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DOSSIER Edited by/Sous la direction de : **P.-L. Carrette**

PART 1

Post Combustion CO₂ Capture Captage de CO₂ en postcombustion

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Aqueous Ammonia (NH₃) Based Post Combustion CO₂ Capture: A Review

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Résumé — Capture de CO₂ en postcombustion par l'ammoniaque en solution aqueuse (NH₃) : synthèse — L'ammoniaque en solution aqueuse (NH₃) est un solvant novateur, prometteur et un challengeur pour la capture du CO₂ émis par les centrales électriques au charbon et au gaz et autres sources industrielles. Au cours des dernières années, d'intenses activités de recherche ont été menées pour tenter de comprendre les propriétés thermo-chimiques et physiques du système CO₂-NH₃-H₂O, ainsi que la chimie et la cinétique associées, afin d'obtenir plus d'informations sur le taux d'absorption, la perte en ammoniaque, les énergies de régénération et les problèmes pratiques, et aussi pour évaluer la faisabilité technique et commerciale des technologies de capture en postcombustion par l'ammoniaque en solution aqueuse. Cet article offre une synthèse de ces activités de recherche, apporte des comparaisons avec le monoéthanolamine (MEA, le solvant de référence) et identifie des opportunités de recherche pour de futures améliorations.

Abstract — Aqueous Ammonia (NH₃) Based Post Combustion CO₂ Capture: A Review — Aqueous ammonia (NH₃) is an emerging, promising and challenging solvent for capture of CO₂ emitted from coal and gas fired power stations and other industrial sources. Over the last few years, intensive research activities have been carried out to understand the thermo-chemical and physical properties of the CO₂-NH₃-H₂O system and the chemistry/kinetics involved, to obtain information on absorption rate, ammonia loss, regeneration energies, and practical issues, and to assess the technical and economical feasibility of the aqueous ammonia based post combustion capture technologies. This paper reviews these research activities, makes comparisons with MonoEthanolAmine (MEA, the benchmark solvent) and identifies the research opportunities for further improvements.

INTRODUCTION

With the rapid industry development globally, excessive amounts of the greenhouse gases in particular CO₂ have been released to the atmosphere, which is believed to be the major contributor to global warming. It is generally agreed that Carbon Capture and Storage (CCS) is the only technology available to make deep cuts in greenhouse gas emissions while still using fossil fuels and much of today's energy infrastructure. Developing an economic and efficient method to capture carbon dioxide is an important objective for successful deployment of effective CCS process chains.

Post Combustion Capture (PCC) is a process that uses an aqueous absorption liquid incorporating compounds such as ammonia or amine to capture CO₂ 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 CO₂ 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 CO₂ from solvents;
- PCC can be used to capture CO₂ 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. \(2009\)](#) shows that retrofitting a 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. Moreover, there is some concern about the formation of carcinogenic nitrosamines from the use of amines in PCC and their possible spread into the environment ([MacDowell et al., 2010](#)).

Aqueous NH₃, as a promising solvent for CO₂ capture, has been receiving increasing attention recently. Compared to traditional amines, NH₃ is a low cost solvent that is not easily decomposed by other gas present in flue gases. Moreover, it has a high CO₂ removal capacity, low absorption heat and low regeneration energy and is less corrosive to instrument. It also has the potential of capturing multiple flue gas components (NO_x, SO_x and CO₂) and producing value added chemicals, such as ammonium sulphate and ammonium nitrate, which are commonly used as fertilizers. However, ammonia is volatile and hence it slips to flue gas

and CO₂ product, thus requiring additional energy and capital costs to reduce ammonia evaporation and/or recover ammonia. This could offset the advantages offered by ammonia.

Over the last few years, there has been a significant amount of research work on the aqueous ammonia based CO₂ capture technologies including experimental investigations at various scales and process modeling to evaluate energy consumption and economics. This paper will briefly review these research activities and make comparisons with other solvents in particular MonoEthanolAmine (MEA), the benchmark solvent, and identify the research opportunities for further improvements.

1 AQUEOUS AMMONIA BASED CO₂ CAPTURE PROCESSES

A number of pilot and demonstration plants has been constructed and operated to evaluate the technical and economic feasibility of NH₃ based PCC processes to remove CO₂ from flue gas being emitted from various industrial sources including both coal and natural gas fired power stations. *Alstom*, *Powerspan*, *CSIRO* and *KIST* (Korean Research Institute of Industrial Science & Technology) are the major players in this area and have tested the technologies at pilot-plant scale ([McLarnon and Duncan, 2009](#); [Rhee et al., 2011](#); [Telikapalli et al., 2011](#); [Yu et al., 2011a](#)).

Powerspan developed an aqueous NH₃ based CO₂ capture process, called ECO₂[®], in which the absorption takes place at ambient temperatures and no slurry is involved in the absorber ([McLarnon and Duncan, 2009](#)). The ammonia concentration used was not given and believed to be between 5 and 15%. Desorption occurs at low pressures. An illustration of how the ECO₂ system is integrated with the ECO multi-pollutant control system is shown in [Figure 1](#). The ECO system uses a barrier discharge reactor, wet scrubber and wet electrostatic precipitator to remove high levels of NO_x, SO₂, mercury and fine particulate matter. The wet scrubber uses aqueous ammonia for SO₂ scrubbing, producing ammonium sulphate fertilizer as a co-product. *Powerspan* initiated a pilot test program with FirstEnergy at the R.E. Burger Plant to demonstrate CO₂ capture through integration with the ECO[®] multi-pollutant control process. A 1-MW pilot demonstration was designed to produce approximately 20 metric tonnes of sequestration ready CO₂ per day. However pilot plant results have not been reported in public domain and there is no further development of this technology reported in the literature.

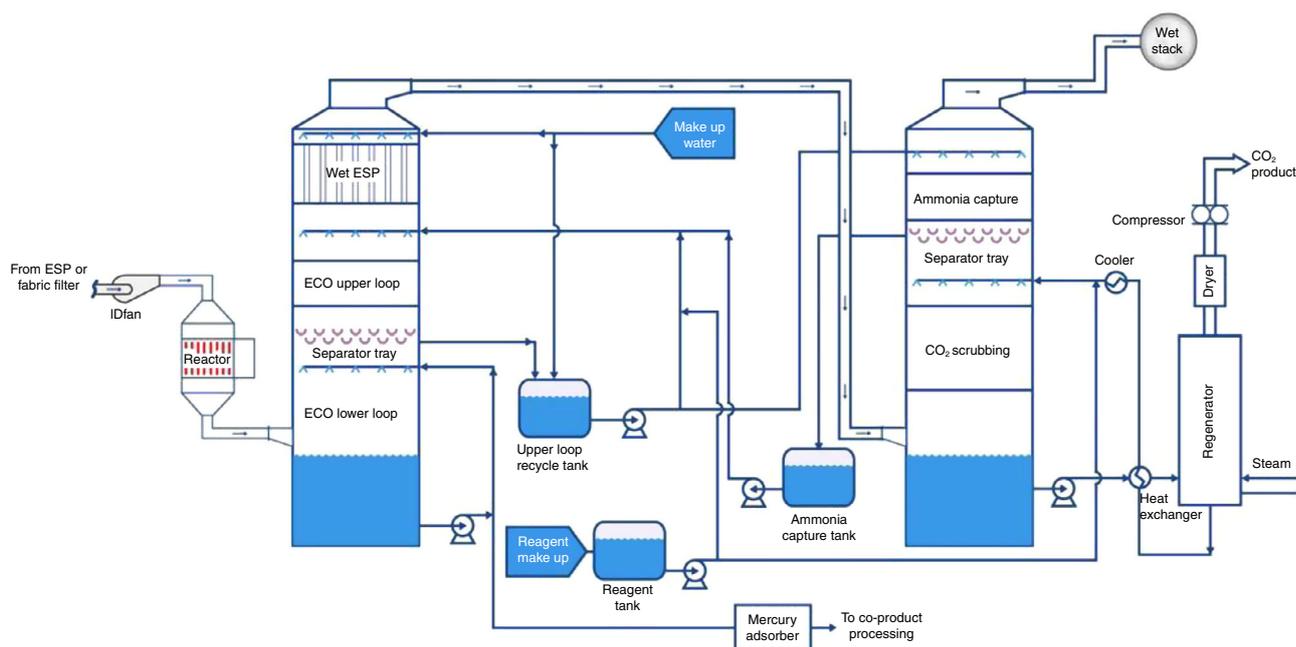


Figure 1

Incorporation of the ECO₂ scrubbing process with Powerspan's commercially available multi-pollutant control ECO process. Figure is copied from McLarnon and Duncan (2009).

Alstom has been playing a leading role in developing and advancing a Chilled Ammonia Process (CAP). In this process as described in the open literature (Darde *et al.*, 2009; Telikapalli *et al.*, 2011), CO₂ is absorbed in a highly ammoniated solution at low temperatures (0-10°C), producing a slurry containing ammonium bicarbonate. In the stripper, ammonium bicarbonate is converted to ammonium carbonate at temperatures above 100°C and pressures of 20-40 bar. Figure 2 shows the simplified chilled ammonia process flow diagram.

Alstom conducted a number of field tests of CAP and completed the demonstration project at American Electric Power's Mountaineer Plant at end of May 2011 after a 21 month period (Jönsson and Telikapalli, 2012). The technology is ready for the next major validation on a gas turbine exhaust as well as industrial (refinery) off-gas with the installation of demonstration plant at Technology Centre Mongstad (TCM). TCM is the world's largest facility for evaluating carbon capture technologies.

The processes investigated by CSIRO and under development at KIST are similar to Powerspan's ECO₂; they both operate at close to ambient temperatures and use ammonia concentrations below 10%.

The major difference is that in the CSIRO research, the desorption takes place under medium pressure and the process combines SO₂ removal and ammonia slip reduction (Yu *et al.*, 2011a, 2012a) while RIST is developing technology for CO₂ capture from Blast Furnace Gas (BFG) generated from iron and steel making process. The process utilises the unrecovered waste heat from a steelmaking process for solvent regeneration and ammonia recovery at low temperatures (Rhee *et al.*, 2011).

2 PROCESS CHEMISTRY

Thermo-chemical properties for the CO₂-NH₃-H₂O system have been reasonably understood thanks to intensive experimental and modeling studies over the years, in particular the last few years. These studies include experimental determination of vapour-liquid-solid equilibrium, speciation, heat of absorption, reaction kinetics, and the thermodynamic model development. Research work in this area has been reviewed by Maurer (2011) and Zhao *et al.* (2012). This section only briefly reviews vapour-liquid-solid equilibrium and reaction mechanism involved in the liquid phase.

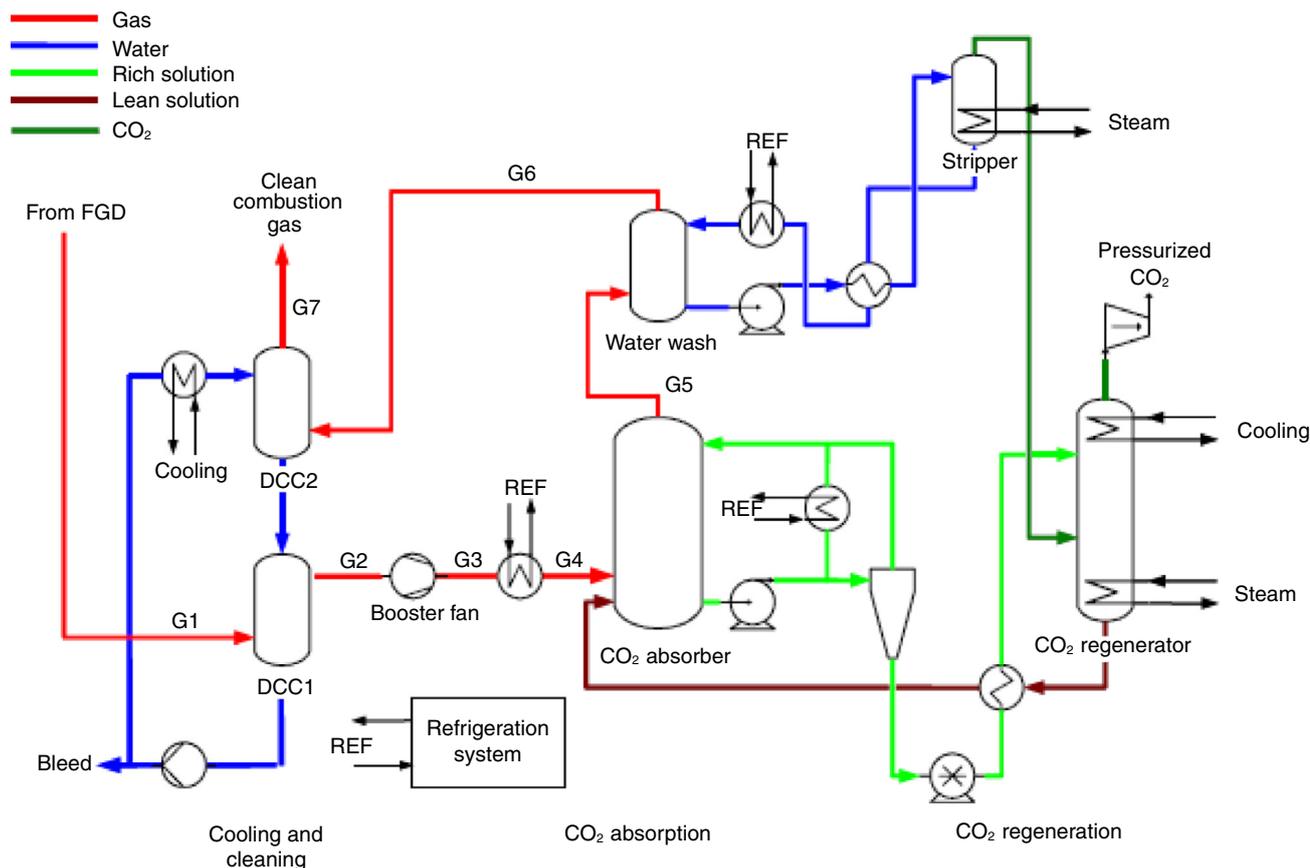


Figure 2

Chilled ammonia process flow diagram. Figure is copied from Jönssona and Telikapalli (2012).

2.1 Vapour-Liquid-Solid Equilibrium (VLSE)

The CO₂-NH₃-H₂O equilibria relevant for the application of aqueous ammonia based CO₂ capture processes are described in Figure 3 (Thomsen and Rasmussen, 1999).

As shown in Figure 3, despite the fact that ammonia can be regarded as the simplest amine, its interaction with CO₂ is quite complex involving the evaporation of ammonia to the gas phase, the formation of carbonate, bicarbonate and carbamate in the liquid phase and solid precipitation. Ammonium bicarbonate is believed to be the major species in the solid, but not all authors agreed on the possible formation and combination of the salts made of (NH₄)₂CO₃, NH₂COONH₄, 2NH₄HCO₃. The complex nature of the CO₂-NH₃-H₂O system makes ammonia an intriguing solvent and it imposes some challenges for its application on CO₂ capture, as discussed in the following sections.

Vapour	CO ₂ (g)	NH ₃ (g)	H ₂ O (g)
	↕	↕	↕
Liquid	CO ₂ (aq)	NH ₃ (aq)	H ₂ O (l)
	$\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-$ $\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{OH}^+$ $\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+$ $\text{HCO}_3^- + \text{NH}_3(\text{aq}) \leftrightarrow \text{NH}_2\text{COO}^- + \text{H}_2\text{O}$ $\text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}^+ + \text{OH}^-$		
Solid	$\text{NH}_4^+ + \text{HCO}_3^- \leftrightarrow \text{NH}_4\text{HCO}_3(\text{s})$ $\text{NH}_2\text{COO}^- + \text{NH}_4^+ \leftrightarrow \text{NH}_2\text{COONH}_4(\text{s})$ $2\text{NH}_4^+ + \text{CO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow (\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}(\text{s})$ $4\text{NH}_4^+ + \text{CO}_3^{2-} + 2\text{HCO}_3^- \leftrightarrow (\text{NH}_4)_2\text{CO}_3 \cdot 2\text{NH}_4\text{HCO}_3(\text{s})$		

Figure 3

Vapour liquid solid equilibria in the CO₂-NH₃-H₂O system.

A number of thermodynamic models has been developed for the NH₃-CO₂-H₂O system in particular models developed by Thomsen and Rasmussen (1999) and Que and Chen (2011) which satisfactorily predict the vapour-liquid-solid equilibria over a wide range. Thomsen and Rasmussen developed a thermodynamic model which includes the aforementioned equilibrium processes (Fig. 3) under the 0-110°C range of temperature and 1-100 bar of the pressure, the ammonia concentration up to 80 molal. This model is not only for the vapour-liquid system but also for vapour-liquid-solid equilibrium including formation of ammonium bicarbonate: NH₄HCO₃; ammonium carbonate: (NH₄)₂CO₃·H₂O; ammonium carbamate: NH₂COONH₄ and ammonium sesqui-carbonate: (NH₄)₂CO₃·2NH₄HCO₃. The thermal properties of the aqueous electrolyte solution are calculated on the basis of the extended UNIQUAC model and the Soave-Redlich-Kwong equation of state. Que and Chen (2011) developed the electrolyte NRTL (Non-Random Two Liquid) activity coefficient model which can satisfactorily represent the thermodynamic properties of the NH₃-CO₂-H₂O system at temperatures up to 473 K, pressures up to 7 MPa, NH₃ concentrations up to 30 wt%, and CO₂ loadings up to unity. However, the model considers ammonium bicarbonate as the only species in the solid.

The availability of these models allows the reliable calculation of thermochemical properties of the CO₂-NH₃-H₂O system under various conditions, assessment of the energy performance of the capture process and even the definition of the best range of operation conditions. For example, Figure 4 shows the predicted solubility curve for ammonium bicarbonate as a function of ammonia concentration and CO₂ loading at various temperatures

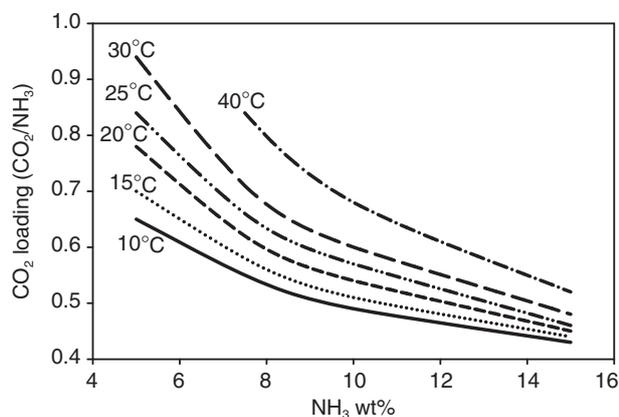


Figure 4
Predicted ammonium bicarbonate solubility operation line.

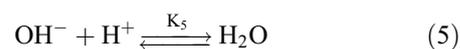
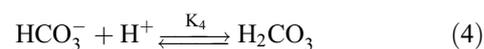
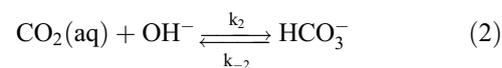
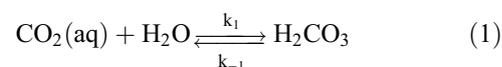
(Yu et al., 2012a). In the region above each curve, ammonium bicarbonate precipitates from the liquid phase. To avoid solid precipitation in the absorber, the ammonia concentration, CO₂ loading and absorption temperatures should be considered carefully.

2.2 Reaction Mechanism/Kinetics in the Liquid Phase

CO₂ absorption in aqueous ammonia is a relatively slow process and limited by the mass transfer in the liquid phase (Darde et al., 2011; Liu et al., 2011; Qi et al., 2013). So it is critical to have a detailed understanding of the reaction mechanism/kinetics involved in the absorption chemistry in order to develop a process model for process evaluation, optimisation and scale-up. A number of researchers investigated the reactions involved in the absorption process and put forward different reaction mechanisms. Similar to the case for the reaction of CO₂ with primary amines, the most important reaction in the presence of free ammonia is the reaction of NH₃ with CO₂. The reaction mechanisms proposed include the zwitterion mechanism (Derks and Versteeg, 2009) and the ter-molecular mechanism (Qin et al., 2010).

A more detailed model was developed by Wang et al. (2011) who studied the kinetics of the reversible reaction of CO₂ with ammonia (instead of irreversible reaction proposed by other researchers) in aqueous solution using stopped-flow techniques and established a complete reaction mechanism, as shown in Figure 5 (Wang et al., 2011).

The interactions of CO₂ (aq) with water and hydroxide ions are indicated in dashed lines. Equations (1-6) summarize this part of the reaction scheme as well as the protonation equilibrium of ammonia:



The formation reactions of the carbamate/carbamic acid included in the mechanism are shown in Equation (7),

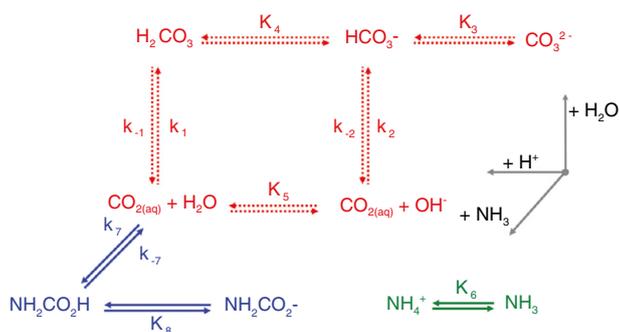
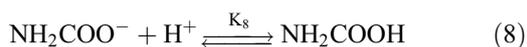
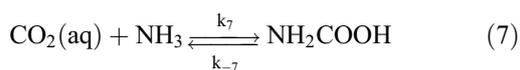


Figure 5

Reaction scheme, including all reactions between ammonia, the CO_2 /carbonate group, and protons (Wang *et al.*, 2011).

while Equation (8) describes the protonation of carbamate to the carbamic acid:



The temperature dependence of all rate and equilibrium constants including the protonation constant of NH_3 between 15 and 45°C were reported by Wang *et al.*

In a CO_2 capture process aqueous ammonia reacts with $\text{CO}_2(\text{aq})$ to form carbamic acid which deprotonates instantly to give a carbamate. Due to the pH changes with continued absorption of CO_2 , the equilibrium is reversed and the carbamate eventually decomposes to generate protonated ammonia and bicarbonate. Table 1 shows the carbamate equilibrium constants and pKa of amines including ammonia. The carbamate equilibrium constants for MEA is much higher than that for ammonia, suggesting that ammonia-derived carbamate is

formed with a lower yield than the equivalent Mono-EthanolAmine carbamate, which contributes to the higher CO_2 loading capacity for aqueous ammonia compared to MonoEthanolAmine.

3 PERFORMANCES OF AQUEOUS AMMONIA BASED POST COMBUSTION CAPTURE PROCESSES

Pilot plant trials and demonstration projects have confirmed the technical feasibility of the aqueous ammonia based CO_2 capture processes and some of the anticipated benefits (Jönsson and Telikapalli, 2012; Rhee *et al.*, 2011; Yu *et al.*, 2011b). The benefits include high CO_2 removal efficiency and high purity of CO_2 product; high stability; high CO_2 loading capacity and high effectiveness for capturing SO_2 (Yu *et al.*, 2011b). This section focuses on absorption rate, regeneration energy, ammonia loss and overall performance.

3.1 CO_2 Absorption Rate

The CO_2 absorption rate is an important parameter which can determine the size of column and hence determine capital cost. It is related to the mass transfer coefficient, the effective surface area for mass transfer and the driving force as described in Equation (9):

$$N_{\text{CO}_2} = K_G A_{\text{int}} (P_{\text{CO}_2} - P_{\text{CO}_2}^*) \quad (9)$$

where N_{CO_2} is the CO_2 absorption rate (mol/s), K_G is the overall gas phase mass transfer coefficient (mol/(s.m².kPa)), P_{CO_2} is the partial pressure of CO_2 in the flue gas (kPa), $P_{\text{CO}_2}^*$ is the CO_2 equilibrium partial pressure in the solvent (kPa) and A_{int} is the effective interfacial surface area of packing (m²).

Mass transfer coefficients are used to assess the CO_2 absorption rates in the solvents. The bench scale studies using wetted wall column and pilot plant studies all suggest that CO_2 mass transfer coefficient in aqueous ammonia are lower than those in MEA (Yu *et al.*, 2011a, 2012b). Figure 6 shows the comparison of overall

TABLE 1
Carbamate equilibrium constants and pKa of amines at 25°C (Fernandes *et al.*, 2012; Puxty *et al.*, 2009)

		NH_3	MEA	AMP	DEA	PIPD	4-PIPD	4-PIPDE
$\text{HCO}_3^- + \text{RNH}_2 \xrightleftharpoons{K_1} \text{RNHCOO}^- + \text{H}_2\text{O}$	Log K_1	0.33	1.76	Very unstable carbamate formed	0.92	1.38	1.39	1.38
$\text{RNH}_3^+ \xrightleftharpoons{K_2} \text{RNH}_2 + \text{H}^+$	pKa	9.24	9.44	8.84	8.88	11.2	10.9	10.6

AMP: 2-amino-2-methyl-1-propanol; DEA: Diethanolamine; PIPD: Piperidine; 4-PIPD: 4-piperidinemethanol; 4-PIPDE: 4-piperidineethanol.
 $K_1 = \frac{[\text{RNHCOO}^-][\text{H}_2\text{O}]}{[\text{RNHCOO}^-][\text{H}^+]}$, M^{-1} ; $K_2 = \frac{[\text{RNH}_2][\text{H}^+]}{[\text{RNH}_3^+]}$, M ; $\text{pKa} = -\log_{10} K_2$

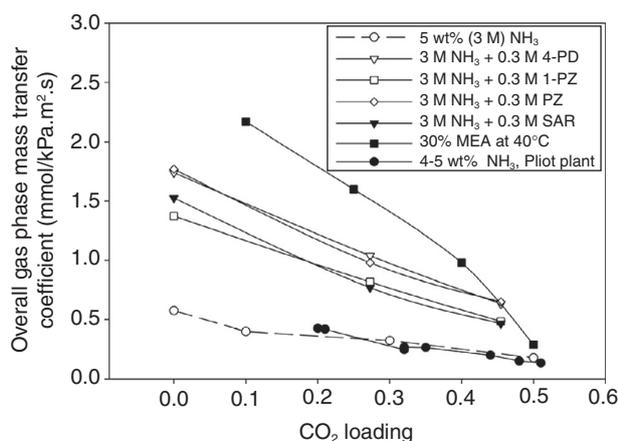


Figure 6

Mass transfer coefficients for CO₂ at various CO₂ loadings obtained from Wetted Wall Column experiments (WWC) and pilot plant trials. WWC: for 30 wt% MEA, absorption temperature = 40°C; for other solvents, absorption temperature = 15°C. Pilot plant: absorption temperature = 10-15°C. 4-PD: 4 amino piperidine. PZ: piperazine. 1-PZ: 1-methyl piperazine. SAR: Sodium Sarcosinate.

gas phase mass transfer coefficient as a function of CO₂ loading in aqueous ammonia and the standard 30 wt% MEA (Yu *et al.*, 2012b). Good agreement between results from pilot plant and wetted wall column experiments for the ammonia solvent was observed. This suggests that the mass transfer coefficients obtained from the wetted wall column can be used to estimate those in large-scale packed columns, at least under the conditions reported here.

The mass transfer coefficients for CO₂ in 3 M aqueous ammonia alone are 3 to 5 times lower than those in MEA solutions at the CO₂ loading range of 0.2-0.4 mole CO₂ per mole amine. The low values for the mass transfer coefficients are due to the low rate constant for the reaction of NH₃ and CO₂ in comparison with that for the reaction between MEA and CO₂. This reaction is the key step for CO₂ absorption in aqueous ammonia (Wang *et al.*, 2011). The reaction of CO₂ + OH⁻, can contribute to CO₂ absorption but its contribution is small due to the low concentration of OH⁻. According to surface renewal theory of mass transfer with chemical reactions, for a pseudo first order reaction and assuming resistance in the gas phase is negligible, the liquid side mass transfer coefficient can be estimated by Equation (10) (Yu *et al.*, 2012b):

$$K_G = \frac{\sqrt{k C_{\text{NH}_3} D_{\text{CO}_2}}}{H_{\text{CO}_2}} \quad (10)$$

k is the rate constant for forward reaction of CO₂ with NH₃, C_{NH_3} is the concentration of free ammonia in the liquid bulk, and D_{CO_2} and H_{CO_2} are diffusivity coefficients and Henry's law constants in aqueous ammonia, respectively.

k values are typically around 200 M⁻¹.s⁻¹ at the temperature of 15°C (Wang *et al.*, 2011). The values are significantly lower than the rate constants for the reaction of MEA with CO₂ at 40°C which are more than 10 000 M⁻¹.s⁻¹ (Versteeg *et al.*, 1996). Both temperature and ammonia concentration can be increased to enhance K_G , but the ammonia loss would increase as well.

There is no publicly available report on the CO₂ absorption rate in the chilled ammonia process. Recently, Alstom power published a paper in which described the rate based model for the chilled ammonia process (Lia *et al.*, 2012). The model used the zwitterion mechanism to explain the reaction between CO₂ and NH₃ and the kinetics parameters in equations were derived by fitting them against experimental data reported by Derks (Derks and Versteeg, 2009). So it is speculated that the mass transfer coefficients for CO₂ in the chilled ammonia process are low, if no promoter/additive is used.

3.2 Regeneration Energy

Table 2 lists the solvent regeneration energies reported in the literature. The regeneration energies refer to the heat requirement for regeneration of solvents (reboiler duty) in the stripper. The values are quite different and vary from less than 1 000 KJ/kg CO₂ to more than 4 200 KJ/kg CO₂. The significant discrepancy is due to under-estimation of heat of desorption in the previous studies and the large variation in operational conditions in particular the solvent concentrations.

During the solvent regeneration, heat is required for:

- CO₂ desorption reaction;
- steam regeneration;
- sensible heat.

Due to the different process conditions, the contribution of the above three parts of energy is various, resulting in the various heat requirements in the CO₂ capture process.

During the stripper process, CO₂ can be desorbed *via* many pathways including the following overall reactions (Jilvero *et al.*, 2012).

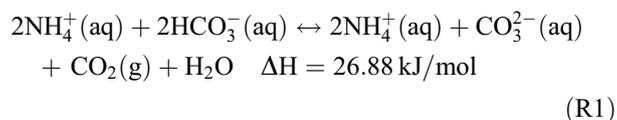
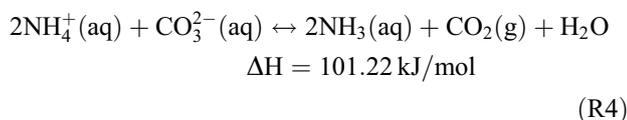
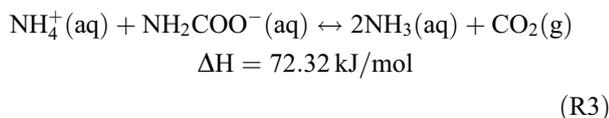
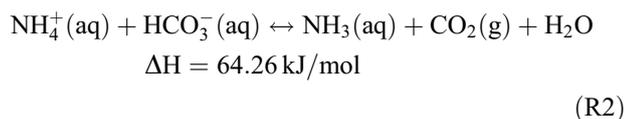


TABLE 2
Heat requirement of desorption processes that use aqueous ammonia

Source	Year	Method	Heat requirement (KJ/kg CO ₂)	Ammonia concentration (wt%)	CO ₂ loading	
					Lean	Rich
EPRI (2006)	2006	Estimate	930	-	-	-
McLarnon and Duncan (2009)	2009	Estimate	1 000	-	-	-
Darde <i>et al.</i> (2009)	2009	Modeling	2 050	28	0.33	0.67
Dave <i>et al.</i> (2009)	2009	Modeling	2 900	7	-	-
Mathias <i>et al.</i> (2010)	2009	Modeling	2 377	26	0.35	0.92
Yu <i>et al.</i> (2011a)	2010	Pilot plant	4 000-4 200	4-5	0.17-0.19	0.35-0.40
Valenti <i>et al.</i> (2012)	2012	Modeling	2 460	15	0.33	-
Darde <i>et al.</i> (2012)	2012	Modeling	~2 500	7.8	0.33	0.66-0.68
Jilvero <i>et al.</i> (2012)	2012	Modeling	2 200	10	0.3	-
Alstom power (Jönsson and Telikapalli, 2012)	2012	Demonstration project	2 200	-	-	-



The previous research reported a low regeneration energy requirement based on the assumption that the regeneration only involves the decompose reaction of ammonia bicarbonate to CO₂ and ammonia carbonate (R1) and the heat of reaction for this reaction is low ($\Delta H = 26.88 \text{ kJ/mol}$). The equilibrium based modeling suggested that one cannot single out only one particular pathway for the solvent regeneration. The experimental and modeling investigations show that the heat of absorption is a function of CO₂ loading and a weak function of temperature and ammonia concentration. Figure 7 shows the experimental and predicted heat of absorption of CO₂ in 5% ammonia solution at the

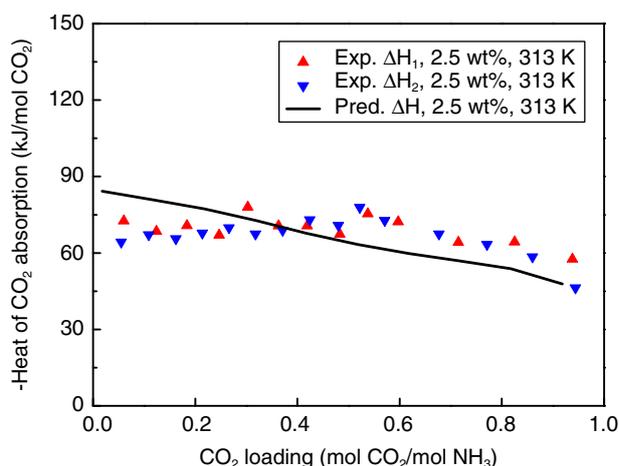


Figure 7

Predicted and experimental heat of CO₂ absorption in 5 wt% NH₃ at $T = 40^\circ\text{C}$.

temperature of 40°C (Qi *et al.*, 2013). The predicted results were obtained using the thermodynamic model for CO₂-NH₃-H₂O developed by Aspentech (Que and Chen, 2011). Over the large CO₂ loading range (0-0.6), the heat of absorption is more than 60 kJ/mol, suggesting that the overall absorption/decomposition pathway

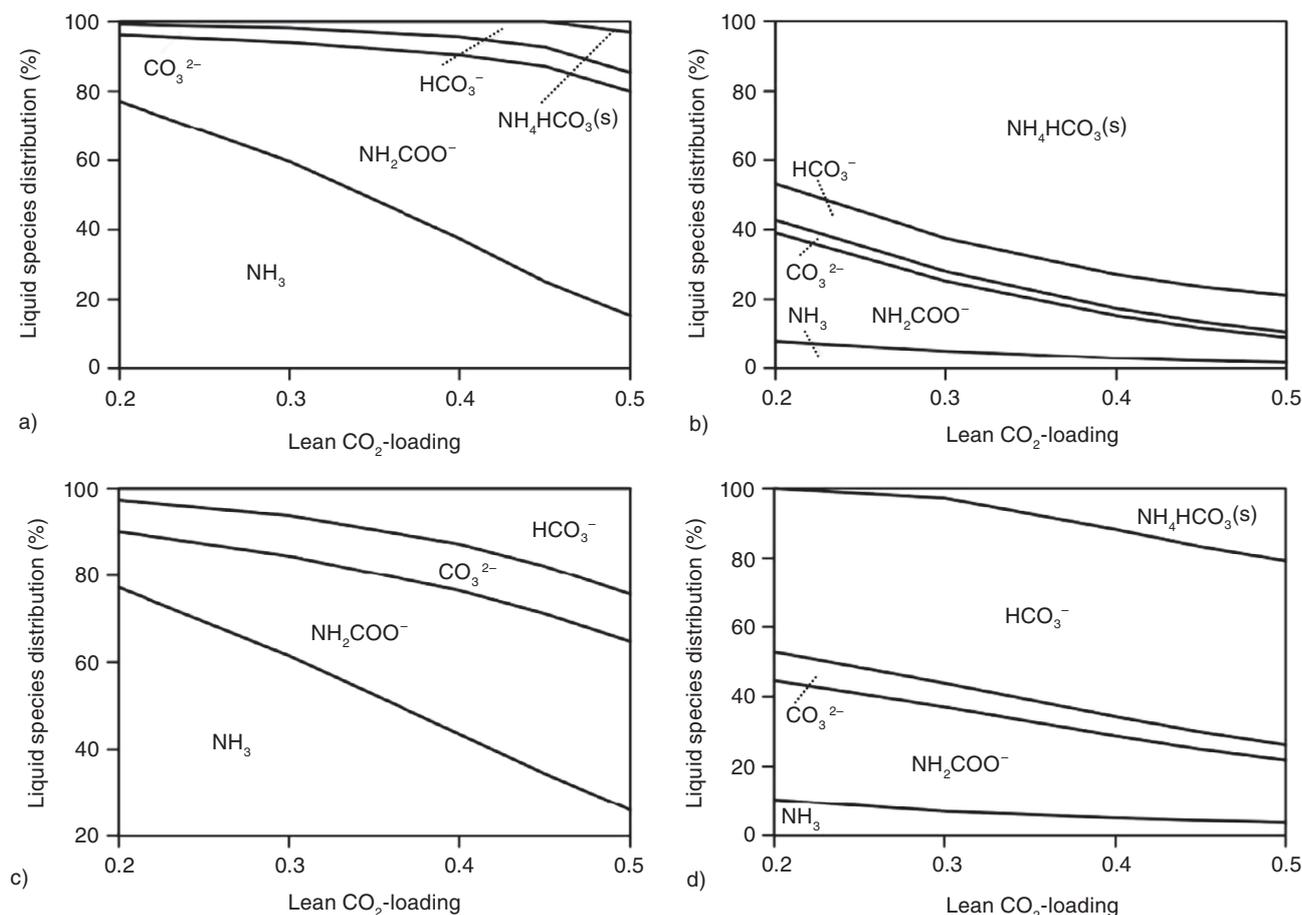


Figure 8

The CO₂-lean solution (a and c) and the CO₂-rich solution (b and d) liquid composition at 15% ammonia (a and b) and 5% ammonia (c and d) are shown as a function of the lean CO₂-loading. The figures exclude water and trace element, such as N₂, OH⁻, H⁺, and CO₂. The process is conducted at a temperature of 10°C and at atmospheric pressure. The figure is copied from [Jilvero et al. \(2012\)](#).

is mainly *via* the formation of ammonium bicarbonate (R2) and carbamate (R3) which is consistent with the conclusion drawn by [Jilvero et al. \(2012\)](#). Through the thermodynamic analysis of the speciation distribution in both lean and rich solvent at NH₃ concentrations 5 and 15% and lean loading of 0.2 to 0.5, it has been found that a large proportion of the CO₂ is absorbed through reactions with free ammonia. As shown in [Figure 8](#), for lean and rich solvents, there are negligible differences with respect to the fractions of carbamate and the carbonate, while the level of free ammonia is decreasing and the amount of bicarbonate is increasing. This suggests that the main reaction pathway for the absorption of CO₂ was identified as the formation of bicarbonate through the reaction of ammonia with CO₂. In other words, the decomposition of bicarbonate to ammonia

and CO₂ is the main reaction for the CO₂ desorption. The heat of reaction required to desorb CO₂ of ammonia was similar to that required for MonoEthanolAmine (MEA). The simulation results show that the heat requirement of ammonia regeneration could be less than 2 500 kJ/kg CO₂ captured. ([Jilvero et al., 2012](#)). The main reason for the lower heat requirement for ammonia compared to MEA is that the thermodynamic properties of the NH₃-CO₂-H₂O system allow for pressurized regeneration, which results in significantly lower water vaporization.

All investigations based on equilibrium-based thermodynamic process modeling are in agreement regarding the potential to achieve a regeneration heat requirement that ranges between 2 000 and 3 000 kJ/kg CO₂ for an aqueous ammonia process. The recent publication from [Alstom](#)

shows a heat requirement of 2 200 KJ/kg CO₂ captured for the chilled ammonia process (Jönsson and Telikapalli, 2012). This result is in line with the modeling prediction. These recent studies show that the aqueous ammonia based CO₂ capture process requires much less heat for the solvent regeneration than MEA based capture processes (Jönsson and Telikapalli, 2012; Jilvero *et al.*, 2012; Valenti *et al.*, 2012; Darde *et al.*, 2012).

The pilot plant trials conducted by CSIRO and Delta Electricity at Delta Electricity's Munmorah power station showed a much higher heat requirement (Yu *et al.*, 2011b). One reason for the high heat requirement is that a diluted ammonia solution was used and the amount of CO₂ captured/released is low. As a result, more than 50% of energy is used to heat up the solvent (sensible heat). The results also show the heat of desorption is around 70-80 kJ/mol, suggesting under the pilot plant conditions where CO₂ loading in stripper varied between 0.4 and 0.1, the major pathway is the formation of carbamate *via* the reaction of CO₂ with free ammonia.

3.3 Ammonia Loss

Ammonia is very volatile and characterised by high equilibrium pressure even in the CO₂ loaded aqueous ammonia solution. Figure 9 shows predicted partial and total pressure at the ammonia concentration of 28% and temperature of 8°C; Figure 10 predicted equilibrium CO₂ and NH₃ partial pressure as a function of CO₂ loading at the ammonia concentration of 5 wt% and

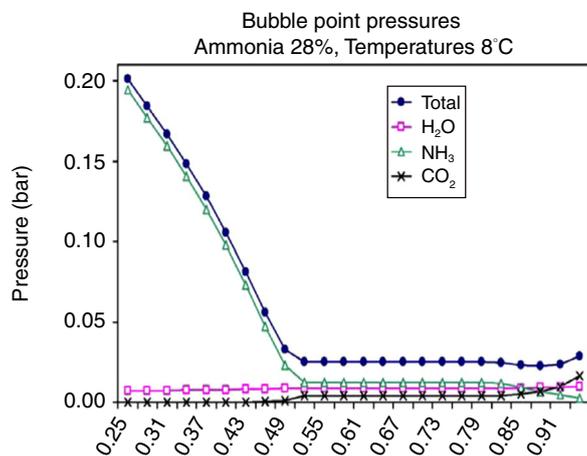


Figure 9

Predicted partial and total pressure at the ammonia concentration of 28 wt% and the temperature of 8°C (Darde *et al.*, 2009).

the temperature of 10, 20 and 30°C; Figure 11 predicted equilibrium NH₃ and CO₂ partial pressure as a function of CO₂ loading at the ammonia concentration of 2.5 and 5% and the temperature of 10°C. The conditions for Figure 9 are relevant for the chilled ammonia process in which precipitation of products is taken into account while the conditions for Figures 10 and 11 are for processes at ambient temperatures, used by Powerspan, CSIRO and KIST at lower ammonia

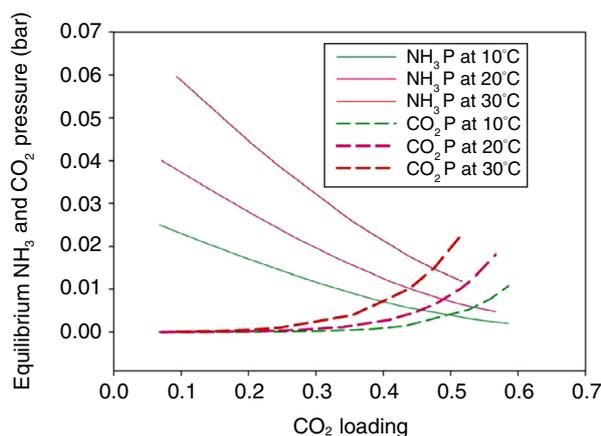


Figure 10

Predicted equilibrium CO₂ and NH₃ partial pressure as a function of CO₂ loading at the ammonia concentration of 5 wt% and the temperature of 10°C. Aspen Plus® V7.3 with a built-in thermodynamic model for CO₂-NH₃-H₂O was used to obtain equilibrium pressure in Figure 10 and Figure 11 (AspenTechnology, 2012; Que and Chen, 2011).

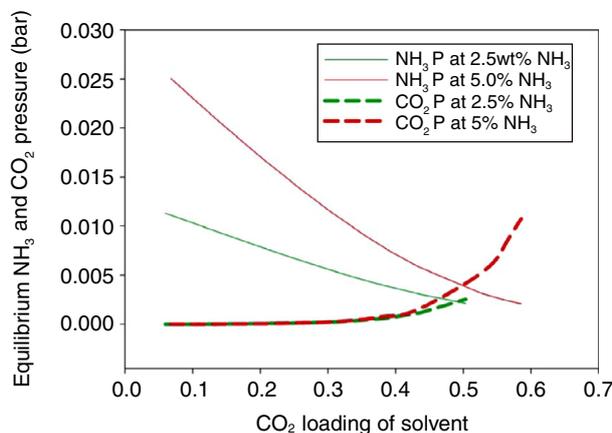


Figure 11

Predicted equilibrium NH₃ and CO₂ partial pressure as a function of CO₂ loading at the ammonia concentration of 2.5 and 5% and the temperature of 10°C.

concentration in which precipitation did not take place. It is clear in all cases, that NH₃ vapour pressures are significant at CO₂ loading below 0.5.

As a result, ammonia will inevitably slip to flue gas in the absorber and to the CO₂ product stream from the stripper in the capture process and measures will have to be taken to recover the ammonia. The operational and capital costs for an ammonia recovery process will be determined by the amount of ammonia slip and the impact of the operational parameters. Despite the fact that it is widely acknowledged that ammonia loss is a big challenge to the aqueous ammonia based CO₂ capture process, there are limited studies on the ammonia loss rate in the literature.

For the chilled ammonia processes, the results available in the literature are all from the modeling work. Mathias *et al.* (2010) studied the effect of ammonia concentration in the gas phase at the outlet of absorber. They found out that the NH₃ slip from the absorber is only weakly dependent on the NH₃ concentration in the range of 15-26% and depends mainly on temperature. At the absorber temperature of 10°C and atmospheric pressure, the NH₃ concentration is approximately constant at 2 230 ppmv at ambient pressure, the ammonia concentration of 26% and CO₂ loading of ca. 0.4 in the lean solvent and reduced to 242 ppm if absorber temperature can drop to -1.1°C. The equilibrium NH₃ partial pressure for a solvent at the ammonia concentration of 28% and CO₂ loading of 0.4 and 8°C is more than 0.05 bar equivalent to 50 000 ppm at atmospheric pressure (Fig. 9), according to Darde *et al.* (2009). The large discrepancy between the two references is most likely indicative of the uncertainty around the thermodynamics of liquid-solid systems.

Versteeg and Rubin (2011) did a thorough analysis of effect of ammonia concentration (0-30%), CO₂ loading (0.25 to 0.67), absorber temperature (5 to 20°C) on ammonia slip in a chilled ammonia process in which rich solvent is not recycled to absorber. An increase in ammonia concentration and absorber temperature as well as a decrease in CO₂ loading can lead to an increase in ammonia slip. Darde *et al.* (2012) also modeled the chilled ammonia process at the low ammonia concentrations up to 12% and investigated the effect of ammonia concentration, CO₂ loading, absorber temperature and process configuration. In a configuration close to the configuration proposed by Alstom (Fig. 2), it has been found that with increase in ammonia concentration in the solvent from 4 to 11%, the ammonia concentration in the gas stream leaving the absorber varies between 4 500 and 19 000 ppm. In Darde's work, a murphy tray efficiency was introduced to account for deviation from the equilibrium.

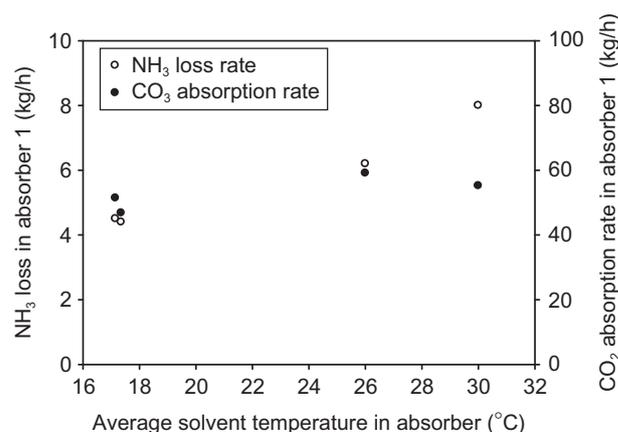


Figure 12

Effect of temperature on the CO₂ absorption rate and NH₃ loss rate in absorber 1 under similar conditions. NH₃ wt% = 3.8-4.2; CO₂ loading in lean solvent = 0.22-0.25. Solvent flow-rate = 134 L/min; Gas flow-rate = 640-820 kg/h; CO₂ in the flue gas = 8-10 vol%. Inner diameter of absorber 1 = 0.6 m; packing height = 3.8 m (Yu *et al.*, 2011a).

Budzianowski (2011), Niu *et al.* (2012) and Yu *et al.* (2012c) conducted experiments to investigate ammonia loss at low ammonia concentrations and relatively high absorber temperatures. All results from these studies observed the trends similar to the modeling studies described above, but the ammonia loss is much higher. For example, Niu *et al.* (2012) studies the absorption at the ammonia concentration of 1-11 wt%, the CO₂ loading of 0.12 and the temperature of 24°C and the ammonia concentrations at outlet were 1-14 vol%. Similar to research work by Niu *et al.*, Yu *et al.* used a pilot scale research facility to investigate the effect of a number of parameters. The pilot plant trials show that the conditions which typically enhance CO₂ absorption rate such as an increase in ammonia concentration and absorption temperature and a decrease in CO₂ loading tend to increase ammonia loss significantly. Among many parameters which affect ammonia loss, temperature is one of the most sensitive parameters. As shown in Figure 12, with the increase in solvent temperature, CO₂ absorption rate in absorber 1 remains similarly but ammonia loss rate increases significantly. From the ammonia loss point of view, the absorption temperature should be as low as possible. However, it is expected that a considerable amount of additional energy is required to produce chilled water. Dave *et al.* (2009) simulated the aqueous ammonia based process by keeping the flue gas and lean solvent temperatures to the absorber at 10°C and solvent concentration at 2.5 and 5 wt%.

The electricity consumption is estimated to be more than 1 400 KJ/kg CO₂.

In addition, the research by Budzianowski (2011) and Qi *et al.* (2013) suggested that the NH₃ desorption process is a fast process and controlled by the vapour liquid equilibrium which could guide future research on process modification to reduce ammonia slip in absorber.

Ammonia is also present in the CO₂ product and requires removal. Yu *et al.* (2012a) investigated the effect of operation conditions on ammonia concentration in the CO₂ product. To reduce ammonia concentration, the high pressure operation and low temperature in the over-head condenser will help reduce ammonia concentration in the CO₂-product. However, this can cause solid precipitation in the stripper where solvent regeneration leads to generation of vapour which contains significant amount of ammonia and CO₂ gas apart from water vapour. When the temperature of vapour drops in the condenser/reflux line or even in stripper when the regeneration stops, part of vapour will condense, leading to formation of the solution/droplet in which ammonia concentration is very high (more than 10 wt%). Since partial pressure of CO₂ is high in stripper, this facilitates formation of a highly carbonated ammonia solution which reaches the ammonium bicarbonate solubility limit. The precipitation of solid will block the stripper condenser and reflux line, causing a shut-down of the plant. Blockage also occurs in instrument tubing, leading to false readings and affecting the operation. For ammonia processes which operate at higher ammonia concentrations, the blockage could also occur in the absorber packing.

3.4 Overall Performance

The aqueous ammonia based CO₂ capture process is quite complex as it involves flue gas cooling, CO₂ absorption and stripping, ammonia capture and recovery. The technology is still under development. So far there are no published results available from optimised pilot plant/demonstration plants, which prevent the rigorous economical assessment of the technologies. In the literature, the assessment of the overall performance was carried out using the equilibrium based process model with the estimated CO₂ absorption rates in the absorber.

Previous studies indicated significant improvements in performance over traditional amine technologies but the analysis was preliminary and based on limited understanding of the system (Bai and Yeh, 1997; Ciferno *et al.*, 2005; Gal *et al.*, 2011). As described above, the understanding of the system has improved significantly over the last few years. Based on improved understanding of the system

thermodynamics model, Versteeg and Rubin (2011) modeled a chilled ammonia-based post-combustion CO₂ capture system processing flue gas from a supercritical coal-fired power plant. The estimated performance and cost were compared to an amine-based capture system. For the ammonia system the absorber CO₂ capture efficiency, NH₃ slip, and solids precipitation were evaluated for changes in lean solution NH₃ concentration, NH₃/CO₂ ratio, and absorber temperature. For 90% CO₂ capture the levelized cost of electricity generation (annual revenue requirement) for the plant with ammonia-based capture was estimated at \$US 105/MWh, which is comparable to the levelized cost of electricity generation for the plant with an amine-based capture system. The ammonia-based CO₂ system benefits from lower steam loads and reduced compressor power requirements, but the chilling loads and associated costs offset these benefits. Versteeg and Rubin (2011) suggest that the viability of ammonia-based CO₂ capture may be location dependent. A plant located in a characteristically cold climate, or with direct access to a large cooling sink such as a deep water lake, would have lower parasitic energy demands for the process chillers.

Linnenberg *et al.* (2012) evaluated the impact of an ammonia-based post-combustion CO₂ capture process on a steam power plant. To study the influence of the cold end of the process, two power plants with different cooling water temperatures are analysed. Additionally, two different process configurations of the capture plant, with either one single absorber or two absorbers connected in series where the first absorber captures the majority of the CO₂ and the second limits the NH₃ slip, are evaluated. The study shows that the configuration of the process with absorption at low temperature (approximately 10°C) with or without precipitation of ammonium bicarbonate compounds leads to a lower net efficiency penalty than an MEA-based process, assuming that low temperature cooling water is available. An estimate of the size of the absorber shows that the absorber columns of an ammonia-based process are significantly higher than the ones required for an MEA-based process. The conclusions are consistent with those by Versteeg and Rubin (2011).

4 OUTLOOK

As highlighted by Zhuang *et al.* (2012), three inherent hurdles with the aqueous ammonia based capture technology have not been fully overcome yet: low CO₂ absorption rate resulting in large absorption equipment; high ammonia vapour pressure leading to ammonia slip into the cleaned flue gas, and ammonium bicarbonate

solid formation in the absorption tower (in stripper condenser as well) which may plug the tower packing, stripper condenser and reflux line. Further research efforts should be focused on these areas in order to improve the technical and economic feasibility of the technologies. Recent research has shown that introduction of additives can enhance CO₂ absorption rate or suppress ammonia vapour (Ahn *et al.*, 2012; Gal *et al.*, 2011; Salentinig *et al.*, 2012; Yu *et al.*, 2012b). For example, a PZ-promoted ammonia solution, which has been patented by Alstom (Gal *et al.*, 2011), is a highly effective promoter of CO₂ absorption in ammonia, as shown in Figure 6. The study by Yu *et al.* (2012b) has shown that alternative additives, which are environmentally friendly, have the potential to significantly increase the CO₂ mass transfer coefficients to a level comparable with MEA at high CO₂ loadings relevant to industrial applications. However, it is not clear about possible side effect of introduction of additives. New processes such as high pressure absorption, rich solvent split, re-engineering of the industrial ammonium bicarbonate fertilizer production process and combined capture of CO₂, SO₂ and other impurities could offer potential for improvement (Yu *et al.*, 2011a; Zhuang *et al.*, 2012). All these research efforts are the early stage of the development.

CONCLUSIONS

The aqueous ammonia based post combustion CO₂ capture processes have gained intensive attention over the last few years thanks to many advantages over amine based solvents. A number of pilot plants and demonstration plants have been constructed and used to assess the technical and economical feasibility of the processes and identify opportunities to further advance the technologies. This paper has reviewed the research work available in the public domain including understanding of the thermo-chemical and physical properties of the CO₂-NH₃-H₂O system, and absorption chemistry/kinetics involved during the absorption, information on absorption rate, ammonia loss, regeneration energies, and practical issues, and assessment of the technical and economical feasibility of the aqueous ammonia based post combustion capture technologies.

Thermo-chemical properties for the CO₂-NH₃-H₂O system have been well understood and an extended UNIQUAC model, described by Thomsen and Rasmussen (1999) and an electrolyte NRTL activity coefficient model by AspenTech (Que and Chen, 2011) can satisfactorily represent the thermodynamic properties of the CO₂-NH₃-H₂O system over a wide range. A comprehen-

sive reaction mechanisms involved in the reaction of CO₂ with ammonia in the aqueous medium has been developed by Wang *et al.* (2011).

Bench scale and pilot plant scale investigations show that aqueous ammonia absorbs CO₂ at a slower rate than the standard MEA solution under their respective operational conditions. Process modeling and experimental results both indicate that ammonia losses can be substantial. All investigations based on equilibrium-based thermodynamic process modeling are in agreement regarding a heat requirement that ranges between 2 000 and 3 000 kJ/kg CO₂. The recent publication from Alstom shows a regeneration heat requirement of 2 200 kJ/kg CO₂ captured for the chilled ammonia process. The assessment of the overall performance using the equilibrium based process models shows that the chilled ammonia process leads to a lower net efficiency penalty than an MEA-based process, assuming that low temperature cooling water is available. An estimate of the size of the absorber shows that the absorber columns of an ammonia-based process will be significantly higher than the ones required for an MEA-based process.

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