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**CO<sub>2</sub> removal by aqueous ammonia scrubbing**

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## Summary

The emission of CO<sub>2</sub> from power plants and other industrial installations can be greatly reduced by removal of the CO<sub>2</sub> from the waste gases such as flue gases. There is a number of commercially available technologies to separate CO<sub>2</sub> from flue gases. These technologies are based on absorption, adsorption, membranes and other physical and biological separation methods.

The leading solvent process is an aqueous solution with mono-ethanolamine (MEA) in 30% by weight as the active ingredient. This amine based process is considered to be the state-of-the-art technology. However, one of the main disadvantages of this technology is the energy required for regeneration of the solvent. This is high, reducing the power plant efficiency, thereby increasing electricity production costs.

From this point of view, the need for a new solvent to improve the capture process becomes an important issue in order to start the large scale application of the CO<sub>2</sub> capture process from power plants flue gases. The solvent that will be investigated in this work is aqueous ammonia which, compared to MEA, has the potential for a higher loading, is less corrosive, not sensitive to oxygen levels, cheap and can also bind SO<sub>2</sub> and NO<sub>x</sub>. Added advantages of the aqua ammonia process are possible saleable fertilizer side-products and simultaneous capture of all three major acid gases (SO<sub>2</sub>, NO<sub>x</sub> and CO<sub>2</sub>) plus HCl and HF.

The general aqueous ammonia process looks promising for capturing CO<sub>2</sub> from flue gas. The aqueous ammonia solvent is expected to be very stable, both thermally and chemically, and some literature references point towards low energy requirement for solvent regeneration. The ability to produce CO<sub>2</sub> at elevated pressure from the regeneration process is another benefit. However, experimental and simulation results from different authors are not always in quantitative agreement with each other.

Important items are whether ammonium carbonate and/or ammonium bicarbonate crystals are formed as well as the extent of ammonia losses and how this influences process operation and process performance. Given the wide variation in study results found in literature, it was decided to carry out a separate preliminary analysis on the aqueous ammonia process using the Aspen Plus flow sheet simulator.

The simulations show that ammonia as a solvent for carbon dioxide removal is promising from the energy requirement point of view. However, more investigation should be done on the washing section to remove the ammonia from the vent gas. Also the effect of ammonium bicarbonate formation and precipitation in the process should be incorporated.

A first estimation of the economical performance of the ammonia process was carried out based on a previous MEA economical study. As a result the net thermal efficiency and the net power output in the power plant after adding the capture process are found to be higher in the case of ammonia comparing to MEA case. And although the investment costs are higher due to lower absorption kinetics of the ammonia, the aqueous ammonia system deserves further consideration. Remaining issues are minimisation of ammonia losses and improvement of mass transfer in the absorber.

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## Appendix

A: Configurations studied

# 1 Introduction

The emission of CO<sub>2</sub> from power plants and other industrial installations can be greatly reduced by removal of the CO<sub>2</sub> from the waste gases such as flue gases. There are a number of commercially available technologies to separate CO<sub>2</sub> from flue gases. These technologies are based on absorption, adsorption, membranes and other physical and biological separation methods.

The relevance and potential of these separation technologies to post-combustion CO<sub>2</sub> capture is subject of research and development efforts world-wide. However, the common conclusion of several assessment studies is that solvent technologies are the separation technologies best suited for post-combustion capture of CO<sub>2</sub> in the near term. They are widely used in industrial applications, although not on the scale required for power stations. In industry also most applications are in high pressure gas streams (natural gas production, syn-gases), which represent conditions (pressures and gas matrix) entirely different from flue gases. The industrial applications in flue gases can be mainly found in the production of CO<sub>2</sub> for use in the food and drinks industry.

The leading solvent process is an aqueous solution with mono-ethanolamine (MEA) in 30% by weight as the active ingredient. Fluor Daniel markets this MEA solution based process under the name Econamine FG. The solution also contains proprietary additives to prevent corrosion and solvent degradation. The presence of these additives is expected to have a negligible effect on the major performance parameters. This amine based process is considered to be the state-of-the-art technology. However, the energy required for regeneration of the solvent is high, reducing the power plant efficiency, thereby increasing electricity production costs [Ciferno 2005].

Other disadvantages of the currently used monoethanolamine (MEA) process are:

- low carbon dioxide loading capacity and therefore sizeable equipment
- equipment corrosion
- amine degradation by SO<sub>2</sub> and O<sub>2</sub>
- the cost of the amine. As an example: on a weight basis an ammonia solution is 6 times cheaper than a MEA solvent [Resnik 2004, Ciferno 2005].

From this point of view the need for a new solvent to improve the capture process becomes an important issue in order to start the large scale application of the CO<sub>2</sub> capture process from power plants flue gases. The solvent that will be investigated in this work is aqueous ammonia which compared to MEA, has the potential for a higher loading, is less corrosive, not sensitive to oxygen levels [Hsu 2003], cheap and can also bind SO<sub>2</sub> and NO<sub>x</sub> [Zhang 2003, Gal 2006]. Added advantages of the aqua ammonia process are possible saleable fertilizer side-products (ammonium bicarbonate) and simultaneous capture of all three major acid gases (SO<sub>2</sub>, NO<sub>x</sub> and CO<sub>2</sub>) as well as HCl and HF [Yeh 2005]. This facilitates or even promotes the use of cheap high-sulphur coal for fuelling power plants [Resnik 2004].

In Chapter 2, a literature review on the aqueous ammonia process is given, while the different types of processes as studied in literature are discussed in Appendix A. The literature review indicated a wide variation in process performance indicator, in particular the thermal energy requirement for solvent regeneration. This necessitated a separate assessment using the Aspen Plus flow sheet simulator. In Chapter 3, the results

of the Aspen Plus simulations are presented as well as the economic performance assessment. In Chapter 4 conclusions are drawn and recommendations for further research and development are presented.

## 2 Literature review

### 2.1 Experimental data

#### 2.1.1 Reactions involved

Below, the reactions that play a role in carbon dioxide absorption in aqueous ammonia are given. The relative importance of each reaction is determined by thermodynamics and the kinetics of the system. Most processes use the conversion of carbonate into bicarbonate reaction (5). This reaction is influenced by pH by reactions 4a/4b. In fact, reactions 3 and 4 act as a buffer. At higher pH more bicarbonate is formed which means that less CO<sub>2</sub> can be bound.

##### *CO<sub>2</sub> absorption*



or



##### *Ammonia absorption*



or



##### *Bicarbonate-carbonate equilibrium*



or



##### *Conversion of carbonate to bicarbonate by binding of CO<sub>2</sub>*



##### *Carbamate formation*



##### *Precipitation of ammonium bicarbonate*

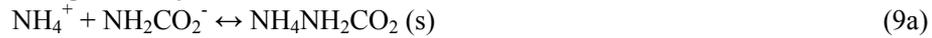


or



##### *Precipitation of ammonium carbonate*



*Precipitation of ammonium carbamate*

or



Starting from an ammonia solution, first the carbonate is formed (Figure 2-1).

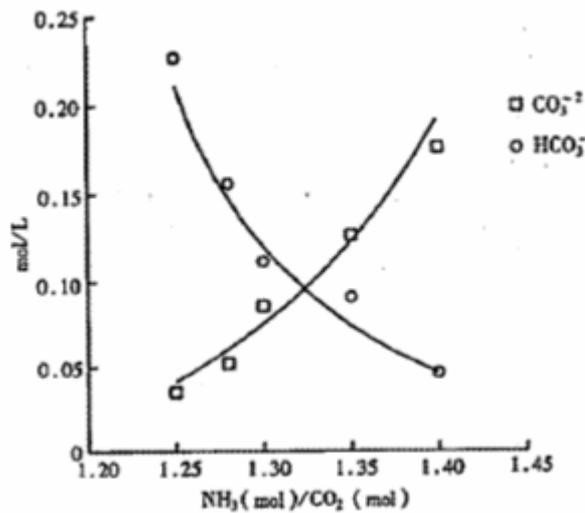


Figure 2-1 Relation of concentrations of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  in produced ammonia solutions to  $\text{NH}_3/\text{CO}_2$  molar ratio [Zhang 2003]

Reaction 6, which forms carbamate, is rather slow as compared to the reactions involving carbonate and bicarbonate. Therefore, Mani *et al.* could identify the carbamate as a separate species using  $^{13}\text{C}$  NMR, but only one combined signal for the carbonate-bicarbonate [Mani 2006]. Carbamate was only found at high  $\text{NH}_3(\text{free})/\text{CO}_2(\text{absorbed})$  ratios and disappeared at higher loadings and lower pH. During continuous operation the pH can be monitored as a way to monitor  $\text{CO}_2$  absorption [Huang 2002].

The precipitation reactions 7 through 9 are a function of the solubility of the salts. These are 320 g/l, 790 g/l and 220 g/l at 20 °C for the carbonate, carbamate and bicarbonate respectively [Merck]. When crystallisation does occur, is not quite clear. Mani *et al.* [Mani 2006] found no solid products, while Diao *et al.* [Diao 2004] did find ammonium bicarbonate crystallisation although they used even more dilute solutions.

### 2.1.2 Carrying capacity

The carrying capacity of aqueous ammonia is not unambiguous. Diao *et al.* found a value of 0.74 g  $\text{CO}_2/\text{g}$   $\text{NH}_3$  [Diao 2004]. Huang *et al.* found a similar value of approximately 0.7 g  $\text{CO}_2/\text{g}$  ammonia solution [Huang 2002]. Zhang *et al.* and Mani *et al.* found a more than twice higher value of 1.7 g  $\text{CO}_2/\text{g}$   $\text{NH}_3$  [Zhang 2003, Mani 2006]. Resnik *et al.* found a similar value of 1.6 g  $\text{CO}_2/\text{g}$   $\text{NH}_3$  for a 7%  $\text{NH}_3$  solution [Resnik 2004].

The reason for this can probably be found in the way the capacities were measured. Resnik *et al.* used a semi-batch process and regenerated the solution by heating. This resulted in loss of capacity to a value of 0.6 g CO<sub>2</sub>/g NH<sub>3</sub> for a 7% solution. This is partly due to loss of NH<sub>3</sub>. Especially during the first regeneration step NH<sub>3</sub> is lost (up to 36% at a 14% solution).

Huang *et al.* also used a batch process and used a resin to regenerate the solution [Huang 2002]. This also resulted in capacity loss to an approximate value of 0.3 g CO<sub>2</sub>/g ammonia solution. Alternatively, Diao *et al.* [Diao 2004] and Zhang *et al.* [Zhang 2003] used a continuous process in a counter-flow tower, but did not regenerate the solution. Zhang *et al.* re-used the solution in which the capacity was reduced only marginally to 1.6 g CO<sub>2</sub>/g NH<sub>3</sub>. This might be due to the compound in which the CO<sub>2</sub> is bound. It was found that with every re-use the carbonate concentration decreased while the bicarbonate concentration is increased. Since the CO<sub>2</sub> to NH<sub>3</sub> molar ratio in carbonate is 0.5 and in bicarbonate 1, weight ratio 1.3 and 2.6 respectively, this makes the bicarbonate a more efficient compound for CO<sub>2</sub> absorption.

Yeh and Bai [Yeh 1999] found that the capacity is a function of temperature. At 10 °C, 1.1 g CO<sub>2</sub>/g NH<sub>3</sub> is possible, at 40 °C this is reduced to 0.8 g CO<sub>2</sub>/g NH<sub>3</sub>.

Gal patented a method that uses a loading up to 1.8-2.6 g CO<sub>2</sub>/g NH<sub>3</sub>, which is the maximum loading possible [Gal 2006].

Table 2-1 gives an overview of the aqueous ammonia solvent capacities

Table 2-1 Solvent carrying capacity comparison.

Solvent and composition	Carrying capacity (g CO <sub>2</sub> /g active component in solvent)
?% NH <sub>3</sub> solution [Diao 2004]	0.74 (28 °C)
15% NH <sub>3</sub> solution [Huang 2002]	0.7 (25 °C)
8 % NH <sub>3</sub> solution [Yeh 1999]	0.8 - 1.1 (40 °C, 10 °C)
14% NH <sub>3</sub> solution [Resnik 2004]	1.1 (27 °C)
7% NH <sub>3</sub> solution [Resnik 2004]	1.6 (27 °C)
?% NH <sub>3</sub> solution [Zhang 2003]	1.7 (35 °C)
4.3% NH <sub>3</sub> -solution [Mani 2006]	1.7 (20 °C)
?% NH <sub>3</sub> solution [Gal 2006]	1.8-2.6 (0-10 °C)
30% MEA-solution	0.2 (cyclic capacity) 0.36 (max. capacity)

The results in Table 2-1 show that the carrying capacity of aqueous ammonia is much larger than for a standard MEA-solution.

### 2.1.3 Rate of absorption

Resnik *et al.* [Resnik 2004] measured CO<sub>2</sub> absorption rates in a semi-continuous reactor. Different sparger types were tested and the experiments were carried out with different ammonia concentrations and at different temperatures. Initial absorption rates, at zero CO<sub>2</sub> loading, were around 0.05 mol/min at 15 °C – 40 °C [Resnik 2004]. This

agrees well with older data from Yeh and Bai [Yeh 1999], who found a rate of 0.03 mol/min at 25 °C. When the solution is getting saturated, the absorption rate is obviously reduced, as the concentration of free ammonia is much lower than initially. The same trend is found by Huang *et al.* [Huang 2002]. However, they found a much lower minimum rate of 0.0017 mol/min at 25°C. The rate found for a solution regenerated by a resin was even lower at 0.0014 mol/min.

Again, Zhang *et al.* found higher values [Zhang 2003]. They found absorption rates of 4.6 mol/min at 35 °C.

Because of the continuous operation, Diao *et al.* could deduce kinetic data in the Arrhenius form [Diao 2004]. They found a value of  $2.4 \cdot 10^5$  l/(mol·s) for the pre-exponential factor and an activation energy of 27 kJ/mol. Under comparable circumstances, this corresponds to similar rates as found by Resnik *et al.* [Resnik 2004].

Hsu *et al.* performed comparative absorption experiments in a stirred tank reaction system with a planar gas-liquid interface [Hsu 2003]. Experiments with MEA, NH<sub>3</sub> and DEA were carried out using different liquid concentrations and at different temperatures. A 30% MEA solution gave the highest absorption rate (see Figure 2-2). A 3% NH<sub>3</sub> solution exhibited an absorption rate which was approximately 50% lower, but still somewhat higher than a 30% DEA solution.

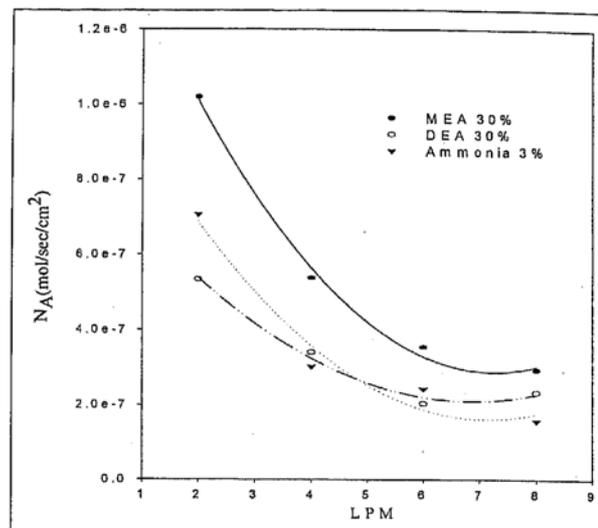


Figure 2-2 The effect of the gas flow rate on the absorption rate of CO<sub>2</sub> in various absorbents

Increasing the concentration in the absorbent led to an increase in absorption rate. However, in case of ammonia this will also increase the evaporative losses (paragraph 2.3). The measured absorption rates were also affected by gas-side mass transfer limitations, but it is clear the absorption rate for NH<sub>3</sub>-solutions at comparable molar concentrations is much lower. The same was concluded by G.T. Rochelle as quoted by Esber [Esber 2006] who estimated that the absorber would be required to be three times the height of a MEA absorber.

## 2.2 Regeneration

### 2.2.1 Methods

The usual method for regenerating the ammonia solution is heating, thus increasing the CO<sub>2</sub> equilibrium partial pressure. However, Huang *et al.* studied an alternative method to regenerate the solution [Huang 2002]. They used different types of an amine-based anion exchange resins to release CO<sub>2</sub> from the ammonium bicarbonate salts. The resins were in turn regenerated using hot (50 °C – 100 °C) water.

### 2.2.2 Energy requirement and power generation efficiency

Resnick *et al.* estimated the thermal energy requirement for solvent regeneration to be in the range 4 – 6 MJ/kg CO<sub>2</sub> for ammonia-concentrations in the range 7-21 % [Resnik 2004]. Yeh *et al.* calculated an energy consumption of approximately 4.3 kJ/kg CO<sub>2</sub> removed [Yeh 2005]. On this basis, Ciferno *et al.* calculated an efficiency reduction of 17% when reducing the carbon dioxide emissions with 90% [Ciferno 2005]. Corti and Lombardi calculated a drastic overall efficiency reduction of power generation for a gas fired power station from 53% to 41% when reducing the CO<sub>2</sub> emission by 89% [Corti 2004]. This was mainly due to the power needed for gas compression. They concluded that the aqueous ammonia process is only a viable alternative for the MEA process when the gas to be treated is already under pressurised conditions, e.g. syn gas purification.

The aforementioned studies indicated an energy requirement for solvent regeneration which is comparable to a start-of-the-art MEA-process. Hence there seems to be little benefit in using ammonia as a solvent from the efficiency point of view. However, more recently Rhudy estimated only 10% power reduction for the chilled ammonia process [Gal 2006] used for CO<sub>2</sub> capture in a ultra-supercritical plant compared to 29% power reduction using the MEA process [Rhudy 2006]. The thermal energy requirement estimated from this study is around 1 MJ/kg CO<sub>2</sub>. Furthermore the CO<sub>2</sub> becomes available at high pressure, reducing the power requirement for compression.

Table 2-2 gives an overview of the thermal energy requirement as given by several authors. A enormous range in requirements is found. This is probably due to difference in process operation and calculation or measurement method.

Table 2-2 Thermal energy requirement

Reference	Thermal energy consumption per kg CO <sub>2</sub>
[Yeh 2005]	4.3 kJ
[Gal 2006]	± 1 MJ
[Resnik 2004]	4-6 MJ
[Corti 2004]	± 6-7 MJ
30% MEA-solution	4 MJ

### 2.2.3 Capacity loss

In the experimental study of Resnik *et al.* where the ammonia solution was regenerated three times, it was found that the solution lost carrying capacity (see Figure 2-3) [Resnik 2004]. This is partly due to  $\text{NH}_3$  loss which is evidenced by a reduction in pH of the solution. The first regeneration step gives the majority loss for any ammonia solution concentration. However, it was found that the lower the initial concentration, the smaller the relative loss in capacity.

On the contrary, Zhang *et al.* hardly suffered capacity loss during the 5 times re-use of the same ammonia solution [Zhang 2003].

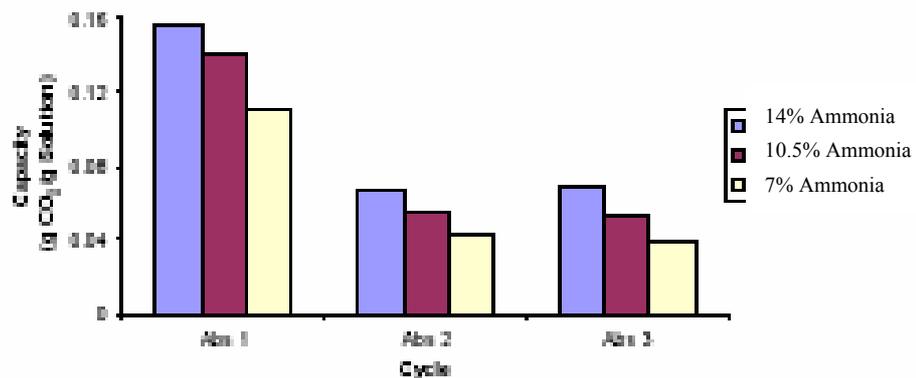


Figure 2-3 Effect of cycling on  $\text{CO}_2$  absorption capacity ( $\text{g CO}_2/\text{g solution}$ ).

The ammonia solution regenerated by an ion-exchange resin also lost carrying capacity during regeneration by boiling water [Huang 2002]. This could be attributed to the inability of the resin to release  $\text{CO}_2$  from ammonium carbonate. This means loss of free ammonia and therefore loss of carrying capacity. The absolute value of regeneration efficiency and thus amount capacity loss depended on the resin used, relative amount of resin to solution (the lower the better) and bicarbonate concentration in the solution (the higher the better).

## 2.3 Ammonia loss

During absorption and regeneration, ammonia is lost to the gas phase. For environmental reasons, this must be kept to a minimum. There are several process parameters that can keep ammonia losses down.

- Using a low concentration  $\text{NH}_3$  in the solution. There exist an almost linear dependency on ammonia loss and concentration in the desorber solution [Corti 2004]. A disadvantage of a low ammonia concentration is that the solution mass flow needs to be increased. Corti and Lombardi found little effect on the solution mass flow needed in the concentration range above 15%.
- Using a moderate pH in the solution. A pH of 9 seems reasonable [Huang 2002]. Hsu *et al.* found an optimum absorption rate at a pH of 11.5-12. Indeed absorption of  $\text{CO}_2$  is increased with increasing pH, but the increase in  $\text{NH}_3$  loss will counteract this effect at the highest pH.

- Using a low absorption temperature, this is mainly determined by the inlet ammonia solution temperature as opposed to flue gas temperature. Corti and Lombardi calculated an optimum temperature of 25 °C [Corti 2004]. However, in view of practical technical limits to reduce cooling water temperatures, 40 °C is suggested. Gal [Gal 2006] has patented a method that uses temperatures below room temperature for absorption. A drawback of a low temperature is reduced solubility of the ammonium salts and therefore possible unwanted precipitation of particles.
- Using a high pressure during absorption. However, this means a higher solution mass flow and therefore a higher external heat duty and higher flue gas compression power consumption [Corti 2004]. Corti and Lombardi found 3 bar to be a good compromise.
- Using a high pressure during regeneration. Usually, a low pressure is beneficial for regeneration, but in this particular case increasing the pressure improves CO<sub>2</sub> and NH<sub>3</sub> separation [Corti 2004]. However, this also means higher compression power consumption. Corti and Lombardi found an optimum where regeneration efficiency is not influenced at 20 bar. Gal [Gal 2006] has patented a method that also uses high pressure regeneration (2-136 bar) and claims an added saving of energy since water desorption is also suppressed at these high pressures.

## 2.4 Synthesis of literature study results

The general aqueous ammonia process looks promising for capturing CO<sub>2</sub> from flue gas. The aqueous ammonia solvent is expected to be very stable, both thermally and chemically, and some literature references point towards low energy requirement for solvent regeneration. The ability to produce CO<sub>2</sub> at elevated pressure from the regeneration process is another benefit. However, experimental and simulation results from different authors are not always in quantitative agreement with each other. It is necessary to perform further absorption and desorption measurements.

Table 2-3 gives an overview of the parameters that determine process performance as used by some authors. The values as used in the power consumption calculations by Yeh *et al.* [Yeh 2005] and Corti and Lombardi [Corti 2004] are included, to illustrate the differences in input and optimum parameters found..

Table 2-3 Parameters that determine power consumption

Parameter	Yeh	Corti
Inlet temperature of flue gas		120 °C
Temperature of adsorption	27 °C	40 °C
Absorption pressure	1 bar	3 bar
Concentration of ammonia solution	8 wt%	3.4 wt%
pH of absorption solution	9-10	Not known
Desorption pressure	1 bar	20 bar
Desorption temperature	82 °C	150 °C

It is clear from Table 2-3 that there is quite a varied range in the operational conditions used in the literature. This also reflects the immature development status of the aqueous ammonia solvent process for post-combustion capture although Alstom is pursuing the commercialisation of a chilled ammonia process [Black 2006]. An important item is whether ammonium carbonate and/or ammonium bicarbonate crystals are formed and how this influences process operation and process performance. Also the claims regarding the energy requirement for thermal regeneration of the solvents vary widely. Some studies [Corti 2004, Yeh 2005, Resnik 2004] indicate energy requirements similar to the standard MEA-process, others indicate much reduced energy requirements down to one quarter of the standard MEA-process. Given the wide variation in study results, it was decided to carry out a separate preliminary analysis on the aqueous ammonia process using the Aspen Plus flow sheet simulator. The analysis and its results are given in Chapter 3.

## 3 Base case definition and simulation

### 3.1 General description

The process simulation was based on the conventional available MEA process. The concentration of ammonia was chosen on the basis of a short sensitivity analysis to investigate the effect of the ammonia weight fraction and the absorption temperature on the ammonia losses in the top of the absorber. This value fell well within the range of 2-4 wt% found in literature in order to have considerable solvent flow rate and in the same time not very high ammonia losses [Corti 2004].

A large reduction in CO<sub>2</sub> concentration in the gas is possible, but at the expense of an increase the height of the absorption vessel. The regeneration of the chemical solvent is carried out in the stripper. This leads to a thermal energy penalty as a result of heating up the solvent, providing the required de-sorption heat for removing the chemically bound CO<sub>2</sub>.

The CO<sub>2</sub>-product has a high purity, with water vapour being the main other component. Due to the selective nature of the chemical absorption process, the concentration of inert gases is low. It is anticipated that one of the main operational problems of ammonia absorption process is the high rate of solvent evaporation. To overcome this problem a washing section using water is required.

### 3.2 Simulation results

The simulation was done using Aspen Plus as a simulation tool with the available NH<sub>3</sub>-H<sub>2</sub>O-CO<sub>2</sub> property set. The focus of this work was to estimate process performance parameters for the carbon dioxide ammonia scrubbing system. The energy required for solvent regeneration is the main factor, which will give a good indication of how good this process is compared to the commercially available MEA process.

The other main parameters are the solvent requirement, the cooling water required in the system including the washing section and the carbon dioxide compression system. The energy requirement results show a clear benefit of using ammonia for carbon dioxide scrubbing. The energy requirement in the ammonia process seems much lower than the well-known MEA process. This reduction in the energy requirement can make the overall process more economic than the conventional available MEA process.

The solvent requirement in the ammonia process is found to be rather high but the ammonia concentration is much times lower than MEA solutions and also the prices of ammonia solution is lower than MEA solvent.

One of the main challenges for the ammonia process is the high evaporation rate of the ammonia. This evaporation can make the ammonia content in the vent gas and the final CO<sub>2</sub> product very high. To remove the ammonia from the vent gas a washing section was added on the top of the absorber. In general we can conclude that using ammonia as a solvent for carbon dioxide removal is a promising method from the energy requirement point of view. However more research should be done on the washing section to remove the ammonia from the vent gas.

The last point that needs to be included is the effect of ammonium bicarbonate formation and precipitation in the process. From literature it is well known that ammonium bicarbonate can form at low temperatures and decompose at elevated temperatures. This solid formation is not included in the used Aspen model, so more study should be done to investigate the effect of this solid on the overall process behaviour.

It has been shown previously in the literature that the formation of precipitates during the absorption process can be advantageous in a technology development based on amino-acid salt solutions [Feron 2004]. Precipitates will result in an advantageous shift of the equilibrium, resulting in a higher CO<sub>2</sub> loading of the solvent. During generation CO<sub>2</sub> pressures are higher than without the formation of precipitates.

### 3.3 Economic evaluation

Since the purpose of adding a capture unit is to reduce the CO<sub>2</sub> emissions per net kWh delivered, the cost of CO<sub>2</sub> avoided relative to a reference plant with no CO<sub>2</sub> control is a widely used economic indicator of the cost for the prevention of CO<sub>2</sub>-emissions. This indicator can also be used to compare different methods of CO<sub>2</sub> emission reduction.

The net power plant capacity and efficiency can be calculated by subtracting the amount of electricity needed for the capture process from the reference power plant capacity. The new cost of electricity was calculated taking into account the reduced output of the power plant.

Equipment sizing and cost estimations were done. The size of the absorber was assumed to be the double the size needed for the conventional MEA process and the size of the stripper was assumed to be the same as MEA process. The rest of the equipment were sized depending on the flow rates and conditions in the ammonia process. The equipment sizing resulted in estimates for the investment costs. The capture investment per ton CO<sub>2</sub> is calculated from total capture investment cost divided by the CO<sub>2</sub> production rate.

As expected, adding the capture process will increase the overall expenses in the power plant. The overall plant efficiency is decreased with capture. However, using ammonia solution as an absorbent had an advantage over MEA on the overall power plant efficiency. The cost of CO<sub>2</sub> avoided and the cost of electricity are almost the same in both the ammonia and MEA.

As an overall conclusion it is clear from this first economical estimation that the ammonia capture process is a promising process. However, a more detailed study should be carried out to obtain a better founded viewpoint.

## 4 Conclusions and recommendations

### 4.1 Conclusions

The solvent investigated in this work was aqueous ammonia which, compared to MEA, has the potential for a higher loading, is less corrosive, not sensitive to oxygen levels, cheap and can also bind SO<sub>2</sub> and NO<sub>x</sub>. Added advantages of the aqueous ammonia process are possible saleable fertilizer side-products (ammonium bicarbonate) and simultaneous capture of all three major acid gases (SO<sub>2</sub>, NO<sub>x</sub> and CO<sub>2</sub>) as well as HCl and HF.

The general aqueous ammonia process looks promising for capturing CO<sub>2</sub> from flue gas. The aqueous ammonia solvent is expected to be very stable, both thermally and chemically, and some literature references point towards low energy requirement for solvent regeneration. The ability to produce CO<sub>2</sub> at elevated pressure from the regeneration process is another benefit. However, experimental and simulation results from different authors are not always in quantitative agreement with each other.

Important items are whether ammonium carbonate and/or ammonium bicarbonate crystals are formed as well as the extent of ammonia losses and how this influences process operation and process performance. Given the wide variation in study results found in literature, it was decided to carry out a separate preliminary analysis on the aqueous ammonia process using the Aspen Plus flow sheet simulator.

The simulations show that using ammonia as solvent for carbon dioxide removal is a promising method from the energy requirement point of view. A first estimation of the economical performance of the ammonia process was also carried out. It was found that the costs for CO<sub>2</sub> capture and electricity for the ammonia solution are comparable to those of MEA. In general it may be concluded that the aqueous ammonia system deserves further consideration.

### 4.2 Recommendations

A focused research and development programme should address the minimisation of ammonia losses in the absorber and improvement of mass transfer in the absorber.

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## 6 Authentication

Names and functions of the cooperators:

Annemieke van de Runstraat - Literature study, reporting  
Mohammad R.M. Abu-Zahra - Aspen Plus simulations  
Paul H.M. Feron - Project coordination

Date upon which, or period in which, the research took place:

4 May till May 2007

Signature:



J. Hopman  
Project leader

Approved by:



S. van der Gijp  
Group leader

## Appendix A: Configurations studied

In the literature found several different configurations for the study of CO<sub>2</sub> removal by ammonia absorption. To understand the results presented, these configurations are described below.

### A.1 Yeh and Resnik [Resnik 2004, Yeh 2005]

Yeh and Resnik used a semi-continuous flow reactor as shown in Figure A.-1 for their CO<sub>2</sub> absorption and regeneration studies. The simulated flue gas consists of 15 vol.% CO<sub>2</sub> and 85 vol.% N<sub>2</sub>. The gases were supplied by compressed gas cylinders and the flow controlled by mass flow controllers. The CO<sub>2</sub> absorber was a 3-l glass container filled with 1500-ml 14% aqueous ammonia solution. Pressure was near atmospheric; total inlet gas flow rate was 7500 sccm. The temperature of the absorber was controlled with a cooling/heating coil, through which temperature-controlled water flowed. The baseline condition for the tests was 27 °C. A mixer operates at 1600 rpm to eliminate mass transfer limits. The simulated flue gas entered the absorber through an open-tube CO<sub>2</sub> gas sparger.

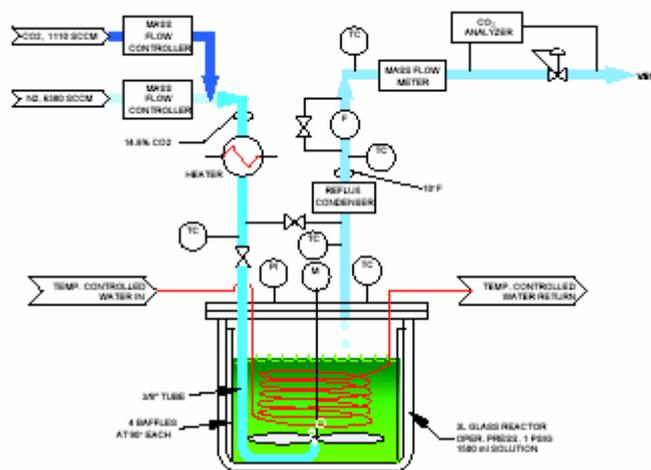


Figure A.-1 Aqua ammonia semi-continuous reactor process flow diagram as used by Yeh *et al.* [Yeh 2005]

The vent gas from the absorber was sent to a reflux condenser, where the gas temperature was reduced to  $-12\text{ }^{\circ}\text{C}$  to condense the vapor escaping from the absorber. The condensed vapor is continuously drained back to the reactor. The vent gas flowrate was measured by a mass flow meter. The gas from the flow meter was then analyzed for unreacted CO<sub>2</sub> gas before being vented.

These authors also did an energy evaluation of a continuous process. The flow diagram is given in Figure A-2. The flue gas enters at the bottom of the absorber with 15% CO<sub>2</sub> (dry basis). In the absorber CO<sub>2</sub> is absorbed by absorbent and the absorbent is recirculated back to the absorber from the regenerator. The aqueous ammonia solution has 8 wt.% NH<sub>3</sub> equivalent. The solution lean loading is 0.08 g CO<sub>2</sub> per g solution from the regenerator. The rich CO<sub>2</sub> loading from the bottom of absorber is 0.15 g CO<sub>2</sub> per g

solution. Therefore, approximately 50% of  $\text{CO}_2$  in the ammonium solution is regenerated. The transfer capacity of ammonium solution is  $0.07 \text{ g CO}_2$  per  $\text{g NH}_3$  solution circulated. Energy usage in ammonium solution regeneration is estimated from heat of reaction and liquid sensible heat at  $4.3 \text{ kJ/g CO}_2$ . Resnik *et.al.* have estimated that the MEA process takes  $11 \text{ MJ/kg CO}_2$  with the solvent being regenerated at a temperature of  $120 \text{ }^\circ\text{C}$ . On the basis of this Resnik *et.al.* concluded that the ammonia process has potential. However, the energy requirement for a process based on a 30% MEA solution is around  $4 \text{ MJ/kg CO}_2$ , which is similar for the ammonia process [Feron, 2005]. Hence, the energy benefits as identified seem to be exaggerated.

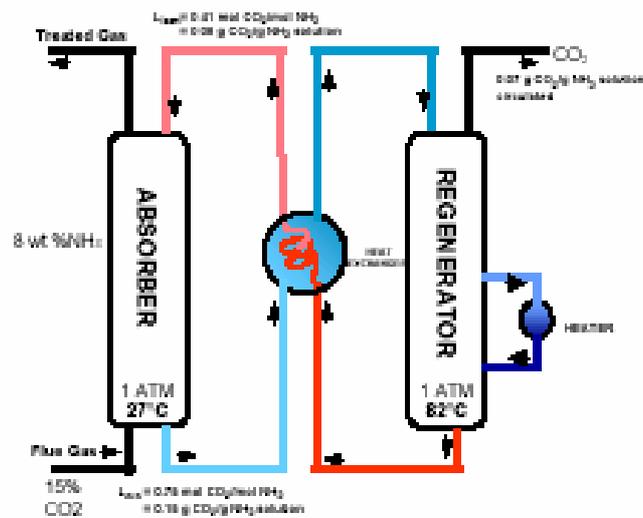


Figure A-2 Process flow diagram for aqua ammonia  $\text{CO}_2$  capture process.

## A.2 Diao [Diao 2004]

The schematic diagram of the experimental system for studying removal of  $\text{CO}_2$  by ammonia scrubbing as used by Diao *et al.* is shown in Figure A-3. The stainless steel reactor had an inside diameter of 250 mm and height of 450 mm. It was installed in a temperature controlled water bath. The main part of their experimental system is composed of a five-layer sieve-plate tower, which is counter-current (ammonia solution from the top and  $\text{CO}_2$  bottom). Its schematic diagram is shown in Figure A-4. All streams are controlled by mass flow controllers. The total flow rates of  $\text{CO}_2$  were kept at 5 l/min. Nitrogen was used as the balance gas.

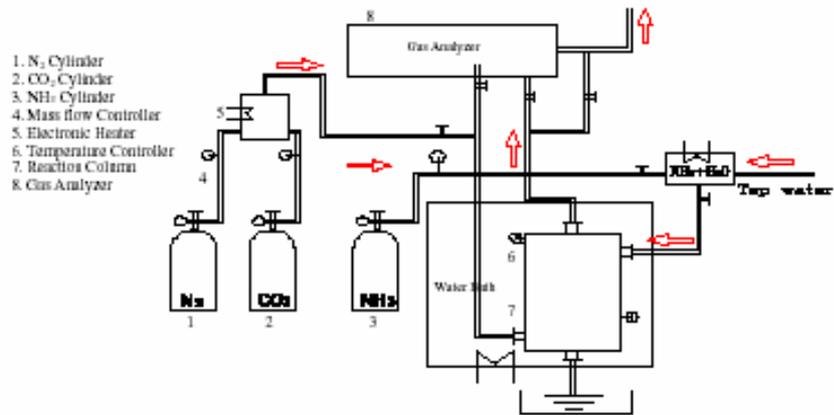


Figure A-3 Schematic diagram of CO<sub>2</sub> removal by ammonia solution scrubbing.

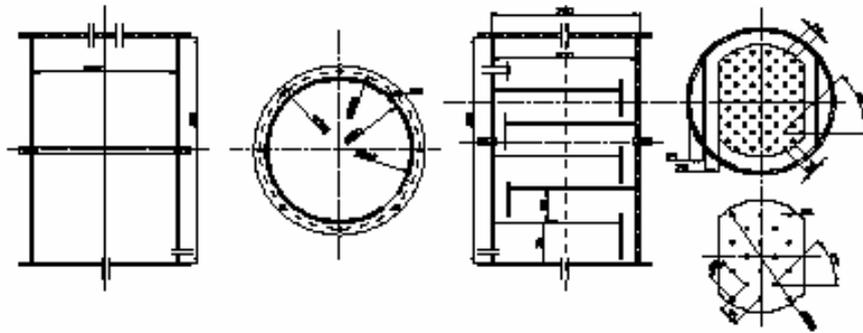


Figure A-4 The structure of the absorption tower.

The simulated flue gases and the connecting pipes were kept at the same temperature as the water bath. To maintain the reaction temperature, the simulated gases were heated again in coiled pipes submerged in the water bath before entering the reactor.

The temperature of the ammonia solution was designed to be in the range from 25 to 55 °C. The inlet concentrations of CO<sub>2</sub> were 10%, 12% and 14% (v/v), and the ammonia solution concentrations were 0.07, 0.10 and 0.14 mol/l, respectively. The solid products in the aqueous solution were collected and dried at 40 °C and analyzed by FTIR.

### A.3 Corti and Lombardi [Corti 2004]

The CO<sub>2</sub> absorption system as used in the analysis by Corti and Lombardi is based on two main units: the absorption column where the CO<sub>2</sub> absorption takes place and the desorption column where the CO<sub>2</sub> load solution is thermally regenerated (see Figure A-5). The absorption and desorption columns are simulated using two equilibrium stages. The absorber unit has no condenser or reboiler.

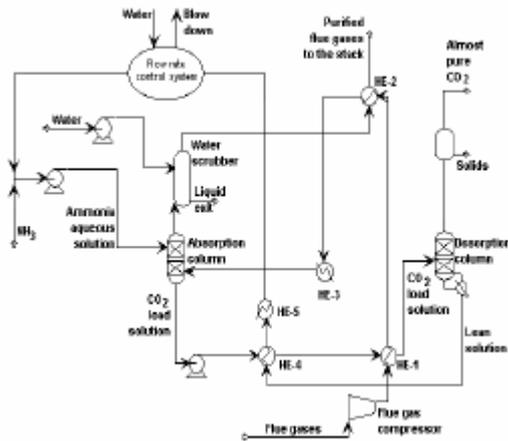


Figure A-5 Corti and Lombardi's CO<sub>2</sub> removal system as used in their Aspen simulations [Corti 2004]

The desorber unit has one inlet stream and two exit streams (regenerated solution and carbon dioxide-rich gaseous stream) and is provided with external heat duty. The heat duty amount is calculated imposing the stream exiting temperature. The flue gas entering stream (180 kg/s,  $T = 120\text{ }^{\circ}\text{C}$ ) needs to be compressed to the absorber working pressure (flue gas compressor) and is then cooled down in a recovery heat exchanger (HE-1) where part of its enthalpy is used to heat up the CO<sub>2</sub> load solution before entering the regeneration column.

Flue gases are further cooled down in a second heat exchanger (HE-2), heating the purified gaseous stream and increasing the buoyancy at the stack; and finally they are cooled down to the defined absorber inlet temperature (HE-3) before entering the bottom stage of the absorption column.

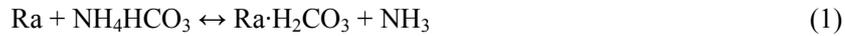
The ammonia aqueous solution enters the top stage of the absorption column, after recirculation, fresh ammonia addition, in the required amount to keep a constant ammonia concentration in the absorber entering solution, and re-pressurisation. The formation of ammonium bicarbonate crystal is neglected in view of the pressures (1-3 bar) and temperatures ( $<50\text{ }^{\circ}\text{C}$ ) studied. The rich solution leaves the absorption column from the bottom stage. It is pressurised up to the desorber working pressure and is heated by means of energy recovery from the lean solution (HE-4) and from the flue gases (HE-1)

The rich solution enters the desorption column, where it is thermally regenerated by an external heat duty. In the desorption unit, the gaseous CO<sub>2</sub> is released and separated from the solid phase: a stream of almost pure CO<sub>2</sub> is obtained. This lean solution is cooled in the HE-4 and further in an externally cooled heat exchanger (HE-5) in order to reach the defined absorber inlet temperature. After a mass flow rate control system (adding fresh water or blowing down part of the solution) and a fresh ammonia make-up, the regenerated solution is recirculated back to the absorber.

#### A.4 Huang *et al.* [Huang 2002]

Instead of thermal regeneration of the rich solution, Huang *et al.* used a weakly basic anion-exchange resin. The resin has a polymer backbone with  $-\text{NH}_2$ ,  $=\text{NH}$  or  $\equiv\text{N}$  side groups, and is abbreviated using Ra. The reactions involved are:

Release of ammonia from ammonium bicarbonate:



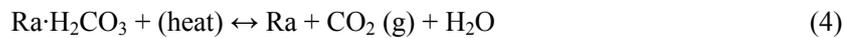
The ammonia can recombine with another bicarbonate to the carbonate



The carbonate in turn can decompose in ammonia and  $\text{CO}_2$



The resin is regenerated using warm water, typically  $50\text{ }^\circ\text{C} - 80\text{ }^\circ\text{C}$ , in which the  $\text{CO}_2$  is released.



#### A.5 Zhang *et al.* [Zhang 2003]

Zhang *et al.* reported on a test facility where flue gas produced by a coal-fired Combustion Research Facility (CRF) was treated with an ammonia spray to remove  $\text{CO}_2$ . The process has been based on the  $\text{CO}_2$  removal used in ammonia synthesis (see Figure A-6).

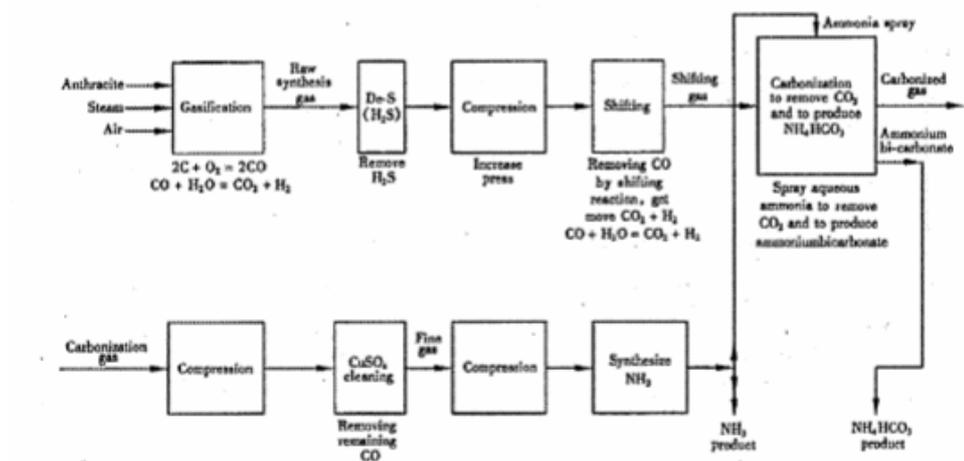


Figure A-6 Flow chart of ammonia synthesis by coal gasification

The CRF used has a cylindrical furnace of 4.2 m height with diameter of 0.4 m.

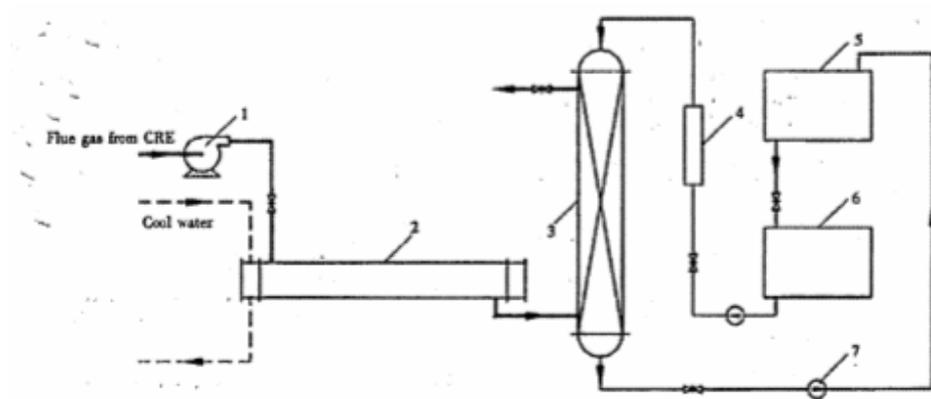


Figure A-7 Schematic of the flow sheet for CO<sub>2</sub> absorption tests from flue gas.

- |                   |                           |
|-------------------|---------------------------|
| 1. Forced fan     | 5. Inlet ammonia storage  |
| 2. Heat exchanger | 6. Outlet ammonia storage |
| 3. Absorber       | 7. Pump                   |
| 4. Flow gauge     |                           |

Figure A-7 shows the schematic of the absorption facility. The flue gas produced (70 m<sup>3</sup>/h) is first cooled to 35 °C using a heat exchanger (2). The gas then enters the packed absorption tower (3) which has an inner diameter of 25 cm and a height of 2 m. It is packed 80 cm high with ceramic rings (25 mm diameter, 25 mm thick). The ammonia is sprayed with 200 l/h, is taken from the ammonia inlet storage (5) and is collected in the outlet ammonia storage (6). The flue gas is vented to the atmosphere. Flue gas and ammonia spray are counter-current. During the series of experiments, inlet storage (5) was refilled using outlet storage (6). Therefore, absorption efficiency data as a function of ammonia content were obtained.

## A.6 Hsu *et al.* [Hsu 2003]

Hsu *et al.* performed experiments to determine the kinetics of absorption of CO<sub>2</sub> in aqueous ammonia and amines. The set-up is shown in Figure A-8.

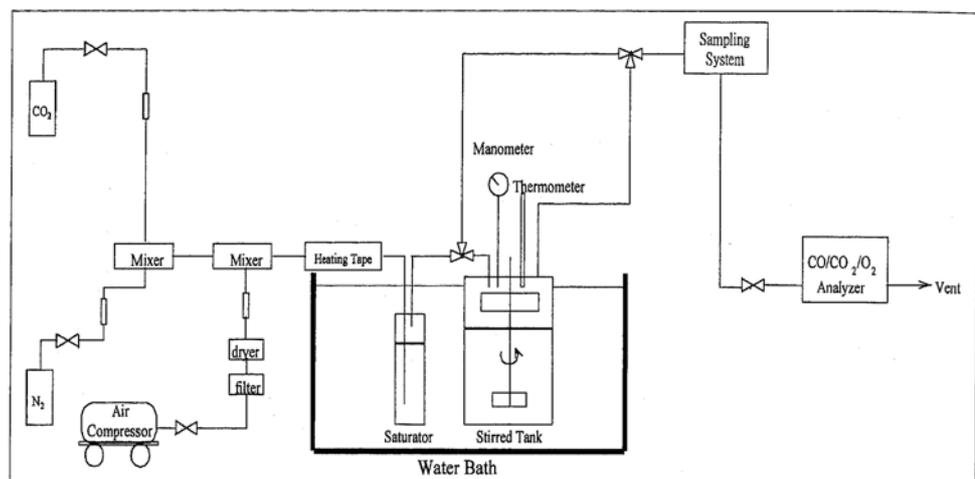


Figure A-8 Set-up as used by Hsu *et al.* [Hsu 2003].

The experiments determining absorption kinetics were carried out in a bench-scale stirred tank reaction system with a plane gas-liquid interface. The system can be divided into three parts: a flue gas simulation system, an absorption reactor and a gas sampling and analyzing system. CO<sub>2</sub> was diluted with N<sub>2</sub> in a plug flow mixer and further diluted by the mass-flow controlled compressed air in another plug flow mixer to the desired concentration and oxygen contents. The simulated flue gas was then heated to 50 °C by an electrical heating tape before entering into the absorption reactor. Gas and liquid temperatures were controlled while the pressure was monitored. The simulated gas was saturated with water in a saturator at 50 °C before entering the reactor.

The results are summarised in Table A-1. However, all these kinetic parameters were probably influenced by mass transfer limitations. This means that the real rates of absorption are probably higher.

Table A-1 Kinetic parameters as found by Hsu *et al.* [Hsu 2003]

Kinetic parameter	Ammonia (3%)	MEA (30%)
Activation energy [kJ/mol]	40	33
Pre-exponential factor [l/mols]	$1.7 \cdot 10^9$	$5.5 \cdot 10^8$
Reaction order in CO <sub>2</sub>	0	0
Reaction order in NH <sub>3</sub> /MEA	1	0.4

#### A.7 Gal, Black and Rhudy [Gal 2006, Black 2006, Rhudy 2006]

Figure A-9 shows a flow diagram as used in the patented process of Gal.

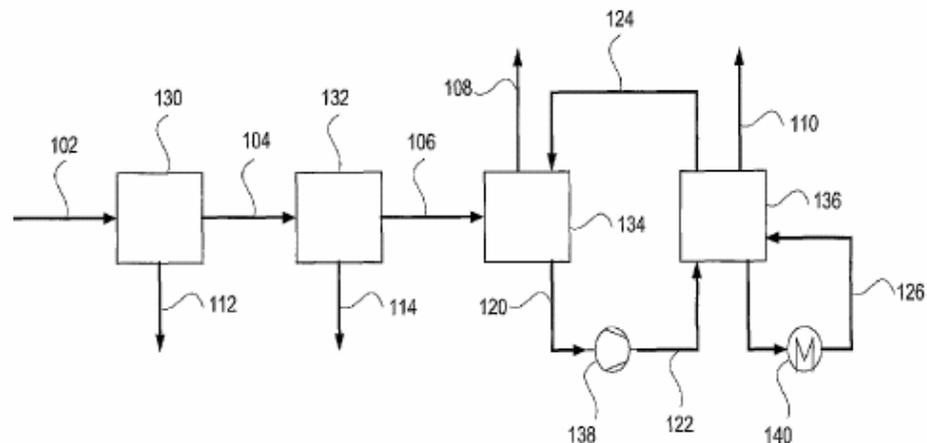


Figure A-9 Schematic of the process patented by Gal.

The meaning of the numbered streams and processes are given below.

- 102: gas stream from combustion of industrial process,
- 104: gas stream conventionally cleaned, water saturated, 40-70 °C
- 106: cooled gas suitable for CO<sub>2</sub> capture
- 108: lean gas release to the atmosphere
- 110: high-pressure CO<sub>2</sub> stream
- 112: waste stream from conventional cleaning

- 114: bleed from direct contact coolers (DCC)
- 120: CO<sub>2</sub>-rich ammonia solution
- 122: high-pressure CO<sub>2</sub>-rich stream
- 124: cooled CO<sub>2</sub>-lean ammonia solution from regeneration unit
- 126: heating stream
- 130: pretreatment cleaning processes to collect particles, capture acid mist, control SO<sub>2</sub>, etc.
- 132: series of direct contact coolers (DCC)
- 134: CO<sub>2</sub> absorber or series of absorbers
- 136: regeneration unit at high pressure and temperature
- 138: high pressure pump
- 140 : heater

The precleaned flue gas is cooled by cold water scrubbing to a temperature of 0-10 °C (typically 2 °C) in 132. It is claimed that condensation of the water in the stream makes this a very efficient process. The reason is that a substantial reduction in volume and mass of the flue gas is obtained and thus the size of downstream equipment [Black 2006]. Moreover, high loadings are possible at these low temperatures. On the other hand, cooling to far below room temperature requires a lot of energy or an abundance of low-temperature water. For comparison Corti and Lombardi [Corti 2004] also wanted to use low temperatures, but had to settle for 50 °C because of heat exchange limitations.

Because of the low temperature, the evaporative ammonia loss in the absorber 134 is suppressed and the mass transfer from CO<sub>2</sub> gas to the liquid is enhanced. During the absorption process, the ammonia loading is increased from 0.8-1.8 g CO<sub>2</sub>/g NH<sub>3</sub> to 1.8-2.6 g CO<sub>2</sub>/g NH<sub>3</sub>. Higher loadings are not possible without precipitation of particles. Alstrom does allow suspended particles this process [Black 2006].

The CO<sub>2</sub>-rich stream 120, which mainly contains ammonium bicarbonate is then pressurised. Stream 122 has a pressure between 3.4 and 172 bar (typically 80-100 bar), which is above the pressure in the regenerator 136 to prevent premature evaporation of CO<sub>2</sub>. The regeneration takes place at pressures between 2 and 136 bar and temperatures between 50 and 200 °C. The high pressure used suppresses ammonia losses and water desorption. The latter effect means that less energy is needed. The patent does not state the ammonia concentration used.

Recently, the US-based Electric Power Research Institute (EPRI) presented an initiative for the development of post-combustion capture technology [Rhudy 2006]. The chilled ammonia process, is the first to be tested in a partnership with Alstom and financially supported by 16 other companies. The chilled ammonia process aims to overcome the disadvantages of conventional ammonia scrubbing, i.e. the ammonia volatility and slow mass transfer in the absorber. This is realised by making sure the absorption process operates at low temperature, i.e. between 2 and 16 °C, but preferably between 0 and 5 °C. The formation of solids is regarded as a benefit, because it enables higher loadings and hence a lower energy requirement for solvent regeneration.

As a result of the high stability of NH<sub>3</sub> the solvent regeneration process can be carried out at high temperature, thereby delivering CO<sub>2</sub> at high pressure (at least 20 bar). The thermal energy requirement is estimated to be only 22% of an MEA process. The data as given by EPRI [Rhudy 2006] do not allow for a good comparison, but the thermal energy requirement can be estimated to be around 1 MJ/kg CO<sub>2</sub>, i.e. if one compares it

with a standard MEA- process. This is less than the binding energy for CO<sub>2</sub>-MEA. Hence an energy requirement as low as 1 MJ/kg CO<sub>2</sub> is not achievable with MEA in a conventional flow sheet. As the reaction with ammonia involves the formation of carbonate, it is possible to achieve a low energy requirement, because the binding energy for carbonates is around 0.5 MJ/kg CO<sub>2</sub>.

Results from a performance comparison with MEA were given by Rhudy [Rhudy 2006]. These results are summarized in Table A-2 do not allow for a direct comparison on a per tonne CO<sub>2</sub> capture basis. The discrepancy in the bottom half of the table is probably due to the power plant auxiliary power consumption of 4-5%, which normally is found in most power plants but is not listed in this table.

Table A-2 Preliminary chilled ammonia process performance prediction in a supercritical PC [Rhudy 2006]

Used Parsons study for basis	Without CO <sub>2</sub> removal	With MEA CO <sub>2</sub> removal	With NH <sub>3</sub> CO <sub>2</sub> removal
LP Steam extraction [kg/h]	0	553,383	122,470
Power loss [KWe]	0	90,000	20,000
<b>Gross power [KWe]</b>	<b>491,000</b>	<b>402,000</b>	<b>471,300</b>
<b>Auxiliary load [KWe]</b>			
Induced draft fan	5,000	19,900	10,000
Pumping CO <sub>2</sub> system	0	1,900	5,000
Chillers	0	0	8,900
CO <sub>2</sub> compressor	0	30,000	9,500
<b>Net power output</b>	<b>462,000</b>	<b>330,000</b>	<b>415,000</b>
<b>% Power reduction</b>		<b>29</b>	<b>10</b>

The whole process is estimated to reduce output of a supercritical coal fired power plant by 10% as compared to 29% in the MEA process [Rhudy 2006]. This is primarily due to the low energy requirement for regeneration but also the power needed for CO<sub>2</sub>-compression, is reduced by a factor of 3. The energy expenditure for flue gas fans is also halved, but there is additional requirement for chillers and also the energy requirement for the "CO<sub>2</sub> pumping system" (presumably solvent pumps) is reduced. This is most likely related to the fact the solvent needs to be brought to a higher desorption pressure.

#### A.8 Mani *et al.* [Mani 2006]

Mani *et al.* studied the speciation of ammonium carbonate, bicarbonate and carbamate upon CO<sub>2</sub> absorption in a ammonia solution by <sup>13</sup>C NMR at room temperature. They found this to be a simple and reliable method to determine the concentrations of these three ionic species. Fast equilibration of the carbonate and bicarbonate anions resulted in a single NMR peaks whose chemical shift depends on the relative concentration of the two species. Integration of the carbamate carbon peak provided the relative amount

of the species with respect to the bicarbonate/carbonate pair. Results as a function pH and  $\text{NH}_3/\text{NH}_4^+$  molar ratio are shown in Figure A.-10 and Figure A-11 respectively.

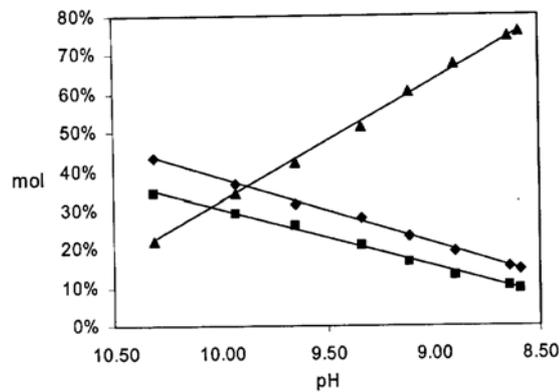


Figure A-10 Variation of the relative amounts (% on molar scale) of carbamate (◆), carbonate (■) and bicarbonate (▲) as a function of pH.

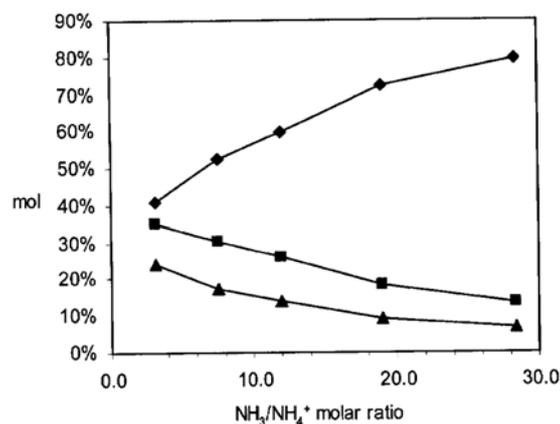


Figure A-11 Variation of the concentrations (% on molar scale) of carbamate (◆), carbonate (■) and bicarbonate (▲) as a function of the  $\text{NH}_3/\text{NH}_4^+$  molar ratio.

They found that a 2.5 M  $\text{NH}_3$  (4.3 wt%) solution represents the better compromise between  $\text{CO}_2$  loadin capacity and ammonia loss. Using an inlet of 15 l/h having 10 vol%  $\text{CO}_2$ , the maximum removal efficiency was near 100% at room temperature. The ammonia loss from the absorber was less than 0.5 vol% in the first steps of absorption going down to approximately 0.1% when the amount of free ammonia in solutions is reduced to 50%. The  $\text{CO}_2$  absorption experiments were stopped when no more than 15-20% of the  $\text{CO}_2$  is absorbed by the residual ammonia and pH values are in the range of 8.5-8.7. Typically, an average removal efficiency of 64 vol% is found, which corresponds to an absorption capacity of 1.76 g  $\text{CO}_2$ /g  $\text{NH}_3$  compared to 0.55-0.58 g  $\text{CO}_2$ /g MEA.