Application of a chilled ammonia-based process for CO₂ capture to cement plants

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Abstract

Cement production accounts for about 5% of the global anthropogenic CO₂ emissions [1]. In contrast to other energy-intensive industrial processes, CO₂ generation is inherent to the cement production: the limestone calcination, i.e. the conversion of CaCO₃ to CaO and CO₂, is responsible for about 60% of the CO₂ emissions from cement production. Accordingly, CO₂ capture and storage (CCS) is needed to reduce the carbon footprint of this industrial application. Among the different possible configurations, CO₂ removal from the flue gas, which is generated in the rotary kiln and in the pre-calciner, is of particular interest as it makes use of the experience acquired in the power plant field and offers retrofit opportunities.

In this context, the Chilled Ammonia Process (CAP) is a promising technology for post-combustion CO₂ capture. Besides a competitive energetic performance compared to conventional amines (MEA), the use of aqueous NH₃ as a solvent offers advantages concerning global availability, environmental footprint and cost compared to most amine processes. Additionally, the aqueous NH₃ solvent is chemically stable in the presence of impurities such as SOₓ and NOₓ, while amines are known to form toxic degradation products and corrosive solutions. A simplified process flow diagram of the CAP is shown in Figure 1.

While the application of the CAP to natural gas and coal-fired power plants has been validated and demonstrated in various facilities of different scale and with CO₂ concentration in the flue gas
ranging from 3 to 16% vol [2,3], the application of the CAP to cement plants, where the CO₂ concentrations can be as high as 30% vol, has not been investigated yet.

The drastic increase in CO₂ concentration in the flue gas is the most important change that the CAP applied to cement has to cope with. Indeed, the CO₂ absorption unit, which is of central importance for the CAP, is largely affected by the higher partial pressure of CO₂ in the inlet stream; changes in the reaction rates and in the energy balance of the column lead to considerably different temperature and concentration profiles.

The higher CO₂ concentration can in principle be confronted with an increase in the liquid to vapour flowrate (L/G) along the absorber, an increase in the ammonia content of the liquid phase and/or a decrease in the CO₂ loading of the CO₂-lean solution with respect to the power plant operating conditions. The liquid composition profiles along the absorber for a power plant and a cement plant are shown in Figure 2. It is worth noting how the larger amount of energy released in the cement case affects the temperature profile of the solution, leading to higher temperature peaks (>50°C) and higher ammonia vaporization from the liquid solvent. Accordingly, an improved management of the heat released inside the column is required for a better control of the temperature and the ammonia slip. Several strategies have been proposed with this goal [4], among which intermediate cooling of the liquid phase or different pumparound configurations have proven to be promising options.

![Figure 2. Weight fraction-based ternary phase diagram for 1 bar and 15°C and apparent composition of the liquid along the CO₂ absorber. V, L, BC, SC and CB refer to vapor, liquid, ammonium bicarbonate, ammonium sesqui-carbonate and ammonium carbonate monohydrate, respectively.](image)

In addition to the new conditions found in the absorber, the higher CO₂ content of the flue gas is a challenge for the modelling tools. As far as rate-based simulations are concerned, different temperature and concentration ranges are conducive to different reaction rates and heat and mass transport along the column, which might be outside the validity range of the available models. As a result, also the Murphree efficiencies, which are frequently applied in combination with equilibrium models to account for kinetic effects while limiting the computational cost [5], call for a revision.

With this work, we provide a comprehensive insight on the needs for the CAP application to the conditions found in cement plants. New operating variables (e.g. pumparound temperature, NH₃ content and CO₂ loading in the CO₂-lean solvent, L/G in the absorber) as well as the absorber
design and the implications on CAP modelling are discussed. The results of the analysis are visualized and rationalized making use of ternary phase diagrams. The overall plant performance in terms of energy consumption and capture efficiency is presented and discussed.

The CAP simulations are carried out in Aspen Plus coupling equilibrium-based simulations together with rate-based simulations of the absorber and are supported by the experimental activity within the Horizon 2020 CEMCAP project. The extended UNIQUAC thermodynamic model [6] is adopted in all simulations.

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