
Chemical Absorption by Aqueous Solution of Ammonia

Gianluca Valenti and Davide Bonalumi

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.78545>

Abstract

Carbon capture is proposed as a viable way of exploiting the fossil resources for power plants and industrial processes. The post-combustion capture by chemical absorption in amine aqueous solutions has been in use in chemical and petrochemical areas for decades. As an alternative, the absorption in aqueous ammonia has received great attention recently. The carbon capture by aqueous ammonia is based on the conventional absorption-regeneration scheme applied to the ternary system $\text{CO}_2\text{-NH}_3\text{-H}_2\text{O}$. It can be implemented in a chilled and a cooled process, depending upon the temperatures in the absorber and, hence, the precipitation of salts. The process simulation can be conducted in two manners: the equilibrium and the rate-based approaches. The specific heat duty is as low as 3.0, for the cooled process, and 2.2 $\text{MJ}/\text{kg}_{\text{CO}_2}$ for the chilled one. Moreover, the index *SPECCA* is as low as 2.6, for the cooled, and 2.9 $\text{MJ}/\text{kg}_{\text{CO}_2}$ for the chilled one. The overall energy performances from the simulations in the rate-based approach, compared against those in the equilibrium approach, result only slightly penalized. From an economic perspective, the carbon capture via chemical absorption by aqueous ammonia is a feasible retrofitting solution, yielding a cost of electricity of 82.4 €/MWh_e and of avoided CO_2 of 38.6 €/t_{CO₂} for the chilled process.

Keywords: carbon capture, post-combustion capture, chemical absorption, aqueous ammonia, salt precipitation, ammonia slip

1. Introduction

The ongoing scientific debate does not focus on whether fossil fuels will have to meet a major portion of the short- and the mid-future energy demand, but rather on how they will be exploited most effectively in terms of primary energy use, environmental impact, and

end-user cost. Meanwhile, renewable sources are expected to be implemented more and more diffusely to allow independence from fossils in a later future.

Carbon capture is proposed as a viable way of effectively exploiting the conventional resources. It can be implemented in a pre-combustion, a post-combustion, or even an oxy-combustion configuration. Among them, the post-combustion option has the large benefit of being readily applicable to the already existing power plants as well as industrial processes that are fueled by coal and natural gas.

The post-combustion carbon capture can be accomplished by adsorption on solid materials or by chemical absorption in liquid solutions. The chemical absorption in amine aqueous solutions has been in use for decades in a number of chemical and petrochemical areas, such as the Oil & Gas or the urea preparation. Currently, the so-called advanced amines are under research with the goal of reducing the energy demand when applied to power plants and industrial processes. As an alternative to amines, the chemical absorption in ammonia aqueous solution has received great attention during the last decade.

This chapter covers the chemical absorption of carbon dioxide by an aqueous solution of ammonia. The next sections will present, in sequence, an overview of a number of works retrieved from the open literature, the simulation by either an equilibrium- or a rate-based approach, the environmental as well as economic assessments and, lastly, the future developments of the process itself.

2. Bibliographic review

The possibility of obtaining carbon dioxide from gas mixtures attracts the attention of inventors and investigators toward the end of the nineteenth century, as narrated by Wellford Martin and Killeffer [1]. In 1937, the two authors turn to be among the first ones to recognize the possibility of producing CO_2 from the flue gases of power plants.

In the first decades of the twentieth century, the process employing aqueous ammonia for the removal of CO_2 and H_2S is used extensively for the purification of coke-oven gas. Carbon dioxide is indeed a major component that must be removed to greatly increase the heating value of that gas. During the following years, amines, specifically alkanolamines, become preferred over ammonia for few reasons [2]. First, the use of amines leads to lower issues of pipe plugging and air polluting. Second, amines are characterized by higher effectiveness in capturing H_2S , which can be used as an affordable source of elemental sulfur. Ultimately, ammonia is still an expensive substance because the industrial ammonia production is still to be established. Historically, the first alkanolamine to become commercially viable is triethanolamine (TEA) in the year 1930.

Through the last few decades, the amines that reach commercial maturity for gas purification are monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanol-amine (MDEA). In particular, MEA is taken frequently as the reference process for the carbon capture in

post-combustion configuration. By contrast, the aqueous ammonia is reconsidered explicitly for carbon capture only quite recently by both research centers and industrial companies.

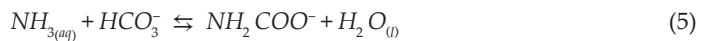
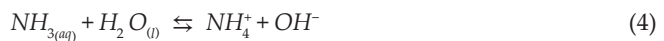
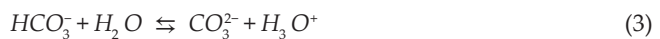
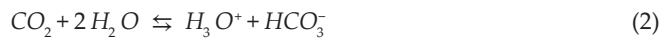
The following sections provide an overview of the information about the general absorption-regeneration scheme, the chemistry of solution, the thermodynamic equilibrium models, the kinetics investigations, and the aqueous ammonia process for carbon capture.

2.1. General absorption-regeneration scheme

The carbon capture by aqueous ammonia as well as aqueous amines is based on the conventional absorption-regeneration scheme, which is illustrated in **Figure 1**. In simple words, the gas to be treated flows upward through the absorber, countercurrent to the falling absorbing solution, and purified from CO₂. The generated rich solution from the bottom of the absorber is heated in a heat exchanger, recovering energy from the lean solution (see subsequent text), and enters the regenerator at a point near to its top. In the regenerator, a heat source (such as steam) releases the captured CO₂, which exits from the top of the column, while the generated lean solution from the bottom. The lean solutions flow, through the mentioned heat exchanger, to the top of the absorber closing the scheme. An exhaustive description of the absorption-regeneration scheme is provided by Kohl and Nielsen [3].

2.2. Chemistry of the solution

The carbon capture by aqueous ammonia is based on the ternary system CO₂-NH₃-H₂O, which yields an electrolyte solution. At the absorber conditions, the main reactions are [4] as follows:



The ternary system is explored by Burrows and Lewis as early as 1912 [5]. In a more recent work, 1982, Pawlikowski et al. [6] investigate vapor-liquid equilibria of many systems, including CO₂-NH₃-H₂O, by way of the gas-liquid chromatography for temperatures ranging from

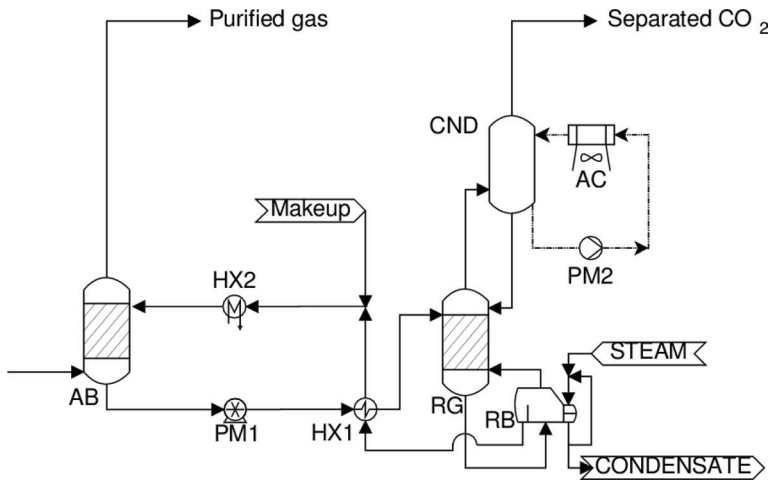


Figure 1. Process flow diagram of the absorption-regeneration scheme for ammonia and amines [3].

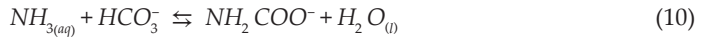
100 to 150°C. Kawazuishi and Prausnitz [7] provide measurements from previous works by other scientists with the scope of calibrating the expressions of dissociation equilibrium constants and Henry's constants for temperatures in the 100–205°C interval and for total liquid-phase concentrations to 10 molal. Göppert and Maurer [8] report vapor-liquid equilibrium data between 333.15 and 393.15 K at pressures up to about 7 MPa for water-rich mixtures and concentrations to about 16 molal for ammonia and 13 molal for carbon dioxide. In 1992, Pelkie et al. [9] use conductivity measurements to estimate the ammonium ion, NH_4^+ , concentration at a temperature of 25°C and over a wide span of pressures and concentrations. The vapor-liquid-solid equilibrium is considered in the work by Kurz et al. [10], which focuses on the solubility of weak electrolyte gases into the aqueous phase in the temperature range from 313 to 353 K at pressures up to 0.7 MPa. In a subsequent study, the enthalpy changes upon partial evaporation of aqueous solutions, including $\text{CO}_2\text{-NH}_3\text{-H}_2\text{O}$, are reported by Rumpf et al. [11] at temperatures from 313 to 393 K. Finally, speciation is measured with ¹³C NMR by Holmes et al. [12] at 25 and 35°C and by Mani et al. [4] at room temperature.

2.3. Thermodynamic equilibrium models

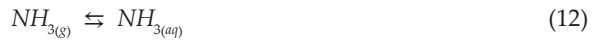
As indicated, the ternary system is an electrolyte solution. The thermodynamic model for such a complex system shall account for the electric interactions among the species, including strong and weak forces. The strong forces are described by long-range terms that represent electrostatic interactions between ions. The weak forces instead by short-range terms that represent the ion dipole interactions and the non-electrostatic interactions.

Two common equilibrium descriptions are the Electrolyte Non-Random Two Liquid (e-NRTL) model [13] and the Extended UNIQUAC model [14]. A comparison between them is proposed

by Darde et al. [15]. The most recent improvement of the Extended UNIQUAC model [16] comprises a full set of equilibrium reactions. First, speciation reactions are as follows:



Moreover, three vapor–liquid equilibrium relations are as follows:



Lastly, the four solid formations are as follows:

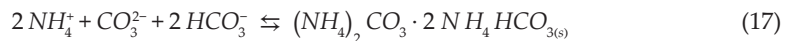
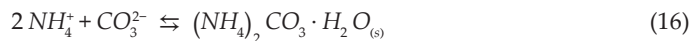
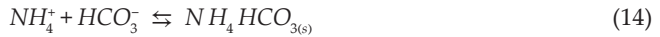


Figure 2 illustrates a comparison of the experimental data by Kurz et al. [10], indicated by hollow markers, and the computed values by way of the improved extended UNIQUAC model, indicated by lines. The agreement is generally high.

2.4. Kinetics investigations

There are relatively few investigations on the kinetics for the ternary system NH_3 – CO_2 – H_2O . Hsu et al. [17] describe the absorption reaction kinetics of amines and ammonia solutions with carbon dioxide in flue gases. The temperature of investigation is 50°C, which is relatively high

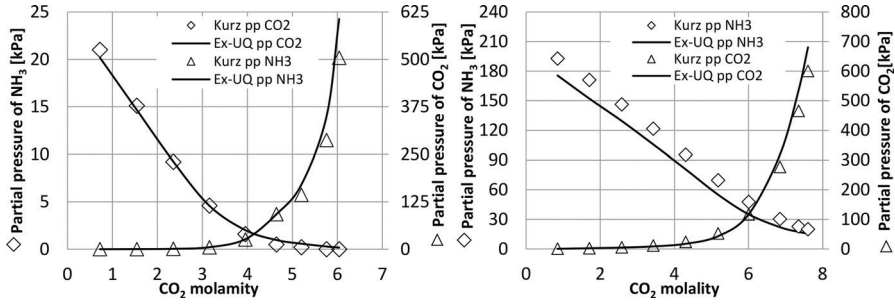
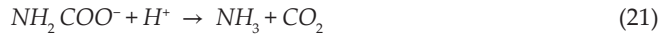
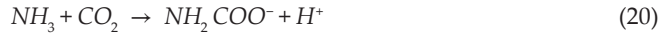


Figure 2. Comparison of the computed values via the Extended UNIQUAC model [16] (indicated by Ex-UQ) of the partial pressure of CO_2 and NH_3 against the experimental data by Kurz et al. [10]. Left: at 313 K and 6.3 molal of NH_3 . Right: at 353 K and 11.8 molal of NH_3 .

for the carbon capture process. Similarly, Diao et al. [18] investigate the removal efficiency of the sole ammonia solution in the 25–55°C interval and regress the parameters of the rate constant for the capture reaction in the Arrhenius form.

Among the reactions that describe the system, only a subset is expected to significantly influence the kinetics of the overall process. These kinetics-affecting reactions are as follows:



Among them, reactions (R18) and (R20) are considered to be the slowest. The first is studied by Pinsent et al. [19], while the second by five different works as discussed subsequently.

Reaction (R18) is investigated by Pinsent et al. [19] via the rapid thermal method in the range 0–40°C. The fitting yields the Arrhenius constant with a second order as follows:

$$\frac{-d\text{CO}_2}{dt} = r = k_2 * [\text{CO}_2][\text{OH}^-] \quad (1)$$

$$k_2 = A * e^{\frac{-E_a}{RT}} \text{ with } A = 4.32 * 10^{13} \frac{\text{kmol}}{(\text{m}^3 * \text{s})} \text{ and } E_a = 13249 \frac{\text{cal}}{\text{mol}} \quad (2)$$

Moreover, Pinsent et al. [20] assess reaction (R20) by the rapid thermal method in the range of ammonia concentration between 0.027 and 0.19 mol/l. By contrast, Puxty et al. [21] study it by measuring the rate of CO_2 absorption into a falling thin film using a wetted wall column

for aqueous ammonia between 0.6 and 6 mol/L, temperature between 5 and 20°C, and the initial thin liquid film CO₂ loading between 0 and 0.8 mol_{CO₂}/mol_{NH₃}. Wang et al. [22] assess the kinetic of reaction (R20) by the stopped flow apparatus in the range of temperature between 15 and 45°C, ammonia concentration between 2.0 and 16 mmol/L, and the initial CO₂ between 3 and 10 mmol/L. Lastly, Jilvero et al. [23] study it by a different perspective. They implement an adsorption column in a commercial code taking the design parameters of an existing pilot plant and they tune the kinetics parameters against the experimental data.

Lillia et al. [24] conduct a comparison of these four investigations and the resulting parameters, reported in **Table 1**, for the Arrhenius equation written as follows:

$$\frac{-dNH_3}{dt} = r = k_2 * [NH_3][CO_2] \quad (3)$$

$$k_2 = A * e^{\frac{-E_a}{RT}} \quad (4)$$

Figure 3 visualizes the trends with respect to the (reciprocal of the) temperature and against the experimental data from the investigations. Each Arrhenius law fits the data well for each work. Apparently, though, the data themselves are not in complete agreement. The results from Pinsent et al. and Wang et al. are in mutual agreement, but in disagreement with those by Puxty et al. and Jilvero et al. Noticeably, Pinsent et al. and Wang et al. measured the data at low ammonia concentrations, while Puxty et al. and Jilvero et al. at high concentrations. In short, there is likely a dependence of the kinetic parameters on the ammonia concentration.

Subsequently, Lillia et al. [25] propose an alternative kinetics based on the two-film theory [26] as represented in **Figure 4**. Their study covers the region typical for the absorption columns: temperatures from 15 to 35°C, NH₃ concentrations from 5 to 15%, and CO₂ loadings from 0.2 to 0.6. The study yields an Arrhenius constant with a pre-exponential factor of 1.41 × 10⁸ [mol/(m³s)] and an activation energy of 60,680 [J/mol]. It has a linear dependence on the CO₂ concentration and a dependence on the NH₃ concentration with an exponent of 1.89.

2.5. Aqueous ammonia process for carbon capture

The concept on what was going to be referred to as the novel ammonia-scrubbing process for the carbon capture is proposed by Bai and Yeh in 1997 based on experimental data [27].

Their work highlights the remarkable potential of high removal efficiencies, over 95%, and absorption capacities, around 0.9 kg of CO₂ per kg of NH₃. Shortly after, Yeh and Bai [28] complete another experimental campaign with the scope of comparing amine and ammonia scrubbing and they confirm the potential of the second over the first solvent. Experiments are conducted at room temperature in their first work and between 10 and 40°C in the later one. In 2005, Yeh et al. [29] publish the results of three-cycle absorption-regeneration tests conducted on MEA and ammonia in a batch reactor maintained at about 25°C. They also reported an approximate estimate of energy usage that is lower than the one for MEA.

Source	Arrhenius parameters of k_2 in Eq. (4)	
	A [kmol/(m ³ s)]	E _A [cal/mol]
Pinsent et al. [20]	1.35×10^{11}	11,585
Puxty et al. [21]	1.66×10^{14}	14,577
Wang et al. [22]	5.01×10^{11}	12,279
Jilvero et al. [23]	6.51×10^{13}	14,362

Table 1. Arrhenius parameters of the rate of reaction (R20) from different experimental works.

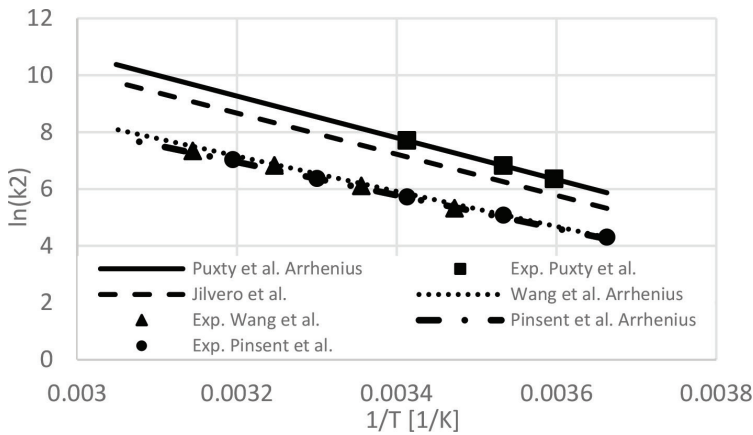


Figure 3. Comparison among values for k_2 and experimental data from cited works: Puxty et al. [21], Wang et al. [22], and Pinsent et al. [20]. The dashed lines are obtained fitting the experimental data. The dashed line for Jilvero et al. [23] is the trend proposed by the authors of that work.

In 2006, EIG Inc. [30] applies for a patent on the chemical absorption of the carbon dioxide into aqueous ammonia at chilled conditions. The company Alstom is engaged in its intensive development, establishing the commercial name Chilled Ammonia Process (CAP). As summarized by Lombardo et al. [31], the chilled process is tested first at bench scale with SRI International. Later, it is verified at pilot scale with the Electric Power Research Institute and two utilities: WE energies in its Pleasant Prairie (WI, USA) and E.ON in its Karlshamm (Sweden) plant. Ultimately, the product validation is executed in the facility of the American Electric Power in Columbus (OH, USA) and in the world's largest test facility of the Technology Center of Mongstad (Norway). The process has evolved during the years and it is still under development by the company General Electric, which has acquired it recently [32].

At the same time, the process is investigated by a number of research centers. Ullah et al. [33] analyze the use of a capacitive deionization in the conventional scheme of the ammonia-based process to reduce the regeneration energy requirement, concluding that the reduction can be as much as 37.5%. Sutter et al. [34] propose instead the controlled solid bicarbonate formation to decrease the energy requirement. Precipitation, separation, and dissolution of the solid

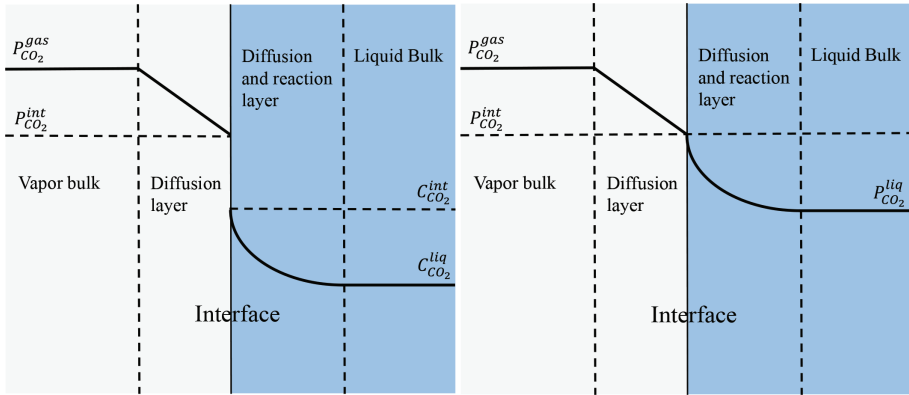


Figure 4. Representation of the two-film theory [26] applied to the ternary system $\text{CO}_2\text{-NH}_3\text{-H}_2\text{O}$. Left: the CO_2 partial pressure profile in the gas and the CO_2 concentration profile in the liquid phase. Right: the CO_2 partial pressure profile in both the gas and liquid phases.

phase are realized in a dedicated process section, while the packed absorption and desorption columns operate free of solids. A similar approach is proposed by Gao et al. [35], pursuing the decreasing energy consumption by the addition of alcohols to reinforce the crystallization.

Bonalumi et al. [36] suggest to operate the process at cool conditions ($20\text{-}35^\circ\text{C}$) rather than chilled ($5\text{-}20^\circ\text{C}$), to minimize the load on the chillers in favor of the load on air coolers. The two processes are visualized in **Figure 5**. In the cool process, one chilling load is still present

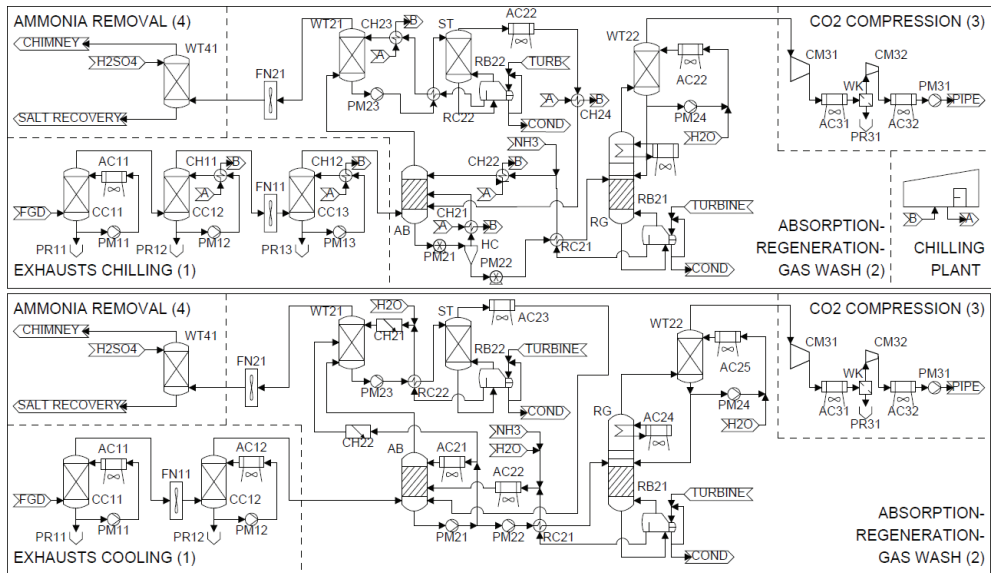


Figure 5. Process flow diagram of the chilled (top) and cooled (bottom) aqueous ammonia process.

for the water wash on top of the absorber. Water wash is required indeed to minimize the tendency of ammonia to escape from the absorber, which is called ammonia slip.

The ammonia-based capture is proposed typically for existing coal- and natural gas-fired power plants. Nonetheless, Bonalumi and Giuffrida [37] consider it for an air-blown integrated gasification combined cycle (IGCC) fired with high-sulfur coal, while Pérez-Calvo et al. [38] for cement plants, both achieving promising indications.

3. Process simulation with the equilibrium approach

In general, the computer simulation of a chemical process can be conducted in two different manners: the equilibrium- and the rate-based approaches, depending on whether the kinetics is not taken or it is taken into consideration, respectively. The results at the equilibrium represent the performance theoretically achievable, while the rate-based the realistic one.

Evaluating the integration of a power plant with the ammonia-based capture using the equilibrium approach, as both chilled and cooled processes, Bonalumi et al. [36] focus on the flue gas from a coal-fired plant, as opposed to a gas-fired. The main difference is the CO₂ concentration, which is in the neighborhood of 15%, on a volume and dry basis, for coal- and of 4% for gas-fired. The reference power plant is the one defined by the European Benchmark Task Force [39] with the scope of establishing a framework for the consistent comparison of capture technologies. The plant has a nominal net electric power output and efficiency of 754 MW_e and 45.5%. The carbon dioxide flow is 160.7 kg_{CO₂}/s at a concentration of 15.2%.

In their evaluation, Bonalumi et al. [36] adopt values of the design parameters differentiated between the chilled and the cooled process, as indicated by **Table 2**. Moreover, in the chilled process, the temperature of the streams entering the absorber is 7°C, leading to a maximum temperature in the absorber of around 18°C, despite the reaction of absorption being exothermic, and promoting the salt precipitation in a wide range of concentrations of the reactants. In the cooled process, instead, the temperature of those streams is 20°C, leading to a maximum temperature in the absorber of around 27°C and preventing the solid formation.

Different indexes can be defined to assess the carbon capture performance. First, the carbon capture efficiency is defined as the ratio of the flow rates [kmol/s or kg/s] of the carbon dioxide exiting the compression island and of that entering the exhaust chilling island. As a second

Parameter	Unit	Chilled	Cooled
Ammonia initial concentration	%(mass)	20	7.5
Ammonia-to-carbon dioxide ratio	kmol/kmol	3.2	5
Recycle fraction	—	0.8	0.2
Regeneration pressure	bar	20	5
Regeneration temperature	°C	95.4	105.6

Table 2. Design parameters for the chilled and the cooled aqueous ammonia capture proposed by Bonalumi et al. [36].

common performance index, the specific heat duty [MJ_{th}/kg_{CO_2}] is defined as the ratio of the reboiler heat duty [MW_{th}] and the mass flow rate [kg_{CO_2}/s] of effectively captured carbon dioxide. However, this second index does not include the information on the capture efficiency (first index) nor on the temperature at which the heat duty is required (or, in equivalent terms, the loss of electric power generation from the steam turbine due to the steam bled for the regenerator).

A third index is adopted to solve this issue about the specific heat duty. Consequently, the new index allows to compare consistently plants characterized by different capture efficiencies, regeneration temperatures, and electric efficiency penalties. The Specific Primary Energy Consumption for Carbon Avoided (*SPECCA*) [MJ_{th}/kg_{CO_2}] is defined as

$$SPECCA \stackrel{def}{=} \frac{HR - HR_{REF}}{E_{REF} - E} \equiv \frac{3600 \left(\frac{1}{\eta_e} - \frac{1}{\eta_{e,REF}} \right)}{E_{REF} - E} \quad (5)$$

where all parameters refer to either the power plant equipped with the carbon capture or the reference plant without it: *HR* is the heat rate [MJ_{th}/MWh_e], *E* the specific CO_2 emission [kg_{CO_2}/MWh_e], η_e [-] the net electric efficiency, and *REF* stays for reference.

Electric power, MW_e	Chilled	Cooled	Electric power, MW_e	Chilled	Cooled
<i>Exhaust cooling (1)</i>					
AC11	2.357	2.351	CH24	0.045	0.000
AC12	0.000	0.132	FN21	3.154	3.342
CH11	4.860	0.000	PM21	1.629	1.410
CH12	1.058	0.000	PM22	2.362	1.121
FN11	3.943	4.177	PM23	<0.001	0.003
PM11	0.597	0.592	PM24	0.010	0.010
PM12	0.201	0.142	Subtotal	64.380	17.219
PM13	0.102	0.000	Power island		
Subtotal	13.148	7.394	RB21	45.131	57.207
<i>ABS-RGN-GW (2)</i>					
AC21	0.220	0.671	RB22	1.878	15.321
AC22	0.144	4.626	Subtotal	47.009	72.528
<i>CO₂ Compression (3)</i>					
AC23	0.018	1.770	AC31	0.226	0.326
AC24	0.000	0.952	AC32	0.775	0.957
AC25	0.000	0.018	CM31	6.771	15.421
CH21	36.349	2.801	CM32	6.019	14.825
CH22	20.310	0.495	PM31	1.784	0.652
CH23	0.139	0.000	Subtotal	15.575	32.181
			Total loss	140.112	129.323

Table 3. Predicted electric consumption of the capture island for the chilled and the cooled aqueous ammonia capture computed by Bonalumi et al. [36].

Parameter	Unit	Reference	MEA	Chilled	Cooled
Electric power loss	MW _e	NA	198.9	140.1	129.3
Net electric power	MW _e	754.0	562.4	613.9	624.7
Net electric efficiency	%	45.5	33.5	37.05	37.70
Specific heat duty	MJ/kg _{CO2}	NA	3.70	2.19	2.98
Specific CO ₂ emission	kg _{CO2} /MWh _e	763	104	141.4	138.9
<i>SPECCA</i>	MJ/kg _{CO2}	NA	4.16	2.86	2.58

Table 4. Overall performances of the chilled and the cooled processes compared against a reference power plant (without carbon capture) and a plant integrated with MEA aqueous solution computed by Bonalumi et al. [36].

Regarding the results for the chilled and the cooled process, **Table 3** compares the predicted electric consumptions. The exhaust cooling and the absorption-regeneration sections are more penalizing for the chilled process due to the major consumption of the chillers. By contrast, the power island is more penalizing for the cooled process, on one side, because of a large contribution due to the higher amount of NH₃ that must be recovered by the water wash section. On the other, because of another major contribution due to the higher specific heat duty and the higher regeneration temperature that require more steam bleeding at a higher value of pressure and enthalpy from the turbine. In addition, the compression stage is more penalizing for the cooled process since the regeneration pressure is lower. Hence, from the electric consumption, the chilled process is less penalizing than the cooled one.

In its turn, **Table 4** summarizes the performances for the chilled and the cooled processes and it compares them against those of the reference power plant (without any carbon capture) and a plant integrated with carbon capture in MEA aqueous solution. From the index *SPECCA*, which is as seen the most consistent perspective for evaluating a capture technology, the cooled process is less penalizing than the chilled one, by far, than MEA.

4. Process simulation with the rate-based approach

In a recent work, Bonalumi et al. [40] adopt the rate-based approach to assess the same cooled aqueous ammonia process that they investigated earlier with the equilibrium approach [36]. **Table 5** summarizes the main results from the comparison of the performances predicted by the two approaches. The overall energy balance for the kinetic study, compared against the equilibrium study, turns to be only slightly penalized. The authors explain that this penalization originates from the larger request of energy to achieve a higher level of CO₂ purity in the lean stream from the regenerator. The differences being moderate, though, the study of an absorption capture plant with the equilibrium approach can be considered a valid method for a preliminary assessment of an ammonia-based process.

Parameter	Unit	Cooled equilibrium	Cooled rate based
Electric power loss	MW _e	129.3	136.4
Net electric power	MW _e	624.7	617.6
Net electric efficiency	%	37.70	37.27
Specific heat duty	MJ/kg _{CO2}	2.98	3.02
Specific CO ₂ emission	kg _{CO2} /MWh _e	138.9	141.2
SPECCA	MJ/kg _{CO2}	2.58	2.77

Table 5. Performances of the cooled process computed with the equilibrium and the rate-based approaches by Bonalumi et al. [34, 36].

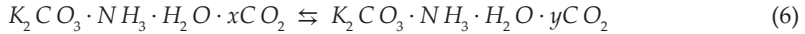
5. Economic and environmental assessments

The integration of the chilled process and an ultra supercritical power plant is analyzed by Valenti et al. [41] via a parametric analysis from the energy and the economic perspectives. The capture island is simulated with an equilibrium approach. In the parametric investigation, five parameters are varied singularly: (1) ammonia initial concentration in the aqueous solution, (2) ammonia-to-carbon dioxide ratio in the absorber, (3) regeneration pressure, (4) regeneration temperature, and (5) absorber chiller evaporation temperature. The economic analysis, with respect to a reference power plant rated at the net electric production of over 750 MW_e, shows that the capital investment of the capture island is estimated to be a relatively small portion of that of the power island. However, due to other costs and due to the performance penalties, the cost of electricity increases significantly by 37.5%, from 59.90 to 82.38 €/MWh_e; ultimately, the resulting cost of avoided CO₂ is approximately 38.64 €/t_{CO2}.

A detailed environmental life cycle analysis for an ultra supercritical power plant with and without carbon capture is proposed by Petrescu et al. [42]. Three capture islands are considered: (1) gas-liquid absorption with MDEA (monodiethanolamine), (2) gas-liquid absorption with aqueous ammonia, and (3) gas-solid absorption with calcium oxide. The environmental evaluation is performed using the “cradle-to-grave” methodology considering several upstream and downstream processes. Eleven environmental impact categories, according to the method CML 2001, are compared using GaBi software. The study highlights that carbon capture technologies decrease the global warming potential indicator, but they may increase other indicators. The amine technology achieves a good performance from the perspective of global warming, but not satisfactory from that of all others. Aqueous ammonia adsorption and calcium looping prove to be better. Some indicators, such as acidification potential, eutrophication potential, or those related to lethal concentrations (e.g., human toxicity potential, freshwater aquatic ecotoxicity potential, and marine aquatic ecotoxicity potential), are better in the case of aqueous ammonia. By contrast, some others, such as abiotic depletion fossil and abiotic depletion elements, are better in the case of calcium looping.

6. Future developments

A highly promising solvent-based CO₂ capture process, named the mixed-salt technology, is being currently developed, as reported by Jayaweera et al. [43]. This technology adds potassium carbonate to the system in order to exploit the advantages of both ammonia-based and potassium carbonate-based technologies. The simplistic representation of the CO₂ absorption and removal reaction is as follows:



where the CO₂ loading is the numerical difference between y and x . The left and right side of the equilibrium represent the lean and rich solutions, respectively. Despite the system being characterized by the presence of several ionic species that could form a solid phase, precipitation is avoided by operating the absorber at relatively high temperatures and at concentrations below the solid-forming conditions. The expected advantages are a limited heat duty at the regenerator and a limited load for the water wash on top of the absorber.

7. Conclusions

This chapter covers the chemical absorption of carbon dioxide by an aqueous solution of ammonia for coal- and natural gas-fired power plants and industrial processes. It reports the literature review, the simulation by equilibrium- or rate-based approach, the economic as well as environmental assessments, and the future developments. Conclusions are as follows:

1. The ammonia-based technology confirms to be attractive compared to conventional amines. It can be implemented in a chilled as well as in a cooled process depending upon the temperature and, consequently, the precipitation of salts in the absorber.
2. The predicted specific heat duty, in the equilibrium approach, is 3.0 for the cooled process and 2.2 MJ/kg_{CO₂} for the chilled one. Moreover, the index *SPECCA* is 2.6 for the cooled and 2.9 MJ/kg_{CO₂} for the chilled. Overall, the cooled process combines the advantage of a moderate energy requirement with the absence of solid formation.
3. The predicted performances in the rate-based approach, compared against those in the equilibrium approach, result slightly penalized. The difference is due to the need of a higher level of CO₂ purity in the lean stream from the regenerator. The index *SPECCA* value changes from 2.6, as seen in the equilibrium, to 2.8 MJ/kg_{CO₂} in the rate-based approach, yielding an increase of the prediction of about 6%. Hence, the study of an absorption capture plant with an equilibrium approach is a valid methodology for a preliminary investigation and optimization process.
4. From an economic perspective, the carbon capture via chemical absorption by aqueous ammonia is a feasible retrofitting solution, yielding a predicted cost of electricity of 82.4 €/MWh_e and a cost of avoided CO₂ of 38.6 €/t_{CO₂} both for the chilled process (those for the cooled process are not reported yet in the open literature).

5. The mixed-salt technology is a promising evolution of the process to further reduce the specific heat duty and the load for the water washing on top of the absorber.

Acknowledgements

The authors gratefully acknowledge Mr. Stefano Lillia of Politecnico di Milano for his help in investigating carbon capture alternatives as well as in reviewing this chapter.

Author details

Gianluca Valenti* and Davide Bonalumi

*Address all correspondence to: gianluca.valenti@polimi.it

Politecnico di Milano, Milano, Italy

References

- [1] Wellford Martin J, Killeffer DH. Carbon dioxide from power plant flue gas. *Industrial and Engineering Chemistry*. 1937;**29**(6):632-636
- [2] Kohl AL, Nielsen RB. Chapter 4 – Removal and use of ammonia in gas purification. In: *Gas Purification*. Houston, Texas, USA: Gulf Professional Publishing; 1997. pp. 278-329
- [3] Kohl AL, Nielsen R. *Gas Purification*. Houston, Texas, USA: Gulf Professional Publishing; 1997
- [4] Mani F, Peruzzini M, Stoppioni P. CO₂ absorption by aqueous NH₃ solutions: Speciation of ammonium carbamate, bicarbonate and carbonate by a ¹³C NMR study. *Green Chemistry*. 2006;**8**(11):995
- [5] Burrows GH, Lewis GN. The equilibrium between ammonium carbonate and ammonium carbamate in aqueous solution at 25°. *Journal of the American Chemical Society*. 1912;**34**(8):993-995
- [6] Pawlikowski EM, Newman J, Prausnitz JM. Phase equilibria for aqueous solutions of ammonia and carbon dioxide. *Industrial and Engineering Chemistry Process Design and Development*. 1982;**21**(4):764-770
- [7] Kawazuishi K, Prausnitz JM. Correlation of vapor-liquid equilibria for the system ammonia-carbon dioxide-water. *Industrial and Engineering Chemistry Research*. 1987; **26**(7):1482-1485
- [8] Göppert U, Maurer G. Vapor-liquid equilibria in aqueous solutions of ammonia and carbon dioxide at temperatures between 333 and 393 K and pressures up to 7 MPa. *Fluid Phase Equilibria*. 1988;**41**(1-2):153-185

- [9] Pelkie JE, Concannon PJ, Manley DB, Poling BE. Product distributions in the carbon dioxide-ammonia-water system from liquid conductivity measurements. *Industrial and Engineering Chemistry Research*. 1992;**31**(9):2209-2215
- [10] Kurz F, Rumpf B, Maurer G. Vapor-liquid-solid equilibria in the system $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ from around 310 to 470 K: New experimental data and modeling. *Fluid Phase Equilibria*. 1995;**104**:261-275
- [11] Rumpf B, Weyrich F, Maurer G. Enthalpy changes upon partial evaporation of aqueous solutions containing ammonia and carbon dioxide. *Industrial and Engineering Chemistry Research*. 1998;**37**(8):2983-2995
- [12] Holmes PE, Naaz M, Poling BE. Ion concentrations in the $\text{CO}_2\text{-NH}_3\text{-H}_2\text{O}$ system from ^{13}C NMR spectroscopy. *Industrial and Engineering Chemistry Research*. 1998;**37**(8):3281-3287
- [13] Chen C-C, Britt HI, Boston JF, Evans LB. Two new activity coefficient models for the vapor-liquid equilibrium of electrolyte systems, thermodynamics of aqueous systems with industrial applications. ACS Symposium Series. American Chemical Society, Washington, DC. October 29, 1980;**133**:61-89. DOI: 10.1021/bk-1980-0133.ch004
- [14] Thomsen K, Rasmussen P. Modeling of vapor-liquid-solid equilibrium in gas-aqueous electrolyte systems. *Chemical Engineering Science*. 1999;**54**(12):1787-1802
- [15] Darde V, Thomsen K, van Well WJM, Bonalumi D, Valenti G, Macchi E. Comparison of two electrolyte models for the carbon capture with aqueous ammonia. *International Journal of Greenhouse Gas Control*. 2012;**8**:61-72
- [16] Bonalumi D, Giuffrida A. Performance Improvement of Cooled Ammonia-based CO_2 Capture in Combined Cycles with Gasification of High-sulfur Coal. *Energy Procedia*. 2017;**114**:6440-6447. <https://doi.org/10.1016/j.egypro.2017.03.1780>
- [17] Hsu CH, Chu H, Cho CM. Absorption and reaction kinetics of amines and ammonia solutions with carbon dioxide in flue gas. *Journal of the Air & Waste Management Association*. 2003;**53**(2):246-252
- [18] Diao YF, Zheng XY, He BS, Chen CH, Xu XC. Experimental study on capturing CO_2 greenhouse gas by ammonia scrubbing. *Energy Conversion and Management*. 2004;**45**(13-14): 2283-2296
- [19] Pinsent BRW, Pearson L, Roughton FJW. The kinetics of combination of carbon dioxide with hydroxide ions. *Transactions of the Faraday Society*. 1956;**52**(1512):1512
- [20] Pinsent BRW, Pearson L, Roughton FJW. The kinetics of combination of carbon dioxide with ammonia. *Transactions of the Faraday Society*. 1956;**52**(2):1594
- [21] Puxty G, Rowland R, Attalla M. Comparison of the rate of CO_2 absorption into aqueous ammonia and monoethanolamine. *Chemical Engineering Science*. 2010;**65**(2):915-922

- [22] Wang X et al. Kinetics of the reversible reaction of $\text{CO}_2(\text{aq})$ with ammonia in aqueous solution. *The Journal of Physical Chemistry. A.* 2011;**115**(24):6405-6412
- [23] Jilvero H, Normann F, Andersson K, Johnsson F. The rate of CO_2 absorption in ammonia—Implications on absorber design. *Industrial and Engineering Chemistry Research.* 2014;**53**(16):6750-6758
- [24] Lillia S, Bonalumi D, Valenti G. Rate-based approaches for the carbon capture with aqueous ammonia without salt precipitation. *Energy Procedia.* 2016;**101**:400-407
- [25] Lillia S, Bonalumi D, Fosbøl PL, Thomsen K, Valenti G. Experimental study of the aqueous CO_2 - NH_3 rate of reaction for temperatures from 15 °C to 35 °C, NH_3 concentrations from 5% to 15% and CO_2 loadings from 0.2 to 0.6. *International Journal of Greenhouse Gas Control.* 2018;**70**(July 2017):117-127
- [26] Lewis WK, Whitman WG. Principles of gas absorption. *Industrial and Engineering Chemistry.* 1924;**16**(12):1215-1220
- [27] Bai H, Yeh AC. Removal of CO_2 greenhouse gas by ammonia scrubbing. *Industrial and Engineering Chemistry Research.* 1997;**36**(6):2490-2493
- [28] Yeh AC, Bai H. Comparison of ammonia and monoethanolamine solvents to reduce CO_2 greenhouse gas emissions. *Science of the Total Environment.* 1999;**228**(2-3):121-133
- [29] Yeh JT, Resnik KP, Rygle K, Pennline HW. Semi-batch absorption and regeneration studies for CO_2 capture by aqueous ammonia. *Fuel Processing Technology.* 2005;**86**(14-15):1533-1546
- [30] Gal E. Ultra cleaning of combustion gases including the removal of CO_2 , Patent number: WO 2006/022885 A1, 2006
- [31] Lombardo G, Agarwal R, Askander J. Chilled ammonia process at Technology Center Mongstad—First results. *Energy Procedia.* 2014;**51**:31-39
- [32] Dube SK. System for Generating Low Pressure Carbon Dioxide in a Chilled Ammonia Process. 2016. European Patent Application: EP3075431A1
- [33] Ullah A, Saleem MW, Kim W-S. Performance and energy cost evaluation of an integrated NH_3 -based CO_2 capture-capacitive deionization process. *International Journal of Greenhouse Gas Control.* 2017;**66**:85-96
- [34] Sutter D, Gazzani M, Mazzotti M. A low-energy chilled ammonia process exploiting controlled solid formation for post-combustion CO_2 capture. *Faraday Discussions.* 2016;**192**:59-83
- [35] Gao J et al. A new technique of carbon capture by ammonia with the reinforced crystallization at low carbonized ratio and initial experimental research. *Fuel Processing Technology.* 2015;**135**:207-211

- [36] Bonalumi D, Valenti G, Lillia S, Fosbøl PL, Thomsen K. A layout for the carbon capture with aqueous ammonia without salt precipitation. *Energy Procedia*. 2016;**86**:134-143
- [37] Bonalumi D, Giuffrida A. Investigations of an air-blown integrated gasification combined cycle fired with high-sulphur coal with post-combustion carbon capture by aqueous ammonia. *Energy*. 2016;**117**:439-449
- [38] Pérez-Calvo J-F, Sutter D, Gazzani M, Mazzotti M. Application of a chilled ammonia-based process for CO₂ capture to cement plants. *Energy Procedia*. 2017;**114**:6197-6205
- [39] Anantharaman R, Bolland O, Booth N, van Dorst E, Ekstrom C, Sanchez Fernandes E, Franco F, Macchi E, Manzolini G, Nikolic D, Pfeffer A, Prins M, Rezvani S, Robinson L. Carbon-free Electricity by SEWGS: Advanced materials, Reactor- and process design. D 4.9 European best practice guidelines for assessment of CO₂ capture technologies. 213206 FP7 - ENERGY.2007.5.1.1, Politecnico di Milano, Alstom UK. 2011
- [40] Bonalumi D, Lillia S, Valenti G, Fosbøl PL, Thomsen K. Kinetic study of a layout for the carbon capture with aqueous ammonia without salt precipitation. *Energy Procedia*. 2017;**114**(November 2016):1352-1359
- [41] Valenti G, Bonalumi D, Macchi E. A parametric investigation of the chilled ammonia process from energy and economic perspectives. *Fuel*. 2012;**101**:74-83
- [42] Petrescu L, Bonalumi D, Valenti G, Cormos A-M, Cormos C-C. Life cycle assessment for supercritical pulverized coal power plants with post-combustion carbon capture and storage. *Journal of Cleaner Production*. 2017;**157**:10-21
- [43] Jayaweera I et al. Results from process modeling of the mixed-salt technology for CO₂ capture from post-combustion-related applications. *Energy Procedia*. 2017;**114**:771-780