

# Ammonia-based post combustion – The techno-economics of controlling ammonia emissions



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## ABSTRACT

An important process consideration in ammonia-based, post-combustion CO<sub>2</sub> capture is the volatility of ammonia. Consequently, there is a need to adopt control measures to minimize the emission (the slip) of ammonia from such processes. This work evaluates techno-economic aspects of methods to reduce the ammonia slip. The emission of ammonia is required to be below 10 ppm while the ammonia slip from the absorber in an ammonia-based process may exceed 10%. The ammonia control methods that are evaluated in this work are staged absorption, ammonia abatement cycle, chilled absorption and acid wash. The control methods are also evaluated with respect to local conditions, such as cooling water temperature and flue gas CO<sub>2</sub> concentration. Rate- and equilibrium-based thermodynamic modelling forms the basis for the evaluation process. A simplified economic estimation method is used to evaluate the utility cost of ammonia control designs under different operating conditions. The economic estimation shows that for the best case conditions the utility cost are as low as 1.5€/tCO<sub>2</sub>. However, the cost of the ammonia control may be more than tenfold when the available cooling water temperature is increased (>5°) or when the flue gas CO<sub>2</sub> concentration is decreased (<15 vol%). Thus, the cost of the slip control measures narrows the range of process conditions at which ammonia-based, post combustion capture is an economically feasible option.

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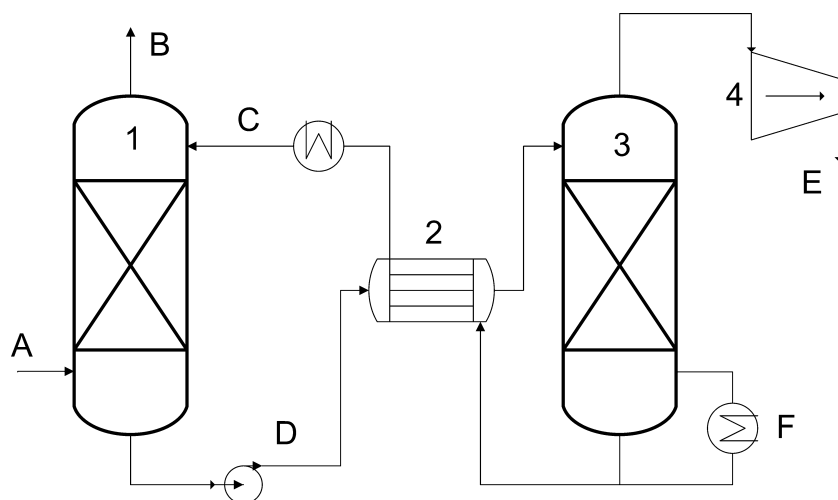
## 1. Introduction

Ammonia is an option to the commonly proposed amine-based absorbent (such as monoethanolamine, MEA) for post-combustion capture. Fig. 1 shows a schematic of a post-combustion capture plant. Downstream the carbon dioxide (CO<sub>2</sub>) emitting process the flue gas stream enters the post-combustion capture process (Units 1–4). The incentive to develop an ammonia-based, post-combustion process is a lower heat requirement for regeneration, less absorbent degradation and a low cost for CO<sub>2</sub> compression. However, one of the main issues with using ammonia as absorbent is that it is far more volatile than other absorbents, for instance MEA. At typical absorber conditions the vapor pressure of ammonia is several thousand times higher than that of MEA. The higher volatility causes a large amount of ammonia to evaporate in the absorption column and leave the absorber (Unit 1) with the flue gases (slip).

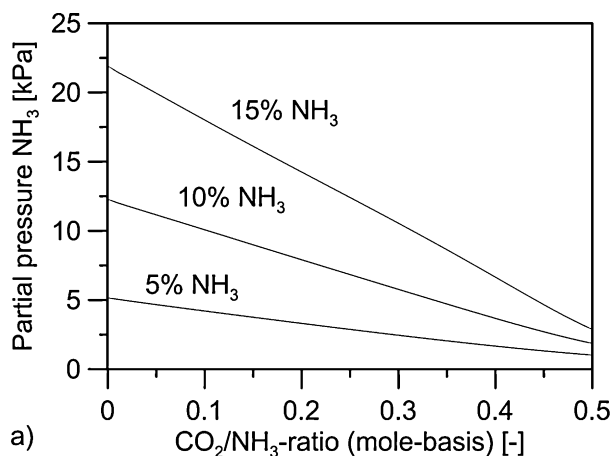
The slip of ammonia is determined by the partial pressure of ammonia in the CO<sub>2</sub>-lean stream entering the absorber. The

partial pressure of ammonia in the CO<sub>2</sub>-lean stream is influenced by a number of parameters such as temperature and the concentration of water and CO<sub>2</sub>. Depending on the conditions in the absorber, the slip of ammonia can differ substantially. Fig. 2 shows how the equilibrium partial pressure of ammonia in the CO<sub>2</sub>-lean stream changes with CO<sub>2</sub>-loading (the molar-ratio between CO<sub>2</sub> and NH<sub>3</sub>) and ammonia concentration (constant amount of ammonia and varying water content) in Fig. 2a and temperature in Fig. 2b. With respect to ammonia slip, a low ammonia concentration, a low temperature and a high CO<sub>2</sub>-loading is desirable. However, optimum operating conditions will become a trade-off between ammonia slip, heat requirement for regeneration, process cooling, reactivity and capture efficiency. Common conditions of the CO<sub>2</sub> lean stream are an ammonia concentration of 5–15 mol% and a CO<sub>2</sub>-loading of 0.25. At these conditions the partial pressure of ammonia is 4–13 kPa, which corresponds to a possible ammonia slip of about 4–13% at the absorber outlet. Another important parameter which is shown in Fig. 2b is the operating temperature. The operating temperature of the absorber is limited by the accessible cooling water temperature. Fig. 2a shows that at 10 mol% ammonia the partial pressure of ammonia is almost 3 times higher at 30 °C compared to 10 °C.

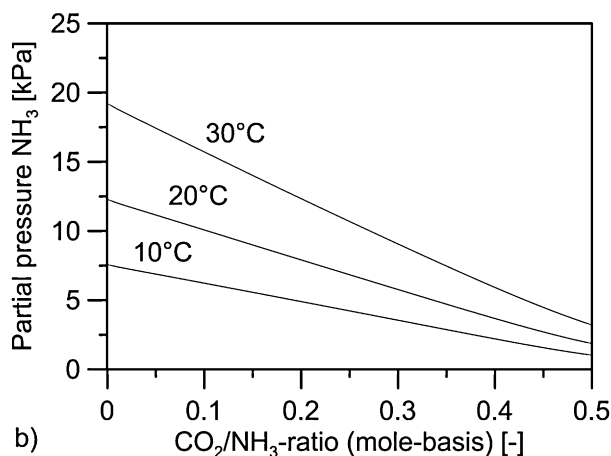
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**Fig. 1.** Schematic of a post-combustion capture process. (1) Absorber, (2) rich/lean heat exchanger, (3) stripper, and (4) CO<sub>2</sub> compression. (A) Flue gases, (B) to stack, (C) CO<sub>2</sub>-lean stream, (D) CO<sub>2</sub>-rich stream, (E) CO<sub>2</sub> stream (F) heat.



a)



b)

**Fig. 2.** The equilibrium partial pressure of ammonia as a function of the CO<sub>2</sub>-loading and the temperature at 10% NH<sub>3</sub> (a) and the ammonia concentration (CO<sub>2</sub>-free) at a temperature of 20 °C (b). The results are based on the model by Que and Chen [1].

A common design target for the discharge ammonia concentration is to be below 10 ppm, i.e., much lower than the absorber outlet concentration. The ammonia emission limitations may vary between different countries and may even be site specific. However, the limitations are always close to 10 ppm. The National Institute for Occupational Safety and Health (NIOSH) has listed

**Table 1**

Methods to reduce ammonia emissions (the ones evaluated in this work are indicated in bold).

Reduction option	Type	Typical application
<b>Steam stripping</b>	Regenerative	Sour water stripping
<b>Acid wash</b>	Destructive	Process gas purification
<b>Chilled absorption</b>	Regenerative	Carbon capture
<b>Staged absorption</b>	Regenerative	Carbon capture
Vapor suppressing additives	Regenerative	Carbon capture
Catalytic/Non-catalytic oxidation	Destructive	Waste water treatment
Zeolite adsorption	Destructive	Waste water treatment
Biodegradation	Destructive	Waste water treatment

25 ppm as the time-weighted average exposure limit for 8 h exposure intervals [2]. Thus, there is a need to reduce the ammonia slip significantly before the bulk gas is emitted to the atmosphere. Table 1 presents options to reduce the ammonia slip. However, not all of the mentioned reduction options are suitable for a post-combustion capture process. There are both regenerative and destructive reduction options. When destructive reduction methods are used, new ammonia is continuously supplied to the capture process and the energy requirement of producing new ammonia from natural gas is 28.82 MJ/kg NH<sub>3</sub> [3].

Vapor suppressing additives are relatively new in connection to control of ammonia volatility [4] and this option is not considered in the present investigation. The method is based on the addition of metal ions to the absorbent and the partial pressure is suppressed by complexation with free ammonia. However, there is concern that this results in a decrease in absorption rate. Oxidation, zeolite adsorption and biodegradation of the ammonia are mostly used for waste-water treatment, when the ammonia concentration is low and ammonia is regarded as a pollutant. In this work four reduction methods are evaluated: staged absorption, ammonia abatement cycle with steam stripping, chilled absorption and acid wash. All of the reduction methods are described more in detail in Section 3.

Control of ammonia emissions will always be associated with an energy penalty. For the ammonia-based capture process, heat and energy requirement of both the CO<sub>2</sub> capture cycle and ammonia control method needs to be added when comparing the thermal performance with other possible post-combustion processes (e.g., monoethanolamine, MEA based post-combustion capture). As a reference, the heat requirement for regeneration in the ammonia based CO<sub>2</sub> capture cycle was evaluated in detail in the work by Jilvero et al. [5] and determined to be as low as 2500 kJ/kg CO<sub>2</sub>

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