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Application of a chilled ammonia-based process for CO_2 capture to cement plants

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Abstract

The chilled ammonia process (CAP) is considered one of the most promising alternatives to amine-based absorption processes for post-combustion carbon capture applied to power plants. This work provides an insight on the CAP adaptations required to meet the conditions found in the flue gas emitted in cement plants, where CO_2 generation is inherent to the manufacturing process. A rate-based model has been validated to simulate the CO_2 absorber of the CAP for cement plant-like flue gas composition in order to obtain the Murphree efficiencies to be used in full CAP simulations in Aspen Plus. A preliminary minimum exergy need of 0.92 MJ/kg$_{CO2}$ has been found for the CAP applied to the cement plant case making use of an optimization algorithm and capturing 85.2% of the emitted CO_2. Higher temperatures (> 45°C) are found in the CO_2 absorber of the CAP when applied to cement plant-like flue gas conditions in comparison to the power plant case (< 40°C), requiring a lower pumparound temperature in order to control the ammonia slip in the CO_2-depleted flue gas exiting the column.

1. Introduction

Cement production accounts for about 5% of the global anthropogenic CO_2 emissions [1]. In contrast to other energy-intensive industrial processes, CO_2 generation is inherent to the cement production: the limestone calcination, i.e. the conversion of $CaCO_3$ to CaO and CO_2, is responsible for about 60% of the CO_2 emissions from

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Nomenclature

e	specific total exergy need (MJ/kg$_{CO2}$)
E_{aux}	exergy losses in the auxiliaries, i.e. pumps and flue gas blowers (MW)
E_{chill}	exergy losses for chilling (MW)
E_{reb}	exergy losses in the reboilers of the CO_2 capture and the FG-WW sections (MW)
f_S	pumparound split fraction (-)
l_{abs}	absorber loading as ratio of CO_2 in the flue gas over the free ammonia in the lean stream (mol$_{CO2}$/mol$_{NH3}$)
l_{lean}	CO_2-loading of the lean stream (mol$_{CO2}$/mol$_{NH3}$)
L/G	liquid to gas mass flowrate ratio (-)
$m_{CO_2}^{abs}$	mass flowrate of CO_2 captured (kg$_{CO2}$/s)
$\dot{Q}_{chill}$	chilling duty (MW)
$\dot{Q}_{reb}$	reboiler duty (MW)
T_{amb}	ambient temperature (= 25 °C)
T_{cool}	temperature of process stream after cooler (°C)
T_{pa}	temperature of the pumparound in the absorber (°C)
T_{reb}	reboiler temperature (°C)
$w_{NH_3}^0$	ammonia concentration in the aqueous binary mixture of the CO_2-lean stream (mass frac.)

cement production. Accordingly, CO_2 capture and storage (CCS) is needed to reduce the carbon footprint of this industrial application. Among the different possible configurations, CO_2 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 CO_2 capture. Besides a competitive energetic performance compared to conventional amines (MEA), the use of aqueous NH_3 as a solvent offers advantages concerning global availability, environmental footprint and cost compared to most amine processes. Additionally, the aqueous NH_3 solvent is chemically stable in the presence of impurities such as SO_x and NO_x, while amines are known to form toxic degradation products and corrosive solutions.

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 CO_2 concentration in the flue gas ranging from 3 to 16%vol [2,3], the application of the CAP to cement plants, where the CO_2 concentrations can be as high as 30%vol, has not been investigated yet. The drastic increase in CO_2 concentration in the flue gas is the most important change that the CAP applied to cement plants has to cope with. The CO_2 absorption unit is largely affected by the higher partial pressure of CO_2 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. In addition to the new conditions found in the absorber, the higher CO_2 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 [4], call for a revision.

In this work, an insight on the needs for the CAP application to the conditions found in cement plants is provided. The overall plant performance in terms of energy consumption and capture efficiency is presented. The resulting operating variables (e.g. pumparound temperature, NH_3 content and CO_2 loading in the CO_2-lean solvent, L/G) and the implications on the conditions found in the CO_2 absorber are analyzed making use of ternary phase diagrams. The CAP simulations are carried out in Aspen Plus, Version 8.6, coupling equilibrium-based simulations of the full process together with rate-based simulations of the CO_2 absorber.

2. CAP plant layout

The overall CAP flow scheme considered for this work is shown in Fig. 1. It consists of four main sections:

(i)   Flue gas cooling. The hot flue gas from the cement plant enters the direct contact cooler. This section serves two purposes: cooling the flue gas to about ambient temperature and removing a significant amount of water contained in the flue gas.

(ii) CO_2 capture. This is the core part of the plant, where CO_2 is removed from the flue gas in an absorber and collected as clean gas in a desorber. Important features of this section are: (i) the CO_2 absorber is cooled by means of a rich solution pumparound, (ii) part of the rich solution is split before entering the regenerative lean-rich solution heat exchanger.

(iii) Flue gas water wash (FG-WW). The CO_2 depleted flue gas exiting the absorber contains significant amounts of ammonia; therefore, this stream is further treated in a flue gas water wash section, which again consists of an absorption and a stripping unit. Although out of the scope of this work, the flue gas exiting the NH_3 absorber should be further treated in an acid wash unit in order to meet the ammonia emission limit value at the stack.

(iv) CO_2 water wash (CO_2-WW). The purity specifications for the CO_2 gas are met by washing the gas out of the desorber with water. Ammonia, water and some CO_2 are separated and recirculated to the desorber.
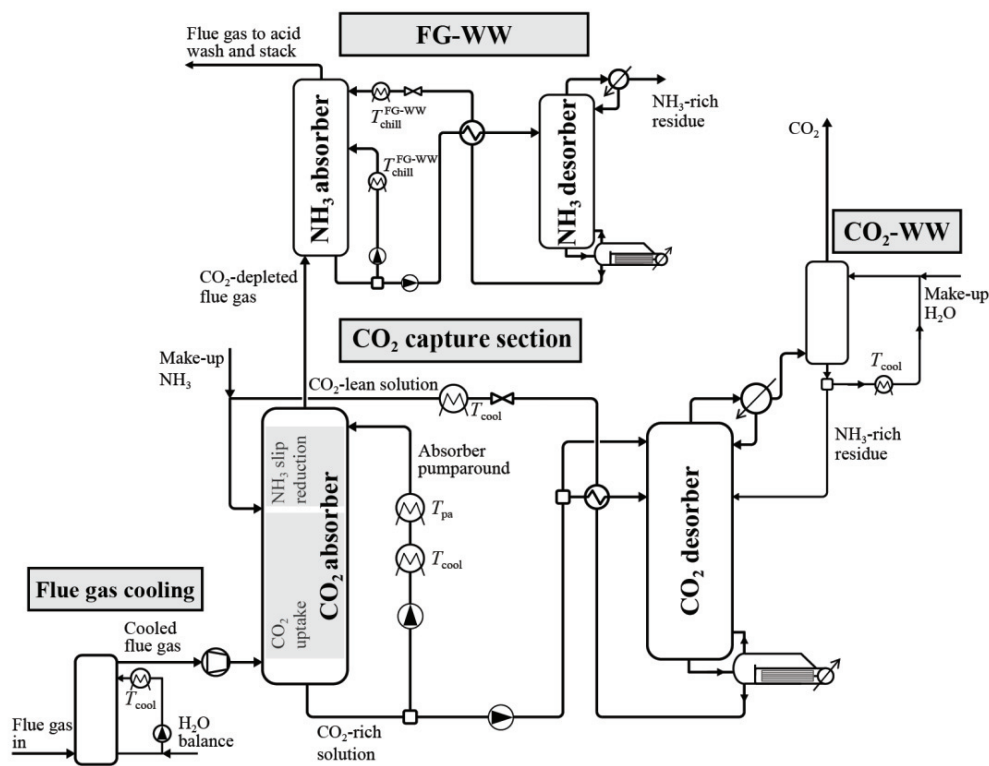

Fig. 1. Flow scheme for the simulated CAP process.

3. Process specifications

The main process specifications and assumptions for the CAP simulations are reported in Table 1. The flue gas conditions considered for this work represent average values of the flue gas produced in a cement plant in Europe, with yearly clinker production of 1 Mt and capacity factor of 0.9, and working with the best available technology (BAT) [5].

Table 1. CAP specifications and assumptions. Other general operating conditions and assumptions not specified here have the same value given by Sutter et al. [6].

Exhaust flue gas specifications	
Total flowrate, t/h	391
Temperature, °C	117
Pressure, bar	1.05
Composition, % vol	
CO_2	18
N_2	63
O_2	10
H_2O	9
CAP process specifications	
CO_2 capture, %	> 85
CO_2 purity before storage, %vol	> 99
Ammonia slip in the flue gas exiting the NH_3 absorber, ppm	< 200
Absorption/Desorption pressure (CO_2 capture section), bar	1.01/10
Utilities	
Cooling water temperature, °C	18
Temperature of chilled streams, °C	
T_{chill}^{FG-WW}	1.5
T_{pa}	5
Heat exchanger $\Delta T_{min,}$ °C or K	3
Auxiliaries	
Pump efficiency, %	80
Isentropic efficiency of compressors, %	85
Driver efficiency	95

4. Process simulation and optimization

As a first effort, the conventional CAP system needs to be adapted to cement plant-like flue gas conditions. This activity was focused on the CO_2 absorber, which is the core piece of equipment in the plant. Firstly, a rate-based model was used to simulate the absorber of the CAP for cement plant-like flue gas composition. As a result, Murphree efficiency values were calculated. Eventually, overall CAP simulations were performed making use of the equilibrium-based model with the updated values of the Murphree efficiencies in order to limit the computational costs related to the full CAP simulation and optimization.

4.1. Rate-based model

A literature research on rate-based models implemented in Aspen Plus for the simulation of CO_2 capture processes with aqueous NH_3 solutions was carried out. Special attention was paid to the selected transport property models, mass transfer correlations and reactions kinetic models. Sensitivity analyses on the Aspen Plus input parameters for the rate-based model such as the liquid film and the column length discretization, and the hydrodynamic model were then performed. Subsequently, the implementation in Aspen Plus and validation of rate-based models was carried out using the data available in the literature for power plant-like flue gas composition, obtained from the Munmorah pilot plant tests [7,8].

The rate-based model selected for this study considers:

(i) The thermodynamic model for the CO_2-NH_3-H_2O system developed originally by Thomsen and Rasmussen [9] and upgraded by Darde et al. [10] (called "Thomsen model" hereinafter), and implemented in Aspen Plus [11]. The Thomsen model has been proven to properly reproduce the experimental VLE results as well as the experimental solubility data accounting for the formation of five different solids within the system. A concise description and extensive application to the CAP of Thomsen model can be found elsewhere [12].

(ii) The flow model "VPlug" available in Aspen Plus with discretization of the column length in segments not longer than 0.1 m.

(iii) A geometrical discretization of the liquid film in 7 segments with increasing length (factor 1.5) from the gas-liquid interface to the liquid bulk.

(iv) Rate-controlled reactions of CO_2 in the liquid phase to form bicarbonate and carbamate ions. Activity-based kinetics for the forward and backward reactions are derived from the kinetic models of Pinsent et al. [13,14] and the Thomsen model.

(v) Mass transfer coefficients and interfacial areas computed with the correlation of Bravo et al. [15].

(vi) Transport property models validated elsewhere for the CO_2-NH_3-H_2O system [8].

The validation of this rate-based model by means of the test results obtained at the Munmorah pilot plant [7] is given by the parity plots shown in Fig. 2 for the CO_2 capture efficiency and the ammonia slip. In general, experimental values are predicted with a deviation smaller than 20%.
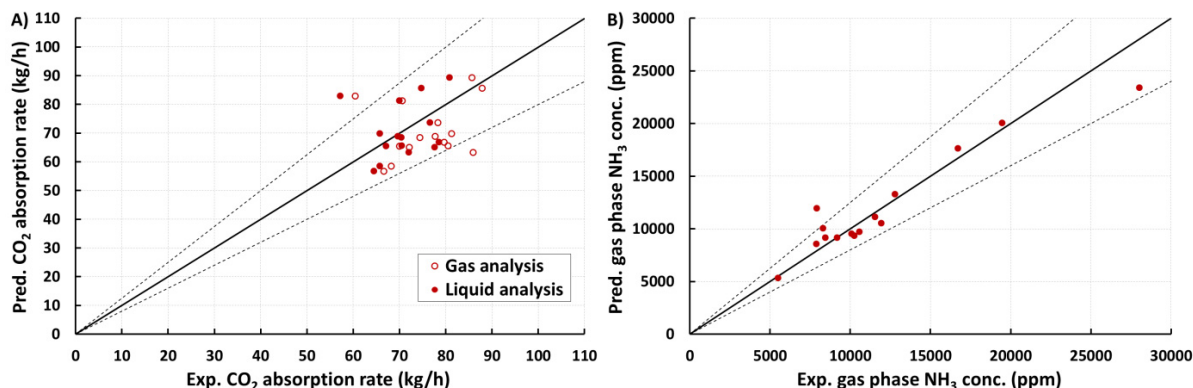

Fig. 2. Predicted vs experimental A) total CO_2 absorption rate, and B) ammonia slip in the gas exiting Absorber 1 of the Munmorah pilot plant. Experimental results are obtained from the Munmorah pilot plant tests [7,8] while the predicted values are obtained by means of the rate-based model implemented in Aspen Plus for this work. The mass transfer coefficients and the interfacial areas are computed by means of the correlation of Onda et al. [16] for the random packing used in the Munmorah pilot plant tests. In A), experimental results from gas and liquid analysis are shown with empty and filled circles, respectively. The dashed lines indicate 20% of deviation with respect to the straight line in bold with slope 1.

Eventually, the Murphree efficiencies obtained from the rate-based simulation of the CO_2 absorber for cement plant-like flue gas conditions were used hereinafter for full CAP simulations. A structured packing of the type Mellapak 350X has been considered for the rate-based simulations of the CO_2 absorber. Average values of the obtained Murphree efficiencies are shown in Table 2.

Table 2. Average Murphree efficiencies obtained from the rate-based simulations of the CO_2 absorber for 5 and 15 stages of the NH_3 removal section and the CO_2 capture section, respectively.

Murphree efficiencies	NH_3 slip reduction section	CO_2 uptake section
CO_2	0.096	0.125
NH_3	0.75	1
H_2O	1	1

4.2. Simulation and optimization methodology

The CAP performance depends on several variables (e.g. solution composition, temperature levels, flowrates), therefore an optimization framework is needed to investigate the different possibilities. The procedure followed here has been firstly presented by Sutter et al. [6] and is briefly described in Fig. 3. First, a base-case simulation that fulfills all specifications and constraints is established. Secondly, the operating conditions of the CO_2 capture section are screened through an extensive, automated sensitivity analysis. Here, five parameters are varied: $w_{NH_3}^0$, l_{lean}, l_{abs}, f_S, and T_{pa}. Finally, the simulations that are successful provide data for the FG-WW section. Here a rigorous optimization based on successive quadratic programming is carried out. In particular, the specific reboiler duty is minimized by changing the pumparound split fraction, the absorber L/G and the absolute reboiler duty.
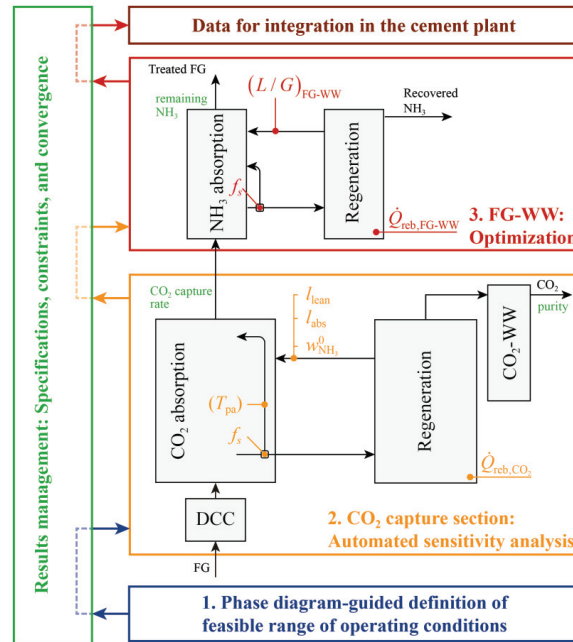

Fig. 3. Scheme of the optimization algorithm. Adapted from Sutter et al. [6].

In order to integrate the results of this three-step optimization with the cement plant in a future stage of the project and obtain the optimal operating conditions of the CAP, the total exergy need is computed for each simulation by means of equation 1.

$$e = \frac{E_{reb} + E_{chill} + E_{aux}}{m_{CO_2}^{abs}} \tag{1}$$

The exergy losses in the reboilers and for chilling are computed by means of equations 2 and 3, respectively, while the exergy requirements in the auxiliaries are obtained in Aspen Plus simulations. The coefficient of performance for a refrigeration unit (COP) has been computed as described by Gazzani et al. [4].

$$E_{reb} = \dot{Q}_{reb}\left(1 - \frac{T_{amb}}{T_{reb} + \Delta T_{min}}\right) \tag{2}$$

$$E_{chill} = \frac{\dot{Q}_{chill}}{COP} \qquad (3)$$

5. Results and discussion

Preliminary results of the aforementioned optimization routine are shown in Fig. 4 for the cement plant case. Each symbol represents one full simulation that has converged and fulfills the specifications. Points are colored according to the exergy expenditure. The two coordinates (i.e. reboiler duty and chilling demand) have by far the strongest effect on the variation of the total exergy need. Also, chilling duty and reboiler duty minimization are opposing objectives. The minimum exergy need is found on the frontier of the ensemble of points closest to the origin. It is also worth noting that the total exergy need is a strong function of the total reboiler duty and only weakly affected by the chilling duty. A minimum exergy need of 0.92 MJ/kg$_{CO_2}$ has been found for the CAP applied to the cement plant case capturing 85.2% of the emitted CO_2.
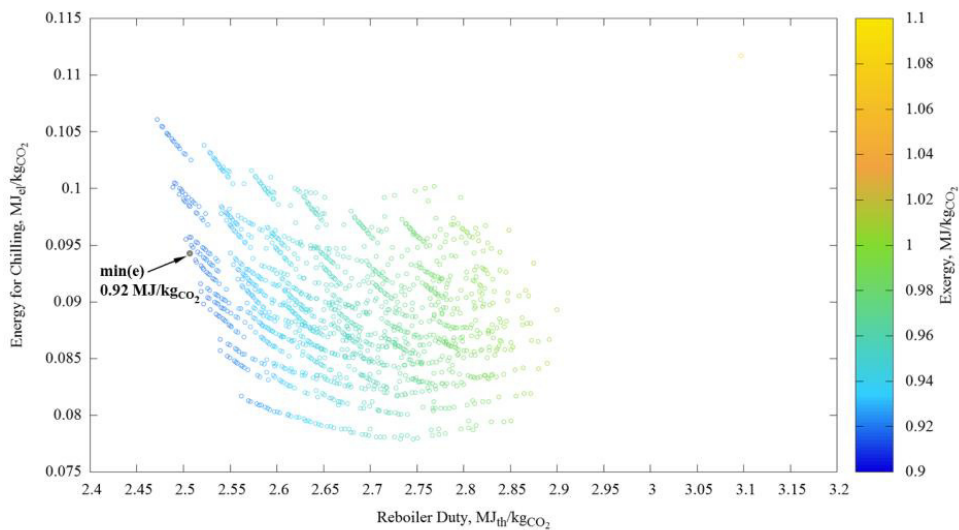

Fig. 4. Resulting exergy value of the preliminary simulations for the cement plant-like case plotted in a chilling duty vs. reboiler duty plan. The reboiler duty is the sum of the thermal energy demand of both reboilers, i.e. the one in the CO_2 capture section and the one in the FG-WW section.

The liquid composition profiles along the CO_2 absorber for a typical cement plant case and for the optimized CAP applied to a power plant case obtained by Sutter et al. [6] are shown in Fig. 5. The higher CO_2 concentration in the flue gas entering the absorber in the cement plant case can in principle be confronted with an increase in the liquid to vapor flowrate ratio (L/G) along the CO_2 absorber, an increase in the ammonia content of the liquid phase and/or a decrease in the CO_2 loading of the CO_2-lean solution with respect to the power plant operating conditions. Comparing the cases shown in Fig. 5, a lower CO_2 loading in the CO_2-lean stream is required for the CAP applied to the cement plant-like flue gas. Additionally, it is worth noting how the larger amount of heat released in the cement case, as a consequence of the greater amount of CO_2 absorbed, affects the temperature profile of the solution, leading to a higher temperature peak (> 45°C). In order to limit the ammonia slip in the CO_2-depleted flue gas exiting the CO_2 absorber, a lower temperature of the pumparound is required in comparison with the CAP applied to the power plant-like flue gas.
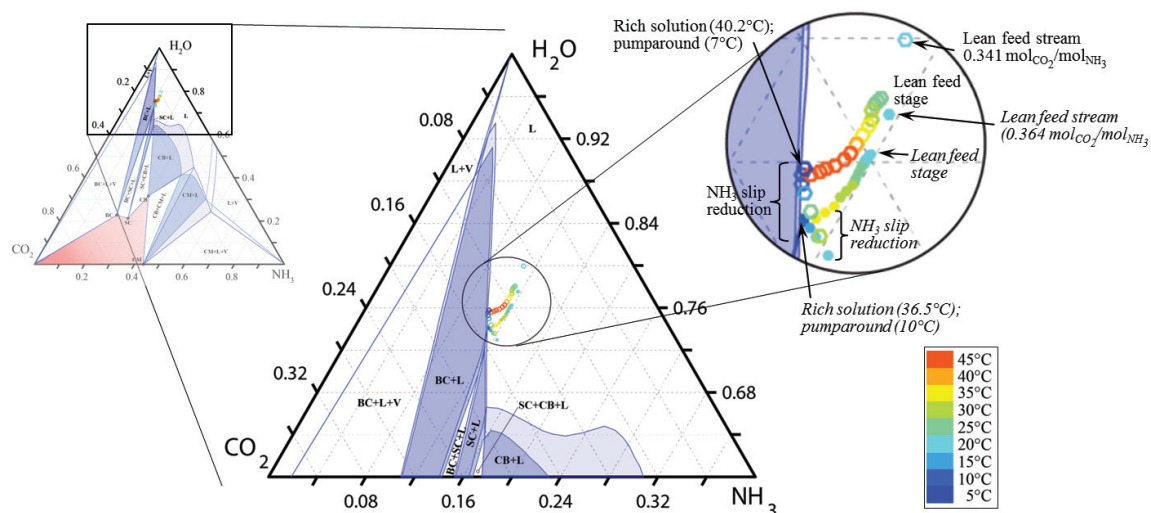
Fig. 5. Stage-wise apparent weight composition profiles on the liquid phase along the CO_2 absorber. The filled and empty circles represent the power plant and cement plant cases, respectively. The temperature has been rounded to 5°C increments. Phase diagram at 1.013 bar and at 5°C and 10°C. V, L, BC, SC, CB and CM refer to vapor, liquid, ammonium bicarbonate (solid), ammonium sesqui-carbonate (solid), ammonium carbonate monohydrate (solid) and ammonium carbamate (solid), respectively.

6. Conclusions

The drastic increase in CO_2 concentration in the flue gas is the most important change that the CAP applied to cement plants has to cope with in comparison with the application to power plant-like flue gases. The larger amount of energy released in the cement case affects the temperature profile of the solution, leading to higher temperature peaks and higher ammonia vaporization from the liquid solvent. Consequently, an improved management of the heat released inside the column is required for a better control of the temperature and the ammonia slip.

On the other hand, the changes in the reaction rates and in the energy balance of the column require different Murphree efficiency values along the absorber with respect to the power plant case. The simulation of the CO_2 absorber by means of a rate-based model validated with experimental results obtained at pilot plant scale has allowed to update the value of the Murphree efficiencies for the cement plant case.

Finally, the optimization routine allows the identification of the conditions of the process that lead to the minimum exergy requirements. Preliminary results have shown that the minimization of the total reboiler duty has a considerably stronger effect on lowering the exergy need than decreasing the chilling duty.

Acknowledgements

References

[1]   Cement Technology Roadmap 2009: Carbon emissions reductions up to 2050. December 2009, International Energy Agency; Paris.
[2]   Bollinger R, Muraskin D, Hammond M, Kozak F, Spitznogle G, Cage M, Sherrick B, Varner M. CCS Project with Alstom's Chilled Ammonia Process at AEP's Mountaineer Plant. Alstom Technical Report, Paper No. 72.

[3] Baburao B, Kniesburger P, Lombardo G. Chilled Ammonia Process Operation and Results from Pilot Plant at Technology Centre Mongstad. Presentation at TCCS-8, Trondheim, Norway, 2015.

[4] Gazzani M, Sutter D, Mazzotti M. Improving the Efficiency of a Chilled Ammonia CO_2 Capture Plant Through Solid Formation: A Thermodynamic Analysis. Energy Procedia 2014; 63:1084-1090.

[5] JRC Reference Reports – Best Available Techniques (BAT) Reference Document for the Production of Cement Lime and Magnesium Oxide. European Commission, 2013.

[6] Sutter D, Gazzani M, Mazzotti M. A low-energy chilled ammonia process exploiting controlled solid formation for post-combustion CO_2 capture. Faraday Discuss 2016. DOI: 10.1039/C6FD00044D

[7] Yu H, Morgan S, Allport A, Cottrell A, Do T, McGregor J, Wardhaugh L, Feron P. Results from trialling aqueous NH_3 based post-combustion capture in a pilot plant at Munmorah power station: Absorption. Chem Eng Res Des 2011; 89:1204-1215.

[8] Qi G, Wang S, Yu H, Wardhaugh L, Feron P, Chen C. Development of a rate-based model for CO_2 absorption using aqueous NH_3 in a packed column. Int J Greenh Gas Control 2013; 17:450-461.

[9] Thomsen K, Rasmussen P. Modeling of vapor–liquid–solid equilibrium in gas–aqueous electrolyte systems. Chem Eng Sci 1999; 54:1787–1802.

[10] Darde V, van Well WJM, Stenby EH, Thomsen K. Modeling of carbon dioxide absorption by aqueous ammonia solutions using the Extended UNIQUAC model. Ind Eng Chem Res 2010; 49:12663-12674.

[11] Darde V, Thomsen K, Well WJMV, Bonalumi D, Valenti G, Macchi E. Comparison of two electrolyte models for the carbon capture with aqueous ammonia. Int J Greenh Gas Control 2012; 8:61-72.

[12] Sutter D, Gazzani M, Mazzotti M. Formation of solids in ammonia-based CO_2 capture processes – Identification of criticalities through thermodynamic analysis of the CO_2-NH_3-H_2O system. Chem Eng Sci 2015; 133:170-180.

[13] Pinsent BRW, Pearson L, Roughton FJW. The kinetics of combination of carbon dioxide with hydroxide ions. Trans Faraday Soc 1956; 52:1512-1520.

[14] Pinsent BRW, Pearson L, Roughton FJW. The kinetics of combination of carbon dioxide with ammonia. Trans Faraday Soc 1956; 52:1594-1598.

[15] Bravo JL, Rocha JA, Fair JR. A comprehensive model for the performance of columns containing structured packings, distillation and absorption. Institution of Chemical Engineers Symposium Series 128; 1992. Institute Chem Eng, 1.

[16] Onda K, Takeuchi H, Okumuto Y. Mass transfer coefficients between gas and liquid phases in packed columns. J Chem Eng Jpn 1968; 1:56-62.