH</td>
<td>1465 (C-C str), 1405 (C-N str)</td>
</tr>
<tr>
<td>8</td>
<td>1172</td>
<td>?</td>
<td>1198 (CH(_2)-CH(_2)-NH(_2) twist)</td>
</tr>
<tr>
<td>9, 10</td>
<td>1081, 1033</td>
<td>C-N, C-O</td>
<td>1101 (C-N str), 1060 (C-N str + tw), 999 (C-O str)</td>
</tr>
</tbody>
</table>

*Could also be due to carbonate formation

Figure 4 IR spectral surface between 2000-900 cm\(^{-1}\) for the reaction between aqueous 30.00 % wt MEA and a gas stream of 1.702 L/min containing 13.04 % CO\(_2\).

Several peak assignments in Table 2 are based on chemical intuition, as there are few examples of IR analysis for carbamate species in the literature, and this is the first report of the IR observation/detection of 2-hydroxyethylcarbamate in aqueous solution. Temporal variation of selected 2-hydroxyethylcarbamate and ethanamine peaks are presented in Figure 6. Referring to Figure 6, the fast increase in the abundance of ['A'] and ['B'], as correlated with the increase in IR peak height, suggests that these peaks are associated with 2-hydroxyethylcarbamate vibrations. Carbamate formation is expected to be rapid upon introduction of CO\(_2\) to the reaction vessel. The abundance of ['7'] increases more slowly with time, and given the frequency of this vibrational peak (1366 cm\(^{-1}\)), it is clearly associated with carbonate formation. Carbonate will form (i) as a hydrolysis product of 2-hydroxyethylcarbamate or (ii) by direct nucleophilic attack by OH\(^-\) on aqueous CO\(_2\) under the high pH conditions induced by the dissolved -or aqueous- MEA. The abundances of ['J'] and ['K'] decrease during the course of the reaction, so these peaks are associated with transformation of the MEA amine group to a carbamate group. It is quite likely these peaks correspond to H\(_2\)C-NH\(_2\) bending or torsions.
Table 2 IR peak assignments for CO₂-loaded MEA solution

<table>
<thead>
<tr>
<th>Peak</th>
<th>Frequency (cm⁻¹)</th>
<th>Assignment</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1564</td>
<td>secondary amine</td>
<td>Software assignment</td>
</tr>
<tr>
<td>B</td>
<td>1491</td>
<td>poss. -HN-C=O</td>
<td>Based on imino-carbonate C-O stretch¹</td>
</tr>
<tr>
<td>C</td>
<td>1464</td>
<td>6</td>
<td>Based on experimental observations²</td>
</tr>
<tr>
<td>D</td>
<td>1385</td>
<td>carbonate</td>
<td>Based on experimental observations</td>
</tr>
<tr>
<td>E</td>
<td>1322</td>
<td>N-C=O(O) in carbamate</td>
<td>Based on organic phosphate P-O stretch³</td>
</tr>
<tr>
<td>F</td>
<td>1226</td>
<td>CO-OH (org. acid)</td>
<td>IR correlation chart</td>
</tr>
<tr>
<td>G</td>
<td>1156</td>
<td>-HN-CO₂ (carbamate)</td>
<td>Based on C-N secondary amine stretch⁴</td>
</tr>
<tr>
<td>H, I</td>
<td>1067, 1019</td>
<td>9,10</td>
<td>Based on experimental observations</td>
</tr>
</tbody>
</table>

¹ IR correlation chart; ² Refer to Table 1; ³ Atomic weight of P = 31 amu, atomic weight of CO = 28 amu, so the vibrations will exhibit similar anharmonicities, and possibly frequencies; ⁴ IR correlation chart. Also close to CO-CN cyanate stretch (weight of OCN = 42 vs CO₂ = 44)

Figure 5 Selected slices of the IR surface, presented in Figure 4, for the aqueous MEA/CO₂ reaction. The legend (RHS) indicates time elapsed since gas admission to the reaction vessel and spectral acquisition. Refer to Tables 1,2 for peak designations.

3.3. A hindered primary amine: AMP + CO₂

AMP, or 2-amino-2-methyl-1-propanol, is a hindered primary amine which reacts with CO₂ to form predominantly carbonate. This outcome is preferable for a CO₂ capture solvent, because the greater stability of carbonate species requires greater heat input to regenerate the parent amine and CO₂, compared with CO₂ regeneration from carbonate/bicarbonate solutions. The frequencies given in Figure 7 compare well with the frequencies for carbonate stretches listed above for the MEA and OH⁻ catalysed CO₂ capture reactions.

Referring to Figure 8, the abundance of [4] decreases as the reaction progresses. Accordingly, this peak corresponds to an AMP vibration (primary amine C-N stretch). Peaks [2] and [3] are observed to increase over the course of the reaction, and the frequencies at which these peaks are observed closely match the carbonate and bicarbonate vibration frequencies reported above. These peaks are clearly representative of carbonate speciation. The peak [1] is observed to increase at the rate of carbonate formation at the reaction onset, however, after a few minutes the rate of generation of this species decreases so that towards the end of the reaction, the rate of generation
is only slightly greater than the rate of consumption and equilibrium is almost established. This suggests ‘[1]’ is due to a vibrational mode of 2-hydroxy-2-methylproplcarbamate.

**Figure 6** Temporal intensity variation for selected MEA/CO₂ IR peaks. For letter designations, refer to Tables 1 and 2. Time axis referenced to t=0, units = min.

**Figure 7** Selected slices of the IR surface for the AMP/CO₂ reaction. The legend (RHS) indicates time interval since t = 0 (gas admission to the reaction vessel) and spectral acquisition. Ball and stick model of AMP [4] at the top right. For peak designations, refer to the text.
3.4. A tertiary amine: MDEA + CO₂

Methyldiethanolamine (CH₃)₂N(C₂H₅OH)₂, is a tertiary amine more often used as a base promoter in a mixture of amines used for CO₂ capture, rather than the principal capture solvent. Tertiary amines can only form carbonates via the base-catalysis pathway, due to the absence of hydrogen atoms bonded directly to the nitrogen atom. Moreover, the base-catalysed bicarbonate pathway is kinetically unfavourable (longer CO₂ gas-capture solution contact times are required).

Referring to Figure 9, in particular the legend (right hand side), it is evident that the CO₂ loading of MDEA occurs extremely slowly, and the paucity of spectral change, aside from the boxed region, is entirely consistent with a single reaction pathway being operative (base-catalysis). Peaks observed to change within the boxed region (eg. ‘1’) are consistent with formation of carbonate and bicarbonate.

4. Conclusion

The results presented in this paper demonstrate the utility of ATR probe-FTIR for the analysis of CO₂ capture by amines in aqueous media. Peaks for four industrial capture solvents have been identified and observed to change with time, and could eventually provide information on the reaction product distribution. This technique will be used in future screening experiments for novel solvents. We also hope to determine kinetic constants by deriving relationships between the product concentrations and FTIR peak heights or areas.

5. Acknowledgements

This CSIRO Energy Transformed Flagship research project has been funded by the Australian Government through the Asia Pacific Partnership on Clean Development and Climate initiative (APP).
Figure 9 Selected slices of the IR surface for the MDEA/CO₂ reaction. The legend (RHS) indicates time interval since t = 0 (gas admission to the reaction vessel) and spectral acquisition. Ball and stick model of MDEA [4], top centre. For peak designations, refer to the text.

References

A Carbon-13 NMR Study of Carbon dioxide Absorption and Desorption with Aqueous Amine Solutions
Qi Yang*, Mark Brown*, Abdelselam Ali*, Dave Winkler*, Graeme Puxty* and Moetaz Attalla*
*Energy transformed Flagship, CSIRO Molecular and Health Technology, Bayview Ave, Clayton, VIC 3168, Australia
*Corresponding author qi.yang@csiro.au
Energy transformed Flagship, CSIRO Energy technology, 10 Murray Dwyer Cct
Steel River Estate, Newcastle, Australia
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Abstract
Quantitative 13C NMR spectroscopy was used to study the reaction of CO2 with aqueous amines. A number of structurally different amines were studied using this method to investigate their CO2 absorption and desorption under different reaction conditions. The results demonstrate that this method is easily applicable to both CO2 absorption and desorption with aqueous amines solutions. The study showed that this technique can be used to investigate the reaction mechanism of amine solvents with CO2, and also give their absorption and desorption capacities. The easy application of this method to monitor speciation of the amine-H2O-CO2 reaction system makes it a useful tool in the development of new amine solvents for post combustion capture (PCC).

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Key word: carbon dioxide, amine, absorption, desorption, NMR

1. Introduction
Climate change is receiving significant attention around the world, with many scientists from different fields working on means to efficiently reduce CO2 emission from human activities, especially from the energy industry. Post combustion capture (PCC) has been demonstrated as a viable process to reduce CO2 released from fossil fuel based electricity generation. Aqueous amines are very promising materials for use in the PCC process, due to their high capacity for CO2 absorption at low CO2 partial pressure and economic affordability. Importantly, this process can be retrofitted to existing power stations or integrated into new ones. There are currently several demonstration pilot plants in operation around the world to study the application of aqueous amines in post combustion CO2 capture from coal fired power station flue gases [1].

The application of aqueous amines for PCC includes two major reactions, CO2 absorption and desorption. The total energy input for PCC using monoethanolamine (MEA) as a “solvent” may be as high as 30% of the power
generated. To make the wide spread application of this technology, commercially viable new amine solvents with lower overall energy requirements must be developed.

The study of speciation in the absorption and desorption processes can provide information about species formation and conversion in the reactions, reveal the relationship between an amine’s capacity for CO₂ capture and its chemical structure, and show the influence of reaction conditions on amine behaviors in CO₂ capture. Speciation of amine-H₂O-CO₂ reactions has not been studied thoroughly and only a few papers have been published [2]. In the most recent speciation study of an amine-H₂O-CO₂ system, Boetinger et al. [2] have described their online NMR spectroscopic study of the species distribution in MEA-H₂O-CO₂ and DEA-H₂O-CO₂ systems. This work required a custom experimental apparatus, and analyzed the species formed in the reactions with online H and C NMR spectroscopy. Hook [3] designed an efficient method to measure CO₂ absorption and desorption in his study of the reaction of sterically hindered aqueous amines with CO₂. He used quantitative C NMR spectroscopy to identify species at the end of an absorption and desorption cycle. These results demonstrate that quantitative C NMR spectroscopy is an efficient tool for use in the study of the amine-H₂O-CO₂ reaction system. By monitoring speciation in whole CO₂ absorption and desorption processes in an open-ended reaction system, it is possible to reveal relationships between amine structures on the one hand, and reaction mechanism and kinetics, influence of reaction conditions and amine capacities of CO₂ capture on the other. The information and knowledge obtained from this study can be used to improve continuous absorbing-desorbing reaction systems and provide guidelines for new amine solvent development for CO₂ capture using the PCC process.

2. Application of Quantitative C NMR and Reaction Apparatus

Aqueous primary and secondary amines react with CO₂ via two major mechanisms: the nucleophilic reaction to generate carbamate derivatives (eq 1) and acid-base neutralization to form bicarbonate compounds (eq 2). The nucleophilic reaction is much faster than the acid-base neutralization according to our observations in this study. Carbamate derivatives formed in this reaction may also generate bicarbonate via a hydrolysis at a suitable stage in the reaction (eq 3). It is apparent that the formation of bicarbonate consumes more CO₂ than the formation of carbamates. Additionally carbamates are thermally more stable than bicarbonates and consume higher energy in the CO₂ desorption process. Tertiary amines do not form carbamates due to the absence of amino-hydrogen atoms, and hence can only undergo acid-base neutralization when they react with CO₂ in aqueous solution (eq 2 where R₃≠ H; R₂≠ H; R₁≠ H). Tertiary amines therefore have potentially higher CO₂ absorbing capacity than primary and secondary amines because they cannot form carbamates; however, they are not an ideal choice for use in PCC as their reaction with CO₂ is slow. The ideal amine solvent to capture CO₂ via PCC should have high speed and high capacity for CO₂ absorption, as well as a high speed, high completion and low energy consumption to release CO₂ in the desorption process. Therefore, a clear picture of the speciation of the amine-H₂O-CO₂ reaction as a function of reaction time can provide a valuable guideline to assist in the design of new amine solvents.

\[ 2R_1R_2NH + CO_2 + H_2O \rightarrow (\text{eq. 1}) \]

\[ R_1R_2NCO_2 + R_1R_2NH_3 \]

\[ R_2R_3N + CO_2 + H_2O \rightarrow \text{eq. 2} \]

\[ HCO_3^- + R_2R_3NH \]

\[ \text{R}_2\text{R}_3\text{NCO}_2 + \text{R}_1\text{R}_2\text{NH} + CO_2 + H_2O \rightarrow \text{eq. 3} \]

\[ 2(\text{HCO}_3^- + \text{R}_1\text{R}_2\text{R}_3\text{NH}_3) \]

The main C NMR resonances used in this quantitative study are those associated with the carbonyl groups of different species at different reaction times. Integration of these resonances allows us to measure the amount of carbonyl group in solution relative to the total amine amount, and from that to calculate the relative amounts of each species present. This data provides the amount of CO₂ reacted with amines in absorption, or carbonyl groups remaining in desorption, their speciation, and reaction rates. After the reaction conditions (concentration,
temperature, CO₂ partial pressure and flow rate, pH, etc.) are standardized, this study will provide information about the relationship between the behaviour of amines in CO₂ absorption and desorption and their chemical structures. Specifically, it will provide us with information on reaction rates, the stability of intermediates and products formed in these reactions, and the reaction mechanism.

In our study samples are taken at different reaction times, sealed, and are analyzed with ¹H and quantitative ¹³C NMR spectroscopy. The quantitative ¹³C NMR provides clear speciation information and is useful in the calculation of the mole percentage of each species relative to the total amine concentration. The ¹H NMR data is used as supporting evidence in this study. The NMR relaxation times (T₁) of carbon atoms, including carbamates and bicarbonates, are measured, and the delay times (Δ) set at ≥5 T₁max (T₁max is the longest T₁ of the carbon among all the carbon atoms in the reaction mixture), in order to ensure that the integration of all the carbon atoms is quantitative. In most cases, the carboxyl carbons of carbamates have longer T₁ values than that of bicarbonate, and of carbon atoms in amines.

The products and intermediates formed in the amine-H₂O-CO₂ system were stable during this quantitative ¹³C and ¹H NMR spectroscopy. The samples were taken directly from the reaction solution to a glass NMR tube (5mm) and then sealed with plastic caps. Our investigation showed that MEA bicarbonate is stable during NMR analysis, and MEA carbamate was more stable, decomposing only partially after being heated with an oil bath at 100°C over night. Different aqueous amines also showed excellent stability once sealed.

Some species generated in the amine-H₂O-CO₂ reaction system are sensitive to the pH of the solution, and their proton and/or carbon NMR signals shift while the reaction pH changes. An external standard reference of 1,4-dioxane was therefore added to the NMR tube for analysis. This reference was calibrated with another external reference of trimethylsilane (TMS) in H₂O via an unlocked run and its ¹³C signal appeared at δ 67.18 ppm.

Absorption reactions were performed in a 50 ml 2-necked pear-shaped flask, with a water condenser topped with a small ice trap. Pure CO₂ gas (99.9%) was bubbled through the amine solution via a Teflon tube (0.028” x 0.07”), and the flow rate set at 5 ml/min after several trial experiments. This flow rate was selected as it was suitable to our study need, to obtain enough details of fast reaction and to complete slow reactions in a planned time frame. The amine solution was stirred at a speed of 900 rpm with an egg-shaped stirring bar (5/8” x ¼”). Desorbing reactions were also carried out in the same apparatus, with CO₂ rich aqueous amine solution obtained from absorption procedure.

3. Results and discussion

MEA was used as the benchmark of our study and aqueous solutions of different concentrations were tested for CO₂ absorption at room temperature (around 25°C) and 40°C. The formation of MEA carbamate was demonstrated by the appearance of carbonyl signal at δ 164.6 ppm. This carbamate carbonyl signal was confirmed by gHMBC 2D NMR spectroscopy which displayed a long range coupling between the carbamate carbonyl carbon atom (C=O) and the proton of the methylene NCH₂ group (figure 1). The carbamate carbonyl resonance increased in intensity and then started to decrease accompanied by the appearance of a new carbonyl resonance at δ 160.8 ppm. The new resonance was assigned to MEA bicarbonate. The carbonyl resonance in this species shows no long range coupling with the methylene NCH₂ protons in the gHMBC 2D NMR spectrum. A stacked quantitative ¹³C NMR spectra of CO₂ absorption with 4M aqueous MEA at room temperature is shown in figure 2. The speciation with reaction time is clearly demonstrated in the spectra.

![Figure 1: gHMBC 2D NMR relationship of δ 164.6 ppm signal of MEA-H₂O-CO₂](image-url)
The absorption of CO₂ by aqueous MEA of different concentrations at different temperatures was studied and some results are shown in figure 3. The graphs in figure 3 show that the 2M MEA (3-b, 3-d) has an earlier and sharper turn on the curve of its carbamate than MEA of 4M at the same reaction temperature (3-a, 3-c). MEA of the same concentration reached maximum concentration of carbamate at a similar time (3-a and 3-c; 3-b and 3-d), but the higher reaction temperature caused a faster decomposition of bicarbonate, and hence gave lower concentration of bicarbonate. These results show the influence of concentration and reaction temperature on MEA's CO₂ absorption capacity, and also revealed a clear pathway of speciation with reaction time.

It is important to note that the timescale in our experiments is hours, rather than the minutes that is typical in PCC pilot plants. This is because the absorbing solution is exposed to a low flux of CO₂, rather than the high flux of a PCC absorption column. This is done to permit accurate and reproducible sampling through the course of the reaction.

The absorption of CO₂ by different amines likewise clearly shows their speciation through their $^{13}$C NMR spectra. The results of CO₂ absorption at room temperature with 4M solutions of monoethanolamine (MEA), N-methyl-ethanolamine (Me-MEA) and N-methyl-diethanolamine (Me-DEA) are shown in figure 4. MEA formed the carbamate and converted partially to bicarbonate during the reaction. Me-MEA also formed a carbamate and this
intermediate converted to bicarbonate faster and to a greater extent. Consistent with its structure, the tertiary amine, Me-DEA, could not form carbamate in the reaction and only formed bicarbonate; it also had the highest CO₂ absorbing capacity of the three amines shown here. However, this was also the slowest to react, especially at the beginning of the reaction. The amount of other (unknown) products formed in the CO₂ absorption with MEA and Me-MEA was very small, and their chemical shift (158.4 ppm) was similar to that of 2-oxazolidinone [2]. The byproduct formed in Me-DEA reaction needs further study for its identification. All these byproducts released CO₂ in the subsequent desorption experiments.

![Graph](image_url)

**Figure 4**: Absorption of CO₂ with MEA (4M), Me-MEA (4M) and Me-DEA (4M) at room temperature

The examples described above illustrate the influence of amine structure on their speciation and total CO₂ absorbing capacity. The following example shows the influence of steric-hindrance of amine structure on amine speciation and CO₂ capture capacity. The CO₂ absorption of a 2M aqueous solution of a sterically-hindered primary amine, 2-amino-2-methyl-propane-1,3-diol (AMPD) was studied at room temperature. The reaction was monitored with the quantitative [¹³C] NMR analysis, and the results showed that the carbamate (δ 164.2 ppm) was formed early in the reaction and then converted rapidly to bicarbonate (see figure 5). When a higher concentration, 4M, was used this amine formed a white precipitate after 1 hour at both room temperature and at 40°C. The formed solid was then dissolved in water and identified with [¹H] and quantitative [¹³C] NMR as the amine carbonate, since the ratio of the amine and carbonyl signals was 2 to 1. This carbonate solution displayed the same carbonyl signal as that which appeared in the NMR spectra at 1 hour in figure 5. This suggests that AMPD carbamate quickly converted to a carbonate, as the instability of the carbamate made the conversion happen at the early stage of the reaction and the pH value at this stage favored the formation of carbonate rather than bicarbonate. As this carbonate only exists for a short time in the reaction before transformed to bicarbonate (δ 161.7 ppm), it can be classified as bicarbonate for the purposes of calculation (figure 6). This classification does not affect the analytical results. The curve in figure 6 showed that maximum amount of AMP carbamate was very low, and was reached at an early stage of the reaction. It had high conversion to bicarbonate, thereby demonstrating a high capacity for CO₂ absorption (106 mole% at 3 hours). It can be expected that this CO₂ rich AMPD solution should perform well in desorption, and that was indeed the case, with a near complete CO₂ release during desorption. These promising results for AMPD suggest that amines with similar structural characteristics should also perform well.

![Graph](image_url)

**Figure 5**: [¹³C] NMR of CO₂ absorption of 2-amino-2-methyl-propane-1,3-diol (2M) at room temperature

**Figure 6**: CO₂ absorption of 2-amino-2-methyl-propane-1,3-diol (2M) at room temperature
We have also applied this method to follow the desorption of CO₂ from the CO₂-rich amine solutions generated during the CO₂ absorption process. By measuring the amount of carboxyl carbons with quantitative ¹³C NMR, the remaining CO₂ can be calculated as a molar percentage, and the species of the molecules which hold the remaining CO₂ as a carboxyl group can also be identified. Hence the total capacity of CO₂ desorption can be obtained and speciation in desorption also observed. The CO₂ desorbing reactions were carried out by heating the CO₂-rich amine solutions in a pear shaped flask in a preheated oil bath at 90°C. At this temperature, most bicarbonate formed in a CO₂ absorption decomposed completely within the first 10 minutes. Examples of CO₂ desorption of MEA, Me-MEA and Me-DEA are shown in figure 7. As expected, both MEA and Me-MEA carbamates are very stable under the desorption conditions used, but Me-DEA released CO₂ faster and to a greater extent due to its higher proportion of bicarbonate formed in the CO₂ absorption step. The results also indicated that both MEA and Me-MEA are able to recapture CO₂ molecules released from bicarbonate decomposition to form more carbamates in desorption step. Although Me-MEA had higher CO₂ absorbing capability (96.2 mole% at 24 hours), it maintained 48.3 mole% of CO₂ at the end of desorption through CO₂ recapture. In comparison MEA retained 55.7 mole% of total CO₂ at the end of desorption. The CO₂ desorption with CO₂ rich Me-DEA was fast and essentially complete as expected. In the future we will lower the CO₂ desorption temperature to reduce the reaction rate and obtain more details about bicarbonate decomposition, in particular the minimum temperature required for bicarbonate decomposition. Lowering the desorption temperature will reduce energy requirements and hence improve the economics of the PCC process.

![Figure 7: CO₂ desorption of MEA, MMEA and MDEA at 90°C](image)

Piperazine is used as a “promoter” in industry for CO₂ capture and we have applied the quantitative ¹³C NMR method of our study to its behaviour in CO₂ absorption and desorption. Piperazine was prepared as a 1M aqueous solution and reacted with CO₂ under our standard conditions at room temperature. The reaction was fast and nearly reached the peak CO₂ absorption at 1 hour reaction time. The CO₂ enriched piperazine solution from this absorption was heated with an oil bath at 90°C to strip the CO₂, but still maintained 61% (mole ratio to amine) of CO₂ in the solution after 60 minutes of desorption time.

![Figure 8: CO₂ absorption and desorption of piperazine (1M)](image)
4. Conclusion

From the above results and discussion, it is clear that the methodology developed in our research is an easy and useful tool to apply to the study of reaction systems of amine-H₂O-CO₂ that does not require any special equipment apart from NMR spectrometers. The application of this method to our study has greatly extended our knowledge about reactions of amines and CO₂ in water solution. We have applied this method of NMR study of CO₂ absorption and desorption to screening a large number of aqueous amines with a wide range of structural diversity, mixed amines of different formulation, and pilot plant samples from absorber and stripper. We have also studied these amines under different reaction conditions including different amine concentrations, reaction temperatures, CO₂ partial pressures, and so on. All of our studies indicate that this method as an easy and reliable tool for investigating amines in PCC, and more results, including kinetic studies, will be forthcoming.

5. Experimental

All the reactions were carried out in standardised reaction apparatus and under standardised conditions as described in Section 2 of this paper. The baths were stabilised at the required temperature before reaction and maintained at the same temperature during reactions. Deionised water was used to make the amine solutions. The data were acquired with Bruker-Biospin Av400 NMR spectrometer and processed with Bruker-Biospin Topspin v2.1 software. All the amines were purchased from major chemical commercial suppliers and used without further purification.

5.1 General method of CO₂ absorption with aqueous amine solutions

An amine compound (0.1 mole) was dissolved in water and made up to 25.00 ml in a 25 ml volumetric flask so that the concentration of the amine solution was 4M unless stated otherwise. Lower concentrations of amine, 2M or 1M, were employed when amines of lower water solubility were used, or when the amines formed precipitates during CO₂ absorption. The amine solution (15 ml) was added to a 25 ml 2-necked pear shaped flask which was linked or equipped with standard attachments as described in section 2. The solution was maintained in a bath of the required temperature and stirred at 900 rpm for 20 minutes. Carbon dioxide was then bubbled through the solution as described in section 2, and the gas outlet was adjusted to just above the stirring bar so that it did not prevent stable and constant stirring. A reaction sample was taken for NMR analysis at different times. For a convenient comparison, reaction samples were taken at 10 minutes, 30 minutes and 60 minutes, and then at every hour to 6 or 7 hours. Most amines were maintained 24 hours for the absorption reaction to achieve equilibrium.

5.2 General method of CO₂ desorption with CO₂ enriched aqueous amine solutions

To make a quick investigation of desorption, the starting solvent was a CO₂-rich solution obtained from the final solution of absorption at room temperature. Concentration of each species and total CO₂ molar percentage was recorded as the starting point. The final CO₂ enriched aqueous amine solutions obtained from the above absorptions were used without changing the flask. The CO₂ supply tube was removed, and the condenser and ice trap were disconnected to let CO₂ gas in the containers escape, and then reconnected with the reaction flask and the free flask neck was sealed with a stopper. The reaction flask was warmed with a preheated oil bath of 90°C. Release of CO₂ was observed immediately and the samples of the reaction were taken for NMR analysis at 10 minutes, 30 minutes and 60 minutes of reaction time.

The CO₂ desorption can also be performed the day after the absorption stage if the CO₂-rich amine solution is kept in a sealed flask and maintained in a fridge of 4°C.

5.3 General method of NMR analysis
All the reaction samples were taken directly into a 5 mm NMR tube. An external standard of 1,4-dioxane was added to the tube. Proton NMR and quantitative proton decoupled $^{13}$C NMR were measured with Bruker-Biospin Av400 without deuterium lock. For most cases, the sample taken at 2 or 3 hours of absorption time were measured for relaxation time as they contained a high concentration of carbamate and bicarbonate as well as amines. However, this time was adjusted for some of the slower or faster reacting amines as required. The delay time (D1) was chosen to be no less than 5 times the longest relaxation time (T1) and 32 scans were collected for each sample. The data was processed with Bruker-Biospin Topspin v2.1 software.

5.4 CO$_2$ absorption with MEA (4M) at room temperature

MEA (6.01 g, 0.1 mole) was dissolved in deionised water and made up to 25.00 ml solution in a volumetric flask. The MEA solution (15 ml) was added to a 50 ml 2-necked pear-shaped flask with standard attachments as described in section 2 and a water bath of 25°C was used to maintain the solvent temperature. CO$_2$ gas was bubbled to the flask through a Teflon tube (described in section 2). The samples were taken at reaction times of 10 min, 30 min, 1 h, 2 h, ... 7 h and 24 h. An external standard of 1,4-dioxane was added to each NMR sample and all the samples were analysed with quantitative $^{13}$C NMR by using the Bruker-Biospin Av400.

5.5 CO$_2$ desorption from CO$_2$-enriched MEA at 90°C

CO$_2$-rich solution from the end of the above absorption experiment was used for CO$_2$ desorption with a preheated oil bath (90°C) as described in the general method. Samples were taken at 10, 30 and 60 minutes of reaction time for quantitative $^{13}$C NMR analysis.

Absorption and desorption of other amines were also carried out using the same method with possible adjustment of their concentration. Reaction temperatures were adjusted according to the study plan.

6. Acknowledgement

We acknowledge the assistance of Drs Roger Mulder and Jo Cosgriff for their invaluable help in methodology development. This CSIRO Energy Transformed Flagship research project has been funded by the Australian Government through the Asia Pacific Partnership on Clean Development and Climate initiative (APP).

7. References


[2] Online NMR spectroscopic study of species distribution in MEA-H$_2$O-CO$_2$ and DEA-H$_2$O-CO$_2$. Wolfgang Boettinger; Michael Maiwald; Hans Hasse; Fluid Phase Equilibria (2008), 263(2), 131-143; references there in.

CO₂ capture by aqueous amines and aqueous ammonia

– A Comparison

N. Dave*, T. Do, G. Puxty, R. Rowland, P.H.M. Feron and M. I. Attalla

CSIRO Energy Technology, P.O.Box 330, Newcastle, NSW 2300, Australia

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Abstract

This paper presents the results of ASPEN simulations of a carbon-dioxide (CO₂) removal and recovery plant that captures CO₂ from a 500 MWe (net) conventional coal-fired power plant flue gas stream. At a constant CO₂ recovery rate of 86.5% by weight, the performance of aqueous ammonia solution as an alternative to various aqueous amino solvents (MEA, AMP and MDEA) is compared in terms of the process scenarios, solvent loadings and overall energy consumption. The overall mass transfer co-efficient and CO₂ loading data generated for aqueous ammonia solutions using a laboratory scale wetted wall gas-liquid contactor are also presented.

The ASPEN simulation results in conjunction with the laboratory data show, that capturing CO₂ from coal-fired power plant flue gas, using aqueous ammonia solvent, will require ammonia concentration no more than 5% by weight and absorber temperature 10°C or lower, if the vapor phase ammonia losses are to be contained and the precipitation of ammonium bi-carbonate in the absorber is to be avoided. Under such an operating scenario, the aqueous ammonia based CO₂ capture process has overall energy requirement comparable to the conventional 30% by weight aqueous MEA based process. The ASPEN results further show that 30% by weight AMP based process has the lowest overall energy requirement among the solvents considered in this paper.

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Keywords: post-combustion capture; power station; coal; absorption processes

1. Introduction

The monoethanolamine (MEA) process, or variations thereof, is currently the most widely used industrial process for capturing CO₂ from pf-fired power plant flue gas streams. In these plants relatively small quantities of CO₂ are captured to meet the industry demands for dry ice, enhanced oil recovery and food processing applications. However, when this process is applied for the greenhouse gas mitigation purposes to such plants, it has been considered too expensive due to large efficiency and cost penalties involved. Studies by the US DOE [1], IEA [2]...
and CSIRO [3] have generally shown that at such scales the net thermal efficiency of the power plant will drop by about 10 absolute percentage points and the cost of CO₂ capture will be around US $30-50 per tonne of CO₂ recovered. One solution to overcome these problems is to find a low cost solvent that has higher CO₂ loading capacity and lower energy requirement for regeneration in comparison with the MEA solvent. Tertiary and hindered amine such as, methyl-diethanolamine (MDEA) and amino-methyl-propanol (AMP), that have theoretical CO₂ loading capacity twice that of MEA and the thermal energy requirement for regeneration lower than MEA have been proposed as alternative solvents [4,5]. Recently, Ciferno et al [6] have shown in their desk-top study of suitability of aqueous ammonia as an alternative solvent, that 7% by weight aqueous ammonia solvent has capacity to halve the energy efficiency and cost penalties that are associated with CO₂ capture from coal-fired power plant flue gas when 30% by weight MEA solvent is used. They have also indicated that aqueous ammonia solvent could potentially be used to remove SOₓ, NOₓ and mercury from flue gas during CO₂ capture. Thus, the aqueous ammonia solvent is a multi-pollutant capture medium.

This paper assesses the CO₂ capture process performance that is likely to result with aqueous solutions of AMP, MDEA and ammonia as solvents and compares each solvent performance with the conventional 30% by weight MEA solvent. The engineering process simulator software ASPEN™ is used to simulate the CO₂ capture plant and estimate the process performance indicators. To ascertain validity of the simulated process conditions for CO₂ capture by aqueous ammonia solvent, the CO₂ loading and overall mass transfer data were also generated using a laboratory scale wetted wall gas-liquid contactor. The ASPEN predicted gas-liquid equilibrium data for the system NH₃-CO₂-H₂O was also compared with the public domain experimental data [7,8].

2. CO₂ capture process flow-sheet

For this study, the coal-fired power plant (500 MWe) is considered to be a typical subcritical type plant in Australia where no flue gas desulphurisation (FGD) systems are installed. A typical Australian bituminous coal with low sulphur content (<1%) is assumed to be the fuel for this plant. The flue gas temperature, pressure and its CO₂ volume content are 120°C, 105 kPa and 12.9% respectively. Figure 1 depicts the general process flow-sheet adopted in the ASPEN process simulation for a CO₂ capture plant that treats the above flue gas. After in-direct heat exchange with the CO₂ lean exhaust gas leaving the absorber, the flue gas (Feed Gas) is pumped into the absorber by a blower. A direct contact type feed gas cooler upstream of the absorber controls the gas temperature at the absorber inlet. After passing through the absorber the flue gas undergoes a water wash section to remove any solvent droplets carried over and then leaves the absorber. The “CO₂ rich” absorbent solution is pumped to the top of a stripper, via a heat exchanger. The regeneration of the solvent is carried out in the stripper. Heat is supplied to the reboiler to maintain the regeneration conditions. The CO₂ product gas leaves the stripper via an overhead condenser. The CO₂-product is a relatively pure product, with water vapour being the main other component. The “CO₂ lean” absorbent solution, containing far less CO₂ is then pumped back to the absorber via the lean-rich heat exchanger and a cooler to bring it down to the absorber temperature level.

3. The CO₂ capture process conditions

With increasing absorption temperature, the physical solubility of CO₂ in the aqueous amino solvent decreases, but the reaction rate of dissolved CO₂ with the amine solvent increases. Hence to strike a balance between physical solubility and reaction kinetics, the flue gas temperature at the absorber inlet is usually kept at around 45°C in the
case of 30% by weight MEA solvent based CO₂ capture process [9]. To keep the comparison basis constant, the “CO₂ lean” AMP and MDEA solvent concentrations and the absorber inlet temperature were also kept same as in the case of MEA based process. In addition, in each case the approach temperatures between the hot and cold fluids were kept at 10°C during the heat exchange. Whilst the CO₂ removal level is set to 86.5% for all the solvents, the process conditions for aqueous ammonia solvent are different from those for the above amino solvents. These conditions were determined separately using the ASPEN™ simulator as explained below. It should be noted that in this paper, the refinement of product CO₂ and its compression for the storage are not considered within the scope of the CO₂ capture plant.

In order to obtain the appropriate operating conditions for the aqueous ammonia based CO₂ capture process, the vapour-liquid equilibrium data was first calculated for the system NH₃-CO₂-H₂O at 120°C and 200°C using the ASPEN™ process simulator and then compared with Müller’s experimental data [7,8]. This was necessary to confirm the validity of ASPEN process simulations. Figures 2 and 3 show close agreement between the ASPEN generated vapour-liquid equilibrium data and Müller’s experimental data. The coloured data points on Figures 2 and 3 represent the Aspen generated values for the total system pressure and the partial pressures of CO₂ and ammonia as a function of total CO₂ molality at the fixed value of ammonia molality.

Using the general process flow-sheet concept depicted in Figure 1, detailed ASPEN process simulations were carried out for the aqueous ammonia based CO₂ capture varying the “CO₂ lean” aqueous ammonia feed stream concentration and its temperature. For each case, the flue gas temperature at the inlet to the absorber was kept the same as the feed aqueous ammonia stream temperature. Under these conditions, both the ammonia loss and the reboiler duty were calculated per kg of CO₂ removed as a function of the feed ammonia concentration for 86.5% CO₂ removal and recovery. In each case, the stripper was assumed to operate at 500 kPa.

Figure 4 shows the results of ASPEN simulations for CO₂ capture using aqueous ammonia solvent at various operating conditions assuming the equilibrium absorption conditions at each stage of the absorber. These results show that both ammonia loss from the system and reboiler duty in the stripper decrease with the decreasing temperature of the absorber. Decreasing the absorber temperature below 5°C has, however, minimum incremental advantages. Increasing the ammonia concentration in the solvent, whilst reducing the reboiler duty at a given absorber temperature, it increases the ammonia loss from the system. The ASPEN simulations additionally showed that with 86.5% CO₂ removal requirement, the ammonia concentration in the aqueous solution at 7.5% and above leads to the ammonium bi-carbonate precipitation in the absorber, if the absorber temperature is 5°C or less.

Figure 2: V-L equilibrium data at 120°C for NH₃-CO₂-H₂O system
Figure 3: V-L equilibrium data at 200°C for NH₃-CO₂-H₂O system
Therefore, for the minimum ammonia loss and reboiler duty with no precipitation of ammonium bi-carbonate in the absorber, the feed ammonia concentration should be kept below 7% by weight, if the absorber is to operate at 5°C.

Whilst the above operating conditions may be generally recommended for the aqueous ammonia based CO₂ capture process, it should be noted that CO₂ absorption at temperatures below the ambient conditions will require chilling the flue gas as well as the "CO₂ lean solvent" using an appropriate refrigerant. This refrigeration system load may not be helpful in reducing the total energy demand associated with the CO₂ capture process when compared with the MEA based process that is currently available commercially. A decision was therefore made to compare the aqueous ammonia based process by keeping the absorber temperature at 10°C and solvent concentration at 2.5% w/w and 5% w/w.

Figure 4: ASPEN simulation results for CO₂ capture at a number of operating conditions with aqueous ammonia solvent

4. Laboratory and ASPEN simulation results

Figure 5 shows the overall mass transfer co-efficient for CO₂ absorption as a function of CO₂ loadings for a number of aqueous ammonia and 30% w/w MEA solvents. These data were generated in a laboratory scale wetted wall column absorber which was operated at atmospheric pressure with CO₂ partial pressure varying from 0 to 20 kPa. The details of the absorber and its operating procedures are given elsewhere [10]. It shows that in an absorber operating at 40°C with 30% w/w MEA as solvent, to achieve similar overall mass transfer rates under identical CO₂ loadings, the aqueous ammonia solvent concentration and temperature will have to be at least 10% and 20°C respectively.

Figure 5: Overall mass transfer co-efficient for CO₂ absorption with aqueous ammonia and 30% w/w MEA solvents as a function of CO₂ loadings

During overall mass transfer measurements at both 5°C and 20°C for 10% w/w aqueous ammonia, the precipitation of solid ammonium bicarbonate was detected at CO₂ loadings of 0.4 mol/mol and higher. This laboratory observation is in-line with the ASPEN predictions shown in Figure 4. Table 1 below shows the ASPEN simulation results for the solvent circulation rate, reboiler heat duty and overall energy demand (includes motive
power) per ton of CO₂ captured in a CO₂ capture plant that uses various solvents for 86.5% CO₂ removal from flue gas. For the amino solvents, the flue gas and the lean solvent inlet temperatures to the absorber were assumed as 45°C and 40°C respectively. In the case of aqueous ammonia solvents, the flue gas and lean solvent inlet temperatures to the absorber were assumed to be 10°C and the refrigeration plant power demand was calculated assuming the co-efficient of performance (COP) equal to 3.

Table 1: Results of ASPEN simulations of a CO₂ capture plant – comparison with amines

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Flow Rate (m³/ton of CO₂)</th>
<th>Reboiler Temperature °C</th>
<th>Reboiler Heat Duty (GJ/ton of CO₂)</th>
<th>Electricity Consumption (GJ/ton of CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30% w/w MEA</td>
<td>18.36</td>
<td>119.8</td>
<td>4.17</td>
<td>0.14</td>
</tr>
<tr>
<td>30% w/w AMP</td>
<td>15.82</td>
<td>115.9</td>
<td>3.18</td>
<td>0.13</td>
</tr>
<tr>
<td>30% w/w MDEA</td>
<td>40.06</td>
<td>112.9</td>
<td>3.82</td>
<td>0.08</td>
</tr>
<tr>
<td>2.5% w/w NH₃</td>
<td>22.32</td>
<td>145.0</td>
<td>4.24</td>
<td>1.87</td>
</tr>
<tr>
<td>5% w/w NH₃</td>
<td>15.88</td>
<td>130.0</td>
<td>2.94</td>
<td>1.42</td>
</tr>
</tbody>
</table>

The simulation results further showed that the total ammonia loss in the vapour phase for 5% w/w aqueous ammonia solvent based CO₂ capture plant is 0.17 kg per ton of CO₂ captured. Whilst the hindered amine AMP has best theoretical performance, the results clearly show that 5% w/w aqueous ammonia solvent has the lowest reboiler heat duty. It is lower than that required for 30% w/w MEA solvent because CO₂ capture via cycling between ammonium carbonate and bi-carbonate has the heat of regeneration 0.61 GJ/ton of CO₂ captured versus 1.92 for MEA. Overall, 5% w/w aqueous ammonia solvent based CO₂ capture has the total energy demand similar to that with 30% MEA based process.

5. Conclusion

The ASPEN simulation results in conjunction with the laboratory data show, that capturing CO₂ from coal-fired power plant flue gas, using aqueous ammonia solvent, will require ammonia concentration no more than 5% by weight and absorber temperature 10°C or less, if the vapor phase ammonia losses are to be contained and the precipitation of ammonium bi-carbonate in the absorber is to be avoided. Under such an operating scenario, the aqueous ammonia based CO₂ capture process has overall energy requirement comparable to the conventional 30% by weight aqueous MEA based process, provided the stripper is operated at 500 kPa and the solvent chiller plant has co-efficient of performance equal to 3. The ASPEN results further show that 30% by weight AMP based process has the lowest overall energy requirement among the solvents considered in this paper.
6. Future work on the aqueous ammonia process

The preliminary results presented here provide an insight into some of the issues related to the use of aqueous ammonia for post-combustion capture of CO₂. Further work will focus on the establishment of a pilot plant operating on a flue gas slipstream, which aims to validate the technical performance predicted by the flow sheet simulations using Aspen Plus. This pilot plant will be located at Lake Munmorah in a power plant operated by Delta Electricity, assisting in the assessment of the use of aqueous ammonia under Australian power plant conditions. Important data to be derived from this pilot plant are the heat requirement for solvent regeneration and the ammonia losses. An experimental programme has been defined to enable the performance validation under a variety of conditions. This is currently underway. In addition to this work a study will be executed aimed at the integration of a full-scale aqueous ammonia process into a typical Australian power plant, including the delivery of CO₂ as a supercritical fluid. This study will provide the input data into an overall economic assessment of the aqueous ammonia process in comparison with conventional amine processes.

7. Acknowledgements

This work was carried out within CSIRO's Energy Transformed Flagship Research stream on Post-Combustion Capture and was supported by the Australian Government through the Asia Pacific Partnership on Clean Development and Climate.

8. References

GHGT-9

Post-combustion capture R&D and pilot plant operation in Australia

A.J. Cottrell\textsuperscript{a*}, J.M. McGregor\textsuperscript{a}, J. Jansen\textsuperscript{b}, Y. Artanto\textsuperscript{b}, N. Dave\textsuperscript{a}, S. Morgan\textsuperscript{a}, P. Pearson\textsuperscript{b}, M.I. Attalla\textsuperscript{a}, L. Wardhaugh\textsuperscript{a}, H.Yu\textsuperscript{a}, A. Allport\textsuperscript{a}, P.H.M. Feron\textsuperscript{a}

\textsuperscript{aCSIRO Energy Technology, P.O.Box 330, Newcastle, NSW 2300, Australia}
\textsuperscript{bCSIRO Energy Technology P.O. Box 312, Clayton South, VIC, 3169, Australia}

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Abstract

Post-combustion capture of CO\textsubscript{2} is a key technology for the reduction of greenhouse gas emissions from Australian coal fired power stations. It is an emerging technology, which still faces significant challenges in scaling up to full commercial scale suitable for power station applications. To increase adoption by the power industry significant cost reductions in capital and operating cost must be realised. CSIRO has developed an integrated post-combustion capture R&D and pilot plant program aimed at bringing down the barriers for commercial deployment. This paper provides an overview of the program and its status.

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Keywords: Type your keywords here, separated by semicolons ;

1. Introduction

The use of post-combustion capture of CO\textsubscript{2} (PCC) followed by geological storage holds the promise of significant CO\textsubscript{2}-emission reductions from existing power stations. The main advantage of PCC is that it is the only practical technology able to reduce emissions from existing power stations and new ones. As it is an end of pipe technology fitted to a power station, it is also the CO\textsubscript{2} capture technology which is the easiest to implement. The leading PCC technology is based on absorption processes, which is further described in the next section. It produces a very pure CO\textsubscript{2} stream and is, in several ways, also a flexible technology with great adaptability. It allows for staged implementation, e.g. via the installation of separate modules, initially only treating a proportion of the power station flue gas. This would also enable rapid pick-up of technology improvements, such as new absorbents with better performance. During operation, it is also possible to vary the rate of CO\textsubscript{2}-removal or to even switch off the capture process. Such flexibility is a desirable feature which enables the power station output to be varied in accordance with the fluctuations in demand and match market conditions. This feature is technically and economically attractive, particularly in liberalised electricity markets and this is not possible with other capture routes. PCC, however, has not yet been demonstrated at full scale in a power plant, nor has it been integrated into a power plant. The application of commercially available PCC-technologies, like all other capture routes, also leads to

\textsuperscript{*}Corresponding author. Tel.: +61-2-4960-6033; fax: +61-2-4960-6021.
E-mail address: aaron.cottrell@csiro.au
large increases in the power generation costs and decreases the power generation efficiency. The development of less expensive capture technologies is therefore needed. Australia’s situation is also somewhat different to other nations, because of the lack of flue gas desulphurisation or denitrification installed at the power stations. Also cooling water constraints are quite severe, because of the ongoing drought. It is against this background that CSIRO has set-up an integrated program of research and pilot plant demonstrations [1].

2. Absorption processes for post-combustion CO₂ capture

Although several different processes are currently under development for the separation of CO₂ from flue gases, absorption processes using aqueous solutions of chemical absorbents is the technology closest to commercialisation at power station scale and likely to be the technology used to make early cuts in global greenhouse gas emissions. The typical flow sheet of CO₂ recovery using chemical absorbents is shown in Figure 1. After cooling the flue gas, it is brought into contact with the chemical absorbent in the absorber. A blower is required to pump the gas through the absorber. At temperatures typically between 40 and 60 °C CO₂ is then bound by the chemical absorbent in the absorber. After the absorption stage the flue gas passes through a water wash section to balance water in the system and to remove any solvent droplets or vapour carried over before it leaves the absorber and vented to the atmosphere. The “rich” absorbent solution, which contains the chemically bound CO₂ is then pumped to the top of a stripper, via a heat exchanger. The regeneration of the chemical absorbent is generally carried out in the stripper at elevated temperatures (100 – 140 °C) and pressures between 1 and 4 bar(a) with some solvents such as ammonia capable of being regenerated at much higher temperatures and pressures. For regeneration to take place, heat is supplied to the reboiler, most likely in the form of steam from the low pressure steam turbine of the power station. The thermal energy required for regeneration is significant and can be be split into three main components; heating up the solution, providing the required energy for removing the chemically bound CO₂ from the solvent and for steam production within the stripper which acts as a stripping gas. Steam is recovered in the condenser and the condensate fed back to the stripper, whereas the CO₂ product gas leaves the condenser. The CO₂-product is a relatively pure (> 99%) product, with water vapour being the main other component. Due to the selective nature of the chemical absorption process, the concentration of inert gases is low. The “lean” absorbent solution, containing a low level of CO₂ is then pumped back to the absorber via the lean-rich heat exchanger and a cooler to bring it down to the absorber temperature level. CO₂ removal is typically between 85 - 95%.

![Figure 1: Generic process flow diagram for CO₂ recovery from flue gas with chemical absorbents](image-url)
3. Post-combustion capture in the Australian electricity sector

Electricity generation in Australia is for 80% based on coal (brown and black). The presence of easy to mine coal reserves, the close proximity of power plants to both coal mines and end users make electricity generation costs in Australia amongst the lowest in the world, but this is possible at the expense of sizeable CO₂-emissions. Table 1 shows key data for Australia’s coal fired power generation fleet [2].

Table 1: Key data for Australian coal fired power stations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generation capacity</td>
<td>28 GW</td>
</tr>
<tr>
<td>Electricity production</td>
<td>170 TWh/a</td>
</tr>
<tr>
<td>Average generation efficiency and emission</td>
<td></td>
</tr>
<tr>
<td>- Black coal</td>
<td>35.6% - 0.9 tonne CO₂/MWh</td>
</tr>
<tr>
<td>- Brown coal</td>
<td>25.7% - 1.3 tonne CO₂/MWh</td>
</tr>
<tr>
<td>Overall CO₂-emissions and no of sources</td>
<td>170 Mtonne CO₂/a from ~ 60 flue gas streams</td>
</tr>
<tr>
<td>Typical SO₂ level range in flue gas</td>
<td></td>
</tr>
<tr>
<td>- Black coal</td>
<td>200 - 600 ppm</td>
</tr>
<tr>
<td>- Brown coal</td>
<td>100 - 300 ppm</td>
</tr>
<tr>
<td>Typical NOₓ level range in flue gas</td>
<td></td>
</tr>
<tr>
<td>- Black coal</td>
<td>300 - 700 ppm</td>
</tr>
<tr>
<td>- Brown coal</td>
<td>100 - 200 ppm</td>
</tr>
<tr>
<td>Typical flue gas temperatures</td>
<td></td>
</tr>
<tr>
<td>- Black coal</td>
<td>120 °C</td>
</tr>
<tr>
<td>- Brown coal</td>
<td>180 °C</td>
</tr>
<tr>
<td>Cooling water requirement</td>
<td>1.5-3.0 m³/MWh</td>
</tr>
</tbody>
</table>

It is important to note that Australian coal fired power stations have limited emission controls - only particulate removal (electrostatic precipitators or bag filters) - and flue gas desulphurization and denitrification has not been installed. In the past Australia’s power generators have not been required to install FGD due to the low sulfur concentration in most of Australia’s coals. This factor, along with the generally remote locations and low population density areas that the stations are operating in, has led to Australia’s fairly unique situation when it comes to CO₂ capture from its flue gases. Now this poses a problem for implementation of CO₂ capture as all commercial processes have limited tolerance to SO₂, ranging from max. 100 ppm for a low concentration MEA-based process down to less than 10 ppm for processes based on new amines or formulated absorbents [3]. This means that in addition to flue gas cooling a separate scrubber will be necessary for deep removal of SO₂ increasing the capital costs of the overall capture system.

4. Post-combustion CO₂ capture at CSIRO

The PCC R&D program at CSIRO consists of two major components which are operated in an integrated manner:
> A pilot plant program

The pilot plant program is aimed at providing hands-on-experience for future operators of PCC plants. The application of emission controls (DeNox and FGD) in the EU, USA and Japan has given those power station operators a familiarity with chemical process technology. There have been no large scale chemical processes applied in the Australian power industry for chemical process experience to be developed. The pilot plants will provide an important opportunity for the industry to gain experience in these types of technologies before going to a large scale. In addition to this the pilot plant program will result in the identification of operational issues and detailed
technology requirement. These issues can be resolved at an early stage and if not straightforward they will lead to the specification of research tasks. A pilot plant operating on real flue gas will also be a testing ground for novel technologies/solvents brought forward by laboratory based research, as these technologies can be tested under realistic flue gas conditions (temperature and composition).

A lab research program

The laboratory based research program will in the first instance support the pilot plant program operation through the provision of analytical services. It will also provide support in the interpretation of research results through e.g. process modelling and detailed chemical analysis and results assessment. The research program is also the starting point for the development of novel chemical absorbents and novel process concepts, which when deemed to be sufficiently qualified can be rolled out to the pilot plants. Within the research the Australian specific requirements related to the flue gas quality and the water limitations can also be addressed.

The research program includes the development of novel chemical absorbents and novel processes for post-combustion capture including the integration with the power plants. Overall, the program is designed to reduce both the capital and operating costs of CO₂ capture under Australian conditions by determining optimum solvent and process configurations. The pilot plant program incorporates the gathering of operational experience with a wide range of flue gases using commercially available chemical absorbents and also novel chemical absorbents developed in the lab research program.

5. Overview of pilot plants

The pilot plant program has established two pilot plants in 2008, in the states of Victoria and New South Wales, with a third being established in Queensland. The capture plant capacities range from 100 kg/h CO₂ to 500 kg/h CO₂ using flue gases from brown and black coal firing. The wide operational scope of the pilot plants is needed to properly prepare next steps in the development of CCS in Australia, which will be a much larger scale demonstration plant incorporating the full chain of capture and storage of CO₂.

Within the Latrobe Valley Post-combustion CO₂ Capture Project the pilot plant technology has been based on amines and will be tested on flue gases from Victorian brown coal. Brown coal flue gases are available at high temperature, have high water content and contain alkaline ash. This provides a challenging environment for chemical absorption processes. This plant is the first of its kind in the southern Hemisphere and was started up in March 2008. The pilot plant is shown in Figure 3. Currently a series of 7-experimental campaigns is being executed using different chemical absorbents. The first campaigns will be based on a 30% MEA aqueous solution to provide the baseline for the process performance.

A second pilot plant, based at Delta Electricity’s Lake Munmorah power station is currently undergoing commissioning and will be operational before the end of 2008. This pilot plant is based on the use of aqueous
ammonia for CO₂ capture and the power station is a black coal fired power station without FGD or deNOx. The design is very flexible allowing the absorber and desorber over a range of different pressures and temperatures. This flexibility is needed to fully explore the benefits and pitfalls of an aqueous ammonia process for CO₂ capture.

A third pilot plant will focus on the determination of an optimum solvent for flue gases from power generation processes using black coal. This pilot plant will be located at Tarong Power station in Queensland and will be constructed in the first half of 2009, ready for operation in the second half of 2009.

CSIRO have also partnered with TPRI and China Huaneng Group in China for the development and operation of a amine based pilot plant at the Huaneng Beijing Cogeneration Power Plant in Beijing. This power station has FGD and deNOx and gives CSIRO the avenue to understand the trade-offs between developing an integrated pollution control system and using separate control technologies for each pollutant. This pilot plant has been operational since June and is based on 20% MEA. Once trials are completed on MEA other solvents and process variations will be incorporated into the operation of the pilot plant.

6. Pilot plant design

The pilot plant design is steered by the requirement to gather sufficient information from its operation to allow the next steps towards scale-up and commercialisation of PCC-technology to be taken. The information can be split up into two separate groups:

- Technical performance
The technical performance data gathered from the pilot plants should give sufficient information to understand the relationships between the CO₂ capture efficiency (described by percentage removal or absorption rate), the CO₂ capture energy consumption (particular the thermal energy requirement) as determined by the operational condition in the absorber (temperature and CO₂ concentration) and the desorber (temperature and pressure). The technical performance is also determined by the liquid absorbent flow rate for a given flue gas flow rate and the liquid CO₂ loadings resulting from this.

- Practical operational performance
  Practical information needed relates to chemical absorbent consumption and degradation rates, fouling and corrosion, the effectiveness of the flue gas conditioning stage, reagent loss rate both to CO₂-product gas and to release with flue gas and system water consumption. This information will require the support from laboratory for the liquid analysis and the determination of the stability of the chemical absorbent.

The performance data gathered can be translated into information needed for the economic assessment of a particular absorbent. Comparison between results derived from the pilot plant with process modelling is needed to provide validation of performances for a range of chemical absorbents. The operational performance will also translate into the selection of equipment materials and chemical usage information, needed for the overall economic assessment.

These requirements have led to a flexible basic design for pilot plants, allowing for testing on several locations as required. The pilot plant has been designed using a simulation software package called Winsim. The Winsim model is based on the process flow diagram shown in Figure 2. It has the following general characteristics:

- capacity of 100-500kg/hr CO₂ capture, depending on location
- capture 85% of the CO₂ in the incoming flue gas stream
- be able to operate with variable reboiler temperatures and pressures
- utilise a prescrubber for removal of SO₂ and NOₓ
- dual absorber columns operable in series or parallel
- single stripper column of sufficient regeneration capacity
- a sophisticated gas analysis to determine flue gas quality and CO₂-product quality.

The pilot plants have been designed for operation with slipstream flue gas from black coal and lignite fired power stations.
7. Loy Yang pilot plant process simulation using Winsim

The Winsim process simulation software has been used to determine the effects on the Loy Yang pilot plant process operation when varying different parameters. The process simulation results will be used to guide operators in setting operational set-points, to compare with results as seen in the pilot plant and to verify the model. They will also aid in understanding any discrepancies between real results and those simulated by the model. Some simulation results are shown in Table 2 for variations in the heat input rate to the reboiler using two different solvent flow-rates. The flue gas composition used for the model is 18.22% H₂O, 6.81% O₂, 65.59% N₂, and 9.38% CO₂ on a volume wet basis, which is the flue gas composition as found at Loy Yang Power Station. The results in Table 2 are in line with the expectations. For instance the expected reduction in lean loading as the heat input into the reboiler increases is observed, although it is clear that there is also a reduction in the reboiler temperature. The thermal energy requirement varies widely but an energy requirement of less than 4 MJ/kg CO₂ is achieved at capture rates between 85% and 95%. This reaffirms that the pilot plant should be operated at capture rates between 85-95% CO₂ capture. Pushing the plant any further results in a significant increase in energy and water required per unit of CO₂ captured. Initial results do not seem to show in any benefit or loss by increasing the solvent flow rate. Continuing work in this area will help firm up conclusions.
Table 2: Simulation results for Loy Yang Pilot Plant

<table>
<thead>
<tr>
<th>Reboiler Heat (MJ/h)</th>
<th>Reboiler Heat Duty (MJ/Kg CO₂ removed)</th>
<th>Lean Solvent (mol/mol)</th>
<th>Rich Solvent (mol/mol)</th>
<th>Solvent (lpm)/Flue Gas rates (m³/h)</th>
<th>Temperature (°C)/P (bar) reboiler</th>
<th>MEA Concentration (mass %)</th>
<th>CO₂ Removed (%)</th>
<th>Cooling Water required m³/h</th>
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<tr>
<td>190</td>
<td>6.2</td>
<td>0.14</td>
<td>0.44</td>
<td>8.5/147</td>
<td>117</td>
<td>29</td>
<td>99.3</td>
<td>5.68</td>
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<tr>
<td>180</td>
<td>5.9</td>
<td>0.15</td>
<td>0.44</td>
<td>8.5/147</td>
<td>116.6</td>
<td>29</td>
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<td>5.06</td>
</tr>
<tr>
<td>150</td>
<td>4.9</td>
<td>0.16</td>
<td>0.46</td>
<td>8.5/147</td>
<td>116</td>
<td>29</td>
<td>98.9</td>
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<tr>
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<td>0.46</td>
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<td>0.49</td>
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<td>0.5</td>
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<td>113</td>
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<td>77.7</td>
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<tr>
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<td>0.21</td>
<td></td>
<td>12.2/147</td>
<td>116/1.68</td>
<td>29.9</td>
<td>99.3</td>
<td>4.9</td>
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<tr>
<td>140</td>
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<td>0.23</td>
<td></td>
<td>12.2/147</td>
<td>115/1.68</td>
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<td>115/1.67</td>
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<td>98.9</td>
<td>4.9</td>
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</table>

8. Preliminary results from Loy Yang pilot plant experiments

Since the commissioning of the Loy Yang pilot plant was completed in May of 2008 the pilot plant has undergone a number of characterisation campaigns to develop a reproducible base line for operation on MEA. This base line will be used to compare solvent and operational changes made in later campaigns and also for verification of process models. The characterization trials entail the achievement of a closed mass balance for CO₂ and water and the assessment of the energy balance.

Figure 3 shows some measured results (temperatures and flow rates) from a typical trial.

Figure 3: Results from a typical pilot plant run
Figure 3 shows that the pilot plant reaches steady state in a fairly short timeframe and that most parameters are fairly stable in operation.

Table 3 shows some results from the characterisation trials carried out since May 2008. These results show that the pilot plant is underperforming terms of the amount of CO₂-recovered compared to the model. The reasons for this are currently investigated.

Table 3: Characterisation trials for the Loy Yang pilot plant

<table>
<thead>
<tr>
<th>Blower flow-rate (m³/h)</th>
<th>Solvent flow-rate (l/min)</th>
<th>Reboiler steam pressure (kPa)</th>
<th>Solvent temp</th>
<th>Recovery (%)</th>
</tr>
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<tr>
<td></td>
<td></td>
<td></td>
<td>ABS-COL1 mid temp (°C)</td>
<td>ABS-COL2 mid temp (°C)</td>
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<tr>
<td>50</td>
<td>8.2</td>
<td>140-150</td>
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<td>75</td>
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<td>167</td>
<td>8.2</td>
<td>140-150</td>
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<td>60</td>
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9. Acknowledgements

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10. References:

Vapour liquid equilibria data for a range of new carbon dioxide absorbents

Graeme Puxty*, Andrew Allport and Moetaz Attalla

CSIRO Division of Energy Technology, PO Box 330, Newcastle NSW 2300, Australia

Abstract

Carbon dioxide (CO₂) is now recognised as the greenhouse gas contributing most to global warming and implicated in climate change model predictions. Electricity generation from fossil fuel combustion is a major source of CO₂ emissions both internationally (32% of total CO₂ emissions) and nationally (50% of total CO₂ emissions). To effectively reduce CO₂ emissions in the short to medium term requires CO₂ capture and storage from these and other point sources as a part of the solution.

The CSIRO Division of Energy Technology has undertaken a major CO₂ capture research program covering many aspects of the technology. On the laboratory scale, the chemical reactions involved in CO₂ capture and release by chemical absorption are being investigated and modelled to identify where and how improvements in efficiency can be made. A large scale screening study in which the CO₂ absorption capacity of over 100 30% w/w amine solutions at 40°C and ~13 kPa CO₂ partial pressure has been carried out. This study has identified a number of novel amines as having outstanding CO₂ carrying capacity. An apparatus has been developed used a stirred glass batch reactor, capable of withstanding pressures up to 1100 kPa, coupled to a pressure controller and gas delivery system from a high pressure reservoir. The apparatus has been used to collect vapour liquid equilibria (VLE) data by measurement of CO₂ consumption from the high pressure reservoir. VLE data has been collected for three amines identified in the screening study at 1 molL⁻¹ and 40°C over the pressure range 0.3 to 900 kPa. The VLE results will be presented along with a comparison with MEA and an interpretation of the behaviour of the amines.

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PACS: Type pacs here, separated by semicolons;

Keywords: post-combustion capture; carbon dioxide solubility; aqueous amine

1. Introduction

The capture, reversible release and storage of carbon dioxide (CO₂) from combustion flue gases (post-combustion capture, PCC) is now recognised by government and industry as a viable near-term option for greenhouse gas...
abatement [2, 3]. It is particularly relevant to electricity generation from fossil fuels (coal, oil and gas) which accounts for approximately 25% of global CO₂ emissions [4] with this figure set to increase drastically in the next 25 years [5]. PCC has a number of practical advantages over other methods such as oxy-firing to produce a pure CO₂ stream and IGCC with pre-combustion capture and is of similar economic cost [6]. In particular, PCC can be retro-fitted to existing power stations and integrated into new ones. Additionally, the parasitic energy demand of a PCC plant on a power station can be reduced (at the cost of CO₂ removal efficiency) according to electricity demand if additional electricity output is required from a power station during times of peak load or optimal electricity pricing. PCC is also applicable to CO₂ capture from other point sources such as steel manufacturing and cement manufacturing. The major difference between applications is the temperature and CO₂ partial pressure of the flue gas.

The application of PCC to combustion flue gases from electricity generation or other point sources poses a number of technical challenges. The main issue is the energy requirement of the process, which using current industry standard technology is expected to reduce the efficiency of a coal fired electricity plant by ~21% [6]. The main energy cost is the heat and steam required for the desorption column and to pump the absorbing solution around the system. By increasing the capacity of a chemical absorbent, in terms of the amount of CO₂ that can be absorbed and desorbed per gram of solution, this energy requirement may be more than halved [7].

In work carried out within CSIRO, Australia over 100 different amine moieties were screened for their ability to absorb CO₂ at 40°C and a CO₂ partial pressure of 13 kPa. Eight amines were identified as showing an outstanding molar absorption capacity, significantly greater than others tested and greater than modeling predictions of capacity as a function of amine basicity. In this work more detailed characterization of three of these amines has been undertaken: 2-amino-2-methyl-1,3-propanediol (AMPD), A1 - a heterocyclic secondary alkanolamine; and A2 - a short chain tertiary alkanolamine. The vapour liquid equilibria between 1 g mol⁻¹ solutions and CO₂ has been determined at 40°C for CO₂ partial pressures covering the range 0.3 - 900 kPa using a newly setup apparatus and compared to monoethanolamine (MEA). This partial pressure range was chosen to provide data relevant to PCC from power stations, as well as PCC in other industries such as steel manufacturing where the gases may be at elevated pressure.

2. Experimental

Chemicals

All chemicals were purchased from Sigma-Aldrich with purities for MEA, AMPD, A1 and A2 of 99%, 99%, 96% and 99.5% respectively. They were used without further purification or preparation. 1 g mol⁻¹ aqueous amine solutions were prepared by weighing appropriate amounts of amine into volumetric flasks and making up to the mark with deionised water. Solutions were prepared freshly for the start of each experiment.

Apparatus and Procedure

The vapour liquid equilibria apparatus consisted of a stirred 160mL jacketed glass reactor vessel capable of operating at pressures up to 1100 kPa (Parr model 5104). The reactor vessel was fitted with a pressure transducer (Swagelok, accuracy 0.5% limit point calibration) and T-type thermocouples for high accuracy pressure and temperature measurements. CO₂ (BOC Australia, 99.5% purity) was delivered to the reactor vessel via a Bronkhorst El-Press forward pressure controller supplied from a high pressure CO₂ reservoir (20 - 65 MPa). The reservoir was suspended below a balance (Mettler-Toledo model PB4002) inside a box to eliminate drafts and the mass loss during an experiment used to determine CO₂ consumption. N₂ was delivered to the reactor from a building supply (BOC Australia, 99.9% purity). The reactor content was thermostated by passing liquid from a water bath (Thermo) through the reactor jacket. A schematic of the apparatus is given in Figure 1. CO₂ was delivered to the reaction vessel via a dip tube located adjacent to the stirrer. As the CO₂ was delivered it became entrained in the stirrer vortex ensuring minimal mass transfer resistance and rapid absorption of the CO₂.
Experiments were completed by charging the reactor vessel with 150 mL of 1 molL\(^{-1}\) aqueous amine solution. The solution was then stirred (1500 rpm) and allowed to equilibrate to the set point temperature of 40°C. Following this the reactor was put under vacuum to degas the solution and remove air from the reactor vessel until all gas evolution ceased. The reactor was filled with 130 kPa N\(_2\) and the experiment was begun by using the pressure controller to deliver CO\(_2\). Depending on the desired range of the CO\(_2\) partial pressure one of the following procedures was used: for pressures below 25 kPa the reactor was rapidly pressurised up to 700 kPa, the gas supply then closed and the reactor allowed to come to equilibrium; and for pressures above 25 kPa the pressure controller was used to maintain a constant pressure set-point in the reactor.

CO\(_2\) consumption was followed using either the reactor pressure or the mass loss from the high pressure CO\(_2\) reservoir with an experiment considered complete when no CO\(_2\) consumption occurred over a 20 minute period. The total CO\(_2\) delivered to the reaction vessel was determined by the mass change in the CO\(_2\) reservoir. The amount of CO\(_2\) occupying the head space of the reactor vessel was determined from the dead volume and pressure using the virial equation of state for CO\(_2\) \([8]\) given in Equation 1 with the remainder assumed to have been absorbed by the solution. To determine the total reactor volume, including inserts, valves, etc, and thus the dead volume (liquid
volume subtracted from the total reactor volume) a calibration was carried out in which known amounts of CO₂ were introduced into the reactor by mass at five different values. Using the measured temperature and pressure the volume of CO₂ was then determined by fitting the virial equation to the pressure versus moles of CO₂.

\[ PV = z n RT \]
\[ z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} \]
\[ B = 137.6 - 87.7 e^{33.7/T} \]
\[ V_m = n/V \]

where \( P \) = absolute pressure (bar), \( V \) = volume (mL), \( n \) = moles, \( R \) = 83.14467 mLbar/Kmol and \( T \) = temperature (K)

3. Results and Discussion

The precision and accuracy of the apparatus was validated by measuring the solubility of CO₂ in water at 26°C and 50°C at four pressures. There is good agreement between measured and literature values as shown in Figure 2. This validated the ability of the apparatus to precisely determine CO₂ absorption capacities of aqueous amine solutions. The amount of CO₂ absorbed by an aqueous amine solution is much greater than pure water, and thus the relative error is lower compared to a solution that absorbs little CO₂ such as water.

The CO₂ absorption capacities, expressed as moles of CO₂ absorbed per mole of amine of the three amines and MEA are given in Table 1 and plotted in Figure 3 and Figure 4. Figure 3 shows the results for CO₂ partial pressures below 100 kPa and Figure 4 for higher pressures. Below 100 kPa the absorption capacity of all the amines varied significantly with CO₂ partial pressure, with molar absorption capacities varying between 0.2 and 0.8 between 0.34 and 30 kPa. This highlights the importance of choosing an amine with optimal behavior for the type of CO₂ partial pressure range it will be exposed to in a real process. In particular, if absorption capacity drops off rapidly with partial pressure in part of the curve, this will limit the amount of CO₂ removal that can be achieved with a particular amine. For example between ~3 and ~25 kPa the absorption capacity of MEA varies between 0.4 and 0.6. However, amine A2 varies between 0.2 and 0.8 over the same pressure range. This would suggest amine A2 would be better.

Figure 2 Measured CO₂ solubility in water at 26°C (blue diamonds) and 50°C (red squares). The solid lines are literature data from [1].
suited to CO₂ removal with pressures at the mid to high end of this range and MEA for pressures at the low end of the range. The results for AMPD over this range suggest it behaves similarly to MEA between ~10 and 25 kPa but the capacity drops rapidly below this. Unfortunately, data for A1 over this range is unavailable due to technical difficulties. In the range ~25 – 100 kPa AMPD, A1 and A2 all have absorption capacities greater than MEA. A1 and A2 have the largest absorption capacities in this range making them a favourable choice for moderate CO₂ partial pressure applications.

### Table 1 Results of molar CO₂ absorption capacity as a function of pressure for 1 molL⁻¹ aqueous amine solutions at 40°C.

<table>
<thead>
<tr>
<th>CO₂ Partial Pressure (kPa)</th>
<th>CO₂ Absorption Capacity (moles CO₂ / moles amine)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.21</td>
<td>0.4111</td>
</tr>
<tr>
<td>24.72</td>
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<tr>
<td>49.79</td>
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<td>679.85</td>
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<td>880.42</td>
<td>1.2339</td>
</tr>
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</table>

At partial pressures above 100 kPa there is little change in absorption capacity with partial pressure for all the amines tested. The change that occurs can be attributed to the increased solubility of CO₂ in water at elevated pressure. At 100 kPa the solubility of CO₂ in water at 40°C is 0.024 molL⁻¹ and at 900 kPa it is 0.21 molL⁻¹ [1]. AMPD, A1 and A2 all achieve absorption capacities greater than MEA. This is consistent with behaviour observed for CO₂ solubility in aqueous MEA elsewhere [9]. The reason for this is likely to be related to the preference of MEA to form a stable carbamate, while all the other amines being sterically hindered primary, secondary or tertiary amines respectively may not. It takes a higher CO₂ partial pressure, and thus larger dissolved CO₂ concentration, to push the CO₂-MEA-H₂O system to favour bicarbonate formation, and even at high pressure this is incomplete. The other amines, being likely to favour bicarbonate formation, achieve their maximum absorption capacity at lower CO₂ partial pressure.
Figure 3 Measured CO₂ molar absorption capacity as a function of CO₂ partial pressure below 100 kPa. Literature data is also shown for 2-amino-2-methyl-1,3-propanediol (open red squares) as it was available at the appropriate concentration. The lines between points are not regression lines but are smoothed curves between points to improve readability.

Figure 4 Measured CO₂ molar absorption capacity as a function of CO₂ partial pressure above 100 kPa. Literature data is also shown for 2-amino-2-methyl-1,3-propanediol (open red squares) as it was available at the appropriate concentration. The lines between points are not regression lines but are smoothed curves between points to improve readability.
In summary, over the pressure range ~10 to 25 kPa MEA and AMPD have similar CO₂ absorption capacities, while below 10 kPa MEA has the highest capacity. A2 has a larger absorption capacities than the others at the mid to high end of this range and a lower absorption capacity towards the low end. AMPD, A1 and A2 all show a higher absorption capacity than MEA over the range ~25 to 900 kPa. All the amine have effectively reached there maximum absorption capacities near 100 kPa, with increases above this pressure attributable to increased CO₂ solubility in water.

4. Conclusions

In previous work a large scale screening study of the CO₂ absorption capacity of over 100 amines at 40°C and CO₂ partial pressure of ~13 kPa was carried with a number of amines identified as showing outstanding absorption capacities. In this work CO₂ absorption data as a function of CO₂ partial pressure for three of these amines (AMPD, A1 and A2) and MEA have been collected using a newly setup apparatus. It was found that the amines showed a large variability in their CO₂ absorption capacity at CO₂ partial pressures below 100 kPa. In particular AMPD and MEA behaved similarly at low pressure, while AMPD, A1 and A2 performed better than MEA at CO₂ partial pressures above 25 kPa.

These results highlight the importance and need to collect CO₂ absorption data in aqueous amines at a range of CO₂ partial pressures. Such information allows prudent amine selection for different CO₂ capture applications depending upon the CO₂ partial pressure in the gas to be cleaned. In particular, to further assess these amines for power station flue gas applications greater resolution of data is required at CO₂ partial pressures between 1.5 kPa - 15 kPa. This information, in conjunction with absorption rate data which will be collected in future work, will allow selection of the best amine to meet any trade off between capital and operating costs for a CO₂ capture process.

5. Acknowledgements

This work was carried out within CSIRO’s Energy Transformed Flagship Research stream on Post-Combustion Capture and was supported by the Australian Government through the Asia Pacific Partnership on Clean Development and Climate.

6. References

Dear Stephen,

The conference is next week, but the deadline for the final papers is 5 December 2008. It is the major event in the area of CO2 Capture and Storage. It's worth to have a look at the conference website.

http://mit.edu/ghgt9/index.html

Best regards,

Paul Feron

Hi Paul

Happy to look through and provide comments. Could you advise the actual time frame as I am not sure of the timing of the conference you refer to below.

Regards
Stephen Woolcott
Manager
APP & Contract Management Section
APP Aluminium Task Force Secretariat
International, Resources Development
\; Taxation Branch
\; Resources Division

Department of Resources, Energy and Tourism
Level 8, 10 Binara Street, Canberra City ACT 2601
GPO Box 1564, Canberra ACT 2601 Australia
PH: 61-2-6276.1890  Fax: 61-2-6213 6026
Mob: 0420 962 726
Email: Stephen.Woolcott@ret.gov.au
Internet: http://www-ret.gov.au
ABN 46 252 861 927

Dear Stephen,
We would like to ask you to review the enclosed papers which will be published after the Greenhouse Gas Technology Conference held in Washington and welcome any comments you might have. The publications relate to work funded through the APP PCC project. Thank you.

Best regards,

Paul H.M. Feron
PCC Science Leader
CSIRO Energy Technology
10 Murray Dwyer Cct, Mayfield West
P.O. Box 330
Newcastle NSW 2300
Australia
Tel +61(0)2 4960 6022
Mob +61(0) 447688747

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Hi Paul

Thank you for providing the attached PCC related papers for comment. While I can't say that I understood every word that I read and some papers were heavy going for me as a non-chemist, there are no problems with the papers from a policy perspective.

I also note that each paper contains an acknowledgement of the Australian Governments funding through the APP as required which is appreciated.

Good luck at the conference.

Regards
Stephen Woolcott
Manager
APP & Contract Management Section
APP Aluminium Task Force Secretariat
International, Resources Development
& Taxation Branch
Resources Division

Department of Resources, Energy and Tourism
Level 8, 10 Binara Street, Canberra City ACT 2601
GPO Box 1564, Canberra ACT 2601 Australia
PH: 61-2-6276 1890 Fax: 61-2-6213 6026
Mob: 0420 962 726
e-mail: Stephen.Woolcott@ret.gov.au
Internet: http://www.ret.gov.au
ABN 46 252 861 927
Dear Paul,

Thank you for your email.

There is the slight chance that the project description template for the Action Plan may change, depending on what feedback we get from other Task Force members on the suggested template. I plan to send a request to all project managers at the end of the week, with the final agreed upon template attached, if no one has raised any objections.

However, you would be more than welcome to start completing the template, as there may not be any major changes, any at all.

I've attached to this email, for your reference, a copy of the project description for the PCC project that is currently in the Action Plan. We were thinking of having just the one project description for both PCC1 and PCC2.

We are still discussing with Korea the program for the meeting and the workshops for Day 1 (31 March). As I mentioned in a previous email, at this stage it is anticipated that the workshop will be a half day workshop in the afternoon that focuses on Korean engagement with existing CFE projects.

Depending on what you would like to do, there may be scope for holding another workshop either on the morning of Day 1 or in parallel with the Korean workshop, so please let me know what ideas you have about presenting on PCC-activities.

Many thanks.

Sent: Tuesday, 20 January 2009 3:31 PM
To: Feron, Paul (DET, Newcastle)
Cc: Princi, Jacqui
Subject: RE: APP Cleaner Fossil Energy Task Force Meeting in Korea, 31 March - 2 April 2009 [SEC=UNCLASSIFIED]
Attachments: CFE 06 06 - current project description.doc

Dear [DELETIONS],

I will not be able to make it to this meeting in Korea, because I have planned my annual leave in April. I gather that the PCC-activities will need to be presented as a minimum and will discuss internally on how to best do this. In the meantime I will fill in the reporting template for both PCC-projects.

Best regards,

Paul H.M. Feron
PCC Science Leader
CSIRO Energy Technology
10 Murray Dwyer Cct, Mayfield West
P.O. Box 330
Newcastle NSW 2300
Australia
From: [DELETION]
Sent: Monday, 19 January 2009 2:25 PM
To: [DELETION]

Subject: APP Cleaner Fossil Energy Task Force Meeting in Korea, 31 March - 2 April 2009 [SEC=UNCLASSIFIED]

Dear Taskforce Members,

I am pleased to advise that we have had a very positive response to our proposal to hold the next CFE Task Force meeting in Seoul, Korea, from 31 March to 2 April 2009. Could you please put these dates in your diary.

We will send out shortly details on the meeting venue, suitable nearby accommodation and visa requirements for travel to Korea.

At the last Taskforce meeting in Melbourne, it was agreed that we would update the Taskforce Action Plan. Unless everyone has any objections, we suggest streamlining the Project Descriptions. I have attached a template for your consideration.

Please do not hesitate to contact me if you have any questions or comments.

Kind Regards,

[DELETION]

Department of Resources, Energy and Tourism
Level 10, 10 Binara Street, Canberra City ACT 2601
GPO Box 1564, Canberra ACT 2601
Ph: 61-2-6213 7888  Fax: 61-2-6213 6934
Email: elizabeth.lim@ret.gov.au
ABN 46 252 861 927

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CFE-06-e6: Assessing Post-Combustion Capture Technologies for Emissions From Coal-Fired Power Stations

Project
This project will progress the development of post combustion capture (PCC) as a technology that can be retrofitted to existing coal power stations to achieve major improvements in environmental performance by capturing SOx, NOx and CO2 emissions. It will establish a post combustion capture (PCC) pilot plant demonstration and laboratory research program in Australia. It will support technology transfer to other Partner countries.

The technical risk and cost of applying the PCC technology are key issues that need to be addressed to facilitate the introduction of this technology. The proposed program will address both issues through targeted research, which will feed into and benefit from the pilot scale plant that will be deployed at several power stations in Australia. This pilot scale testing is crucial, as only assessment under real flue gas conditions will ensure the development of realistic and cost effective emission control technologies. The project also includes laboratory research on developing new sorbents, technologies and processes to improve the economic and environmental performance.

Participation
CSIRO will lead the project and partner with research organizations in Australia and other member countries. CSIRO will also encourage direct participation from industry from both the Coal Producing and Electricity Generating Sectors.

Objectives
The overall objective of the PCC program is to support the adoption of PCC technology through research, development and demonstration. The program will aim to reduce the costs of deploying PCC technology by improving the science associated with the capture of CO2 and also by increasing the engineering process experience in using PCC technology as it is applied to Australian power station conditions. Scientists from other member countries will share engineering process experience through their participation in field trials. This program will also provide direct benefits for power station in other Partner countries that do not have de-SOx and de-NOx emission control on their power stations.

Pilot and Research Program
- Operation of mobile 1000 tpa PCC pilot plant at several Australian power stations to obtain process data, solvent performance testing and practical experience. Scientists from other member countries will be invited to take an active role in the operation and evaluation of pilot plant research at Australian power stations.
- Assessment of different solvents including but not limited to, amines, amino acids, room temperature ionic liquids and aqueous ammonia.
- Modeling, synthesis and development of improved solvents based on laboratory research of representative flue gases and then assessment under pilot scale testing.

Future Developments
• Assuming a favorable outcome from the research program and pilot scale testing, development of the following process designs for ongoing staged demonstration and application of the technology:
  - A small demonstration; 50,000 tpa.
  - A full demonstration PCC plant of 225,000 tpa capacity (with both capture and compression).
  - A concept design for a PCC plant of 3.3 Mtpa capacity.

• This project could be extended to other member countries, but only if there is approval by the host government. This could involve the supply of a mobile pilot PCC plant to be operated at various power stations in that country, training of field operatives and laboratory support.

Milestones
• 12/2006 Finalize establishment of CSIRO laboratory facilities.
• 02/2007 Installation of CSIRO PCC mobile pilot plant at the first power station to undertake field trials in Australia.
• 01/2008-12/2010: Operation and testing on real flue gases to obtain performance data for a range of existing and developed solvents.
• 10/2007 Implement training and technology transfer program that will be open to participants from other member countries.
• Annual - Undertake program technical exchange workshops for all parties.

Location
The initial work will be undertaken in Australia. The pilot plant project demonstrations will be undertaken at several power stations in NSW and Queensland and the research component will also be conducted in Australia at a number of different research locations particularly Newcastle and Melbourne.

Resources
The project will be funded by Australia and supplemented as appropriate by other Partner countries.
Dear Lindsey,

We would like to request the Department's approval for the enclosed paper due to be presented at the 2009 Australia-China Symposium on Advanced Coal and Biomass Utilisation Technologies on 9 – 11 December 2009 in Wuhan, China. The publication is the first with some results from the ammonia PCC pilot plant at Delta Electricity's Munmorah power plant. Thank you in advance.

Best regards,

Paul H.M. Feron  
CSIRO Energy Technology  
10 Murray Dwyer Cct, Mayfield West  
P.O. Box 330  
Newcastle NSW 2300  
Australia  
Tel +61(0)2 4960 6022  
Mob +61(0) 447688747

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AQUEOUS AMMONIA BASED POST COMBUSTION CAPTURE PILOT PLANT AT MUNMORAH: RESULTS OF PRELIMINARY TESTS

Hai Yu1, *, Scott Morgan1, Anthony Callen2, Aaron Cottrell1, James McGregor1, Peter Coombes3, Andrew Allport1, Thong Do1, Narendra Dave1, Rob Rowland1, Graeme Puxty1, Moetaz Attalla1, Paul Feron1

1CSIRO Energy Centre, 10 Murray Dwyer Circuit, Mayfield West Circuit, NSW 2304, Australia
2 Delta Electricity, Scenic Drive, Doyalson, NSW 2262, Australia

*Corresponding author: hai.yu@csiro.au (Dr Hai Yu)

ABSTRACT

Aqueous ammonia based CO2 capture is a promising technology for reduction of CO2 emission from power station and research work in this area is reviewed briefly. CSIRO and Delta Electricity have jointly constructed a research scale Post Combustion Capture (PCC) pilot plant at the Munmorah Power Station. The pilot plant is designed to capture up to 3,000 tonnes of CO2 per annum, using aqueous solution ammonia to capture CO2 in the flue gas.

Functionality and preliminary tests at Munmorah pilot plant suggest that the pilot plant is functioning appropriately and steady state operation can be achieved under conditions specified. The comparison of pilot plant data and lab studies confirms the pilot plant performs as predicted. The NH3 process proves to be very effective for SO2 removal but not for NOx. Relatively high ammonia loss is ascribed to its volatility and in particular low absorption of CO2 in the solvent.

KEY WORDS: Post combustion CO2 capture, aqueous ammonia, pilot plant trial

1 INTRODUCTION

Research efforts have been intensified worldwide to develop technologies which are technically and economically feasible for capturing CO2 emitted from coal fired power stations and thus to mitigate global warming. CO2 capture by chemical solvents is believed to be the most promising technologies if the urgent actions are required to reduce CO2 emission. The advantages of this technology include

- An established technology and low technological risk. It has been widely adopted for CO2 separation in natural gas sweetening and ammonia production.
- Effective for capture of CO2 with low partial pressure
- Flexible in operation and can be retrofitable to the existing power stations

However, the currently used solvents suffer degradation in the oxidative environment and are not tolerant to many species in the flue gas such as SOx and NOx. The processes using traditional amines require significant energy for regeneration and are economically unfavourable. The intense development efforts on novel solvents for improved performance and reduced energy consumption during regeneration, as well as process designs incorporating new contacting devices such as hybrid membrane-absorbent systems, solid adsorbents and high temperature regenerable sorbents, may lead to the use of more energy efficient post combustion capture systems 1.

1.1 OVERVIEW OF AQUEOUS AMMONIA BASED CO2 CAPTURE

Aqueous ammonia, as one of novel solvents for CO2 capture, has received increasing attention recently, due to the potential benefits:

- Low cost of solvent
- Higher CO2 removal capacities
- Lower absorption heat and less regeneration energy
- Less corrosive and damage to equipment
Possibility of capturing multicomponents (NOx, SOx, CO2) which is of particular interest to Australian power stations since flue gas desulphurisation (FGD) and selective catalytic reduction (SCR) of NOx are not implemented in Australia.

The biggest challenge facing aqueous ammonia process is that ammonia is very volatile, which requires a large amount of cooling water to recover NH3 which slips to the flue gas. To minimize ammonia loss, the absorption of NH3 needs to take place at low temperatures. Cooling of the flue gas and solvent and regeneration of NH3 from wash water requires significant energy. In addition, the absorption rate is low for NH3 at low temperatures, which means that a much bigger size of absorber is required. Research efforts are underway worldwide to explore the potential of ammonia based process as a viable solution for capture of CO2 and/or other pollutants in the flue gas emitted from power stations.

The chemistry involved in the CO2 capture by aqueous ammonia is relatively well understood, particular from a thermodynamic point of view (equilibrium product distribution including solid species under various conditions). It is worth noting that Thomson and Rasmussen developed a thermodynamic model which combines extended UNIQUAC model for electrolytes and the Soave-Redlich-Kwong cubic equation of state and applies it to aqueous systems containing ammonia and/or carbon dioxide along with various salts. Model parameters prove to be valid in the temperature range 0-110°C, the pressure range from 0-100 bar, and the concentration range up to approximately 80 molal ammonia. The model parameters were evaluated on the basis of more than 7000 experimental data points.

However, limited research efforts focus on the actual process and understand the mass transfer rate in both absorption and desorption. Table 1 summarizes lab scale research reported in the open literature for CO2 capture by aqueous ammonia solution.

Among all these studies, only one research work studied absorption and desorption in a continuous mode. It is generally agreed that during the absorption, ammonium bicarbonate is the one of major products, but there is still disagreement on the composition of other products such as carbonate, and carbonate. The understanding of reaction kinetics and mass transfer involved in the process is very limited and requires further research work. Doing so can improve our understanding of the process and facilitate the development of a model to accurately describe the process and help scale up the process.

Due to the potential benefits associated with the ammonia process, power industry has shown a strong interest. A number of pilot plants have been constructed and operated to test the technical and economical feasibility. Alstom and Powerspan are the major players. Alstom designed and constructed a chilled ammonia pilot plant that captures CO2 from a portion of coal fired boiler fuel gas at We Energies' Pleasant Prairies Plant, 1,210-megawatt coal fired generating station. The We Energies facility is designed to capture over 35 tonnes/day of CO2 at design rates. As described in the patent, CO2 is absorbed in highly ammoniated solution at low temperatures 0-10°C, producing slurry containing ammonia bicarbonate. In the stripper, ammonia bicarbonate is converted to ammonia carbonate at high temperatures above 100°C and pressure of 20-40 bar. Powerspan has been developing a CO2 capture process, called ECO2® and initiated a pilot test program with First Energy at the R.E. Burger Plant. A 1-MW pilot demonstration is scheduled to begin in 2008, which will produce approximately 20 tons of sequestration ready CO2 per day. The ECO2® process is similar to that of Alstom but the absorption takes place at relatively high temperature, above 20°C, and does not involve the precipitation in the absorber.

1.2 MUNMORAH PCC PILOT PLANT

CSIRO and Delta Electricity have jointly constructed a $7 million (AUD) research scale Post Combustion Capture (PCC) pilot plant at the Munmorah Power Station. The pilot plant is part of and supported by the Asia Pacific Partnership on Clean Development and Climate (APP). It is designed to capture up to 3,000 tonnes per annum of CO2 from the black coal fired power station using aqueous ammonia as the chemical absorbent.

The Aims of the pilot plant campaign include
- Determine the interdependent relationship between thermal energy use for solvent regeneration, solvent flow rate, feed gas conditions, process temperature and pressure.
- Optimize the overall process performance for the given power plant flue gas and standard ammonia solution.
- Determine the fate of acid components in the flue gas (SO\textsubscript{x} and NO\textsubscript{x}) including production of chemical byproducts.
- Identify opportunities for optimizing process performance and where possible demonstrate them in prolonged service.
- Formulate novel process options and where possible validate them in prolonged service.
- Explore the potential of using aqueous ammonia solution to simultaneously capture CO\textsubscript{2} and other acid components from coal fired power plants under Australian conditions.

To achieve aims of the pilot plant, a detailed experimental program has been developed and is divided into three stages.

Stage 1- Functionality and preliminary tests. In these tests, the functionality of all components of pilot plant is tested and interdependent relationship among different components to achieve desired operation conditions determined. Preliminary tests using flue gas and low concentration of ammonia will also be conducted to ensure that analytic facilities are appropriate and adequate and pilot plant performs as expected and to define and achieve steady state operations.

Stage 2- Operational tests. These tests will determine the interdependent relationship between thermal energy use for solvent regeneration, solvent flow rate, feed gas conditions, process temperature and pressure, ammonia loss and consumption of utilities. The fate of SO\textsubscript{x}/NO\textsubscript{x}, and other elements present in the flue gases will be also investigated in this stage.

Stage 3- Optimization tests. Based on information gathered from operational tests, we will establish the experimental conditions for a range of conditions which might be optimum, and validate the expected performances under these conditions. Novel processes will be developed and tested in either lab or pilot plant.

The pilot plant was operational in January 2009 and functionality and preliminary tests were completed recently in April. This paper presents and discusses results obtained in these tests.

2 EXPERIMENTAL

Figure 1 is the simplified schematic diagram of pilot plant. Briefly, the pilot plant consists of one pretreatment column, two absorbers with an additional wash column at the top, and one stripper. The pretreatment works as a direct contact cooler for flue gas and also serves as a scrubber for removal of SO\textsubscript{x} in the flue gas. The two absorbers provide flexibility in operation with different arrangements (single column or two columns in series or parallel). In wash column, water is used to removal ammonia which slips to the flue gas and the resultant wash liquid is sent to pretreatment column for scrubbing SO\textsubscript{x}. The rich solvent is regenerated in the stripper and rich CO\textsubscript{2} is released from the top of stripper.

Table 2 summarizes test conditions for some of pilot plant trials. A typical flue gas composition is listed in Table 3.

The pilot plant operation is composed of two stages. In the first stage (absorption only), the stripper is off and fresh ammonia is circulated between absorber and stripper, contacting flue gas in the absorber until pH of ammonia before and after the absorption equals, indicating that the solution is close to saturation or CO\textsubscript{2} mass transfer rate is very low. Then in the second stage (full mode), the steam from boiler is introduced to the reboiler and stripper bottom temperature increases to the set value. Gradually the pilot plant reaches a steady state under conditions studied. During the tests, the following parameters will be measured on-line:
Flue gas flow rate
- Liquid flow rate of solvent and various condensate streams
- CO₂ flow rate from the stripper
- Pressure at various locations
- Pressure drop across the columns
- Temperatures around all major equipment
- Concentrations of CO₂, NH₃, O₂, SO₂, NOₓ, H₂O at various locations.

Solvent samples are to be taken at various points and will be analysed off-line for:
- CO₂ content
- NH₃ content
- Speciation of rich and lean solvents.
- SOₓ, NOₓ-content and other trace elements, including particulate materials.

The Gasmet® analyser (FTIR) equipped with a ZrO₂ oxygen analyser allows online identification and quantification of gases species in the flue gas. Standard wet chemistry titration is performed for the determination of CO₂ and NH₃ content in the liquid samples. The speciation involves the use of C¹³ NMR and other techniques, which are currently tested in the lab.

3 RESULTS AND DISCUSSION

3.1 CO₂ REMOVAL EFFICIENCY FOR FRESH AMMONIA AND VALIDATION OF EXPERIMENTAL DATA FROM PILOT PLANT TRIALS.

It is important to ensure that the pilot plant functions appropriately and experimental data obtained are valid. To this end, pilot plant experimental data are compared to the estimation based on wetted wall column results [1]. The CO₂ absorption rate within the column can be calculated by the following equation.

\[ N_{CO₂} = K_o A (P_{CO₂} - P_{CO₂}^*) \]  

Where
- \( N_{CO₂} \), CO₂ absorption rate, mmol/s.
- \( K_o \), overall gas mass transfer coefficient, mmol/(s m² kPa).
- \( P_{CO₂} \), partial pressure of CO₂ in the flue gas, kPa
- \( P_{CO₂}^* \), CO₂ equilibrium partial pressure with respect to the solvent, kPa
- \( A \), effective interfacial surface area, m².

\( K_o \) values are obtained from the lab scale wetted wall experiments which are conducted under the similar reactions conditions (similar T, P, CO₂ loading and partial pressure of CO₂) to those for pilot plant operations. The separate investigation using MEA/CO₂ system has confirmed that \( K_o \) values obtained from the wetted wall experiments can be applied to pilot plant investigations, at least in our case. The process for CO₂ absorption in MEA solvent is well understood and chemical and physical properties of the system are available. Based on well established mass transfer model for CO₂/MEA [2], we developed a rate based model to calculate the overall mass transfer coefficient for CO₂/MEA system in the pilot plant. The model involves use of film theory model to describe mass transfer in the interface and enhancement factor to account for the effect of chemical reactions on the mass transfer. The excellent agreement was achieved between model calculation and wetted wall data (Results are not included for the purpose of brevity).

\( P_{CO₂} \) can be estimated by taking log mean of inlet and outlet CO₂ partial pressure in case that the variation of partial pressure cross the column is small. \( P_{CO₂}^* \) can be negligible for fresh ammonia or with ammonia solvent with a low CO₂ loading.
A, effective interfacial surface area, is estimated using Onda’s correlation \(^2\) and ca. 61% of packing surface is wet and available for mass transfer under conditions studied. Table 4 show the CO\(_2\) removal efficiencies estimated from wetted wall date.

CO\(_2\) removal efficiency obtained for fresh ammonia in the pilot plant is used for the purpose of comparison. In this case, the operation conditions are relatively well defined, in particular with regards to NH\(_3\) concentration in the solvent which can be determined more accurately than loaded solvents. The CO\(_2\) removal efficiency for the fresh ammonia is calculated as follows,

\[
\text{CO}_2 \text{ removal efficiency } \% = \frac{\text{Difference of } \text{CO}_2 \text{ mass flow rate at wash column outlet for saturated and fresh } \text{NH}_3 \text{ solutions}}{\text{CO}_2 \text{ mass flow rate at wash column outlet for saturated } \text{NH}_3 \text{ solution}} \times 100%\]

Figure 2 shows the variation of CO\(_2\) mass flowrate at the top of wash column and CO\(_2\) removal efficiency in Test 2. The saturated ammonia is used as reference to minimise the effect of system flashing on CO\(_2\) concentration at the outlet of absorption system. Since the total volume of solvent is 400 L and the solvent flowrate is 134, it is estimated that in the initial 3 minutes, flue gas contacts with fresh ammonia solution and CO\(_2\) removal efficiency calculated during this period are those for the fresh solution. As shown in Figure 2, the CO\(_2\) removal efficiency for the fresh 1.0% ammonia is 18-20.0%, which agrees well with estimation from wetted wall data. The good agreement was also achieved for the fresh ammonia of 1.4% in Test 1, suggesting that the pilot plant performs as expected and the results obtained are valid.

3.2 CO\(_2\) REMOVAL EFFICIENCY AT THE STEADY STATE

Figure 3 shows the variation of stripper bottom temperature, absorber inlet solvent temperature and NH\(_3\) vol% at the stripper gas outlet with time after approximately 1 h operation of reboiler (the introduction of steam to reboiler). These parameters remain relatively constant, suggesting that the pilot plant has reached the steady state.

As shown in Figure 3, the gas leaving the stripper contains predominately CO\(_2\) with the volume concentration of more than 99%. Other species in the gas include H\(_2\)O (0.5%), O\(_2\) (0.2%), NH\(_3\) (30 ppm), NO\(_x\) (30 ppm) and balance N\(_2\) (0.2-0.3 %).

The status of steady state operations were also confirmed by the constant flowrate of gaseous species at various locations including CO\(_2\) shown in Figure 4. The carbon balance of CO\(_2\) at the steady state remains close to 100% at the steady state. The CO\(_2\) removal efficiency in Test 2 and 3 were calculated and included in Table 4. The lower CO\(_2\) removal efficiency compared to that in case of fresh ammonia is due to the loss of ammonia with time and loading of CO\(_2\) in the lean solvent, confirmed by the liquid analysis (not included in this paper).

3.3 FATE OF OTHER SPECIES IN THE FLUE GAS AND AMMONIA LOSS

3.3.1 NH\(_3\) A relatively high concentration of ammonia is present in the flow gas during the start up period. At the steady state, as shown in Figure 5, more than 1000 ppm of NH\(_3\) is present in the flue gas leaving the absorber and it is estimated that 2 kg of ammonia will be lost to the caustic solution or return flue gas in a 5 h operation time, which is equivalent to loss of up to 10% of ammonia in the fresh solution. At the stripper gas outlet, ammonia concentration is relatively low (20-40 ppm). We suggest that the high NH\(_3\) concentration of ammonia in the flue gas is primarily due to volatile nature of ammonia and low CO\(_2\) loading and more free NH\(_3\) in the aqueous ammonia solvent. Increase CO\(_2\) absorption rate at low temperature is the key for minimisation of ammonia loss for the current configuration of pilot plant.

3.3.2 SO\(_2\) Figure 6 shows the change of SO\(_2\) concentration in the flue gas at various locations with time in Test 3. More than 95% of SO\(_2\) is removed in the pre-treatment. The similar results were observed in all
other tests conducted. It is believed that high SO₂ removal efficiency is ascribed to high solubility of SO₂ in water and availability of NH₃ in the wash circuit which is trapped in the wash column.

3.3.3 NOₓ
The NOₓ concentrations at various location in Test 3 (day 2) are presented in Figure 7. As can be seen, there is no appreciable effect on NOₓ removal which is also the case in all other tests conducted because NOₓ, in the flue gas comprises primarily NO which has a very low solubility in water.

3.3.4 H₂O
The flowrate of H₂O decreases significantly after the pretreatment and remain constant afterwards, as showed in Figure 8. In the pretreatment, flue gas temperature decrease markedly, resulting in water condensation, while in absorber and wash column, flue gas and liquid temperature remains relatively constant and condensation of water from flue gas is minimal.

3.3.5 O₂
As shown in Figure 9, the mass flowrate of O₂ decrease slightly after pre-treatment, which is possibly due to absorption of O₂ in the caustic solution. More O₂ was removed from flue gas in the absorber, which is consistent with the fact that solvent flowrate (134 L/min) is much higher than that of caustic solution (39 L/min) and it is expected that more O₂ is dissolved in the solvent. Interestingly, after wash column, O₂ mass flowrate increased, which may indicate the desorption of O₂ from the caustic solution in the wash column. The solubility of O₂ in water is actually very low, even lower than that of NO. So we expect that the O₂ flowrate at various locations should be constant. Further efforts (more experimental runs and investigation) will be required to understand behaviour of O₂.

3.4 CONCLUSION
The functionalist and preliminary tests at Munnorah pilot plant suggest that the pilot plant is functioning appropriately and steady state operation can be achieved under conditions studied. The comparison of pilot plant data and lab studies confirms the pilot plant performs as predicted. CO₂ removal efficiencies are low since low concentration of NH₃ is used in the test. The NH₃ process proves to be very effective for SO₂ removal in the pretreatment but not for NOₓ. Relatively high loss of ammonia is ascribed to its volatility and in particular low absorption of CO₂ in the solvent. Future work will symmetrically investigate the effect of NH₃ concentration, solvent flowrate, process T, P and packing on the process performance.

ACKNOWLEDGMENTS
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REFERENCES

Table 1 Summary of lab scale research reported in the open literature for CO\textsubscript{2} capture by aqueous ammonia solution.

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<tr>
<th>Investigator</th>
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<th>NH\textsubscript{3} concentration wt%</th>
<th>Absorber T °C</th>
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<th>Absorption products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yeh and Bai, 1999\textsuperscript{13}</td>
<td>Semi batch absorber</td>
<td>7-35%</td>
<td>10-40</td>
<td>Not applicable</td>
<td>1</td>
<td>Bicarbonate</td>
</tr>
<tr>
<td>Diao et al., 2004\textsuperscript{14}</td>
<td>Sieve tower</td>
<td>0.1-0.2%</td>
<td>25-55</td>
<td>Not applicable</td>
<td>1</td>
<td>Bicarbonate</td>
</tr>
<tr>
<td>Yeh et al., 2004\textsuperscript{15}</td>
<td>Semi batch absorber</td>
<td>7-14%</td>
<td>16-38</td>
<td>49-90</td>
<td>1</td>
<td>Bicarbonate Carbonate</td>
</tr>
<tr>
<td>Pesnik et al., 2005\textsuperscript{16}</td>
<td>Continuous flow system</td>
<td>10.5-21%</td>
<td>15-38</td>
<td>77-83</td>
<td>1</td>
<td>Bicarbonate Carbonate</td>
</tr>
<tr>
<td>Kim et al., 2008\textsuperscript{17}</td>
<td>Semi batch absorber</td>
<td>7-17%</td>
<td>10-80</td>
<td>Not applicable</td>
<td>1</td>
<td>Carbamate Carbonate Bicarbonate</td>
</tr>
</tbody>
</table>

Table 2 Experimental condition for three pilot plant trials

<table>
<thead>
<tr>
<th>Operation Mode</th>
<th>Test 1</th>
<th>Test 2</th>
<th>Test 3\textsuperscript{*}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue gas flowrate, kg/h</td>
<td>Absorption only</td>
<td>Full mode</td>
<td>Full mode</td>
</tr>
<tr>
<td>Flowrate of caustic solution, L/min</td>
<td>39</td>
<td>39</td>
<td>39</td>
</tr>
<tr>
<td>Flowrate of solvent, L/min</td>
<td>134</td>
<td>134</td>
<td>134</td>
</tr>
<tr>
<td>Initial NH\textsubscript{3} concentration, wt %</td>
<td>1.4</td>
<td>1.0</td>
<td>2.35</td>
</tr>
<tr>
<td>Treatment inlet gas temperature, °C</td>
<td>35-45</td>
<td>40-45</td>
<td>22-28</td>
</tr>
<tr>
<td>Absorber solvent inlet temperatures, °C</td>
<td>10</td>
<td>10-20\textsuperscript{*}</td>
<td>10-20\textsuperscript{*}</td>
</tr>
<tr>
<td>Stripper bottom temperature, °C</td>
<td>n.a.</td>
<td>130-136</td>
<td>130</td>
</tr>
<tr>
<td>Absorber and pretreatment inlet gas pressure, bar</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Stripper pressure, bar</td>
<td>3</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

\* In the initial stage where the reboiler is off, the temperature is 10\textdegree C, while at the steady state when reboiler is on, the temperature is 20\textdegree C.

\textsuperscript{*} In test 3, the pilot plants were tested in two consecutive days without change of solvent.
Table 3 A typical flue gas composition

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>11.4 vol%</td>
</tr>
<tr>
<td>O₂</td>
<td>7.4 vol%</td>
</tr>
<tr>
<td>H₂O</td>
<td>3.4 vol%</td>
</tr>
<tr>
<td>NO</td>
<td>231.2 ppm</td>
</tr>
<tr>
<td>NO₂</td>
<td>2.1 ppm</td>
</tr>
<tr>
<td>SO₂</td>
<td>251.1 ppm</td>
</tr>
<tr>
<td>N₂</td>
<td>77.7 vol%</td>
</tr>
</tbody>
</table>

Note: The flue gas is measured at between blower and pre-treatment column.

Table 4 CO₂ removal efficiencies estimated from wetted wall date and from experiments under different conditions (fresh ammonia and steady state).

<table>
<thead>
<tr>
<th>Ammonia concentration (fresh solution)</th>
<th>1.4 wt %</th>
<th>1.0 wt%</th>
<th>2.35 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estimation from wetted wall for fresh solution</td>
<td>21</td>
<td>17%</td>
<td>23%</td>
</tr>
<tr>
<td>Experimental date for fresh solution</td>
<td>20-25</td>
<td>18-20</td>
<td>n.a.</td>
</tr>
<tr>
<td>Experimental results for spent solution at steady state</td>
<td>n.a.</td>
<td>10-12</td>
<td>15-17 (day one)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>13-15 (day two)</td>
</tr>
</tbody>
</table>
Figure 1 Simplified schematic of Munmorah pilot plant with the configuration of two absorbers in parallel. Please note: only one absorber, absorber 1, is used in recent tests.

Figure 2 Variation of CO₂ mass flowrate at the top of wash column and CO₂ removal efficiency in Test 2.
Figure 3  Stripper bottom temperature, absorber inlet solvent temperature and CO\textsubscript{2} volume percentage at the stripper gas outlet vs time on stream in Test 3 (day 2).

Figure 4 CO\textsubscript{2} mass flowrate at various locations vs time on stream in Test 3 (day 2).
Figure 5 Ammonia concentrations at various locations vs time on stream in Test 3 (day 2).

Figure 6 SO₂ concentration at various locations vs time on stream in Test 3 (day 2).
Figure 7 NOx concentration at various locations vs time on stream in Test 3 (day 2).

Figure 8 H2O mass flowrates at various locations vs time in Test 3 (day 2).
Figure 9  O₂ mass flowrates at various locations vs time in Test 3 (day 2).
Hi Paul

We are happy to approve the attached paper for the 2009 Australia-China Symposium on Advanced Coal and Biomass Utilisation Technologies. The document is a good read and the results show promising signs for PCC technology.

However, in reviewing the paper we noticed several apparent typos and grammatical errors eg. Page 2 - para 4 third line refers to products then uses carbonate twice; p3 'sate operations', 'Stage 2 - Operational'-s. These testses will determine'. As such, it may be worthwhile to have the document proofread for grammar/spelling before it is distributed at the Symposium later this year.

Kind regards

Lindsey Tibbles
Asia-Pacific Partnership (APP) & Contract Management
International, Resources Development & Taxation Branch

Department of Resources, Energy and Tourism
Level 8, 10 Binara Street, Canberra City ACT 2600
Ph: +61-2-6213 7476
Email: lindsey.tibbles@ret.gov.au
ABN 46 252 861 927
AQUEOUS AMMONIA BASED POST COMBUSTION CAPTURE PILOT PLANT AT MUNMORAH: RESULTS OF PRELIMINARY TESTS

Hai Yu1,*, Scott Morgan1, Anthony Callen2, Aaron Cottrell1, James McGregor1, Peter Coombes2, Andrew Allport1, Thong Do1, Narendra Dave1, Rob Rowland1, Graeme Puxty1, Moetaz Attalla1, Paul Feron1

1CSIRO Energy Centre, 10 Murray Dwyer Circuit, Mayfield West Circuit, NSW 2304, Australia
2Delta Electricity, Scenic Drive, Doyalson, NSW 2262, Australia

*Corresponding author: hai.yu@csiro.au (Dr Hai Yu)

ABSTRACT
Aqueous ammonia based CO2 capture is a promising technology for reduction of CO2 emission from power station and research work in this area is reviewed briefly. CSIRO and Delta Electricity have jointly constructed a research scale Post Combustion Capture (PCC) pilot plant at the Munmorah Power Station. The pilot plant is designed to capture up to 3,000 tonnes CO2 per annum, using aqueous solution ammonia to capture CO2 in the flue gas.

Functionality and preliminary tests at Munmorah pilot plant suggest that the pilot plant is functioning appropriately and steady state operation can be achieved under conditions specified. The comparison of pilot plant data and lab studies confirms the pilot plant performs as predicted. The NH3 process proves to be very effective for SO2 removal but not for NOx. Relatively high ammonia loss is ascribed to its volatility and in particular low absorption of CO2 in the solvent.

KEY WORDS: Post combustion CO2 capture, aqueous ammonia, pilot plant trial

1 INTRODUCTION
Research efforts have been intensified worldwide to develop technologies which are technically and economically feasible for capturing CO2 emitted from coal fired power stations and thus to mitigate global warming. CO2 capture by chemical solvents is believed to be the most promising technologies if the urgent actions are required to reduce CO2 emission. The advantages of this technology include

○ An established technology and low technological risk. It has been widely adopted for CO2 separation in natural gas sweetening and ammonia production.
○ Effective for capture of CO2 with low partial pressure
○ Flexible in operation and can be retrofittable to the existing power stations

However, the currently used solvents suffer degradation in the oxidative environment and are not tolerant to many species in the flue gas such as SO2 and NOx. The processes using traditional amines require significant energy for regeneration and are economically unfavourable. The intense development efforts on novel solvents for improved performance and reduced energy consumption during regeneration, as well as process designs incorporating new contacting devices such as hybrid membrane-absorbent systems, solid adsorbents and high temperature regenerable sorbents, may lead to the use of more energy efficient post combustion capture systems.

1.1 OVERVIEW OF AQUEOUS AMMONIA BASED CO2 CAPTURE
Aqueous ammonia, as one of novel solvents for CO2 capture, has received increasing attention recently, due to the potential benefits:

○ Low cost of solvent
○ Higher CO2 removal capacities
○ Lower absorption heat and less regeneration energy
○ Less corrosive and damage to equipment
Possibility of capturing multicomponents (NOx, SO2, CO2) which is of particular interest to Australian power stations since flue gas desulphurisation (FGD) and selective catalytic reduction (SCR) of NOx are not implemented in Australia.

The biggest challenge facing aqueous ammonia process is that ammonia is very volatile, which requires a large amount of cooling water to recover NH3 which slips to the flue gas. To minimize ammonia loss, the absorption of NH3 needs to take place at low temperatures. Cooling of the flue gas and solvent and regeneration of NH3 from wash water requires significant energy. In addition, the absorption rate is low for NH3 at low temperatures, which means that a much bigger size of absorber is required. Research efforts are underway worldwide to explore the potential of ammonia based process as a viable solution for capture of CO2 and/or other pollutants in the flue gas emitted from power stations.

The chemistry involved in the CO2 capture by aqueous ammonia is relatively well understood, particular from a thermodynamic point of view (equilibrium product distribution including solid species under various conditions). It is worth noting that Thomson and Rasmussen developed a thermodynamic model which combines extended UNIQUAC model for electrolytes and the Soave-Redlich-Kwong cubic equation of state and applies it to aqueous systems containing ammonia and/or carbon dioxide along with various salts. Model parameters prove to be valid in the temperature range 0-110°C, the pressure range from 0-100 bar, and the concentration range up to approximately 80 molal ammonia. The model parameters were evaluated on the basis of more than 7000 experimental data points.

However, limited research efforts focus on the actual process and understand the mass transfer rate in both absorption and desorption. Table 1 summarizes lab scale research reported in the open literature for CO2 capture by aqueous ammonia solution.

Among all these studies, only one research work studied absorption and desorption in a continuous mode. It is generally agreed that during the absorption, ammonium bicarbonate is the one of major products, but there is still disagreement on the composition of other products such as carbonate, and carbonate. The understanding of reaction kinetics and mass transfer involved in the process is very limited and requires further research work. Doing so can improve our understanding of the process and facilitate the development of a model to accurately describe the process and help scale up the process.

Due to the potential benefits associated with the ammonia process, power industry has shown a strong interest. A number of pilot plants have been constructed and operated to test the technical and economical feasibility. Alstom and Powerspan are the major players. Alstom designed and constructed a chilled ammonia pilot plant that captures CO2 from a portion of coal fired boiler fuel gas at We Energies' Pleasant Prairies Plant, 1,210-megawatt coal fired generating station. The We Energies facility is designed to capture over 35 tonnes/day of CO2 at design rates. As described in the patent, CO2 is absorbed in highly ammoniated solution at low temperatures 0-10°C, producing slurry containing ammonia bicarbonate. In the stripper, ammonia bicarbonate is converted to ammonia carbonate at high temperatures above 100°C and pressure of 20-40 bar. Powerspan has been developing a CO2 capture process, called ECO2 and initiated a pilot test program with First Energy at the R.E. Burger Plant. A 1-MW pilot demonstration is scheduled to begin in 2008, which will produce approximately 20 tons of sequestration ready CO2 per day. The ECO2 process is similar to that of Alston but the absorption takes place at relatively high temperature, above 20°C, and does not involve the precipitation in the absorber.

1.2 MUNMORAH PCC PILOT PLANT

CSIRO and Delta Electricity have jointly constructed a $7 million (AUD) research scale Post Combustion Capture (PCC) pilot plant at the Munmorah Power Station. The pilot plant is part of and supported by the Asia Pacific Partnership on Clean Development and Climate (APP). It is designed to capture up to 3,000 tonnes per annum of CO2 from the black coal fired power station using aqueous ammonia as the chemical absorbent.

The Aims of the pilot plant campaign include
o Determine the interdependent relationship between thermal energy use for solvent regeneration, solvent flow rate, feed gas conditions, process temperature and pressure.

o Optimize the overall process performance for the given power plant flue gas and standard ammonia solution.

o Determine the fate of acid components in the flue gas (SO\textsubscript{x} and NO\textsubscript{x}) including production of chemical byproducts.

o Identify opportunities for optimizing process performance and where possible demonstrate them in prolonged service.

o Formulate novel process options and where possible validate them in prolonged service.

o Explore the potential of using aqueous ammonia solution to simultaneously capture CO\textsubscript{2} and other acid components from coal fired power plants under Australian conditions.

To achieve aims of the pilot plant, a detailed experimental program has been developed and is divided into three stages.

Stage 1- Functionality and preliminary tests. In these tests, the functionality of all components of pilot plant is tested and interdependent relationship among different components to achieve desired operation conditions determined. Preliminary tests using flue gas and low concentration of ammonia will also be conducted to ensure that analytic facilities are appropriate and adequate and pilot plant performs as expected and to define and achieve steady state operations.

Stage 2- Operational tests. These testes will determine the interdependent relationship between thermal energy use for solvent regeneration, solvent flow rate, feed gas conditions, process temperature and pressure, ammonia loss and consumption of utilities. The fate of SO\textsubscript{x}/NO\textsubscript{x} and other elements present in the flue gases will be also investigated in this stage.

Stage 3- Optimization tests. Based on information gathered from operational tests, we will establish the experimental conditions for a range of conditions which might be optimum, and validate the expected performances under these conditions. Novel processes will be developed and tested in either lab or pilot plant.

The pilot plant was operational in January 2009 and functionality and preliminary tests were completed recently in April. This paper presents and discusses results obtained in these tests.

2 EXPERIMENTAL

Figure 1 is the simplified schematic diagram of pilot plant. Briefly, the pilot plant consists of one pretreatment column, two absorbers with an additional wash column at the top, and one stripper. The pretreatment works as a direct contact cooler for flue gas and also server as a scrubber for removal of SO\textsubscript{2} in the flue gas. The two absorbers provide flexibility in operation with different arrangements (single column or two columns in series or parallel). In wash column, water is used to removal ammonia which slips to the flue gas and the resultant wash liquid is sent to pretreatment column for scrubbing SO\textsubscript{2}. The rich solvent is regenerated in the stripper and rich CO\textsubscript{2} is released from the top of stripper.

Table 2 summarizes test conditions for some of pilot plant trials. A typical flue gas composition is listed in Table 3.

The pilot plant operation is composed of two stages. In the first stage (absorption only), the stripper is off and fresh ammonia is circulated between absorber and stripper, contacting flue gas in the absorber until pH of ammonia before and after the absorption equals, indicating that the solution is close to saturation or CO\textsubscript{2} mass transfer rate is very low. Then in the second stage (full mode), the steam from boiler is introduced to the reboiler and stripper bottom temperature increases to the set value. Gradually the pilot plant reaches a steady state under conditions studied. During the tests, the following parameters will be measured on-line:
Flue gas flow rate
Liquid flow rate of solvent and various condensate streams
CO₂ flow rate from the stripper
Pressure at various locations
Pressure drop across the columns
Temperatures around all major equipment
Concentrations of CO₂, NH₃, O₂, SO₂, NOₓ, H₂O at various locations.

Solvent samples are to be taken at various points and will be analysed off-line for:

- CO₂ content
- NH₃ content
- Speciation of rich and lean solvents.
- SO₄, NO₃-content and other trace elements, including particulate materials.

The Gasmet® analyser (FTIR) equipped with a ZrO₂ oxygen analyser allows online identification and quantification of gases species in the flue gas. Standard wet chemistry titration is performed for the determination of CO₂ and NH₃ content in the liquid samples. The speciation involves the use of C¹³ NMR and other techniques, which are currently tested in the lab.

3 RESULTS AND DISCUSSION

3.1 CO₂ REMOVAL EFFICIENCY FOR FRESH AMMONIA AND VALIDATION OF EXPERIMENTAL DATA FROM PILOT PLANT TRIALS.

It is important to ensure that the pilot plant functions appropriately and experimental data obtained are valid. To this end, pilot plant experimental data are compared to the estimation based on wetted wall column results.

The CO₂ absorption rate within the column can be calculated by the following equation.

\[ N_{CO₂} = K_G A (P_{CO₂} - P_{CO₂}^*) \]  \( (1) \)

Where

\[ N_{CO₂}, \text{ CO₂ absorption rate, mmol/s.} \]
\[ K_G, \text{ overall gas mass transfer coefficient, mmol/(s m}^2 \text{ kPa).} \]
\[ P_{CO₂}, \text{ partial pressure of CO₂ in the flue gas, kPa.} \]
\[ P_{CO₂}^*, \text{ CO₂ equilibrium partial pressure with respect to the solvent, kPa.} \]
\[ A, \text{ effective interfacial surface area, m}^2. \]

\( K_G \) values are obtained from the lab scale wetted wall experiments which are conducted under the similar reactions conditions (similar T, P, CO₂ loading and partial pressure of CO₂) to those for pilot plant operations. The separate investigation using MEA/CO₂ system has confirmed that \( K_G \) values obtained from the wetted wall experiments can be applied to pilot plant investigations, at least in our case. The process for CO₂ absorption in MEA solvent is well understood and chemical and physical properties of the system are available. Based on well established mass transfer model for CO₂/MEA \(^{12}\), we developed a rate based model to calculate the overall mass transfer coefficient for CO₂/MEA system in the pilot plant. The model involves use of film theory model to describe mass transfer in the interface and enhancement factor to account for the effect of chemical reactions on the mass transfer. The excellent agreement was achieved between model calculation and wetted wall data (Results are not included for the purpose of brevity).

\( P_{CO₂} \) can be estimated by taking log mean of inlet and outlet CO₂ partial pressure in case that the variation of partial pressure cross the column is small. \( P_{CO₂}^* \) can be negligible for fresh ammonia or with ammonia solvent with a low CO₂ loading.

4
A, effective interfacial surface area, is estimated using Onda's correlation and ca. 61% of packing surface is wet and available for mass transfer under conditions studied. Table 4 show the CO₂ removal efficiencies estimated from wetted wall date.

CO₂ removal efficiency obtained for fresh ammonia in the pilot plant is used for the purpose of comparison. In this case, the operation conditions are relatively well defined, in particular with regards to NH₃ concentration in the solvent which can be determined more accurately than loaded solvents. The CO₂ removal efficiency for the fresh ammonia is calculated as follows,

\[
\text{CO}_2 \text{ removal efficiency %} = \frac{\text{Difference of CO}_2 \text{ mass flow rates at wash column outlet for saturated and fresh NH}_3 \text{ solution}}{\text{CO}_2 \text{ mass flow rate at wash column outlet for saturated NH}_3 \text{ solution}} \times 100\%
\]

Figure 2 shows the variation of CO₂ mass flowrate at the top of wash column and CO₂ removal efficiency in Test 2. The saturated ammonia is used as reference to minimise the effect of system flashing on CO₂ concentration at the outlet of absorption system. Since the total volume of solvent is 400 L and the solvent flowrate is 134, it is estimated that in the initial 3 minutes, flue gas contacts with fresh ammonia solution and CO₂ removal efficiency calculated during this period are those for the fresh solution. As shown in Figure 2, the CO₂ removal efficiency for the fresh 1.0% ammonia is 18-20.0%, which agrees well with estimation from wetted wall data. The good agreement was also achieved for the fresh ammonia of 1.4% in Test 1, suggesting that the pilot plant performs as expected and the results obtained are valid.

3.2 CO₂ REMOVAL EFFICIENCY AT THE STEADY STATE

Figure 3 shows the variation of stripper bottom temperature, absorber inlet solvent temperature and NH₃ vol% at the stripper gas outlet with time after approximately 1 h operation of reboiler (the introduction of steam to reboiler). These parameters remain relatively constant, suggesting that the pilot plant has reached the steady state.

As shown in Figure 3, the gas leaving the stripper contains predominately CO₂ with the volume concentration of more than 99%. Other species in the gas include H₂O (0.5%), O₂ (0.2%), NH₃ (30 ppm), NO₃ (30 ppm) and balance N₂ (0.2-0.3 %).

The status of steady state operations were also confirmed by the constant flowrate of gaseous species at various locations including CO₂ shown in Figure 4. The carbon balance of CO₂ at the steady state remains close to 100% at the steady state. The CO₂ removal efficiency in Test 2 and 3 were calculated and included in Table 4. The lower CO₂ removal efficiency compared to that in case of fresh ammonia is due to the loss of ammonia with time and loading of CO₂ in the lean solvent, confirmed by the liquid analysis (not included in this paper).

3.3 FATE OF OTHER SPECIES IN THE FLUE GAS AND AMMONIA LOSS

3.3.1 NH₃ A relatively high concentration of ammonia is present in the flue gas during the start up period. At the steady state, as shown in Figure 5, more than 1000 ppm of NH₃ is present in the flue gas leaving the absorber and it is estimated that 2 kg of ammonia will be lost to the caustic solution or return flue gas in a 5 h operation time, which is equivalent to loss of up to 10% of ammonia in the fresh solution. At the stripper gas outlet, ammonia concentration is relatively low (20-40 ppm). We suggest that the high NH₃ concentration of ammonia in the flue gas is primarily due to volatile nature of ammonia and low CO₂ loading and more free NH₃ in the aqueous ammonia solvent. Increase CO₂ absorption rate at low temperature is the key for minimisation of ammonia loss for the current configuration of pilot plant.

3.3.2 SO₂ Figure 6 shows the change of SO₂ concentration in the flue gas at various locations with time in Test 3. More than 95% of SO₂ is removed in the pre-treatment. The similar results were observed in all
other tests conducted. It is believed that high SO₂ removal efficiency is ascribed to high solubility of SO₂ in water and availability of NH₃ in the wash circuit which is trapped in the wash column.

3.3.3 NOₓ 

The NOₓ concentrations at various location in Test 3 (day 2) are presented in Figure 7. As can be seen, there is no appreciable effect on NOₓ removal which is also the case in all other tests conducted because NOₓ in the flue gas comprises primarily NO which has a very low solubility in water.

3.3.4 H₂O

The flowrate of H₂O decreases significantly after the pretreatment and remain constant afterwards, as showed in Figure 8. In the pretreatment, flue gas temperature decrease markedly, resulting in water condensation, while in absorber and wash column, flue gas and liquid temperature remains relatively constant and condensation of water from flue gas is minimal.

3.3.5 O₂

As shown in Figure 9, the mass flowrate of O₂ decrease slightly after pre-treatment, which is possibly due to absorption of O₂ in the caustic solution. More O₂ was removed from flue gas in the absorber, which is consistent with the fact that solvent flowrate (134 L/min) is much higher than that of caustic solution (39 L/min) and it is expected that more O₂ is dissolved in the solvent. Interestingly, after wash column, O₂ mass flowrate increased, which may indicate the desorption of O₂ from the caustic solution in the wash column. The solubility of O₂ in water is actually very low, even lower than that of NO. So we expect that the O₂ flowrate at various locations should be constant. Further efforts (more experimental runs and investigation) will be required to understand behaviour of O₂.

3.4 CONCLUSION

The functionalist and preliminary tests at Munmorah pilot plant suggest that the pilot plant is functioning appropriately and steady state operation can be achieved under conditions studied. The comparison of pilot plant data and lab studies confirms the pilot plant performs as predicted. CO₂ removal efficiencies are low since low concentration of NH₃ is used in the test. The NH₃ process proves to be very effective for SO₂ removal in the pretreatment but not for NOₓ. Relatively high loss of ammonia is ascribed to it volatility and in particular low absorption of CO₂ in the solvent. Future work will symmetrically investigate the effect of NH₃ concentration, solvent flowrate, process T, P and packing on the process performance.

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<td>Semi batch absorber</td>
<td>7-14%</td>
<td>16-38</td>
<td>49-90</td>
<td>1</td>
<td>Bicarbonate Carbonate</td>
</tr>
<tr>
<td>Pesnik et al., 2005₁⁶</td>
<td>Continuous flow system</td>
<td>10.5-21%</td>
<td>15-38</td>
<td>77-83</td>
<td>1</td>
<td>Bicarbonate Carbonate</td>
</tr>
<tr>
<td>Kim et al., 2008₁⁷</td>
<td>Semi batch absorber</td>
<td>7-17%</td>
<td>10-80</td>
<td>Not applicable</td>
<td>1</td>
<td>Carbamate Carbonate Bicarbonate</td>
</tr>
</tbody>
</table>

Table 2 Experimental condition for three pilot plant trials

<table>
<thead>
<tr>
<th>Operation Mode</th>
<th>Test 1</th>
<th>Test 2</th>
<th>Test 3*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue gas flowrate, kg/h</td>
<td>Absorption only</td>
<td>Full mode</td>
<td>Full mode</td>
</tr>
<tr>
<td>Flowrate of caustic solution, L/min</td>
<td>760</td>
<td>760</td>
<td>810</td>
</tr>
<tr>
<td>Flowrate of solvent, L/min</td>
<td>39</td>
<td>39</td>
<td>39</td>
</tr>
<tr>
<td>Initial NH₃ concentration, wt %</td>
<td>1.4</td>
<td>1.0</td>
<td>2.35</td>
</tr>
<tr>
<td>Pretreatment inlet gas temperature, °C</td>
<td>35-45</td>
<td>40-45</td>
<td>22-28</td>
</tr>
<tr>
<td>Absorber solvent inlet temperatures, °C</td>
<td>10</td>
<td>10-20⁺</td>
<td>10-20⁺</td>
</tr>
<tr>
<td>Stripper bottom temperature, °C</td>
<td>n.a.</td>
<td>130-136</td>
<td>130</td>
</tr>
<tr>
<td>Absorber and pretreatment inlet gas pressure, bar</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Stripper pressure, bar</td>
<td>3</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

*: In the initial stage where the reboiler is off, the temperature is 10°C, while at the steady state when reboiler is on, the temperature is 20°C.
⁺: In test 3, the pilot plants were tested in two consecutive days without change of solvent.
Table 3 A typical flue gas composition

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>11.4 vol%</td>
</tr>
<tr>
<td>O₂</td>
<td>7.4 vol%</td>
</tr>
<tr>
<td>H₂O</td>
<td>3.4 vol%</td>
</tr>
<tr>
<td>NO</td>
<td>231.2 ppm</td>
</tr>
<tr>
<td>NO₂</td>
<td>2.1 ppm</td>
</tr>
<tr>
<td>SO₂</td>
<td>251.1 ppm</td>
</tr>
<tr>
<td>N₂</td>
<td>77.7 vol%</td>
</tr>
</tbody>
</table>

Note: The flue gas is measured at between blower and pre-treatment column.

Table 4 CO₂ removal efficiencies estimated from wetted wall date and from experiments under different conditions (fresh ammonia and steady state).

<table>
<thead>
<tr>
<th></th>
<th>1.4 wt %</th>
<th>1.0 wt%</th>
<th>2.35 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estimation from wetted wall for fresh solution</td>
<td>21</td>
<td>17%</td>
<td>23%</td>
</tr>
<tr>
<td>Experimental date for fresh solution</td>
<td>20-25</td>
<td>18-20</td>
<td>n.a.</td>
</tr>
<tr>
<td>Experimental results for spent solution at steady state</td>
<td>n.a.</td>
<td>10-12</td>
<td>15-17 (day one)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>13-15 (day two)</td>
</tr>
</tbody>
</table>
Figure 1 Simplified schematic of Munmorah pilot plant with the configuration of two absorbers in parallel. Please note: only one absorber, absorber 1, is used in recent tests.

![Flue gas flow diagram](image)

Figure 2 Variation of CO₂ mass flowrate at the top of wash column and CO₂ removal efficiency in Test 2.
Figure 3  Stripper bottom temperature, absorber inlet solvent temperature and CO$_2$ volume percentage at the stripper gas outlet vs time on stream in Test 3 (day 2).

Figure 4 CO$_2$ mass flowrate at various locations vs time on stream in Test 3 (day 2).
Figure 5 Ammonia concentrations at various locations vs time on stream in Test 3 (day 2).

Figure 6 SO₂ concentration at various locations vs time on stream in Test 3 (day 2).
Figure 7  NO\textsubscript{x} concentration at various locations vs time on stream in Test 3 (day 2).

Figure 8  H\textsubscript{2}O mass flowrates at various locations vs time in Test 3 (day 2).
Figure 9  O$_2$ mass flowrates at various locations vs time in Test 3 (day 2).
No worries Paul,

It is much appreciated.

Kind regards
Lindsey Tibbles

-----Original Message-----
From: Paul.Feron@csiro.au [mailto:Paul.Feron@csiro.au]
Sent: Wednesday, 6 May 2009 11:20 AM
To: Tibbles, Lindsey
Cc: Woolcott, Stephen; Anjana.Narasimhan@csiro.au
Subject: RE: Approval request [SEC=UNCLASSIFIED]

Dear Lindsey,

Thanks for your comments. In my hastiness to clear my mailbox after coming back from leave I overlooked the fact that the paper actually did not go through the official CSIRO internal review procedure, who would have picked up the spelling mistakes. I apologise for this and will correct this. Should the required corrections be more than spelling mistakes and/or grammatical errors, I will submit a new version for your approval. Obviously you will get a corrected version anyway for your records.

Best regards,

Paul H.M. Feron
PCC Science Leader
CSIRO Energy Technology
10 Murray Dwyer Cct, Mayfield West
O. Box 330
Newcastle NSW 2300
Australia
Tel +61(0)2 4960 6022
Mob +61(0) 447688747

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