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## Comparative study of chemical absorbents in postcombustion CO<sub>2</sub> capture

G. Pellegrini\*, R. Strube, G. Manfrida

Department of Energy Engineering "Sergio Stecco", University of Florence, 50134 Florence, Italy

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### ABSTRACT

In order to reduce CO<sub>2</sub> emissions from a power plant, CO<sub>2</sub> can be captured either from the syngas that is to be burned or from the flue gases exiting the energy conversion process. Postcombustion capture has the advantage that it can be applied to retrofit existing power plants. In this paper the authors compare two primary amines (MEA and DGA) to ammonia with respect to their capability to capture CO<sub>2</sub> from a flue gas stream. The ammonia process captures CO<sub>2</sub> by formation of stable salts, which are separated from the solvent stream by filtration or sedimentation. These salts can be used commercially as fertilizers. Energy requirements are greatly reduced, since no heat is required for solvent regeneration, and no compression of the separated CO<sub>2</sub> is necessary. Energy, however, is required for the reduction of ammonia emissions. In order to obtain the solid ammonia salts, their solubility has to be reduced by modification of the solvent and by lowering absorption temperature. With and without separation of the salt products, ammonia proved to be an alternative solvent with high CO<sub>2</sub> removal efficiency. Simulation of all processes was carried out with Aspen Plus<sup>®</sup> and compared to experimental results for CO<sub>2</sub> scrubbing with ammonia.

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### 1. Introduction

The still rising demand for energy and the increase in CO<sub>2</sub> emissions typically involved has become one of the most important environmental topics.

In order to reduce the environmental impact of power generation from fossil fuels, CO<sub>2</sub> can be captured either from the syngas stream that is to be burned or from the flue gases exiting the energy conversion process. Postcombustion capture has the advantage that it can be applied for retrofitting existing power plants. The most mature technology of CO<sub>2</sub> absorption in gas purification processes uses amines such as Monoethanolamine (MEA) as absorbent [1]. Due to the high economic and efficiency penalties this technology is still not applied to CO<sub>2</sub> absorption in commercial power plants. Especially MEA is easily degraded in the presence of SO<sub>2</sub> and O<sub>2</sub> by the formation of irreversible byproducts, reducing the absorption capacity of the amine and making its recovery difficult [2].

A novel method of reducing CO<sub>2</sub> emissions from power plants is given by the use of an aqueous ammonia solution, which makes it possible to capture CO<sub>2</sub> as a valuable solid product [3–5]. Thus we focused our research on the capture of ammonia salts, as this allows for a much more rational use of the CO<sub>2</sub> than the liquefaction and

necessary storage of the gaseous carbon dioxide leaving the absorption process in the case of MEA (Monoethanolamine) and DGA (Diglycolamine). The produced salts are a basic ingredient of fertilizers [6] and could hence be exploited commercially. NH<sub>3</sub> has frequently been used as reactant for the De-NO<sub>x</sub> process in power plants, and it is also interesting for the removal of SO<sub>2</sub> and HCl from flue gases [7].

In this paper the authors compare two primary amines – MEA and DGA – to ammonia, all in aqueous solution, with respect to their CO<sub>2</sub> capture performance.

The energy penalty for postcombustion CO<sub>2</sub> capture with amines is currently in the range of 4–5 GJ/t CO<sub>2,captured</sub> [8,9]. This penalty is mainly due to the necessary input of thermal energy for the regeneration of the solvent in the traditional absorber–desorber process (see Fig. 1).

Energy requirements are greatly reduced in the absorption process with ammonia, since no heat for solvent regeneration and no compression of the separated CO<sub>2</sub> are necessary. However, a great amount of water is required for washing the exhaust gas stream in order to reduce emission of ammonia into the atmosphere.

CO<sub>2</sub> scrubbing with ammonia is economically very attractive [10], if salts can be separated, since the conventional production of the ammonia salts requires an energy input of around 32 GJ/t salt [11].

For the analysis of the capture processes we used the flowsheet simulation program Aspen Plus<sup>®</sup> [12]. The reactions used for CO<sub>2</sub>

\* Corresponding author. Tel.: +39 055 4796737; fax: +39 055 4224137.

E-mail addresses: [giacomo.pellegrini@unifi.it](mailto:giacomo.pellegrini@unifi.it) (G. Pellegrini), [robertstrube@gmail.com](mailto:robertstrube@gmail.com) (R. Strube).

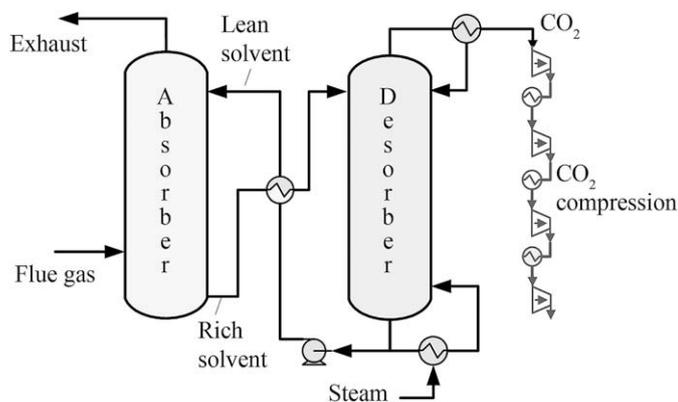


Fig. 1. Schematic diagram of absorption section for CO<sub>2</sub> scrubbing with MEA and DGA solutions [10].

absorption with the MEA, the DGA and the ammonia solvents are listed in Table 1. This table also shows the parameters for the calculation of the equilibrium constants and the kinetic parameters of the slower reactions 13 and 14. The important reaction of carbamate formation (Reactions 5, 7, and 12) was described to proceed very fast by a so-called shuttle mechanism [13] via a zwitterionic intermediate. Reactions 13 and 14 are slower than the other reactions considered here. Therefore, the kinetic parameters [14] of these reactions are important for a more accurate simulation of the capture process.

Table 1

Chemical reactions of all investigated systems with equilibrium constants  $K_{eq}$  and kinetic factors  $k$ .

		A	B	C	D
<b>CO<sub>2</sub>-MEA-H<sub>2</sub>O system (reactions 1 to 5, and 13 – 14)</b>					
CO <sub>2</sub> + 2H <sub>2</sub> O ↔ H <sub>3</sub> O <sup>+</sup> + HCO <sub>3</sub> <sup>-</sup>	(1)	132.899	-13445.9	-22.4773	0.0
2H <sub>2</sub> O ↔ H <sub>3</sub> O <sup>+</sup> + OH <sup>-</sup>	(2)	216.049	-12431.7	-35.4819	-12431.7
HCO <sub>3</sub> <sup>-</sup> + H <sub>2</sub> O ↔ H <sub>3</sub> O <sup>+</sup> + CO <sub>3</sub> <sup>2-</sup>	(3)	-0.52135	-2545.53	0.0	0.0
MEA <sup>+</sup> + H <sub>2</sub> O ↔ MEA + H <sub>3</sub> O <sup>+</sup>	(4)	-3.03833	-7008.36	0.0	-0.00313489
MEACOO <sup>-</sup> + H <sub>2</sub> O ↔ MEA + HCO <sub>3</sub> <sup>-</sup>	(5)	231.466	12092.1	36.7816	0.0
<b>CO<sub>2</sub>-DGA-H<sub>2</sub>O system (in addition to reactions 1 – 3, and 13 – 14)</b>					
DGAH <sup>+</sup> + H <sub>2</sub> O ↔ DGA + H <sub>3</sub> O <sup>+</sup>	(6)	-13.3373	-4218.71	0.0	0.0
DGACOO <sup>-</sup> + H <sub>2</sub> O ↔ DGA + HCO <sub>3</sub> <sup>-</sup>	(7)	3.66110	-3696.17	0.0	0.0
<b>CO<sub>2</sub>-NH<sub>3</sub>-H<sub>2</sub>O system (in addition to reactions 1 – 3, and 13 – 14)</b>					
NH <sub>3</sub> + H <sub>2</sub> O ↔ NH <sub>4</sub> <sup>+</sup> + OH <sup>-</sup>	(8)	-1.25656	-3335.7	1.4971	-0.0370566
NH <sub>3</sub> + HCO <sub>3</sub> <sup>-</sup> ↔ NH <sub>2</sub> COO <sup>-</sup> + H <sub>2</sub> O	(9)	-4.58344	2900	0.0	0.0
NH <sub>4</sub> HCO <sub>3</sub> $\xrightleftharpoons{SALT}$ NH <sub>4</sub> <sup>+</sup> + HCO <sub>3</sub> <sup>-</sup>	(10)	554.818	-22442.5	-89.0064	0.0647321
(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> $\xrightleftharpoons{SALT}$ 2NH <sub>3</sub> + CO <sub>2</sub> + H <sub>2</sub> O	(11)	By minimization of Gibbs free energy			
NH <sub>2</sub> COONH <sub>4</sub> $\xrightleftharpoons{SALT}$ NH <sub>4</sub> <sup>+</sup> + NH <sub>2</sub> COO <sup>-</sup>	(12)	By minimization of Gibbs free energy			
$\ln(K_{eq}) = A + \frac{B}{T} + C \cdot \ln(T) + D \cdot T$ , T in Kelvin					
<b>Kinetic reactions for all solvent systems</b>					
CO <sub>2</sub> + OH <sup>-</sup> → HCO <sub>3</sub> <sup>-</sup>	(13)	$4.3152 \times 10^{13}$	0.0	13,249	
HCO <sub>3</sub> <sup>-</sup> → CO <sub>2</sub> + OH <sup>-</sup>	(14)	$3.7486 \times 10^{14}$	0.0	25271.76	
$r = k \cdot T^n \cdot \exp(-\frac{E}{RT}) \cdot \prod_{i=1}^N C_i^{a_i}$ , k in kmol/(K <sup>n</sup> ·m <sup>3</sup> ·s), E in cal/mol					

Values for the solubility of the ammonia salts are differing between manufacturers. Data sets for two major manufacturers are given in Table 2 [15,16].

Due to the presence of ionic species in these multi-component volatile weak electrolyte systems [17,18], liquid and vapour properties were computed by the electrolyte NRTL method. Henry's law was used to calculate the solubility of CO<sub>2</sub> in water.

## 2. Process simulations

All simulations were carried out with Aspen Plus<sup>®</sup>, which has become a widely used standard application for computerized flowsheet simulations in the chemical industry. The model configuration for CO<sub>2</sub> scrubbing with ammonia included a packed absorber column of 10 theoretical stages and a filter for the extraction of salt products from the rich solvent leaving the absorber. The lean solvent is recycled to the absorber after inserting fresh solvent to make up for the losses attributed to the removal of ammonia salts.

A standard absorber–desorber configuration (with a packed absorption column of 6 theoretical stages and a packed desorption column of 10 theoretical stages) was used for the simulation of the absorption process with MEA and DGA as reacting amines (see Fig. 1). All columns were of the type RadFrac<sup>®</sup> [12], which is used in Aspen Plus<sup>®</sup> for the calculation of chemical equilibrium processes.

For all capture processes we assumed the flue gas stream to exit from a combined cycle, consisting of a methane fired 5.2 MW GE5 gas turbine and a two-pressure steam cycle. The flue gas is composed mainly by nitrogen; steam, oxygen, and carbon dioxide (ca. 7% wt.) are the other gases into the flue gas.

**Table 2**  
Salt solubilities [15,16].

Salts	BASF (g/l)	Sigma-Aldrich (g/l)
NH <sub>4</sub> HCO <sub>3</sub>	178	220
NH <sub>4</sub> COONH <sub>2</sub>	423	790
(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	320	320

A simplified diagram of the combined cycle is shown in Fig. 2.

The relevant parameters of the gas turbine and of the two pressure level of combined cycle can be found in Table 3.

For the thermal solvent regeneration in a desorber column, steam can be extracted from the low pressure steam turbine. This steam condenses in the reboiler of the column and releases heat in order to break the chemical bond between solvent and CO<sub>2</sub>.

### 3. Simulation results

In this section we compare the performance of the solvents ammonia, MEA, and DGA in the simulations.

Fig. 3 shows that the removal efficiency of MEA was higher than of DGA, as was expected. Ammonia has by far the best absorbent qualities among the substances investigated. For this comparison, the solvent flow was held constant for every individual solvent while the solvent concentration was raised (range of concentrations in % wt.: MEA: 0.17–0.33, DGA: 0.17–0.5, NH<sub>3</sub>: 0.02–0.2). The simulations for NH<sub>3</sub> showed a very high removal efficiency at ambient temperature. For a CO<sub>2</sub> removal efficiency of 80% an ammonia to CO<sub>2</sub> ratio of ca. 1.5 (a solvent concentration of 7% wt.) is sufficient, while for the same removal efficiency using MEA an amine to CO<sub>2</sub> ratio greater than 3 (solvent concentration of 20% wt.) is necessary.

For a removal efficiency of 90% the temperature profiles inside the absorber are shown in Fig. 4 for all solvents entering at 20 °C. In all cases the flue gas inlet temperature was 137 °C.

Due to the exothermic nature of absorption reactions, the temperature profile can serve as an indicator for the progress of the reactions inside the absorber column. These temperature profiles show that after the first 4–5 stages most of the fresh solvent has reacted with the CO<sub>2</sub> from the flue gas, so that a larger absorption column of more than 6 stages does not give a significantly higher absorption efficiency in our simulations.

**Table 3**  
Gas turbine and combined cycle parameters.

GE5 gas turbine	
Heat rate (kJ/kWh)	13,400
$M_{\text{fluegas}}$ (kg/s)	24.5
$T_{\text{fluegas}}$ (K)	850
$p_{\text{fluegas}}$ (bar)	1.3
$\eta_{\text{GT,el}}$	0.27
Pressure ratio ( $\beta$ )	9.1
$P_{\text{el}}$ (kW)	5220
Combined cycle	
$T_{\text{fluegas,out}}$ (K)	410
$p_{\text{fluegas,out}}$ (bar)	1.1
$\eta_{\text{CC, el}}$	0.5
$p_{\text{hp}}/p_{\text{lp}}/p_{\text{condenser}}$ (bar)	120/15/0.05
$P_{\text{el,max}}$ (kW)	10,100
$T_{\text{pinch}}$ in HRSG and reboiler	20

The ammonia process captures CO<sub>2</sub> forming stable salts. As shown in Fig. 5, salt formation increases logarithmically with solvent loading (mol CO<sub>2</sub>/mol solvent agent). The salts are separated from the solvent stream by filtration or by sedimentation and have commercial appeal for fertilizer production.

We studied the effect of thermal solvent regeneration on the performance of the combined cycle power plant as described in the introduction. Thermal regeneration is achieved by heating the reboiler of the desorber column with low quality steam from the low pressure steam turbine. To reduce the impact on power plant efficiency, the outtake pressure is chosen as low as possible. The temperature, which the steam can deliver by condensation, however, depends on reboiler pressure. In our simulations, the drop in power output from the combined cycle changed from 0.2 MW per MW of reboiler duty at a regeneration temperature of 90 °C to 0.26 MW per MW of reboiler duty at a regeneration temperature of 120 °C. Changing the reboiler duty from 2.5 MW to 8.5 MW for different solvents resulted in the bottom temperatures of the desorber as shown in Fig. 6, which demonstrates the effect of reboiler temperature on the regeneration efficiency of the desorber. The limits for the reboiler duty used here correspond to the limitations of the combined cycle used in our simulations. In this figure we also present additional results for ammonia in a standard absorber–desorber configuration.

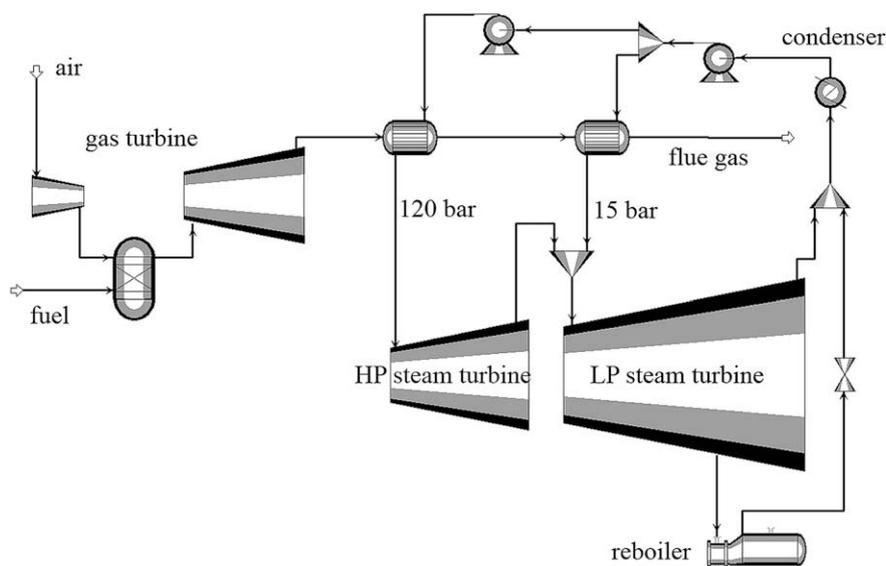


Fig. 2. Schematic diagram of combined cycle with 5.2 MW gas turbine and steam turbines of 120 bar and 15 bar inlet pressure in Aspen Plus®.

A great part of the CO<sub>2</sub> is released from the solvent in case of ammonia desorption without requiring a greater energy input. In our simulations, an 80% regeneration of the ammonia solvent would lead to a reduction of about 5% in electrical power output from the power plant. MEA has the strongest bonding to CO<sub>2</sub>. Therefore, a higher energy input is needed for breaking these bonds. The same regeneration efficiency would lead to a power reduction of ca. 25% in case of the MEA and of ca. 18% in case of DGA as a solvent. A high regeneration efficiency is, however, required for the reduction of the solvent flow.

#### 4. Experimental setup

Subsequently, we investigated the CO<sub>2</sub> removal with ammonia by a series of experiments carried out in a small-scale setup in the laboratory of the Inorganic Chemistry department at the University of Florence.

The semi-continuous flow reactor (see Fig. 7) consisted of a glass column containing 240 ml of aqueous ammonia solution (5% wt. ammonia concentration).

A substitute flue gas stream (10% vv. CO<sub>2</sub> in N<sub>2</sub>) of ca. 4.2 ml/s was fed continuously to the bottom of the absorber through a sintered glass diffuser (Ø 16–40 µm pores). The exhaust gas left the absorber at the top. The inlet gas mixture was humidified by bubbling it through water before it entered the reactor. All experiments were carried out at atmospheric pressure.

The CO<sub>2</sub> capture performance of the system is easily determined by weight measurements of all system components before the tests and after certain time intervals. The pH-value and the species in solution have been analysed with a <sup>13</sup>C NMR (Nuclear Magnetic Resonance spectroscopy) apparatus. A gas chromatograph is used to measure the losses of CO<sub>2</sub> from the system.

#### 5. Experimental results

In the results of the <sup>13</sup>C NMR, in Fig. 8, the peak on the right represents the combined contribution from carbonate and bicarbonate ions. These two ions appear as a single peak whose position depends on the relative concentration of the two ions:

$$\frac{[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = \frac{160.82 - S}{S - 168.24} \quad (15)$$

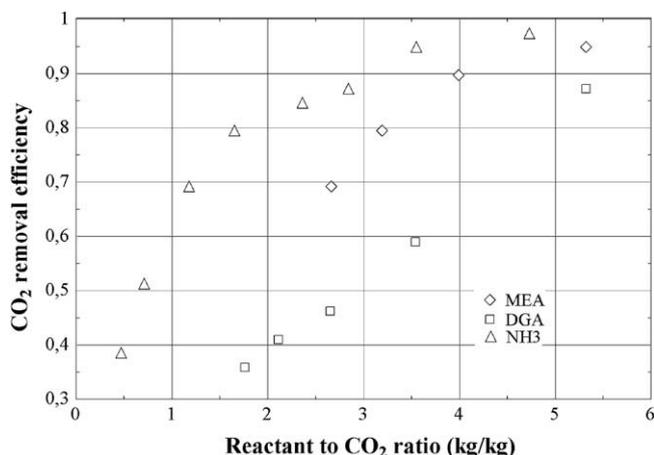


Fig. 3. CO<sub>2</sub> removal efficiency at  $T = 20\text{ }^\circ\text{C}$  of MEA, DGA and NH<sub>3</sub> at different amine to CO<sub>2</sub> ratios.

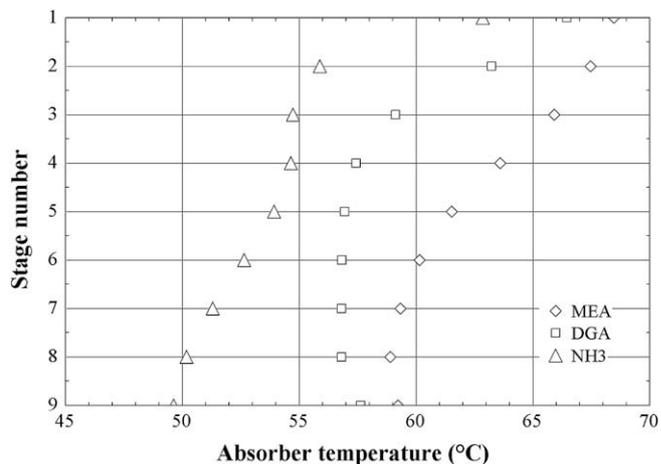


Fig. 4. Absorber temperature profiles for 90% CO<sub>2</sub> removal with MEA, DGA and NH<sub>3</sub>.

where  $S$  is the shift of the carbonate/bicarbonate peak in ppm, and the two constants represent 100% bicarbonate (160.82) and 100% carbonate (168.24), respectively. These constants were determined by measuring the spectra of solutions that only contained bicarbonate or carbonate. The other peak in Fig. 8 results from the carbamate [19,20].

Although the reaction between carbonate and bicarbonate reached equilibrium very fast, this was not the case for the reaction of carbamate with its carbonate and bicarbonate products. Thus, the solution was given at least 1 h to react, allowing for the measurement of the equilibrium concentrations of bicarbonate, carbonate and carbamate ions. The concentrations of the components in solution after different time intervals are shown for two different absorption temperatures in Table 4. The loss of ammonia from the absorber proved to be very low (ca. 0.01%).

Temperatures of down to  $-5\text{ }^\circ\text{C}$  were investigated due to the expected reduction in salt solubility. However, the CO<sub>2</sub> removal efficiency was nearly independent of absorber temperature, as shown in Fig. 9, and pH-measurements of the solution verified this behaviour.

Contrary to the simulation results, the experiments showed that at such low ammonia concentrations, due to the high solubility of salts, it was not possible to separate them from the solution. The resulting lower removal efficiency of ammonia in the experiments

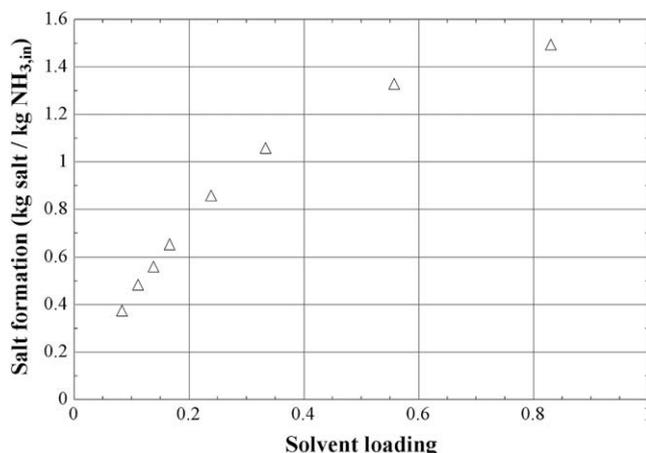


Fig. 5. Ammonia salt formation for different loadings (mol/mol) of the ammonia solvent.

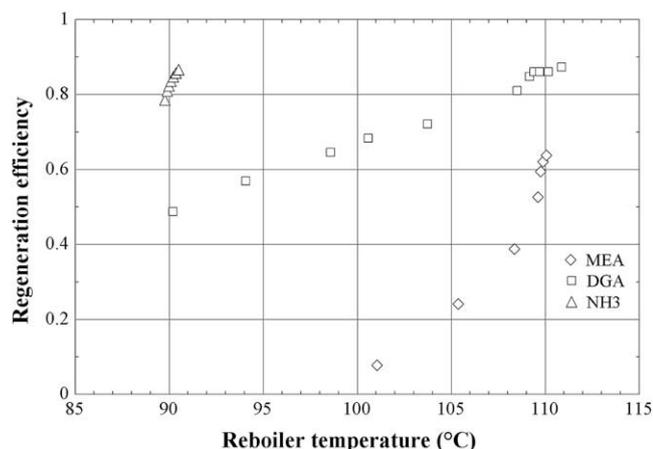


Fig. 6. Regeneration efficiency in the desorber for a reboiler duty of 2.5–8.5 MW.

(ca. 1.26 kgCO<sub>2,removed</sub>/kgNH<sub>3,in</sub>), however, is still higher than the simulation results for MEA and DGA.

In order to be able to separate the ammonia salts it is necessary to lower their solubility. This can be achieved by either raising the concentration of ammonia in the solvent stream [21,22] or by using an alternative solvent. In this work, the latter option was chosen, as otherwise ammonia losses with the exhaust gas become very large. Aiming at a reduction of these losses, the authors then investigated the hydro-alcoholic solvent EtOH–H<sub>2</sub>O–NH<sub>3</sub>, resulting in a so-called Ethano-Aqueous-Ammonia (EAA) solution. Ethanol was chosen due to its similar characteristics to water and its good availability. A new series of tests was carried out for various ammonia concentrations and absorber temperatures without changing the described experimental setup.

While the removal efficiency and thus the amount of produced salts with the hydro-alcoholic solution improved with the increase of ammonia concentration.

After giving the solution 3 h to react, the CO<sub>2</sub> outlet concentration exceeded 20% wt. for an ammonia concentration of 2% wt., while it took more than 6 h until the same outlet concentration of CO<sub>2</sub> was observed at ammonia concentrations of 4% wt. and 6% wt.

Also the amount of produced salts confirmed that removal efficiency improved with increasing ammonia concentration. At the end of the experiment, when the CO<sub>2</sub> outlet concentration exceeded 25% wt., the salts are removed from the absorption column.

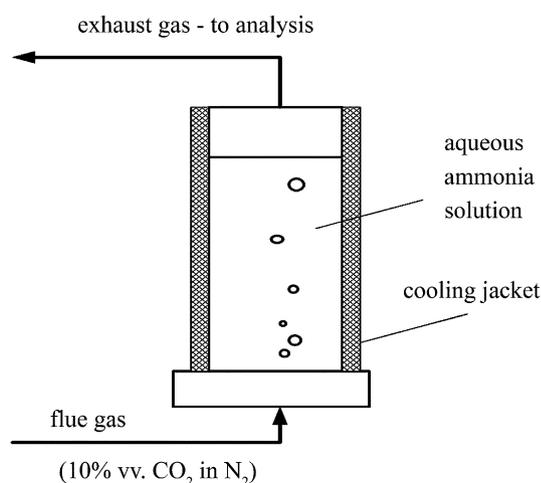


Fig. 7. Schematic diagram of absorber assembly.

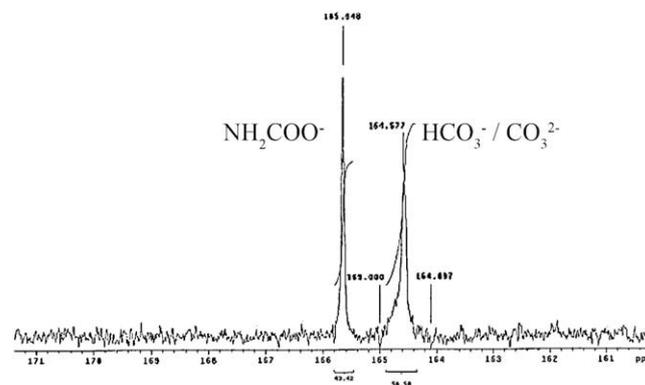


Fig. 8. Results of <sup>13</sup>C NMR analysis.

Then, they are dried and weighed to measure their relative amount and a sample of the produced salts is sent to an NMR analysis to determine the salt composition. In the end, the absorption column is weighed again and the test is restarted. At an absorber temperature of –5 °C, about 8.3 g were obtained for a solvent concentration of 2% wt., while it were 12.8 g and 13.7 g respectively for solvent concentrations of 4% wt. and 6% wt. However, higher ammonia concentrations in the entering solvent stream also lead to elevated losses of ammonia with the exiting gas stream.

The results for different absorber temperatures clearly show a reduced formation of ammonia salts at higher temperatures (above 0 °C). At a solvent concentration of 2% wt. the amount of salts formed amounted to ca. 8.3 g at –5 °C, while at temperatures of 0 °C and 20 °C these values were reduced to 6.2 g and even 1.8 g respectively. A reduced salt formation consequently leads to lower CO<sub>2</sub> removal efficiencies and higher losses of the solvent components with the exhaust gas. The CO<sub>2</sub> outlet concentration exceeded 20% wt. already after a reaction time of 90 min for an absorption temperature of 20 °C, while it took more than 150 min until the same outlet concentration of CO<sub>2</sub> was observed for the lower temperatures.

The experiments carried out with the EtOH–H<sub>2</sub>O–NH<sub>3</sub> (EAA) solvent confirmed the trends of the previous experiments without ethanol as to the response of component concentrations to the absorption conditions, i.e. absorption temperature.

As the amount of free (or excess) NH<sub>3</sub> in the solution increased, the same trend could be observed for carbamate formation, while the formation of bicarbonate decreased with higher concentrations of free NH<sub>3</sub> (see Table 5).

The development of CO<sub>2</sub> removal efficiency of the ammonia solution (AA) and the EAA solution are compared in Fig. 10 for an absorption temperature of 20 °C and an ammonia concentration of 5% wt. in the solvent stream. At any time, the removal efficiency of the salt-forming EAA is higher than the performance of AA.

Table 4

Development of component concentrations (% wt.) in ammonia solution (5% wt. NH<sub>3</sub> in H<sub>2</sub>O) at –5 °C and at 20 °C.

Time (h)	T = –5 °C			T = 20 °C		
	Component concentrations (% wt.)					
	HCO <sub>3</sub> <sup>–</sup>	CO <sub>3</sub> <sup>2–</sup>	NH <sub>2</sub> COO <sup>–</sup>	HCO <sub>3</sub> <sup>–</sup>	CO <sub>3</sub> <sup>2–</sup>	NH <sub>2</sub> COO <sup>–</sup>
2	28.1	28.6	43.3	28.2	28.8	43.0
3	42.8	21.9	35.3	45.3	22.7	32.0
7	52.0	18.3	29.7	60.2	16.5	23.3
8	63.3	14.8	21.9	71.0	11.9	17.1

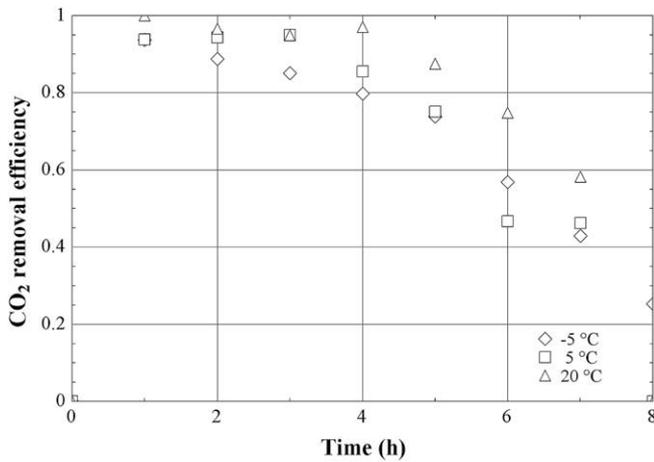


Fig. 9. CO<sub>2</sub> removal efficiency by ammonia solution (5% wt. NH<sub>3</sub> in H<sub>2</sub>O) at different temperatures.

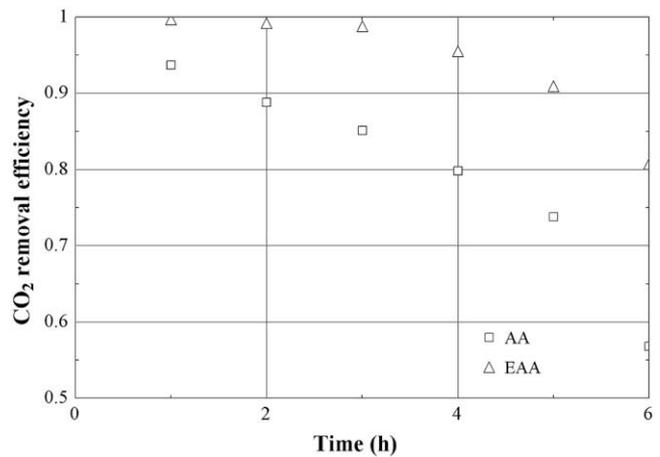


Fig. 10. Removal efficiency of AA and EAA at 20 °C with 5% wt. NH<sub>3</sub>.

The measurements are effected by an experimental error. The precision of the balance, used to weigh all the components, is  $\pm 0.01$  g, corresponding to an error of ca. 1%. The accuracy of the gas chromatograph, used to measure the losses of CO<sub>2</sub> from the system, is ca. 5% around the value of calibration (a flow containing 10% vol. CO<sub>2</sub> and 90% vol. N<sub>2</sub> produced by Italian gas company Rivoira). This leads to an error of up to 4% in mass of CO<sub>2</sub> lost, depending on the total amount of CO<sub>2</sub> that has left the system. The NMR instrument measures frequency signals and compares them to a reference frequency, showing the composition of the produced salts.

## 6. Comparison of experiments and simulations

In a final comparison (see Fig. 11), for an aqueous ammonia solution (AA) of 5% wt. and at an absorption temperature of 20 °C, the Aspen Plus® model (AA with salt formation) demonstrated the highest CO<sub>2</sub> removal efficiency. The last value in Fig. 11 represents the result for 90% CO<sub>2</sub> removal in an absorber–desorber configuration with a reboiler duty of 8 MW. For the same parameters, the amount of CO<sub>2</sub> removed per unit mass of solvent agent was 0.18 kg/kg of MEA and 0.17 kg/kg of DGA.

The removal efficiency per kg of ammonia was significantly lower if a regenerative cycle was used. This seems to confirm that the greatest problem in using ammonia for CO<sub>2</sub> removal is the high solubility of the ammonia salts.

In the non-regenerative ammonia process, at 20 °C approximately 20% of the ammonia exits the absorber with the gas stream and has to be removed. The energy requirements for the gas treatment in order to reduce ammonia emissions are in the same range as for the regeneration of the amines. This value can be reduced by lowering the temperature, which would lead, however, to a higher energy consumption for cooling.

Another important factor to be taken into account is the amount of energy needed for the production of the solvents. With the

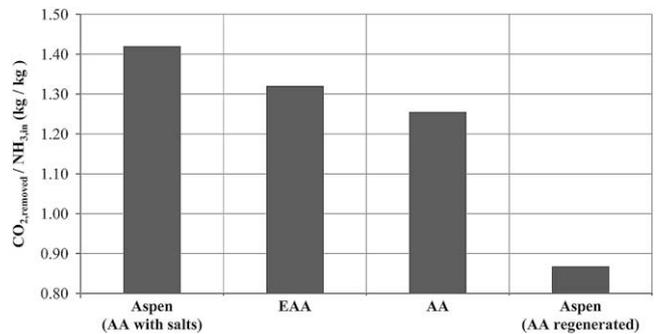


Fig. 11. Comparison of Aspen Plus® models to experiments with AA solution and EAA solution at  $T = 20$  °C.

secondary gas treatment after the salt forming absorption, around 20% of the ammonia would be recuperated. The rest would have to be supplied fresh with a production cost of 19.4 MJ/kg of NH<sub>3</sub> [11]. Producing the fertilizer salts in a separate process would require 32 MJ/kg of ammonia salt [11]. Around 2% of the MEA mass flow have to be added to the process due to unavoidable solvent losses and degradation [23]. The production costs of MEA are approximately 88 MJ/kg of MEA [11].

Compression of the CO<sub>2</sub> for transport and storage is necessary in all regenerative cycles. This requires around 0.4 MJ/kg CO<sub>2</sub>.

Comparing the investigated processes one can state that despite the necessary high solvent makeup, capturing the CO<sub>2</sub> in the form of ammonia salts has a clear energetical advantage over the regenerative processes.

First rate-based models have been used in simulations with Aspen Plus® for the absorption of CO<sub>2</sub>. In these simulations no salt formation could be observed when using the ammonia solvent AA, while it was not possible to simulate absorption with the Ethanol–Ammonia solvent EAA. Using an absorber–desorber configuration, the absorption efficiency of ammonia is lower than in the corresponding model based on equilibrium. This indicates that the reaction time and thus the height of the absorber play an important role in the absorption of CO<sub>2</sub>. Results of the rate-based model will be published in the future.

## 7. Conclusions

In this study, comparative flowsheet simulations for the CO<sub>2</sub> capture performance of three different solvents (MEA, DGA, and

**Table 5**  
Development of component concentrations (% wt.) in EtOH–H<sub>2</sub>O–NH<sub>3</sub> solution at –5 °C and at 20 °C.

Cycle	$T = -5$ °C		$T = 20$ °C	
	HCO <sub>3</sub> <sup>-</sup> + CO <sub>3</sub> <sup>2-</sup>	NH <sub>2</sub> COO <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup> + CO <sub>3</sub> <sup>2-</sup>	NH <sub>2</sub> COO <sup>-</sup>
1	13.8	86.2	35.4	64.6
2	20.8	79.2	69.6	30.4
3	73.5	26.5	100	
4	100			

NH<sub>3</sub>) were carried out. The simulations show that ammonia is a superior absorbent, which yields high removal efficiencies at low solvent concentrations.

In the experiments the excellent absorbing qualities of ammonia could be verified. Crystalline salts (which may be used as a commercial product) could only be obtained, however, by a reduction of the very high solubility of the ammonia salts. This reduction was achieved by using a mixture of ethanol, water and ammonia.

Even if no salt formation occurs and the ammonia solvent is thermally regenerated in an absorber–desorber arrangement, the much lower absorption temperatures (due to the reactions between the CO<sub>2</sub> and the solvent) imply much lower energy requirements for solvent regeneration as compared to MEA and DGA.

Using low concentrations of ammonia in the solution for CO<sub>2</sub> removal proved to be a good compromise between high removal efficiency and low ammonia losses with the exhaust gas stream. Any capture process using ammonia, either by salt production or in an absorber–desorber configuration, benefits clearly from lower temperatures. This greatly reduces ammonia losses from the absorber and hence the necessary energy input for emission reduction. However, the energy requirements for cooling the solution and the absorber remain to be investigated.

The production of fertilizers using the ammonia salts produced in the aforementioned process would of course lead to implications on the fertilizer market and on the producers of these fertilizers. This option will therefore only be implemented until the level of demand for fertilizers is met and probably in cooperation with the fertilizer producers, which this way could obtain an economical base ingredient from the power plant sector.

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