CO₂ CAPTURE PERFORMANCE OF MEA AND BLENDED AMINE SOLVENTS IN CSIRO’S PILOT PLANT WITH FLUE GAS FROM A BROWN COAL-FIRED POWER STATION

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ABSTRACT

Post-combustion Carbon Capture (PCC) is a key technology in a complete CO₂ capture and storage (CCS) chain. Reactive liquid absorption processes are currently the most advanced, both in commercial and technological terms. The area of improved solvents for CO₂ is a focal point in many R&D programmes, in addition to more efficient PCC process engineering and optimised process integration. CSIRO’s R&D programme in Australia is investigating all these areas and this paper discusses solvent testing results with real flue gases.

The performance of the solvents is determined by the inter-dependent relationships between the following three parameters:
1. CO₂ removal efficiency;
2. heat requirement for solvent regeneration; and
3. solvent loss as a result of evaporation/carry-over or solvent deterioration.

The trials were conducted in CSIRO’s transportable PCC Pilot Plant - hosted by Loy Yang Power, Australia - that has been capturing CO₂ from flue gas from the brown coal-fired power station since May 2008. After obtaining a base-line for the pilot plant using MEA, other promising amine blends have been tested in the plant during several campaigns. This paper describes the results to-date regarding the performance of the solvents in absolute terms and relative to the MEA base case.

The pilot plant results show that both MEA and blended amine solvent trials exhibit a good CO₂ balance (<10% deviation). Both systems indicate a similar trend of increasing ratio of the liquid flow rate over the gas flow rate (L/G) and successive increase in CO₂ removal. A remarkable reduction (4-34%) in heat-duty can be obtained by using blended amine solvents instead of a 30 wt-% of MEA solution. A minimum reboiler heat-duty versus L/G ratio is clearly observed for the MEA-baseline.

INTRODUCTION

Post-combustion Carbon Capture (PCC) is a key technology in a complete CO₂ capture and storage (CCS) chain. Amongst the technologies that can capture CO₂, reactive liquid absorption processes are the most advanced, both in commercial and technological terms. This paper summarizes the CSIRO programme on PCC on pilot plants [1] and focuses on results from comparison of several solvents trialled in the PCC pilot plant at Loy Yang Power.

The following pilot plants have been commissioned by CSIRO at three power plant locations in Australia and one was realised in Beijing supporting TPRI and Huaneng:
- Loy Yang Power focusing on application of amines for CO₂ capture in brown coal operations;
- Delta Electricity Munmorah power station focusing on the application of cooled ammonia for CO₂ capture in black coal operations;
- Tarong Energy power station focusing on application of amines for CO₂ capture in black coal operations (currently under commissioning; note: not in Figure 1).
- Huaneng Beijing Cogeneration Plant was supported by CSIRO through the provision of design documents, a hands-on training programme for the future Chinese operators and practical assistance during start-up. This pilot plant uses conventional amine technology on a flue gas from a black coal fired power station, which has FGD installed.

![Loy Yang Power – since ‘08](image1)
Brown coal-fired power station

![Munmorah – since ‘09](image2)
Black coal-fired power station

![Beijing – since ‘08](image3)
Supporting TPRI and Huaneng

Figure 1. Photographs of pilot plants in Loy Yang Power, Munmorah and Beijing (Huaneng).

**PCC on Brown Coal-fired Power Stations in Latrobe Valley (Australia)**

Lignite-fuelled power stations in Victoria (Australia) share 92% of Victoria’s total electricity generation market in 2009, which is reduced by 1% compared to the year of 2000. However, the absolute value of the power generated by lignite increased by 9% from 2000 (47 GWh) to 2009 (52 GWh) [2]. Loy Yang Power generates 2.2 GW and is one of the lignite-fuelled power stations situated in Latrobe Valley of Victoria, which generate in total 6.7 GW. It is also reported that lignite-fuelled power generation is the source of about half of Victoria’s current greenhouse gas emissions [3]. It is therefore clear CO₂-emission reduction strategies aimed at the existing power station are urgently needed to provide a path towards environmental sustainability of the Victorian brown coal industry. The use of CCS is essential for this path and PCC an important first part of the chain. The implementation of PCC in the Victorian case requires specific focus towards its technological development in regards of three following issues:

- Brown coal is not sold into a world market due to its high moisture content in contrast to black coal, oil or natural gas. Therefore, it is expected that brown coal prices will remain at low price levels thus continuing to provide the basis for low cost electricity for Victoria. The capture of CO₂ will result in a large increase in the cost of electricity generation, which needs to be addressed.
- 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.
- The combined process of coal mining, power generation and PCC should use less water than current power generation as ground water level retreats to an unsustainable situation.
For the Latrobe Valley Post-combustion Capture project CSIRO operates the pilot plant, based on amine technology, which is connected to flue gases from Victorian brown coal-fired power station at Loy Yang Power. This plant is the first of its kind in the Southern Hemisphere and has been capturing CO₂ since May 2008. The project aims to conduct research and pilot scale deployment of prospective technologies for the post-combustion capture of carbon dioxide (PCC) from the flue gases of brown coal-fired power stations. In direct support of this aim the objective of the PCC pilot plant trial program is to set a baseline based on 30 wt% MEA and benchmark other solvents against this baseline.

TECHNICAL SECTION

Description and Operation of PCC Pilot Plant at Loy Yang Power

The first CSIRO PCC pilot plant was designed to capture CO₂ from real flue gases and as such, it is currently fed with flue gas from unit 2 of the power station operated by Loy Yang Power. One particularly unique aspect of this pilot plant is its absorber columns which could be operated in series, in parallel or individually. It has an additional benefit of being easily transportable.

The PCC pilot plant has been designed to receive 150 kg/h real flue gas from the power plant. The plant consists of one flue gas pre-treatment unit, two absorber columns to capture the CO₂, a stripper column for solvent regeneration equipped with a plate reboiler for stripping off the CO₂ from the solvent and a 120 kW electric-boiler unit to generate steam for heating media in the stripper’s reboiler.

The absorber columns are made from 200DN stainless steel pipe (211 mm ID). Each column height is 9.4 m and each column consists of two 1.35 m packed bed sections, totalling to 5.4 m for the absorption section. The stripper column is 6.9 m high and made from 150DN stainless steel pipe (161 mm ID). The height of stripper packing is 3.9 m. Packing type used in all columns is Pall rings (0.5”). General characteristics of packing material are (i) packing size in every section is 160 mm, (ii) specific area of packing is 338 m²/m³ and (iii) packing factor (1/m) is 306. A 60 kW condenser (with 20% allowable to enhance the capacity) is also installed to condense water and amine vapour from the top vapour-product of the stripper column. The vapour and liquid is separated in flash drum before the liquid phase is returned to the solvent feed tank after prior mixing with hot lean solvent from stripper’s bottom product. The vapour phases, contains about 98 vol% CO₂, flows through a coriolis mass-flow meter and released to the atmosphere.

A concentration of 30 wt% mono-ethanolamine (MEA) is initially used for a baseline study. MEA is chosen because it is proven and well-documented worldwide. It is a common solvent for the capturing of CO₂ not only from natural gas and in refinery operations but also has been used for coal-fuelled power plants [4].

Figure 2 describes a simplified flow sheet of CSIRO PPC pilot plant at Loy Yang Power. The flue gas is pumped into a cooler and then passed to a knock-out drum where condensates and particulates are separated. Because none of the Victorian power stations are equipped with a flue gas desulphurisation unit (FGD), the flue gas impurities such as particulates, SOₓ and NOₓ can cause solvent deterioration [5]. Therefore, these components have to be removed by blowing the flue gas into a caustic scrubber (flue gas pre-treatment) before it enters the absorber where the flue gas counter-currently contacts with an amine based solvent at around 35-55°C and atmospheric pressure. In series operation mode, the treated-flue gas firstly enters absorber column 2 and is contacted with
CO₂-rich solvent from the bottom of absorber 1. The CO₂-less gas exits from the absorber 2 is then fed to the absorber 1 where it is contacted with the fresh lean solvent. Generally speaking, in these two absorber columns, CO₂, a weak acid, is absorbed into the aqueous MEA-solution and reacts exothermically with the MEA, a weak base. The exit flue gas from absorber 1 which contains less CO₂ is returned to the power plant’s stack.

The CO₂-rich MEA stream from the bottom of the absorber 2 and is pumped and preheated to 90-100 °C (depend on ΔT approach setting) in a cross-solvent heat exchanger, where exchanging the heat is occurring between the hot lean solvent from the stripper’s bottom product and the cold-rich solvent from the bottom of the absorber 2, before it enters the stripper column where the CO₂ is unfettered from the solvent (through endothermic reaction) by heating via reboiler (typically >110°C). The reboiler heat is obtained from steam latent heat (at a range steam pressures of 135-150 kPa). The hot lean solvent after exchanging the heat in the heat exchanger is recycled to the solvent feed tank after which it is mixed with the liquid phases/reflux as explained earlier.

In two further campaigns blended amines were trialled, Blended Amine 1 and 2, and compared to the MEA-baseline. Blended Amine 1 was developed to reducing the energy consumption when compared to MEA, while Blended Amine 2 was developed by RITE (Japan) and focussed on improving kinetics as well as reducing energy consumption.

In our baseline operation, we generally achieved adequate CO₂ balance throughout the operation. The CO₂ balance is fluctuating around ± 10% [6].

**Gas and Liquid Analysis**

The PCC pilot plant is well supported with instrumental analysers in order to analyse gas and liquid samples. The gas analysis is conducted on-site by using GASMET CEMS and the liquid analysis is by pH monitoring while samples are collected and sent for analysis elsewhere.
Flue gas from the pilot plant, treated flue gas such as lean gas (cleaned gas) from the absorbers column and product gases from stripper column are measured. In total, there are five GASMET installed throughout the plant as shown in Figure 2.

The GASMET CEMS system incorporates a Fourier Transform Infrared spectrometer, a temperature controlled sample cell, and signal processing electronics. The gas analyser is designed for continuous emission monitoring (CEM). Gas components that has been detected are H$_2$O, CO$_2$, CO, N$_2$O, NO, NO$_2$, SO$_2$, NH$_3$, HCl, CH$_4$, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_8$, C$_6$H$_{14}$, Formaldehyde, Acetaldehyde, Ethanol, Ethanol amine, HF and O$_2$.

Liquid/solvent analysis is carried out in order to determine total/free amine and CO$_2$ concentrations. Figure 2 also shows that four liquid sampling points which comprise of lean solvent entering the absorber 1, rich solvent from absorbers 1 and 2 and finally lean solvent as bottom product of the stripper column. Liquid samples are usually collected within a range of time, in which the absorption process shows constant temperature and CO$_2$ concentration values, before the trial is stopped.

**Experimental Program**

A series of trials with different solvents was carried out at the pilot plant until the end of 2009. The aim of the first campaign was to evaluate the performance of 30 wt% MEA to capture CO$_2$ from real flue gas in the pilot plant under nominal conditions and to achieve adequate CO$_2$ balance. This campaign will be referred to as the baseline.

In the second campaign MEA was used blended with a different primary amine with a lower binding energy with CO$_2$ than MEA. This blended solvent was named Blended Amine 1. In the third campaign a novel proprietary amine blend was trialed; so-called ‘Blended Amine 2’, which has been developed by RITE (Japan). The two blended amines were examined in the pilot plant aiming at similar percentage of CO$_2$ recovery as compared to the baseline case with 30 wt% MEA. This paper focuses on comparison between MEA baseline and these two different blended amines in the domain of CO$_2$ recovery efficiency and heat duty (MJ/kg CO$_2$) required for solvent regeneration.

**Table 1. Process conditions and typical gas composition of the pilot plant trial using 30 wt% MEA solution**

<table>
<thead>
<tr>
<th>Process Parameters</th>
<th>Process conditions</th>
<th>Process conditions</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>MEA baseline</td>
<td>MEA at 112 °C</td>
</tr>
<tr>
<td>Solvent flow rate (m$^3$/h)</td>
<td>0.24 – 0.42</td>
<td></td>
</tr>
<tr>
<td>Flue gas flow rate (m$^3$/h)</td>
<td>100 – 140</td>
<td></td>
</tr>
<tr>
<td>Solvent Temp. to Absorber (°C)</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Bottom Stripper temperature (°C)</td>
<td>115</td>
<td>112</td>
</tr>
<tr>
<td>Lean solvent loading (mol CO$_2$/mol MEA)</td>
<td>0.19 ± 0.01</td>
<td>0.24 ± 0.02</td>
</tr>
<tr>
<td>Composition (wt %volume)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>20 - 23</td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>10 - 11</td>
<td></td>
</tr>
<tr>
<td>O$_2$</td>
<td>4.5 – 5</td>
<td></td>
</tr>
<tr>
<td>Impurities (wt ppm volume)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO$_2$</td>
<td>120-200</td>
<td></td>
</tr>
<tr>
<td>NO$_x$ (~99% NO, balance NO$_2$ and N$_2$O)</td>
<td>150-250</td>
<td></td>
</tr>
</tbody>
</table>
Evaluation of Data

Calculation method to determine CO$_2$ recovery

The pilot plant data sets can be employed in three different ways to determine CO$_2$ recovery as follows:

1. By using GASMET data, we can calculate the mass of CO$_2$ going into the absorber 2 and going out from the absorber 1. The CO$_2$ recovery (removed CO$_2$) is then calculated according equation 1

$$
100 \times \frac{CO_2^{\text{after pretreatment (to ABS column 2) \ − CO_2^{\text{in treated fluegas}}}}}{CO_2^{\text{after pretreatment (to ABS column 2)}}}
$$

(1)

2. By using GASMET data and gas product flow measurement, we calculate the mass of CO$_2$ produced from the stripper. After correcting for the water content in the gas stream the CO$_2$-recovery (produced CO$_2$) is determined according equation 2.

$$
100 \times \frac{CO_2^{\text{produced from stripper}}}{CO_2^{\text{after pretreatment (to ABS column 2)}}}
$$

(2)

3. From the solvent analysis and solvent flow rate data, we can calculate CO$_2$ absorbed in the two absorber columns and also determine the CO$_2$ produced from the stripper via the difference between the rich solvent entering the stripper column and lean solvent leaving the stripper column. This is similar to equation 1, where the mass flow of CO$_2$ in the solvent from the absorber is substracted from the mass flow of CO$_2$ in the solvent going into Absorber column 1.

For most of the pilot plant data sets, these three methods gave similar values within the limit of error. The final value of CO$_2$ recovery is the average of three values. At points when the CO$_2$ mass flow from the top of stripper column was fluctuating too much, the average value of numbers 1 and 3 was used.

Calculation method to determine heat duty correction

Heat duty, so-called reboiler heat duty, in this paper is presented as corrected basis by ignoring the heat loss. The heat duty after ignoring heat loss can be written as follow:

$$
Q_{\text{reboiler}} = Q_{\text{condenser}} + Q_{\text{solventheat}} + Q_{\text{desorption}}
$$

(3)

where,

$$
Q_{\text{condenser}} = m_{\text{cooling water}} \times C_p^{\text{water}} \times \Delta T
$$

(4)

$m_{\text{cooling water}}$ = mass flow of cooling water (kg/h)

$C_p^{\text{water}}$ = specific heat of cooling water (kJ/kg K)

$\Delta T$ = $T$ cooling water at outlet condenser − $T$ cooling water at inlet Condenser (K)
\[ Q_{\text{solvent heat}} = m_{\text{solvent}} \times C_{p_{\text{solvent}}} \times \Delta T \]  \hspace{1cm} \text{(5)}

- \[ m_{\text{solvent}} = \text{mass flow of solvent (kg/h)} \]
- \[ C_{p_{\text{solvent}}} = \text{specific heat of solvent (kJ/kg K)} \]
- \[ \Delta T = \text{T of solvent at bottom stripper – T of solvent at inlet stripper (K)} \]

\[ Q_{\text{desorption}} = m_{\text{CO}_2} \times \Delta H_{\text{desorption}} \]  \hspace{1cm} \text{(6)}

- \[ m_{\text{CO}_2} = \text{mass flow of CO}_2 \text{ product from the stripper column (kg/h)} \]
- \[ \Delta H_{\text{desorption}} = \text{Heat of desorption (kJ/kg)} \]

**RESULTS**

Initially, we carried out trials with 30 wt% MEA to set a baseline at 115 °C. The baseline is set by altering L/G, where L/G is the ratio of the liquid flow rate and the flue gas flow rate standardized to normalised conditions (0 °C and 1 atm) at a certain bottom temperature of the stripper column, while measuring CO\textsubscript{2} recovery and heat duty. Another reference line for 30 wt-% MEA was set at a bottom temperature of 112 °C, because we learnt that solvent blends operate optimal at lower boiler temperatures, in contrast to MEA, due to the lower binding energy of the CO\textsubscript{2} with the blended solvents, as shown further in this paper.

Figure 3 shows the effect of a variation of the L/G ratio on the CO\textsubscript{2} recovery at two different stripper bottom temperatures. With an increase in the L/G value the CO\textsubscript{2}-recovery is increased as more solvent is available for the flue gas to capture CO\textsubscript{2}. Figure 3, furthermore, confirms that increasing the lean loading by lowering stripper’s bottom temperature, leads to a reduction of the CO\textsubscript{2} recovery.

![Figure 3. Effect of L/G on CO\textsubscript{2} recovery at two different stripper’s bottom temperatures for 30 wt% MEA.](image-url)
Results for the heat duty for solvent regeneration as a function of L/G are shown in Figure 4, again at the two stripper bottom temperatures. These results have been corrected for heat losses from the stripper. At a stripper bottom temperature of 115 °C there appeared to be a minimum in the heat duty. Such a minimum could not be discerned for a stripper bottom temperature of 112 °C. However, the heat duty for the stripper bottom temperature of 112 °C was lower than that of 115 °C, except for L/G around 3.2 that the heat duty of 112 °C was slightly lower than that of 115 °C. This is probably due to the lean solvent loading for both temperatures were similar. The heat duty of MEA-baseline at 115 °C reduced as L/G increased until reaching a minimum at L/G between 3.2 and 3.5. Further increase in L/G resulted in a gradual increase of the heat duty. This was also observed on lab-scale and discussed by Cifre et al. [7].

![Figure 4](image)

**Figure 4.** Effect of L/G on heat duty at different stripper’s bottom temperatures for MEA baseline conditions of 115 °C and a variation of 112 °C (corrected for heat losses to the environment)

**Solvent Comparison**

Typical flue gas compositions from the power station during the operation of the blended amines campaigns was within the range of flue gas composition used for MEA baseline. For Blended Amine 1, a lean solvent loading of 0.19±0.02 mol CO₂/mol amine was obtained at stripper’s bottom temperature of 112 °C, which is similar to MEA baseline operated at temperature of 115 °C. However, Blended Amine 2 at similar stripper’s bottom temperature produced much lower lean solvent loading, 0.05±0.01 mol CO₂/mol amine.

As expected, the performance of the different solvents indicates that CO₂ recovery increases as liquid to gas ratio increases. This is due to the larger amount of circulated liquid in the absorber columns which in turn increases the driving force for absorption, thereby increasing the CO₂-removal per unit of time.
It is also shown that the recovery of CO$_2$ for the baseline MEA 30 wt% and Blended Amine 2 are similar, while they are both significantly higher than that of the Blended Amine 1. This suggests that Blended Amine 1 exhibits a lower absorption rate for CO$_2$ from the gas phase compared to the other solvents.

The heat duty for the blended amines was lower compared to MEA-baseline which is expected. This finding (with a different blending system) is also reported by previous workers [8, 9].

**Figure 5.** CO$_2$ recovery as a function of L/G for different solvents operated at a stripper bottom temperature of 112 °C for the blended amines and 115 °C for the MEA baseline.

In Figure 6 the heat duty of the blended amines relative to the MEA baseline has been depicted as a function of the CO$_2$ recovery. It shows that at a CO$_2$ recovery of 85%, the relative heat duty required for the solvent regeneration of Blended Amine 1 and 2 is dropped by 4% and 14% respectively. This is probably due to the lower heat of desorption of the blended solvents than that of MEA, ca. 85 kJ/mol of CO$_2$. Another possibility is MEA requires the largest energy to evaporate water (because MEA has the lowest CO$_2$ partial pressure compare to those of blended solvents) in order to create driving force to strip-off CO$_2$ than the blended amine solvents.
In case the CO$_2$ recovery is reduced to 70%, the heat duty of Blended Amine 1 and 2 is further decreased by 21% and 34% respectively (note: the heat duty of Blended Amine 1 at CO$_2$ recovery of 65% is used in comparison because the heat duty's value at 70% CO$_2$ recovery is not available). This significant reduction is due to the heat duty in the MEA-baseline at low L/G (L/G = 2.3) being much higher compared to the heat duty of the MEA baseline at L/G = 4.1. Hence, this reduction for comparison of the blended solvents with the MEA baseline is also much larger. It is possible that the heat required for water vaporization and L/G have important influence for this significant reduction, which will be addressed in detail in a following paper.

**CONCLUSION**

CSIRO’s transportable PCC pilot plant is fed with flue gas from a brown coal-fired power station of Loy Yang Power in the Latrobe Valley, Victoria, Australia, since May 2008. Several campaigns have been carried out for setting a comprehensive baseline based on MEA. Further campaigns dealt with comparing blended amines to MEA regarding CO$_2$ recovery and heat duty. The pilot plant results show that both MEA and blended amine solvent trials exhibit a good CO$_2$ balance (<10% deviation). Both systems indicate a similar trend of increasing L/G ratio and successive improvements in CO$_2$ removal. A remarkable reduction in heat-duty can be obtained by using blended amine solvents instead of MEA alone (4-34%). A minimum reboiler heat-duty versus L/G ratio is observed for the MEA baseline and this phenomenon will be discussed in further papers regarding the blended amines.
ACKNOWLEDGEMENTS

The authors wish to acknowledge the team from RITE for their very valuable and constructive cooperation during campaign 4 – ‘Blended Amine 2’, which solvent has been developed by RITE within the COCS project supported by Ministry of Economy, Trade and Industry in Japan. Also Loy Yang Power is gratefully acknowledged for hosting CSIRO’s PCC pilot plant and valuable discussions. CSIRO’s contribution in the LVPCl project was carried out within CSIRO’s Coal Technology Portfolio on Post-Combustion Capture and it is supported by the Victorian State Government through the Energy Technology Innovation Subsidy (ETIS) and Loy Yang Power Management Pty Ltd.

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