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UPDATE ON AQUEOUS AMMONIA BASED POST COMBUSTION CAPTURE PILOT PLANT AT MUNMORAH

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Abstract
CSIRO and Delta Electricity have jointly constructed an A$5 million research scale Post Combustion Capture (PCC) pilot plant at the Munmorah black coal fired power station. The results from the pilot plant trials will be used to assess the potential of using aqueous ammonia solution to capture CO_2 and other acid components such as SO_x and NO_x from coal fired power plants under Australian conditions. This paper reports and discusses the experimental results obtained from the pilot plant trials.

Keywords: Post combustion carbon capture, pilot plant trials, aqueous ammonia, CO_2, SO_x, and NO_x.

1 Introduction

Aqueous ammonia, as one of the promising solvents for CO_2 capture, has recently received increasing attention[1-4]. Compared to traditional amines, ammonia is a low cost solvent and does not degrade in the presence of O_2 and other species present in the flue gas. Moreover, it has a high CO_2 removal capacity, low absorption heat and hence low regeneration energy. It has also the potential of capturing multicomponents (NO_x, SO_x and CO_2), which is of particular interest to Australian power stations since flue gas desulphurisation (FGD) of SO_x and selective catalytic reduction (SCR) of NO_x are not implemented in Australia. A number of pilot and demonstration plants have been constructed and operated in the last few years to test the technical and economic feasibility of the ammonia based PCC processes. Alstom and Powerspan are the two major players in this area. Alstom has patented a chilled ammonia process in which CO_2 is absorbed in 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[5]. Powerspan has developed a CO_2 capture process, called ECO2®, in which the absorption takes place at relatively high temperature, above 20°C, and no slurry is involved in the absorber[6].

The chemistry involved in the CO_2 capture by aqueous ammonia is relatively well understood, particular from a thermodynamic point of view (equilibrium product distribution including solid species under various conditions). However, information on e.g. absorption rates, ammonia loss rates and practical experience is, scarcely available in the public domain, which complicates the establishment of a good basis for plant design. To address the gap in know-how on aqueous ammonia for CO_2 capture, CSIRO and Delta Electricity have jointly constructed an A$5 million research scale PCC pilot plant at Munmorah Power Station. It is designed to capture up to 3,000 tonnes per annum of CO_2 from the power station using aqueous ammonia as the chemical absorbent. The objectives of the pilot plant trials include:

- Determination of the interdependent relationship between solvent and feed gas conditions, absorption and regeneration conditions, column packing, CO_2 capture efficiency, ammonia loss, and consumption of energy and cooling water.
- Determination of the fate of acid components present in the flue gas (SO_x and NO_x) including production of chemical bi-products.
- Optimisation of the overall process performance for the given power plant flue gas conditions.
- Identification of opportunities for thermal/process integration or novel approaches to minimize the energy requirements and loss of ammonia, and potential to remove other species such as SO_x and NO_x in the flue gas simultaneously.
- Exploring the potential of using aqueous ammonia solution to simultaneously capture CO_2 and other acid components from coal fired power plants under Australian conditions.

A series of experimental campaigns have been developed to investigate and understand the behaviour of aqueous ammonia for PCC. In particular the application of aqueous ammonia for PCC in hot and dry climates, like Australia, is needed. The construction and commissioning of the pilot pant was completed in early 2009 and the pilot plant trials are underway and are expected to be completed by Mid-2010. This paper reports and discusses the experimental results obtained from the pilot plant trials to date.

2 Experimental

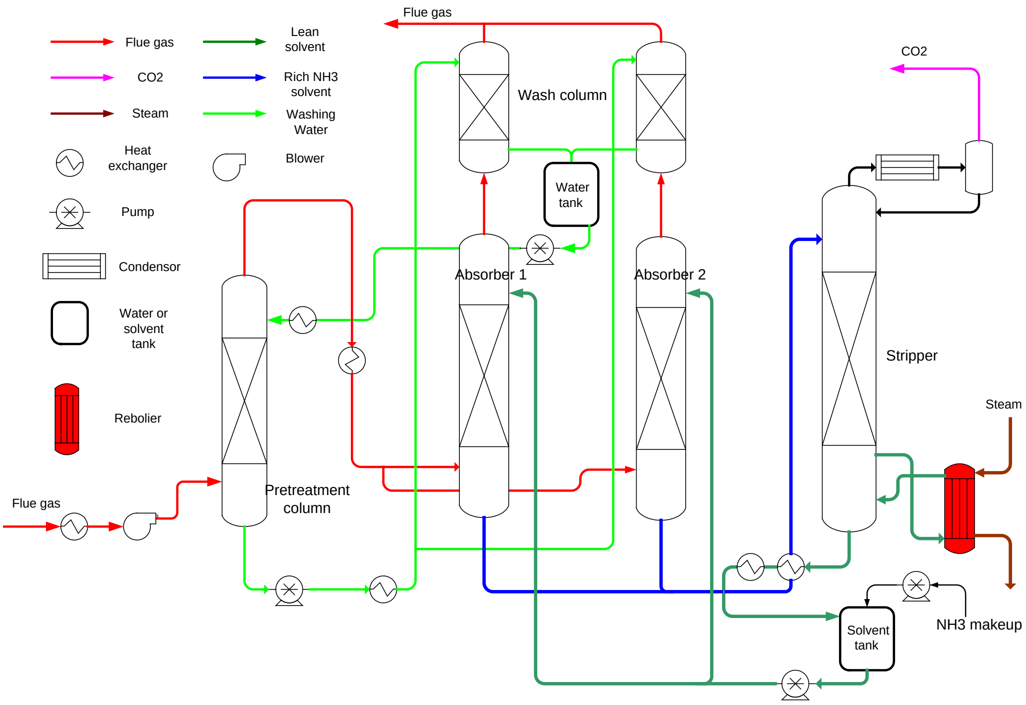

Figure 1. Simplified flowsheet of Munmorah pilot plant with operation of two columns.

Figure 1 show the simplified flowsheet of the Munmorah pilot plant, which consists of one pretreatment column, two absorber columns with a separate washing 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).

Table 1. Inner diameters of columns and packing heights.

Columns	Diameter, mm	Packing height, m
Pretreatment column	500	3
Absorber	600	2
Wash column	500	1.8
Stripper	400	3.5

The columns are constructed with stainless steel and randomly packed with 25 mm Pall ring (Rhine Ruhr Pty Ltd) which has the volumetric surface area of 207 m^2/m^3. The inner diameters of columns and packing heights are listed in Table 1. The experimental conditions for the campaigns so far are summarized in Table 2. Table 3 lists the typical composition of the flue gas measured at a point between blower and the pretreatment column. The Gasmet® analyser (FTIR) equipped with a ZrO_2 oxygen analyser allowed online identification and quantification of gas species in the flue gas at various locations of pilot plant. Standard wet chemistry titration was performed for the determination of CO_2 and NH_3 content in the liquid samples.

Table 2. Summary of the experimental conditions.

	Overall operational range	Condition 1	Condition 2
Configuration of absorbers	One or two columns	One column	One column
Ammonia concentration (wt%)	0-5	2-3	4-5
CO_2 loading of lean solvent (mole CO_2/mole ammonia)	0-0.6	0.2-0.5	0.3-0.5
Washing water flowrate, L/min	39	39	39
Liquid temperature in pretreatment and wash columns, ^oC	10-15	10-15	10-15
Solvent flowrate, L/min	50-134	134	134
Gas flowrate, Nm^3/h	510-700	700	700
Liquid temperature in absorber, ^oC	15-30	15-20	15-20
Gas pressure in absorber, kPa	101-105	101-105	101-105
Stripper bottom liquid temperature, ^oC	100-150	100-150	100-150
Stripper top gas pressure, kPa	300-600	300-600	300-600

Table 3. Typical inlet flue gas composition.

CO_2	H_2O	O_2	NO	NO_2	SO_2	N_2
9-12 vol%	3-5 vol%	6.5-10 vol%	200-250 ppm	<10 ppm	190-260 ppm	76-78 vol%

3 Results and Discussion

3.1 Functionality and Preliminary Tests.

In these tests, the functionality of all components of the pilot plant were tested and steady state operation conditions were defined and achieved.

3.2 Operational Tests.

These tests aim to investigate the effect of feed gas conditions, solvent conditions, process temperature and pressure, and column configuration on the CO_2 recovery, energy consumption, ammonia loss and consumption of utilities. The fate of SO_x/$NO_{x,}$ will be also investigated in this stage.

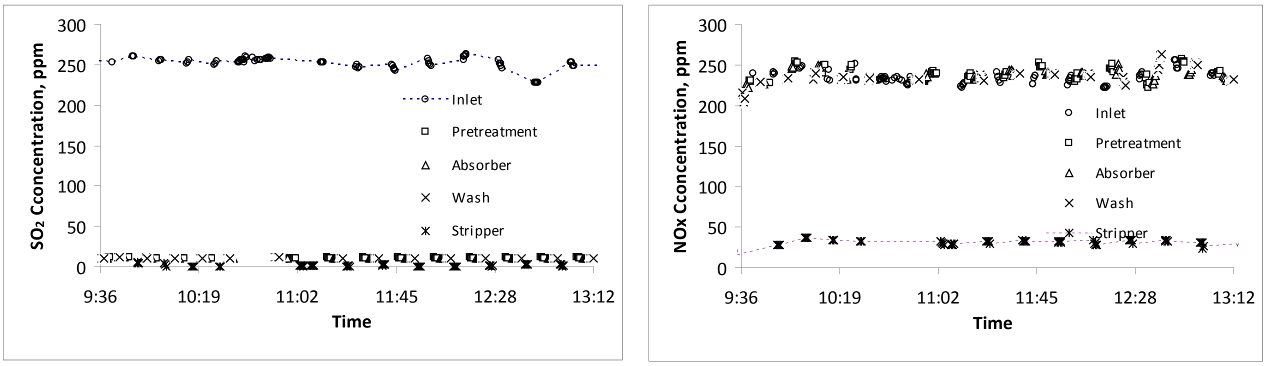

Figure 2. Typical SO_2 and NO_x concentrations at various locations of pilot plant versus time.

3.2.1 SO_2 and NO_x removal.

Figure 2 shows the typical SO_2 and NO_x concentration profiles versus time at various locations of the pilot plant. The SO_2 removal efficiency in the pretreatment column is more than 95% under all experimental conditions listed in Table 3. High SO_2 removal efficiency is due to the high solubility of SO_2 in the water and the enhanced absorption by NH_3 present in the washing water. It has been found that more than 500 ppm of NH_3 is trapped in the washing water in the wash column, which results in the excess of NH_3 in the washing water for SO_2 absorption. However, there is no appreciable effect on NO_x removal. That is because NO_x in the flue gas primarily comprises NO which has a very low solubility in water and does not react with NH_3 in the solvent.

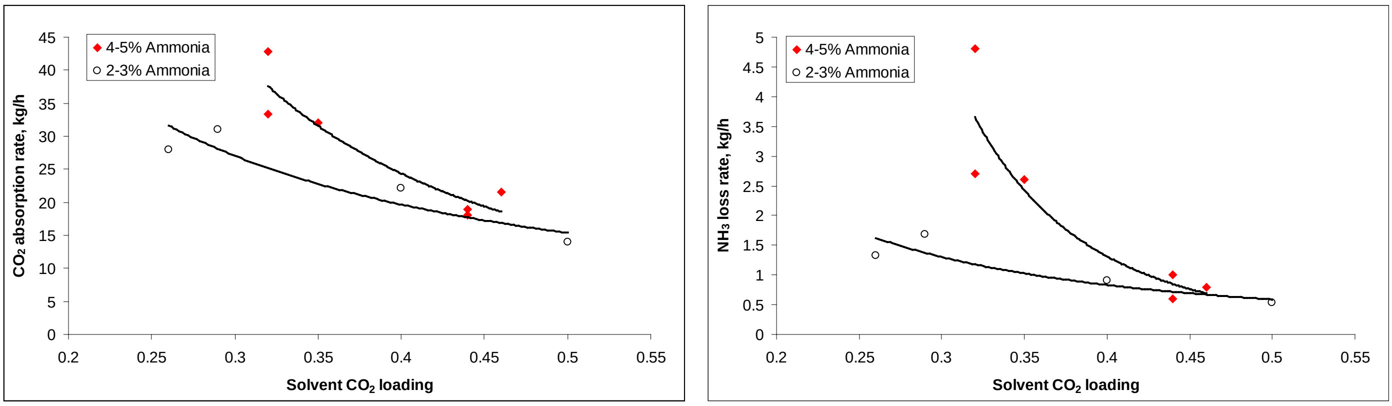

Figure 3. Effect of CO_2 loading of the solvent on the CO_2 absorption rate and ammonia loss rate in the absorber at two ammonia concentration ranges under Condition 1 for 2-3% ammonia and Condition 2 for 4-5% ammonia listed in Table 2, respectively. Packing height in the absorber is 2 m.

3.2.2 Effect of NH_3 concentration and loading on the CO_2 absorption rate and NH_3 loss rate.

Figure 3 shows the effect of CO_2 loading in the absorber on the CO_2 absorption rate and ammonia loss rate at two ammonia concentration ranges (2-3% and 4-5%). The CO_2 loading refers to the molar ratio of CO_2 to NH_3 in the solvent and the arithmetic average of CO_2 loading of lean and rich solvent is used. CO_2 absorption rate is defined as the amount of CO_2 absorbed in the solvent in the absorber per unit time. The NH_3 loss rate is defined as the amount of NH_3 slipping to flue gas in the absorber per unit time. The results in Figure 3 show that, as expected from theory, a decrease in CO_2 loading leads to an increase in both CO_2 absorption rate and ammonia loss rate. At relatively high loadings (above 0.45), ammonia concentration has little effect on the CO_2 absorption rate and ammonia loss rate at two ammonia concentrations, while within decrease in loading in the loading ranges below 0.45, the effect of ammonia concentration on CO_2 absorption rate and ammonia loss rate is more pronounced, in particular on the ammonia loss rate. The CO_2 absorption rate within the column can be calculated by Equation 1:

$$N_{CO2} = K_G A(P_{CO2} - P^*_{CO2}) \qquad (1)$$

Where

N_{CO2}, CO_2 absorption rate, mmol/s.

K_G, overall gas mass transfer coefficient, mmol/(s m^2 kPa).

P_{CO2}, partial pressure of CO_2 in the flue gas, kPa.

P^*_{CO2}, CO_2 equilibrium partial pressure in the solvent, kPa.

A, effective interfacial surface area, m^2.

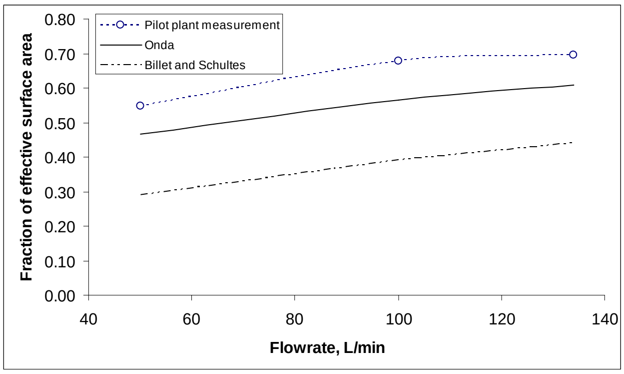

Figure 4. The measured and predicted fraction of effective surface area as a function of liquid flowrate. NaOH concentration: 0.1-0.7 mol/L; CO_2 concentration in the gas: 1000-5000 ppm. Gas flowrate: 700 Nm^3/h; Liquid flwarate: 50-134 L/min; Absorption temperature: 15-20°C.

The knowledge of K_G and *A* is critical for the prediction of CO_2 absorption rate and for the plant design and scale up. Figure 4 shows the fraction of the effective surface area of packing in the absorber as a function of liquid flowrate. The predicted values from two correlations are also included in Figure 4[7,8]. The effective surface area measurement was conducted by following the procedures described by Rejl et al.[7]. The correlations for the CO_2 diffusion, Henry's constant and reaction rate constant for the reaction of CO_2 and OH^- in the NaOH solution were based on work by Pohorecki and Moniuk[8]. As shown in Figure 4, the effective surface increases slightly with increase of solvent flow rate and between 50 and 70% of the total packing area is available for the mass transfer under the conditions studied. The measured values are significantly higher than the prediction by Billet and Schultes' correlation[9] and relatively close to those from Onda's[10]. Once the surface area is determined, K_G can be calculated by Equation 2.

$$K_G = \frac{N_{CO2}}{A(P_{CO2} - P^*_{CO2})} \tag{2}$$

Figure 5 shows the effect of NH_3 concentration and loadings on K_G. At high loadings above 0.45, the effect of ammonia concentration on K_G is minimal, indicating that in the high loading range, the CO_2 mass transfer in the absorption process is controlled by the diffusion process. In the loading range below 0.45 and with the availability of more free ammonia, the enhancement of CO_2 absorption by the reaction of CO_2 and NH_3 is more evident. The K_G values increase with both decrease of loading and increase of ammonia concentration, which can explain what is observed in Figure 3. For the purpose of comparison, Figure 5 includes the K_G values obtained from the wetted wall column experiments under the conditions similar to those for the pilot plant trials[11]. Compared to K_G values obtained from the wetted wall column experiments, K_G values from the pilot plant are halved in the loading range 0.2-0.5. This illustrates that results from wetted wall experiments are only indicative of absorption rates determined in packed columns, as the hydraulic conditions are not identical.

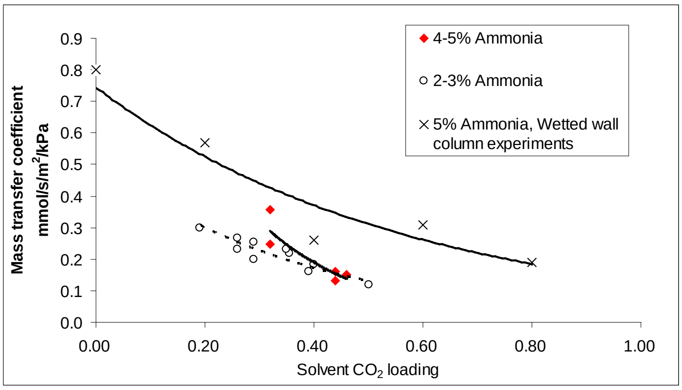

Figure 5. Effect of NH_3 concentration and loadings on the mass transfer coefficients in the absorber under conditions listed in Table 1. Packing height in the absorber is 2 m.

Figure 6 shows the trend in the ammonia concentration in the flue gas after the CO_2 absorber as a function of CO_2 loading. Also shown is the equilibrium concentration of the lean solvent entering the absorber. An Increase in the ammonia concentration in the solution and a decrease in the CO_2 loading lead to an increase in the free ammonia concentration and consequently an increase in driving force for ammonia desorption. The ammonia concentrations in the flue gas leaving the absorber is found to be as high as 1/2 of the equilibrium concentrations.

So far we have achieved 60% CO_2 removal efficiency under the design flue gas conditions at low ammonia concentrations up to 5%. In the following campaigns, we will extend the current investigation to high ammonia concentrations and low CO_2 loading ranges and increase the column packing to achieve the targeted 85% recovery. Finally, during the optimization test, based on information gathered from operational tests, we will establish the experimental conditions for a range of conditions which might be optimum, validate the expected performances under these conditions, and assess the consumption of energy and utilities.

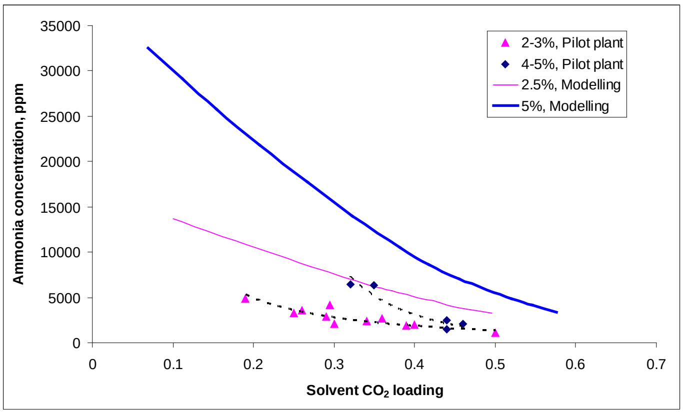

Figure 6. Measured and equilibrium ammonia concentrations in the flue gas at the outlet of absorber as a function of CO_2 loading of lean solvent at two ammonia concentration ranges. The experimental conditions are listed under Conditions 1 and 2 in Table 2. The equilibrium NH_3 concentrations at 15°C are obtained using Aspen Plus® in aspenONE V7.1[12].

4. Conclusions

The functionality and preliminary tests with the Munmorah PCC pilot plant suggest that the pilot plant is functioning appropriately and steady state operation can be achieved under the conditions studied. More than 95% of SO_2 in the flue gas is removed in the pre-treatment column while there is little removal of NO_x. High ammonia concentration and low CO_2 loading in the solvent favour the CO_2 absorption but to a greater extent enhance ammonia loss to the flue gas. The mass transfer coefficients for CO_2 in the absorber under various conditions are obtained based on pilot plant data and are found to be half of those measured using wetted wall columns. Ammonia loss is generally high and the concentrations of ammonia in the flue gas leaving the absorber are equivalent to up to half of the equilibrium NH_3 concentrations with respect to the lean solvent.

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