Concentrated Piperazine based Post-Combustion-Capture for Australian coal-fired power plants

Summary Report

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Contents

Figures

Tables

1 Summary

This project was designed to evaluate the use of concentrated piperazine (PZ) for post-combustion capture of CO_2 (PCC) in black-coal fired power stations in Australia. Concentrated PZ is an alternative to the standard MEA-based processes and based on extensive laboratory based research has shown attractive attributes such that they have the potential to reduce the costs of capture and compression of CO_2 by more than 50%, according to the University of Texas. Their laboratory research has shown that:

- The PZ solvent is more reactive than the standard, that should lead to a reduction in absorber sizes and hence capital cost.
- The PZ solvent is robust enough to allow regeneration at high temperature resulting in the release of CO_2 at high pressure, thus reducing compression costs.
- The thermal energy for solvent regeneration is less than for MEA.
- The solvent vapour pressure is lower than that of MEA resulting in lower solvent losses.

CSIRO have assessed this solvent on a pilot scale with real flue gases at the Tarong PCC pilot plant in Queensland. The PCC pilot plant, owned by Stanwell, has been designed, built and is operated by CSIRO. It is CSIRO's third pilot plant in Australia and has benefited from its predecessor designs in New South Wales and Victoria by taking the learnings of these pilot plant operations into account.

A program of risk and safety assessments, plant modifications, experimental activities and desktop studies have been completed, assessing the anticipated benefits of the concentrated PZ process culminating in techno-economic comparison between the concentrated PZ process and the standard MEA process.

2   Introduction

2.1 Post-combustion capture in Australia

Post-combustion capture of CO_2 (PCC) is an important part of a technology chain to reduce emissions from existing and new coal fired power stations, which also involves the subsequent storage of the product CO_2 underground. As the capture step is the most expensive step, there is a considerable interest in reducing the costs of this part of the chain. The most advanced technology for PCC uses a liquid absorbent to extract the CO_2 from the flue gas of a power station. The commonly used liquid absorbent is a 30% (7 molal) aqueous solution of monoethanolamine (MEA). CSIRO has developed baseline costs for this process utilising commercially available software tools for the power plant and PCC process plant [(Dave et al 2011a, Dave et al 2011b).]. An overview of these costs is given in table 1(Feron and Hooper 2009).

Table 1: Typical efficiencies, costs of generation and avoided CO_2-emission costs under Australian conditions (Feron and Hooper 2009).

Generation efficiency without PCC	35 – 41 %	Efficiency range determined by type of steam cycle and type of cooling
Generation efficiency with PCC	25 – 29 %	
Capital costs without PCC	2300-3000 $/kW$_e$	Cost range determined by type of steam cycle and type of cooling
Capital costs with PCC	4900-5900 $/kW$_e$	
Cost of generation without PCC	21 - 66 $/MWh	Lower costs refer to fully amortised power plant; higher costs to new-built power plant
Cost of generation with PCC	75 - 129 $/MWh	
Avoided CO_2 emissions cost	68 - 92 $/ton	

From Table 1 it can be seen that the implementation of PCC with 90% capture of the CO_2-emissions from a coal fired power plant resulted in an increase of the cost of generation of 55 – 63 $/MWh and avoided emissions costs of 68 – 92 $/ton CO_2. The higher costs of generation are only to a small extent due to the decreased power generation efficiency (typically 30 % equivalent to 10-12 %-points decrease). Table 1 clearly shows that the capital costs will double with the implementation of PCC and this constitutes the main component in the increased costs of generation. The detailed analysis of the cost contributions has

demonstrated that more than half of the capital costs are related to the equipment in the flue gas path, in particular the CO_2 absorber (Dave et al 2011a, Dave et al 2011b).

2.2 Piperazine for PCC applications

Alternative liquid absorbents are being developed to reduce the costs of PCC. A promising alternative to a 7 molal MEA solution is a concentrated (8 molal) solution of piperazine (PZ) under development in the group led by Prof. Gary Rochelle at the University of Texas in Austin. PZ is a secondary amine and a diamine, i.e. with two amine groups in the same molecule. The overall reactions between CO_2 and PZ in an aqueous solution are more complex than those for MEA (Conway et al 2013). However the theoretical maximum loading of 1 mol CO2 per mol amine for PZ is twice that of MEA. In table 1 some key properties are shown for MEA and PZ.

Table 2: Properties of mono-ethanolamine and piperazine

	Monoethanolamine	Piperazine
Formula	C_2H_7NO	$C_4H_{10}N_2$
Structure		
Molecular mass	61.08 g/mol	86.14 g/mol
Melting point	10.3 ^{o}C	106 ^{o}C
Boiling point	170 ^{o}C	146 ^{o}C
Cost	~$2/kg	~$6/kg
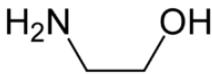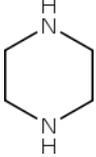
The studies by the University of Texas have indicated that the solvent possesses the following benefits under laboratory conditions (Freeman et al 2009, Freeman et al 2010, Rochelle et al 2011):

> ➢ It has an absorption rate which is twice as fast as MEA with the potential to halve absorber columns sizes,
> ➢ It has nearly a double absorption capacity for CO_2 compared to MEA with the potential to reduce the liquid absorbent regeneration energy requirement by 15-20%

- It is thermally stable at 150 $^{\circ}$C, allowing for absorbent regeneration at high pressure thereby reducing the energy requirement for CO_2-compression,
- It exhibits much lower oxidative degradation than MEA at a given temperature.

Overall, the combined impact of these benefits means that the PZ solution has the potential to reduce the cost of capture by more than 50% compared to the state-of-the-art MEA baseline solvent. This is due to the following synergetic contributions:

- A smaller absorber column and therefore reduced equipment costs,
- The possibility of using a simpler regeneration system and therefore an equipment cost reduction compared to a conventional stripper system based on a packed column,
- A lower thermal energy requirement for regeneration of the liquid absorbent,
- Reduced electricity consumption for compression,
- Reduced investment costs for the compressor as the first compression stage is not required.

These anticipated benefits have never been demonstrated in a real plant operating on flue gases from coal fired power stations. Therefore the effect of flue gas components such as NO_x and SO_2 in addition to trace elements present on the performance of the PZ-based process is unknown. This also entails the formation of degradation products from operation with PZ in real flue gases, particularly as recently concerns have been raised regarding the formation of harmful products from the PCC processes (Shao and Stangeland 2009, Jackson and Attalla 2011).

The attractive properties of PZ as a solvent for CO_2 capture have been known for some time. It is used as an absorption rate promoter in commercially available solvent blends used in natural gas treating (BASF aMDEA). However, solubility issues have meant that its concentration typically has to be restricted to concentrations less than 2 molal (10 wt%). As can be seen in Figure 1 (DOW chemical company, 2001), concentrated 40 wt% (8 molal) PZ is only in solution at temperatures above 40°C.

Concentrated (40 wt%) PZ has evolved as an alternative process from ten years of bench-scale and modelling effort on amine scrubbing by the University of Texas (UT) in Austin. Initial work focused on the use of PZ in concert with potassium carbonate (Chen, Rochelle, Seibert, 2006). Further work has revealed that, in reality, the volatility of 40 wt% PZ is less than that of 30 wt% MEA, despite the lower boiling point of PZ (Table 1). As can be seen in Figure 2 (Freeman et al. 2010), when a concentrated piperazine solution is loaded with CO_2, the operating temperatures required to form a solution without precipitates are reduced. However, it should be noted that operation is restricted to a narrow band of CO_2 loadings. At low CO_2 loadings, piperazine hydrate (Pz.6H_2O(s)) is noted to precipitate from solution. In addition, at high CO_2 loadings, protonated piperazine carbamate (H^+PZCOO^-.H_2O(s)) is thought to precipitate out of solution. Thus at typical operating temperatures (e.g. 40 - 150°C) CO_2 loadings should be maintained between 0.1 – 0.4 mol CO_2 / mol alkalinity (for an 8 molal solution). When temperatures drop below 40°C, CO_2 loadings

need to be restricted to a narrower range to avoid precipitation issues (0.32 – 0.37 mol CO_2 / mol alkalinity for an 8 molal solution).
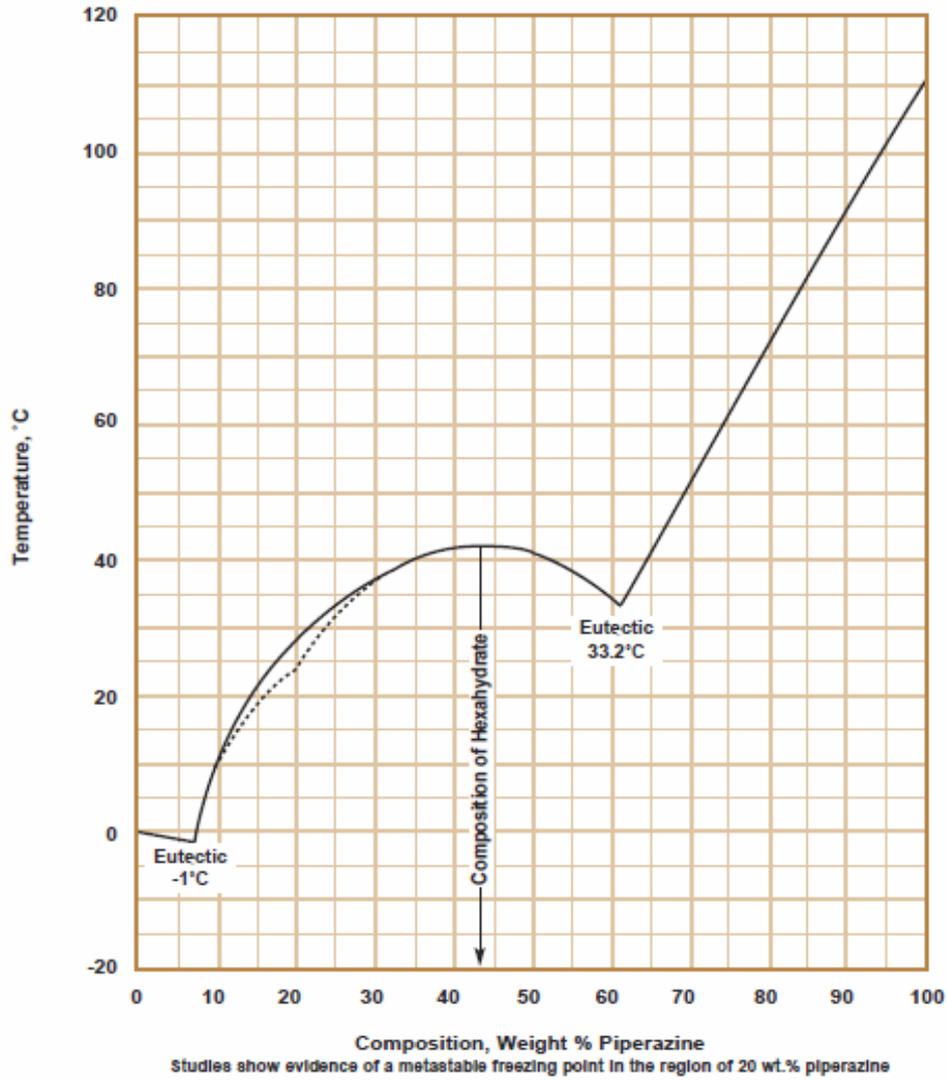
Figure 1: Piperazine aqueous solutions, freezing point vs. composition (Diagram taken from Ethyleneamines overview, DOW chemical company 2001)
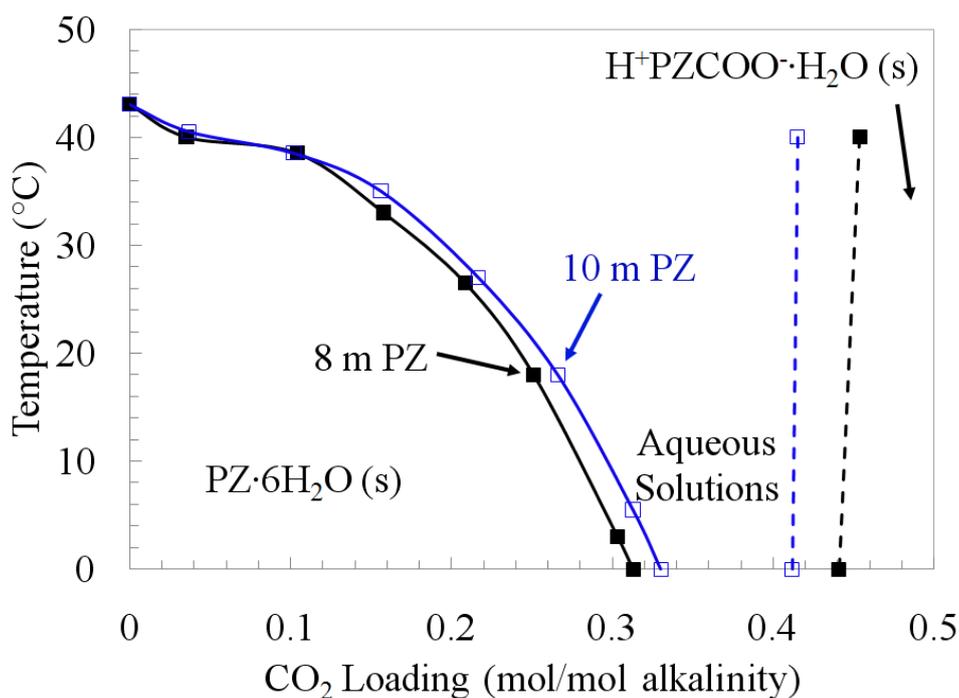
Figure 2: Solid-liquid transition temperature for aqueous piperazine (Diagram taken from Freeman et al. 2010)

Continued research by the UT has furthermore indicated that the concentrated PZ process will have significantly better energy performance than MEA because it has larger CO_2 capacity and faster absorption rates. Further, PZ does not have an alcohol group that could promote thermal degradation; hence it can be regenerated at higher temperature/pressure than MEA. This also enables the reduction of the CO_2 compression costs.

Understanding solvent stability and robustness is an important feature to understand when scaling up a PCC process. Solvent degradation can increase plant operating costs through solvent make-up costs and reduced capture capacity (Freeman et al. 2010). Being a secondary amine, piperazine (PZ) will form a stable nitrosamine. These are of concern as many nitrosamines are anticipated to be carcinogenic (Shao and Stangeland 2009). Currently, modelling predictions suggest that the level of nitrosamine emission from CO_2 capture facilities will be low. However, the majority of this work has been completed for the commonly used monoethanolamine (MEA) process. MEA is a primary amine, and as such does not form a stable nitrosamine. Nitrosamines will still form in the MEA process however through reaction with contaminants and solvent degradation products. Currently the authors know of no publicly available predictions or emissions data relating to the formation and emission of nitrosamines from CO_2 capture plant running on concentrated PZ. Thus monitoring nitrosamine formation is of interest at the Tarong pilot plant during operation with concentrated piperazine.

2.3 Project goal

The overall project objective was to evaluate the performance of the concentrated piperazine based process for post-combustion CO_2 capture in Australian coal fired power stations. This evaluation has considered the following aspects:

- o The energy requirement for liquid absorbent regeneration,
- o The CO_2-absorption rates,
- o The stability of the piperazine solvent and formation of degradation products from prolonged operation of the process
- o The impact on the power generation efficiency and costs of a typical Australian coal fired power station equipped with piperazine based technology
- o The potential use of emission reduction technologies for harmful compounds.

The project intended to progress the development of a PCC process that can potentially significantly reduce operating and capital costs by up to 50%. Furthermore it was considered that the project would provide valuable information for the scale up and operation of this process.

2.4 Project scope and link to report content

The scope of work consisted of the following activities:

1.   Preparation for pilot plant experiments with concentrated piperazine
2.   Modification of the Tarong PCC pilot plant
3.   Commissioning of the modified PCC pilot plant at Tarong Power Station with concentrated PZ

The results from these three activities are described in Chapter 3.

4.   Parametric variation of process operating conditions

The results from the parametric pilot plant operation are summarised in Chapter 4.

5.   Duration experiments at preferred conditions
6.   Methodologies for reduction of harmful emissions

The results from these activities are given in Chapter 5

7.   Overall process evaluation

The results of the techno-economic assessment are given in Chapter 6.

3 Operation of the pilot facility with concentrated Piperazine

3.1 Description of the Tarong Pilot Plant

The Tarong pilot plant treats a slip stream of flue gas from Unit 3 at Tarong Power Station, capturing CO_2 at a rate of ~100 kg/hr (roughly 1000 tpa). The pilot plant consists of three main columns, shown in their standard configuration in Figure 3. The first column is a pre-treatment column. Here the hot flue gases (~100-110°C and 1 atm) are scrubbed with a dilute caustic wash, cooling the flue gases (to ~ 45°C) and reducing the SOx/NOx and particulate matter content. The cooled flue gases then pass through the blower, raising their temperature slightly before entering the absorber column. In the absorber the flue gasses are contacted with the absorption solvent (in this case aqueous piperazine of concentrations up to 8 molal) in order to capture the CO_2. The CO_2 lean flue gas passes into a water wash section at the top of the absorber column to remove any traces of solvent carried over in the gas stream. The CO_2 laden solvent enters the stripping column for regeneration and separation of the CO_2. Hot gases leaving the stripping section enter the condenser section at the top of the column. Lean solvent leaving the bottom of the stripping column is cooled and recycled to the absorption column.

Lean and rich solvent samples are collected just prior to and after the absorber column respectively. Gas measurements are recorded either side of the pre-treatment column, prior to and after the absorber wash column, and in the gas stream exiting the stripping column condenser section. The gas composition is determined by Fourier Transform Infra-Red Spectroscopy (FT-IR) with an accuracy of 2% of the measurement range for each species. Solvent CO_2 loadings and piperazine concentration are determined offline by acid-base titration. Detailed descriptions of the Tarong pilot plant have been provided previously (Cousins et al. 2011).
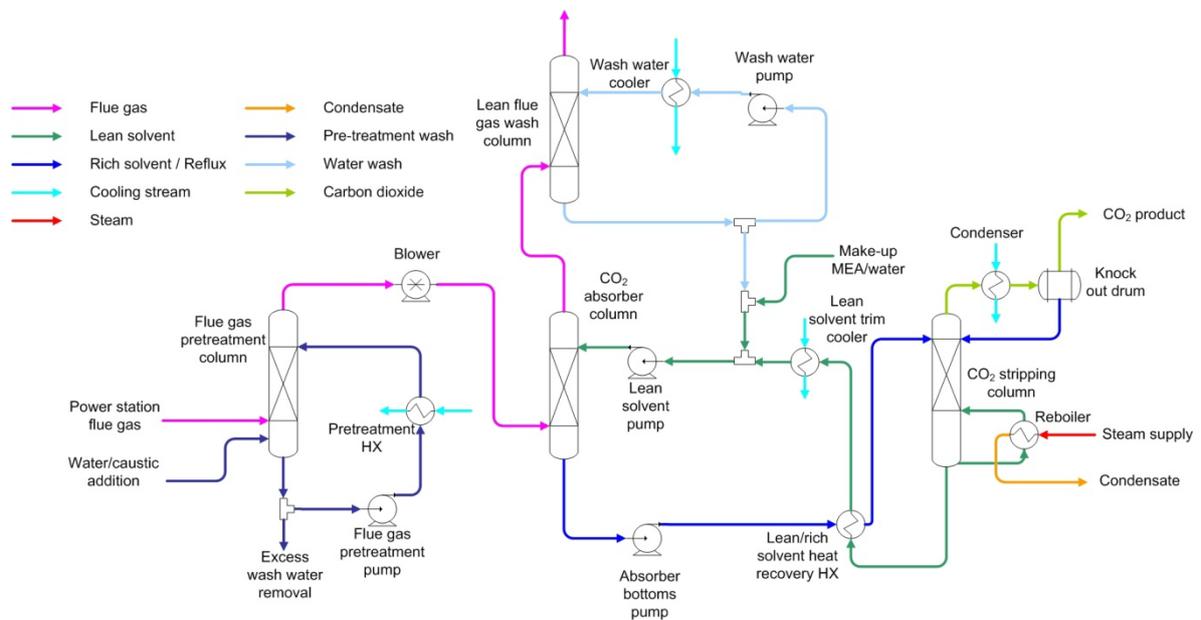
Figure 3: Process Flow Diagram of the Tarong CO$_2$ capture pilot plant

The Tarong PCC pilot plant has been designed specifically for use with amine based absorbents but also enables the evaluation of a range of process modifications (Cousins et al 2010). It is therefore ideally suited for a trial with alternative solvents, such as PZ, allowing the options such as intercooling to be evaluated experimentally. Initial pilot plant experiments with concentrated piperazine were carried out prior to this project. The results from these experiments led to the following modifications to facilitate a fuller investigation of the solvent performance:

➢ Replacement of column packing materials aiming to provide better mass transfer performance with the more viscous piperazine based solvent

➢ Replacement of gasket materials to allow safe operation with piperazine at higher temperatures

➢ Installation of heat exchanger to improve the absorber intercooling needed for the higher capacity liquid absorbent.

➢ Installation of a larger lean-rich heat exchanger to accomodate the lower heat transfer coefficients of the more viscous piperazine based solvent

The introduction of each new solvent brings a series of engineering and safety checks to ensure that the plant is able to operate with the new solvent. For piperazine we found that a new collection of HSE guidelines and procedures for the operation of the plant were necessary. These were mostly concerned with the safety aspects of using piperazine and handling its degradation. The review of the Health, Safety and Environmental procedures was undertaken in conjunction with Stanwell staff. As a result of this review the pilot plant Environmental Management Plan (EMP), Emergency Response Plan (ERP), and Risk Management Assessment (RMA) were updated for the new solvent. This highlighted that a number of plant operating procedures either needed to be created or modified as well as informing the Queensland

Government Department of Environment and Resource Management of this new solvent on site and the expected emissions as a result of its use.

Due to the physical and chemical characteristics of PZ some engineering modifications were required for the plant to be effectively and safely operated. For practical purposes in terms of restarting the pilot plant in the case of a precipitation event the pilot plant was progressively fitted with heat tracing on key solvent lines. These modifications were performed with other maintenance items.

3.2   Defining preferred operational conditions for Tarong PCC pilot plant

One of the key characteristic in terms of operation for 8 molal concentrated piperazine is its change in solubility with a change in loading, solvent concentration and temperature. For normal operating conditions the solvent generally sees temperatures in excess of 40°C giving an operating window with respect to CO_2 loading between 0.16 to 0.43 mol/mol of alkalinity. Some allowances need to be made for fluctuations in solvent concentration due to changes in the water balance and CO_2 loadings so it is important not to go too close to the solubility limits of the solvent.

While it is possible to operate at the conditions stated above, due to the nature of the loading curve and the impact resulting from e.g. an unscheduled plant shutdown there is potential for the solvent composition to drift into the precipitation zone as the solvent cools which can cause a major disruption to the operation due to the blocking of solvent lines and pumps. Therefore it is important to position the operating window with this in mind while also accounting for the ambient conditions.

Therefore the preferred operating CO_2 loading conditions is 0.26 to 0.42 mol CO_2/mol of alkalinity during periods when the plant is manned as the operators can act rapidly to overcome any operational issues. At Tarong power station ambient conditions can reach very close to 0°C particularly during the winter period an operating window of 0.32 - 0.41 mol CO_2/mol alkalinity was adopted during periods when the plant is unmanned and the plant will shutdown to a status that is easy to recover from.

The operational areas for the solvent are shown in Figure 4. The red box shows the afterhours operation window, the blue box shows the staffed operating window and the green area shows the technically possible operating window.
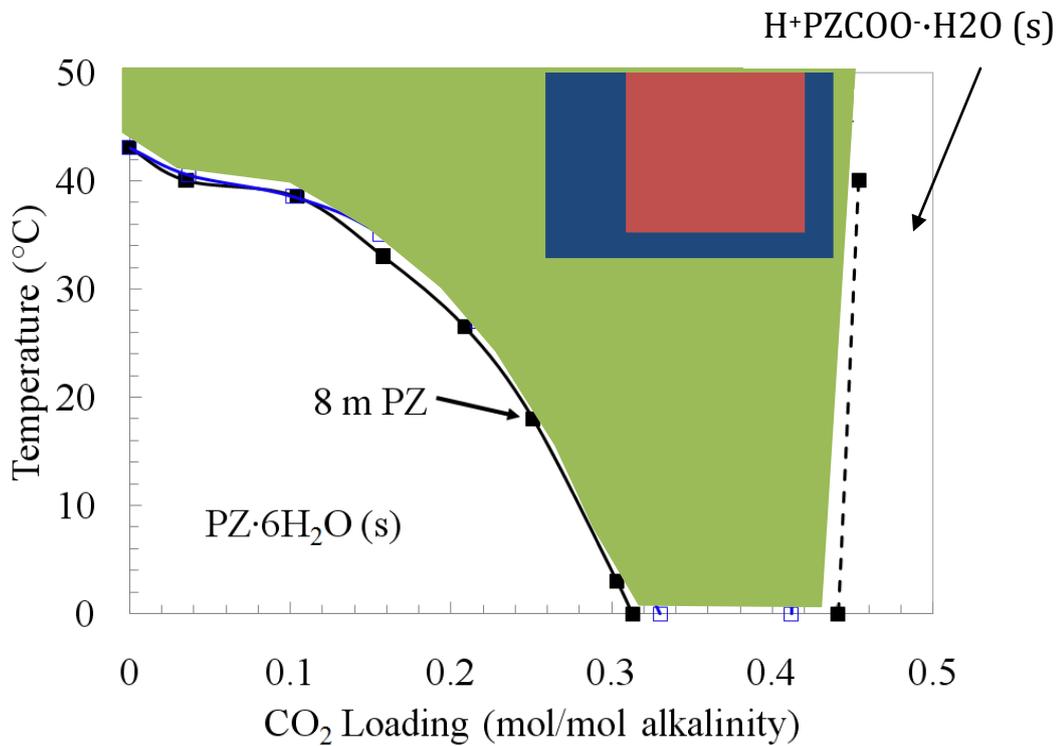
16

Figure 4: Operating zones for 8m concentrated piperazine

The operators have gained an excellent awareness of the solubility characteristics of the solvent through systematic experiential learning particularly during the early phases of the project. This has enabled the team to successfully operate the pilot plant for extended periods without precipitation events resulting in unscheduled shut-downs. An important aspect for successful piperazine operation is the additional investment into heat tracing of pipes which can be activated in the event of an unexpected shutdown. This will limit the detrimental impact from the formation of precipitates and facilitate the restart of the plant.

3.3   Solvent preparation for new system or as make-up

Piperazine is available commercially as a solid flake or as 68% solution. In either case the solvent has a solid component at ambient conditions and therefore requires additional preparation before it can be added to the plant. In our operations we have shown that we can most effectively handle piperazine by preparing solid piperazine flake into a 10 wt% solution for easy handling and avoidance of precipitation down to temperatures of 10°C (as shown in Figure 1). The drawback of having the solvent prepared at 10 wt% is that there excess water in the solvent in the pilot plant.

To overcome this the pilot plant was operated in such a way as to allow for the excess of water to leave the the pilot plant as water vapour in the lean flue gas compared by appropriately controlling the upstream and downstream absorber temperatures. Using this method we were able to effectively achieve and maintain the desired composition. Whilst it was also possible to remove water from the system using the condensate

collected in the knock out drum on the stripping column overhead, this was not used due to concern that nitrosamines could potentially condense and collect in this fluid.

When additional PZ is required as make-up solvent it was added incrementally to ensure solution temperature/concentration/CO_2 loading did not change significantly, thus avoiding precipitation issues.

3.4 Verification of volatile piperazine measurement

Due to the safety concerns and experimental requirements of using piperazine it was important to verify that our Gasmet gas analyser was able to detect trace levels of piperazine in and around the pilot plant. To verify that the Gasmet was an effective tool for measuring volatile piperazine a sample probe was removed from the pilot plant and exposed to a heated (40°C) 28 wt% piperazine solution prepared in the laboratory. With this test we showed that the Gasmet was able to detect volatile piperazine above this solution. It should be noted that the Gasmet gas analyser is only considered reliable to 5 ppm PZ concentration. This level was considered to be satisfactory from a safety and environmental point of view, bearing in mind that all gases from the pilot plant are pumped back into the power plant flue gas duct and hence heavily diluted.

Initial measurements in the pilot plant have shown levels of PZ to be at <5 ppm (1 ppm measured) at the top of the absorber before the water wash which corresponds with the expectations of lower vapour pressures of the solvent that have been measured in the laboratory. During the previous MEA campaigns typical emissions of MEA at the top of the absorber section of the pilot plant were in the range 50-150 ppm and these were typically reduced to <10ppm at the exit of the water wash.

3.5 Nitrosamine sampling and testing

Another important safety and experimental aspect of the piperazine based process is the monitoring of the formation of nitrosamines in the solvent over operational time. Being a secondary amine, the reaction of piperazine with nitrites (NO_2^-) in the solvent is of concern. Nitrites can enter the solvent from a number of sources, including trace NO_2 dissolved from the flue gas. As a result, weekly samples of solvent were collected into Ultra Violet (UV) protected sample jars and sent to CSIRO laboratories in Newcastle as well as the University of Texas for analysis. Samples sent to the University of Texas were analysed by High Pressure Liquid Chromatography (HPLC) and those sent to CSIRO were measured using a group extraction method. The extraction method is approximately 30% efficient for N-Nitrosopiperazine, thus the raw data is increased by a factor of 3 to provide the approximate concentration in the solvent samples. The method has been developed as a quick way to determine an indicative concentration for total nitrosamine content (Azzi et al. 2011)

4 Parametric Evaluation

4.1 Experimental Methodology

There are a number of different strategies available to the plant operator when running a CO_2 capture facility. Changing plant parameters will affect resource requirements including: cooling water flow rates, pumping requirement, and steam usage (energy input). For a CO_2 capture facility, around 2/3 of the energy requirement is that used to regenerate the solvent. Thus it is important to determine the operating conditions which minimise this energy consumption.

In order to better understand the PZ based process and to identify optimal operating conditions the PCC pilot plant was operated at various setpoints, referred to as a parametric evaluation. This involved variation of plant parameters:

- liquid flow rate (L/G ratio)
- regenerator pressure and temperature, and
- use of absorber inter-cooling.

The aim was to determine the impact of these operating conditions on regeneration energy and capture performance of the pilot plant with this solvent.

4.2 Results

For CO_2 capture efficiencies of 82 ± 5%, regeneration energies of 2.9 – 3.6 MJ/kgCO_2 were determined from the experimental results for 8 molal PZ at a regeneration pressure of 155 ± 2 ^{o}C. Regeneration energy decreased with a decrease in solvent flow rate (L/G ratio). The regeneration energy determined for the Tarong pilot plant when operating on 30 wt% MEA was in the range 3.4.- 4.5 MJ/kgCO_2. Despite the scatter in the data, concentrated PZ was noted to have consistently lower regener tion energy requirements than the standard 30 wt% MEA, by around 15%.
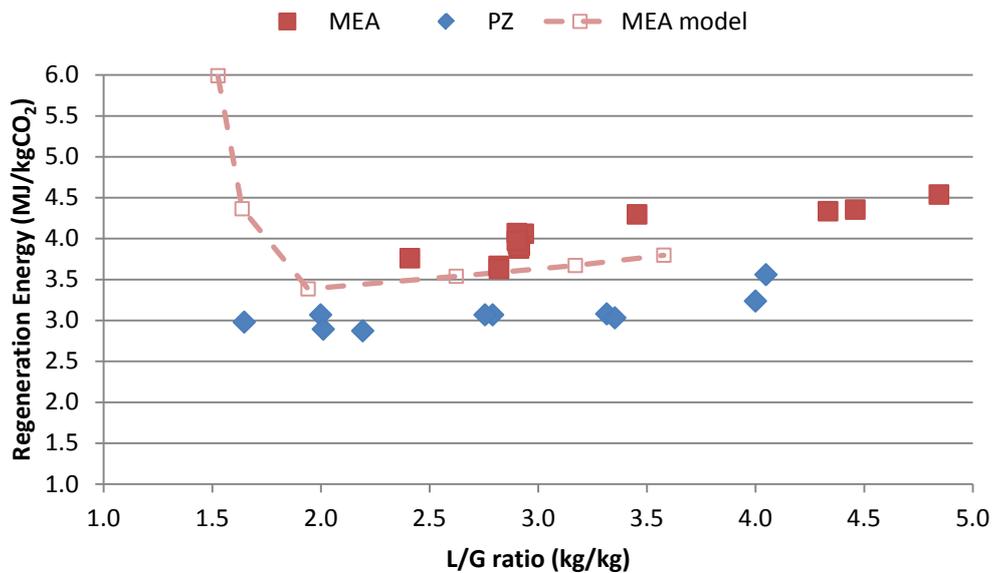
Figure 5: Effect of L/G ratio on regeneration energy for runs completed with 30wt% MEA and 8m PZ

Operation with inter-cooling on the absorber was also achieved as part of the parametric evaluation. A standard 'in and out' inter-cooling method was used, achieving inter-cooling temperatures of 30-35 °C. A reduction in regeneration energy requirements was achieved, with the effect being more pronounced at higher solvent flow rates (high L/G ratio). The use of inter-cooling allowed for a slight reduction in regeneration energy of around 0.2GJ/t CO_2 captured and as this was not fully optimised in terms of both the position in the column and solvent loadings we believe that there was likely to be more to benefit from inter-cooling.

Inter-cooling was noted to decrease regeneration energy requirements between 5-10 % depending on the solvent flow rate used and was able to maintain these regeneration energies across a wider range of solvent flow rates. Regeneration energies when operating with inter-cooling were calculated to be 2.8 – 2.9 MJ/kgCO_2 for solvent flow rates of 15 – 30 L/min (L/G 1.6-3.5). Inter-cooling was noted to increase the carrying capacity of the solvent, particularly when operating with higher solvent flow rates.

5   Duration experiments

5.1 Experimental methodology

For the duration tests one operating set-point was maintained for an extended period of time. Two duration tests were conducted that differed only in the regeneration temperature used (125 or 155 ^{o}C). The parametric studies with the solvent in the Tarong CO_2 capture pilot plant finished on 4/12/2012 after 856 hours of operation on the solvent. For the duration experiments flue gas flow rate (600 kg/hr) and lean solvent flow rate (20 L/min) were held constant. Subsequently 425 hours of operation were achieved on the solvent with a regeneration temperature of 125 ^{o}C. This was followed by a further 421 hours of operation with a regeneration temperature of 155 ^{o}C, giving a total operating time on the solvent of 1702 h by the end of the project.

Despite the formation of degradation products with operation at the Tarong pilot plant, regeneration energy requirements were not notably effected, despite the noticeable changes in the solvent's appearance as show in Figure 5. For operation times up to 1700 h on a real coal flue gas, no loss of plant performance was observed.
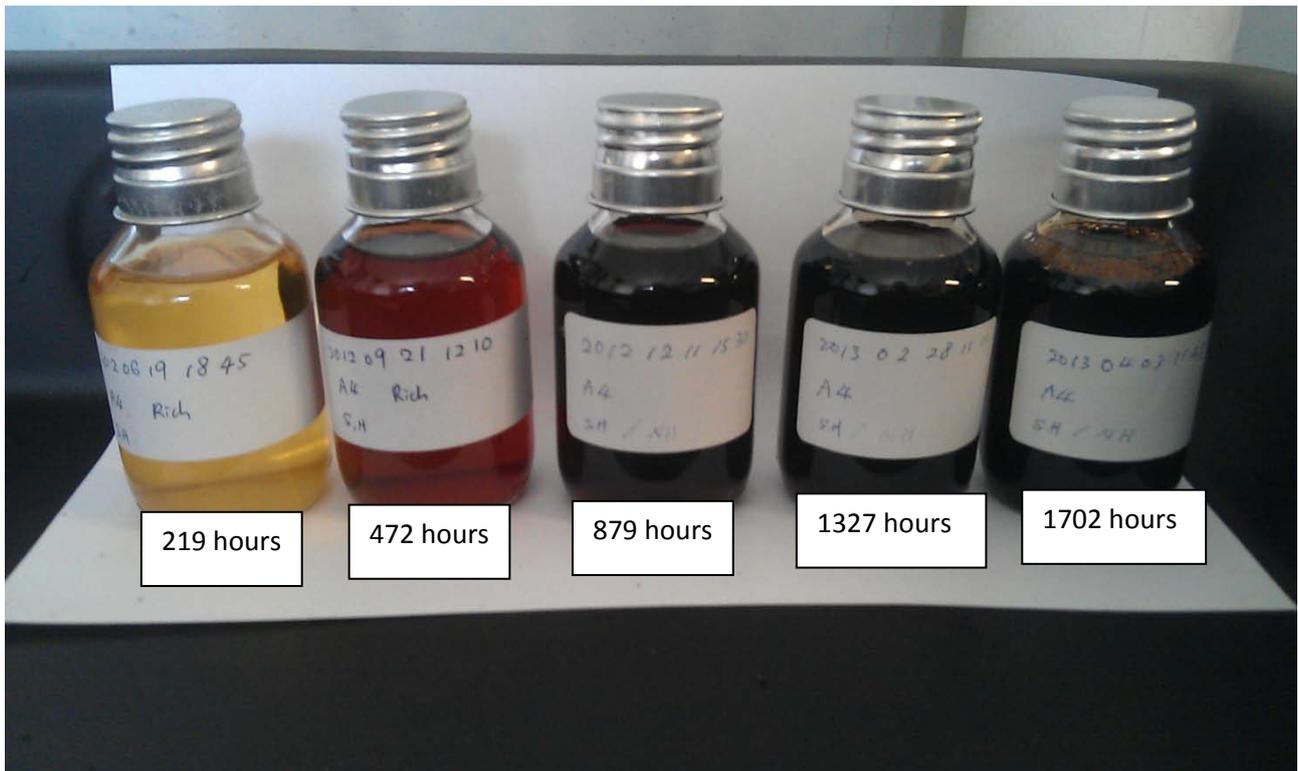
| 219 hours | 472 hours | 879 hours | 1327 hours | 1702 hours |

Figure 6: Visual appearance of the piperazine solvent at various stages of the duration experiment

5.2 Pilot plant emissions

Gas samples are analysed at various locations around the Tarong pilot plant by Fourier Transform Infra-red Spectroscopy. The Gasmet system has an accuracy of 2% of the measurement range for each species. As such, concentrations < 5 ppmV tend to be below the limit of quantification. Figure 5 contains results for NH_3, PZ, NO and NO_2 measured in the CO_2 lean flue gas exiting the absorber wash during the duration operation. The NO is unaffected by the change in plant operating conditions. NO_2 appears similarly unaffected, however its concentration is below the level of quantification. There is a spike in PZ concentration at the start of the 125 ^{o}C operation. This is thought to be caused by re-start of the plant after an unexpected shut-down. During re-start, the inlet flue gas flow rate spiked to 670 kg/hr. It is suggested that this spike in flow carried some solvent from the absorber, causing the spike in PZ concentration seen leaving the absorber wash. For the remainder of the operation, very little PZ is measured leaving the absorber wash section in the CO_2 lean gas. This shows the effectiveness of the water wash for removing PZ from the CO_2 lean flue gas, despite the wash water containing a small concentration of PZ (Figure 3).

The NH_3 concentration is seen to increase with operating time, with a spike in concentration after operating conditions were changed to 155 ^{o}C. At 125 ^{o}C regeneration temperature the ammonia concentration steadily increase from 12 to 17 ppm; At 155 ^{o}C regeneration temperature the ammonia concentration steadily increase from 22 to 31 ppm.The rate of increase of NH_3 concentration in the CO_2 lean flue gas

seems to approximately double from 125 °C, to 155 °C. NH_3 is a product of the oxidative degradation of the solvent. As a comparison, the Niederaussem pilot plant measured NH_3 concentrations in the range 26.9-46.6 mg/Nm^3 (39 – 67 ppm) in their CO_2 lean flue gas when operating with MEA (Moser et al 2011a). At the Niederaussem pilot plant, fresh water is added to the wash water, which will enhance the absorber wash stage. No make-up water was added to the absorber wash stage at the Tarong pilot plant.
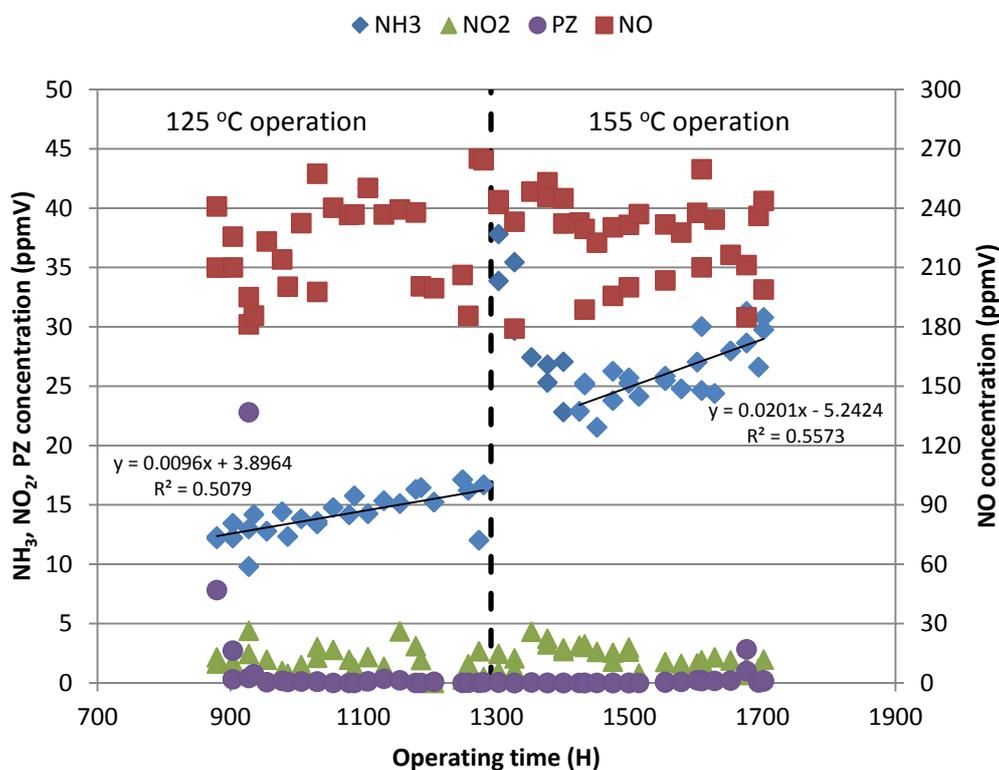

Figure 7: Concentration of NH_3, NO_2, PZ and NO in measured in CO_2 lean flue gas exiting absorber wash section

5.3 Formation of Heat Stable Salts

Solvent, absorber wash water and stripping column condensate samples were collected weekly in amber sample bottles at the pilot plant and sent to CSIRO Energy Centre in Newcastle and to the University of Texas in Austin for analysis. Solvent samples sent to the University of Texas were analysed for some key HSS's (formate, acetate and oxalate), N-formyl-PZ (FPZ), sulphates, and nitrates, by anion IC. These results are provided in Figures 6 and 7. Results from the University of Texas showed that the Heat Stable Salt (HSS) in highest concentration was formate, with the rate of formation increasing with regeneration temperature (0.05 mmol/kg/hr at 125°C and 0.167 mmol/kg/hr at 155°C). The effect of pre-treatment could be seen with sulphate concentration in the solvent increasing sharply when caustic supply to the pre-treatment column was interrupted.
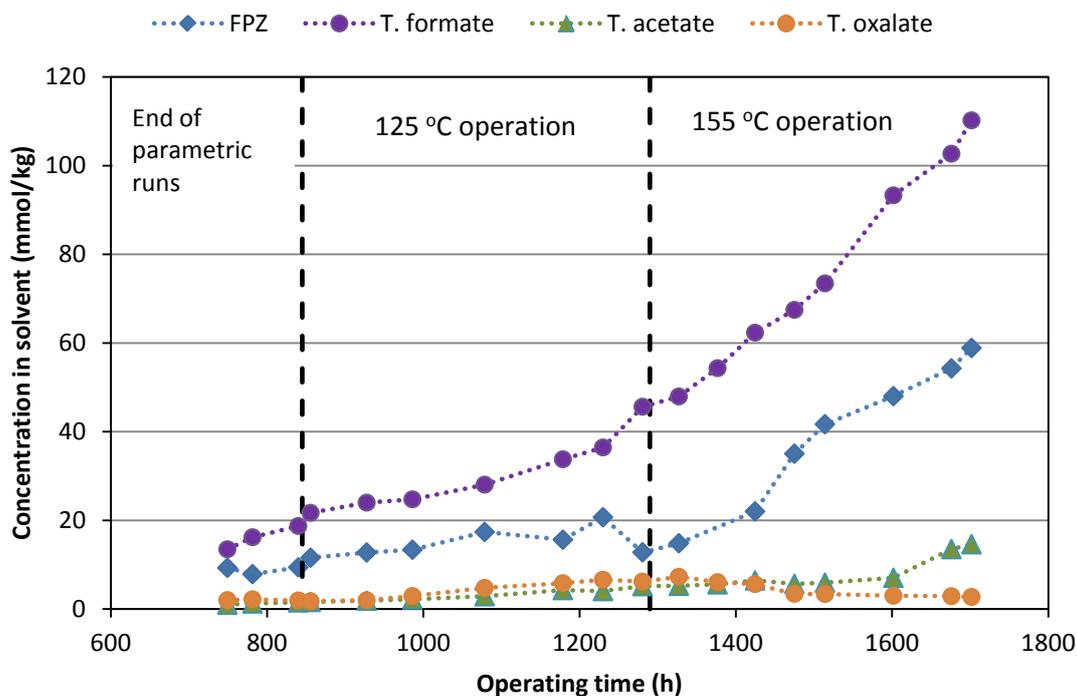
Figure 8: Formation of FPZ, total formate, total acetate and total oxalate in the lean piperazine solvent with extended operation. Solvent analysis performed at the University of Texas

Sulphates and nitrates in the solvent also increase with operating time. Sulphate is formed from absorption of SOx in the flue gas (Nielsen 2013). Its concentration is fairly steady, except for two jumps occurring at operating times of approximately 900 and 1250 h. The first increase corresponds to a loss of caustic supply to the flue gas pre-treatment. As a result, the pilot plant was shut down. The loss of caustic in the pre-treatment will have allowed higher than normal levels of SOx into the absorber, corresponding to the increase in sulphate levels seen in the solvent. The second increase corresponds to failure of the caustic dosing pump that occurred on 18 January 2013. Again, the loss of caustic to the pre-treatment will have resulted in higher levels of SOx entering the absorber. Nitrate concentration in the solvent is seen to gradually increase with operation, most likely from NOx absorption (Nielsen 2013). This is something that will need to be kept in mind when CO_2 capture facilities are operated commercially, particularly if they use a secondary amine solvent (such as piperazine) which can react with nitrate in the solvent and form nitrosamines. The accumulation rate of nitrate in the solvent is 0.016 mmol/kg/hr
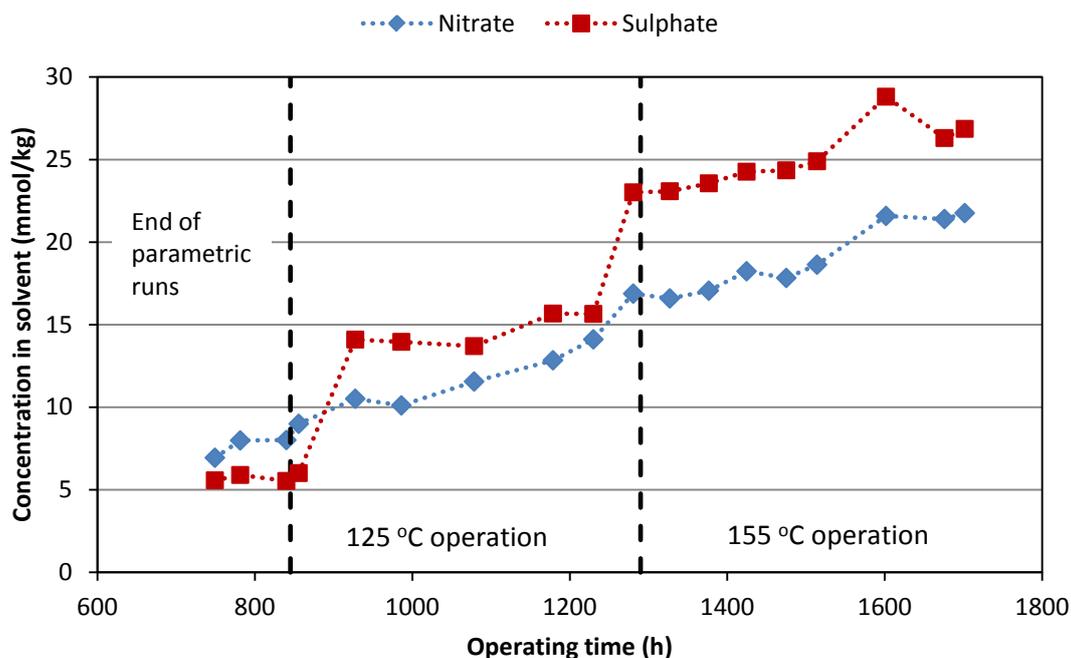
Figure 9: Formation of sulphates and nitrates in the lean piperazine solvent with extended operation. Solvent analysis performed at the University of Texas

5.4 Nitrosamine formation

Nitrosopiperazine concentration results provided by the University of Texas and CSIRO are of similar magnitude. Figure 10 shows the concentration mononitrosopiperazine (MNPZ) with the operating time of the pilot plant as measured the University of Texas. The results show a strong correlation for MNPZ formation with regeneration temperature, with concentration decreasing sharply when the regeneration temperature was increased from 125 to 155 ^{o}C. A similar trend is observed in the results from CSIRO, however scatter in the dataset make identification of the trend less clear. Figure 11 shows some MNPZ is also observed in the absorber wash water and in the stripping column condensate. The present results suggest that nitrosopiperazine concentration in the stripping column condensate does not increase appreciably when the regeneration temperature is increased.
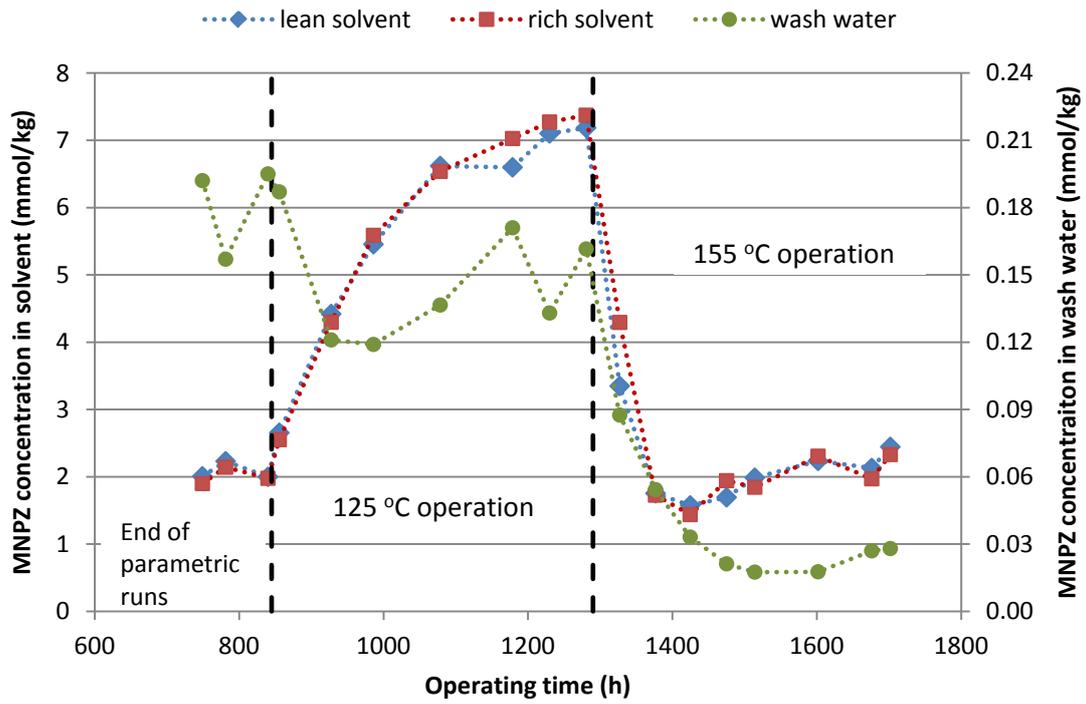
Figure 10: Formation of MNPZ in rich and lean solvent samples and in absorber wash water with extended operation. Solvent analysis performed at the University of Texas
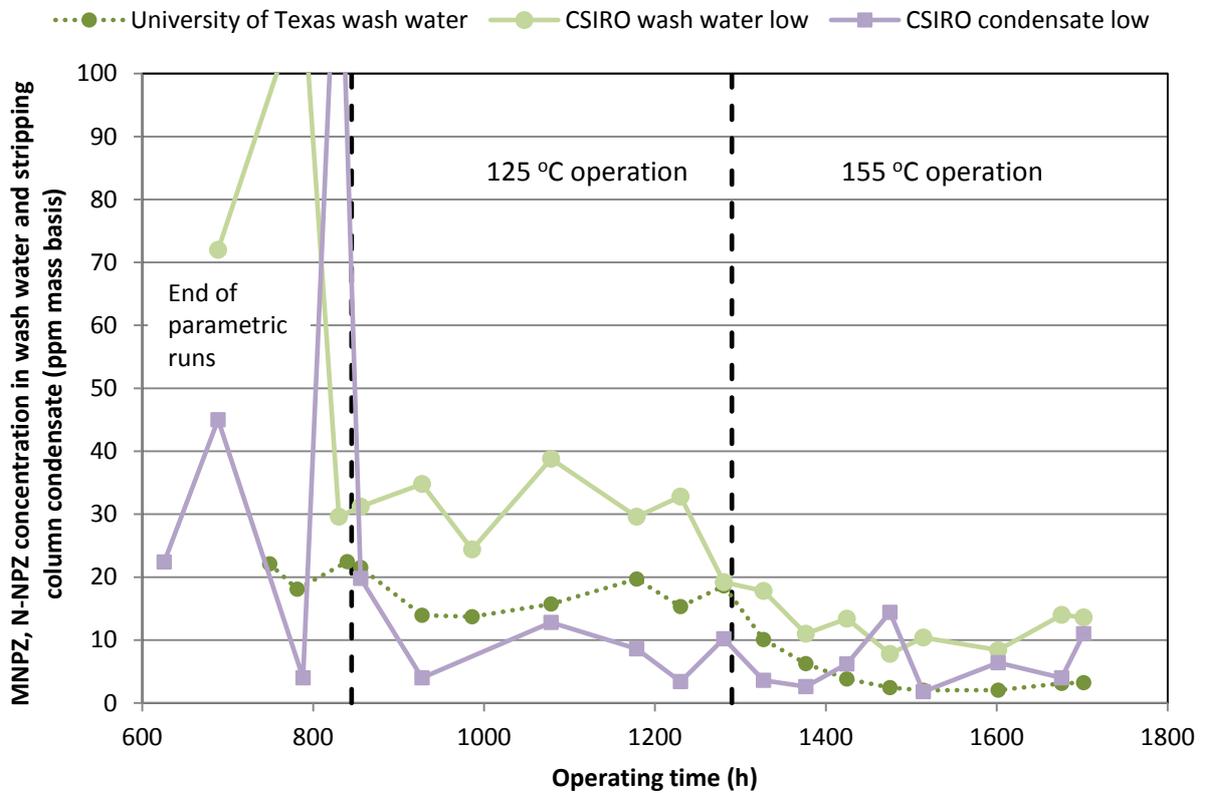

Figure 11: MNPZ and N-NPZ concentration measured in the absorber wash water and stripper condensate . Solvent analysis performed at the University of Texas and at CET laboratories

It is critical to operation with piperazine that nitrosamine formation minimisation and nitrosamine destruction are key to successful safe operation. The indications so far is that the simplest method of management is to minimise incoming NO_2 as well as using thermal destruction as demonstrated above by operating the stripper at elevated temperatures and ensuring solvent residence time at those temperatures is sufficient to limit the nitrosamines to a manageable level. There are however a number of other techniques that may need to be applied such as nitrite scavenging, ultraviolet degradation, inhibition and catalytic hydrogenation. The success and applicability of many of the methods suggested in the literature is currently under debate. In addition, much of the experimental work completed to date has been at laboratory scale. The simplest method to implement and evaluate at this stage is thermal degradation.

6   Techno-Economic Assessment

An assessment has been performed comparing the industry standard MEA process with the concentrated PZ process. The comparison has been based on the basic process only and utilising operating conditions to take advantage of specific solvent. The analysis uses non optimised pilot plant data for the concentrated piperazine process and optimised data for the MEA process. It should also be noted there are advanced process integration and energy minimisation techniques which this assessment does not cover which could be incorporated into either of these processes.

To carry out the capital cost estimations both processes have been modelled using ASPEN as it contains a built in costing package called the ASPEN Economic Analyser which enables the costing of the components of the PCC process. Before we could use this software we needed to validate the pilot plant results against the process model for concentrated piperazine. A process model was developed using ASPEN based on the pilot plant and compared to the results from the plant and it was shown to predict some aspects of the operation of the pilot plant well and overestimated some key parameters such as regeneration energy.

Once the validated process model for the pilot plant using concentrated was completed, it was scaled up to match the flue gas output of the 443 MW Tarong North Power Station. A similar process model was developed for the MEA based capture process. With results from the process modelling a steam and electrical requirement of the pilot plant was determined and found that the piperazine process was more efficient to operate than the comparable MEA process but required a higher grade of steam to regenerate the solvent at the higher temperature and pressures. The piperazine process also had a significantly lower compressor electrical load requirement.

Both process models were costed and the concentrated PZ process was found to be slightly more expensive mostly as a result of the increased viscosity and operating pressure of the solvent. The increased viscosity requires a greater surface area in heat exchangers, particularly the lean-rich cross heat exchanger, as well requiring additional column due to the different flooding characteristics of a higher viscosity solvent. Taking advantage of the solvents high thermal stability allows the process to regenerate CO_2 at a higher temperature and pressure which ultimately saves on compression costs. This however does lead to additional costs in the construction of the stripping column to handle up to 10bar of pressure. Some of this additional expense was recovered due to only requiring a smaller compressor as a result of being able to operate at a higher pressure but overall the capital cost of the concentrated piperazine process is higher based on the ASPEN Economic Analyser. The MEA process estimated cost was $239 million and the PZ process estimated cost was $258 million.

To determine the impact of withdrawing steam from the power station steam cycle the power station was modelled using a steam turbine modelling package called STEAM-PRO using the steam consumption data of the PCC models and compared to the base power station case. The power station operated most efficiently with the piperazine process but less than was indicated by the capture process modelling due to the requirement of a higher grade steam for the piperazine process. Incorporating the electrical requirements of the PCC plant the overall sent out efficiency including capture comes to 26.95% for piperazine and 26.31% for MEA.

Performing the economic calculations using the information from the models showed that the piperazine process is still slightly cheaper at $79.55 per MWh compared to the MEA based process at $80.15 per MWh but due to the closeness of the results would be taken as being equal. Additionally both processes could be optimised further which would bring down the costs of both processes and it is envisaged that there is still significant savings to be had in optimising the concentrated piperazine process over the MEA process as the MEA process has had far greater level of development to date.

7   Conclusions and recommendations

This project aimed to investigate the potential of the concentrated PZ process for Australian conditions to reduce the cost of electricity production with CO_2 capture. The project showed that the solvent did deliver some aspects as indicated by laboratory studies such as lower volatility, more thermally stable and lower regeneration energy requirements but did not clearly show improvements in reaction rates as predicted. Operation of solvent regeneration at higher temperature's and pressures proved successful with some increased degradation but this is still small compared to MEA. The higher temperature and pressure operation should allow a reduction in the number of stages required for compression of the product CO_2.

Practical issues dealing with solvents tendency to precipitate when CO2 loading and temperatures fall outside of the optimal range were very real and require careful consideration if this solvent is chosen as the operating fluid for PCC. Although with careful operation and appropriate plant modifications and additions the solvent can be successfully and reliably utilised for PCC and energetically performs better than the standard MEA process by around 15%.

Piperazine being a secondary amine is prone to forming stable nitrosamines in the presence of nitrite. The project has shown that using concentrated piperazine on a coal combustion flue gas containing NO_2 does form nitrosamines which build up and seem to reach equilibrium over time. It was also shown that the nitrosamine concentration can be successfully managed by implementing an effective flue gas pre-treatment stage before CO2 absorption as well as operating the solvent regeneration at a higher temperature which is thought to increase the rate of thermal degradation of the nitrosamine compound.

Assessing the piperazine process using a techno economic approach showed that the piperazine process is, while be more capital intensive, only slightly cheaper at $79.55 per MWh compared to the MEA based process at $80.15 per MWh. Additionally both processes could be optimised further which would bring down the costs of both processes and it is envisaged that there is still significant savings to be had in optimising the concentrated piperazine process over the MEA process as the MEA process has had far greater level of development to date. It should also be noted that the techno-economic models were based on models produced in ASPEN and the MEA process predicts accurately as it is a well known solvent but based on our pilot experience the ASPEN model over predicted regeneration energies for PZ which were used in these economic models and hence we anticipate the real operational cost for PZ would be lower.

As more knowledge is gained about the concentrated PZ process further optimisations and process configurations to fully take advantage of the solvents properties can be explored. With this more reliable

assessments of the technology can take place. This report does show however that the PZ process is no worse than the MEA process and has the potential to be better.

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