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The 8th Trondheim Conference on CO₂ Capture, Transport and Storage

Dynamic Operation and Simulation of Post-Combustion CO₂ Capture

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Abstract

Thermal power need to operate, on a daily basis, with frequent and fast load changes to balance the large variations of intermittent energy sources, such as wind and solar energy. To make the integration of carbon capture to power plants economically and technically feasible, the carbon capture process has to be able to follow these fast and large load changes without decreasing the overall performance of the carbon capture plant. Therefore, dynamic models for simulation, optimization and control system design are essential.

In this work, we compare the transient behavior of the model against dynamic pilot data for CO₂ absorption and desorption for step-changes in the flue gas flow rate. In addition we investigate the dynamic behavior of a full-scale post-combustion capture plant using monoethanolamine (MEA) and piperazine (PZ). This analysis demonstrates the good agreement between the developed model (dCAPCO₂) and the pilot measurements at both, transient and steady-state conditions. It outlines how the time needed to reach a new steady-state varies with respect to amine type and concentration. The simulation study reveals that it is essential to control the lean solvent flow to avoid sudden changes in the CO₂ removal rate and to avoid increased heat demand of solvent regeneration. In addition, it shows how storage tanks (liquid hold-up of the system) can be designed to accommodate significant upstream changes in the power plant management. This flexibility is especially needed for operation in future mixed green energy market.

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Keywords: Dynamic modeling; flexible operation; post-combustion CO₂ capture; model validation; pilot plant operation.

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1. Introduction

Renewable energy sources may change the energy market and become the next generations of power production however the energy infrastructure is not yet ready to shut-down the fossil-fuel fired power plants. Thermal power plants supply our daily energy needs and they will dominate the market in the coming decades, especially in developing countries. Therefore, the growing focus on reducing CO₂ emissions requires implementation of CO₂ capture units in fossil-fueled power plants.

Several carbon capture alternatives are under development. Solvent based post-combustion capture is one of the most promising technologies. Various experimental and modeling studies have demonstrated its maturity and they have shown that it is ready to be implemented on a large scale [1-8]. However, most of these studies focus on steady-state operation of the thermal power plant with integrated CO₂ capture.

Full-load operation of thermal power plants and capture units is unrealistic. Power plants need to handle fluctuations resulting from various sources, such as peak in energy demand, change in green energy production, raw material heterogeneity, malfunctioning of equipment, etc. Dynamic response studies are essential to gain knowledge about possible bottlenecks during dynamic operation and they are needed to enable flexible and economically efficient operation of a power plant with integrated CO₂ capture. The dynamics of the entire plant must be understood. Consequently, dynamic models for CO₂ absorption and desorption as well as dynamic testing in experimental setups such as pilot plants are essential in order to investigate the operation of such plants, for optimization and for control system studies [6]. Moreover, implementing flexible operation features, such as solvent storage tanks, flue gas bypass or venting systems may improve the energy efficiency of the carbon capture process [9]. Flexible operation will significantly reduce the capture process energy penalty while insuring that both, the CO₂ capture level and energy demand, are met.

The solvent storage tanks system is one of the flexible operation configurations which consist of two tanks: (i) rich storage tank to collect the solvent exiting the absorber before it is regenerated, (ii) lean storage tank of the same size to collect the lean solvent leaving the stripper. The role of the lean and rich solvent tanks is to decouple the operation of the power plant and capture plant [10] to make it more flexible. Moreover, it partially decouples the operation of the absorber and the desorber. During periods of high electricity price, the rich solvent is stored, allowing high electricity output. During periods of off-peak electricity price, the stored rich solvent from the storage tank is fed and regenerated. Unlike a bypass/venting system, the solvent storage systems allows meeting the CO₂ emission regulations.

The aim of this work is two-fold: to compare the developed mechanistic first principle based dynamic mathematical model for CO₂ absorption and desorption to pilot plant dynamic data and to investigate the transient behavior of a carbon capture plant for large load changes. In addition, we investigate the importance of the solvent storage tank configuration for flexible operation of the post-combustion capture plant. The simulations are carried out using the dCAPCO₂ in-house dynamic model [11]. This model applies the General Method (GM) enhancement factor [12] to calculate the CO₂ mass transfer rate and it uses the extended UNIQUAC thermodynamic model [13,14] for thermal properties and equilibrium prediction.

2. Data acquisition for dynamic operation of a CO₂ pilot absorber

Performing dynamic pilot CO₂ absorber and desorber experiments to validate dynamic models is a complex task. A step-change in process parameters like gas or solvent flow rate, reboiler heat input, etc. results in fluctuating process parameters. These conditions cannot be matched by a model since they are caused by instantaneous measured and unmeasured disturbances. Therefore, online monitoring and adequate control of pilot plants is essential to produce suitable dynamic data for model validation. A good approach, to avoid highly fluctuating systems, is to introduce incremental step changes to the process parameters instead of sudden changes in the inputs [15]. Reducing the step size minimizes the process disturbances and reduces the noise and the fluctuations in the data.

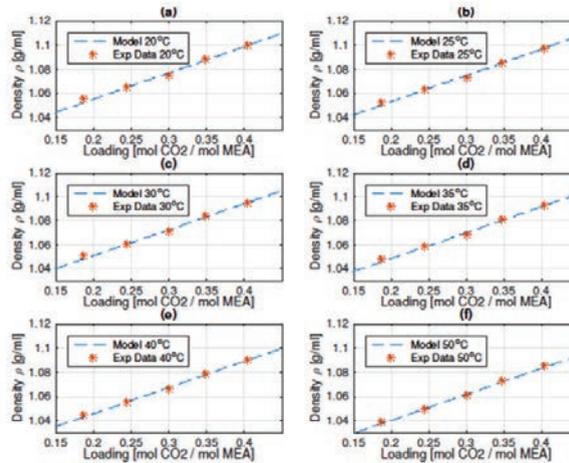


Fig. 1. Density correlation of 30 wt% MEA at different loadings for temperatures ranging from 20 to 50 °C.

Due to fast changes in the outlets when changing the inlets, online monitoring is needed. While the inline measurement of gas and liquid phase temperature and flow are relatively simple, other important parameters, such as composition of the gas and of the liquid phase are complicated to measure. NDIR probes are generally used for determining the CO₂ content of a gas mixture. However, they cannot handle liquid and they must be placed in a bypass, outside the column. Moreover, some probes are not suitable to measure in wet gases and they require a gas conditioner. Sønderby et al. [5] have shown that CO₂ probes give the highest fluctuations after changing a process parameter and they are the last to stabilize. Therefore these probes are not suitable for monitoring the dynamic behavior of a pilot plant.

The solvent CO₂ loading cannot be measured inline. Offline titration is a possible solution for determining the liquid phase CO₂ concentration. However, the workload of this method is unreasonable high for dynamic operations and the experimental error is in the order of $\pm 4\%$ [5]. A promising solution is correlating the CO₂ loading to properties like density, conductivity, pH, etc. Especially density correlates strongly with CO₂ concentration [16] and measurements can be performed easily. It is important to note that these properties are highly temperature dependent. Optical measurements can also be used to estimate the CO₂ loading in real time [16]. For example, Fourier transform infrared spectrometry (FTIR) provides very high accuracy, but the cost of this equipment is more than 20-fold of a density-meter [16].

Density measurements give an acceptable balance between accuracy and cost. However, correlations which account for the concentration of CO₂ and amine as well as the temperature of the sample must be developed and validated. Therefore, experiments for measuring the density of a 30 wt% MEA solution at different CO₂ loadings, from 0.2 to 0.4, for temperatures ranges from 20 to 50 °C were performed. These experiments were compared to experimental data and density correlations from Weiland [17] and Amundsen [18]. Fig. 1 shows the measured values against the density correlation by Weiland et al. [17]. This figure demonstrates the good agreement between Weiland model and the measured values. An analysis, not shown in this work, demonstrated that the Amundsen correlation deviates from the data and from the Weiland's model, especially for lower CO₂ loadings.

It can be concluded that the Weiland et al. [17] correlation can be used with certainty for correlating density of loaded MEA solution to CO₂ loading.

3. The used dynamic CO₂ capture model

This section briefly presents the dCAPCO₂ mechanistic first principle based dynamic model for CO₂ absorption and desorption using monoethanolamine (MEA) and piperazine (PZ). The proposed model describes the space and time variation of the state variables, i.e. temperature and composition of the gas phase and liquid phase. The two film model gives the mass transfer flux between the gas and liquid phase. An enhancement factor accounts for the reaction between CO₂ and MEA respectively PZ.

In the development of the model, we assume:

- Mass transfer between the phases is bi-directional.
- The flow fields of the column are turbulent.
- No fluid accumulation in the gas and liquid films.
- MEA is non-volatile.
- Reaction takes place only in the liquid film.
- Heat loss to the surroundings is negligible.

The models developed for CO₂ absorption and desorption are similar with the exception that the desorber requires a reboiler unit. With the above assumptions, the mass balances for the gas phase and the liquid phase are:

$$\frac{\partial y_i}{\partial t} = -\frac{1}{C_g} \frac{\partial N_{i,g}}{\partial z} - \frac{a}{\varepsilon(1-h_L)} J_{i,gl} \quad (1)$$

$$\frac{\partial X_i}{\partial t} = \frac{1}{C_l} \frac{\partial N_{i,l}}{\partial z} + \frac{a}{\varepsilon h_L} J_{i,gl} \quad (2)$$

where y_i is the mole fraction of component i in the gas phase; X_i is the apparent mole fraction of component i in the liquid phase. $N_{i,g}$ and $N_{i,l}$ denotes the gas and liquid flux of component i ; $J_{i,gl}$ is the mass transfer flux of component i through the gas-liquid interface. Component i can be CO₂, H₂O and amine, e.g. MEA, PZ, etc.

In addition, we assume that the volatile components condense at the gas-liquid interface releasing the heat to the liquid. Therefore, the conservation of energy for the gas phase and the liquid phase are:

$$\frac{\partial U_g}{\partial t} = -\frac{\partial Q_g}{\partial z} - \frac{a}{\varepsilon(1-h_L)} q_{cond} \quad (3)$$

$$\frac{\partial U_l}{\partial t} = \frac{\partial Q_l}{\partial z} + \frac{a}{\varepsilon h_L} (q_{conv} + q_{cond} + q_{gen}) \quad (4)$$

U_g and U_l are the internal energy of the gas and liquid phase; Q_g and Q_l are the heat flux; q_{conv} refers to the heat transported through the gas-liquid interface; q_{cond} is the heat flux by conduction; and q_{gen} gives the generated heat by reaction or condensation/evaporation. The dynamic model uses the [19,20] mass transfer and hydraulic models and an in-house physical-chemical property package secures the accuracy of the calculations [21]. The extended UNIQUAC thermodynamic model gives the vapor-liquid equilibrium and thermal properties [14]. More details can be found in [11,22].

4. Results and discussion

In this study, first we compare the transient response of the model to dynamic pilot plant data for step-changes in the flue gas flow rate. We show calculated and measured absorber CO₂ outlet concentrations, CO₂ removal rates and temperature profiles for the absorber and for the desorber. Secondly, we simulate a 200 t/h CO₂ capacity post-

combustion capture plant using MEA and PZ. We investigate the open-loop behavior of this capture plant for large load changes of the power plant and we evaluate the importance of the storage tank capacity on the load following capabilities of a capture plant.

4.1. Validation of the dynamic CO₂ capture model

In this section, we simulate a 1 t/h CO₂ capacity pilot plant using 30 wt% MEA. We compare the dynamics of the absorber and of the desorber to model predictions for two scenarios: (test 1) flue gas flow ramp down from 5000 Nm³/h to 3500 Nm³/h and (test 2) flue gas flow rate ramp up from 4100 Nm³/h to 5000 Nm³/h.

These scenarios represent a change in the power plant load, considering only the change in the flue gas flow rate. It is important to note that the pilot plant was operated in open-loop control. At the beginning of each test case, approximately 90% CO₂ removal rate was reached, and then the flue gas flow rate was changed, keeping all other variables constant.

The dynamic campaign was carried out using an approximately 13.7 dry mol% CO₂ flue gas and it was saturated with water before entering the absorber. The gas flow was contacted with a 30 wt% MEA solution with a loading of 0.21 mol CO₂/mol MEA. Both of the packed columns, absorber and stripper, have a diameter of 1.1 m. The height of the absorber is 17 m and the height of the stripper is 10 m. The heat to the reboiler was supplied by utility steam from the power plant at 2.5 barg. More details regarding the pilot campaign can be found in [23].

Fig. 2A and Fig. 2B show the variation over time of the main inlet parameters for the absorber and the desorber for test 1 and test 2. Fig. 2A presents the flow rate and the CO₂ concentration of the flue gas entering the absorber. Fig. 2B shows the flow rate of the rich solvent and the CO₂ loading of the rich feed entering the stripper. These figures outline how the inlet parameters had some variations during the tests since the flue gas originates from a real power plant. For example, the absorber inlet CO₂ concentration fluctuated in the range of 12.92 to 14.35 mol% (test 1) respectively 13.12 to 14.35 mol% (test 2).

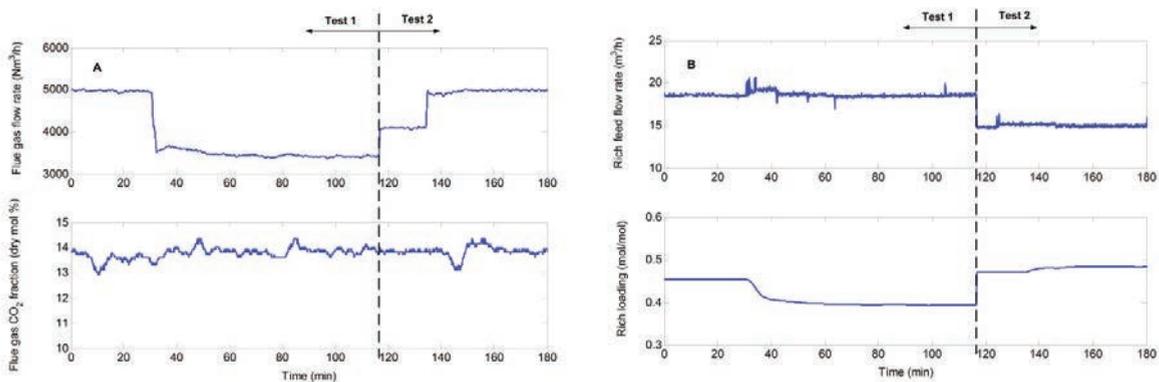
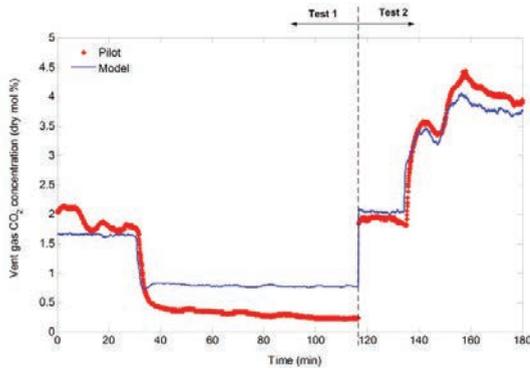
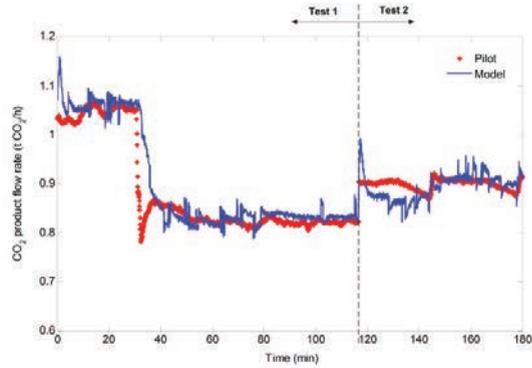


Fig. 2. (A) Absorber inlet flue gas flow rate and CO₂ mol fraction; (B) Desorber feed flow rate and rich CO₂ loading.

Fig. 3 compares the change in the vent gas CO₂ concentration predicted by the model to pilot plant data. It can be seen that the pilot and the model almost overlap during transition from one steady-state to another. This is a remarkable result, especially considering the fluctuations in the inlet parameters, see fig. 2A. The deviation between model and experiment is the most visible at low CO₂ concentrations, below 0.5 mol % when steady-state is approached. It may be due to greater measurement errors at low concentrations. It may also be due to higher uncertainty of the physical and thermodynamic model at low CO₂ concentrations. For increased flue gas flow rate (test 2) when the CO₂ capture rate decreases below 90%, the model and the pilot results almost overlap. The model predicts very accurately the CO₂ capture rate for flue gas ramp-up conditions.

Fig. 3. Vent gas CO₂ mol fraction (dry basis).Fig. 4. CO₂ product flow leaving the stripper.

The CO₂ flow rate exiting the top of the stripper is presented in fig. 4. This figure demonstrates that the model follows quite well the changes in the CO₂ flow rate. However, the pilot plant has a smoother behavior compared to model predictions. This is most likely due to the fact that the sump of the absorber is not modelled in this work. Therefore, the rich feed from the absorber directly enters the stripper leading to the absence of mixing effects.

These results demonstrate how the model is able to capture the trend of CO₂ mass transfer rate in the absorber and desorber. The standard deviation in the vent CO₂ concentration is 1.46 % and it is 0.08 t/h for the CO₂ product flow rate. An off-set can be seen in fig. 3 and fig. 4 for the initial (t = 0 min) simulation time. It is most likely due to biased steady-state starting point. In this analysis, we assume that the pilot plant was at complete steady-state before the step-change, which is not necessarily true. It is hard to ensure steady-state in real pilot plant, especially when the flue gas results from a real power plant.

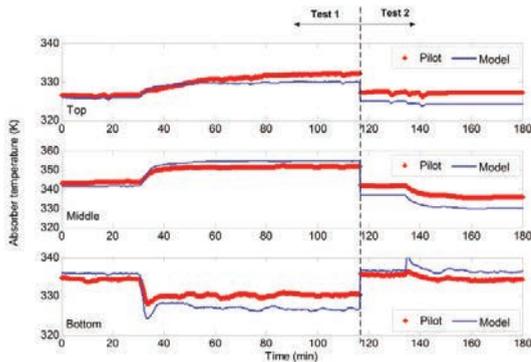


Fig. 5. Liquid temperature at the top, middle and bottom of the absorber.

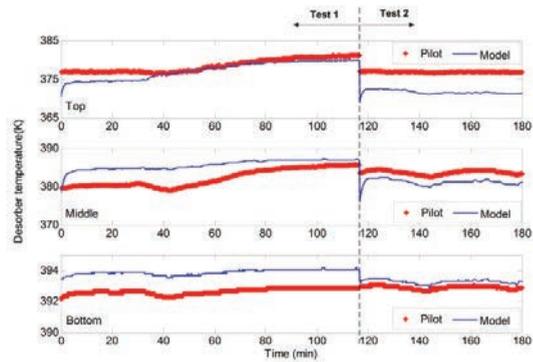


Fig. 6. Liquid temperature at the top, middle and bottom of the desorber.

The accuracy of the heat balance for the absorber and the desorber is reflected in fig. 5 and fig. 6. They present the calculated temperature of the absorber respectively desorber at the top, middle and bottom of the column. The simulation results are compared to pilot measurements.

This analysis reveals the good agreement between model and pilot. The model captures well the dynamics of the plant. The deviation between model and experiment for the absorber generally is less than 4 K. The greatest deviation can be seen for the middle temperature value, up to 6.1 K. As expected, the difference between calculated and measured temperature in the stripper is a bit higher [24]. The deviations are around 3 – 5 K for the top and

middle temperatures. However, the temperature of the liquid entering the reboiler is determined very accurately with a deviation of 0.2 to 1.4 K.

Fosbøl et al. [24] have investigated the expected predictability and variation of some calculated simulation properties. They have concluded that a 5 – 10% deviation should be expected when comparing model to experimental data. Some properties, such as outlet temperature (top respectively bottom), solvent temperature to reboiler are more trustworthy than other properties such as stripper top CO₂ flow, reboiler temperature, in the mid sections of a column, etc.

Therefore, it can be concluded that the model captures very accurately the transient behavior of the pilot plant and also predicts well the steady state values. The predictions fall in the expected range of accuracy.

4.2. Simulation of a full-scale CO₂ post-combustion capture plant

4.2.1. Process boundaries

In this paper, we investigate the flexibility of a traditional post-combustion capture process configuration with the option of storing a fraction of the lean solvent in a buffer tank during start-up, periods of peak electricity prices and shut down operations. The base case load operating conditions correspond to a 200 t/h CO₂ capacity post-combustion capture plant using MEA and PZ solutions. The loading of the lean solvent is 0.21 mol CO₂/mol alkalinity. The flue gas is specific for a coal-fired power plant, i.e. a flue gas containing 14.1 mol% CO₂, saturated with water. The carbon capture plant is designed for 90% CO₂ removal rate and 70 % flooding at full load operation of the thermal power plant. Moreover, the carbon capture unit is equipped with heat exchangers to secure the cooling of the lean solvent and to provide constant preheating of the rich solution entering the stripper.

4.2.2. Sensitivity analysis of CO₂ post-combustion capture

We investigate the open-loop behavior of the process when the power plant is ramped down to 50% and it is ramped up to 30% above the base load. We assume that a change in the power plant load changes the flue gas flow rate but not the CO₂ composition of the flue gas. In this simulation scenario, the liquid flow rate is kept constant, while the reboiler duty is adjusted to reach an equivalent lean loading of 0.21. Note that the steam input to the reboiler is relatively constant, only small adjustments, (up to 10%) are needed. The flue gas flow rate varies according to the specifications in fig. 7A.

Fig. 7B and fig. 7C show the simulation results for CO₂ capture using 30 and 40 wt% MEA and PZ solution.

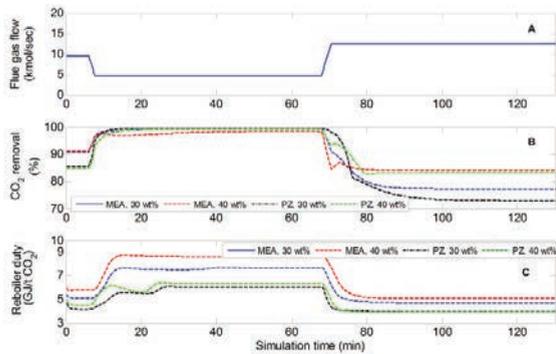


Fig. 7. Dynamics of the post-combustion capture plant during load changes for the MEA and PZ case.

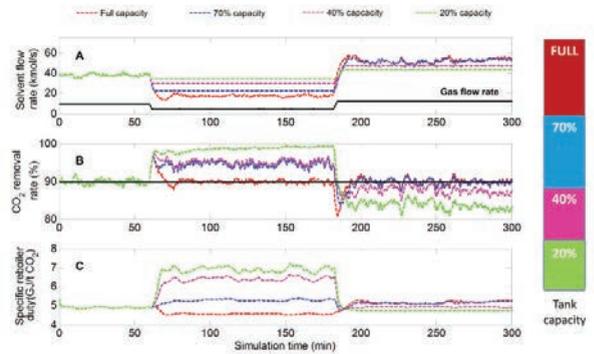


Fig. 8. (A) Flue gas and lean solvent flow rate; (B) CO₂ removal rate and (C) Specific reboiler duty for different storage tank capacities.

The results reveal that a decrease of the flue gas flow rate results in a significant increase of the CO₂ removal rate and vice versa. This was expected since a smaller gas flow is contacted with the same amount of solvent.

Furthermore, fig. 7B substantiates that the process reaches a new steady-state in less than 25 min when the flue gas flow rate decreases.

For increased flue gas flow, the system stabilizes more slowly, more than 30 min. The time needed to reach a new steady-state varies with solvent type (MEA, PZ) and concentration. MEA reaches a new steady state faster than piperazine for both concentrations, 30wt% respectively 40 wt%, when the flue gas flow is ramped up. However, for flue gas ramp down, PZ reaches steady-state conditions before MEA. This behavior may be related to the stronger influence of the flue gas flow on the temperature for the PZ system compared to MEA.

Fig. 7C outlines that the specific reboiler duty (SRD) increases sharply by 40% to 50% when the flue gas flow rate is reduced. This behavior is related to the rich loading of the stream leaving the absorber. At reduced gas flow rate, less CO₂ is captured and the CO₂ loading of the rich stream is reduced. Therefore, smaller amount of CO₂ will be removed in the stripper which gives a higher SRD.

The ramp-up of flue gas flow in Fig. 7, 30% above base load, increases the SRD only by 5 to 15 %. Even though the CO₂ removal percentage reduces, the CO₂ absorption rate increases compared to the base case and it leads to increased rich loading. The model behaves as expected, higher rich loading gives a lower SRD and vice versa, see [25]. Fig. 7C shows how the increase in the SRD (flue gas ramp down scenario) is up to 10% higher for MEA and the decrease of the SRD (flue gas ramp up scenario) is the greatest for the 40 wt% MEA and PZ solutions. Therefore, 30 wt% MEA corresponds to the worst case scenario from an economic point of view due to high heat demand of solvent regeneration.

4.2.3. Load following operation for limited storage tank capacity

In this section, we highlight the importance of the solvent storage configuration for flexible operation. Similar to the above described scenarios, a 50% gas flow decrease respectively 30% increase, compared to the base load, is simulated. The focus is on exemplifying the effect of the tank hold-up (capacity) on CO₂ removal efficiency and specific reboiler duty. We apply a random noise (disturbance) to the CO₂ concentration (± 0.3 mol%) and to the flow rate (± 0.3 kmol/s) of the flue gas in order to mimic a flue gas flow coming from a real power plant. In this analysis, we implement a decentralized control structure to keep the CO₂ removal rate at 90% and the lean loading out of the reboiler at 0.21. The removal rate is controlled by changing the solvent flow to the absorber and the lean loading is regulated by manipulating the steam flow to the reboiler. More details regarding the design and performance of the implemented controller can be found in [22].

In this study, we simulate four scenarios. The first scenario, full capacity, corresponds to a tank designed to accommodate changes in the liquid flow rate, necessary to maintain the CO₂ removal at 90%, while the flue gas flow changes between 50% and 130% of its base load value. Three scenarios are discussed for under-designed buffer tanks: 70%, 40% and 20 % of the full capacity scenario. Fig. 8A shows the variation of the flue gas and solvent flow rate for all of the cases.

In practice, an under-designed storage tank may result in: (a) excess solvent volume for CO₂ capture for flue gas ramp down and (b) limited solvent volume available for CO₂ capture for flue gas ramp up. In case of excess of solvent (case a), the removal rate surpass the 90% CO₂ removal set-point while for limited solvent volume (case b), the 90% CO₂ removal set-point cannot be met. This is exemplified in fig. 8B.

Fig. 8 underlines that in order to keep the 90% removal rate, the solvent flow rate must decrease to 17 kmol/s when the flue gas flow reduces and it has to increase to approximately 52 kmol/s for flue gas ramp up scenario. However, for limited storage tank capacity, the hold-up of the system is less than required for operating the CO₂ capture plant at the desired set points. For example, the 20% capacity case has a minimum solvent flow of 34.3 kmol/s and a maximum solvent flow of 43.7 kmol/s. One might see that this is considerably smaller range than for sufficient hold-up (full capacity).

Fig. 8C shows the effect of various tank capacity cases on the heat demand of solvent regeneration. It demonstrates that the specific heat duty slightly reduces when 90% CO₂ capture is met for decreased flue gas flow. However, for under-designed storage tanks, the specific reboiler duty increases noticeably, see figure 8C from 70 to 180 minutes. This is especially true when the liquid hold-up is less than 70% of the design value (70 % capacity). Furthermore, the analysis reveals that the liquid hold-up (capacity of the storage tanks) has little effect on the heat

demand when the capture plant is operated 30% above the base load, seen on operation minutes 200-300 in the figure. However, the SRD at 20% capacity is slightly lower compared to full capacity which is due to the lower solvent recirculation flow rate. It is important to note that generally the 90% CO₂ removal percentage cannot be met if the storage tank capacity is less than 50% of the design value.

These findings are in accordance with the open-loop analysis of the post-combustion capture process, as shown in fig. 7. It can be concluded that it is essential to control the solvent flow to avoid sudden increase of the specific reboiler duty. Therefore, storage tanks (liquid hold-up of the system) must be designed to accommodate changes in the flue gas flow.

5. Conclusions

In this paper, we validate the dCAPCO₂ mechanistic dynamic mathematical model for CO₂ absorption and desorption. We demonstrate the accuracy of the model against real dynamic data obtained at a 17 meter absorber and 10 meter desorber with a diameter of 1.1 m pilot plant. In addition, we investigate the open-loop response of the process using 30 respectively 40 wt% MEA and PZ and we evaluate the effect of the liquid hold-up (solvent storage tank capacity) on the CO₂ removal rate and specific reboiler duty. Results for large load changes of the power plant are shown. Furthermore, we compare the Weiland et al. [17] density correlation against experimental data at various temperatures and CO₂ loadings. The analysis shows that the model proposed by Weiland [17] predicts well the density of loaded MEA solution at different temperatures. This model can be used to determine the solvent CO₂ loading from density measurement.

We compare the predicted and measured vent gas CO₂ concentration, the CO₂ product flow rate and the temperature (top, middle and bottom) of the absorber and of the desorber. The analysis reveals that the model describes fairly well the transient behavior of the pilot plant. It outlines how the model follows well the changes in the vent gas CO₂ concentration. However, it under-predicts the CO₂ concentration of the clean gas for low L/G ratio when the CO₂ concentration is lower than 0.5 mol%. This discrepancy between the model and pilot may be due to measurement errors which become more significant at low concentrations.

The variations in the CO₂ product flow are also very well captured by the model. However, the pilot shows a smoother behavior compared to the predictions. One possible explanation of the observed fluctuations in the flow rate may be that the sump of the absorber is not modelled. Therefore, any variation in the absorber outlet directly propagates to the stripper. The predicted temperature of the absorber and desorber agrees well with the measured values. The deviations are in the range of 1 to 6 K. Therefore they fall in the expected range of accuracy.

This study also shows the simulation of a 200 t CO₂ /h capacity post-combustion capture plant with and without storage tank. It presents two operation scenarios: (a) flue gas ramp down to 50% and (b) ramp up to 30% above the base load. The open-loop simulation of the CO₂ capture plant using 30 and 40 wt% MEA and PZ demonstrates how the time needed to reach a new steady state differs as function of solvent type and concentration. Note, the solvent flow rate is kept constant during this analysis. Furthermore, it outlines that the specific heat duty increases significantly with respect to solvent flow rate when the capture percentage exceeds 90%. The change in the removal rate is less for the flow rate down scenario when the capture rate falls way below 90%.

An additional closed-loop simulation of the same 200 t CO₂ /h capacity post-combustion capture plant was carried out. During this analysis the CO₂ removal rate is kept at 90% by manipulating the lean solvent flow rate. The lean loading out of the reboiler was adjusted to 0.21 by varying the steam flow to the reboiler. The simulation shows how the implemented control structure is able to keep the plant at the desired set points for large load changes.

An additional evaluation exemplifies the effect of under-designed storage tanks. In practice, an under-designed storage tank corresponds to insufficient liquid hold up of the capture plant. Therefore, the solvent flow rate cannot be decreased enough and the removal rate exceeds 90% for decreased flue gas flows. In case of increased gas flow, the available solvent volume is insufficient and it leads to lower CO₂ capture. It is important to note that any change in the capture rate leads to higher heat demand of CO₂ stripping.

This work demonstrates that the implemented model and its numerical implementation enables transient simulation of a post-combustion capture plant and it can be used for dynamic optimization and control strategies

development. It reveals that the storage tank configuration is a viable option for flexible operation of the power plant with integrated carbon capture plant, without additional increase of the operational cost. Moreover, this option enables regenerating of the rich solvent at off-peak electricity prices, therefore it can significantly reduce the overall energy penalty of post-combustion CO₂ capture.

References

- [1] Goto K, Yogo K, Higashii T. A review of efficiency penalty in a coal-fired power plant with post-combustion CO₂ capture. *Appl Energy* 2013;111:710-20.
- [2] Hossein Sahraei M, Ricardez-Sandoval LA. Controllability and optimal scheduling of a CO₂ capture plant using model predictive control. *International Journal of Greenhouse Gas Control* 2014;30:58-71.
- [3] Linnenberg S, Darde V, Oexmann J, Kather A, van Well WJM, Thomsen K. Evaluating the impact of an ammonia-based post-combustion CO₂ capture process on a steam power plant with different cooling water temperatures. *International Journal of Greenhouse Gas Control* 2012;10:1-14.
- [4] Oexmann J, Hensel C, Kather A. Post-combustion CO₂-capture from coal-fired power plants: Preliminary evaluation of an integrated chemical absorption process with piperazine-promoted potassium carbonate. *International Journal of Greenhouse Gas Control* 2008;539-52.
- [5] Sonderby TL, Carlsen KB, Fosbol PL, Kiorboe LG, von Solms N. A new pilot absorber for CO₂ capture from flue gases: Measuring and modelling capture with MEA solution. *International Journal of Greenhouse Gas Control* 2013;12:181-92.
- [6] Bui M, Gunawan I, Verheyen V, Artanto Y, Meuleman E, Feron P. Dynamic Modeling and Validation of Post-combustion CO₂ Capture Plants in Australian Coal-fired Power Stations. *Energy Procedia* 2013;37:2694-702.
- [7] Tobiesen FA, Svendsen HF, Juliussen O. Experimental validation of a rigorous absorber model for CO₂ postcombustion capture. *AIChE J* 2007;53:846-65.
- [8] Tobiesen FA, Juliussen O, Svendsen HF. Experimental validation of a rigorous desorber model for post-combustion capture. *Chemical Engineering Science* 2008;63:2641-56.
- [9] Chalmers H, Lucquiaud M, Gibbins J, Leach M. Flexible Operation of Coal Fired Power Plants with Postcombustion Capture of Carbon Dioxide. *Journal of Environmental Engineering-Asce* 2009;135:449-58.
- [10] Bui M, Gunawan I, Verheyen V, Feron P, Meuleman E, Adeloju S. Dynamic modelling and optimisation of flexible operation in post-combustion CO₂ capture plants-A review. *Comput Chem Eng* 2014;61:245-65.
- [11] Gaspar J, Jørgensen JB, Fosbol PL. A Dynamic Mathematical Model for Packed Columns in Carbon Capture Plants. *Proceedings of ECC conference 2015*, 15-17 of July.
- [12] Gaspar J, Fosbol PL. A general enhancement factor model for absorption and desorption systems: A CO₂ capture case-study. *AIChE Journal* (under review).
- [13] Thomsen K, Rasmussen P, Gani R. Correlation and prediction of thermal properties and phase behaviour for a class of aqueous electrolyte systems. *Chemical Engineering Science* 1996;51:3675-83.
- [14] Thomsen K, Rasmussen P. Modeling of vapor-liquid-solid equilibrium in gas-aqueous electrolyte systems. *Chemical Engineering Science* 1999;54:1787-802.
- [15] Bui M, Gunawan I, Verheyen TV, Meuleman E, Feron P. Dynamic Operation of Post-combustion CO₂ Capture in Australian Coal-fired Power Plants. *Energy Procedia* 2014;63:1368-75.
- [16] van der Ham LV, van Eekveld AC, Goetheer ELV. Online Monitoring of Dissolved CO₂ and MEA Concentrations: Effect of Solvent Degradation on Predictive Accuracy. *Energy Procedia* 2014;63:1223-8.
- [17] Weiland RH, Dingman JC, Cronin DB, Browning GJ. Density and viscosity of some partially carbonated aqueous alkanolamine solutions and their blends. *J Chem Eng Data* 1998;43:378-82.
- [18] Amundsen TG, Oi LE, Eimer DA. Density and Viscosity of Monoethanolamine plus Water plus Carbon Dioxide from (25 to 80) degrees C. *J Chem Eng Data* 2009;54:3096-100.
- [19] Rocha JA, Bravo JL, Fair JR. Distillation-Columns Containing Structured Packings - a Comprehensive Model for their Performance .1. Hydraulic Models. *Ind Eng Chem Res* 1993;32:641-51.
- [20] Rocha JA, Bravo JL, Fair JR. Distillation columns containing structured packings: A comprehensive model for their performance .2. Mass-transfer model. *Ind Eng Chem Res* 1996;35:1660-7.
- [21] Gabrielsen J. CO₂ Capture from Coal Fired Power Plants. 2007.
- [22] Gaspar J, Jørgensen JB, Fosbol PL. Control of a post-combustion CO₂ capture plant during process start-up and load variations. *Proceedings of ADCHEM conference 2015*, 8-11 of September.
- [23] Faber R, Köpcke M, Biede O, Knudsen JN, Andersen J. Open-loop step responses for the MEA post-combustion capture process: Experimental results from the Esbjerg pilot plant. *Energy Procedia* 2011;4:1427-34.
- [24] Fosbøl PL, Gaspar J, Ehlers S, Kather A, Briot P, Nienoord M et al. Benchmarking and comparing first and second generation post combustion CO₂ capture technologies. *Energy Procedia* 2014.
- [25] Ding J, Lin Y, Rochelle GT. Optimization of Stripping Piperazine with Variable Rich Loading. *Energy Procedia* 2014;63:1842-53.