Simulation, modelling and optimization of different chilled ammonia-based process configurations for CO₂ capture applied to cement plants

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Introduction

Cement manufacturing accounts for approximately 6-7% of CO₂ emissions produced by anthropogenic activity worldwide. About 60% of these CO₂ emissions are intrinsic to the production of clinker, the main constituent of cement, as the calcination of limestone to produce CaO, one of the reactants required to produce clinker, leads to the formation of CO₂. As a consequence, CO₂ capture and storage (CCS) is essential to decrease the carbon footprint of this industrial process effectively. Among the different options, CO₂ removal from the flue gas generated in the pre-calciner and the rotary kiln is of particular interest as it makes use of the extensive existing experience in post-combustion capture technologies applied to power plants while leaving the cement process unchanged. Within this framework, the Chilled Ammonia Process (CAP) technology is a promising candidate, since it shows a competitive energetic performance with respect to conventional amines, and because aqueous NH₃ solutions offer significant advantages concerning global availability, environmental footprint, costs and chemical stability. A simplified flow scheme of the standard CAP is shown in Figure 1.

Figure 1. Simplified flow scheme of the standard CAP.
CAP application to cement plants

Although the CAP is on the verge of commercialization for natural gas- and coal-fired power plants with CO₂ concentrations in the flue gas ranging from 3 to 16%vol [1], the application of the CAP to cement plants, where the CO₂ concentrations can be as high as 35%vol, has not been developed yet. Considering constant capture rate and inlet flue gas flowrate, the higher CO₂ concentration in the flue gas requires a larger amount of CO₂ to be captured in the CO₂ absorber, leading to a higher heat release. As a consequence, the operating conditions in the CO₂ absorber have to be modified such that the temperature, and hence, the evaporation of ammonia from the liquid solvent can be controlled. Based on detailed process simulations and pilot plant experimental results, we will show that these requirements can be fulfilled by combining an increase in the liquid-to-vapor flowrate ratio along the absorber (L/G) with a decrease in the ammonia concentration in the CO₂-lean solution (w_{NH₃,lean}).

Process optimization

A set of operating parameters have been identified as key variables for the optimization of the energy penalty: in addition to L/G and w_{NH₃,lean}, the CO₂ loading of the CO₂-lean solution, the split fraction and temperature of the pumparound recycled to the top of the CO₂ absorber, the flue gas temperature entering the CO₂ absorber, the split fraction of the cold CO₂-rich stream sent to the top of the CO₂ desorber and the CO₂ desorber working pressure. Consequently, the combination of operating variables that minimizes the energy needs of the CAP has been found applying a heuristic optimization framework [3]. The Specific Primary Energy Consumption for CO₂ Avoided (SPECCA), as defined for a reference cement plant by Anantharaman et al. [4], has been used as the objective function to be minimized. Additionally, some advanced CAP configurations with respect to the standard CAP shown in Figure 1 have been studied with the aim of minimizing the energy requirements of the process, namely: (i) the CAP with controlled solid formation [5]; (ii) the CAP with an advanced flash stripper [6]; and (iii) the CAP with lean or rich vapor compression [7]. Preliminary results of this work regarding energy demand of the CAP for a flue gas containing 22%vol CO₂ are shown in Figure 2.

![Figure 2](image-url)

**Figure 2.** Contributions of the key energy consumers to the total SPECCA value considering a cement plant-like flue gas composition containing 22%vol CO₂, for different cases: (A) Standard CAP, as shown in Figure 1, with an initial set of operating conditions derived from the CAP as described by Sutter et al. [5] (optimized for a flue gas containing 15%vol CO₂); (B) Standard CAP, as shown in Figure 1, with the optimized set of operating conditions minimizing the value of the SPECCA obtained in this work; and (C) Advanced CAP configuration with the initial set of operating conditions used in case (A).

As shown in Figure 2, the optimization of the operating conditions of the standard CAP has led to a reduction of the SPECCA of about 15%, while the application of an advanced CAP configuration has led to a 20% decrease. Further reductions can be expected for the latter case (Figure 2, case C).
after optimizing the operating conditions for the advanced CAP configurations. In all cases, the main contributor to the SPECCA is the thermal energy required in the reboiler of the CO₂ desorber, whose value has been decreased from 2.36 MJ/kg of CO₂ in case (A) to 2.07 and 1.81 MJ/kg in cases (B) and (C), respectively.

Rate-based model development
On the other hand, the design of the absorption units requires the use of rate-based process simulations. Concerning the absorbers, such a model should include both heat and mass transfer between vapor and liquid, as well as the reaction kinetics of CO₂ in the liquid phase. Rate-based models for the CO₂-NH₃-H₂O system available in the literature have been validated with pilot plant CO₂ absorption tests performed with flue gases containing only up to 12%vol CO₂ [8]. However, the higher partial pressure of CO₂ in the inlet stream in the case of cement plants will affect the CO₂ absorption unit considerably, leading to different temperature and concentration profiles along the column [3], which are outside the validity range of the available models. Consequently, new CO₂ and NH₃ absorption experiments have been performed at pilot plant scale with synthetic flue gases to reproduce the conditions found in cement plants. The experimental results have then been used to develop and validate a new rate-based model that covers the temperature and concentration ranges in the CO₂ absorber and in the NH₃ absorber according to the new application. The new model enables the detailed design of the CAP for cement plant applications.

Summary
With this work, we provide a comprehensive analysis of the new requirements when applying the CAP to CO₂ capture from cement plants. Modifications of the standard CAP flow scheme have been implemented and compared, and the optimum set of operating conditions have been found for different CO₂ concentration levels in the flue gas with the aim of minimizing the energy consumption. Additionally, the design of the absorption columns is determined based on a new rate-based model for the absorption of CO₂ with aqueous NH₃ solutions that has been developed making use of new pilot plant scale experiments mimicking cement plant-like flue gas conditions.

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References

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