Development of an Aqueous Ammonia Based PCC Technology for Australian Conditions

Process modelling of combined SO$_2$ and CO$_2$ capture using aqueous ammonia

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# Executive Summary

This research project focuses on the development of the advanced aqueous ammonia (NH₃) 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. 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 (NOₓ) 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 a $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, 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 4.
A rigorous rate-based model for the system of NH₃-CO₂-SO₂-H₂O was developed in Aspen Plus® and validated by the experimental results from open literature and pilot plant trials at Munmorah Power Station. The model can satisfactorily predict the CO₂ absorption, CO₂ desorption and SO₂ removal in packed columns.

We have proposed a novel and effective process for the combined SO₂ removal and ammonia recycle, which can be integrated with the aqueous ammonia based CO₂ capture process to achieve flue gas cooling, SO₂ and CO₂ removal and ammonia recycle simultaneously in one process. The process simulation using the rate-based model showed that under the typical flue gas conditions, the proposed process has a SO₂ removal efficiency of over 99.9% and an ammonia reuse efficiency of 99.9%. The novel process can not only simplify the flue gas desulfurization, but also resolve the problems of ammonia loss and SO₂ removal, thus holding the potential of cutting the CO₂ capture costs significantly. The separate experiments on SO₂ and ammonia absorption using a bubble column were carried out to further evaluate the technical feasibility of the combined process. The experimental results qualitatively confirmed the simulated results and the technical feasibility of the process.

The amino acid salts studied in this work can significantly enhance CO₂ absorption in aqueous ammonia at low CO₂ loadings but their role in promotion of CO₂ absorption rate becomes much smaller with an increase in CO₂ loading. The mass transfer coefficients of CO₂ in amino acid salts and ammonia mixtures are close to those in MEA but generally lower under the conditions studied. In comparison, ammonia mixed with piperazine or 2-methyl piperazine can achieve mass transfer coefficients higher than those in MEA.

In an attempt to develop a rate-based model for the promoted ammonia solvents which is not available in Aspen Plus, we used an in-house software tool implemented in the Matlab® to model the mass transfer of CO₂ in the ammonia and piperazine mixtures in a wetted wall column. The software tool incorporates the reaction kinetic model developed from stopped flow kinetic study and solves partial differential equations and nonlinear simultaneous equations that define the diffusion, reaction and equilibrium processes occurring in a thin liquid film. It has been found that both calculated and experimental mass transfer coefficients increases with the concentration of piperazine added to the blended ammonia/piperazine solutions with constant ammonia and CO₂ concentrations in solutions. However, the calculated values underestimate the measured values by a relative error of approximately 30-40%. Further investigation is required to understand the reasons for the discrepancy and improve the mass transfer simulations.

The milestones of the project for the report period have been achieved and the project is on track to achieve the milestones which are due on 30 March 2015.
2 Recent Advancement of Solvent Development for Post-Combustion Capture

Post combustion capture (PCC) is a process that uses an aqueous absorption liquid incorporating compounds such as ammonia or amine to capture CO$_2$ from power station flue gases and many other industrial sources. It is the leading capture technology as a result of the potential benefits, such as,

- It can be retrofitted to existing power plants or integrated with new infrastructure to achieve a range of CO$_2$ reductions, from partial retrofit to full capture capacity;
- It has a lower technology risk compared with other competing technologies;
- Renewable technologies can be integrated with PCC, for example, low cost solar thermal collectors can provide the heat required to separate CO$_2$ from solvents;
- PCC can be used to capture CO$_2$ from a range of sources – smelters, kilns and steel works, as well as coal- and gas-fired power stations.

Currently, the commercially available PCC technology is mainly based on alkanol/alkyl amine solutions. A study by Dave et al. shows that retrofitting a monoethanolamine (MEA) based PCC plant to the existing/new mechanical draft water cooled black coal fired plants will reduce the power plant efficiency by 10 absolute percentage points and involves significant capital investment costs (Dave et al., 2011). The research work has been intensified in recent years to improve the existing solvents or developed novel solvents to reduce the capital and running costs of the PCC technologies. The report from Global CCS institute summaries the status of near term PCC technologies up to Jan 2012 (Global CCS Institute, 2012). This report provides an update on the recent development of these near term technologies.

<table>
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<tr>
<th>Technology provider</th>
<th>Solvent</th>
<th>Comments</th>
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<tbody>
<tr>
<td>Cansolv</td>
<td>Cansolv chemical solvents</td>
<td>As part of a retrofit of SaskPower’s Boundary Dam 3 unit, a post combustion carbon dioxide (CO$_2$) capture facility based on Cansolv chemical solvent will be installed to capture up to 1 million metric tons per annum (Mtpa) of CO$_2$. Captured CO$_2$ in excess of that to be delivered to oil fields for enhanced oil recovery will be injected into a deep saline formation as part of the Aquistore Project. Mechanical completion of the carbon capture facilities was in December 2013 with commissioning activities beginning thereafter. The completion of the power plant refurbishment occurred in the second quarter of 2014. Overall operation of the Demonstration Project is planned for late in the second quarter or early third quarter of 2014 (Boundary dam, 2014). In addition, Cansolv has recently developed a new solvent, DC-201. Pilot plant trials showed the new solvent can achieve a reduction of regeneration energy consumption by 35% compared to MEA. The new solvent will be tested in Cansolv SO$_2$ CO$_2$ Demonstrated Plant in Wales, UK (Just, 2013).</td>
</tr>
<tr>
<td>Fluor</td>
<td>Econamine FG Plus</td>
<td>Fluor’s Econamine FG Plus$^\text{SM}$ technology is claimed to reduce steam consumption by over 30% compared to ‘generic’ MEA technology and has been used in more than 25 commercial plants for the recovery of CO$_2$ from</td>
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<tr>
<td>Company</td>
<td>Technology/Process</td>
<td>Details</td>
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<tr>
<td>MHI</td>
<td>KS-1 sterically hindered amine solvent</td>
<td>MHI KM-CDR process was employed in the world’s first integrated CCS project for flue gas from a coal-fired power plant. The CO₂ capture facility, which was built jointly by MHI and Southern Company, is the world’s largest in scale and is able to capture 500 metric tons per day, with CO₂ recovery efficiency above 90%. (Hirata et al., 2013). The captured and compressed CO₂ has been injected since August, 2012. As of October 2013 the plant had operated for a cumulative 10,600 hrs and during that time achieved 198,000 tonnes of CO₂ captured and 101,700 tons of CO₂ stored (Hirata, 2014). NRG Energy and JX Nippon Oil &amp; Gas Exploration are jointly carrying out Petra Nova Carbon Capture Project at W.A. Parish power plant at Thompsons, near Houston, Texas. The WA Parish project will utilize the KM-CDR Process and uses a proprietary KS-1 high-performance solvent for the CO₂ absorption and desorption. The CO₂ capture capacity is 1.4 million tonnes per annum. The plant is expected to be operational in 2016. (Petra Nova, 2014) MHI claims that KM-CDR circulation rate is 60% of that for (unspecified) MEA, regeneration energy is 68% of MEA, and solvent loss and degradation are 10% of MEA. MHI is working on process improvements that are said to have potential to reduce the regeneration heat requirement to 1860 kJ/kg CO₂ from 2790 kJ/kg CO₂ (Global CCS Institute, 2012).</td>
</tr>
<tr>
<td>Alstom Power</td>
<td>Aqueous ammonia</td>
<td>Alstom conducted a number of field tests of chilled ammonia process (CAP) and completed the demonstration project at American Electric Power’s Mountaineer Plant at end of May 2011 after a 21 month period. The results shows the heat requirement of 2.2 MJ/kg CO₂ captured for the chilled ammonia process (Jönsson and Telikapalli, 2012). Gassnova awarded Alstom a concept study for a full-scale CO₂ capture plant to be located at Mongstad near Bergen, Norway. The Alstom test plant recently commissioned at TCM continues the overall validation programme for CAP. CAP operation at TCM tuning first results is: CO₂ capture rates from 80% to as high as 87%, CO₂ purity of greater than 99.9%, low NH₃ emissions (Lombardo G., 2014).</td>
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<tr>
<td>Alstom Power</td>
<td>Advanced amine solvent</td>
<td>Dow Oil &amp; Gas and Alstom are jointly developing advanced amine process (AAP) technology that utilizes UCARSO™ FGC 3000, an advanced amine solvent from Dow, in combination with advanced flow schemes to provide a cost-effective post-combustion, carbon capture technology for application in power plants worldwide. The carbon capture demonstration plant was located at the EDF thermal power plant in Le Havre, France, and captured its first tonne of CO₂ in July 2013. The test programme was completed in March 2014. The technology has successfully been demonstrated in the field at &gt; 99.9% pure CO₂ product quality at 90% capture rates. The AAP design has been optimized for emissions mitigation and control and has less solvent degradation as compared to Monoethanolamine (MEA) solvent (Baburao, 2014).</td>
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| Babcock & Wilcox  | OptiCap™                                    | Babcock & Wilcox Power Generation Group, Inc. (B&W PGG) completed a three months test campaign from September 2011 to December 2011 using OptiCap solvent. The test run spanned approximately 2,000 hours. The OptiCap solvent has many benefits including low corrosivity, low regeneration energy, and an expected high resistance to solvent degradation.
The lowest OptiCap regeneration energy measured was 2.55 MJ/Kg CO$_2$. In addition, it offers the ability to operate the capture process at elevated pressures due to its thermal stability, which will have a significant favourable impact on mechanical compression energy (Gayheart, 2013).

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<th>Aker Clean carbon (ACC)</th>
<th>ACC proprietary solvents</th>
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<td>ACC has been testing its solvent on the CO$_2$ technology Centre Mongstad since 2012. The test campaigns have shown that ACC advanced solvents S21 and S26 show good energy performance and are superior to 30 wt% MEA with respect to solvent degradation, ammonia emission and nitrosamine formation. For example, the reboiler duty for solvents S21 and S26 was found to be approximately 10% lower than that for MEA. Solvent amine losses have been quantified to approximately 2.6 kg amine/ton CO$_2$ captured for MEA, 0.5-0.6 kg amine/ton CO$_2$ captured for ACCTM advanced solvent S21, and 0.2-0.3 kg amine/ton CO$_2$ captured for ACCTM advanced solvent S26 (Gorset, 2014).</td>
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In addition to further development of the near term technologies, intensive research work has been carried out to develop novel solvents. The focus of these researchers is primarily on increase in absorption capacity and reduction of energy consumption of the solvents. These novel solvents include ionic liquids, enzyme catalysed solvents, and phase change solvents. The novel solvents mentioned above are still at the early stage development and have not been tested in the pilot plant under the real flue gas conditions.

References


Gorset, O., et al., 2014. Results from testing of Aker Solutions advanced amine solvents at CO$_2$ Technology Centre Mongstad, to be presented in the 12nd International Conference on Greenhouse Gas Control Technologies (GHGT 12).


PCC is one of the leading capture technologies for significant reduction of \( \text{CO}_2 \) 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 \( \text{CO}_2 \) 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 \( \text{CO}_2 \) 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 (Figure 1 a). As shown in Figure 1b, the significant increase is due to increase in capital (plant cost), fuel, O&M and \( \text{CO}_2 \) 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 \( \text{CO}_2 \) 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 \( \text{CO}_2 \) capture and compression facilities.

![Figure 1](image.png)

Figure 1 (a) Levelised cost of electricity (LCOE) for a new plant with and without CCS; (b) Incremental LCOE with the amine based CCS (The results are derived from (a)). The estimated incremental LCOE with the advanced ammonia based CCS is also included in (b) to demonstrate the potential benefits from using ammonia based CCS. The estimation is made in this work and based on assumption that the expected advancements for ammonia CCS can be achieved.

The advanced amine solvent has poor \( \text{SO}_x \) tolerance which requires a deep cut in \( \text{SO}_2 \) 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 CO\textsubscript{2} removal and compression is $888 M AUD while capital increase due to clean up costs (installation of FGD) is $90 M AUD (EPRI, 2010). FGD alone will count for more than 9% of the increased capital costs.

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. The low energy consumption means the use of less coal and treatment of less gas, which results in a smaller facility, and has 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 CO\textsubscript{2} 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 O\textsubscript{2} 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 CO\textsubscript{2} removal capacity and a low regeneration energy. It also has the potential of capturing multiple components (NO\textsubscript{x}, SO\textsubscript{x}, CO\textsubscript{2} 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\textsubscript{x} are not implemented in Australia. It has been estimated by Powerspan (McLarnon, 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. It has to be pointed out that these reports assumed the availability of low temperature cooling water for solvent and flue gas cooling and recovery of ammonia. In Australia where ambient temperature is generally high, the energy consumption for production of low temperature cooling water is expected to be high, thus partially offsetting the energy saving from the solvent regeneration.

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 $7 M 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 CO\textsubscript{2} removal efficiency (more than 85%) and production of high purity of CO\textsubscript{2} (99-100 vol%), and effectiveness of the combined SO\textsubscript{2} 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 CO$_2$ 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 CO$_2$ 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.

References


4 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 \( N_{\text{CO}_2} = K_G A (P_{\text{CO}_2} - P^*_{\text{CO}_2}) \), where \( N_{\text{CO}_2} \) is CO₂ absorption flux, \( K_G \) mass transfer coefficient, \( P_{\text{CO}_2} \) partial pressure of CO₂ in the flue gas, \( P^*_{\text{CO}_2} \) 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 \( (P_{\text{CO}_2} - P^*_{\text{CO}_2}) \), 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 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 higher 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 and 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 (Saleem, 1993). 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 years and divided into six stages with each stage being approximately 6 months. This report includes the results from the following research activities in Stage 4:

1. Development and validation of a rate-based model for the system of \(\text{NH}_3\)-\(\text{CO}_2\)-\(\text{SO}_2\)-\(\text{H}_2\text{O}\) using Aspen Plus.
2. Process modelling of a combined \(\text{SO}_2\) removal and \(\text{NH}_3\) recycle process. \(\text{SO}_2\) and \(\text{NH}_3\) absorption experiments on a bubble column were carried out to qualitatively confirm the modelling results.
3. Development of ammonia-based solvents which can match the standard MEA-based solvents in terms of \(\text{CO}_2\) absorption rate.
4. Modelling of \(\text{CO}_2\) absorption in piperazine promoted \(\text{NH}_3\) solutions in a wetted wall column. This is the extension of the work on the elucidation of promotion mechanism reported in the last progress report.

References


5 Approaches and Methodologies

This section describes the approaches and methodologies used for the following research activities:

(a) Development and validation of a rate-based model for the system of NH₃-CO₂-SO₂-H₂O using Aspen Plus
(b) Process modelling of a combined SO₂ removal and NH₃ recycle process using the developed rate-based model
(c) SO₂ and NH₃ absorption experiments on a bubble column to qualitatively validate the modelling results
(d) Modelling of CO₂ absorption in piperazine/ammonia mixture in a wetted wall column

5.1 Development of a rate-based model for the system of NH₃-CO₂-SO₂-H₂O

The rigorous rate-based process model is built within the RateFrac module in Aspen plus. The process model consists of a thermodynamic model, a transport model and a rate-based model. Thermodynamic model must be able to describe accurately the chemical equilibrium, vapour–liquid equilibrium, speciation and many other chemical and physical properties. The reliable transport model is required to calculate the density, viscosity, thermal conductivity, diffusion coefficient and surface tension of the electrolyte ammonia solvent. The rate-based model needs to completely characterise the material and energy balance, chemical kinetics, mass and heat transfer, hydrodynamics and column properties of the whole absorption and desorption system.

5.1.1 Thermodynamic and transport model

The Pitzer property method embedded in Aspen Plus is employed to calculate the chemical physical properties of the liquid phase including the fugacity coefficient, entropy, enthalpy and Gibbs energy, while the Redlich-Kwong-Soave equation of state is used to calculate the vapor phase fugacity coefficient. NH₃, CO₂, SO₂, N₂ and O₂ were defined as Henry components and the Henry’s law constants of these species were retrieved from Electrolytes Expert System in Aspen plus. The Pitzer parameters for the binary interactions in the NH₃-CO₂-H₂O system are regressed against the literature experimental data of vapor-liquid equilibrium, heat capacity, ion speciation, which are automatically retrieved from the Aspen Plus databank (Aspen Technology, 2010a and 2010b).

The electrolyte solution characteristics and the liquid-vapor behaviors of the NH₃-CO₂-SO₂-H₂O system were modeled with an equilibrium chemistry package. Table 2 list all the reactions included in the package and their corresponding equilibrium constants. The chemical equilibrium constants of these reactions are expressed as:

\[ \ln K_{eq} = A + B/T + C\ln(T) + DT \]

where \( K_{eq} \) is the equilibrium constant of each reaction; \( T \) is the temperature, \( K \); constants \( A, B, C, D \) were adjustable parameters. The parameters for reactions 1-10 are available in the Aspen databank (Aspen Technology, 2010b) and those for the reaction 2HSO₃⁻ <--> S₂O₅²⁻ + H₂O were obtained from Ermatchkov et al. (2005).
Transport properties are required when describing mass and heat transfer in the rate-based model for aqueous ammonia-based CO$_2$ capture. Various transport property models and corrections are embedded in Aspen Plus, and can be applied to calculate the density, viscosity, thermal conductivity, diffusion coefficient and surface tension of the NH$_3$–CO$_2$–SO$_2$–H$_2$O system. In this work, the liquid density of the electrolyte solutions is calculated using the Clarke model. 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. 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. The thermal conductivity is calculated by the Sato–Riedel and DIPPR models and the Vredeveld mixing rule, and adjusted using the Riedel model. The diffusivity of each species is determined using the Wilke–Chang model for molecular species and the Nernst–Hartley model for ions.

### 5.1.2 Rate-based model

The rate-based model embedded in the Aspen Plus RadFrac module is used to model CO$_2$ and SO$_2$ absorption in 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 absorption and desorption system.

The module allows users to divide the column into a number of stages along the column and perform material and energy balances at each stage, and integrate across the entire column. The model adopts the two-film theory and considers mass and heat transfer resistance in the liquid and gas phase (Whitman, 1923). The liquid film at each stage is discretised into several segments, as shown in Figure 2.
Figure 2 Schematic of discretised two-film model for the rate-based model in each stage

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/desorber column to be calculated. The rate-based model uses the Maxwell–Stefan theory to solve multi-component mass and heat transfer (Alopaeus, 1999).

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 et al. 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 operational conditions. Correlations from both Onda et al. (1999) and Billet and Schultes (1985) underpredict the effective interfacial area by approximately 20% and 40%, respectively, compared with the experimental results in the pilot plant. It is not clear why there are large discrepancies between the model prediction and the measurements. All correlations are empirically obtained and subject to the experimental conditions, packing materials used and the way how the materials are packed in the column. The pilot plant conditions are not exactly the same as those used for determination of the correlations. It is also possible that some pilot plant specific issues are responsible. But we were not able to determine which particular factor contributes most in the pilot plant campaigns. So we adopt a realistic approach: select the correlation from Onda et al. and set the interfacial area factor as a scaling factor for the effective interfacial area in the rate-based model 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 suitable for
random packing 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.

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 the 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 chemical reaction model for the NH$_3$-CO$_2$-SO$_2$-H$_2$O system includes the equilibrium reactions listed in Table 2 and those kinetically controlled reactions listed in Table 3. We assume that reactions of CO$_2$ with OH$^-$ and NH$_3$ are kinetically controlled. The power law expressions are used to express the kinetically-controlled reactions.

$$r = kT^n e^{-\frac{E}{RT}} \prod_{i=1}^{n} C_{i}^{a_i}$$

where $r$ is the rate of reaction; $k$ is the pre-exponential factor; $n$ is the temperature exponent which is chosen as zero for this simulation; $E$ is the activation energy; $R$ is the universal gas constant; $T$ is the absolute temperature; $C_i$ is the molarity concentration of component $i$; $a_i$ is the stoichiometric coefficient of component $i$ in the reaction equation. The kinetic parameters $k$ and $E$ for kinetic reactions in Table 3 are derived from the work of Pinsent et al. (1956a and b).

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Parameters</th>
<th>$K$</th>
<th>$E$(cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CO$_2$ + OH$^-$ --&gt; HCO$_3^-$</td>
<td>4.32e+13</td>
<td>13249</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>HCO$_3^-$ --&gt; CO$_2$ + OH$^-$</td>
<td>2.38e+17</td>
<td>29451</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>NH$_3$ + CO$_2$ + H$_2$O --&gt; NH$_2$COO$^-$ + H$_3$O$^+$</td>
<td>1.35e+11</td>
<td>11585</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>NH$_2$COO$^-$ + H$_3$O$^+$ --&gt; NH$_3$ + CO$_2$ + H$_2$O</td>
<td>4.75e+20</td>
<td>16529</td>
<td></td>
</tr>
</tbody>
</table>

5.1.3 Pilot plant tests on Munmorah pilot plant

The results obtained from Munmorah pilot plant were used for model validation. In 2008 -2010, CSIRO in collaboration with Delta Electricity designed, constructed and operated a pilot plant at Munmorah Power Station and tested the aqueous ammonia based capture process under real flue gas conditions. The objectives were to address the gap in know-how on application of aqueous ammonia for post-combustion capture of CO$_2$ and to provide high quality pilot plant results for process model development and subsequent process optimisation and assessment.

Figure 1 shows the simplified flow-sheet of the Munmorah pilot plant, which consists of one pretreatment column, two absorber columns each with a separate wash column at the top, and one stripper. The pretreatment column works as a direct contact cooler for the flue gas and also serves as a scrubber for removal of SO$_2$ in the flue gas. The two absorbers provide flexibility in operation with different arrangements (single column or two columns in series or parallel). In case of series operation, the solvent
enters absorber 2 first and then absorber 1. The columns used in the pilot plant are constructed of stainless steel pipe (grade 304) and randomly packed with 16 or 25 mm Pall rings (Rhine Ruhr Pty Ltd.) which have the volumetric surface area of 340 or 207 m$^2$/m$^3$. The diameter of the columns, their packing heights and packing materials are listed in Table 4.

![Figure 3 Simplified flowsheet of Munmorah pilot plant with operation of two columns in parallel](image)

Table 4 Inner diameters of columns and packing heights

<table>
<thead>
<tr>
<th>Columns</th>
<th>Diameter, mm</th>
<th>Packing height, m</th>
<th>Packing materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pretreatment column</td>
<td>500</td>
<td>3</td>
<td>25 mm Pall ring</td>
</tr>
<tr>
<td>Absorber$^a$</td>
<td>600</td>
<td>2 or 3.9 (one column alone)</td>
<td>25 mm Pall ring</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.8 or 7.8 (two columns in series)</td>
<td></td>
</tr>
<tr>
<td>Wash column</td>
<td>500</td>
<td>1.8</td>
<td>25 mm Pall ring</td>
</tr>
<tr>
<td>Stripper</td>
<td>400</td>
<td>3.9</td>
<td>16 mm Pall ring</td>
</tr>
</tbody>
</table>

$^a$ The column packing heights can be varied which allows investigation of the effect of packing height on CO$_2$ removal.

Table 5 Typical inlet flue gas composition

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$</th>
<th>H$_2$O</th>
<th>O$_2$</th>
<th>NO</th>
<th>NO$_2$</th>
<th>SO$_2$</th>
<th>N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8.5-12 vol%</td>
<td>3-6 vol%</td>
<td>6.5-10 vol%</td>
<td>200-330 ppm</td>
<td>&lt;10 ppm</td>
<td>190-280 ppm</td>
<td>76-78 vol%</td>
</tr>
</tbody>
</table>
Table 6 Summary of the experimental conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Operational range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia concentration, wt%</td>
<td>0-6</td>
</tr>
<tr>
<td>CO₂ loading of lean solvent (mole CO₂/mole ammonia)</td>
<td>0-0.6</td>
</tr>
<tr>
<td>Wash water flow-rate, L/min</td>
<td>39</td>
</tr>
<tr>
<td>Liquid temperature in pretreatment and wash columns, °C</td>
<td>10-15</td>
</tr>
<tr>
<td>Solvent flow-rate, L/min</td>
<td>50-134</td>
</tr>
<tr>
<td>Gas flow-rate, kg/h</td>
<td>650-1000</td>
</tr>
<tr>
<td>Liquid temperature in absorber, °C</td>
<td>10-30</td>
</tr>
<tr>
<td>Gas pressure in absorber (absolute), kPa</td>
<td>101-150</td>
</tr>
<tr>
<td>Stripper bottom liquid temperature, °C</td>
<td>90-150</td>
</tr>
<tr>
<td>Stripper pressure (absolute), kPa</td>
<td>300-850</td>
</tr>
</tbody>
</table>

The detailed pilot trials have been described elsewhere (Yu, 2011 and 2012).

SO₂ removal experiments

Apart from CO₂ absorption and regeneration tests described above, an NH₃ dosing experiment was designed and carried out in the pilot plant to understand the characteristics of SO₂ removal by NH₃ and collect additional results for the model validation. The experiment was performed in the pretreatment column. The flue gas was introduced to the bottom of the column initially without liquid circulation. About 40 minutes after the introduction of flue gas, fresh water was introduced to the column from the top and circulated between the column and the wash water tank. The NH₃ was dosed into the wash water at different flow rates to investigate the effect of the NH₃ concentration in the solution on SO₂ removal. A Gasmet™ analyzer (FTIR) (CX-4000) allowed online identification and quantification of gas species including CO₂, SO₂, NH₃ and H₂O in the flue gas at the inlet and outlet of the pretreatment column. pH of the solution at the outlet of the pretreatment column was measured online using an industrial pH meter (Rosemount). The detailed experimental activities and observations during the NH₃ dosing experiment are listed in Table 7.
Table 7 Experimental activities and observations in the SO$_2$ removal experiment. Flue gas flow-rate = 936 kg/h, CO$_2$ flow-rate = 120 kg/h, SO$_2$ concentration = ca. 200 ppmv, liquid flow-rate = 39 L/min, gas inlet temperature = 35-38°C, inlet wash water temperature = 25°C

<table>
<thead>
<tr>
<th>Stage</th>
<th>Time</th>
<th>Activities</th>
<th>pH</th>
<th>SO$_2$ removal</th>
<th>CO$_2$ removal</th>
<th>NH$_3$ outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9:04</td>
<td>Flue gas on</td>
<td>Not available</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>2</td>
<td>9:53</td>
<td>Water circulation</td>
<td>Drop to 2.5</td>
<td>Partial</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>3</td>
<td>11:40</td>
<td>Dosing NH$_3$ at 0.2 kg/h</td>
<td>Increase to 2.7</td>
<td>Partial</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>4</td>
<td>12:30</td>
<td>Dosing NH$_3$ at 0.5 kg/h</td>
<td>Increase to 7.2</td>
<td>Almost</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>5</td>
<td>13:33</td>
<td>Dosing NH$_3$ at 1 kg/h</td>
<td>Increase to 8.2</td>
<td>Complete</td>
<td>possible</td>
<td>Some</td>
</tr>
<tr>
<td>6</td>
<td>14:20</td>
<td>Dosing NH$_3$ at 1.8 kg/h</td>
<td>Increase to 8.6</td>
<td>Complete</td>
<td>possible</td>
<td>Sharp increase</td>
</tr>
</tbody>
</table>

5.2 Rate based modelling of combined SO$_2$ removal and NH$_3$ recovery

Figure 4 shows the process flow-sheet diagram of the combined removal and NH$_3$ recycling system integrated with an aqueous ammonia based CO$_2$ capture unit (stripper is not shown). The whole system consists of a pretreatment column, an NH$_3$ wash column and a CO$_2$ absorber. Briefly, the vaporized NH$_3$ from CO$_2$ absorber was absorbed in the wash column. The NH$_3$-rich solution was collected at the bottom of the wash column and sent to the pretreatment column. In the pretreatment column, the hot flue gas directly contacted with the NH$_3$-rich solution. SO$_2$ was absorbed by the NH$_3$-rich solution and the captured NH$_3$ was desorbed by waste heat contained in the high temperature flue gas. The released NH$_3$ was recycled back to the CO$_2$ absorber as the make-up NH$_3$. The NH$_3$ lean solution was pumped to the top of the wash column for re-capturing the slipped NH$_3$. This was
one cycle. The solution was continuously circulated between the pretreatment column and wash column, and SO\textsubscript{2} was absorbed and accumulated in the SO\textsubscript{2}-rich solution. After a number of circulations, the entire system reached a semi steady state when temperature in each stream remained constant while the concentrations of some species such as SO\textsubscript{2} increased. As shown in the analysis in the following section, the major species in the solution was (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{3} and its concentrations increased with circulation times. When the (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{3} concentration reached the saturation point, part of the solution will be transferred to the ammonium sulfate production unit. It should be mentioned that the fresh water was introduced into the wash column to maintain the water balance in the NH\textsubscript{3} recycle and SO\textsubscript{2} recovery system. A chiller was used to cool down the NH\textsubscript{3}-lean solvent in order to achieve high NH\textsubscript{3} capture efficiencies, while a heater was used to heat up NH\textsubscript{3}-lean solvent to further enhance NH\textsubscript{3} desorption and recycling.

We used the developed rate-based model to simulate the proposed process and assess its technical feasibility. The typical flue gas conditions from the power station and the CO\textsubscript{2} absorber are shown in Table 8 respectively. For the given flue gas conditions, the preliminary modelling of the process was carried out to determine a base case scenario under which the efficiencies of SO\textsubscript{2} removal and NH\textsubscript{3} recovery were high, the column sizes are small and there is no flooding in the columns. The conditions are as follows: 350 kg/hr wash water circulation rate; 10 °C wash water inlet temperature; wash column size \( \varnothing \text{ (inner diameter)} 0.5m \times h \text{ (height)} 3.0m \text{ with 16mm pall ring}; \) pretreatment column size \( \varnothing 0.5m \times h 3.0m \text{ with 25mm pall ring}, \) 5°C temperature approach of the heat exchanger between the hot inlet and the cold outlet streams.

**Table 8 The properties of the flue gas from power station and CO\textsubscript{2} absorber**

<table>
<thead>
<tr>
<th>Source</th>
<th>Flow-rate Kg/hr</th>
<th>Temperature °C</th>
<th>Composition, vol/% CO\textsubscript{2}</th>
<th>H\textsubscript{2}O</th>
<th>O\textsubscript{2}</th>
<th>N\textsubscript{2}</th>
<th>NH\textsubscript{3}</th>
<th>SO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power station</td>
<td>760</td>
<td>120</td>
<td>10.7</td>
<td>6.0</td>
<td>7.8</td>
<td>75.5</td>
<td>-</td>
<td>200ppmv</td>
</tr>
<tr>
<td>CO\textsubscript{2} absorber</td>
<td>656</td>
<td>16.9</td>
<td>3.23</td>
<td>1.83</td>
<td>9.0</td>
<td>84.2</td>
<td>1.20</td>
<td>-</td>
</tr>
</tbody>
</table>

5.3 SO\textsubscript{2} and NH\textsubscript{3} absorption experiments
The SO$_2$ and NH$_3$ absorption experiments were carried out separately in a bubble column to help validate the simulation results. The schematic flow-sheet diagram of the experimental setups is shown in Figure 5. Carbon dioxide (99.8%), Nitrogen (99.9%), sulphur dioxide (1.0 % in N$_2$) and NH$_3$ (1.06 % in N$_2$) were used to produce the gas mixtures. The flow rates of the gases were controlled by mass flow controllers (Bronkhorst). The total gas flow rate was fixed at 5.0 L/min in the SO$_2$ removal experiments and 3.0 L/min in the NH$_3$ absorption experiments. The gases went through a mixer before entering the bubble column. Both the mixer and the bubble column were placed in the water bath to ensure that the gas temperature was close to the solvent temperature before the gas mixture entered the bubble column. The simulation results to be presented in the following section showed that the major species in the wash water is ammonium sulphite (NH$_4$)$_2$SO$_3$. Therefore the ammonium sulphite monohydrate ((NH$_4$)$_2$SO$_3$·H$_2$O, 92% purity from Sigma Aldrich) was used to prepare (NH$_4$)$_2$SO$_3$ solutions in the experiments to simulate the real process. The gas mixture was dispersed at the bottom of the bubble column and contacted the solvent with a short residence time. The FTIR gas analyzer (Gasmet™ Dx-4000) was used to determine the gaseous CO$_2$, SO$_2$, and NH$_3$ concentrations before and after absorption. The SO$_2$ and NH$_3$ removal efficiency can be expressed as the following equation. \[ \eta \% = \frac{c_{i,inlet} - c_{i,outlet}}{c_{i,inlet}} \times 100\% \] where $\eta$ is the removal efficiency; $i$ represents the component SO$_2$ or NH$_3$; $c_{i,inlet}$ is the inlet concentration of component $i$, ppmv; and $c_{i,outlet}$ is the outlet concentration of component $i$, ppmv. NH$_3$ removal efficiency is also called NH$_3$ reuse efficiency. The slipped NH$_3$ from the CO$_2$ absorber will go to three destinations: one is to be discharged into the atmosphere after the wash column (gas phase); the second is to be recycled to the CO$_2$ absorber (gas phase); and the third will be dissolved in the solution (liquid phase). The NH$_3$ in the second and third can be regarded as reuse (recycle). In each experiment, 200 ml of solution was placed in the bubble column. During the absorption experiments, either SO$_2$ or NH$_3$ will build up in the solutions and the composition of the solution will change with time. As a result, the SO$_2$ and NH$_3$ removal efficiency will change accordingly. In this work, the
average value in the first one minute of the measurement was used. In this short period of time, the composition of the solution changed little.

5.4 Modelling of CO₂ absorption in piperazine/NH₃ mixture in a wetted wall column

The availability of the detailed reaction scheme for the Piperazine (PZ)-NH₃-CO₂-H₂O system also makes it possible to rigorously simulate the mass transfer process in a gas–liquid contactor including the wetted wall column. The simulated results including CO₂ absorption flux or CO₂ mass transfer coefficients can be compared with experimental results to confirm the validity of the simulation and help identify and understand the factors which can influence the mass transfer. This exercise could help develop a rate based model for CO₂ absorption which can be used for process optimisation. The commonly used process simulation packages such as Aspen Plus requires thermodynamic, transport and rate-based models for the studied system in order to simulate the absorption process. However, for the new solvent system, these models are not available and the development of these models requires significant efforts. In this work, an in-house software tool implemented in the Matlab® was used to model the CO₂ mass transfer behavior in the NH₃ and PZ mixtures. The software tool solves partial differential equations and nonlinear simultaneous equations that define the diffusion, reaction and equilibrium processes occurring in a thin liquid film as a function of time and film depth (Puxty and Rowland, 2011). Axial dispersion and heating effects are neglected and the equations are solved in one dimension perpendicular to the gas-liquid interface. It is also assumed that physical properties such as viscosity and density remain invariant within the film.

In brief, the system of partial differential equations to be solved are defined as a combination of Fick’s law (diffusion) and chemical reaction (Cussler, 2009; Danckwerts, 1970):

\[
\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} - r_i
\]

where \(D_i\) is the diffusion coefficient of species i (m²·s⁻¹), \(C_i\) is the concentration of species i in molarity (M), \(x\) is the distance from the gas-liquid interface (m), \(t\) is time (s) and \(r_i\) is the rate of formation or destruction of i by chemical reaction (M·s⁻¹). The chemical model used was identical to that described the previous report. The Matlab® function pdepe, which relies on the method of lines, was used to numerically solve the complete system of partial differential equations assuming slab geometry. The pdepe function automatically determines the grid spacing in both time and space to achieve results of a specified accuracy. Once the solution of this equation has been calculated for a given gas-liquid exposure time (\(t_e\)) the time average CO₂ absorption flux can be calculated at the gas-liquid interface (\(x = 0\)) according to the following equation.
\[ r_{CO_2}^{\text{calc}} = -A \frac{D_{CO_2}}{t_e} \int_0^t \frac{\partial C_{CO_2}}{\partial t} dt \]

Diffusion coefficients for CO\(_2\) and all other species and the exposure time were calculated as previously described (Dubois and Thomas, 2011) based on the measured viscosity and density and the wetted-wall operating conditions. The concentration of CO\(_2\) at the gas-liquid interface was calculated using the Henry constant from Crovetto et al. (1991). The \( \rho \) is the density of the solutions.

\[
H_{CO_2} = \frac{\exp(9.4052 + \frac{3934.40}{T} - \frac{941290.2}{T^2})}{1801} \rho
\]

The liquid side mass transfer coefficient, \( k_L \), can be determined from the calculated results in the same manner as \( K_e \) is determined from the wetted-wall data. If the gas-side resistance to mass transfer is assumed negligible (which is the case for the 5 L.min\(^{-1}\) gas flow rate used) \( k_L \) (liquid phase mass transfer coefficient) \( \approx K_G \).

References


Aspen Technology. 2010b. Rate-based model of the CO\(_2\) capture process by NH\(_3\) using Aspen Plus. Burlington, MA, USA.


Ermatchkov, V., Kamps, A. P.S., Maurer, G., 2005. The chemical reaction equilibrium constant and standard molar enthalpy change for the reaction: \{HSO₃⁻(aq) ⇌ S₂O₅²⁻(aq) + H₂O(l)\}. a spectroscopic and calorimetric investigation, The Journal of Chemical Thermodynamics, 37, 187–199.


Tsai, T.C., 1985. Packed tower program has special features, Oil and Gas Journal, 83, 77.


6 Results and Discussion

6.1 Validation of a rate-based model for the system of NH$_3$-CO$_2$-SO$_2$-H$_2$O using Aspen Plus

The validation of the thermodynamic model is one of the pre-requisites and foundation for the development of a rigorous rate-based model. We used the developed thermodynamic model of the NH$_3$-SO$_2$-CO$_2$-H$_2$O system to predict chemical and physical properties in ternary systems of NH$_3$-CO$_2$-H$_2$O (CO$_2$ capture process) and NH$_3$-SO$_2$-H$_2$O (SO$_2$ capture process) and quaternary system of NH$_3$-SO$_2$-CO$_2$-H$_2$O (combined CO$_2$/SO$_2$ removal and NH$_3$ recycling). The predicted results are compared with experimental data available in the literature.

6.1.1 Validation of thermodynamic model

(a) NH$_3$-CO$_2$-H$_2$O system

Figure 6 shows comparison of experimental total pressure and predicted data as a function of CO$_2$ molality at various ammonia concentrations and temperatures. Experimental data (point) from Göppert et al. (1988) and Kurz et al. (1995)

Figure 6 shows comparison of experimental total pressure and predicted data as a function of CO$_2$ molality at various ammonia concentrations and temperatures. Figure 7 shows comparison of experimental and predicted CO$_2$ partial pressure as a function of CO$_2$ molality at various ammonia concentrations and two temperatures, 333 K and 353 K. The experimental and predicted species profiles as a function of CO$_2$
molality at the ammonia concentration of 6.3 mol NH$_3$/kg H$_2$O and 313 K are presented in Figure 8. The good agreement between the experimental and modelling results are obtained.

Figure 7 Comparison of experimental (point) and predicted (line) CO$_2$ partial pressure as a function of CO$_2$ molality at various NH$_3$ concentrations and (a) T=333 K; (b) T=353 K. Experimental CO$_2$ partial pressure results are from GÖppert et al (1988).

Figure 8 Comparison of experimental (point) and predicted (line) liquid species distribution as a function of CO$_2$ molality at the ammonia concentration of 6.3 mol/kg H$_2$O and 313 K. Experimental results are from Lichtfers [25]

(b) NH$_3$-SO$_2$-H$_2$O system

Figure 9 plots the modelled and experimental total pressures in the NH$_3$-SO$_2$-H$_2$O system as a function of SO$_2$ molality at two ammonia concentrations. The predicted total pressures agree reasonably well with the experimental measurements. Overestimation of the total pressure is observed at high SO$_2$ concentrations (above 6 mol/kg H$_2$O). This is likely due to the limitation of Pitzer model in which the electrolytes concentration in the solution should be no more than 6 mol/L (Aspen Technology, 2010). Another possibility of the deviations might be due to the uncertainty of measurements at high temperature and high loading. Considering that the proposed process was carried out in the electrolytes concentration
range of 0-6 mol/L and at temperatures below 353 K, the model is suitable for the prediction of vapor-liquid equilibrium.

\[ \text{Figure 9 Total pressure of NH}_3\text{-SO}_2\text{-H}_2\text{O for different temperatures at (a) mNH}_3\text{=}3.19 \text{ mol/kg H}_2\text{O , (b) mNH}_3\text{=}6.08 \text{ mol/kg H}_2\text{O with model data and experiment data from Rumpf et al [26]}} \]

The solution pH can reflect the species distribution such as HSO\(^{-}\), SO\(^{2-}\), S\(_2\)O\(_5\)^{2-}\. As shown in Figure 10, the modelled pH values agree well with the experimental results at the electrolytes concentrations ranging from 0.001 mol/L to 6 mol/L. This implies that the proposed thermodynamic model also has the capability to predict the ionic species concentration in the NH\(_3\)-SO\(_2\)-H\(_2\)O system.

\[ \text{Figure 10 pH of solutions at a function of SO}_2 \text{ concentrations at different NH}_3/\text{SO}_2 \text{ (N/S) molar ratios and 293 K. Experimental data are obtained from Scott & McCarthy (1967)} \]

(c) NH\(_3\)-CO\(_2\)-SO\(_2\)-H\(_2\)O

Figure 11 compares the predicted and experimental CO\(_2\) partial pressure in the SO\(_2\) loading range of 0-0.3 (mol SO\(_2\)/mol NH\(_3\)) and temperature range of 293-333 K. These conditions are relevant to the actual conditions of the combined SO\(_2\) recovery and NH\(_3\) recycling process. As shown in Figure 11, the model prediction agrees reasonably well with the experimental results, although a small deviation was observed at CO\(_2\) molality over 0.5 mol/kg H\(_2\)O. Considering that the SO\(_2\) removal and NH\(_3\) recycling process will be carried out at low CO\(_2\) concentrations (below 0.5 mol/kg H\(_2\)O), the effect of the deviation can be neglected.
Figure 11 Predicted and measured CO$_2$ partial pressure of NH$_3$-CO$_2$-SO$_2$-H$_2$O system as a function of CO$_2$ molality at various SO$_2$ loadings (molar ratio of SO$_2$ to NH$_3$) and the ammonia concentration of 5 wt%. (a) 293 K, (b) 313 K and (c) 333 K. Experimental data are obtained from Qi (2014)
In summary, the developed thermodynamic model can satisfactorily predict the vapor-liquid equilibrium and ions speciation not only for the ternary systems, NH$_3$-CO$_2$-H$_2$O system and NH$_3$-SO$_2$-H$_2$O system, but also for the quaternary NH$_3$-CO$_2$-SO$_2$-H$_2$O system.

6.1.2 Validation of the rate-based model

The rate-based model was validated using pilot plant results from CO$_2$ absorption, CO$_2$ regeneration and NH$_3$ dosing experiments respectively.

(a) CO$_2$ absorption in a packed column

Table 9 shows the comparison of pilot plant and predicted results under a variety of experimental conditions. As shown in Table 9, the average relative error for the overall CO$_2$ absorption rate in 30 tests is ±6.0%, and for NH$_3$ loss rate in 24 tests is ±11.1%. The comparison of the CO$_2$ absorption rate and ammonia loss rate between the modelling and experimental results are also presented in Figure 12. Generally good agreement between the experimental and modelling results was obtained.

![Comparison of experimental and predicted CO$_2$ absorption rate](image1)

![Comparison of experimental and predicted NH$_3$ loss rate](image2)

**Figure 12** Comparison of (a) CO$_2$ absorption rate and (b) ammonia loss rate between pilot plant tests and rate-based model under the conditions listed in Table 9
Table 9 Summary of rate-based model predictions and pilot-plant trial results conducted under a variety of experimental conditions in absorber

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Comparison of test results and simulation results

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</table>

Comparison of test results and simulation results

| Exp. CO₂ absorption rate ⁶, kg/h | 69.6 | 69.1 | 67.3 | 65.9 | 71.2 | 79.9 | 86.2 | 72.1 | 83.9 | 99.6 | 65.3 | 80.2 | 89.7 | 85  |
| Pred. CO₂ absorption rate, kg/h | 71.9 | 71.4 | 71.2 | 69.8 | 71.0 | 82.2 | 81.4 | 74.5 | 72.1 | 94.8 | 63.6 | 84.5 | 82.5 | 75.4|
| Relative error, % | 3.3% | 3.3% | 5.8% | 5.6% | 0.3% | 2.9% | 5.7% | 3.3% | 14.1%| 4.8% | 2.6% | 5.4% | 8.0% | 11.3%|
| Exp. NH₃ loss rate, kg/h | 5.27 | 6.72 | 7.19 | 7.70 | 11.7 | 13.6 | 12.4 | 6.21 | 11.7 | 12.1 | 9.4  | 10.4 | 8.2  | 9.8 |
| Pred. NH₃ loss rate, kg/h | 4.1  | 5.2  | 4.3  | 4.8  | 9.5  | 9.5  | 11.5 | 8.9  | 12.6 | 11.0 | 11.3 | 12.3 | 12.1 | 9.1 |
| Relative error, % | 22.2%| 22.6%| --   | --   | 18.8%| 7.2% | 7.7% | 9.1% | 20.2%| 18.2%| --   | 7.1% |

Note: ‘a’: more details on test 30-38 in Qi (2013); ‘c’: defined as the molar ratio of total C-containing species to the total N-containing species (C/N molar ratio, mol/mol). ‘--’: great error between test and simulation; ‘g’: CO₂ absorption rate based on gas analysis; ‘l’: CO₂ absorption rate based on liquid analysis; ‘n.a’: not
(b) CO$_2$ regeneration in a packed column

Table 10 lists pilot plant and predicted results obtained from solvent regeneration experiments under a variety of experimental conditions. In the process simulation, the Design Specs embedded in Aspen Plus were used. The variable parameters were condenser duty and reboiler duty; the design specifications were condenser temperature and the flow rate of CO$_2$ product. Aspen Plus automatically finds the accurate value of variable parameters to achieve design specifications during the simulation process.

Figure 13 shows the parity plot of energy requirement obtained experimentally and from the rate-based simulation in Aspen Plus. The energy consumption in pilot plant trials was calculated by two methods (Yu et al., 2012a), which are marked as Regeneration Energy (solvent) and Regeneration Energy (Steam) in Table 10 and Figure 13.

\[ Q_R = H_S + H_D - Q_C - Q_L \]

$H_S$ represents the sensible heat required to heat the solvent from the stripper inlet temperature to the stripper outlet temperature (stripping temperature), and $H_D$ is the energy required to desorb CO$_2$ from the solvent, which can be calculated by multiplying the heat of desorption by the CO$_2$ desorption rate. The CO$_2$ heat of desorption was estimated using Aspen Plus. $Q_C$ is the heat duty of condenser, and $Q_L$ stands for stripper heat loss, which can be estimated from the water-only experiments. From the steam side, energy consumption can be calculated directly from the steam consumption rate and latent heat of evaporation of water.

Good agreement has been achieved between the results. The relative deviations between the predicted and experimental results for most of the 30 cases considered are below 15%. Significant deviations are observed for several cases, which may be caused by discontinuous operation of the pilot plant, resulting from solid formation in the condenser and reflux lines (Yu et al., 2012b).
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**Comparison of test results and simulation results**

| Exp., ºC | 129.2 | 131.6 | 129.1 | 129.8 | 129.7 | 128.5 | 131.6 | 132 | 130.2 | 119.63 | 131.97 | 111.5 | 113.6 | 121.1 | 118.9 |
| Pred., ºC | 127.9 | 130.6 | 130.2 | 130.4 | 128.2 | 128.6 | 131.8 | 131.9 | 130.1 | 118 | 130.7 | 114.3 | 114.9 | 120.1 | 117.3 |
| Exp. average, ppm | n.a | n.a | n.a | 446 | 523 | 1621 | 906 | 1421 | 1173 | 1135 | 998 | 374 | 625 | 658 | 1033 |
| Pred., ppm | 1569 | 1690 | 1563 | 733 | 955 | 1514 | 1283 | 1260 | 1196 | 1122 | 1094 | 899 | 1091 | 1386 | 1306 |
| Exp. (solvent), kW | 143.5 | 150.6 | 146.8 | 156.9 | 142.4 | 164.5 | 167.1 | 139.4 | 112.2 | 96.8 | 109 | 128.2 | 147.7 | 160.4 | 156.1 |
| Exp. (steam), kW | 159.9 | 143 | 163.1 | 164.1 | 163.3 | 178.2 | 179.4 | 144.1 | 130.6 | 112.8 | 113.1 | 106.2 | 143.3 | 168.1 | 163.4 |
| Pred., kW | 143.3 | 153.4 | 166.3 | 168.5 | 135.1 | 172.4 | 178.4 | 148.6 | 117.4 | 99.3 | 107.4 | 151.2 | 157.6 | 153.6 | 149.5 |
Table 10 continued

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**Comparison of test results and simulation results**

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More details on pilot plant trials can be found in Yu et al., 2012a

n.a = not available
Figure 14 Parity plot of measured and predicted stripping temperature under conditions listed in Table 10

Figure 14 shows the parity plot of stripping temperature measured experimentally and obtained from simulation. The relative deviations between them are below 7% for all 30 cases considered, and below 3% in most cases.

Figure 15 shows the parity plot of the average value of ammonia concentration in product stream measured experimentally and the value obtained from simulation. Reasonable agreement has been achieved between the results.

Figure 15 parity plot of the average value of ammonia concentration in product stream measured experimentally and the value obtained from simulation
(c) **SO₂ removal by aqueous ammonia**

The results from the dosing experiments are used to validate the model for the absorption of SO₂ by aqueous ammonia. The model settings for the pretreatment column were based on the conditions of pilot plant trials, including the column size, packed materials, operating conditions.

It is well-known that during the SO₂ absorption process, the oxidation process of S(IV) → S(VI) inevitably occurs in the presence of oxygen. In our simulation, we assume that the SO₂ in the gas phase and SO₃²⁻ in aqueous solution are not oxidated by the oxygen during the capture process. This assumption is based on the following considerations (Miller, 1972; Hegg, 1978; McKay, 1971): (1) the oxidation of S(IV)→S(VI) primarily takes place in the liquid phase after SO₂ is dissolved into the solution generating SO₃²⁻ species, and thus the oxidation will have little influence on the SO₂ transportation from gas phase to liquid phase; (2) the oxidation rate of SO₃²⁻ to SO₄²⁻ is kinetically controlled and can be generally expressed as
\[
\frac{d[SO₄²⁻]}{dt} = K[SO₃²⁻].
\]
This means the rate of production of SO₄²⁻ is proportional to the concentration of SO₃²⁻. While in the pilot plant testing, the SO₃²⁻ concentration was very low and below 0.011 mol/L; [3] the SO₂ removal process was carried out in the oxygen-deficit environment due to the relatively low oxygen concentration below 8.0% in the flue gas, which does not favor the oxidation process. Therefore the assumption will have a minor influence on the simulation of SO₂ removal by aqueous ammonia in the pilot plant. This is verified by the excellent agreement between model predictions and experimental results in terms of the solution pH, NH₃, SO₂ and CO₂ concentration at the pretreatment column outlet (Figure 16).

**Outlet solution pH:** Absorption of the acidic gas SO₂ into the aqueous solution will lead to a decrease of solution pH due to the low dissociation constant of H₂SO₃ (pKa=1.81). As shown in Figure 16(a), the solution pH dropped quickly with the SO₂ absorbed by the circulated water due to the increasing solution acidity. The pH value then increased step by step with the increasing ammonia dosing rate. The simulation curve matches experimental results very well. As the solution pH is a very important indication of the species distribution, the validation of solution pH to some extent reflects that the model enables the predication of the solution species in the system of NH₃-CO₂-SO₂-H₂O.

**Gas outlet SO₂ concentration:** The SO₂ level in the outlet flue gas directly reflects the SO₂ removal efficiency by aqueous ammonia. As shown in Figure 16(b), upon water circulation, the outlet SO₂ concentration experienced a rapid drop but quickly increased to a level close to the inlet SO₂ concentration. This implies that the fresh water has a relatively low SO₂ removal capacity. With the increasing NH₃ dosing rate over 0.5 kg/hr, the SO₂ concentration dropped to a very low level. The simulation results agree reasonably well with the experiment data at these NH₃ dosing stages.

**Gas outlet ammonia concentration:** The ammonia introduced into the water was used to neutralize the acidic gas SO₂. If the dosed ammonia was excessive for SO₂ absorption, part of ammonia will slip to the flue gas due to the intrinsic property of high volatility and high pH of the wash water. As shown in Figure 16(c), ammonia started to slip at the dosing rate of 1.0 kg/hr NH₃, above which ammonia evaporation increased dramatically. The trend of outlet ammonia concentration is in good consistence with the modelling results.

**Gas outlet CO₂ flow rate:** As shown in Figure 16(d), there is no appreciable CO₂ removal in the test. This suggests that under the conditions studied, SO₂ is absorbed in the solution in preference to CO₂. The simulation results were in good agreement with the experimental results.
Figure 16 Comparison of pilot plant data with simulation results (a) solution pH; (b) gas SO$_2$ concentration; (c) gas ammonia concentration; (d) gas CO$_2$ flow rate outlet.

The good agreement between the experimental and modelling results suggests that the established model can well predict the SO$_2$/CO$_2$ absorption process by aqueous ammonia. This, in turn, confirms that the assumptions are reasonable at the studied conditions.

6.2 Rate based modelling of SO$_2$ removal and NH$_3$ recycling

Figure 17 (a) NH$_3$ reuse efficiency and emission concentration (b) SO$_2$ removal efficiency and emission concentration as a function of number of cycles.

Using the validated rate-based model, we simulated the proposed combined SO$_2$ removal and NH$_3$ recycle process under the conditions listed in section 4.2. Figure 17 shows the ammonia reuse efficiency and SO$_2$ removal efficiency as a function of number of cycles. The ammonia slipped from the CO$_2$ absorber was
either reused (recycled back to the CO$_2$ absorber or remain in the wash water for SO$_2$ removal) or emitted in the combined SO$_2$ removal and NH$_3$ recycle system. Ammonia reuse efficiency (removal efficiency) is defined as percentage of ammonia which is recycled back to the CO$_2$ absorber and remains in the wash water. At steady state 96.62% of ammonia was recycled to CO$_2$ absorber, while 3.36% of ammonia was used for SO$_2$ capture. So the total ammonia reuse efficiency reached as high as 99.98%.

Figure 17(b) shows that the proposed process achieved a high SO$_2$ capture efficiency constantly over 99.98% and the SO$_2$ emission concentration was in trace level varied from 10 ppbv to 30 ppbv. This high efficiency removal is primarily attributed to the fast reaction between SO$_2$ and H$_2$O and the fact that the generated HSO$_3^-$ was quickly neutralized by basic aqueous ammonia.

Figure 18 shows the concentration profiles of sulfur-containing species in wash water at the outlet of the pretreatment column as a function of number of cycles. SO$_2$ and ammonia were accumulated in the solution in the forms of (NH$_4$)$_2$SO$_3$, NH$_4$HSO$_3$ and (NH$_4$)$_2$S$_2$O$_3$. (NH$_4$)$_2$SO$_3$ was persistently the dominant species in the wash water and the concentration increased gradually to 35% (saturated concentration of (NH$_4$)$_2$SO$_3$ at 10 °C) while the NH$_4$HSO$_3$ and (NH$_4$)$_2$S$_2$O$_3$ remained at relatively low levels. The concentrated SO$_2$ solution is expected to undergo a further treatment, e.g. producing ammonium sulfate/fertilizers. It should be pointed out that CO$_2$ was not absorbed in the combined capture process. In other words, the process achieves selective removal of SO$_2$ and ammonia in preference to CO$_2$.

![Figure 18 Concentration of major SO$_2$ containing species at the pretreatment column outlet as a function of number of cycles](image-url)

Wash column

To gain the insight of how the ammonia is removed, the wash column profiles with respect to the ammonia removal efficiency and temperature were studied. The vaporised ammonia from CO$_2$ absorber was scrubbed in the wash column using the circulated ammonium sulphite solution. As shown in the Figure 19 (a), the ammonia removal efficiency increases along the packed column and the value can reach over 99.9%. This means that almost all the slipped ammonia was scrubbed in the solution in the forms of free ammonia and NH$_4^+$ ion species.
Figure 19 (a) NH₃ removal efficiency and (b) temperature profile as a function of packed height

It is well known that the NH₃ absorption by aqueous solution is an exothermic process, leading to an overall temperature increase of the solution (Figure 19 (b)). This will decrease the NH₃ solubility in the solvent and reduce the driving force for ammonia absorption. So the low temperature is required in order to achieve a high removal efficiency for ammonia. In this simulation, the 10 °C wash water was used to obtain a high ammonia removal efficiency. The liquid temperature profile along the column experienced two peaks. One was caused by the exothermic process of NH₃ absorption by the wash solution. The other was caused by the 10 °C fresh makeup water that was introduced into the top of washing column. The makeup water played two roles: One was to maintain the H₂O balance of the system; the second was to have a deep removal of NH₃. The simulated temperature profile shows that the liquid temperature ranged from 10 °C to 32 °C in the wash column. This temperature range provides the reference for the separate NH₃ absorption in the bubble column.

Pretreatment column

After the slipped NH₃ was absorbed in the wash column, the solution was sent to the pretreatment column which played three significant roles in the proposed SO₂ removal and NH₃ recycle process. The first was to cool down the high temperature flue gas from power station. As shown in Figure 20 (a), the flue gas temperature experienced a sharp decrease after contact with the relatively low temperature solvent along the packed column. The outlet gas temperature from the pretreatment column decreased to 43.6 °C and the gas can be directly transported to the CO₂ absorber without further cooling. Our simulation has confirmed that the flue gas temperature from 15 °C to 50 °C had little influence on the CO₂ absorption process including absorption rate and ammonia vaporization rate. This is due to the small heat capacity of the gas and the fact that the latent heat in the high temperature flue gas has been released and transferred to the solvent.
Figure 20 (a) liquid and gas temperature profile, (b) SO$_2$ removal efficiency and NH$_3$ recycling efficiency, (c) solution pH profile, (d) N/S ratio profile as a function of the packed height

The second role was to remove the SO$_2$ in the flue gas. The result in Figure 20(b) shows that SO$_2$ removal efficiency increased sharply to 95% in the first 1.0 m packed height and slightly in the remaining 2.0 m packing.

The third role was to recycle the scrubbed ammonia to the CO$_2$ absorber by making use of latent heat in the flue gas. As shown in Figure 20(b), the NH$_3$ recycling (reuse) efficiency increased steadily along the column and reached the maximum of 99.9% at the top of column. In the pretreatment column, the solution was heated by the high temperature flue gas and released the NH$_3$ vapor. The solution pH decreased as the wash water flowed down along the column, as shown in Figure 20(c). The decrease was due to the absorption of SO$_2$ and evaporation of ammonia. Figure 20(d) describes the N/S ratio profile in the liquid phase (the molar ratio of N-containing species to the S-containing species) as a function of packing height. Initially, the solution at the column top contained the free NH$_3$ and had a high N/S ratio. With the liquid falling down along the column, the ratio decreased gradually due to the release of molecular NH$_3$ from the solution. The vaporized ammonia was then recycled back to the CO$_2$ absorber as make up. It is worth mentioning that the N/S ratio can be below 2.0 at the bottom stage. This implies that all the free ammonia was recycled and part of (NH$_4$)$_2$SO$_3$ was decomposed to release the NH$_3$ vapor. The decomposition of (NH$_4$)$_2$SO$_3$ occurring at the column bottom was partly attributed to the high temperature flue gas in the bottom stage (Figure 20(a)).

In summary, the multi-function pretreatment column acted as: (1) a cooler to cool down the high temperature flue gas; (2) a heater to recycle almost all the escaped NH$_3$ to the CO$_2$ absorber; and (3) an
efficient desulphurization facility to deeply remove \( \text{SO}_2 \). Accordingly, this advanced process would hold the advantages of (1) saving the energy consumption for the flue gas cooling; (2) reducing the energy and capital cost for the \( \text{NH}_3 \) recovery system; (3) and simplifying the flue gas desulphurization (FGD) process which is particularly important in Australia as the FGD system is not installed in Australian power plants.

6.3 \( \text{SO}_2 \) and ammonia absorption experiments

Based on the modelling results, the experimental work using bubble column was carried out to qualitatively verify the prediction results on \( \text{SO}_2 \) and ammonia absorption separately.

6.3.1. \( \text{SO}_2 \) absorption and \( \text{NH}_3 \) vaporization

![Graph](image)

**Figure 21** (a) \( \text{SO}_2 \) and \( \text{CO}_2 \) removal efficiency and (b) \( \text{SO}_2 \) concentration at the column outlet as a function of \((\text{NH}_4)_2\text{SO}_3\) concentration at various \( \text{SO}_2 \) inlet concentrations and the temperature of 313 k (40°C).

The modelling results in Section 6.2 suggests that the \( \text{SO}_2 \) absorption process was performed in the liquid temperature range of 42-48°C. The temperature of 40°C was used to test the \( \text{SO}_2 \) absorption in the bubble column. The \( \text{SO}_2 \) inlet concentration varied from 58 ppmv to 833 ppmv, which covers the typical \( \text{SO}_2 \) level in the flue gas from Australian coal-fired power stations. As shown in Figure 21(a), the \((\text{NH}_4)_2\text{SO}_3\) solution had excellent \( \text{SO}_2 \) removal efficiency for the high \( \text{SO}_2 \) level flue gas, while a relatively low \( \text{SO}_2 \) removal efficiency for the low \( \text{SO}_2 \) level flue gas. Figure 21(b) shows that the outlet \( \text{SO}_2 \) concentrations from the bubble column were very small, generally below 20 ppm. The values changed little with variation of \((\text{NH}_4)_2\text{SO}_3\) concentration and increased slightly with an increase in inlet \( \text{SO}_2 \). This means the \((\text{NH}_4)_2\text{SO}_3\) concentration has a high \( \text{SO}_2 \) absorption capacity. It should be pointed out that the \( \text{CO}_2 \) removal efficiencies were negligible under all conditions studied. One of examples is shown in Figure 22 which shows the \( \text{SO}_2 \) and \( \text{CO}_2 \) removal efficiency and outlet ammonia concentration as a function of \((\text{NH}_4)_2\text{SO}_3\) concentration at two temperatures (25°C and 40°C) and inlet \( \text{SO}_2 \) concentration of 445 ppm. There was virtually no \( \text{CO}_2 \) removal while \( \text{SO}_2 \) removal efficiencies were above 95% and slightly higher at low temperatures. This clearly indicates that the \((\text{NH}_4)_2\text{SO}_3\) solutions can selectively remove \( \text{SO}_2 \) in preference to \( \text{CO}_2 \).
Figure 22 (a) SO\textsubscript{2} and CO\textsubscript{2} removal efficiency and (b) outlet NH\textsubscript{3} concentration as a function of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{3} concentration at two temperatures (25\textdegree C and 40\textdegree C) and inlet SO\textsubscript{2} concentration of 445 ppm. CO\textsubscript{2} inlet concentration was 10.4 %

Figure 22 (b) shows the ammonia evaporation occurred in the SO\textsubscript{2} absorption process and the amount of NH\textsubscript{3} in the gas increased with increasing (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{3} concentration, in particular with increasing temperature. This suggests that high temperature absorption does not affect SO\textsubscript{2} and CO\textsubscript{2} removal but significantly facilitate ammonia evaporation and thus its recycle.

6.3.2 NH\textsubscript{3} absorption

The modelling results in Section 6.2 show that the ammonia absorption process occurred at temperatures between 10 and 32 \textdegree C. 10 \textdegree C and 25 \textdegree C were selected to represent the temperature swing during absorption process.

Figure 23 (a) NH\textsubscript{3} removal efficiency and (b) NH\textsubscript{3} concentration at the column outlet as a function of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{3} concentration at 10 and 25\textdegree C. NH\textsubscript{3} concentration at the inlet is ca. 2000 ppm and CO\textsubscript{2} inlet concentration was 2.0 %

Figures 23 shows the ammonia removal efficiency and ammonia concentration at the column outlet as a function of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{3} concentration at 10 and 25\textdegree C respectively. It is evident that the ammonia removal efficiency decreased and the corresponding NH\textsubscript{3} concentration at the column outlet increased with an
increase in \((\text{NH}_4)_2\text{SO}_3\) concentration. The ammonia removal efficiency was over 85% at 10 °C, while at 25 °C the absorption efficiency drop significantly, especially at high \((\text{NH}_4)_2\text{SO}_3\) concentrations.

The experiments proved the concept of the combined capture process and demonstrated the feasibility of \(\text{SO}_2\) removal and ammonia recycling through the application of the proposed process configuration.

### 6.4 Solvent development

The previous results have showed that both amino acid salts including sarcinate and prolinate, piperazine and its derivatives including 1-methyl piperazine and 2 methy piperazine can promote \(\text{NH}_3\) absorption. The promotion mechanism has been elucidated by stopped flow kinetic study of the reaction of \(\text{CO}_2\) with ammonia, promoters and ammonia/promoter mixture. The previous study has also showed that the reaction of \(\text{CO}_2\) with ammonia/promoter mixture is a simply combination of the two individual reaction system and there is no catalytic effect from promoters. In other words, the promoter itself acts as a reactant and can react with \(\text{CO}_2\) in a similar way to ammonia. These promoters have much higher reaction kinetics with \(\text{CO}_2\) than ammonia, which is the major reason why introduction of these promoters can significantly enhance \(\text{CO}_2\) absorption in aqueous \(\text{NH}_3\). In case of amino acid salts, the extent of promotion is pronounced at low \(\text{CO}_2\) loadings but becomes smaller with an increase in \(\text{CO}_2\) loading. Figure 24 shows the mass transfer coefficient of \(\text{CO}_2\) in the mixture of ammonia with potassium prolinate as a function of \(\text{CO}_2\) loading at the temperature of 288 K. For comparison purpose, the mass transfer coefficient of \(\text{CO}_2\) in 3 M \(\text{NH}_3\) and 30% MEA are included.

![Figure 24 Mass transfer coefficient of \(\text{CO}_2\) in the mixture of ammonia with potassium prolinate as a function of \(\text{CO}_2\) loading at the temperature of 288 K. The data for 30% MEA was obtained at 313 K](image)

At \(\text{CO}_2\) loadings below 0.1, the mass transfer coefficients of \(\text{CO}_2\) in both 2 M prolinate/3 MNH$_3$ and 3 M prolinate/2M NH$_3$ match those in MEA. But the values drop rapidly with an increases in \(\text{CO}_2\) loading and are lower those in MEA at \(\text{CO}_2\) loadings between 0.1 and 0.5. At loadings close to 0.5, mass transfer coefficients in all solutions are similar. Similar results were observed in sarcinate/NH$_3$ mixture, as reported previously.
Figure 25 Mass transfer coefficient of CO$_2$ in the mixture of ammonia with piperazine as a function of CO$_2$ loading at the temperature of 288 K. The data for 30% MEA was obtained at 313 K.

Figure 26 Mass transfer coefficient of CO$_2$ in the mixture of ammonia with 2-methyl piperazine as a function of CO$_2$ loading at the temperature of 288 K. The data for 30% MEA was obtained at 313 K.

Figures 25 and 26 show mass transfer coefficients of CO$_2$ in the mixture of ammonia with piperazine and ammonia with 2-methyl piperazine as a function of CO$_2$ loading at the temperature of 288 K respectively. Mass transfer coefficient of CO$_2$ in 1.5 piperazine/3 M ammonia mixture and 3 M 2-methyl piperazine/2 M ammonia can match those in MEA in a wide CO$_2$ loading range. As discussed in the previous reports, these diamines have two advantages. One is that these amines have 2 amino functional groups both of which react with CO$_2$ faster than ammonia, thus enhancing CO$_2$ absorption at CO$_2$ loaded solutions. pKa values of these amines are close or even lower than that of ammonia. Protons released from the CO$_2$ dissolution or depronotation of carbamic acid can react with ammonia in preference to amines. So more free amines are available to react with CO$_2$. While in case of sarcosinate and prolinate, pKa of these amino acid salts are much higher than ammonia and have only one amino group. With an increase in CO$_2$ loading (amount of CO$_2$ in the solution), the concentration of the free amino acid salts in amino acid salts/ammonia mixture decrease to a larger extent than those in the single amine and the role of these amino acid salts in promotion of CO$_2$ absorption becomes much smaller.
So it can be concluded that the amino acid salts studied in this work can significantly enhance CO₂ absorption in aqueous ammonia at low CO₂ loadings but their role in promotion of CO₂ absorption rate becomes much smaller with an increase in CO₂ loading. The mass transfer coefficients of CO₂ in amino acid salts and NH₃ mixtures are close to those in MEA but generally lower under the conditions studied. In comparison, ammonia with piperazine or 2-methyl piperazine can achieve mass transfer coefficients higher than those in MEA. Our focus on the solvent development in this project will be piperazine or 2-methyl piperazine promoted ammonia solution. We are currently developing rate-based models for the piperazine-NH₃-CO₂-H₂O system and 2-methyl piperazine-NH₃-CO₂-H₂O system. The available of models will allow evaluation of the performance of the piperazine or 2-methyl piperazine based capture process.

6.5 Modelling of CO₂ absorption in piperazine/ammonia mixture in a wetted wall column

Estimated values of $K_G$ are compared to wetted-wall measured values in Figure 27. This comparison is for various piperazine concentrations and a constant CO₂ concentration of 0.9 M. When using the value of $k_7$ (the rate constant for the forward reaction of ammonia with CO₂) from Wang et al. (2011) in the calculations (determined by stopped-flow spectrometry at low NH₃ concentration, 469 M⁻¹.s⁻¹), the calculated $K_G$ values underestimate the measured $K_G$ by a relative error of approximately 30-40%. Alternatively, when using a value of $k_7$ determined from two previous studies using a similar wetted-wall column to that used in this work (1170 M⁻¹.s⁻¹ (Li et al., 2013), and 3369 M⁻¹.s⁻¹ (Puxty et al., 2010), the calculated $K_G$ values are in closer agreement to the measured values. When using the smaller value of the two, the agreement is better at lower piperazine concentrations, and when using the larger value, a better agreement is achieved at higher piperazine concentrations. The reason for this discrepancy is not clear. Of the $k_7$ values, that determined in a homogeneous single phase by stopped-flow spectrometry is likely the most reliable as the assumptions and errors introduced when studying gas-liquid reactions are eliminated. However, this determination was done at mM (millimolar) NH₃ concentrations rather than the M (molar) concentrations used in the wetted-wall studies. The larger $k_7$ values determined in the wetted-wall studies could be due to the volatility of NH₃ leading to additional reaction occurring at the gas-liquid interface or in the gas phase that is not captured in the mass transfer simulations. Further investigation is required to understand the reasons for the discrepancy and improve the mass transfer simulations.
Figure 27 The mass transfer model estimated value of $K_G$ (solid lines) compared to the wetted-wall measured values (diamonds) for different concentrations of PZ at a constant CO$_2$ loading of $\frac{[CO_2]}{[NH_3]} = 0.3$ and using different values of $k_7$.

It should be noted that, for both calculated and experimental values listed in Figure 27, $K_G$ increases with the concentration of piperazine added to the blended ammonia/piperazine solutions with constant ammonia and CO$_2$ concentrations in solutions. The reason for the increase is the increasing contribution from the reaction of CO$_2$ with PZ/PZH$^+$ and PZCO$_2^-$/PZCO$_2$H as outlined in the last progress report.

6.6 Impact of research achievements from this project

The research has so far led to the following advancements:

(1) Development of a rigorous rate-based model for the system of NH$_3$-CO$_2$-SO$_2$-H$_2$O. The model has been validated using the experimental results from open literature and pilot plant trials at Munmorah Power Station.

(2) Development of a combined SO$_2$ removal and NH$_3$ recycle process which can be integrated with the aqueous ammonia based CO$_2$ capture process.

(3) Development of aqueous ammonia based solvents which can match MEA based solvents in terms of CO$_2$ absorption rate. Ammonia blended with piperazine or 2-methyl piperazine can achieve mass transfer coefficients higher than those in MEA.

The availability of the rigorous rate-based model will allow a reliable process evaluation and guide process improvement and optimisation. The combined SO$_2$ removal and NH$_3$ recycle process can simply the flue gas desulphurization (FGD) process, save the energy consumption for the flue gas cooling and reducing the energy and capital cost for the NH$_3$ recovery system. Currently we are assessing the technical and energy performance of an advanced aqueous ammonia-based CO$_2$ capture technology for a 500 MW coal fired power station and comparing the energy consumption with those in chilled ammonia process and MEA based process (Li, 2014). The technology is still based on aqueous ammonia (no promoters are
added) but includes the combined SO\textsubscript{2} removal and NH\textsubscript{3} recycle process. It has been found that the advanced ammonia based process has a net efficiency penalty of 7.9\% points, which is lower than that for modified CAP process (8.5\%) and much lower than that for the MEA process (10.9\%). The results will be reported in the following reports.

Development of aqueous ammonia based solvents which can match MEA based solvents in terms of CO\textsubscript{2} absorption rate can significantly reduce the column size and the capital costs associated with the ammonia based capture process. We are currently developing rate-based models for the piperazine-NH\textsubscript{3}-CO\textsubscript{2}-H\textsubscript{2}O system and 2-methyl piperazine-NH\textsubscript{3}-CO\textsubscript{2}-H\textsubscript{2}O system. The models will allow a more realistic evaluation of the performance of the piperazine or 2-methyl piperazine promoted ammonia capture processes.

References


Kurz F.; Rumpf B.; Maurer G. 1995. Vapor-liquid-solid equilibria in the system NH\textsubscript{3}-CO\textsubscript{2}-H\textsubscript{2}O from around 310 to 470 K: New experimental data and modeling. 104, 261-275.


The project has made a good progress and has completed the milestones listed in the reporting period.

Using Aspen Plus®, we have developed a rigorous rate-based model for the system of $\text{NH}_3$-$\text{CO}_2$-$\text{SO}_2$-$\text{H}_2\text{O}$ and validated the model against the experimental results from open literature and pilot plant trials at Munmorah Power Station. The model can satisfactorily predict the $\text{CO}_2$ absorption, $\text{CO}_2$ desorption and $\text{SO}_2$ removal processes in packed columns and thus guide process evaluation and optimisation.

We have proposed a novel process to combine $\text{SO}_2$ removal and ammonia recycling. The process can be integrated with the aqueous ammonia based $\text{CO}_2$ capture process to achieve flue gas cooling, $\text{SO}_2$ and $\text{CO}_2$ removal and ammonia recycle simultaneously in one process. The process simulation using the rate-based model shows that under the typical flue gas conditions, the proposed process has a $\text{SO}_2$ removal efficiency of over 99.9% and an ammonia reuse efficiency of 99.9%. The novel process can not only simplify the flue gas desulfurization, but also resolve the problems of ammonia loss and $\text{SO}_2$ removal, thus holding the potential of cutting the $\text{CO}_2$ capture costs significantly. The separate experiments on $\text{SO}_2$ and ammonia absorption using a bubble column were carried out to further evaluate the technical feasibility of the combined $\text{SO}_2$ removal and ammonia recycling process. The experimental results qualitatively confirmed the simulated results and the technical feasibility of the process.

In terms of solvent development, the amino acid salts studied in this work can significantly enhance $\text{CO}_2$ absorption in aqueous ammonia at low $\text{CO}_2$ loadings but their role in promotion of $\text{CO}_2$ absorption rate becomes much smaller with an increase in $\text{CO}_2$ loading. The mass transfer coefficients of $\text{CO}_2$ in amino acid salts and ammonia mixtures are close to those in MEA but generally lower under the conditions studied. In comparison, ammonia mixed with piperazine or 2-methyl piperazine can achieve mass transfer coefficients higher than those in MEA.

In an attempt to develop a rate-based model for the promoted ammonia solvents which is not available in Aspen Plus, we used an in-house software tool implemented in the Matlab® to model the mass transfer of $\text{CO}_2$ in the ammonia and piperazine mixtures in a wetted wall column. The software tool incorporates the reaction kinetic model developed from stopped flow kinetic study and solves partial differential equations and nonlinear simultaneous equations that define the diffusion, reaction and equilibrium processes occurring in a thin liquid film. It has been found that both calculated and experimental mass transfer coefficients increases with the concentration of piperazine added to the blended ammonia/piperazine solutions with constant ammonia and $\text{CO}_2$ concentrations in solutions. However, the calculated values underestimate the measured values by a relative error of approximately 30-40%. Further investigation is required to understand the reasons for the discrepancy and improve the mass transfer simulations.

The milestones of the project for the report period have been achieved and the project is on track to achieve the milestones which are due on 30 March 2015.
8 Future work

In the next 6 months, we will follow the plan specified in the proposal and carry out the following work:

- Use the developed rate-based model to assess the technical and energy performance of an aqueous ammonia-based CO\textsubscript{2} capture technology for a 500 MW coal fired power station and comparing the energy consumption with those in chilled ammonia process and MEA based processes. The technology integrates the combined SO\textsubscript{2} removal and NH\textsubscript{3} recycle with the capture process.

- Develop rate-based models for the piperazine-NH\textsubscript{3}-CO\textsubscript{2}-H\textsubscript{2}O system and 2-methyl piperazine-NH\textsubscript{3}-CO\textsubscript{2}-H\textsubscript{2}O system. The models will allow a more realistic evaluation of the performance of the piperazine or 2-methyl piperazine promoted ammonia capture processes. In addition, we will use the model to assess the performance of a complete CO\textsubscript{2} absorption system and identify the optimal conditions to be used for the demonstration of the advanced aqueous ammonia based PCC at a CO\textsubscript{2} capture rate of at least 10 kg/h with CSIRO’s process development facility at Newcastle.

- Carry out the experiments on CO\textsubscript{2} absorption under pressure and investigate the effect of pressure on CO\textsubscript{2} mass transfer and ammonia loss.