



Development of the Advanced Aqueous Ammonia Based Post Combustion Capture Technology

Progress Report

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Contents

1 Executive Summary	6
2 Introduction	8
3 Scope of the Project	12
4 Activities and Methodologies	15
5 Results and Discussion	24
6 Status of Milestones	34
7 Conclusions	37
8 Future work	38

List of Figures

Figure 1: Levelised cost of electricity (LCOE) for a new plant with and without CCS. Incremental LCOE with the amine based CCS and estimated incremental LCOE with the advanced ammonia based CCS are also included to demonstrate the potential benefits from using ammonia based CCS.	8
Figure 2: Schematic of discretised two-film model for the rate-based model in each segment.....	18
Figure 3: Schematic flow-sheet of the CO ₂ absorbers in series.....	20
Figure 4: Comparison of predicted (a) CO ₂ and (b) NH ₃ partial pressure and experimental data (symbols) from Krevelen et al. (1949) as a function of CO ₂ molality in the NH ₃ -CO ₂ -H ₂ O system at 20 °C	26
Figure 5: Comparison of predicted (a) CO ₂ -containing and (b) ammonia-containing speciation and experimental data (symbols) from Lichtfers (2000) as a function of CO ₂ molality in the NH ₃ -CO ₂ -H ₂ O system with 6.3 mol NH ₃ /kg H ₂ O at 40 °C.....	27
Figure 6: Comparison of predicted heat of CO ₂ absorption and experimental data (symbols) from Qin et al. (2011) as a function of CO ₂ loading in the NH ₃ -CO ₂ -H ₂ O system at (a) 40 °C, 2.5wt% NH ₃ and (b) 40 °C, 5wt% NH ₃	29
Figure 7: Comparison of predicted transport properties of aqueous ammonia and experimental data (symbols) as a function of NH ₃ mass fraction: (a) density; (b) viscosity; and (c) surface tension	30
Figure 8: Mass transfer coefficients for CO ₂ at an absorption temperature of 15 °C in NH ₃ (3 M), additive only (0.3 M), and 0.3 M additive + 3 M NH ₃ . PZ: piperazine, 4-PD: 4 amino piperidine, SAR: sarcosine, PRO: proline, 2-PZ: 2-methyl piperazine, DAP: 1,3-diaminopropane, DACH: trans-1,4-diaminocyclohexane, ASP: L-asparagine, ALA: β-alanine, EDA: ethylenediamine, BZ: benzylamine	32

List of Tables

Table 1: Summary of rate-based model predictions and some of pilot plant trials results conducted under a variety of experimental conditions	31
Table 2: List of new additives tested in the wetted wall screening tests	21
Table 3: Comparison of CO ₂ content between standard and measured values using CM150	24
Table 4: Comparison of NH ₃ content between standard and measured values using the titration method	25

1 Executive Summary

This research project focuses on the development of the advanced aqueous ammonia based post combustion capture (PCC) technology for significant reduction of CO₂ emission from coal fired power stations in Australia.

Currently, the commercially available PCC technology is mainly based on alkanol/alkyl amine solutions. This technology will reduce the power plant efficiency by 25-30% and involve significant capital/investment costs including the expensive flue gas desulfurization which is not installed in Australian power plants. Moreover, there is a concern about the potential formation of harmful compounds from the use of amines in PCC and their environmental impact. As a promising solvent, aqueous ammonia has many advantages over amine-based capture technologies, including no degradation in the presence of O₂, a higher CO₂ absorption capacity than monoethanolamine (MEA), a low regeneration energy. It also has a potential to capture oxides of nitrogen (NO_x) and sulphur dioxide (SO₂) from the flue gas of coal-fired power plants, and to produce value-added chemicals, such as ammonium sulfate and ammonium nitrate, which are commonly used as fertiliser.

This research project is based on CSIRO PCC pilot plant trials with an aqueous ammonia based liquid absorbent under real flue gas conditions in an 7M AUD pilot plant at Delta Electricity's Munmorah power station and ongoing work in this area. The pilot plant trials have confirmed the technical feasibility of the process and confirmed some of the expected benefits. The pilot plant trials have also highlighted some of the issues when using aqueous ammonia in a PCC process. These include a relatively low CO₂ absorption rate and high ammonia loss. These issues currently limit the economical feasibility of the aqueous ammonia based PCC process.

The strategy of the research proposed here is to extend a number of novel approaches developed previously by CSIRO to address the issues identified and make the process economically favourable. These novel approaches to be further explored in this project include promotion of CO₂ absorption rate through the introduction of additives, in particular those stable and environmentally friendly additives, combined removal of SO₂ and CO₂ and recovery of ammonia, and absorption under pressure to further enhance CO₂ absorption and suppress ammonia loss. In addition, the research project will combine an experimental and modelling approach to develop a rigorous rate based model for the aqueous ammonia based capture process which allows for reliable process simulation, optimisation and scale up. The outcomes of this research project will include the demonstration of the advanced aqueous ammonia based PCC at a CO₂ capture rate of at least 10 kg/h with CSIRO's process development facility in Newcastle. The advanced technology is expected to achieve a CO₂ absorption rate that is comparable with the standard MEA based solution, limit the power plant efficiency loss below 20%, and achieve the combined removal of SO₂ and recovery of ammonia to produce ammonium sulphate and eliminate additional flue gas desulfurization and reduce wash water consumption. The combined outcomes will enable the advanced technology to achieve a significant reduction in incremental levelised cost of electricity compared to state of the art, advanced amine based PCC technology.

This project is planned over a three-year time frame and is divided into 6 stages. This report summaries the progress of the projects and presents the results obtained in stage 1.

The milestones of the project for the report period have been achieved and the three key activities in the report period have been completed.

Analytic methods for liquid and gas analysis have been established and confirmed to be adequate.

The framework for a rigorous rate-based model for CO₂ absorption using aqueous ammonia in a packed column has been established and the rate-based model was developed and used to simulate results from pilot plant trial of an aqueous ammonia-based post-combustion process at the Munmorah Power Station, New South Wales. The model is based on RateSep module, a rate-based absorption and stripping unit operation model in Aspen Plus, and uses the available thermodynamic, kinetic and transport property models for the NH₃-CO₂-H₂O system to predict the performance of CO₂ capture. The thermodynamic and transport property models satisfactorily predict experimental results from the published literature. The modelling results from the rate-based model also agree reasonably well with selected pilot plant results on CO₂ absorption rate.

The project investigates the effect of eight additives as potential promoters of CO₂ absorption in aqueous ammonia. The additives were 2-methyl piperazine, 1,3-diaminopropane, ethylenediamine, benzylamine, trans-1,4-diaminocyclohexane, the potassium salts of three amino acids: L-proline, L-asparagine and β-alanine. Experiments were performed on a wetted wall column at an absorption temperature of 15 °C using 3 M (mol/L) NH₃ in the presence and absence of 0.3 M of each additive. CO₂ mass transfer coefficients increased to different extents in the presence of different additives. L-proline potassium salt promoted CO₂ absorption in aqueous NH₃ to a greater extent than the other additives. L-proline together with piperazine and sarcosine has been identified in the following stopped flow kinetic study to elucidate the role of these additives.

2 Introduction

PCC is one of the leading capture technologies for significant reduction of CO₂ emission from coal fired power stations. Currently, the state of the art PCC technology is based on amine solutions, MEA in particular. A report by US Department of Energy (Ramezan, 2007) shows that the advanced amine technology will reduce the power plant efficiency by 30% and involve significant capital investment costs for retrofitting an existing coal fired power station (Conesville unit 5 in Ohio, subcritical, 90% capture). The incremental levelized cost of electricity (LCOE) is estimated to USD \$69/MWh. Recent studies of low CO₂ emission technologies for power generation in the Australian context (EPRI, 2010) show that addition of an advanced amine PCC process (state of the art) and CO₂ transport and storage to a new coal fired power station (pulverised black coal, supercritical, 750 MW sent out) will lead to a decrease in plant efficiency from 38% to 28.4 % (25.3% decrease) and an increase in LCOE from 77 AUD/MWh to 167 AUD/MWh. As shown in Figure 1, the significant increase is due to increase in capital (plant cost), fuel, O&M and CO₂ transport and storage. The capital cost increase accounts for almost 60% of the total incremental LCOE. High capital costs are due to the fact that the new plants have to process more than 33% of coal extra to have the same power output and need to remove a large amount of CO₂ from an even larger amount of flue gas and compress it. This involves an increase in the size of the existing equipment and introduction of flue gas desulfurization (FGD) unit and CO₂ capture and compression facilities.

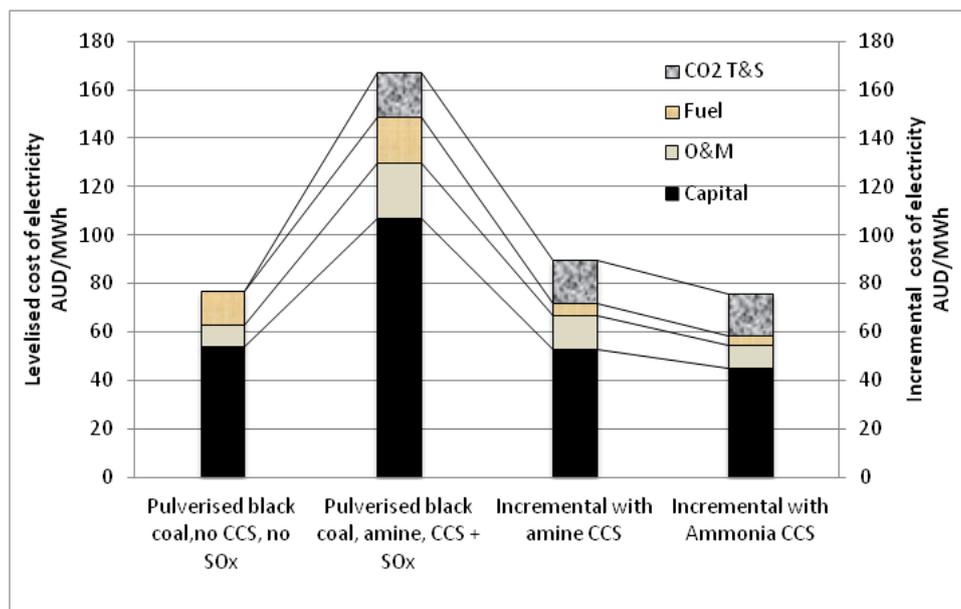


Figure 1 Levelised cost of electricity (LCOE) for a new plant with and without CCS. Incremental LCOE with the amine based CCS and estimated incremental LCOE with the advanced ammonia based CCS are also included to demonstrate the potential benefits from using ammonia based CCS.

The advanced amine solvent has poor SO_x tolerance which requires a deep cut in SO₂ content to levels below 10 ppm. The cost of building a desulfurization unit is substantial. According to the EPRI report, in a new plant in Australia in which the bare erected capital cost increase due to CO₂ removal and compression is AUD 888M AUD while capital increase due to clean up costs (installation of FGD) is AUD 90 M AUD (EPRI, 2010). FGD alone will count for more than 9% of the increased capital costs.

In addition, there has been concern regarding the potential formation of harmful compounds from the use of amines in PCC and their possible negative environmental impact.

It is clear that to make CCS technologies, and in particular PCC, economically more feasible, the research focus will be on the reduction of capital costs by using more efficient, smaller and cheaper units and development of solvents which require low parasitic energy consumption and thus consume less coal and have less gas to treat which results in a smaller facility, and have less environmental and health effects. In this context, the current submission is proposed, aiming at the development of advanced aqueous ammonia based PCC to achieve a significant cost reduction and reduce environmental risks.

Advantages of aqueous ammonia based PCC

Aqueous ammonia is a promising emerging solvent for CO₂ capture. Compared to other amines, ammonia, as one of the most widely produced chemicals in the world, is a low cost solvent, does not degrade in the presence of O₂ and other species present in the flue gas, and is less corrosive. The environmental and health effects of ammonia are well studied and are more benign than amines. Ammonia has a high CO₂ removal capacity and a low regeneration energy. It also has the potential of capturing multiple components (NO_x, SO_x, CO₂ and Hg) (Ciferno, 2005) and producing value added products such as ammonium sulphate and ammonium nitrate, which are widely used as fertilisers. This potential is of particular interest to Australian power stations since desulfurization and DeNO_x are not implemented in Australia. It has been estimated by Powerspan (MacDowell, 2009) that the power plant efficiency loss is below 20% for an ammonia based capture process. A scoping study by US Department of Energy (Ciferno, 2005) suggested that the incremental cost of electricity using ammonia is less than half of that using traditional amines.

CSIRO has identified the aqueous ammonia based technology as a promising low cost technology for significant reduction of multiple components emissions from coal fired power stations in Australia. CSIRO and Delta Electricity completed pilot plant trials of the aqueous ammonia based capture technology under the real flue gas conditions in 7M AUD pilot plant scale research facility at Delta's Munmorah Power

Station in 2010. The pilot plant trials have confirmed the benefits and technical feasibility of the process and its potential for application in the Australian power sector. The benefits include high CO₂ removal efficiency (more than 85%) and production of high purity of CO₂ (99-100 vol%), and effectiveness of the combined SO₂ removal (more than 95%) and ammonia recovery, high stability of ammonia solvent and low regeneration energy. Part of the results were published in a number of conferences and journal papers (Yu, 2011a and 2011b). It is the first time that results from an actual aqueous ammonia plant operating on real flue gases have been published.

Areas for improvement

The pilot plant trials have identified a number of research opportunities to further develop aqueous ammonia based capture technologies.

- Relatively low CO₂ absorption rate compared to amine based solvent, which results in 2-3 times the number of absorbers compared to monoethanolamine (MEA, the benchmark solvent) and thus higher capital costs.
- Relatively high ammonia loss at high CO₂ absorption rate. The consumption of wash water is high.
- Operating the desorption process in a similar pattern to regular amine processes will result in the formation of ammonium-bicarbonate solids in the condenser, resulting in blockage.
- The available process simulation models were insufficient to support the process optimisation and scale up.

This limits the economical feasibility of the aqueous ammonia based PCC process. In this research project, CSIRO will collaborate with the University of Newcastle and Curtin University of Technology (by way of student exchange or other collaboration), exploring and evaluating novel approaches and concepts to further advance the aqueous ammonia based PCC process in Australian context.

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3 Scope of the Project

This research project will further develop a promising aqueous ammonia (NH₃) based post combustion capture (PCC) process to achieve a significant reduction of investment and running cost in the Australian context and reduce potential environmental risks resulting from the implementation of PCC technologies.

The objectives of the project are:

1. Develop a novel aqueous ammonia based solvent which has fast CO₂ absorption rate equivalent to MEA while maintaining a low regeneration energy requirement.
2. Further advance the combined SO₂ removal and ammonia recovery technology to eliminate additional FGD, reduce the ammonia slip in the exiting flue gas to acceptable levels and produce a value added fertiliser, i.e. ammonium sulphate.
3. Further develop CSIRO technology (patent application no WO/2010/020017) to enhance CO₂ absorption, reduce ammonia loss and cooling water consumption.
4. Develop and validate a rigorous rate based model for the capture process which will guide process modification to achieve further savings on capture costs.

The research proposed here is to extend a number of novel approaches developed previously by CSIRO to address the issues identified, achieve the project objectives and thus make the process economically favourable. The new ideas and approaches include;

Promotion of CO₂ absorption rate through addition of promoters. Ammonia has been confirmed as a high loading capacity solvent and has a theoretically 1:1 ratio with CO₂ on a molar basis. It has been reported in a study by DOE (Ciferno, 2005) that the CO₂ carrying capacity in g CO₂ per g of ammonia solution (8 wt.%) circulated is 0.07 as compared with 0.036 g CO₂ per g MEA solution (20 wt.%). However, the CO₂ absorption rate is much lower in ammonia than in MEA, as identified by our recent pilot plant investigation (Yu, 2011a). This is preventing ammonia of achieving its high loading capacity and low regeneration energy potential.

The CO₂ absorption flux within the column can be correlated by $N_{CO_2} = K_G A (P_{CO_2} - P^*_{CO_2})$, where N_{CO_2} is CO₂ absorption flux, K_G mass transfer coefficient, P_{CO_2} partial pressure of CO₂ in the flue gas, $P^*_{CO_2}$ CO₂ equilibrium partial pressure in the solvent and A , effective interfacial surface area. For a given CO₂ absorption flux to achieve a typically 85-90% CO₂ removal efficiency, K_G and $(P_{CO_2} - P^*_{CO_2})$, need to be high in order to reduce A , which is directly related to the size of column (capital cost).

Recent studies by CSIRO showed that with introduction of a small amount of additive such as an amino acid salt which is environmentally friendly, stable and cheap, the CO₂ mass transfer coefficients increase significantly (Yu, 2012). With the introduction of 0.3 M additive to 3 M ammonia, the mass transfer coefficients increase dramatically compared to ammonia alone. They are comparable with MEA at high CO₂ loadings which are relevant to industrial applications. It is expected that further tests of new additives and optimisation of the solvent will lead to the development of the novel ammonia based solvent with

high mass transfer coefficients which match and are even high than those for MEA while maintaining its low regeneration energy.

The promotion of CO₂ absorption in ammonia is relatively new and the mechanism involved is unknown. Recently CSIRO has developed a new software tool in Matlab® to model CO₂ absorption into aqueous MEA, PZ, ammonia and binary mixtures of PZ with AMP or ammonia (Puxty, 2011). The tool solves partial differential and simultaneous equations describing diffusion and chemical reaction automatically derived from reactions written using chemical notation. It has been demonstrated that by using reactions that are chemically plausible the mass transfer in binary mixtures can be described by combining the chemical reactions and their associated parameters determined for single amines. The observed enhanced mass transfer in binary mixtures can be explained through chemical interactions occurring in the mixture without need to resort to using additional reactions or unusual transport phenomena (e.g. the shuttle mechanism). Such a tool in conjunction with a stopped flow reactor at the University of Newcastle will help elucidate the promotion mechanism (Wang, 2011).

Combined removal of SO₂ and recovery of ammonia. This research project also tests a hypothesis that an integrated approach can be used to achieve the combined removal of SO₂ and recovery of ammonia. In this approach, as described in our publication (Yu, 2011a), the wash water is circulated between the pre-treatment column (before absorber) and wash column (after absorber). Ammonia recovered from the flue gas in the wash column is used to capture SO₂ in the pre-treatment column. The results from the pilot plant trials have demonstrated the effectiveness of the approach. More than 95% SO₂ in the flue gas and more than 80% ammonia which slips to flue gas in the absorber can be removed from the gas phase by the wash water. The removal of SO₂ from flue gas by ammonia is the established technology and its fundamentals have been well documented (Kohl, Nielsen, 1997). Ammonia has a strong affinity for SO₂, thus permitting a compact absorber with a very low liquid-to-gas ratio. The high-purity, high-market value ammonium sulphate crystals were successfully compacted into a premium granular by-product. The combined removal of SO₂ and ammonia has a potential of reducing or offsetting the cost involved for removal of SO₂ and ammonia with production of saleable ammonium sulphate. The focus of the research project is to identify conditions under which SO₂ and ammonia are selectively removed at high efficiencies in preference to CO₂, understand the mechanism involved for oxidation of sulphite to sulphate, and explore more efficient methods for separation of ammonium sulphate from the aqueous ammonia solvent.

Absorption under pressure. This research project will also further develop a new concept developed by CSIRO. The flue gas is pressurised and absorption of CO₂, SO₂ and recovery of ammonia can take place under pressure. The flue gas cooling requirement is provided by the expansion of the flue gas after pressurisation. It is well known that pressurisation of flue gas will lead to high energy penalties but the size of absorption columns and ammonia loss as well as energy consumption for production of cooling water can be reduced significantly. In the Australian context, capital costs are the major contributors to the capture costs while fuel contribution is relatively small. The proposed high pressure absorption experiments and the rigorous process model to be developed will allow an evaluation of the feasibility of the concept and its economic viability.

Development of rate based absorption model. The available process simulation models were insufficient to support the process optimisation and scale up. The project will develop a rigorous rate based model for the advanced aqueous ammonia based capture process and validate the model with results from previous pilot plant trials and from experiments with the CSIRO's processes development facility. The developed

model will be used to evaluate novel process concepts such as rich solvent recycle in the absorber and identify approaches to further reduce ammonia loss and energy and water consumption.

The research plan has been developed to carry out the proposed research activities. The project is planned over three year and divided into 6 stages with each stage being approximately 6 months. This report is the progress report of Stage 1 of the project.

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4 Activities and Methodologies

Three key activities listed in stage 1 of the project have been conducted.

1. Establish the analytic methods for gas and liquid analysis

Gas analysis. The concentrations of CO₂, SO₂, NH₃, and H₂O in the gas need to be determined. A portable FTIR gas analyser DX 4000 from Gaset Technologies was purchased for this purpose. The instrument allows online analysis of up to 50 gases with a single analyser. The gas analyser is supplied with analysis software-Calmet that is designed in-house by Gaset Technologies own software development team for data processing. In addition, a Horiba CO₂ gas analyser is used if only CO₂ concentration in the gas phase needs to be determined, for example, in the wetted wall column experiments for the measurement of CO₂ absorption rate.

Liquid analysis. A carbon analyser CM150 from UIC was purchased and used to determine the total CO₂ content in the CO₂ loaded solution. The instrument is equipped with an acidification module and a CO₂ Coulometer. The acidification module allows the complete desorption of CO₂ from the CO₂ loaded solution and the amount of CO₂ will be measured by the CO₂ Coulometer. An auto titrator (Mettler Toledo T50) is employed to determine the total ammonia content. A sample of ammonia solution is weighed accurately and diluted with water to ~ 50 ml. A known excess of HCl is added to the sample to liberate any bound CO₂. The mixture is then titrated against NaOH (0.5 M) until the equivalence point is reached. The titration gives the amount of HCl in excess. The difference between the total amount of HCl added and amount of HCl in excess is the amount of the total NH₃ in the solution.

2. Establish the framework for the rate based model and compare the modelling work with pilot plant results

The CO₂ capture by aqueous ammonia involves absorption and desorption. Since desorption takes place at very high temperature, the equilibrium based process model can be used. In the absorber where the absorption temperature is low, a rate based model is required to predict the absorption performance. The framework for the rate based model requires thermodynamic model for the NH₃-CO₂-H₂O system, transport properties of species involved and the rate-based model which characterise the material and energy balance, chemical kinetics, mass and heat transfer, hydrodynamics and column properties of the whole absorption system.

2.1 Thermodynamic model

Calculations of thermodynamic properties are required to evaluate the performance of the CO₂ capture process using aqueous ammonia. The model must be able to describe accurately the chemical equilibrium, vapour-liquid equilibrium, speciation, enthalpy change of the NH₃-CO₂-H₂O system and many other chemical and physical properties. We use a recently developed the thermodynamic model for

CO₂-NH₃-H₂O (Que et al. 2011) which has been implemented in Aspen Plus V 7.3. The model is described briefly here.

The electrolyte NRTL model is used to calculate activity coefficients, enthalpies, and Gibbs energies for non-ideal, CO₂-loaded ammonia liquid phase thermodynamic behavior. The RK (Redlich-Kwong) equation of state is applied to the calculation of fugacity coefficients for the vapour phase.

Dissolved CO₂ in the aqueous ammonia solvent is determined by both its physical and chemical solubility. A chemistry model is consequently included in the electrolyte NRTL model, which considers the following reactions occurring in the NH₃-CO₂-H₂O system:



NH₄HCO₃ may precipitate in the system, so reaction 6 is also included:



The chemical equilibrium constants of reactions 1–6 can be expressed in the form:

$$\ln K_{\text{eq},j} = a + b/T + c \ln(T) + d * T + e * ((P - P_{\text{ref}}) / P_{\text{ref}}) \quad (7)$$

where $K_{\text{eq},j}$ is the equilibrium constant of reaction j ; T is the temperature in Kelvin; P_{ref} is the reference state pressure; and constants a , b , c , d and e are regressed against experimental data reported in the public domain (Austgen, 1989).

CO₂, NH₃ and N₂ are declared as Henry's law components, and Henry's Law parameters are retrieved by the electrolytes expert system. The vapour–liquid equilibrium and liquid phase speciation distribution of the NH₃-CO₂-H₂O system are calculated by a flash model. The apparent component approach is chosen to solve the vapour–liquid equilibrium.

The enthalpies of CO₂ absorption are calculated from temperature derivatives of activity coefficients in Aspen Plus. The enthalpies of CO₂ absorption are estimated from the vapour–liquid equilibrium data obtained from the flash calculations, using the commonly used equation derived from the Gibbs-Helmholtz Equation (Kim, 2009; Mathias et al. 2009; Qin et al. 2011):

$$\left[\frac{\partial \ln \hat{f}_i}{\partial (1/T)} \right]_{P,x} = \frac{\Delta H_s}{R} \quad (8)$$

where \hat{f}_i is the fugacity coefficient, and equilibrium partial pressures of CO₂ are used to replace the fugacity coefficient in the calculation; ΔH_s is the enthalpy of CO₂ absorption; R is the gas constant.

Mathias and O'Connell (2012) provided a clear definition of enthalpy of absorption and rigorous derivation of G-H equation to relate the commonly used form (equation 8) to the rigorous form. The rigorous form includes two terms: one is the f term (common form) and the other is P-term. The calculation by Mathias and O'Connell (2012) showed that the contribution of P-term to the heat of absorption is negligible for MEA-CO₂-H₂O system. It is assumed to the case for the NH₃-CO₂-H₂O system considering the similarity of the two systems.

2.2 Transport properties model

The transport properties of aqueous ammonia are required when describing mass and heat transfer in the rate-based model for CO₂ capture by aqueous ammonia. Different transport property models and corrections can be chosen to calculate the density, viscosity, thermal conductivity, diffusion coefficient and surface tension of the electrolyte ammonia solvent. The liquid density of the electrolyte solutions is calculated using the Clarke model (Aspen Technology, 2009). The liquid viscosity is computed by the Andrade and DIPPR (Design Institute for Physical Properties) models and an electrolyte correction is applied using the Jones-Dole model for the presence of the NH₃-CO₂-H₂O system (Aspen Technology, 2010). The surface tension of the aqueous ammonia solvent is calculated by the Hakim–Steinberg–Stiel and DIPPR models and corrected with the Onsager–Samaras model (Aspen Technology, 2010). The thermal conductivity is calculated by the Sato–Riedel and DIPPR models and the Vredeveld mixing rule, and adjusted using the Riedel model (Riedel, 1951). The diffusivity of each species is determined using the Wilke–Chang model for molecular species and the Nernst–Hartley model for ions (Aspen Technology, 2010b).

2.3 Rate-based model

The rate-based model embedded in the Aspen Plus RadFrac distillation model (RateSep) is used to model CO₂ absorption using aqueous ammonia. The rate-based model can completely characterise the material and energy balance, chemical kinetics, mass and heat transfer, hydrodynamics and column properties of the whole absorption system. The model flow-sheet, inputs and specifications are based on the pilot-plant trials at Munmorah Power Station.

The rate-based model allows users to divide the absorber into a number of stages along the column height, perform material and energy balances at each stage, and integrate across the entire column. The model also considers mass and heat transfer resistance in the liquid and gas phase. The two-film theory is adopted, and the liquid film at each stage is discretised into several segments, as shown in Figure 2. The segments near the interface are thinner than those close to the liquid bulk phase. This non-homogeneous discretisation allows more accurate calculation of species concentration profiles in the film. In this work, the film discretisation option is set to geometric sequence, the film discretisation ratio (ratio of film thickness of adjacent discretisation segments from bulk to interface) is set at 2, and the number of discretisation segments is 4. Combining the film equations with the material and heat balance equations

at each stage allows the performance of the entire absorber column to be calculated. The rate-based model uses the Maxwell–Stefan theory to solve multi-component mass and heat transfer (Alopaeus et al, 1999).

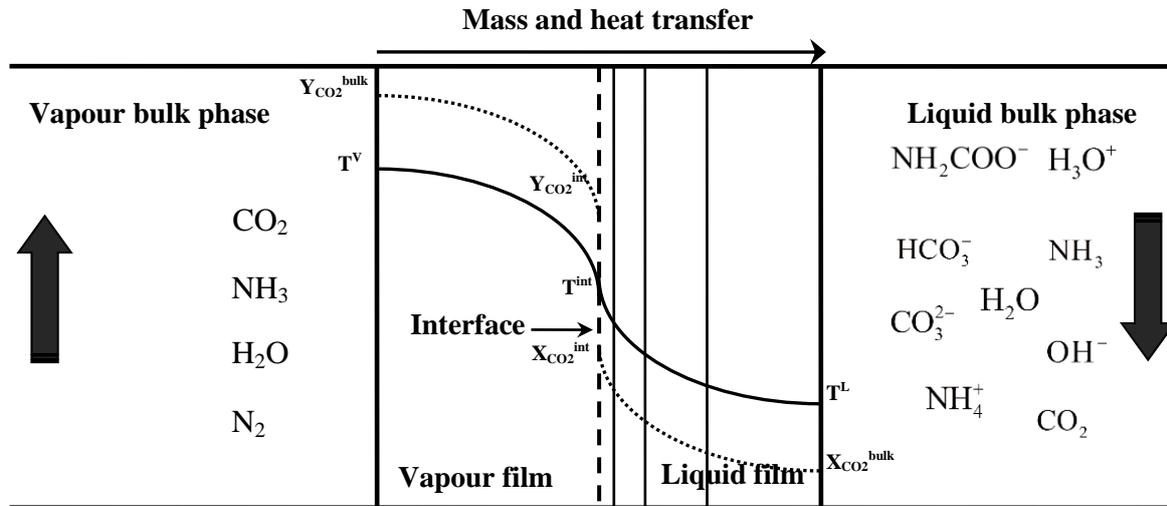
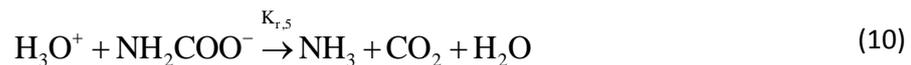


Figure 2 Schematic of discretised two-film model for the rate-based model in each segment

The chemical reaction model for the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system is consistent with the electrolyte NRTL model, which we described above. The equilibrium reactions 1–5, and the salt precipitation reaction 6, are necessarily involved in the kinetic model, which is the same as the chemistry model. The model also includes the reactions of CO_2 with NH_3 (reactions 9 and 10) and the reactions of CO_2 with OH^- (reactions 11 and 12), which are kinetically controlled (Aspen Technology, 2009).



The kinetic reaction rate can be expressed by power law equations in Aspen Plus:

$$r_j = k_j \left(\frac{T}{T_0} \right)^n \exp \left[\left(\frac{-E_j}{R} \right) \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \prod_{i=1}^N C_i^{\alpha_i} \quad (13)$$

where r_j is the reaction rate of reaction j ; k_j is the pre-exponential factor; T is the absolute temperature; T_0 is the reference temperature; n is the temperature exponent; E_j is the activation energy; C_i is the concentration of component i ; α_i is the stoichiometric number of component i ; N is the number of components in reaction j ; R is the gas constant. k_j , n and E_j are derived from the work of Pinsent et al. (1956) who determined the rate constants for reactions 9 and 11 temperatures of 0–40 °C.

The rate constants from Pinsent et al. (1956) have been used by a number of researchers in their modeling work involving the two reactions (Brettschneider et al. 2004; Yu et al. 2011; Niu et al. 2012). The background rate constants were calculated using forward rate constants and the equilibrium constants. This can ensure that all forward and backward reaction rates are available and consistent with chemical equilibrium. The detailed description of the approach used has been described by Zhang et al. (2009).

For the calculation of mass and heat transfer, the rate-based model provides several built-in correlations to compute the gas and liquid mass and heat transfer coefficients for different packing types. Three mass transfer correlations developed by Onda et al. (1968), Billet and Schultes (1999) and Bravo and Fair (1985) can be selected. In this work, we chose the correlation proposed by Onda et al. (1968) to calculate the mass transfer properties for the random ring packing used in the Munmorah pilot plant. The Chilton–Colburn correlation is used to calculate the heat transfer in the absorber (Chilton and Colburn, 1934).

The effective interfacial area is a critical parameter for both mass and heat transfer in the rate-based model. Yu et al. (2011) measured the effective interfacial areas as a function of the liquid flow rate for the packing used in the Munmorah pilot plant under typical operating conditions. Correlations from both Onda et al. (1968) and Billet and Schultes (1999) underpredicted the effective interfacial area by approximately 20% and 40%, respectively, compared with the experimental results in the pilot plant (Yu et al. 2011). The interfacial area factor as a scaling factor for the effective interfacial area in the rate-based model is set at 1.2 to match the pilot plant measurements.

Four different flow models can be used to evaluate the liquid bulk properties: mixed, countercurrent, VPlug and VPlug-Pavg models. We chose the countercurrent model for this work, because it is recommended to be more accurate for packed columns (Chen, 2007). The countercurrent model determines the mass and heat transfer using the arithmetic average of gas and liquid phase bulk properties at the inlet and outlet of each stage. Under the conditions studied, there is not too much difference with the four flow models.

Liquid holdup is used to calculate the kinetic reaction rate in the rate-based model. The correlation by Stichlmair et al. (1989) is applied to the holdup calculations. The liquid holdup value is set to 3% of the free volume under the reaction tab used for model initialisation. The Tsai method is used to calculate pressure drop in the packed absorber (Tsai, 1985). The rate-based model uses the specific correlations for the mass transfer coefficients, interfacial area, liquid holdup and pressure drop to characterise the column hydrodynamics.

The Munmorah pilot plant consists of one pretreatment column serving as the scrubber for SO₂ removal; two absorber columns, each with one separate wash column at the top; and one stripper. Detailed information about the experimental conditions for the pilot plant trials has been described elsewhere (Yu et al. 2011). In this paper, we focus on modeling CO₂ absorption in the two absorbers.

The flow-sheet for the rate-based absorber model is shown in Figure 3. The two absorbers are operated in series. The flue gas containing CO₂ is introduced into the bottom of Absorber 1, and the lean solvent to the top of Absorber 2. Since aqueous ammonia is used to remove SO₂ in the pretreatment column, the flue gas at the inlet of the absorber contains a certain amount of ammonia and water. One cooler is used between the two absorbers in order to reduce the temperature of the semi-rich solvent that leaves Absorber 2.

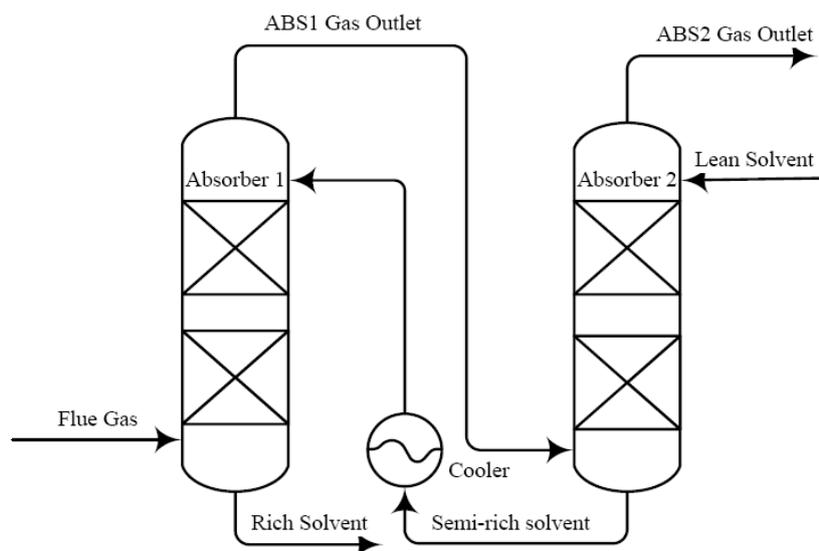


Figure 3 Schematic flow-sheet of the CO₂ absorbers in series

In the pilot plant, the packing is separated into two beds in each absorber column, connected with a liquid re-distributor. In the model, one continuous column is used and packing height for each absorber is 3.8 m (1.8 m, if one packing bed alone), divided into 25 stages for each 3.8-m-high absorber considering no significant change of absorber performance and more intensive computation when the stage number is over 25. The inner diameter of the absorbers is set to 0.6 m. 25-mm Pall rings are used as packing materials, with a specific surface area of 207 m²/m³. The flue gas and lean solvent streams specifications in the rate-based model are given in Table 1; they are the same as those used in the pilot plant trials in Campaign 3 (Yu et al. 2011).

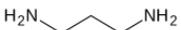
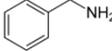
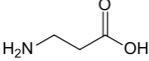
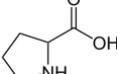
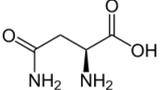
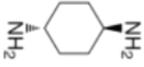
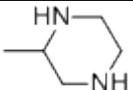
3. Carry out the wetted wall column screening experiments and identify promoters for stopped flow reactor study

In our previous research, we investigated the effect of seven additives as potential promoters of CO₂ absorption in aqueous ammonia. The additives were monoethanolamine, piperazine (PZ), 1-methyl piperazine (1-PZ), 4-amino piperidine (4-PD) and the sodium salts of three amino acids: sarcosine, taurine and glycine (Yu et al., 2012)). In this research, we screen tested a number of new promoters and compared with those tested prior to ANLEC project to determine if the new additives have a better performance in terms of promotion of CO₂ absorption rate in aqueous ammonia.

The wetted wall column used is identical to the one reported previously (Puxty, 2010) except that an ammonia scrubber containing concentrated phosphoric acid solution was installed immediately after the column outlet. Ammonia is volatile and will inevitably slip to the gas during the wetted wall column experiments. An ammonia scrubber was used to remove ammonia in the gas. This prevented ammonia from dissolving in the water which condensed in the cooler before the gas entered the Horiba gas analyser and avoided the absorption of CO₂ in the ammonia solution in the cooler. Otherwise a superficially high CO₂ absorption rate will be obtained.

The screening tests were performed at an absorption temperature of 15 °C using 3 M (mol/L) NH₃ in the presence and absence of 0.3 M of each additive. A gas flow rate of 5 L/min at 15°C was used to minimise the gas phase resistance, and solvent flow rate was kept at 100–120 ml/min to produce a laminar and ripple-free flow. Table 2 lists the additives tested. Ammonia solvents in the presence of additives at various CO₂ loadings were prepared by mixing the concentrated ammonia solution with ammonium bicarbonate and additives. The amino acids were neutralized with an equimolar amount of NaOH before use.

Table 2 List of new additives tested in the wetted wall screening tests.

Name	Molecular formula	Molar mass g/mol	pKa at 25°C	Imagine
1,3-Diaminopropane (DAP)	C ₃ H ₁₀ N ₂	74.1	10.55 8.88	
Ethylenediamine (EDA)	C ₂ H ₈ N ₂	60.1	9.92 6.86	
Benzylamine (BZ)	C ₇ H ₉ N	107.2	9.34	
β-alanine (ALA)	C ₃ H ₇ NO ₂	89.1	10.08	
L-Proline (PRO)	C ₅ H ₉ NO ₂	115.1	10.47	
L-Asparagine (ASP)	C ₄ H ₈ N ₂ O ₃	132.1	8.73	
trans-1,4-Diaminocyclohexane (DACH)	C ₆ H ₁₄ N ₂	114.2	9.94 6.47	
2-Methylpiperazine (2-MP)	C ₅ H ₁₂ N ₂	100.2	9.57 5.24	

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5 Results and Discussion

1. Establish the analytic methods for gas and liquid analysis

The availability of FTIR allows the simultaneous analysis of a number of species including CO₂, H₂O, SO₂ and NH₃ and determines their concentration with the program Calmet. The accuracy of the measurement is $\pm 2\%$ of the measurement range for each species. The use of FTIR analysis during the pilot plant trials of aqueous ammonia based CO₂ capture at Munmorah Power Station has confirmed that Gasmet FTIR is suitable for the analysis involved in the proposed research.

Table 3 lists the CO₂ content in the standard samples and measured values using CM150. Table 4 shows the comparison of NH₃ content between the standard samples and measured values using the titration method. Generally the measured values of both CO₂ and ammonia contents agree reasonably well with the standard samples. The measured values are slightly lower than the expected values most likely because of the volatile nature of the samples. Both ammonia and CO₂ will desorb in the open environment during measurement, resulting in loss of a small portion of ammonia and CO₂. Further improvement on the analysis of CO₂ and ammonia contents should consider minimisation of their loss during measurement.

Table 3 Comparison of CO₂ content between standard and measured values using CM150

Sample	CO ₂ contents in standard samples (mg/g solution)	Measured CO ₂ contents (mg/g solution)	Deviation, %
Sodium carbonate solution	65.0	65.2	0.31
7 wt% NH ₃ , CO ₂ loading 0.5	90.4	83.6	-7.6
3 wt% NH ₃ , CO ₂ loading 0.5	38.8	37.9	-2.3
1 wt% NH ₃ , CO ₂ loading 0.5	12.9	12.7	-1.6

Table 4 Comparison of NH₃ content between standard and measured values using the titration method

Sample	Sample Mass (g)	NH ₃ content in standard samples(wt%)	NH ₃ content measured (wt%)	Deviation (%)
10% NH ₄ HCO ₃ solution	1.0052	2.1	2.07	-1.43
1% NH ₄ HCO ₃ solution	4.0197	0.21	0.19	-9.52
0.1% NH ₄ HCO ₃ solution	6.005	0.021	0.02	-4.76
3% NH ₃ solution, Loading 0.5	2.0113	3.0	2.83	-5.67

2 Establish the framework for the rate based model and compare the modelling work with pilot plant results

2.1 Validation of thermodynamic and transport model

Figure 4 compares the predicted CO₂ and NH₃ partial pressures and the measured results at various ammonia and CO₂ molalities (mol/kg H₂O) at 20 °C (van Krevelen et al. 1949). These conditions are close to the experimental conditions used in the pilot plant absorber. In general, there is a good agreement between the model's prediction and the experimental results. A notable deviation is observed at higher NH₃ and CO₂ molalities (Figure 4b), perhaps caused by the imperfect interactions parameters regression from the published experimental vapour–liquid equilibrium data. Considering that the CO₂ loadings used in the pilot plant tests were below 0.6 (molar ratio of CO₂/NH₃), the effect of the deviation on the modeling results is expected to be small.

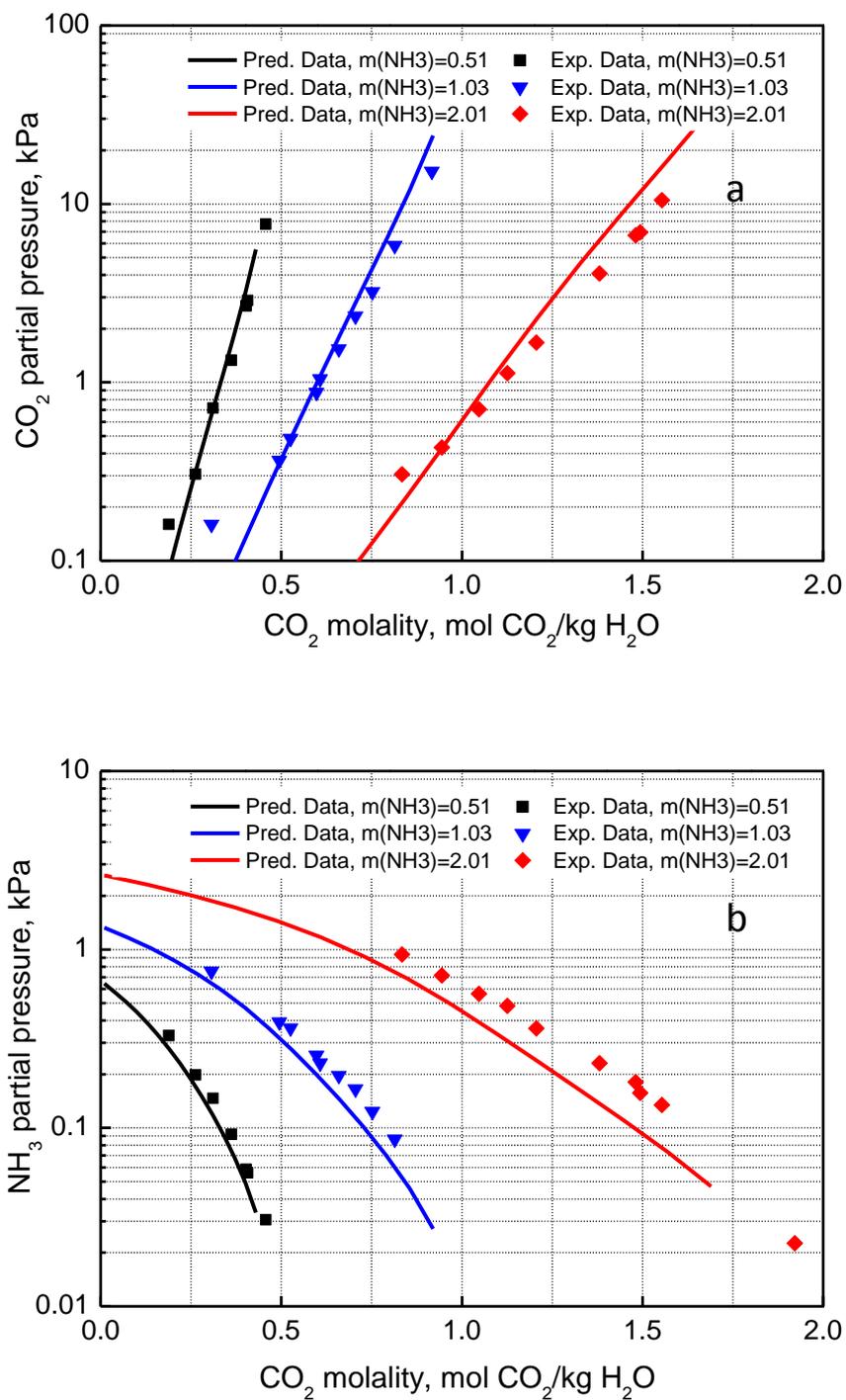


Figure 4 Comparison of predicted (a) CO₂ and (b) NH₃ partial pressure and experimental data (symbols) from Krevelen et al. (1949) as a function of CO₂ molality in the NH₃-CO₂-H₂O system at 20 °C

The predicted speciation data were compared to the experimental results in the temperature range 40–120 °C (Lichtfers, 2000). Figure 5 shows the predicted and experimental speciation profiles at a NH_3 molality of 6.3 mol/kg H_2O and temperature of 40 °C. The model’s prediction agrees very well with the experimental measurements.

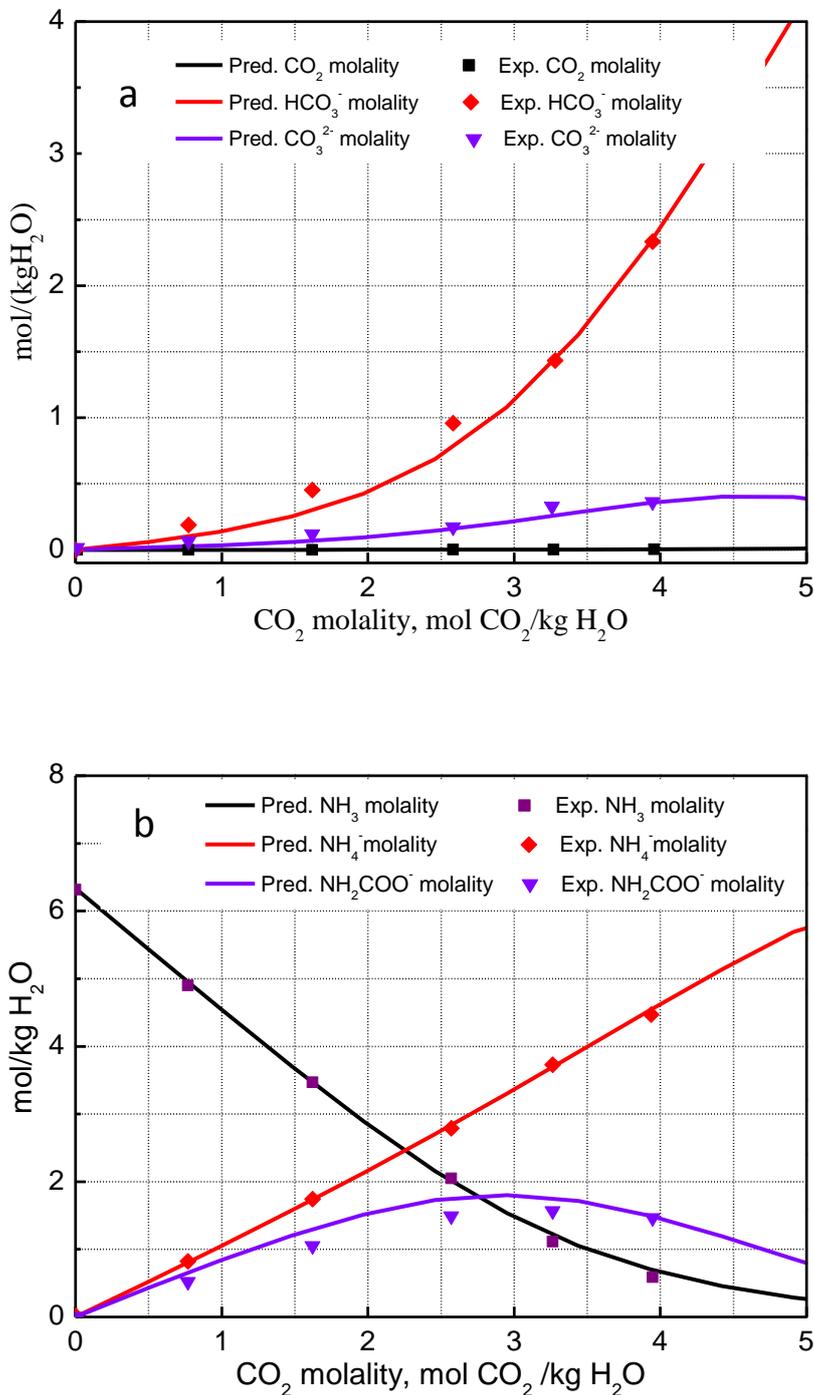


Figure 5 Comparison of predicted (a) CO_2 -containing and (b) ammonia-containing speciation and experimental data (symbols) from Lichtfers (2000) as a function of CO_2 molality in the NH_3 - CO_2 - H_2O system with 6.3 mol NH_3 /kg H_2O at 40 °C

The heat of CO₂ absorption results were compared with the experimental calorimetric data measured using a reaction calorimeter by Qin et al. (2011). The experimental data are differential in temperature and semi-differential in loading. Figure 6 shows that the predicted enthalpies of CO₂ absorption are in a good agreement with the experimental data at 40 °C. A relatively large deviation occurs at loadings below 0.2. This is possibly caused by the calculation accuracy of the van't Hoff equation, whose disadvantages were discussed by Kim et al. (2009). In addition, the uncertainties in the experimental measurement are not clear. It is also likely that experimental errors at low CO₂ loadings contribute to the deviations. The main contribution to the heat of absorption comes from the reaction of ammonia protonation and carbamate formation, which are proportional to the concentrations of the respective species in the mixture. Figure 5 shows that with an increase in CO₂ loading, the fraction of bicarbonate in the mixture increases, while that of carbamate decreases. We therefore would expect that the enthalpies of CO₂ absorption decrease. However, the experimental result shows little change or even an increase at low CO₂ loadings.

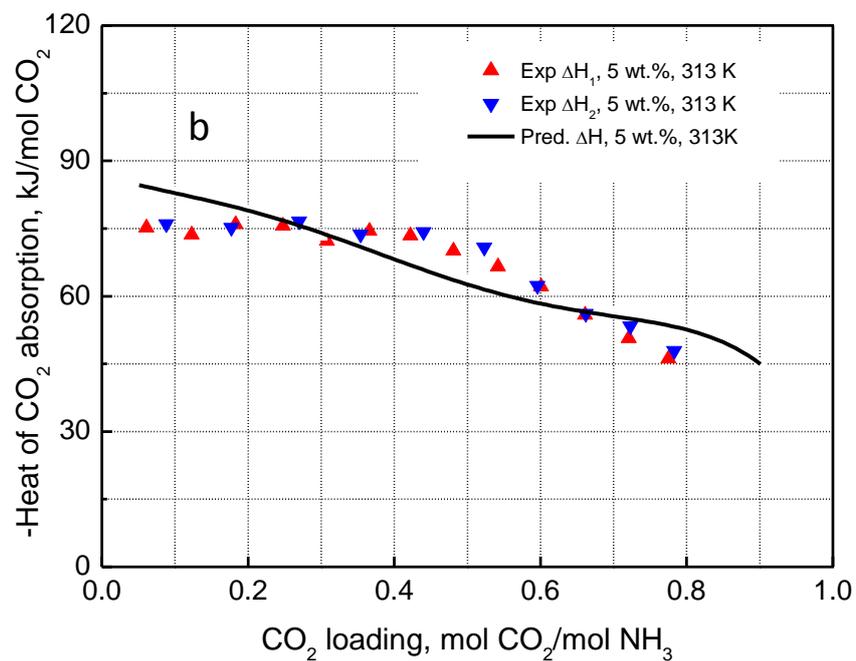
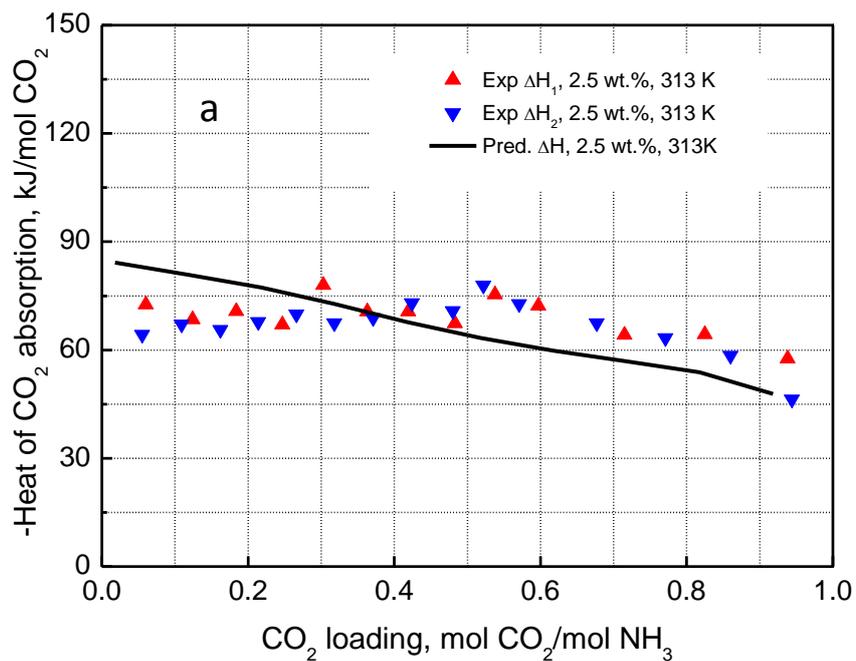


Figure 6 Comparison of predicted heat of CO₂ absorption and experimental data (symbols) from Qin et al. (2011) as a function of CO₂ loading in the NH₃-CO₂-H₂O system at (a) 40 °C, 2.5wt% NH₃ and (b) 40 °C, 5wt% NH₃

Figure 7 compares (a) the predicted solvent density data with the experimental results from Pleskov and Igamberdyev (1939), King et al. (1930) and Rice et al. (1928); (b) the predicted viscosity results and the experimental results of Pleskov and Igamberdyev (1939) and Frank et al. (1996); and (c) the surface tension prediction results and those obtained experimentally by King et al. (1930) and Rice et al. (1928). The model can satisfactorily predict these properties at the low ammonia concentrations relevant to the pilot plant trials.

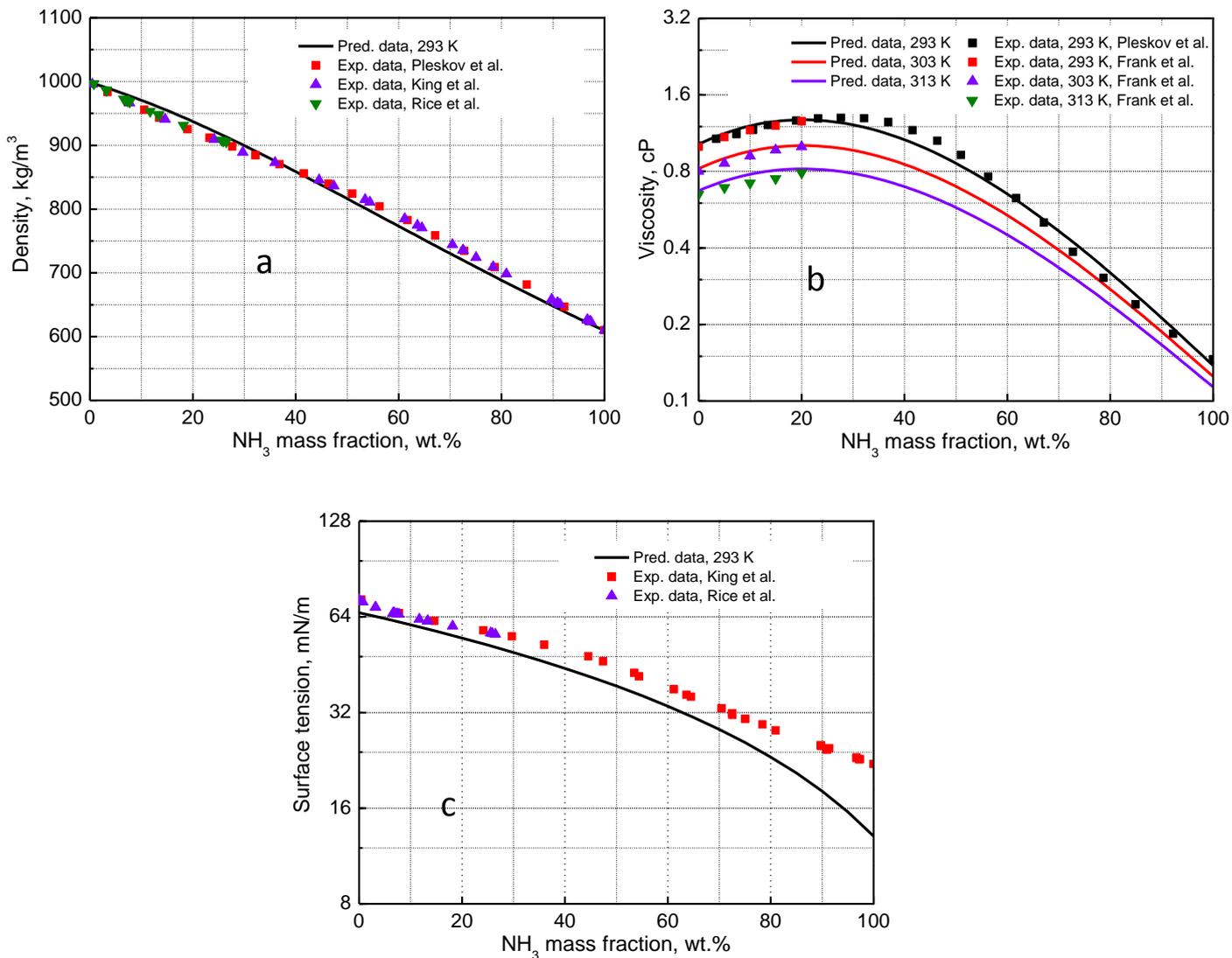


Figure 7 Comparison of predicted transport properties of aqueous ammonia and experimental data (symbols) as a function of NH₃ mass fraction: (a) density; (b) viscosity; and (c) surface tension

3.2 Validation of absorber model- comparison of CO₂ absorption rate

The rate-based model specifications and simulation results based on the pilot plant trials are summarised in Table 1, along with the experimental results of the pilot plant absorber performance.

CO₂ absorption rates based on the gas analysis are generally higher than those based on the liquid analysis. This is because the liquid samples were analysed offline, and it is likely that a small portion of CO₂

was lost during sample collection and measurement. So we use the CO₂ absorption rate based on the gas analysis to compare with the model prediction. As shown in Table 1, the predicted CO₂ absorption rates agree well with the experimental values for selected experiments, suggesting that the rate based model implemented is valid and promising. The work is underway to validate the model with more experimental results from pilot plant trials.

Table 1 Summary of rate-based model predictions and some of pilot plant trials results conducted under a variety of experimental conditions

Test ID	30	31	31R	31B
NH ₃ weight percentage, wt%	4.91	4.08	4.21	3.80
CO ₂ loading of lean solvent	0.240	0.240	0.229	0.250
Flue gas flow rate, kg/hr	646	646	632	750
CO ₂ volume concentration in flue gas, vol%	8.624	9.395	9.765	7.583
NH ₃ volume concentration in flue gas, vol %	0.521	0.433	0.473	0.211
H ₂ O volume concentration in flue gas, vol %	2.213	3.217	3.043	1.391
Liquid flow rate, L/min	134	134	134	134
Absorber 1 gas inlet temperature, °C	21.81	27.99	30.02	16.61
Absorber 2 liquid inlet temperature, °C	23.89	26.98	32.28	16.38
Cooler outlet temperature, °C	23.10	26.65	31.41	15.27
Absorbers operation pressure, bar	1	1	1	1
Exp. CO ₂ loading (rich ^b), mol CO ₂ / mol NH ₃	0.296	0.345	0.319	0.332
Pred. CO ₂ loading(rich), mol CO ₂ / mol NH ₃	0.315	0.336	0.331	0.331
Exp.CO ₂ absorption rate (overall, gas analysis) ^c , kg/hr	66.6	79.6	77.7	68.2
Pred. CO ₂ absorption rate (overall, rate-based), kg/hr	70.9	76.3	80.1	61.0

3 Carry out the wetted wall column screening experiments and identify promoters for stopped flow reactor study

Our previous study has suggested that aqueous solutions of additives with high CO₂ mass transfer coefficients generally had even higher mass transfer coefficients when mixed with ammonia. Based on this, we have tested a number of new additives (shown in Table 2) which can react with CO₂ at fast rates. Figure 8 shows the mass transfer coefficients for CO₂ in NH₃ (3 M), additive only (0.3 M), and 0.3 M

additive + 3 M NH₃, with zero CO₂ loading. For the comparison purpose, the results for PZ, 4-PD and SAR are also included. In terms of promotion effect, the additives increase mass transfer coefficients of CO₂ in aqueous ammonia at zero loading according to the following order

PZ > 4-PD ~ PRO > SAR ~ 2-PZ ~ BZ > DAP ~ EDA > DAH ~ ASP ~ ALA

Apart from PZ, 4-PD and sarcosine which were identified as the effective promoters in our previous study (Yu, 2012), L-proline has a high potential of enhancing CO₂ absorption in aqueous ammonia. Considering that the prices of 4-PD is high, the following wetted wall study will focus on PZ, sarcosine and L-proline and investigate the effect of amount of additives, CO₂ loading, absorption temperature on the mass transfer coefficients of CO₂ in aqueous ammonia. The kinetics of the reactions of CO₂ with mixture of ammonia with additives (PZ, sarcosine and L-proline) will be investigated on a stopped flow reactor facility, available at the University of Newcastle, to understand the promotion mechanism.

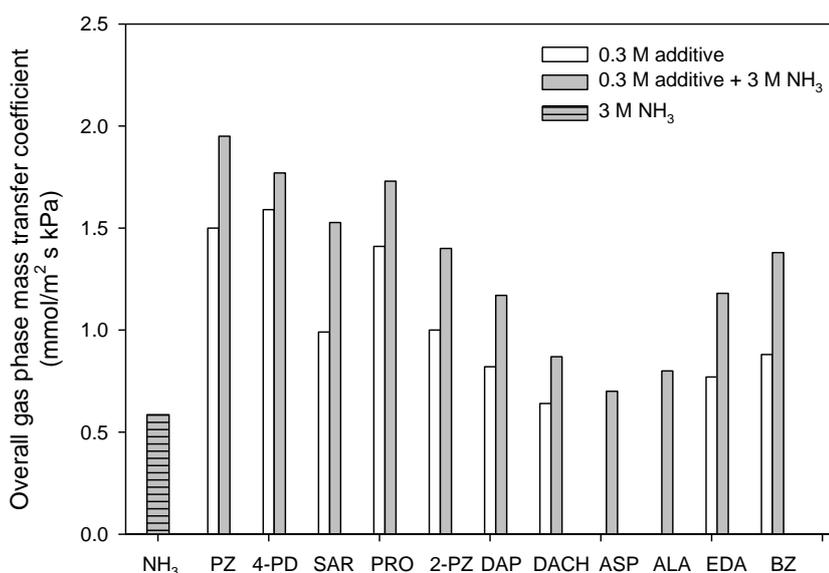


Figure 8 Mass transfer coefficients for CO₂ at an absorption temperature of 15 °C in NH₃ (3 M), additive only (0.3 M), and 0.3 M additive + 3 M NH₃. PZ: piperazine, 4-PD: 4 amino piperidine, SAR: sarcosine, PRO: proline, 2-PZ: 2-methyl piperazine, DAP: 1,3-diaminopropane, DACH: trans-1,4-diaminocyclohexane, ASP: L-asparagine, ALA: β-alanine, EDA: ethylenediame, BZ: benzylamine.

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6 Status of Milestones

Date Due	Description	ANLEC Funding (\$)	Status
15/06/2012	Contract signing	\$ 212,630	Complete
30/03/2013	<p>Completion of recruitment of PhD students and research project officer</p> <p>Delivery of a progress report approved by ANLEC R&D which shows the following:</p> <p>(1) Results have been generated from wetted wall column screening experiments and promoters for stopped flow reactor experiments have been identified.</p> <p>(2) The framework for the rate based model has been established and the comparison between the modelling work and pilot plant results has been made.</p> <p>(3) Analytic methods for gas and liquid analysis have been established.</p>	\$ 68,042	<p>Complete</p> <p>PhD student Lichun Li from University of Newcastle and Research Assistant Hung Nam Vo from Curtin University of Technology are working on the project. This report</p>
30/09/2013	<p>Completion of experiments for screening promoters and optimisation of solvent formulation on wetted wall column</p> <p>Delivery of a progress and technical report approved by ANLEC R&D which includes:</p> <p>(1) Status of the research activities and milestone</p> <p>(2) Approaches and methodologies used in the screening experiments</p> <p>(3) Results obtained</p> <p>(4) Evidence that the following has been achieved:</p> <p>a. The new aqueous ammonia based solvent can absorb CO₂ as least 2 times as fast as the solvent based on aqueous ammonia alone</p> <p>Delivery of an industry report approved by ANLEC R&D which includes a description of:</p> <p>(1) Recent advancement of solvent development for post combustion capture including aqueous ammonia around the world</p> <p>(2) Results from this research project</p> <p>(3) The impact of research achievements from this project on the advancement of aqueous ammonia based PCC processes for application in Australia</p>	\$ 68,042	Not yet started
31/03/2014	<p>Completion of experiments on stopped flow reactor</p> <p>Delivery of a progress and technical report approved by ANLEC R&D which includes:</p> <p>(1) Status of the research activities and milestones</p> <p>(2) Approaches and methodologies used in the stopped flow reactor experiments</p> <p>(3) Results from stopped flow reactor experiments and discussion</p>	\$ 59,537	Not yet started
30/09/2014	<p>Completion of process modelling for elucidation of promotion mechanism and completion of SO₂ and NH₃ absorption experiments</p> <p>Delivery of a progress and technical report approved</p>	\$ 59,537	Not yet started

by ANLEC R&D which includes:

- (1) Status of the research activities and milestone
- (2) Approaches and methodologies used in the process modelling and SO₂ and NH₃ absorption experiments
- (3) Results obtained
- (4) Evidence that the following has been achieved:
 - a. Develop a novel aqueous ammonia based solvent which can achieve a CO₂ absorption rate that can match the standard MEA based solvent
 - b. Develop a rigorous rate based model for the aqueous ammonia based CO₂ capture process and validate the model with results from previous pilot plant trials
 - c. Achieve the combined removal of SO₂ and recovery of ammonia and eliminate additional flue gas desulfurization. This includes:
 - Identification and validation of experimental conditions under which SO₂ in the flue gas is selectively removed in preference to CO₂ by ammonia (flue gas pre-treatment). More than 90% of SO₂ will be removed in the pre-treatment stage in which CO₂ removal is negligible.
 - Ammonia in the flue gas can be reduced to an acceptable level by SO₂ solution (flue gas post-treatment).

Delivery of an industry report approved by ANLEC R&D which includes a description of:

- (1) Recent advancement of solvent development for post combustion capture including aqueous ammonia
- (2) Summary of results obtained from this research project
- (3) Impact of the research achievements from this project on the advancement of aqueous ammonia based PCC processes for application in Australia

31/03/2015	Completion of high pressure experiments. Delivery of a progress and technical report approved by ANLEC R&D which includes: (1) Status of the research activities and milestone (2) Approaches and methodologies used in the high pressure experiments (3) Results obtained	\$ 59,537	Ongoing 10% complete
31/08/2015	Submit Draft of Final Report to ANLEC R&D for review	\$ 68,042	Not yet started
30/09/2015	Completion of process modification, evaluation and demonstration of advanced ammonia technology; Completion of development of rigorous process development and delivery of scale up design. Final Report submitted as acceptable to ANLEC R&D Delivery of an industry report which includes a description of:	\$ 255,157	Not yet started

- (1) Recent advancement of solvent development for post combustion capture including aqueous ammonia
 - (2) Summary of results obtained from this research project
 - (3) Impact of the research achievements from this project on the advancement of aqueous ammonia based PCC processes for application in Australia
 - (4) Evaluation of technical and economic feasibility for application of the improved process developed from this project
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7 Conclusions

The project has made a good progress and has completed three activities listed in the reporting period. The project is on track to achieve next milestones.

Analytic methods for the determination of ammonia and CO₂ contents in the solvents and gas composition have been established and confirmed to be adequate. The measured CO₂ and ammonia contents in the solvents are slightly lower than the actual values most likely due to desorption of CO₂ and ammonia during measurement. Further improvement on the liquid analysis should minimise CO₂ and ammonia loss during measurement.

The framework for a rigorous rate-based model for CO₂ absorption using aqueous ammonia in a packed column has been established and the rate-based model was developed and used to simulate results from pilot plant trial of an aqueous ammonia-based post-combustion process at the Munmorah Power Station, New South Wales. The model is based on RateSep module, a rate-based absorption and stripping unit operation model in Aspen Plus, and uses the available thermodynamic, kinetic and transport property models for the NH₃-CO₂-H₂O system to predict the performance of CO₂ capture. The thermodynamic and transport property models satisfactorily predict experimental results from the published literature. The modelling results from the rate-based model also agree reasonably well with selected pilot plant results on CO₂ absorption rate.

The project investigated the effect of eight new additives as potential promoters of CO₂ absorption in aqueous ammonia. The additives were 2-methyl piperazine, 1,3-Diaminopropane, Ethylenediame, Benzylamine, trans-1,4-Diaminocyclohexane, the potassium salts of three amino acids: L-proline, L-Asparagine and β-alanine. CO₂ mass transfer coefficients increased to different extents in the presence of different additives. L-proline potassium salt promoted CO₂ absorption in aqueous NH₃ to a greater extent than the other additives. The kinetics of the reactions of CO₂ with mixture of ammonia with PZ, sarcosine and L-proline will be investigated on a stopped flow reactor facility to understand the promotion mechanism.

8 Future work

In the next 6 months, we will carry out the following work

- Validation of the rate based model using the previous pilot plant results
- Ongoing solvent formulation and wetted wall column experiments to develop the aqueous ammonia based solvent which absorb CO₂ as least 2 times as fast as the solvent based on aqueous ammonia alone
- Stopped flow kinetic study of the reaction of CO₂ with ammonia in the presence of selected additives to understand the promotion mechanism for CO₂ absorption in aqueous ammonia by additives
- Setting up the research facility for the SO₂ and NH₃ absorption experiments