Dynamic operation of liquid absorbent-based post-combustion CO_2 capture plants

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24.1 Introduction

Previous techno-economic studies of post-combustion CO_2 capture (PCC) focus on full-time operation and capture of 85–90% of CO_2 from flue gas (Pauley, 1983; Rao and Rubin, 2002; Abu-Zahra et al., 2007a,b; Artanto et al., 2009; Dave et al., 2011a,b; Gibbins et al., 2011; Dillon et al., 2012). Under full-load CO_2 capture conditions, a PCC plant imposes a considerable energy penalty on a power station, decreasing electricity output by 30% (Eslick and Miller, 2011; Zaman and Lee, 2015). For power plants that must maintain a baseline electricity output, the PCC energy penalty will increase fuel requirements (House et al., 2009). During periods of high electricity demand, PCC operation can reduce the technical and economic performance of the power station.

Dynamic (or flexible) operation has been proposed as a strategy to reduce the impact of integrating PCC into power plants. The concept of flexible capture accounts for dynamic variations in the demand and price of electricity. For example, in periods of low energy demand, electricity prices will be lower and capture rates may be ramped up accordingly. During high-demand periods, electricity prices will be higher, and thus capture may be turned down or switched off completely (Wiley et al., 2010). Flexible PCC operation provides a compromise between generating electricity for profit and abating CO_2 emissions, enabling the PCC plant to respond to load changes without sacrificing power plant performance. It can also coordinate the balance between electricity demand and legislative requirements for CO_2 emission reductions (Chen et al., 2010) to improve the economic feasibility of PCC (Garðarsdóttir et al., 2015). This approach postpones the energy penalty from PCC to ensure that electricity market demands are met (Wiley et al., 2010; Patiño-Echeverri and Hoppock, 2012).

Economic studies demonstrate that flexible operation strategies can substantially improve the economic feasibility of PCC (Cohen et al., 2010a,b; Wiley et al., 2010; Husebye et al., 2011; Cohen et al., 2012a,b,c). These studies are case specific, with different model constraints and assumptions (eg, CO_2 pricing, government regulations,

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fuel price, and application to electricity grid versus single plant). The comparison of actual cost results across different studies is only possible under similar conditions and constraints.

Dynamic PCC operation imposes process disturbances when the CO_2 capture plant is ramped up or turned down, and the immediate and long-term effects of these disturbances are unclear. Thus, recent research focuses on the feasibility of flexible PCC operation on a technical basis. Dynamic modeling and pilot plant studies will improve our understanding of dynamic behavior, enabling optimization of process control for dynamic PCC conditions.

24.2 Dynamic operation of post-combustion CO_2 capture

24.2.1 Strategies to improve flexibility

Proposed strategies that address the demand for flexibility within the PCC process include:

- flexible operation modes (partial, part-time, or variable CO_2 capture)
- venting flue gas
- bypass system
- liquid absorbent storage
- optimized steam cycle and heat integration designs.

These strategies and their functions are discussed in the following sections. As discussed in Section 24.3.2, economic analyses indicate that these flexible operation strategies can provide significant financial advantages.

24.2.2 Flexible operation modes

The most commonly studied PCC operation mode is full-time complete CO_2 capture mode, where CO_2 capture percentage (90% or higher) and energy penalty are maintained at constant levels. Additional flexible operation modes for PCC plants include partial, part-time, or variable capture, as explained in the following sections. These are summarized in Table 24.1 (Wiley et al., 2010).

Partial CO_2 capture is the full-time capture of CO_2 from flue gas at a constant recovery rate below 90%. This mode vents the remainder of the exhaust flue gas containing residual CO_2 to the atmosphere (Wiley et al., 2010). Part-time CO_2 capture is the operation of the capture plant for chosen periods of time, usually in accordance with electricity demand. During periods when capture is not running, the flue gas is directly vented (Cohen et al., 2010b). Variable CO_2 capture uses different capture rates for selected time intervals (based on trends in the electricity market). For periods of high demand, the capture plant will run at a low capture rate. Conversely, a high

Table 24.1 **Summary of operating modes for a post-combustion CO_2 capture plant**

Operating mode	CO_2 capture rate	Definition
Full-time complete CO_2 capture	One capture rate >90%	Full-time continuous capture with constant CO_2 capture rate and energy penalty
Partial CO_2 capture	One capture rate <90%	Full-time capture of CO_2 at constant recovery rate, residual portion of CO_2 is vented with exhaust flue gas
Part-time CO_2 capture	One capture rate Any percentage	Capture is on for selected intervals of time, and flue gas is vented when capture is off
Variable CO_2 capture	Multiple capture rates Each percentage is different	Different CO_2 capture rates for selected time intervals, based on the trends of the electricity market

capture rate is used for periods of low demand, while an intermediate CO_2 capture rate is used for moderate electricity demand. The capture plant will be designed to the capacity of the maximum CO_2 capture rate (Wiley et al., 2010).

Recently, model simulations of dynamic conditions demonstrated that reboiler duty can be significantly reduced by partial CO_2 capture. The implementation of load variation scenarios in a PCC plant improved the capture efficiency and energy requirements of CO_2 capture (Garðarsdóttir et al., 2015). From a technical perspective, large disturbances will impose significant process instability (Bui et al., 2014a). Consequently, a part-time operating mode that involves frequently turning CO_2 capture on and off would not be practical. The partial or variable CO_2 capture modes are preferable from a technical operating perspective, since they avoid completely switching off the CO_2 capture plant.

The trends of electricity demand may be represented on a basis of hours, days, or seasons. A baseload power station could redirect energy capacity to the PCC process during any of these time frames. For example, a flexible operation strategy could redirect energy consumption from CO_2 capture to electricity generation, increasing power plant output during periods of high electricity demand (Cohen et al., 2010b). Conversely, when electricity demand is low, PCC plants will require the capacity to ramp up CO_2 capture within the appropriate time frame.

24.2.3 Start-up venting and bypassing the post-combustion CO_2 capture system

The PCC system is not essential for the operation of a power plant. Even with optimal energy use and integration, a power station needs to have the capacity to operate without CO_2 capture (Chalmers et al., 2009). The ability to vent flue gas or bypass PCC enables a power station to operate independently of the PCC process.

The operation of a PCC unit can prolong power plant start-up time, due to the extraction of steam from power generation. Start-up venting of excess flue gas avoids CO_2 capture completely and significantly reduces the impact on the power plant. The start-up time will depend on the proportion of flue gas being vented and the power generator's capacity for varied steam flow rates. With the implementation of carbon pricing, the cost of electricity generation may be greater without CO_2 capture, due to the cost associated with CO_2 emissions. Due to the limited amount of liquid storage in the absorption system, venting may be necessary and start-up costs should consider CO_2 emission costs (Chalmers and Gibbins, 2007).

During normal operation of the power plant, the PCC bypass configuration (Fig. 24.1) can be used for partial CO_2 capture or zero-load operation modes. The bypass system proportionally decreases the flow of steam and rich absorbent to the stripper simultaneously. The bypass redirects the rich absorbent to the absorber, increasing power output and decreasing CO_2 capture rate. The CO_2 removal capacity of the rich absorbent is much lower than the lean absorbent. Thus, the bypass system extracts less CO_2 from the flue gas compared with normal CO_2 capture operation. Overall CO_2 emissions will be higher when the bypass is operational, and thus the cost of CO_2 emissions may increase, but this is offset by the electricity generation revenue. Additionally, if the retrofit capture unit is adequately sized for the available steam flows from the power plant, the additional capital cost of a bypass system is negligible (Rao and Rubin, 2006; Cohen et al., 2010a).

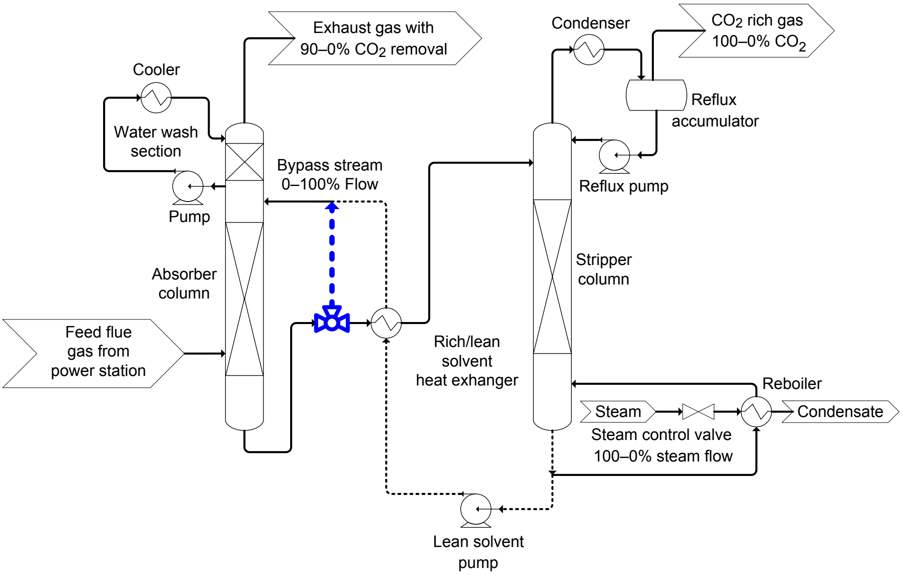

Figure 24.1 The bypass system (*blue valve and stream*) within the post-combustion CO_2 capture process provides added flexibility for partial or part-time CO_2 capture (Bui et al., 2014b).

Coal-fired subcritical power generators are operationally flexible, and can vary steam flows if CO_2 capture bypass is implemented (Cohen et al., 2010a). During periods of high electricity prices and low CO_2 emissions penalty, a bypass of the CO_2 capture system is practical, because it restores the retrofitted power plant to its original capacity (Chalmers et al., 2010). It will be more economically desirable to install a CO_2 capture bypass system in an existing power plant than to construct new peaking capacity plants to compensate for higher electricity demand periods. New power generators with CO_2 capture can also benefit from a voluntary bypass of the PCC unit. The new power plants may be oversized for the additional CO_2 capture process. Thus, with a bypass installed, a power plant could meet higher electricity demand in the future (Chalmers et al., 2009).

24.2.4 Liquid absorbent storage

The ability to store absorbent provides flexibility in the regeneration process, allowing desorption energy requirements to be varied. As shown in Fig. 24.2, the absorbent storage tanks between the absorber and stripper columns facilitate the delay of absorbent regeneration and CO_2 compression. The capacity to accumulate liquid absorbent has the additional benefit of enabling unequal absorbent flow rates through the absorber and stripper (Husebye et al., 2011). Another advantage of storage capacity is the ability to vary the load of the CO_2 compression train at a different rate to the power plant. Even so, this load variation requires careful process control (Chalmers and Gibbins, 2007).

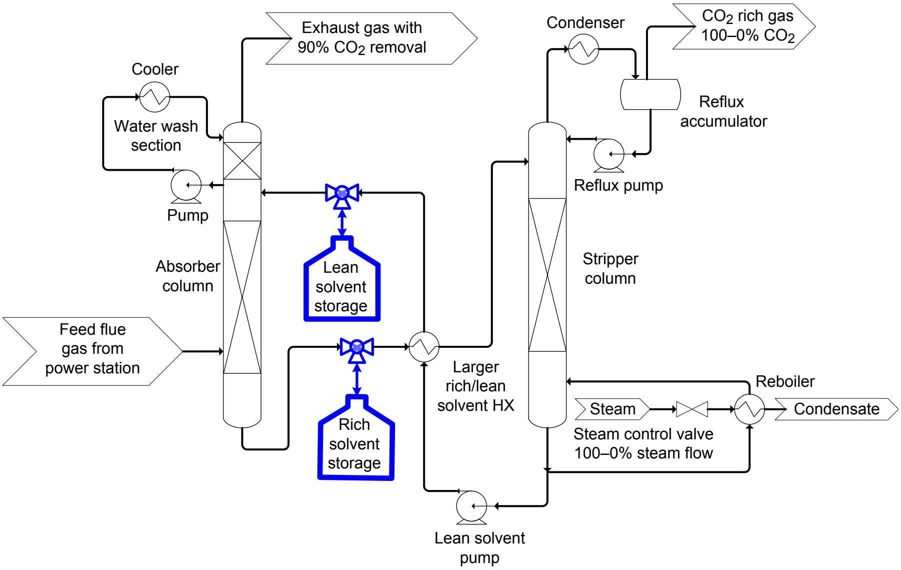

Figure 24.2 Flexible operation of post-combustion CO_2 capture using absorbent storage (*blue components*) (Bui et al., 2014b).

The proposed absorbent storage system consists of two tanks. One tank collects rich absorbent as it exits the absorber before it is regenerated, while a second tank of the same size gathers lean absorbent as it exits the stripper after regeneration (Husebye et al., 2011). While CO_2 is captured during periods of high electricity demand, rich absorbent gathers in one storage tank, allowing for higher electricity output and low CO_2 production (Gibbins and Crane, 2004a; Cohen et al., 2010b). Simultaneously, stored lean absorbent from the other tank can be fed into the absorber to maintain high CO_2 removal rates, even though the loads for the stripper and compressor have decreased. Conversely, during off-peak periods, when electricity demand is low, stored rich absorbent is fed into the stripper to be regenerated and lean absorbent is collected for storage (Cohen et al., 2010a).

The absorbent storage system requires upsizing of the stripper column and compressor to ensure adequate regeneration of the regular rich absorbent load and additional stored load. Since high CO_2 capture levels can be maintained, the reduced CO_2 emissions from a PCC plant operating with a flexible absorbent storage system are comparable to a plant operating full-time at high capture rates. However, capital costs increase significantly with increased absorbent inventory, additional storage tanks, a larger stripper column, and a larger CO_2 compressor (Cohen et al., 2010a).

24.2.5 Optimization of the steam cycle design and heat integration

The energy requirements for absorbent regeneration can range from 0.72 to 1.74 thermal megawatts per megawatt electricity generated by a coal-fired power plant (Alie et al., 2006). One optimized approach extracts steam from the intermediate pressure/low pressure (IP/LP) crossover pipe and expands the steam through a new auxiliary turbine. This process reduces efficiency losses and obtains steam conditions suitable for the reboiler (Gibbins and Crane, 2004b; Romeo et al., 2008). The optimal location to extract saturated steam is the middle of the LP section in the turbine, where the pressure ranges from 1.8 to 2.8 bar. To recover 90% of CO_2, at least 40–60% of this low-grade steam in the IP/LP crossover pipe is required for extraction. However, steam turbines in existing power plants do not usually enable extraction at this pressure range (Stöver et al., 2010). Consequently, optimal integration is only possible if the steam turbine is designed for a future PCC installation (Romeo et al., 2008); existing power plants require steam turbine retrofits. Other strategies to improve energy efficiency include, optimized heat integration between the power plant and CO_2 capture plant (Harkin et al., 2009, 2010; Khalilpour and Abbas, 2011), and waste heat recovery from flue gas (Chawla, 1999; Zhelev and Semkov, 2004; Blarke and Dotzauer, 2011).

The implementation of an optimized steam cycle design and heat integration will depend on whether CO_2 capture is inbuilt in new generators or retrofitted to existing power plants. For retrofits of CO_2 capture, the LP steam turbine and generator must have the capacity to increase net power and meet electricity demand. This can be achieved at low cost with a CO_2 capture bypass, or at a much higher cost with an LP steam turbine upgrade (Chalmers et al., 2010). A number of retrofit steam cycle designs have been developed for power plants with PCC (Lucquiaud and Gibbins, 2010). In new power stations inbuilt with PCC, the additional revenue gained from greater electricity generation with the larger LP turbine, larger generator, and bypass of the PCC system should justify the extra capital cost (Chalmers et al., 2010).

24.3 Design considerations for dynamic post-combustion CO_2 capture operation

24.3.1 Motivation for flexible operation of post-combustion CO_2 capture

Dynamic operation capabilities in PCC plants are inevitable, with the two main financial drivers being volatility in the electricity market and high CO_2 prices (see Section 24.3.2). The rise in electricity generation from intermittent renewable energy sources and the inflexibility of nuclear power plants are encouraging the need for flexible operation of coal-fired power plants (Lawal et al., 2010b; Kumar, 2014; Schiffer, 2014; van der Wijk et al., 2014; Mac Dowell and Shah, 2015). In Europe and the United States, many fossil fuel-fired power plants already operate flexibly (Kumar, 2014; Schiffer, 2014).

The energy output of electricity generators varies depending on market demand, which is influenced by daily and seasonal changes. Consequently, the flow rate and CO_2 level of flue gas emitted by the power plant can fluctuate significantly. Thus, flexible operation of PCC plants in response to these variations can be of significant benefit (Chen et al., 2010). Larger fossil-fired power stations traditionally operate at baseload, and thus rarely operate flexibly. Despite baseload power stations having relatively constant output (Kumar, 2014), a PCC plant will require capabilities for flexibility due to the inherent variability of the feed flue gas and absorbent conditions. The emitted flue gas from power plants will vary in properties depending on the fuel type, coal heterogeneity, and changing ambient conditions (Hasan et al., 2012). Additionally, absorbent properties change due to amine degradation. These technical motivations for flexible PCC operation are discussed in Section 24.3.3.

24.3.2 Economic benefits of post-combustion CO_2 capture dynamic operation

24.3.2.1 Volatility of electricity demand and prices

A major financial driver for dynamic PCC operation is the volatility of electricity prices (Husebye et al., 2011). The dynamic electricity market presents opportunities to improve the financial benefits and efficiency of PCC. Wiley et al. (2010) demonstrate the advantage of using different flexible CO_2 capture modes (partial, part-time, and variable capture) in accordance with seasonal trends in the New South Wales electricity grid (Australia). Compared with partial and part-time capture scenarios, variable CO_2 capture mode is the most economically and technically efficient

(Wiley et al., 2010), because it takes advantage of any capture opportunities while minimizing process disturbances.

Cohen et al. (2010b) demonstrate the effect of part-time CO_2 capture with different response times (hourly, daily, and seasonal) to demand trends of the Texan electricity grid (United States). In comparison with full-time CO_2 capture, daily or seasonal response times offered small reductions in generation costs without sacrificing electric grid efficiency. Hourly response times for part-time CO_2 capture offered the greatest reductions in CO_2 emissions (50%) compared with daily (28%) or seasonal (40%) response times. However, the cost for hourly part-time capture was higher than full-time CO_2 capture. Larger reductions in CO_2 emissions led to higher average generation cost. The economic value of dynamic CO_2 capture is therefore dependent on response time.

24.3.2.2 CO_2 pricing

A major determinant for the economic benefit of flexible PCC operation is CO_2 pricing. Fig. 24.3 illustrates the affect of CO_2 price on annual operating profits of a 500 MW coal-fired power station with flexible CO_2 capture (in Texas). Flue gas venting is economically advantageous at moderate CO_2 prices (US\$20–70/tonne CO_2); however, benefits diminish at high CO_2 prices. Liquid absorbent storage is profitable at low to high CO_2 prices, where US\$30–100/tonne CO_2 increases profits by 9–29% compared with inflexible CO_2 capture (Cohen et al., 2010a). Similar trends were observed when considering the influence of variable natural gas prices (Cohen et al., 2012c). In comparison with flexible operation using venting only, absorbent storage provides greater operating profits and reductions in CO_2 emissions. However, the profit advantages of absorbent storage are offset by higher capital costs (Cohen et al., 2012b).

In advanced electricity grids, where coal may be replaced by natural gas, nuclear, or renewable energy options, the source of electricity can vary depending on fuel prices.

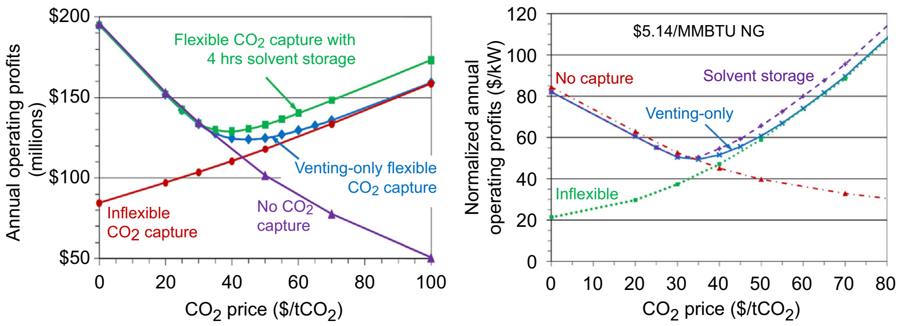

Figure 24.3 Affect of flexible operation on: (left) annual operating profits at different CO_2 emission prices (Cohen et al., 2010a), (right) normalized annual operating profits at different CO_2 emission prices, with consideration to natural gas prices (2010 average of US\$5.14 per million metric British thermal units) (Cohen et al., 2012c).

Cohen et al. (2012a) demonstrate that coal-fired power plants with CO_2 capture can remain economically competitive with the use of a flexible operation (absorbent storage and venting). Coal-fired power plants with flexible CO_2 capture can reduce electricity dispatch costs, and have reliable, low-cost reserve capacity with adequate response times, which reduces the need for ancillary services. These economic benefits will increase further with increased CO_2 and natural gas pricing, even with the existence of grid-scale energy storage (Cohen et al., 2012a).

The studies mentioned previously are case specific, with different model constraints and assumptions (eg, CO_2 pricing, government regulations, fuel price, and application to electricity grid versus single plant). Thus, comparison of actual cost results across different studies is only possible under similar conditions and constraints. At high CO_2 prices, flexible CO_2 capture provides the greatest economic benefit and electricity generation without CO_2 capture becoming unprofitable. Additionally, deployment of energy options (ie, coal, natural gas, or renewables) is dependent on fuel prices and generation costs, which can significantly affect the financial performance of power plants using PCC. For example, the financial benefit of using PCC in coal-fired power plants improves when natural gas costs more than coal (Cohen et al., 2012a; Mac Dowell and Shah, 2015).

24.3.3 Dynamically changing physical properties

24.3.3.1 Flue gas composition and properties

The characteristics of the feed flue gas significantly affect the efficiency and cost of a CO_2 capture plant. The physical properties and composition of flue gas streams vary with different plant processes and combustion fuels (eg, brown/black coal or natural gas). The amount of CO_2 in flue gas from power generation and industrial processes varies significantly, ranging from tens to thousands of tonnes CO_2 per day. Depending on the type of source or fuel, the flue gas may contain CO_2, N_2, O_2, H_2O, CO and H_2, and contaminants such as SO_X or NO_X (Hasan et al., 2012).

Important considerations for PCC technology applicability and performance include flue gas stream specifications and the scale of capture. Table 24.2 shows that the CO_2 composition of flue gases from power plants is typically 3.4—14%, depending on the fuel type, where N_2 is the main constituent. The flue gases from other industrial processes (eg, urea, hydrogen, steel, and cement production plants) can have a CO_2 composition of 7—44%. Some industrial processes (eg, ethanol or ethylene production) can produce exhaust gas streams of almost pure CO_2 (Mahasenan and Brown, 2004). Chemical absorption processes are most appropriate for flue gas streams with low CO_2 concentration, where control measures have been implemented to remove contaminants such as SO_X, NO_X, and fly ash (Mahasenan and Brown, 2004). In power stations, coal combustion generates higher CO_2 emissions in the flue gas than natural gas or oil. Hence, a large emphasis is placed on PCC research for coal-fired power stations.

Flue gas from a power station is usually derived from a single coal type (ie, brown or black coal), sourced either from nearby coal mines or imported from overseas. The

Table 24.2 Volumetric composition (%) of process streams from various industrial plants (Mahasenan and Brown, 2004; Hasan et al., 2012)

Plant	CO_2	N_2	O_2	H_2O	CO	H_2	NO_X	SO_X	Other
Coal-fired power plant	12.6–14	71.4–74	3–4.3	8–10.8	—	—	0	0–0.1	0.9–1
Natural gas-fired power plant	8.6–9	70–71	2.4–13	7.8–17.3	—	—	0	0	0–0.9
Gas turbine power plant	3.4–3.8	74.4–75.7	12.6–13.8	6.9–8.3	—	—	0	0	0–0.9
Fuel oil-fired power plant	11	73	3	13	—	—	Trace	Trace	—
Liquid natural gas	0.1–8	0–5	0–0.2	—	—	—	0	0	87–99
Urea plant	8	68	1	22	—	—	Trace	Trace	1
Refinery	7	77	3	14	—	—	—	—	—
Hydrogen plant (steam–methane reforming)	12	—	—	29	1	50	0	0	8
Steel plant (blast furnace)	20	56	—	—	21	3	0	0	—
Steel plant (Corex)	24	12	0	1	44	17	0	—	2
Steel plant (cyclone converter furnace)	44	9	—	—	24	20	0	—	—
Cement plant	19	61	8	13	—	—	—	Trace	—
Ammonia production (before CO_2 removal)[a]	18.9	19.9	—	—	0.1	60.1	—	—	1
Ethanol (fermentation)	100								
Ethylene oxide (vented stream)	100								

[a] Composition from Copplestone et al. (2008).

coal itself is heterogeneous, and its properties can vary at different locations within the mine and even throughout the same coal seam (Li, 2004). Thus, the properties of the flue gas exiting the power station will also vary. Flexible operation of the PCC plant can accommodate this variation in flue gas properties to improve CO_2 capture efficiency.

The CO_2 concentration of the incoming flue gas has a direct influence on the CO_2 concentration in the rich absorbent (van der Ham et al., 2014a). Thus, variable flue gas composition affects the CO_2 capture performance. Hasan et al. (2012) show that for any given feed flue gas flow rate, an increase in CO_2 concentration in the feed increases the investment and operating costs. As CO_2 concentration increases, the greater feed flow of CO_2 requires higher absorbent flow rates and reboiler heat duty for absorbent regeneration (Hasan et al., 2012). More recently, Khakharia et al. (2015) studied a dynamic pilot plant operation with an amine absorbent using a monoethanolamine (MEA) and 2-amino-2-methyl-1-propanol—piperazine (AMP—PZ) mix, where flue gas CO_2 content was incrementally decreased. Decreasing the flue gas CO_2 concentration reduces the amount of CO_2 absorbed, which in turn decreases temperature within the absorber (Fig. 24.4). Additionally, gradual decreases in flue gas CO_2 composition from 12.7 to 6 vol% increased amine aerosol emissions (Fig. 24.5). However, flue gas CO_2 concentrations below 6 vol% decreased amine emissions (Khakharia et al., 2015).

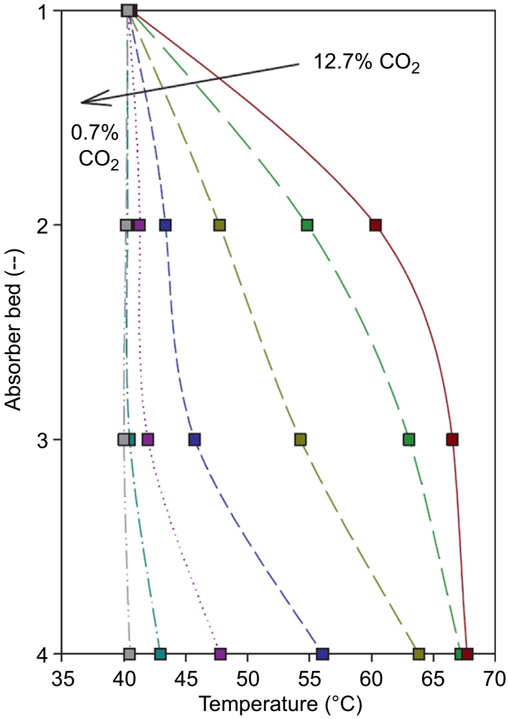

Figure 24.4 Absorber column temperature during variation of flue gas CO_2 concentration from 12.7 to 0.7 vol% in a post-combustion CO_2 capture mini-plant operating with 2-amino-2-methyl-1-propanol—piperazine amine absorbent (Khakharia et al., 2015).

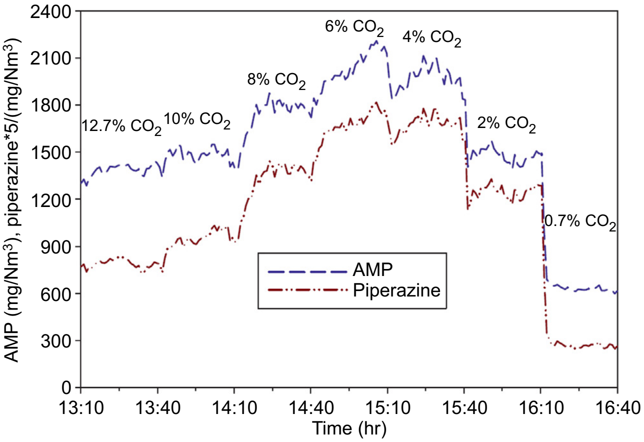

Figure 24.5 Emissions of 2-amino-2-methyl-1-propanol (AMP) and piperazine (PZ) amine absorbents from a post-combustion CO_2 capture plant during decreasing step-changes in CO_2 concentration from 12.7 to 0.7 vol.% (Khakharia et al., 2015).

All PCC plants are likely to experience variable flue gas properties as a result of power plant load changes, even when using just one fuel type. To compensate for these ongoing changes, flexible PCC operation is essential. However, most PCC experimental and modeling studies are based on fixed CO_2 composition (usually corresponding to either coal or natural gas). Some studies have examined the influence of flue gas CO_2 composition on amine degradation (Supap et al., 2006; Voice and Rochelle, 2013; Bougie and Iliuta, 2014). However, only a few studies have investigated the impact of variable CO_2 composition in the feed flue gas on the CO_2 capture performance of chemical absorption (Hasan et al., 2012; Khakharia et al., 2015). Further research is required to investigate the impact of variable flue gas properties (particularly CO_2 composition) on the performance of flexible PCC systems.

24.3.3.2 Absorption liquid properties

Plant operability can significantly affect the feasibility of flexible operation in terms of technical performance and cost. Factors that influence plant operability should therefore be considered in the early process design phases. For example, the products formed from amine degradation generally have a negative impact on plant operability, and can reduce the life of a PCC plant (Islam et al., 2011). Depending on the type of degradation products, the operation problems that may arise include:

- poor plant performance (reduces capture capacity)
- amine loss (increases operating costs)
- changes to viscosity
- foaming effects
- fouling effects
- corrosion effects

- construction type (material selection affects capital costs)
- negative environmental impact.

Only the first five issues will be discussed, because they directly affect PCC operability and hence might hinder the ability for flexible operation.

Plant performance

Amine degradation decreases plant performance due to the reduction in CO_2 absorption capacity (Supap et al., 2006; Lepaumier et al., 2008; Islam et al., 2011). It can also reduce the rate of CO_2 absorption and increase the heat of CO_2 absorption (van der Ham et al., 2014b). The presence of heat-stable salts in MEA solutions increases the time required to reach equilibrium, for example, heavily degraded MEA solutions might have slower reaction kinetics than fresh MEA solutions. Existing 30% MEA vapor—liquid equilibrium models are unable to adequately represent highly degraded solutions, and may require calibration to compensate for degradation effects. Typically, the degraded MEA solution will be reclaimed and replaced with makeup to improve plant performance (Geers et al., 2011). Consequently, amine degradation increases process energy requirements and costs.

Amine loss

Amine can be lost through evaporation, entrainment, and amine degradation. Chapel et al. (1999) estimates total absorbent losses to average 1.6 kg/tonne of CO_2 captured in well-maintained PCC plants. The Esbjerg pilot plant (Denmark) reports a specific MEA consumption of 1.4 kg/tonne CO_2 captured (Knudsen et al., 2009). The specific MEA consumption of the PCC plant at RWE Power (Niederaussem, Germany) is only 0.3 kg/tonne CO_2 captured, significantly lower than the Esbjerg plant (Moser et al., 2011, 2012, 2014).

The most significant loss of amine occurs through evaporation and entrainment from the absorber. Mist eliminators can control entrainment, and water wash sections on the absorber column can recover as much as 95% of the evaporated absorbent (Veltman et al., 2010). Other technologies that can recover volatile compounds at the top of absorbers include adsorption processes (Dwivedi et al., 2004) and scrubbing with demineralized water, acidic water, alkali, or proprietary reagents (Sharma and Azzi, 2014).

Changes to viscosity

Amine degradation significantly increases solution viscosity (Lepaumier et al., 2008; Islam et al., 2011). Viscous solutions increase pumping duty (Islam et al., 2011) and can lead to difficulties with maintaining process stability (Bui et al., 2014a). Generally, the viscosity of a liquid decreases as the liquid temperature increases (Masuko and Magill, 1988; Seeton, 2006). Ye et al. (2013) report that increases to temperature reduces the viscosity of the MEA solution, which promotes the diffusion of CO_2 into the liquid phase. Thus, as the temperature rises, the rate of CO_2 absorption increases. Conversely, a higher solution viscosity would hinder the diffusion of CO_2 into the liquid phase, thereby reducing the CO_2 absorption rate.

Foaming effects

The foaming tendency and foam stability of amine solutions is mostly affected by the liquid's surface tension, viscosity, and density. Liquid viscosity has the greatest impact on foam height, followed by density and surface tension (Thitakamol and Veawab, 2008; Thitakamol et al., 2008; Thitakamol and Veawab, 2009; Islam et al., 2011). The foaming behavior of MEA solution is influenced by many process parameters, such as gas flow rates, temperature, CO_2 loading, amine concentration, amine degradation products, and corrosion inhibitors (Thitakamol and Veawab, 2008; Thitakamol et al., 2008; Thitakamol and Veawab, 2009).

Thitakamol and Veawab (2008) investigated the influence of PCC process parameters on the foaming behavior of amines under simulated environments in a laboratory. As gas flow rate increases, foam formation is disrupted due to increased gas turbulence. Subsequently, both foam stability and the foaminess coefficient decrease. Solution temperature has the greatest impact on the foaming tendency; as it increases, the foaminess coefficient decreases (due to lower foaming tendency). The foaminess coefficient also increases and eventually decreases with increasing amine concentration and CO_2 loading (Thitakamol and Veawab, 2008; Thitakamol et al., 2008; Thitakamol and Veawab, 2009).

The presence of the following amine degradation products increases the foaming coefficient (listed in order of increasing foam volume): ammonium thiosulfate, glycolic acid, sodium sulfite, malonic acid, oxalic acid, sodium thiocyanate, sodium chloride, sodium thiosulfate, bicine, hydrochloric acid, formic acid, acetic acid, and sulfuric acid. Some corrosion inhibitors (eg, sodium metavanadate and copper carbonate) can reduce the solution surface tension and increase foaming tendency, whereas sodium sulfite has no apparent affect (Thitakamol and Veawab, 2008; Thitakamol et al., 2008; Thitakamol and Veawab, 2009). Surface tension typically increases in the presence of small halogen anions (F^-) (Levin et al., 2009), large cations, and divalent anions $\left(SO_4{}^{2-}\right)$. Conversely, acetate ions and large halogen anions (I^- or Br^-) act as surfactants and reduce surface tension (Lima et al., 2013). Thus, an important factor in foaming tendency is the potential introduction of ions or salts that change surface tension.

Some amine types have a tendency to generate foams (Thitakamol and Veawab, 2008). For example, MEA, methyl diethanolamine (MDEA), and MEA + AMP (2:1 mixing mole ratio) generate foams. However, the following amines do not foam: diethanolamine (DEA); AMP, blends of MEA + MDEA, DEA + MDEA, and MEA + AMP (1:1 and 1:2 mixing mole ratios). Thus, amine selection plays an important role in the foaming tendency of the absorbent in the PCC process.

Fouling effects

Solid products may form as a result of amine degradation or corrosion during the PCC process. The solid products form sludge in the liquid phase (Sharma and Azzi, 2014). The solids carried by the liquid phase cause fouling when deposits form in process piping, heat exchangers, and the reboiler. Fouling in PCC plants can increase energy costs due to higher pressure drops in process equipment and lower heat transfer coefficients. Cleaning fouling deposits from piping and process equipment is expensive (Islam et al., 2011). The Esbjerg PCC pilot plant uses a carbon filter to remove organic degradation products from a slipstream of absorbent (Knudsen et al., 2009). The use of carbon beds and/or filters in PCC processes to remove particulates and amine degradation products is recommended (Chapel et al., 1999).

24.4 Developments in dynamic modeling of post-combustion CO_2 capture

24.4.1 Dynamic post-combustion CO_2 capture models

Flexible operation can improve the economic viability of PCC technology. Recently, there has been growing interest in the development of dynamic models to understand flexible operation and transient behavior of PCC plants. PCC modeling studies employ a number of commercial computer programs to develop dynamic PCC models, including Aspen Plus Dynamics, gPROMS, MATLAB, UniSim, and Aspen Custom Modeller. Fosbøl et al. (2014) demonstrate significant variability among modeling results from different software tools and different approaches. Thus, researchers should be wary of results from models that have not been validated against experimental or pilot plant results.

This section discusses the development of dynamic PCC models, including simplified, stand-alone column models and complex, fully integrated process models. For an extensive review and discussion of dynamic modeling and optimization of flexible PCC operation, see Bui et al. (2014b).

24.4.2 Comparison of equilibrium-based and rate-based approaches

PCC process models may use either equilibrium-based or rate-based approaches. In the equilibrium-based approach, the liquid and vapor phases at every theoretical stage are assumed to reach equilibrium and mix perfectly (Lawal et al., 2009b). This approach neglects the restrictions of mass and heat transfer to simplify the system (Léonard et al., 2013). The rate-based (or nonequilibrium) approach is based on the two-film theory and the Maxwell—Stefan formulation (Krishna and Standart, 1976; Taylor and Webb, 1981; Krishnamurthy and Taylor, 1985b; Higler et al., 1998; Schneider et al., 1999; Peng et al., 2002; Lawal et al., 2010b). This approach is more rigorous than the equilibrium-based approach, and provides greater accuracy for detailed column design (Krishnamurthy and Taylor, 1985a,b).

Zhang and Chen (2012) demonstrate that the rate-based approach provides accurate predictions of concentration and temperature profiles in the absorption and stripper columns, while the equilibrium-based approach overestimated the rate of CO_2 absorption and underestimated the reboiler heat duty. Other modeling studies also report improved accuracy of the rate-based approach compared with equilibrium-based models (Treybal, 1969; Feintuch and Treybal, 1978; Krishnamurthy and Taylor, 1985a,b; Lawal et al., 2009b; Biliyok et al., 2012a,b). The required complexity of a model will depend on the intended application, as well as the tool capacity and limitations (eg, computational time and memory), resulting in a trade-off between model accuracy and complexity (Prölß et al., 2010; Åkesson et al., 2012).

Although the steady-state solutions from rate-based and equilibrium-based models are significantly different, these models have similar dynamic responses (Peng et al., 2003). Thus, the equilibrium approach to modeling PCC should provide adequate accuracy for dynamic simulations. Although the rate-based approach is more rigorous, its unnecessary complexity may slow down model simulations. For users investigating overall dynamic performance, an equilibrium-based approach to dynamic modeling is sufficient. However, the rate-based approach is recommended when steady-state and absorption results are of particular interest.

24.4.3 Stand-alone dynamic models

To reduce complexity, many researchers model only one section of the PCC process as a stand-alone column. Stand-alone dynamic models of the absorber column provide important information about the chemical absorption reactions and behavior (Kvamsdal et al., 2009; Lawal et al., 2009b; Kvamsdal et al., 2010; Gáspár and Cormoş, 2012; Jayarathna et al., 2013b; Mac Dowell et al., 2013; Posch and Haider, 2013). They also enable optimization of the desorption section to minimize reboiler heat duty and improve efficiency (Ziaii et al., 2009; Greer et al., 2010; Enaasen et al., 2012).

Kvamsdal et al. (2009) developed a dynamic equilibrium-based model of the absorber column in the gPROMS software. The specifications for this model are based on the pilot plant at the University of Texas (Dugas, 2006). Although the model may provide some valuable predictions, it was not validated against operational data, due to a lack of availability (Kvamsdal et al., 2009). Because model validation is required to ensure accurate results, Kvamsdal et al. (2010) reimplemented their model in MATLAB and solved it using the ODE15s solver. This improved modeling approach validated the dynamic absorber model against both steady-state and dynamic operational data from a pilot plant at the Norwegian University of Science and Technology (NTNU) and Norway’s Stiftelsen for industriell og teknisk forskning (SINTEF) laboratory. Operation of this pilot plant under dynamic mode was challenging, and may potentially be the reason for a lack of published dynamic pilot plant data. The study demonstrated that a model calibrated with data from one specific plant may not necessarily simulate behavior representative of other plants with different geometry and operating conditions (Kvamsdal et al., 2010).

Lawal et al. (2009b) used a dynamic absorber model to conduct a comparative investigation of the equilibrium-based (Aspen Plus software) and rate-based (gPROMS software) modeling approaches. Pilot plant data from the Separations Research Program (University of Texas at Austin) was used to validate the two absorber models (Dugas, 2006). More recent studies tend to use the rate-based approach to model dynamic stand-alone absorbers (Jayarathna et al., 2013b;

Mac Dowell et al., 2013; Posch and Haider, 2013). Lawal et al. (2009b), Jayarathna et al. (2013b), and Mac Dowell et al. (2013) were only capable of conducting steady-state model validations, due to the limited availability of dynamic operational data. On the other hand, Posch and Haider (2013) were able to conduct a dynamic validation of their absorber model against dynamic pilot plant results from the CO_2 Separation Plant (CO_2SEPPL) at the Dürnrohr power station in Austria.

Unlike previous modeling research, which focused on a conventional MEA absorbent, Gáspár and Cormoş (2012) assessed the dynamic behavior and performance of four different absorbents: MEA, DEA, MDEA, and AMP. The study found that several published mass transfer and hydraulic correlations are absorbent type-specific. When modeling systems of different absorbent types, the following considerations are important when selecting mass transfer and hydraulic correlations for a model: (1) suitability for a specific absorbent type and (2) design boundaries and conditions of the chemical system (Gáspár and Cormoş, 2012). Consideration of these factors will ensure reliability and accuracy of predictions.

The stand-alone, rate-based stripper model by Ziaii et al. (2009) was developed in Aspen Custom Modeller. Upon optimizing for steady-state conditions, the stripper model was used to analyze dynamic behavior in response to changes to reboiler duty. When making changes to heat input once the reboiler reaches steady-state conditions, liquid residence time is the most significant factor that determines system response time. The model indicates that stripper column packing height has a direct correlation with stripper efficiency and steam consumption (Ziaii et al., 2009). In contrast, Greer et al. (2010) suggest that stripper column height has little influence on desorption, and that the steam flow rate supplied to the stripper has a significant impact on the efficiency of absorbent regeneration. The dynamic mathematical model of the stripper section was developed in MATLAB and used the ODE15s solver (Greer et al., 2010). Similarly, Enaasen et al. (2012) developed a dynamic mathematical stripper model in the MATLAB software, which was verified against steady-state simulations from another model in CO2SIM. For these three dynamic stripper models (Ziaii et al., 2009; Greer et al., 2010; Enaasen et al., 2012), the lack of validation against actual operational data raises concerns about the reliability of their predictions.

Stand-alone column models can provide useful predictions, particularly if validated against experimental or pilot plant data. However, consideration of both the absorber and stripper sections is required for completeness of a modeling study. To extend beyond modeling single columns, Lawal et al. (2009a) developed dynamic stand-alone models for both the absorber and stripper columns. Each of these models was implemented in gPROMS software using the rate-based approach. As previously undertaken by Lawal et al. (2009b), the validation of the models against pilot plant data by Dugas (2006) demonstrated that dynamic stand-alone models reasonably predict the steady-state column temperature profiles and CO_2 loading. Modeling accuracy could be improved by coupling the absorber and stripper columns with a recycle loop that is more representative of the actual process (Lawal et al., 2009a). Subsequently, the development of dynamic models has progressed to the integration of submodels to simulate the complete PCC process.

24.4.4 *Integrated dynamic models of the post-combustion CO_2 capture process*

An integrated dynamic model describes the complete PCC process and couples the absorber and stripper columns with a recycle loop. Lawal et al. (2010b) developed a dynamic model of the absorber and stripper integrated with the recycle loop, using gPROMS software. The integrated model was used to investigate PCC performance in coal-fired power plants operating under the context of the United Kingdom's energy grid requirements. Steady-state pilot plant data used previously (Lawal et al., 2009a,b, 2010a) was used for model validation. Again, the lack of available pilot plant data prevented dynamic validation of the integrated model. This integrated model had greater predictive accuracy than stand-alone models published by Lawal et al. (2009a). Although the stand-alone models can provide a general prediction for temperature profiles, inaccuracies are amplified when discrepancies in the absorber model are carried through to the stripper model calculations (Lawal et al., 2010b).

The integrated dynamic model developed in gPROMS was scaled up to full-scale dimensions by Lawal et al. (2012). The model validation was conducted at steady-state at pilot plant-scale, since commercial-scale and dynamic data was unavailable. The dynamic model was extended to include both the PCC plant and the subcritical coal-fired power generator. Dynamic simulations of coupled models revealed that the PCC plant has a slower response time than the power plant. More importantly, the control loop interaction between the PCC and power generator models hindered the ability to achieve steady power output (Lawal et al., 2012). This highlights the disadvantage of fully integrating the PCC process with the power plant.

Jayarathna et al. (2013a) and Karimi et al. (2012) also validated integrated, rate-based PCC models against steady-state, pilot plant data from Dugas (2006). Jayarathna et al. (2013a) implemented a mathematical model of the MEA-based PCC process in MATLAB. In contrast, Karimi et al. (2012) used UniSim Design software to model the dynamic behavior of MEA-based PCC plants with various stripper configurations. Shifting the focus away from conventional MEA absorbent, Dietl et al. (2012) analyzed the dynamic performance of a PCC plant using amino acid absorbent. Object-oriented Modellica language was used to develop three rate-based models for the: (1) absorber column, (2) stripper column, and (3) integrated PCC process. The dynamic behavior of the stand-alone models and the integrated model was compared over short and long timescales. The short-term responses (ie, first few minutes) of the stand-alone models and integrated model were similar, while the long-term responses diverged (Dietl et al., 2012).

Biliyok et al. (2012a,b) used dynamic pilot plant data to validate an integrated PCC model previously developed by Lawal et al. (2010b). This was the second dynamic validation to be performed after Kvamsdal et al. (2010). The pilot plant results were derived from the research at The University of Texas in Austin (Dugas, 2006). The dynamic validation compared pilot plant and model results for the (1) absorber temperature profile, (2) CO_2 capture rate, and (3) reboiler heat duty. Although the dynamic model over or underestimated in some cases, the predicted trends and dynamic behavior were generally in good agreement with the pilot plant results.

Biliyok et al. (2012a) suggested that flue gas moisture content significantly affected CO_2 capture rate. The prediction of the absorber temperature profile was similar to the findings of Mac Dowell et al. (2013).

A dynamic PCC model developed by Enaasen Flø et al. (2015) in MATLAB was validated against steady state and dynamic data from the Gløshaugen (NTNU/SINTEF) PCC pilot plant. Of the six dynamic pilot plant cases available, two data sets were used for dynamic model validation, a 17% step-change in reboiler duty, and a 22% step-change in absorbent flow rate. The integrated PCC process model consisted of submodels for the absorber, regeneration, and cross heat exchanger. To avoid the propagation of errors through the system, each submodel was validated separately. This involved using pilot plant data as inputs for each submodel and the model predictions were compared to the measured pilot plant response (Enaasen Flø et al., 2015).

24.4.5 Dynamic modeling for process optimization and control

Dynamic PCC modeling is beginning to explore the technical and economic impact of process integration into the power generation. Proposed approaches to improving efficiency include optimized heat integration between the power plant and CO_2 capture plant (Harkin et al., 2009, 2010; Khalilpour and Abbas, 2011), waste heat recovery from flue gas (Chawla, 1999; Zhelev and Semkov, 2004; Blarke and Dotzauer, 2011), and optimized steam cycle retrofit (Romeo et al., 2008; Lucquiaud and Gibbins, 2010; Sipöcz et al., 2011).

Integrated dynamic models are now being used to develop robust process control and online operational strategies for efficient flexible PCC operation (Prölß et al., 2010; Lin et al., 2011, 2012; Åkesson et al., 2012; Panahi and Skogestad, 2012; Léonard et al., 2013; Hossein Sahraei and Ricardez-Sandoval, 2014; Nittaya et al., 2014b; Luu et al., 2015). Further developments in dynamic PCC process modeling include the incorporation of economic models to consider both technical and financial performance (Gibbins and Crane, 2004b; Botero et al., 2008; Wiley et al., 2010; Mac Dowell and Shah, 2013).

Although pilot-scale models and plant studies offer invaluable insight into the transient behavior of PCC processes, researchers are recognizing the need to move toward commercial-scale processes. Thus, dynamic PCC models are now being applied to simulate and design industrial-scale processes (Lawal et al., 2012; Nittaya et al., 2014a). One commercial-scale PCC plant already exists in Boundary Dam, Canada (Stéphenne, 2014) and another is under construction at W.A. Parish power station in Texas (DOE, 2015). The predictive accuracy of larger-scale, dynamic PCC models will be improved through model validation as commercial-scale operational data becomes available.

24.5 Developments in dynamic operation of pilot plants

24.5.1 Role of post-combustion CO_2 capture plants in dynamic model development

Operational pilot plant data provides researchers with insights into process performance and ideal operation strategies, and also has a role in model development. The validation or calibration of a model against real operational data under a wide range of plant operational conditions can demonstrate the validity and accuracy of simulation results (Campbell, 2014). Additionally, PCC demonstrations need to process flue gas derived from actual fuel combustion (eg, coal) to accurately represent commercial-scale processes. Validated theoretical models are valuable tools for the optimization of further pilot plant experiments and accurate upscaling of industrial processes.

Few pilot plant studies have published data from pilot plants operating under dynamic conditions (Bui et al., 2014b). Subsequently, most existing dynamic models have only been validated with steady-state pilot plant data (Kvamsdal et al., 2009; Lawal et al., 2009a,b, 2010b, 2012). In these studies, pilot plant validation cases were selected to cover a broad range of liquid to gas (L/G) ratios. A high L/G ratio corresponds to high absorbent flow rate and high CO_2 capture level, while a low L/G ratio is associated with low absorbent flow rate and low CO_2 capture level. For each validation case, the data required included: (1) absorber column temperature profiles, (2) stripper column temperature profiles, and (3) CO_2 loading of amine absorbent at different positions in the pilot plant. Simulation results from the dynamic models were compared with pilot plant data to verify the accuracy of the model (Kvamsdal et al., 2009; Lawal et al., 2009a,b, 2010b, 2012).

Some dynamic PCC modeling studies have successfully validated models against transient pilot plant data (Kvamsdal et al., 2010; Biliyok et al., 2012a; Enaasen Flø et al., 2015). The transient pilot plant scenarios used by Kvamsdal et al. (2010) to validate a dynamic PCC model include: (1) changing liquid and gas flow rate and (2) changing CO_2 content at the gas inlet. The validation procedure involved comparing the model simulation results and the pilot plant measurements for the absorber column temperature profile and the change in CO_2 recovery % with time (Kvamsdal et al., 2010). The dynamic model validation by Biliyok et al. (2012a) used transient pilot plant data for increasing moisture in flue gas and absorber intercooling. To obtain reliable dynamic pilot plant data for model validation, Enaasen Flø et al. (2015) conducted step-changes in the reboiler duty and absorbent flow rate of the pilot plant. For these studies, dynamic models could not predict absolute values from pilot plant data, indicating some model adjustments may be necessary. There was reasonable agreement between the modeled trends and dynamic pilot plant measurements.

Although larger demonstration plants provide a better representation of industrial processes, small-scale pilot plants also provide extensive operating data and valuable information. Smaller demonstrations provide ease and flexibility for operation and process control (Wilson et al., 2005a,b). Smaller testing facilities are also advantageous when studying novel absorbents, because the volume available for testing may be limited (Mangalapally et al., 2008). Some studies demonstrate that laboratory-scale pilot plants can also provide reliable data for validation of process models (Tobiesen et al., 2007, 2008). Ideal candidate pilot plants for the study of dynamic PCC operation would:

- have relatively fast dynamics (ie, small-scale PCC plants)
- be equipped with sensors and indicators to monitor process conditions (eg, temperature and pressure), particularly along the absorber column
- be fitted with a system that provides online measurements of liquid phase CO_2 concentration and CO_2 loading (eg, density meters).

24.5.2 Dynamic operation approach

Transient behavior during large process disturbances (eg, uncontrolled shut-down or large increase of liquid flow) is highly variable and difficult to reproduce (Bui et al., 2014a). Consequently, the process may need a significant amount of time to stabilize from the fluctuations. Thus, large disturbances should be avoided if reliable and reproducible dynamic data is required. Dynamic behavior of incremental disturbances is more predictable, and process control is more easily managed; thus, it is more suitable for the validation of dynamic process models. In outdoor pilot plants that treat real flue gas, measurements are influenced by external factors, such as (1) weather or ambient temperature affecting columns, pipelines, and cooling water, (2) temperature change of flue gas from the power station, and (3) changes in flue gas composition. These factors introduce variability into pilot plant results, and hence need to be monitored.

The step-change dynamic operation approach has been developed to address variability issues in pilot plant studies. This approach involves sequential incremental changes to one process parameter. Upon making a change, the process is allowed to reach steady-state (ie, constant and stable measurements). The steady-state snapshots in time can be plotted in sequence for an overview of the dynamic plant behavior, an example of an absorber column temperature profile is given in Fig. 24.6. The step-change approach minimizes disturbances to the process, and its application to pilot plant operation significantly improves the consistency and reproducibility of dynamic results. This approach has been used in PCC pilot plants including, Esbjerg Power Station (Faber et al., 2010), RWE Power (Moser et al., 2011), CSIRO PCC pilot plant at AGL Loy Yang (Bui et al., 2014a, 2016), and at the Gløshaugen (NTNU/SINTEF) pilot plant (Enaasen Flø et al., 2015).

Process parameters used for dynamic step-change operation will require relatively fast response times and will generate observable effects in CO_2 capture performance.

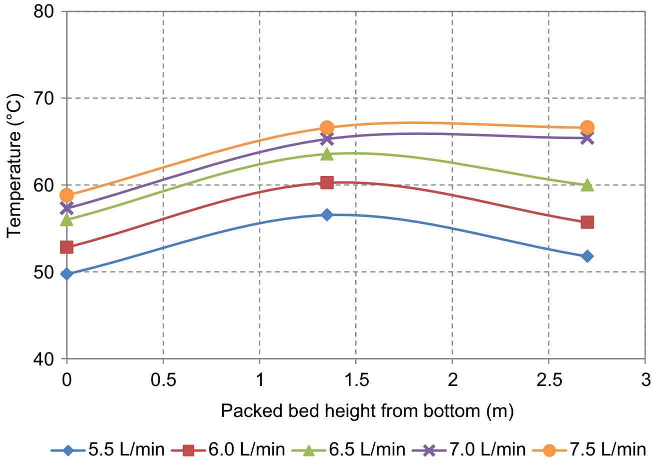

Figure 24.6 Absorber column temperature profiles during step-change in monoethanolamine absorbent flow rate (Bui et al., 2016).

To capture the full dynamics of the PCC process, step-changes should be conducted on a number of process parameters (eg, gas flow, liquid flow, and reboiler duty). The dynamic operating range of step-changes for each process parameter is set at the minimum and maximum limits (Bui et al., 2016). This can reveal the operational boundaries with the greatest stability, which will vary with plants of different scales and configuration. Dynamic operation within this stable range will improve the reliability of pilot plant results.

Operating a pilot plant under the same process conditions does not necessarily yield reproducible results, due to external factors such as ambient temperature. To ensure reproducibility of dynamic data from PCC plants, the following conditions need to be monitored and controlled:

- Operating set-point conditions – ensure major parameters are consistent (eg, liquid and gas flow rates, stripper reboiler temperature, and heating and cooling duties).
- Absorbent concentration in the liquid – should be carefully monitored and adjusted.
- Heat loss – ensure adequate thermal insulation for appropriate pipes and equipment.
- Ambient temperature – monitor weather forecasts and select days with similar ambient conditions.
- Amine degradation – ensure the same degree of degradation (eg, conduct runs on same day or across consecutive days).

24.5.3 Online monitoring

PCC pilot plant and laboratory studies are optimizing data measurement techniques to improve the reliability of results. Most parameters, such as temperature, pressure flow, and gas composition can be measured online in a pilot plant. Few pilot plants are equipped for real-time liquid analysis; thus, most pilot plant studies measure liquid phase CO_2 loading, density, and amine concentration using offline laboratory analysis (Dugas, 2006; Artanto et al., 2009; Seibert et al., 2010; Simon et al., 2011; Artanto et al., 2012). However, such techniques are unable to illustrate dynamic changes in liquid absorbent composition (van der Ham et al., 2014a; van Eckeveld et al., 2014). For dynamic PCC operation, the ability to monitor transient behavior in the liquid phase will be critical.

A number of studies are investigating alternative methods for online monitoring of liquid composition that are robust, low cost, and provide accurate measurements. Pilot plants have implemented calibrated density meters for real-time measurements of liquid CO_2 loading. Although this method is limited in accuracy, it enables operators to observe the instantaneous CO_2 composition changes in the liquid phase for better process control (Seibert et al., 2010; Bui et al., 2014a). Predictive accuracy of absorbent composition measurements can be improved using Fourier transform infrared (FTIR) spectroscopy combined with a multivariate chemometric method (Einbu et al., 2011; Geers et al., 2011). However, FTIR is expensive and the results are inadequate when concentrations are beyond the calibration limits, or when a noncalibrated component is present in the solution (van der Ham et al., 2014a; van Eckeveld et al., 2014).

Another approach to determine absorbent composition uses simple inline analytical techniques to measure real-time absorbent properties (eg, density, viscosity, and conductivity) in combination with a multivariate chemometric method. Depending on the liquid phase component, concentration will have a strong correlation with one or more different absorbent properties. For example, MEA concentration demonstrates a strong relationship with the liquid properties of sonic speed and refractive index, while CO_2 concentration strongly correlates with density, conductivity, and refractive index. Measurements of multiple absorbent properties have been incorporated with a multivariate chemometric technique to develop models that can predict real-time CO_2 and MEA concentration very accurately (van der Ham et al., 2014a,b; van Eckeveld et al., 2014). Under pilot plant conditions, the chemometric method can determine CO_2 concentration within 4.3% accuracy, whereas AMP and PZ concentrations are measured within 2.1% and 3.5% accuracy, respectively. Such a strategy significantly improves accuracy of measurements and reduces costs due to the simplicity of the analytical techniques (Kachko et al., 2015).

The presence of acid gases (H_2SO_4 and HNO_3 in liquid) can have a small effect on the measurement accuracy of online techniques. UV—visible spectroscopy, in particular, is highly sensitive to HNO_3. The effectiveness of most online monitoring techniques is affected by the presence of oxidative degradation products (ammonia, formic acid, formaldehyde, acetic acid, and oxalic acid) (van der Ham et al., 2014a; van Eckeveld et al., 2014). Conversely, 1-(2-hydroxyethyl)-2-imidazolidinone, a product from carbamate polymerization, has little affect (van Eckeveld et al., 2014). Previous studies of online liquid analysis have reduced the impact of amine degradation by reclaiming degraded absorbent (Kachko et al., 2015) or applying corrective calibration to measurements (van der Ham et al., 2014b). The corrective calibration model by van der Ham et al. (2014b) improved liquid concentration measurements for the laboratory set-up; however, MEA measurements in the industrial process were unreliable. Additional contaminants (eg, particulates or high levels of amine degradation products) in industry may reduce the reliability of measurements.

Although various online liquid analysis techniques have been successfully demonstrated experimentally, further development is necessary before they can be applied to commercial-scale PCC plants. Detailed economic analysis is also required to determine the balance between cost and accuracy of the proposed techniques. Online monitoring techniques can become more robust if the following are considered: (1) affect of all types of pollutants (degradation products, acid gases, and particulates), (2) degree and type of amine degradation, (3) calibration with already available process data, and (4) development of techniques for various absorbents (van der Ham et al., 2014b). Furthermore, research is required in PCC plants to define optimal locations for the placement of probes and measurement devices.

24.6 Concluding remarks and outlook

Dynamic (or flexible) PCC operation is necessary due to the transient nature of electricity demand and CO_2 pricing. It can also counteract the changes that occur in flue gas composition and absorbent over time. Current studies on the feasibility of flexible PCC operation focus on the influence of either economic or technical motivations, and assume that these motivations act independently. Future research should consider both the economic and technical influences when optimizing dynamic operation strategies. The selection of appropriate response times and flexible operation strategies is a balance between satisfying both the economic benefits provided through electricity/CO_2 pricing, and the inherent technical changes in the composition of feed flue gas and amine liquid absorbent.

Dynamic modeling and pilot plant experiments both have a critical role in the optimization of dynamic PCC operation. The predictive accuracy of a model depends on the reliability of the operational plant data used for model validation and calibration. Thus, dynamic PCC models require validation with dynamic operational data (eg, from a laboratory or pilot plant). There is an urgent need for more dynamic pilot plant results to become available for model validation. The accuracy of previously developed dynamic PCC models can be improved by iteratively validating them with dynamic data sets from various PCC pilot plants.

A lack of practical experience makes dynamic operation of PCC plants challenging. A key focus is assurance of reliable data. Thus, important considerations when designing a dynamic pilot plant operating procedure include the following:

- Equip the PCC plant with optimal measurement techniques for online monitoring of vital process parameters, particularly those essential for model validation (eg, absorbent CO_2 concentration).
- Take into account the affect of plant scale on the process dynamics (ie, smaller scale equals faster dynamics).
- Conduct replicate runs. This requires consistent operating set-point conditions for liquid and gas flow rates, stripper reboiler temperature, and heating and cooling duties.
- Reduce heat losses by using adequate thermal insulation.
- Keep the absorbent concentration constant; it needs careful monitoring and consequential adjustment to reach the desired value.
- Minimize ambient temperature effects; operation days should have similar ambient conditions.
- Reduce the influence of absorbent degradation; conduct runs on same day or across consecutive days to ensure the same degree of degradation.

Future research into dynamic PCC operation should investigate the:

1. technical implications of process disturbances during flexible operation
2. affect of variable input streams (flue gas and absorbent)
3. feasibility of proposed flexible operation strategies on a basis of both economic and technical criteria
4. optimization of dynamic PCC operation for industrial-scale application
5. affects of amine degradation on PCC operability.

References

Abu-Zahra, M.R.M., Niederer, J.P.M., Feron, P.H.M., Versteeg, G.F., 2007a. CO_2 capture from power plants: part II. A parametric study of the economical performance based on monoethanolamine. International Journal of Greenhouse Gas Control 1 (2), 135−142.

Abu-Zahra, M.R.M., Schneiders, L.H.J., Niederer, J.P.M., Feron, P.H.M., Versteeg, G.F., 2007b. CO_2 capture from power plants: part I. A parametric study of the technical performance based on monoethanolamine. International Journal of Greenhouse Gas Control 1 (1), 37−46.

Åkesson, J., Laird, C.D., Lavedan, G., Prölß, K., Tummescheit, H., Velut, S., Zhu, Y., 2012. Nonlinear model predictive control of a CO_2 post-combustion absorption unit. Chemical Engineering & Technology 35 (3), 445−454.

Alie, C., Douglas, P., Croiset, E., 2006. Simulation and optimization of a coal-fired power plant with integrated CO_2 capture using MEA scrubbing. In: The 8th International Conference on Greenhouse Gas Control Technologies (GHGT-8), Trondheim, Norway.

Artanto, Y., Attalla, M.I., Cottrell, A., Jansen, J., McGregor, J.M., Meuleman, E.E.B., Morgan, S., Osborn, M., Pearson, P., Wardhaugh, L., Feron, P.H.M., 2009. A preliminary evaluation of post-combustion CO_2 capture performance in a pilot plant test using monoethanolamine at a lignite-fuelled power station in Australia. In: Fourth International Conference of Clean Coal Technologies for Our Future (CCT2009), Dresden, Germany.

Artanto, Y., Jansen, J., Pearson, P., Do, T., Cottrell, A., Meuleman, E., Feron, P., 2012. Performance of MEA and amine-blends in the CSIRO PCC pilot plant at Loy Yang power in Australia. Fuel 101, 264−275.

Biliyok, C., Lawal, A., Wang, M., Seibert, F., 2012a. Dynamic modelling, validation and analysis of post-combustion chemical absorption CO_2 capture plant. International Journal of Greenhouse Gas Control 9, 428−445.

Biliyok, C., Lawal, A., Wang, M., Seibert, F., 2012b. Dynamic validation of model for post-combustion chemical absorption CO_2 capture plant. In: Ian David Lockhart, B., Michael, F. (Eds.), 22nd European Symposium on Computer Aided Chemical Engineering, London, UK, Computer Aided Chemical Engineering, vol. 30, pp. 807−811.

Blarke, M.B., Dotzauer, E., 2011. Intermittency-friendly and high-efficiency cogeneration: operational optimisation of cogeneration with compression heat pump, flue gas heat recovery, and intermediate cold storage. Energy 36 (12), 6867−6878.

Botero, C., Finkenrath, M., Bartlett, M., Chu, R., Choi, G., Chinn, D., 2008. Redesign, optimization, and economic evaluation of a natural gas combined cycle with the best integrated technology CO_2 capture. 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9), Washington DC, United States. Energy Procedia 1, 3835−3842 (2009).

Bougie, F., Iliuta, M.C., 2014. Stability of aqueous amine solutions to thermal and oxidative degradation in the absence and the presence of CO_2. International Journal of Greenhouse Gas Control 29, 16−21.

Bui, M., Gunawan, I., Verheyen, T.V., Meuleman, E., Feron, P., 2014a. Dynamic operation of post-combustion CO_2 capture in Australian coal-fired power plants. 12th International Conference on Greenhouse Gas Control Technologies (GHGT-12), Austin, Texas, USA. Energy Procedia 63, 1368−1375.

Bui, M., Gunawan, I., Verheyen, V., Feron, P., Meuleman, E., Adeloju, S., 2014b. Dynamic modelling and optimisation of flexible operation in post-combustion CO_2 capture plants—A review. Computers & Chemical Engineering 61, 245−265.

Bui, M., Gunawan, I., Verheyen, V., Feron, P., Meuleman, E., 2016. Flexible operation of CSIRO's post-combustion CO_2 capture pilot plant at the AGL Loy Yang power station. Int. J. Greenhouse Gas Control, http://dx.doi.org/10.1016/j.ijggc.2015.12.016.

Campbell, M., 2014. Technology innovation & advancements for Shell Cansolv CO_2 capture solvents. 12th International Conference on Greenhouse Gas Control Technologies (GHGT-12), Austin, Texas, United States. Energy Procedia 63, 801−807.

Chalmers, H., Gibbins, J., 2007. Initial evaluation of the impact of post-combustion capture of carbon dioxide on supercritical pulverised coal power plant part load performance. Fuel 86 (14 SPEC. ISS.), 2109−2123.

Chalmers, H., Leach, M., Gibbins, J., 2010. Built-in flexibility at retrofitted power plants: what is it worth and can we afford to ignore it?. 10th International Conference on Greenhouse Gas Control Technologies (GHGT-10), Amsterdam, The Netherlands Energy Procedia 4, 2596−2603 (2011).

Chalmers, H., Lucquiaud, M., Gibbins, J., Leach, M., 2009. Flexible operation of coal fired power plants with postcombustion capture of carbon dioxide. Journal of Environmental Engineering 135 (6), 449−458.

Chapel, D.G., Mariz, C.L., Ernest, J., 1999. Recovery of CO_2 from flue gases: commercial trends. In: Canadian Society of Chemical Engineers Annual Meeting. Fluor Daniel Inc., Saskatchewan, Canada.

Chawla, J.M., 1999. Waste heat recovery from flue gases with substantial dust load. Chemical Engineering and Processing: Process Intensification 38 (4−6), 365−371.

Chen, Q., Kang, C., Xia, Q., 2010. Modeling flexible operation mechanism of CO_2 capture power plant and its effects on power-system operation. IEEE Transactions on Energy Conversion 25 (3), 853−861.

Cohen, S.M., Rochelle, G.T., Webber, M.E., 2010a. Optimal operation of flexible post-combustion CO_2 capture in response to volatile electricity prices10th International Conference on Greenhouse Gas Control Technologies (GHGT-10), Amsterdam, Netherlands. Energy Procedia 4, 2604−2611 (2011).

Cohen, S.M., Rochelle, G.T., Webber, M.E., 2010b. Turning CO_2 capture on and off in response to electric grid demand: a baseline analysis of emissions and economics. Journal of Energy Resources Technology 132 (2), 021003-1−021003-8.

Cohen, S.M., Rochelle, G.T., Webber, M.E., 2012a. Optimal CO_2 capture operation in an advanced electric grid. 11th International Conference on Greenhouse Gas Control Technologies (GHGT-11), Kyoto, Japan. Energy Procedia 37, 2585−2594 (2013).

Cohen, S.M., Rochelle, G.T., Webber, M.E., 2012b. Optimizing post-combustion CO_2 capture in response to volatile electricity prices. International Journal of Greenhouse Gas Control 8, 180−195.

Cohen, S.M., Webber, M.E., Rochelle, G.T., 2012c. The impact of electricity market conditions on the value of flexible CO_2 capture. Proceedings from ASME International Mechanical Engineering Congress and Exposition (IMECE), Texas, United States. The American Society of Mechanical Engineers (ASME) 6, 581−593.

Copplestone, J.C., Kirk, C.M., Death, S.L., Betteridge, N.G., Fellows, S.M., 2008. Production of Chemicals: Ammonia and Urea Production. New Zealand Institute of Chemistry, NZIC.

Dave, N., Do, T., Palfreyman, D., Feron, P.H.M., 2011a. Impact of liquid absorption process development on the costs of post-combustion capture in Australian coal-fired power stations. Chemical Engineering Research and Design 89 (9), 1625−1638.

Dave, N., Do, T., Palfreyman, D., Feron, P.H.M., 2011b. Impact of post combustion capture of CO_2 on existing and new Australian coal-fired power plants. Energy Procedia 4, 2005−2019.

Dietl, K., Joos, A., Schmitz, G., 2012. Dynamic analysis of the absorption/desorption loop of a carbon capture plant using an object-oriented approach. Chemical Engineering and Processing: Process Intensification 52, 132−139.

Dillon, D., Grace, D., Maxson, A., Børter, K., Augeli, J.N., Woodhouse, S.N., Aspelund, G., 2012. Post-combustion capture on natural gas combined cycle plants: a technical and economical evaluation of retrofit, new build, and the application of exhaust gas recycle.

11th International Conference on Greenhouse Gas Control Technologies (GHGT-11), Kyoto, Japan. Energy Procedia 37, 2397–2405 (2013).

DOE, 2015. Petra Nova - W.A. Parish Project (Online). Office of Fossil Energy, U.S. Department of Energy (DOE), Washington DC, US. Available: http://energy.gov/fe/petra-nova-wa-parish-project (accessed 04.08.15.).

Dugas, R.E., 2006. Pilot Plant Study of Carbon Dioxide Capture by Aqueous Monoethanolamine (Masters thesis). The University of Texas at Austin.

Dwivedi, P., Gaur, V., Sharma, A., Verma, N., 2004. Comparative study of removal of volatile organic compounds by cryogenic condensation and adsorption by activated carbon fiber. Separation and Purification Technology 39 (1–2), 23–37.

van Eckeveld, A.C., van der Ham, L.V., Geers, L.F.G., van den Broeke, L.J.P., Boersma, B.J., Goetheer, E.L.V., 2014. Online monitoring of the solvent and absorbed acid gas concentration in a CO_2 capture process using monoethanolamine. Industrial & Engineering Chemistry Research 53 (13), 5515–5523.

Einbu, A., Ciftja, A.F., Grimstvedt, A., Zakeri, A., Svendsen, H.F., 2011. Online analysis of amine concentration and CO_2 loading in MEA solutions by ATR-FTIR spectroscopy. The 6th Trondheim Conference on CO_2 Capture, Transport and Storage, Trondheim, Norway. Energy Procedia 23, 55–63 (2012).

Enaasen Flø, N., Knuutila, H., Kvamsdal, H.M., Hillestad, M., 2015. Dynamic model validation of the post-combustion CO_2 absorption process. International Journal of Greenhouse Gas Control 41, 127–141.

Enaasen, N., Tobiesen, A., Kvamsdal, H.M., Hillestad, M., 2012. Dynamic modeling of the solvent regeneration part of a CO_2 capture plant. 11th International Conference on Greenhouse Gas Control Technologies (GHGT-11), Kyoto, Japan. Energy Procedia 37, 2058–2065 (2013).

Eslick, J.C., Miller, D.C., 2011. A multi-objective analysis for the retrofit of a pulverized coal power plant with a CO_2 capture and compression process. Computers & Chemical Engineering 35 (8), 1488–1500.

Faber, R., Köpcke, M., Biede, O., Knudsen, J.N., Andersen, J., 2010. Open-loop step responses for the MEA post-combustion capture process: experimental results from the Esbjerg pilot plant. 10th International Conference on Greenhouse Gas Control Technologies (GHGT-10), Amsterdam, The Netherlands. Energy Procedia 4, 1427–1434 (2011).

Feintuch, H.M., Treybal, R.E., 1978. The design of adiabatic packed towers for gas absorption and stripping. Industrial & Engineering Chemistry Process Design and Development 17 (4), 505–513.

Fosbøl, P.L., Gaspar, J., Ehlers, S., Kather, A., Briot, P., Nienoord, M., Khakharia, P., Moullec, Y.L., Berglihn, O.T., Kvamsdal, H., 2014. Benchmarking and comparing first and second generation post combustion CO_2 capture technologies. 12th International Conference on Greenhouse Gas Control Technologies (GHGT-12), Austin, Texas, United States. Energy Procedia 63, 27–44.

Garðarsdóttir, S.Ó., Normann, F., Andersson, K., Prölß, K., Emilsdóttir, S., Johnsson, F., 2015. Post-combustion CO_2 capture applied to a state-of-the-art coal-fired power plant—the influence of dynamic process conditions. International Journal of Greenhouse Gas Control 33, 51–62.

Gáspár, J., Cormoş, A.-M., 2012. Dynamic modeling and absorption capacity assessment of CO_2 capture process. International Journal of Greenhouse Gas Control 8, 45–55.

Geers, L.F.G., van de Runstraat, A., Joh, R., Schneider, R.D., Goetheer, E.L.V., 2011. Development of an online monitoring method of a CO_2 capture process. Industrial & Engineering Chemistry Research 50 (15), 9175–9180.

Gibbins, J., Chalmers, H., Lucquiaud, M., Li, J., McGlashan, N., Liang, X., Davison, J., 2011. Techno-economic assessment of CO_2 capture retrofit to existing power plants. Energy Procedia 4, 1835−1842.

Gibbins, J.R., Crane, R.I., 2004a. Preliminary assessment of electricity costs for existing pulverized fuel plant retrofitted with an advanced supercritical boiler and turbine and solvent CO_2 capture. Proceedings of the Institution of Mechanical Engineers, Part A. Journal of Power and Energy 218 (7), 551−555.

Gibbins, J.R., Crane, R.I., 2004b. Scope for reductions in the cost of CO_2 capture using flue gas scrubbing with amine solvents. Proceedings of the Institution of Mechanical Engineers, Part A. Journal of Power and Energy 218 (4), 231−239.

Greer, T., Bedelbayev, A., Igreja, J.M., Gomes, J.F., Lie, B., 2010. A simulation study on the abatement of CO_2 emissions by de-absorption with monoethanolamine. Environmental Technology 31 (1), 107−115.

van der Ham, L.V., Bakker, D.E., Geers, L.F.G., Goetheer, E.L.V., 2014a. Inline monitoring of CO_2 absorption processes using simple analytical techniques and multivariate modeling. Chemical Engineering & Technology 37 (2), 221−228.

van der Ham, L.V., van Eckeveld, A.C., Goetheer, E.L.V., 2014b. Online monitoring of dissolved CO_2 and MEA concentrations: effect of solvent degradation on predictive accuracy. 12th International Conference on Greenhouse Gas Control Technologies (GHGT-12), Austin, Texas, United States. Energy Procedia 63, 1223−1228.

Harkin, T., Hoadley, A., Hooper, B., 2009. Process integration analysis of a brown coal-fired power station with CO_2 capture and storage and lignite drying. Energy Procedia 1 (1), 3817−3825.

Harkin, T., Hoadley, A., Hooper, B., 2010. Reducing the energy penalty of CO_2 capture and compression using pinch analysis. Journal of Cleaner Production 18 (9), 857−866.

Hasan, M.M.F., Baliban, R.C., Elia, J.A., Floudas, C.A., 2012. Modeling, simulation, and optimization of postcombustion CO_2 capture for variable feed concentration and flow rate. 1. Chemical absorption and membrane processes. Industrial & Engineering Chemistry Research 51 (48), 15642−15664.

Higler, A., Taylor, R., Krishna, R., 1998. Modeling of a reactive separation process using a nonequilibrium stage model. Computers and Chemical Engineering 22 (Suppl. 1), S111−S118.

Hossein Sahraei, M., Ricardez-Sandoval, L.A., 2014. Controllability and optimal scheduling of a CO_2 capture plant using model predictive control. International Journal of Greenhouse Gas Control 30, 58−71.

House, K.Z., Harvey, C.F., Aziz, M.J., Schrag, D.P., 2009. The energy penalty of post-combustion CO_2 capture & storage and its implications for retrofitting the U.S. installed base. Energy & Environmental Science 2 (2), 193−205.

Husebye, J., Anantharaman, R., Fleten, S.-E., 2011. Techno-economic assessment of flexible solvent regeneration & storage for base load coal-fired power generation with post combustion CO_2 capture. Energy Procedia 4, 2612−2619.

Islam, M.S., Yusoff, R., Ali, B.S., Islam, M.N., Chakrabarti, M.H., 2011. Degradation studies of amines and alkanolamines during sour gas treatment process. International Journal of Physical Sciences 6 (25), 5877−5890.

Jayarathna, S.A., Lie, B., Melaaen, M.C., 2013a. Amine based CO_2 capture plant: dynamic modeling and simulations. International Journal of Greenhouse Gas Control 14, 282−290.

Jayarathna, S.A., Lie, B., Melaaen, M.C., 2013b. Dynamic modelling of the absorber of a post-combustion CO_2 capture plant: modelling and simulations. Computers & Chemical Engineering 53, 178−189.

Kachko, A., van der Ham, L.V., Geers, L.F.G., Huizinga, A., Rieder, A., Abu-Zahra, M.R.M., Vlugt, T.J.H., Goetheer, E.L.V., 2015. Real-time process monitoring of CO_2 capture by aqueous AMP-PZ using chemometrics: pilot plant demonstration. Industrial & Engineering Chemistry Research 54 (21), 5769–5776.

Karimi, M., Hillestad, M., Svendsen, H.F., 2012. Investigation of the dynamic behavior of different stripper configurations for post-combustion CO_2 capture. International Journal of Greenhouse Gas Control 7, 230–239.

Khakharia, P., Brachert, L., Mertens, J., Anderlohr, C., Huizinga, A., Fernandez, E.S., Schallert, B., Schaber, K., Vlugt, T.J.H., Goetheer, E., 2015. Understanding aerosol based emissions in a post combustion CO_2 capture process: parameter testing and mechanisms. International Journal of Greenhouse Gas Control 34, 63–74.

Khalilpour, R., Abbas, A., 2011. HEN optimization for efficient retrofitting of coal-fired power plants with post-combustion carbon capture. International Journal of Greenhouse Gas Control 5 (2), 189–199.

Knudsen, J.N., Jensen, J.N., Vilhelmsen, P.-J., Biede, O., 2009. Experience with CO_2 capture from coal flue gas in pilot-scale: testing of different amine solvents. Energy Procedia 1 (1), 783–790.

Krishna, R., Standart, G.L., 1976. A multicomponent film model incorporating a general matrix method of solution to the Maxwell-Stefan equations. AIChE Journal 22 (2), 383–389.

Krishnamurthy, R., Taylor, R., 1985a. A nonequilibrium stage model of multicomponent separation processes. Part I: model description and method of solution. AIChE Journal 31 (3), 449–456.

Krishnamurthy, R., Taylor, R., 1985b. A nonequilibrium stage model of multicomponent separation processes. Part II: comparison with experiment. AIChE Journal 31 (3), 456–465.

Kumar, N., 2014. Improving the flexibility of coal-fired power plants. Power Engineering (Online). Available: http://www.power-eng.com/articles/print/volume-118/issue-9/features/improving-the-flexibility-of-coal-fired-power-plants.html (accessed 16.07.15.).

Kvamsdal, H.M., Chikukwa, A., Hillestad, M., Zakeri, A., Einbu, A., 2010. A comparison of different parameter correlation models and the validation of an MEA-based absorber model. 10th International Conference on Greenhouse Gas Control Technologies (GHGT-10), Amsterdam, Netherlands. Energy Procedia 4, 1526–1533 (2011).

Kvamsdal, H.M., Jakobsen, J.P., Hoff, K.A., 2009. Dynamic modeling and simulation of a CO_2 absorber column for post-combustion CO_2 capture. Chemical Engineering and Processing: Process Intensification 48 (1), 135–144.

Lawal, A., Wang, M., Stephenson, P., 2010a. Investigating the dynamic response of CO_2 chemical absorption process in enhanced-O_2 coal power plant with post-combustion CO_2 capture. 10th International Conference on Greenhouse Gas Control Technologies (GHGT-10), Amsterdam, The Netherlands. Energy Procedia 4, 1035–1042 (2011).

Lawal, A., Wang, M., Stephenson, P., Koumpouras, G., Yeung, H., 2010b. Dynamic modelling and analysis of post-combustion CO_2 chemical absorption process for coal-fired power plants. Fuel 89 (10), 2791–2801.

Lawal, A., Wang, M., Stephenson, P., Obi, O., 2012. Demonstrating full-scale post-combustion CO_2 capture for coal-fired power plants through dynamic modelling and simulation. Fuel 101, 115–128.

Lawal, A., Wang, M., Stephenson, P., Yeung, H., 2009a. Dynamic modeling and simulation of CO_2 chemical absorption process for coal-fired power plants10th International Symposium on Process Systems Engineering-PSE2009, Brazil. Computer Aided Chemical Engineering 27, 1725–1730.

Lawal, A., Wang, M., Stephenson, P., Yeung, H., 2009b. Dynamic modelling of CO_2 absorption for post combustion capture in coal-fired power plants. Fuel 88 (12), 2455−2462.

Léonard, G., Mogador, B.C., Belletante, S., Heyen, G., 2013. Dynamic modelling and control of a pilot plant for post-combustion CO_2 capture. In: Kraslawski, A., Turunen, I. (Eds.), 23rd European Symposium on Computer Aided Process Engineering (ESCAPE 23), Lappeenranta, Finland. Computer Aided Chemical Engineering 32, 451−456.

Lepaumier, H., Picq, D., Carrette, P.L., 2008. Degradation study of new solvents for CO_2 capture in post-combustion. 9th International Conference on Greenhouse Gas Control, Washington DC, USA. Energy Procedia 1, 893−900 (2009).

Levin, Y., dos Santos, A.P., Diehl, A., 2009. Ions at the air-water interface: an end to a hundred-year-old mystery? Physical Review Letters 103 (25), 257802.

Li, C.-Z., 2004. Chapter 1-Introduction. In: Li, C.-Z. (Ed.), Advances in the Science of Victorian Brown Coal. Elsevier Science, Amsterdam, pp. 1−10.

Lima, E.R.A., Melo, B.M.D., Baptista, L.T., Paredes, M.L.L., 2013. Specific ion effects on the interfacial tension of water/hydrocarbon systems. Brazilian Journal of Chemical Engineering 30, 55−62.

Lin, Y.-J., Pan, T.-H., Wong, D.S.-H., Jang, S.-S., Chi, Y.-W., Yeh, C.-H., 2011. Plantwide control of CO_2 capture by absorption and stripping using monoethanolamine solution. Industrial & Engineering Chemistry Research 50 (3), 1338−1345.

Lin, Y.-J., Wong, D.S.-H., Jang, S.-S., Ou, J.-J., 2012. Control strategies for flexible operation of power plant with CO_2 capture plant. AIChE Journal 58 (9), 2697−2704.

Lucquiaud, M., Gibbins, J., 2010. Steam cycle options for the retrofit of coal and gas power plants with postcombustion capture. 10th International Conference on Greenhouse Gas Control Technologies (GHGT-10), Amsterdam, The Netherlands. Energy Procedia 4, 1812−1819 (2011).

Luu, M.T., Abdul Manaf, N., Abbas, A., 2015. Dynamic modelling and control strategies for flexible operation of amine-based post-combustion CO_2 capture systems. International Journal of Greenhouse Gas Control 39, 377−389.

Mac Dowell, N., Samsatli, N.J., Shah, N., 2013. Dynamic modelling and analysis of an amine-based post-combustion CO_2 capture absorption column. International Journal of Greenhouse Gas Control 12, 247−258.

Mac Dowell, N., Shah, N., 2013. Identification of the cost-optimal degree of CO_2 capture: an optimisation study using dynamic process models. International Journal of Greenhouse Gas Control 13, 44−58.

Mac Dowell, N., Shah, N., 2015. The multi-period optimisation of an amine-based CO_2 capture process integrated with a super-critical coal-fired power station for flexible operation. Computers & Chemical Engineering 74, 169−183.

Mahasenan, N., Brown, D.R., 2004. Beyond the big picture: characterizaton of CO_2-laden streams and implications for capture technologies. In: Wilson, M., Morris, T., Gale, J., Thambimuthu, K. (Eds.), 7th International Conference on Greenhouse Gas Control Technologies, Greenhouse Gas Control Technologies, vol. 7. Elsevier Science Ltd., Vancouver, Canada, pp. 1817−1820 (2005).

Mangalapally, H.P., Notz, R., Hoch, S., Asprion, N., Sieder, G., Garcia, H., Hasse, H., 2008. Pilot plant experimental studies of post combustion CO_2 capture by reactive absorption with MEA and new solvents. 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9), Washington DC, USA. Energy Procedia 1, 963−970 (2009).

Masuko, T., Magill, J.H., 1988. A comprehensive expression for temperature dependence of liquid viscosity. Nihon Reoroji Gakkaishi (Journal of the Society of Rheology, Japan) 16 (1), 22−26.

Moser, P., Schmidt, S., Sieder, G., Garcia, H., Stoffregen, T., 2011. Performance of MEA in a long-term test at the post-combustion capture pilot plant in Niederaussem. International Journal of Greenhouse Gas Control 5 (4), 620−627.

Moser, P., Schmidt, S., Stahl, K., Vorberg, G., Lozano, G.A., Stoffregen, T., Rösler, F., 2014. Demonstrating emission reduction − results from the post-combustion capture pilot plant at Niederaussem. 12th International Conference on Greenhouse Gas Control Technologies (GHGT-12). Energy Procedia 63, 902−910.

Moser, P., Schmidt, S., Wallus, S., Ginsberg, T., Sieder, G., Clausen, I., Palacios, J.G., Stoffregen, T., Mihailowitsch, D., 2012. Enhancement and long-term testing of optimised post-combustion capture technology - results of the second phase of the testing programme at the Niederaussem pilot plant. 11th International Conference on Greenhouse Gas Control Technologies (GHGT-11), Kyoto. Japan. Energy Procedia 37, 2377−2388 (2013).

Nittaya, T., Douglas, P.L., Croiset, E., Ricardez-Sandoval, L.A., 2014a. Dynamic modeling and evaluation of an industrial-scale CO_2 capture plant using monoethanolamine absorption processes. Industrial & Engineering Chemistry Research 53 (28), 11411−11426.

Nittaya, T., Douglas, P.L., Croiset, E., Ricardez-Sandoval, L.A., 2014b. Dynamic modelling and control of MEA absorption processes for CO_2 capture from power plants. Fuel 116, 672−691.

Panahi, M., Skogestad, S., 2012. Economically efficient operation of CO_2 capturing process. Part II. Design of control layer. Chemical Engineering and Processing: Process Intensification 52, 112−124.

Patiño-Echeverri, D., Hoppock, D.C., 2012. Reducing the energy penalty costs of postcombustion CCS systems with amine-storage. Environmental Science & Technology 46 (2), 1243−1252.

Pauley, C.R., 1983. Feasibility of CO_2 recovery from flue gas. In: American Institute of Chemical Engineers, Summer National Meeting, Denver, USA, pp. 1−19.

Peng, J., Edgar, T.F., Bruce Eldridge, R., 2003. Dynamic rate-based and equilibrium models for a packed reactive distillation column. Chemical Engineering Science 58 (12), 2671−2680.

Peng, J., Lextrait, S., Edgar, T.F., Eldridge, R.B., 2002. A comparison of steady-state equilibrium and rate-based models for packed reactive distillation columns. Industrial and Engineering Chemistry Research 41 (11), 2735−2744.

Posch, S., Haider, M., 2013. Dynamic modeling of CO_2 absorption from coal-fired power plants into an aqueous monoethanolamine solution. Chemical Engineering Research and Design 91 (6), 977−987.

Prölß, K., Tummescheit, H., Velut, S., Åkesson, J., 2010. Dynamic model of a post-combustion absorption unit for use in a non-linear model predictive control scheme. 10th International Conference on Greenhouse Gas Control Technologies (GHGT-10), Amsterdam, The Netherlands. Energy Procedia 4, 2620−2627 (2011).

Rao, A.B., Rubin, E.S., 2002. A technical, economic, and environmental assessment of amine-based CO_2 capture technology for power plant greenhouse gas control. Environmental Science and Technology 36 (20), 4467−4475.

Rao, A.B., Rubin, E.S., 2006. Identifying cost-effective CO_2 control levels for amine-based CO_2 capture systems. Industrial & Engineering Chemistry Research 45 (8), 2421−2429.

Romeo, L.M., Espatolero, S., Bolea, I., 2008. Designing a supercritical steam cycle to integrate the energy requirements of CO_2 amine scrubbing. International Journal of Greenhouse Gas Control 2 (4), 563−570.

Schiffer, H.-W., 2014. The flexibility of German coal-fired power plants amid increased renewables. Cornerstone - The Official Journal of the World Coal Industry (Online). Available: http://cornerstonemag.net/the-flexibility-of-german-coal-fired-power-plants-amid-increased-renewables/ (accessed 15.07.15.).

Schneider, R., Kenig, E.Y., Górak, A., 1999. Dynamic modelling of reactive absorption with the Maxwell-Stefan approach. Chemical Engineering Research and Design 77 (7), 633−638.

Seeton, C., 2006. Viscosity−temperature correlation for liquids. Tribology Letters 22 (1), 67−78.

Seibert, F., Chen, E., Perry, M., Briggs, S., Montgomery, R., Rochelle, G., 2010. UT/SRP CO_2 capture pilot plant — operating experience and procedures. 10th International Conference on Greenhouse Gas Control Technologies, Amsterdam, The Netherlands. Energy Procedia 4, 1616−1623 (2011).

Sharma, S.D., Azzi, M., 2014. A critical review of existing strategies for emission control in the monoethanolamine-based carbon capture process and some recommendations for improved strategies. Fuel 121, 178−188.

Simon, L.L., Elias, Y., Puxty, G., Artanto, Y., Hungerbuhler, K., 2011. Rate based modeling and validation of a carbon-dioxide pilot plant absorbtion column operating on monoethanolamine. Chemical Engineering Research and Design 89 (9), 1684−1692.

Sipöcz, N., Jonshagen, K., Assadi, M., Genrup, M., 2011. Novel high-performing single-pressure combined cycle with CO_2 capture. Journal of Engineering for Gas Turbines and Power 133 (4), 041701-1−041701-8.

Stéphenne, K., 2014. Start-up of world's first commercial post-combustion coal fired CCS project: contribution of Shell Cansolv to Sask Power Boundary Dam ICCS Project. 12th International Conference on Greenhouse Gas Control Technologies (GHGT-12), Austin, Texas, United States. Energy Procedia 63, 6106−6110.

Stöver, B., Bergins, C., Klebes, J., 2010. Optimized post combustion carbon capturing on coal fired power plants. 10th International Conference on Greenhouse Gas Control Technologies, Amsterdam, The Netherlands. Energy Procedia 4, 1637−1643 (2011).

Supap, T., Idem, R., Tontiwachwuthikul, P., Saiwan, C., 2006. Analysis of monoethanolamine and its oxidative degradation products during CO_2 absorption from flue gases: A comparative study of GC-MS, HPLC-RID, and CE-DAD analytical techniques and possible optimum combinations. Industrial & Engineering Chemistry Research 45 (8), 2437−2451.

Taylor, R., Webb, D.R., 1981. Film models for multicomponent mass transfer; computational methods: the exact solution of the Maxwell-Stefan equations. Computers & Chemical Engineering 5 (2), 61−73.

Thitakamol, B., Veawab, A., 2008. Foaming behavior in CO_2 absorption process using aqueous solutions of single and blended alkanolamines. Industrial & Engineering Chemistry Research 47 (1), 216−225.

Thitakamol, B., Veawab, A., 2009. Foaming model for CO_2 absorption process using aqueous monoethanolamine solutions. Colloids and Surfaces A: Physicochemical and Engineering Aspects 349 (1−3), 125−136.

Thitakamol, B., Veawab, A., Aroonwilas, A., 2008. Foaming in amine-based CO_2 capture process: experiment, modeling and simulation. 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9), Washington DC, USA. Energy Procedia 1, 1381−1386 (2009).

Tobiesen, F.A., Juliussen, O., Svendsen, H.F., 2008. Experimental validation of a rigorous desorber model for post-combustion capture. Chemical Engineering Science 63 (10), 2641−2656.

Tobiesen, F.A., Svendsen, H.F., Juliussen, O., 2007. Experimental validation of a rigorous absorber model for CO_2 postcombustion capture. AIChE Journal 53 (4), 846−865.

Treybal, R.E., 1969. Adiabatic gas absorption and stripping in packed towers. Industrial & Engineering Chemistry 61 (7), 36−41.

Veltman, K., Singh, B., Hertwich, E.G., 2010. Human and environmental impact assessment of postcombustion CO_2 capture focusing on emissions from amine-based scrubbing solvents to air. Environmental Science and Technology 44 (4), 1496−1502.

Voice, A.K., Rochelle, G.T., 2013. Products and process variables in oxidation of monoethanolamine for CO_2 capture. International Journal of Greenhouse Gas Control 12, 472−477.

van der Wijk, P.C., Brouwer, A.S., van den Broek, M., Slot, T., Stienstra, G., van der Veen, W., Faaij, A.P.C., 2014. Benefits of coal-fired power generation with flexible CCS in a future northwest European power system with large scale wind power. International Journal of Greenhouse Gas Control 28, 216−233.

Wiley, D.E., Ho, M.T., Donde, L., 2010. Technical and economic opportunities for flexible CO_2 capture at Australian black coal fired power plants. 10th International Conference on Greenhouse Gas Control Technologies (GHGT-10), Amsterdam, The Netherlands. Energy Procedia 4, 1893−1900 (2011).

Wilson, M., Tontiwachwuthikul, P., Chakma, A., Idem, R., Veawab, A., Aroonwilas, A., Gelowitz, D., Henni, A., Mahinpey, N., 2005a. The International Test Centre for carbon dioxide capture (ITC). In: Rubin, E.S., Keith, D.W., Gilboy, C.F., Wilson, M., Morris, T., Gale, J., Thambimuthu, K. (Eds.), Greenhouse Gas Control Technologies 7, Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies - September 2004. Oxford: Elsevier Science Ltd, Vancouver, Canada, pp. 1807−1810.

Wilson, M., Tontiwachwuthikul, P., Chakma, A., Idem, R., Veawab, A., Aroonwilas, A., Gelowitz, D., Stobbs, R., 2005b. Evaluation of the CO_2 capture performance of the University of Regina CO_2 technology development plant and the boundary dam CO_2 demonstration plant. In: Rubin, E.S., Keith, D.W., Gilboy, C.F., Wilson, M., Morris, T., Gale, J., Thambimuthu, K. (Eds.), Greenhouse Gas Control Technologies 7, Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies - September 2004. Oxford: Elsevier Science Ltd, Vancouver, Canada, pp. 55−61.

Ye, C., Dang, M., Yao, C., Chen, G., Yuan, Q., 2013. Process analysis on CO_2 absorption by monoethanolamine solutions in microchannel reactors. Chemical Engineering Journal 225, 120−127.

Zaman, M., Lee, J.H., 2015. Optimization of the various modes of flexible operation for post-combustion CO_2 capture plant. Computers & Chemical Engineering 75, 14−27.

Zhang, Y., Chen, C.-C., 2012. Modeling CO_2 absorption and desorption by aqueous monoethanolamine solution with Aspen rate-based model. 11th International Conference on Greenhouse Gas Control Technologies (GHGT-11), Kyoto, Japan. Energy Procedia 37, 1584−1596 (2013).

Zhelev, T.K., Semkov, K.A., 2004. Cleaner flue gas and energy recovery through pinch analysis. Journal of Cleaner Production 12 (2), 165−170.

Ziaii, S., Rochelle, G.T., Edgar, T.F., 2009. Dynamic modeling to minimize energy use for CO_2 capture in power plants by aqueous monoethanolamine. Industrial and Engineering Chemistry Research 48 (13), 6105−6111.