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Flexible operation of post-combustion CO2 capture at pilot scale with demonstration of capture-efficiency control using online solvent measurements.

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Abstract
Flexible post-combustion carbon capture and storage (CCS) has the potential to play a significant part in the affordable decarbonisation of electricity generation portfolios. PCC plant operators can modify capture plant process variables to adjust the CO_2 capture level to a value which is optimal for current fuel cost, electricity selling price and CO_2 emissions costs, increasing short-term profitability. Additionally, variation of the level of steam extraction from the generation plant can allow the capture facility to provide additional operating flexibility for coal-fired power stations which are comparatively slow to change output.
A pilot-scale test campaign investigates the response of plant operating parameters to dynamic scenarios which are designed to be representative of pulverized coal plant operation. Online sensors continuously monitor changes in rich and lean solvent CO_2 loading (30%wt monoethanolamine). Solvent loading is likely to be a critical control variable for the optimisation of flexible PCC operation, and since economic and operational boundaries can change on timescales 30mins or shorter, the development of methods for rapid, continuous online solvent analysis is key. Seven dynamic datasets are produced and insights about plant response times and hydrodynamics are provided. These include power output maximization, frequency response, power output ramping and a comparison between two plant start-up strategies.
In the final dynamic operating scenario, control of CO_2 capture efficiency for a simple reboiler steam decoupling and reintroduction event is demonstrated using only knowledge of plant hydrodynamics and continuous measurement of solvent lean loading. Hot water flow to the reboiler is reduced to drop the capture efficiency. The "target" value for the minimum capture efficiency in the scenario was set at 30%, but a minimum CO_2 capture efficiency of 26.4% was achieved. While there remains scope for improvement this represents a significant practical step towards the control of capture plant using online solvent concentration and CO_2 measurements, and the next steps for its further development are discussed.

1. Introduction
Despite the continuing phase-out of coal power generation in Europe it is likely to remain an important source of electricity in Asia, Africa and the Americas through 2040 and beyond (IEA, 2015) Carbon capture and storage (CCS) has the potential to significantly limit the emissions from coal and gas-fired power stations, reducing the cost and mitigating the worst effects of dangerous climate change (IPCC, 2014). Post-combustion capture (PCC) applied to coal-fired power stations is a proven technology for the reduction of CO_2 from flue gas, but there are outstanding questions regarding how the process responds to changes in generation plant output.
Coal-fired plants are less likely to provide dispatchable services for rapid response to spikes in electricity demand due to their slower ramp rate than modern NGCCs. However, the plants are capable to do so if needs be, and are increasingly likely to participate in load-following operations or operate in a two-shifting regime. In this regime the plant is shut down at night due to reduced demand and restarted in the morning when the demand is higher. Flexibility in capture plant operation is critical if it is to respond to these dynamic generation events effectively.
Capture plant flexibility also allows coal-fired power stations to maximise the electricity available for transmission while the plant is operating at baseload. Errey et al (2014) demonstrates the value of CO_2 capture plants varying their capture efficiency in response to changes in electricity selling price. Mac Dowell (2015) and Flø (2016) use dynamic models to investigate various capture plant operation strategies to capitalise on volatile electricity selling price while maintaining an average CO_2 capture efficiency which is close to 90% over 24 hours. The model used by Flø (2016) is validated against flexibility tests done at the Brindisi pilot published previously by Mangiaracina et al. (2014). However, the availability of dynamic plant performance data in open literature in very limited and the lack of public-domain dynamic plant data

makes the validation of these strategies problematic (Bui, 2014), especially for dynamic scenarios which are more complex than a step-change in a single plant parameter.

Furthermore, the implementation of these operational strategies requires a robust process control system to achieve optimised performance when manipulating reboiler steam input to capitalise on fluctuating electricity selling price, or responding to a dynamic generation plant event (Mac Dowell, 2015; Flø 2016). Tait et al (2016) suggest that active control of the real-time solvent capacity via manipulation of solvent flow rate and/or reboiler heat input, combined with continuous measurement of lean and rich solvent CO_2 loading could be used to control CO_2 capture efficiency during dynamic operations.

This work details the implementation of dynamic scenarios at pilot plant scale. The test campaign shares some similarity with previously published work on post-combustion capture on NGCC plant by Tait et al (2016) but with several key differences. This work focuses on coal generation; the dynamic scenarios are based on operating data from real coal plant and on operating modes which are most relevant to post-combustion capture on coal. The test facility is purpose-built for CO_2 capture and the reboiler design is significantly different to that described in Tait et al (2016), allowing comparisons to be made between how different pilot-plant design and configuration affects the response to dynamic operations. The deployment of two online solvent sensors allows for continuous measurement of both rich and lean loading to be made. Seven dynamic operating scenarios are implemented. This includes two different shutdown-startup couplings, frequency response, load-following and two capture bypass events. These scenarios are used to provide insights about plant hydrodynamics and response to dynamic scenarios while passively monitoring changes in solvent loading with the online solvent sensors. The knowledge of plant dynamics gained over the course of the test campaign is used in a final scenario in which online lean solvent loading measurements are used to demonstrate control of CO_2 capture efficiency following a steam decoupling event.

2. Overview of Test Facility

The amine technology CO_2 capture plant which was previously installed at Didcot power station by RWE is now located at the PACT facilities of the UKCCSRC at the University of Sheffield. The plant is purpose-built for CO_2 capture operations and has been upgraded several times since 2012. A simplified layout of the capture plant is shown in Fig. 1. The absorber contains 6.50m of 300mm diameter Sulzer Mellapak CC3 packing, while the desorber contains 6m of Intalox IMTP 25 random packing and is 300mm in diameter. There are several options for flue gas injection – the facility can be connected to a biomass burner, a gas turbine or a gas mixing skid which can create synthetic flue gas from air/N_2 and CO_2. For the duration of the test campaign, a mixture of ambient air with approx. 12% CO_2 from the gas mixing skid is used to simulate flue gas from a coal-fired power station. Gas ordinarily flows through an FGD wash column prior to entering the absorber (Akram, 2016), but due to consistent problems with water condensation and buildup in the pipework between the FGD and absorber inlet, the FGD is bypassed for the duration of the test campaign. For all tests, the flue gas entering the absorber is unsaturated and has water content approx. 1% of total volume. This causes the plant to lose water through the absorber gas outlet, resulting in an increase in nominal amine concentration of 2-3% w/w per day. The effect of this on plant reboiler duty is discussed in section 3.2.

To make up for these water losses the plant is topped up with water manually if necessary at the beginning of the operating day.

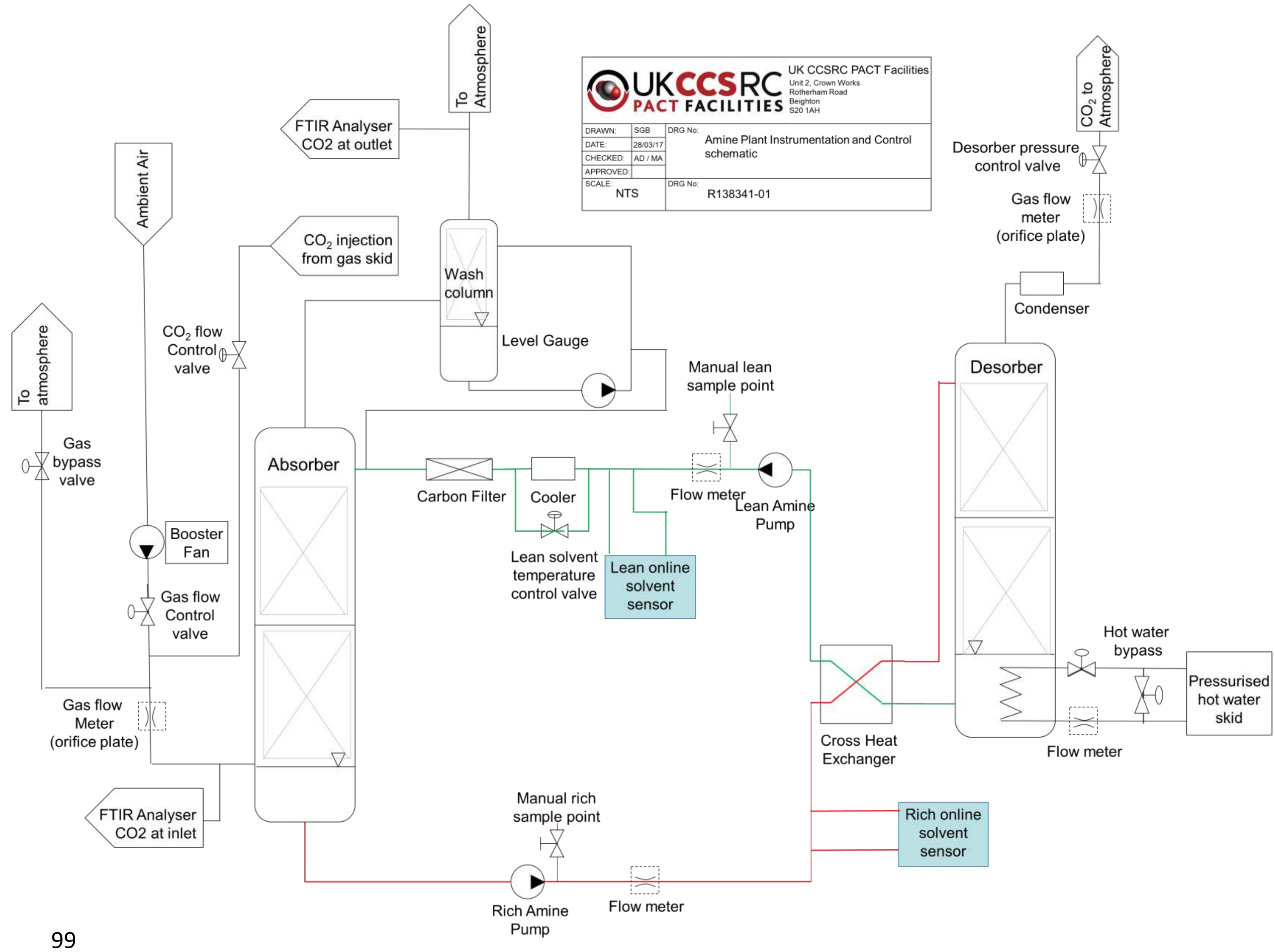


Fig. 1. Process flow diagram of amine plant (Akram, 2017)

The plant uses pressurised hot water to regenerate rich solvent. The reboiler, shown in Fig. 2, consists of a large overspill tank containing a heating element, through which pressurised water at approx. 124°C is pumped. At the end of the reboiler tank furthest from the desorber, solvent spills over a baffle to feed the lean solvent pump. The pump is protected by a sensor which will trip if the liquid level in this section falls below a given threshold, shutting down the plant. The total solvent inventory of the plant is approx. 600l, the majority of which resides in the reboiler during operation. The absorbing solvent used for the duration of the test campaign is 30% Monoethanolamine (MEA), though the nominal amine concentration varies between 28% and 35% due to the aforementioned water losses.

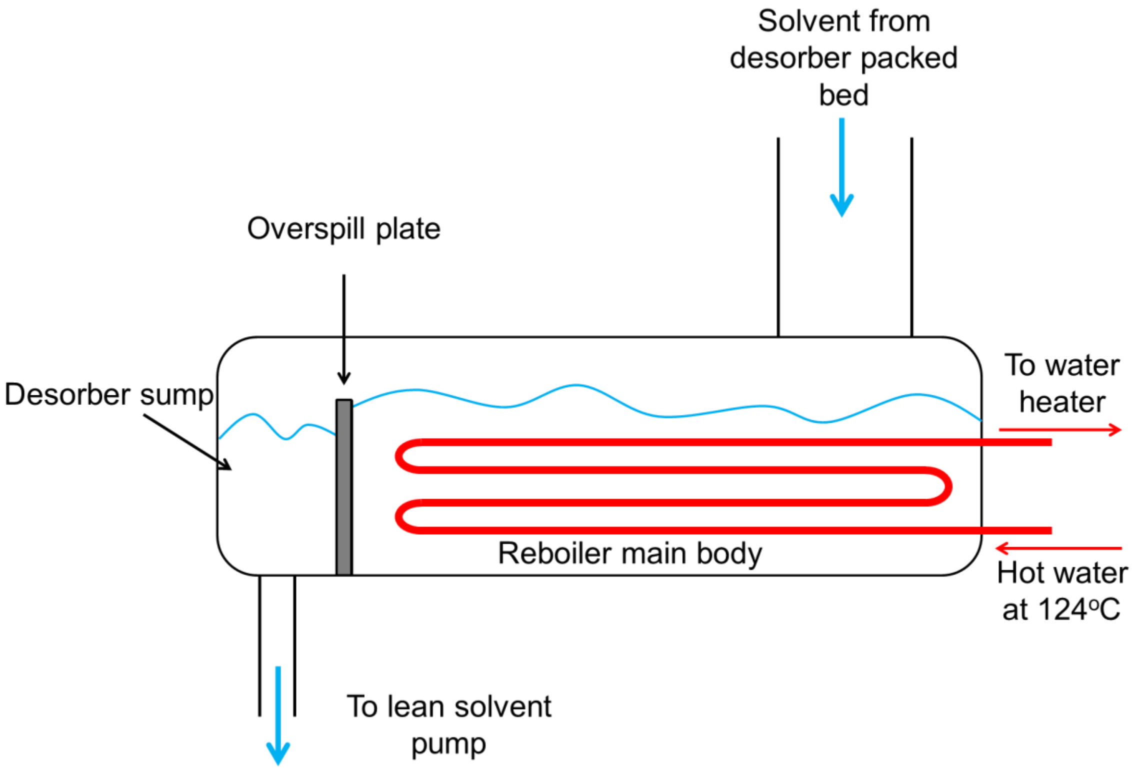


Fig. 2. Reboiler design at UKCCSRC PACT

The gas flow is comprised of ambient air which is enriched with CO_2 to the required concentration via injection and checked via a Fourier Transform infra-red (FT-IR) spectroscopy analyser at the absorber gas inlet. A second FT-IR device analyses the gas composition at the absorber outlet. As the only two available FT-IR systems are required at the absorber inlet and outlet for the determination of CO_2 capture efficiency, it is not possible to determine the CO_2 mass flow at the desorber outlet.
Solvent flow rate is controlled via individually-controlled valves located after the rich and lean solvent pump. The valves can be controlled via a flow rate setpoint or opened and closed manually. During solvent flow rate changes there is a considerable risk of plant shutdown as the solvent level in the absorber sump may fall below the trip switch threshold, making fine control and ramping very difficult to implement. For this reason only large step-changes in solvent flow are used in the test campaign.
A bypass valve allows the flow of pressurised hot water to the reboiler to be adjusted using a PID controller. The hot water pump has an operating range of 0-10m^3/hr and while the flowmeter is unable to detect any flow below approx. 3.0m^3/hr, below this value the PID controller can be switched off allowing the valve position to be adjusted manually. However, as there is no flow measurement determining the hot water flow rate between 0-3m^3/hr is a matter of guesswork.
Desorber pressure setpoint is adjusted via a PID controller by opening or closing the valve at the top of the desorber. For all scenarios in this work, the desorber pressure setpoint was 0.4 bar$_g$. Desorber pressure fluctuates between around 0.37-0.47 bar$_g$ at baseload flow conditions.

At baseload conditions the cross-flow heat exchanger provides a temperature increase of approx. +47°C to the rich solvent entering the desorber and a decrease of approx. -47°C to the lean solvent entering the absorber. This is sufficient to bring the lean solvent down from 99°C at the desorber sump outlet to around 52°C, so further cooling is required to reduce the temperature to 40°C at the absorber inlet. Solvent enters the desorber at approx. 98°C at baseload conditions. Absorber inlet temperature is maintained at 40°C using a PID-controlled cooler and bypass valve which is connected to the PLC system. There is very little variation in lean solvent temperature at the absorber inlet once the temperature of lean solvent coming from the cross-heat exchanger is greater than 40°C.

3. Methodology and Preparation

3.1 Solvent Mixing Experiments

Solvent circulation times and mixing effects have been shown to affect plant response to dynamic operations (Tait et al, 2016), so prior knowledge of plant hydrodynamics is required to fully account for changes in capture efficiency, absorber temperature profile, lean loading and rich loading over the course of each dynamic scenario.

Four conductivity probes, two on each of the rich and lean solvent lines, were installed. The pair of probes installed on the rich line monitored the outlet of the absorber and inlet of the desorber, while the pair of probes installed on the lean solvent line monitored the outlet of the desorber and the inlet of the absorber. Ideally the conductivity probes would be installed as close as possible to the inlets and outlets of the absorber and desorber. However, due to difficulties in installing the conductivity probes at heights all of the probes were installed at ground level. This meant that the distance between the pair of probes was shorter as compared to if they were installed at the inlets to absorber and desorber columns. For this reason it is not possible to determine the circulation between the lean solvent pump > absorber inlet or rich solvent pump > desorber inlet, but valuable information about solvent mixing and total circulation time can still be obtained.

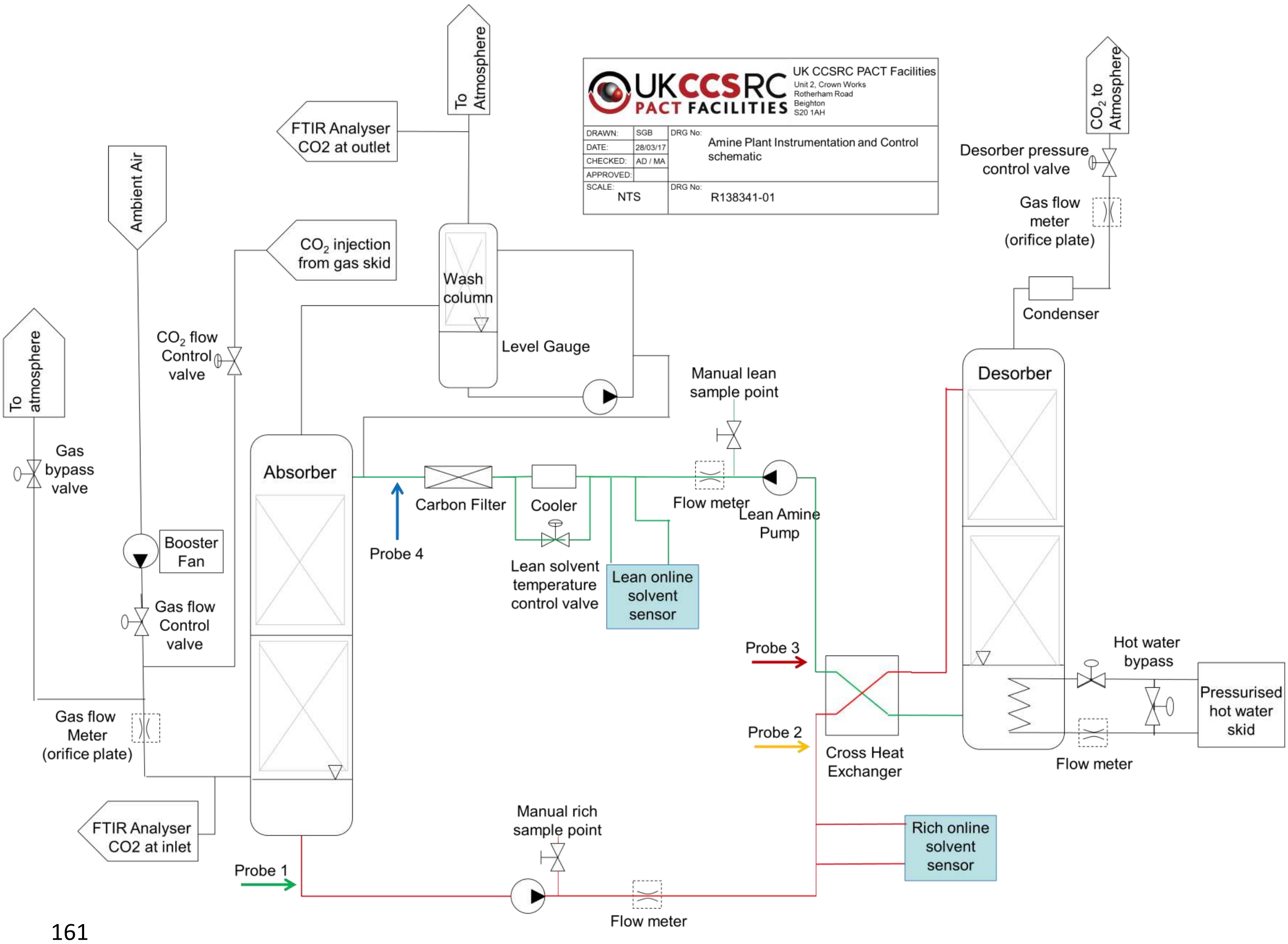


Fig. 3 Plant PFD with conductivity probe locations

A batch of amine solvent (between 30-40%wt MEA, approx. 400l) is isolated in the desorber sump. Deionised water (approx. 70l) is added to the absorber sump. The solvent pumps are started at t=0. As pure water mixes with amine solvent, the conductivity decreases. By observing the conductivity at each of these points it is possible to estimate the circulation time between them and the duration required for the solvent inventory to become fully mixed.

Tests were carried out at the initially proposed baseload flowrate (1200l of solvent/hr), but a flow rate of only 1000l/hr was necessary to achieve >90% capture (see section 3.2).

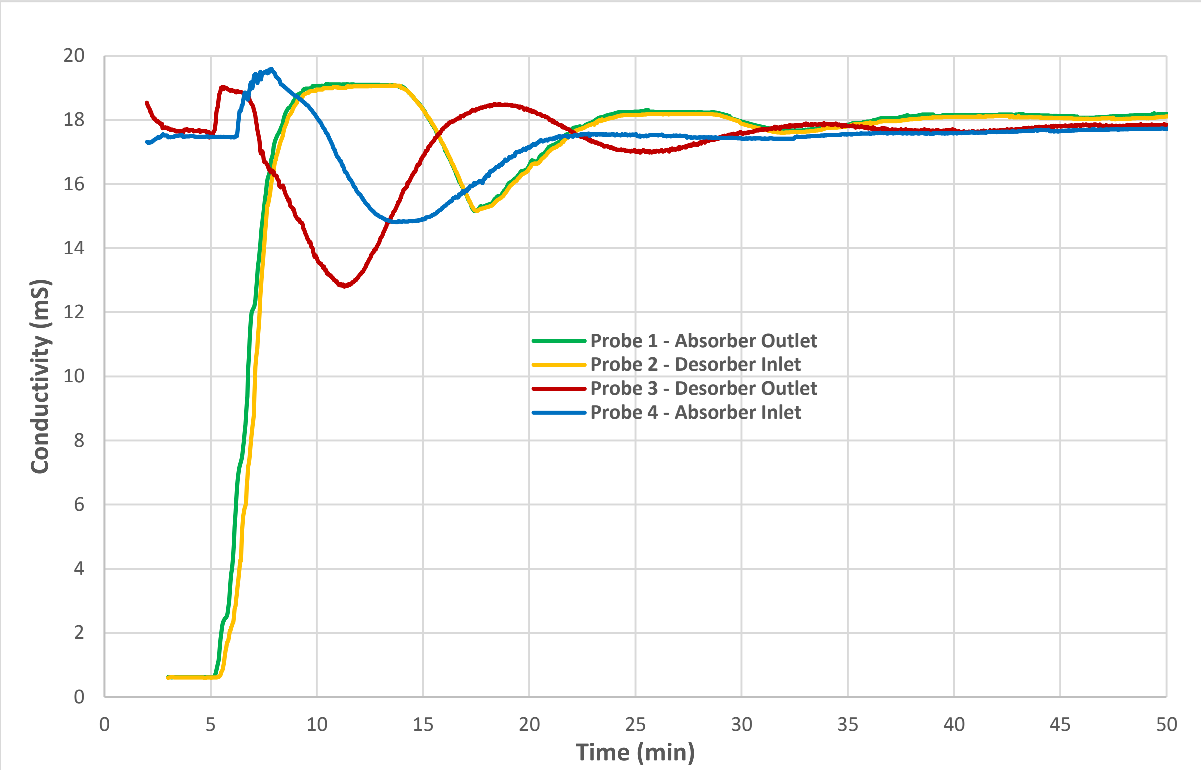


Fig. 4. Liquid circulation experiments

Due to their close proximity in the liquid line (see fig. 3), pair of probes installed on the rich solvent line (probe 1-absorber outlet/probe 2- desorber inlet), conductivity values measured by the pair follow each other closely (see fig. 4). However, there is a noticeable difference in the conductivity values measured by the pair of probes installed on the lean solvent line (probe 3- desorber outlet/probe 4-absorber inlet) which may indicate a small amount of solvent mixing taking place within the line, or may be due to the lean solvent pump starting up and stabilising more slowly than the rich.

Conductivity at the absorber outlet (probe 1) begins to increase at t=5min. This indicates that the minimum time required for a small batch of solvent located at the desorber outlet (probe 3) to circulate to the absorber sump and begin mixing with the sump's existing solvent inventory is 5min. Conductivity at the desorber outlet (probe 3) begins to decrease at t=5min 30sec, indicating that the time required for a batch of solvent to circulate from the absorber outlet (probe 1) to the reboiler and begin mixing with the solvent inventory is 5min 30sec. The entire solvent inventory requires 37-38min to become fully mixed, which is 7min more than the estimated time of 30 min required for a batch of solvent to fully circulate the plant at this flow condition, based on vessel volumes and total solvent inventory. The implications for dynamic operations are:

1. During operation, the solvent spends approx. 2/3 of the time residing in the reboiler or absorber sump. This allows ample time for the solvent to become well mixed. Therefore it is not anticipated

that after, for example, reintroduction of hot water to the reboiler after a decoupling event, large additional fluctuations in solvent loading or capture efficiency will be observed following a return to baseload flow conditions, as observed by Tait et al. (2016)

2. The solvent becomes fully mixed within approx. 1.25 circulations of the entire solvent inventory.
3. The circulation time between desorber outlet and absorber inlet is less than 5min. Any changes in solvent loading at the desorber outlet due to step-changes in reboiler heat input should induce a CO_2 capture efficiency response within 5min.

As this test was carried out at a solvent flowrate of 1200l/hr and the eventual baseload condition has a flow rate of 1000l/hr, a reasonable approximation is to multiply the circulation times obtained in this test by 1.2 to obtain circulation times at 1000l/hr (fig.5).

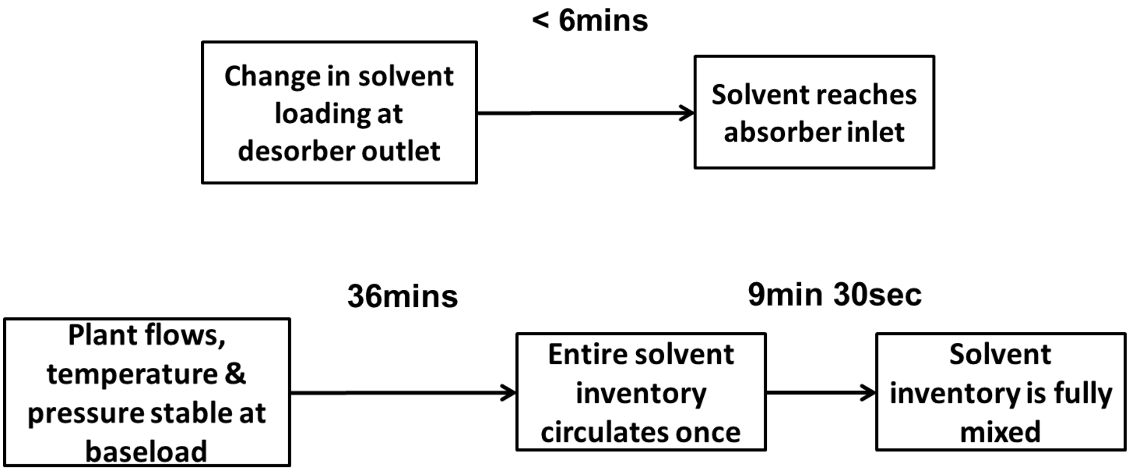


Fig. 5. Important solvent circulation times for dynamic operation, scaled to 1000m^3/hr

These circulation tests provide a reasonable estimate of solvent circulation times, and are useful in the planning of experiments and analysis of plant response early in the test campaign. However, as demonstrated in section 5 it is possible to use online solvent sensors, plant temperatures and capture efficiency to build on this initial analysis and construct a much clearer picture of plant response.

3.2 Baseload Operating Conditions

Due to changes in ambient conditions, general flow variability and varying nominal MEA concentration due to water losses these baseload conditions should be regarded as approximate.

Controlled Variable	**Value**
Gas Flowrate at absorber inlet (Nm^3/h)	200
Gas inlet temperature (^oC)	42
Inlet gas CO_2 concentration (% v/v)	12
Pressurised hot water flow rate (m^3/hr)	10
Solvent flowrate (l/h)	1000
Pressurised hot water inlet temperature (^oC)	124
Pressurised hot water outlet temperature (^oC)	118.5
Liquid inlet temperature, Absorber (^oC)	40
Liquid inlet temperature, Desorber (^oC)	98
Measured Parameter	
CO_2 capture efficiency (%)	91.5-95
Reboiler duty (GJ/tCO_2)	6.2-6.8
L/G ratio (l/m^3)	5.0
Nominal amine concentration (% w/w)	28-34
Rich Solvent Loading (mol CO_2/mol amine)	0.36-0.40
Lean Solvent Loading (mol CO_2/mol amine)	0.13-0.17

Table 1. Baseload Operating Conditions

The baseload liquid-to-gas flow ratio (L/G) is established as 5 l/m^3. The minimum solvent flow rate achievable without risking damage to solvent pumps is 400l/hr so a flow rate of 1000l/hr allows solvent flow to be reduced to 50% of its baseload value (500l/hr) while affording the operators a reasonable margin for error. The gas flow is operating close to its maximum for this plant at 200m^3/hr.

It is worth noting that the baseload operating conditions reported here correspond to a necessary reference point, which allow for large changes in amplitude of key operating variables, such as solvent flowrate, gas flow rate, etc. It does not necessarily correspond to the optimised conditions for minimising reboiler duty. This is one reason explaining why the reboiler duty is higher than reported for other comparable facilities. The other reason is due to the small size of the cross-flow heat exchanger. In most CO_2 capture facilities the approach temperature for the cross-heat exchanger is approx. 10^{o}C. For this pilot facility the process fluid (rich solvent) exits the heat exchanger at approx. 98^{o}C while the working fluid (lean solvent) enters the heat exchanger at approx. 118^{o}C, for an approach temperature of 20^{o}C. A lower desorber inlet temperature requires more energy input from the reboiler as sensible heat to bring the incoming solvent up to stripping temperature. The additional contribution to the reboiler duty due to the undersized heat exchanger (ΔQ_{reb}) can be calculated as follows.

$$\Delta Q_{reb} = \frac{m_{rich} Cp_{rich} \Delta T_a}{m_{CO2}} \qquad \text{(Equation 1)}$$

Where m_{rich} is the mass flow rate of rich solvent in kg/s, Cp_{rich} is the specific heat capacity of the rich solvent in J/kg.K, ΔT_a is the difference in approach temperature between this facility and one with an optimised heat exchanger in K and m_{CO2} is the CO_2 capture efficiency in kg/s. With ΔT_a = 10K the additional contribution to the reboiler duty ranges between 1.033GJ/tCO_2 and 1.084GJ/tCO_2, accounting for changes in capture efficiency and nominal MEA concentration (see table 1).

Due to water losses through the absorber and desorber gas outlets the nominal MEA concentration of the solvent increases over time. An automatic, batch-wise water topup system exists, but to avoid additional perturbations during dynamic testing it is not used over the duration of the test campaign. Instead, water levels are topped up in a single large batch at the start of each test day if MEA concentration becomes too high.

This variation in amine concentration appears to reduce the reboiler duty as the solvent becomes more concentrated in amine (see fig. 6). Increased amine concentration may also have the effect of lowering the lean and rich solvent CO2 loading and increasing the capture efficiency. Although the volumetric flow of solvent remains constant, the molar flow rate of lean amine into the absorber increases thus decreasing the lean solvent CO2 loading. Additionally, the baseload plant conditions are such that the solvent never reaches a saturated rich CO2 loading (around 0.5 mol MEA/mol CO_2), therefore a reduction in lean solvent CO2 loading entering the absorber can also correspond to a reduction of rich solvent CO2 loading leaving the absorber. The mass ratio of CO_2 in reaction products to H_2O in the rich solvent is increased, reducing the energy lost into the water as sensible or latent heat per mole of CO_2 liberated. Finally, leaner solvent entering the absorber results in a larger driving force for CO_2 absorption and therefore a higher capture efficiency.

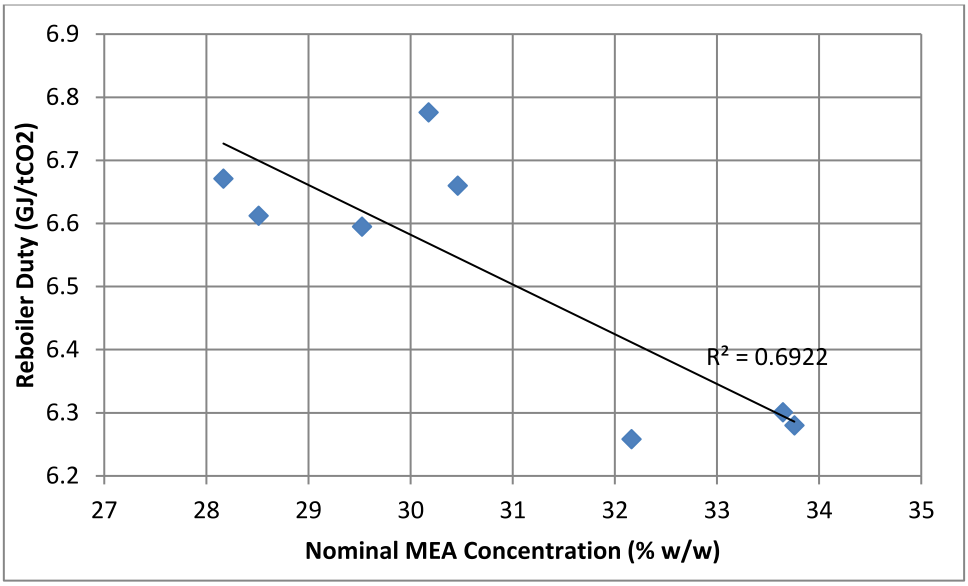


Fig. 6 Reboiler Duty Variance with amine concentration

Figure 6 shows how the reboiler duty appears to decrease with nominal amine concentration at steady-state, baseload flow conditions. To minimise uncertainty due to short-term variations in temperature, capture efficiency and flow, the reboiler duties are calculated using the average hot water inlet/outlet temperature, CO_2 capture efficiency and hot water flow rate over a 20 minute period. The nominal amine concentration is the average of four measurements (2x lean, 2x rich) taken at the beginning and end of this 20 minute period.

3.2.1 Titration measurements and uncertainty

Lean and rich solvent samples are taken at regular intervals during dynamic testing and analysed for MEA and CO_2 content using a Mettler Toledo T90 auto-titrator. Determination of CO_2 concentration in amine solvents using MEA is well-established, and is first described by Wonder et al. (1959). Samples were titrated against 0.2M HCl to determine total amine concentration, then 0.5M NaOH to determine CO_2 concentration. The titration method measures the total concentration of free amine and CO_2 in each sample. These measurements are then used to calculate the nominal amine concentration, which neglects the mass of CO2 in the sample to determine the mass ratio of free amine to water. This is a useful measurement to make as the concentration of CO_2 in samples varies depending on operating conditions, and the nominal concentration indicates if the solvent has degraded from its optimal value (in the case of MEA, 30% by mass).

To determine the uncertainty of titration measurements a solution of 29.40%wt MEA (nominal) and 8.04%wt CO_2 equivalent is made up gravimetrically by bubbling CO_2 through MEA solution in a dreschel flask. The loaded solution is titrated for MEA and CO_2 content in triplicate. The uncertainty in bench CO_2 loading measurements is found to be +/- 3.15% relative, summarised in table 2.

MEA concentration (% wt, via titration)	CO_2 concentration (%wt, via titration)	MEA concentration (% wt nominal, calculated)	CO2 loading (mol CO_2/mol MEA, calculated)
27.068	7.876	29.38	0.403
26.942	7.936	29.26	0.409
27.307	7.751	29.60	0.395

Table 2. Titration measurements for determination of uncertainty

3.2.2 Online solvent sensors

Two online solvent composition sensors are located in the lean and rich solvent lines (see fig. 1). In-situ measurements of solvent physical properties are used to determine amine concentration and CO_2 loading in real-time. The sensor used by Tait et al. (2016) is modified to comply with site safety regulations and to add remote operation capability. It was deployed along with a second device which has the same design. A detailed account of sensor development is provided by Buschle (2015). The specifics of the method by which the sensor operates are currently restricted as the University of Edinburgh is in the process of commercialising the technology, but it operates on similar principles to others which can be found in the literature (example: van Eckeveld et al., 2014). Continuous rich solvent measurements are provided for 8 of 9 dynamic scenarios and continuous lean solvent measurements for 7 of 9.

3.3 Selection of dynamic scenarios

Dynamic operations are selected to be representative of scenarios which may be encountered during the operation of a supercritical coal power unit fitted with post-combustion capture.

3.3.1 Generation plant shutdown

This scenario is designed to be a realistic representation of how a post-combustion capture plant would respond to generation plant shutdown, with flue gas and regeneration "steam" (in this case pressurised hot water) ramp rates based on real operating procedures for supercritical coal units with stated power outputs of 500 MW or greater (NETL, 2014). In this scenario and all others, flue gas flow is approximated as being proportional to generation plant output. Flue gas flow is ramped down until it reaches 30% of baseload, which is defined as minimum stable generation (MSG). Below MSG the flue gas contains too many impurities due to incomplete combustion (DECC and Parsons Brinckerhoff, 2014), so to avoid polluting the solvent the gas flow is reduced to zero at this time. Hot water (i.e. "steam") is fed to the reboiler for as long as possible so the solvent is lean in preparation for startup. Once gas flow reaches zero, solvent flow is reduced to 50% of baseload and for practical reasons is allowed to circulate until rich and lean loading have converged, simulating a scenario in which solvent flow is left running overnight to make use of the plant site's cooling water. A similar shutdown procedure is described in Ceccarelli et al. (2014) as applied to PCC on NGCC plant – in this case it is applied to coal. The comparative benefits of continuing to circulate solvent overnight as opposed to immediate shutdown as soon as the flue gas flow has stopped are discussed in section 4.1.1 The shutdown method has a direct impact on capture plant response on the next startup. Two plant startup methods were investigated, both of which were preceded by this method of shutdown.

3.3.2 Generation plant startup 1

Ramp rates for plant startup are taken from PACE (2014), with minimum stable generation defined as 30% of baseload. Two startup scenarios are simulated, both preceded by the shutdown method described in 3.3.1 and intended to simulate a "hot start" of a coal plant, in which the plant is shut down in response to falling demand (DECC and Parsons Brinckerhoff, 2014). The first startup scenario simulates a situation in which the low-pressure steam turbine is allowed to reach full load before any steam is introduced to the reboiler. This results in an extended period during which the CO_2 capture efficiency is low and the plant requires several hours to reach the desired capture efficiency.

3.3.3 Generation plant startup 2

In the second startup scenario steam (i.e. hot water) is introduced to the reboiler as soon as it becomes available, resulting in a smaller drop in capture efficiency and the plant reaching steady state more rapidly. This kind of operating mode may be useful in cases where there are restrictive laws on large, short-term spikes in CO_2 emissions from point sources. This may also be a more cost effective start-up method at very high carbon prices.

3.3.4 Frequency response via pressurised hot water flow reduction

A coal power station which is equipped with post-combustion capture can provide additional flexibility in output via manipulation of the steam flow to the reboiler (Lucquiaud, 2009; Haines, 2014). In this scenario the flow of hot water to the reboiler is reduced to 50% of baseload as the other 50% is redirected to the LP steam turbine. In a power plant equipped with PCC this would result in a rapid, but marginal increase in plant output which would allow the coal plant to be used in grid balancing operations such as frequency response. After the hot water flow has been at 50% of baseload for 2 hours it is ramped back up to baseload.

3.3.5 Capture bypass via pressurised hot water flow decoupling

This scenario simulates the plant operator taking actions at the capture plant level in order to maximise electricity power output and capitalise on high electricity selling price. Two capture bypass scenarios are implemented – Bypass scenario 1 maintains both solvent and gas flow rates at baseload while reducing the hot water flow rate to zero. Bypass scenario 2 maintains gas flow rate at baseload, but reduces the solvent flow to 50% of baseload while reducing the hot water flow rate to zero. This is to reduce the power consumption of the pumps, and to reduce the power consumption of the flue gas booster fan via minimisation of absorber pressure drop. The period of this event lasts 2 hours.

3.3.6 Capture plant ramping

This scenario simulates the operation of a load-following plant, which is identified as one of the five typical modes of operation for coal-fired power stations in the UK as of 2012 (Mac Dowell and Shah, 2015). The generation plant ramps down its output from 100% of baseload to 70% for a period of 2 hours, then ramps back up. Hot water flow and solvent flow are matched as closely as possible to the gas flowrate to maintain the baseload L/G flow ratio, and to maintain consistency with the conclusion of Mac Dowell and Shah (2015) that less steam is available for solvent regeneration during these events.

3.3.7 Capture efficiency control using online solvent measurements

Future advanced control systems for both coal and gas CCS plants are likely to require real-time measurements of solvent composition to anticipate changes in capture efficiency and respond in a manner which is optimised in terms of environmental, economic and operational boundaries (Luu, 2015). For example, there could be a situation in which the operator wishes to maximise revenue by providing an ancillary service such as fast reserve balancing by reducing the level of steam abstraction to the reboiler, but at the same time wishes to minimise CO_2 emissions charges for the duration. Optimised capture plant operation in such a scenario is not possible without discrete knowledge of capture plant dynamics (process gain, dead time, time constants), so a simplified version is implemented.
This scenario envisions a situation in which the operator has to drive the CO2 capture efficiency to 30% via a steam decoupling event and immediately return to the baseload capture efficiency of 90% or higher. With flue gas and solvent flow kept constant at baseload, the hot water flow to the reboiler is shut down. The lean solvent sensor is used in combination with knowledge of plant hydrodynamics and response times to predict when the flow of hot water must be turned back on to achieve a minimum capture efficiency of 30%.

4. Discussion of dynamic operating scenarios

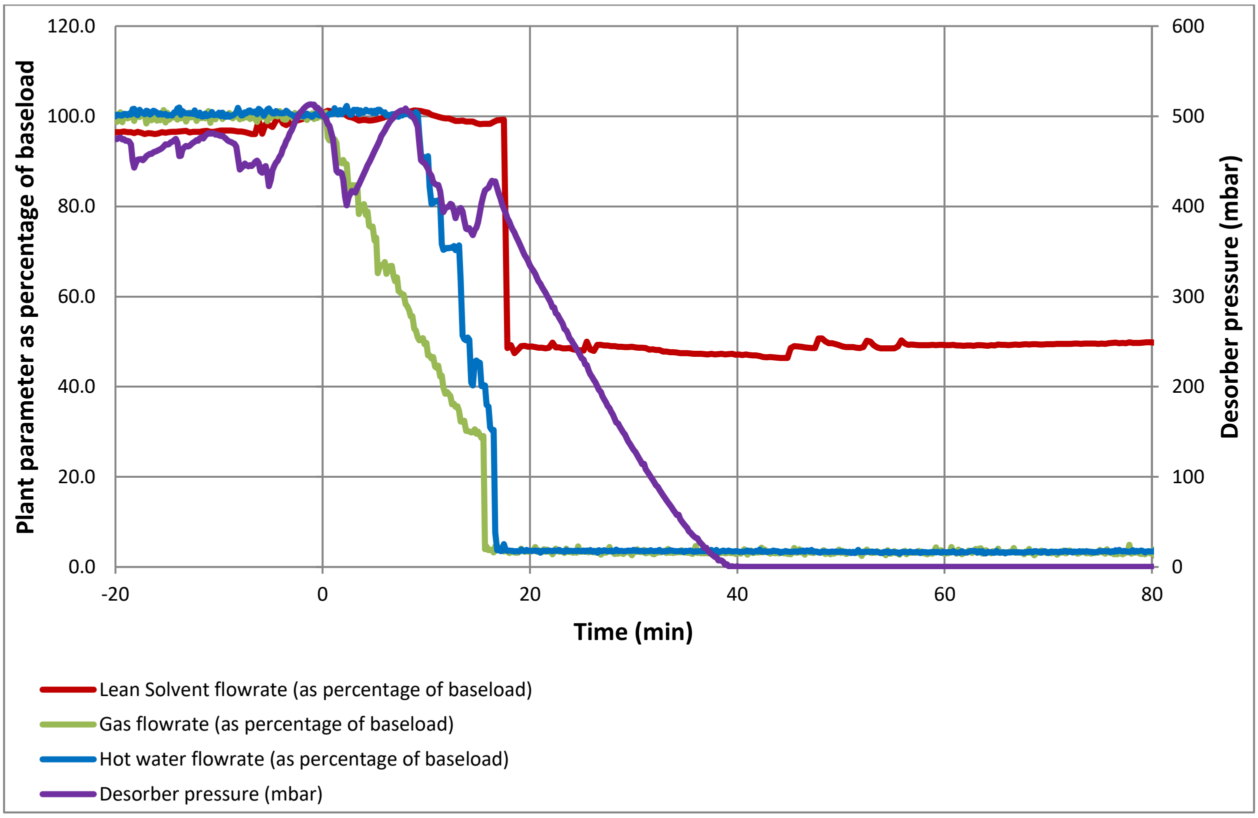
In this section, plant trends from the dynamic scenarios are discussed in detail. Rich and lean titration measurements are based on solvent samples taken from the absorber outlet and desorber outlet, respectively. At baseload conditions the circulation time from lean solvent sampling port to absorber inlet and rich solvent sampling port to desorber inlet is approximately 3 minutes. The circulation time between the lean solvent sensor and the absorber inlet is also around 3 minutes at baseload flow conditions.

4.1 Shutdown/Startup coupling 1

4.1.1 Shutdown

Plant shutdown is initiated at t=0min (fig. 7a). Gas flow is ramped down at a rate of 5% of the baseload flow per minute (10 m^3/hr) until it reaches 30% of baseload flow (60m^3/hr), then reduced to zero. At t=9min, the flow of pressurised hot water to the reboiler is ramped down at a rate of around 10% of baseload per minute (1m^3/hr) until it reaches zero at t=19min. The hot water flowmeter is unable to detect any flow below approx. 3m^3/hr, accounting for the apparent immediate reduction of hot water flow to zero once it reaches 30% of baseload at t=16min. The flow of hot water was controlled by the position of a proportional solenoid valve, so it is assumed the hot water flow continued on a similar trajectory between t=16 mins and t=19 mins. Once the flow of gas has been reduced to zero, solvent flow is reduced to 50% of baseload (500kg/hr) and allowed to continue circulating until the reboiler has cooled to under 80°C and lean & rich loadings have converged. This simulates the first part of a scenario in which the plant operator has allowed the solvent inventory to continue circulating so that the plant is cool for the subsequent startup event. In practice at a full-scale capture facility the operator may allow the solvent to continue circulating overnight, making use of additional cooling to ensure the solvent is at ambient temperature for the subsequent startup operation (Ceccarelli et al, 2014).

The CO_2 capture efficiency increases slightly over the course of the shutdown operation until the flow of gas is switched off (fig. 7b). The gas flow rate is decreasing while the liquid flow rate remains constant, resulting in a gradually increasing L/G ratio and higher capture efficiency. This also results in a decrease in rich solvent CO_2 loading which, due to effective solvent mixing within the plant, rapidly converges with lean loading and stabilises at around 0.18mol CO_2/mol amine (fig. 7b)._The volume of rich solvent contained in the absorber sump is around 70l while the desorber contains around 400l of lean solvent, so the loading of the fully mixed solvent inventory is closer to that of the lean. Continuous lean solvent measurement was not available during this scenario.



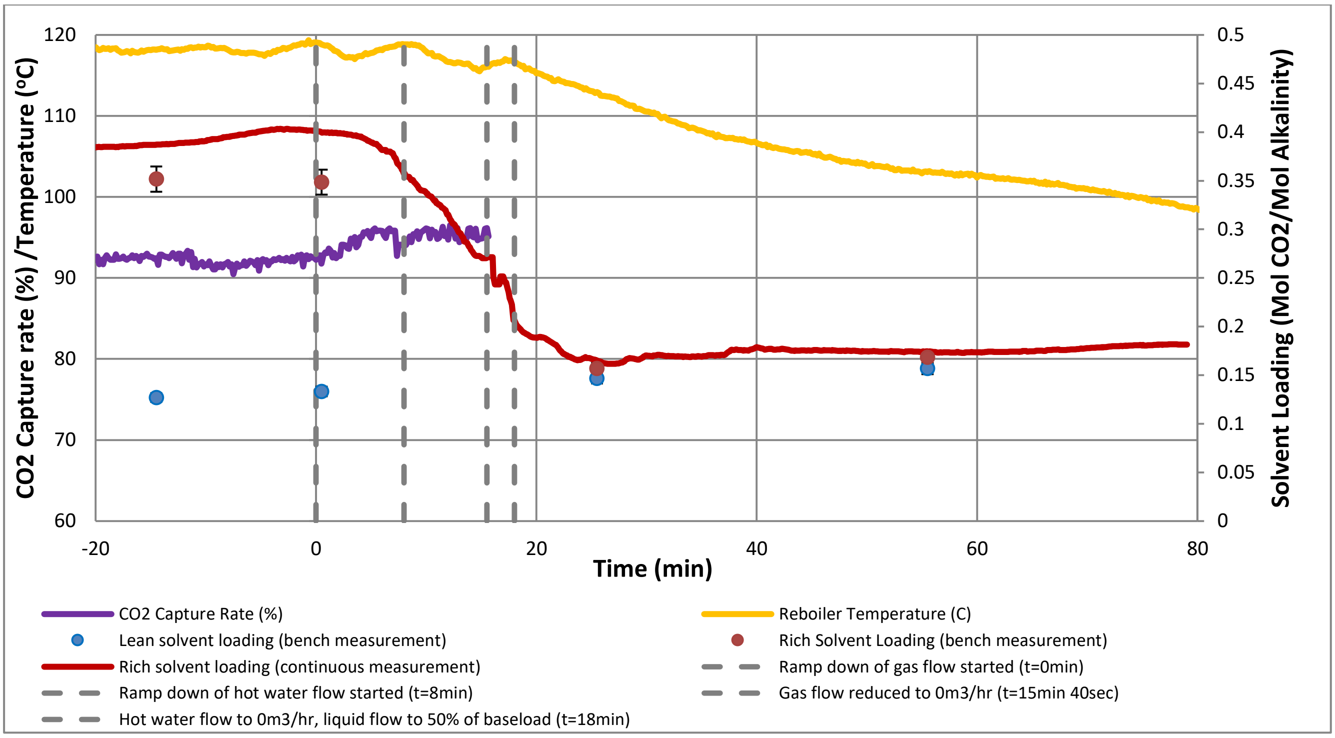


Fig. 7a. Gas, solvent hot water flow rate and desorber pressure as percentage of baseload operation, shutdown scenario 1

Fig. 7b. Rich and lean solvent loading, reboiler temperature and CO_2 capture efficiency, shutdown scenario 1

The absorber temperature bulge decreases in magnitude and moves towards the base of the packed bed over the course of the shutdown operation (fig. 8). The rate of CO_2 absorption per unit of column volume decreases due to the decrease in gas flow rate, and a proportionally larger amount of CO_2 is absorbed close to the gas inlet. Hot solvent holdup residing in the upper regions of the packed bed also flows down the packing as time progresses, increasing the temperature closer to the base.

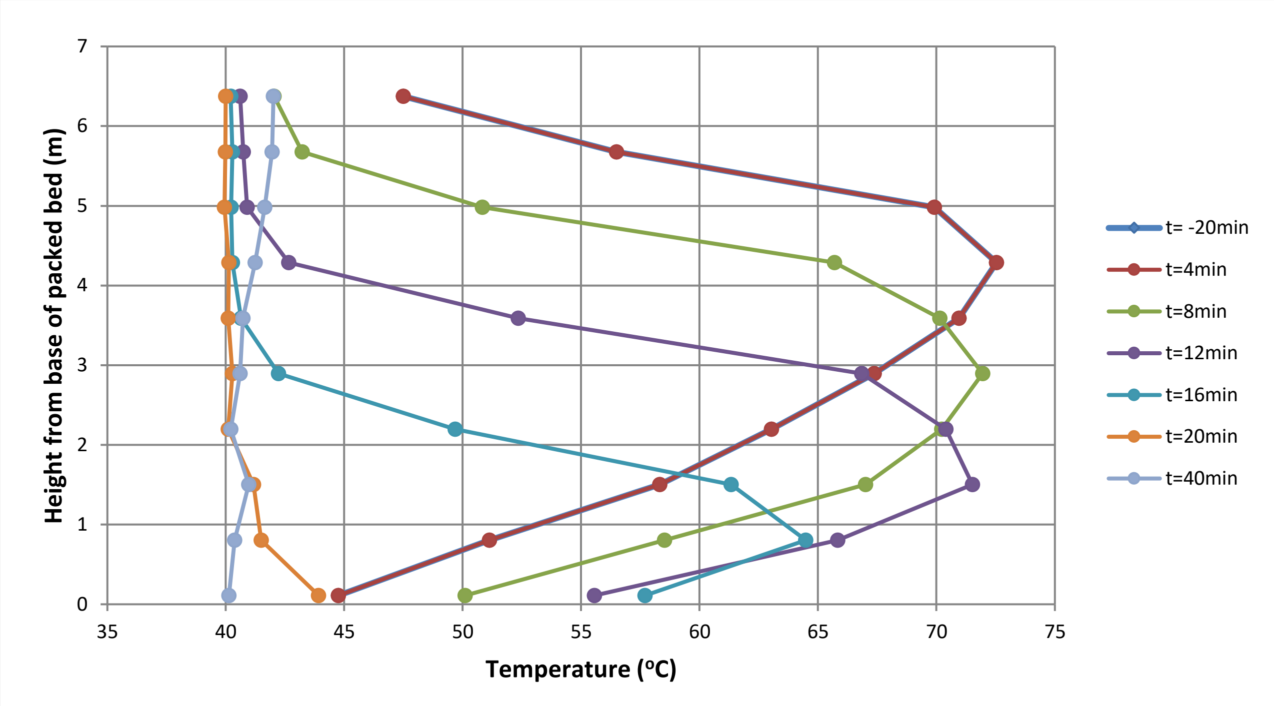
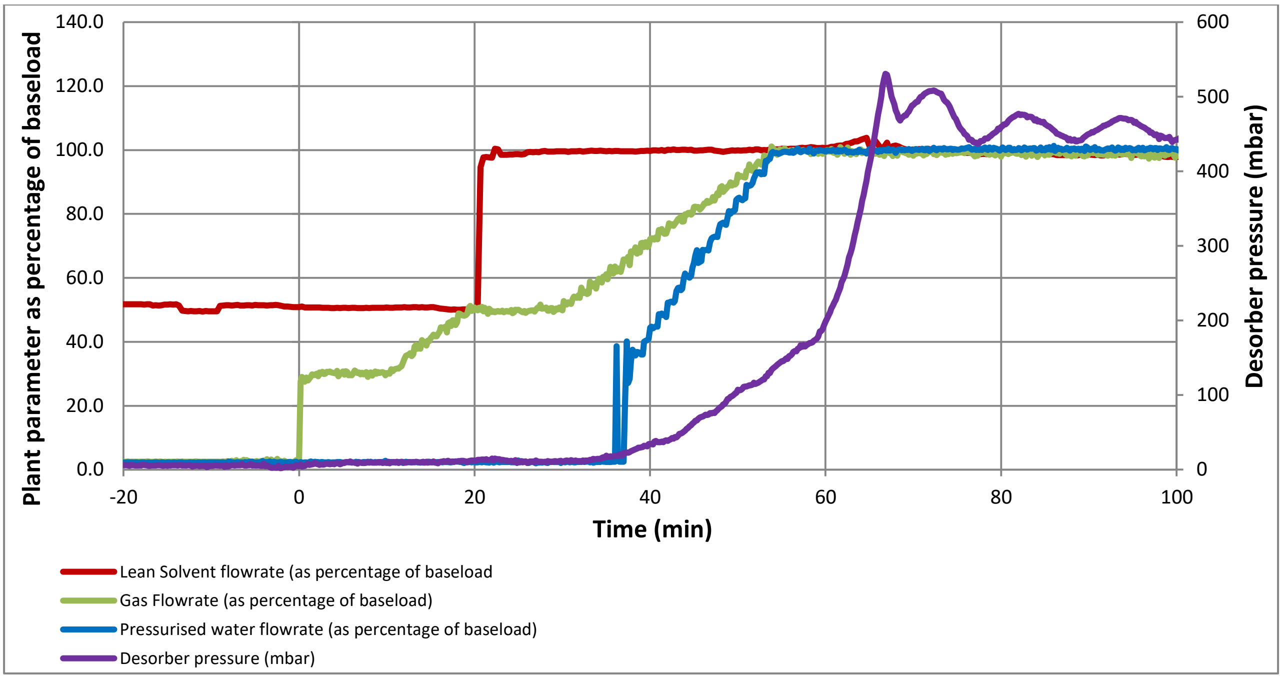


Fig. 8 Absorber temperature profile during plant shutdown scenario #1

4.1.2 Startup – standard procedure

This plant startup scenario intends to simulate a situation in which the low-pressure steam turbine achieves full power output before the introduction of steam to the reboiler. The startup procedure is based on real pulverised coal plant data (NETL, 2014). In anticipation of plant startup, the flow of solvent is stabilised at 50% of baseload. Titration measurements show that the lean and rich loadings are initially approx. 0.18 mol CO_2/molamine. Gas is introduced to the absorber at t=0min (fig. 9a), when the hypothetical generation plant reaches minimum stable generation (30% of its stated power generation capacity). Once the gas flow is stabilised at 50% of baseload (100m^3/hr) at t=20min, the solvent flow is increased to 100% of baseload (1000 l/hr) in anticipation of the next gas flow ramp, which is initiated at t=28min. Pressurised hot water is ramped at a rate of approx. 0.4m^3/hr per minute from t=29min to t=54min. As mentioned previously, the hot water flow meter does not detect flow below around 30% of baseload (3m^3/hr), but the hot water flow rate increase is assumed to have the same rate throughout the ramp. Hot water and gas flowrates both reach 100% of baseload at t=54min.
CO_2 capture efficiency is initially higher than at baseload due to the higher L/G ratio, but drops off rapidly at t=35min as lean loading at the absorber inlet rises (fig. 9b). At this time, lean solvent CO_2 loading at the absorber inlet becomes high enough to diminish the driving force for CO_2 absorption, reducing the capture efficiency. Solvent lean loading reaches a maximum at t=69min, while capture efficiency reaches a minimum at t=72min. If it is assumed that mixing effects in the pipework between the desorber sump outlet and absorber inlet are negligible, solvent which is analysed by the lean solvent sensor at t=x min will reach the absorber inlet at t=x+3 min.
Due to an error with the data-logging programme at t =200min, certain datasets after this time are unavailable. There is also a large spike in the rich solvent CO_2 loading online measurement at t=260-280min, but since the measured value exceeds 0.5mol/mol and a similar spike in titration measurements is not observed, this may be attributed to an instability of the rich loading sensor.



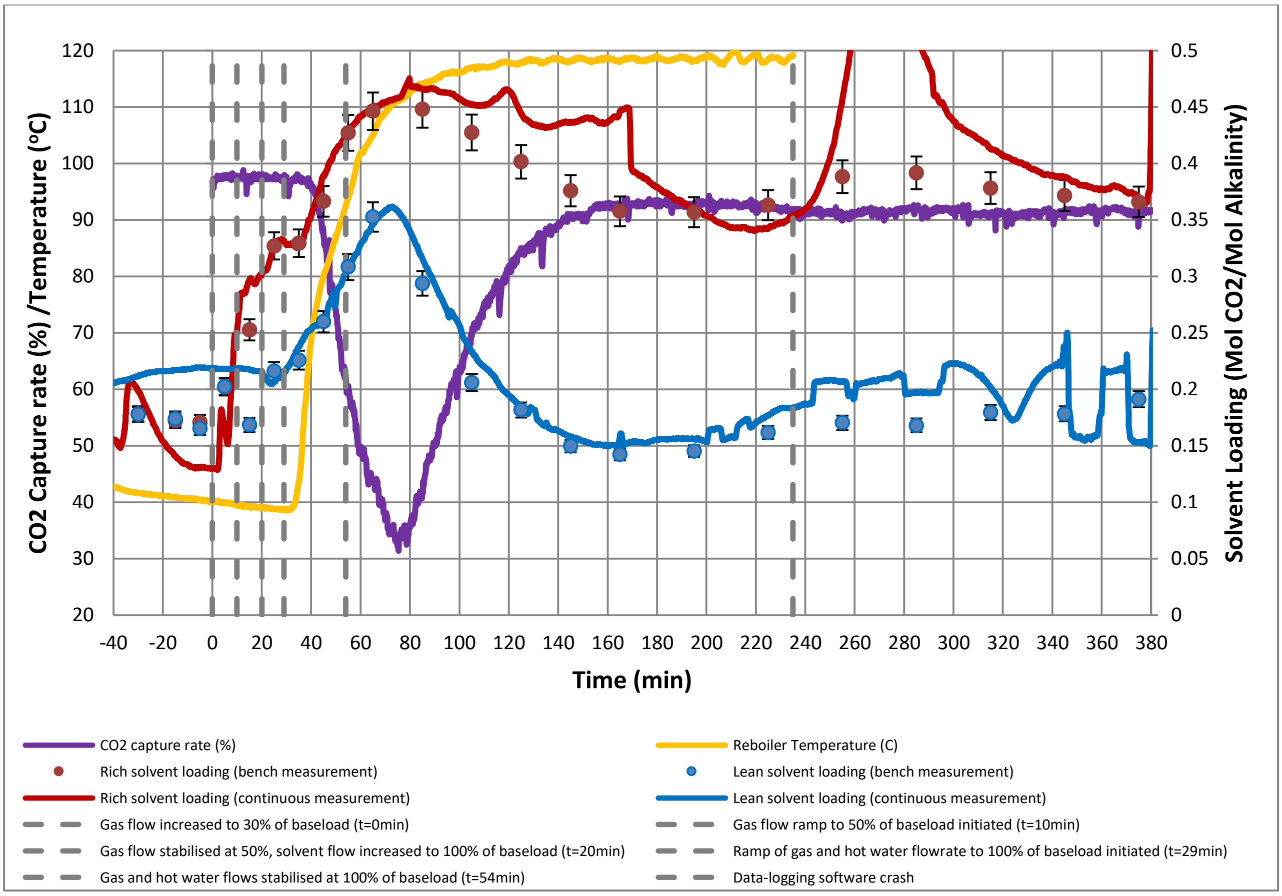
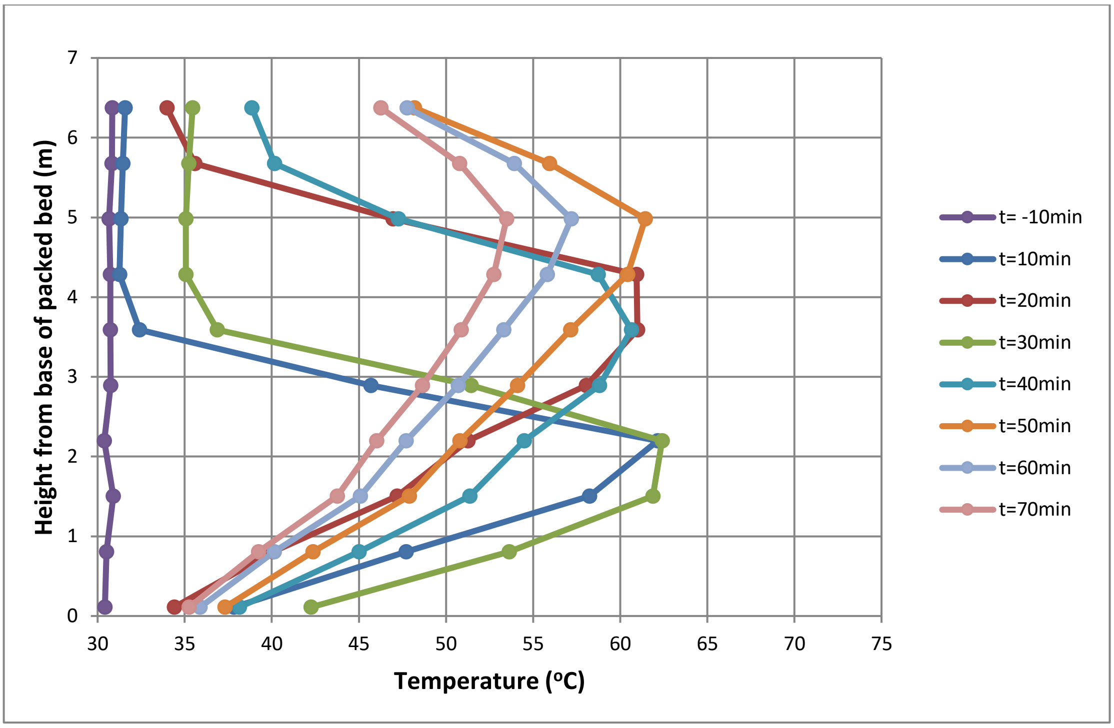


Fig. 9a Gas, solvent hot water flow rate and desorber pressure as percentage of baseload operation, startup scenario 1

Fig. 9b Rich and lean solvent loading, reboiler temperature and CO_2 capture efficiency, startup scenario 1



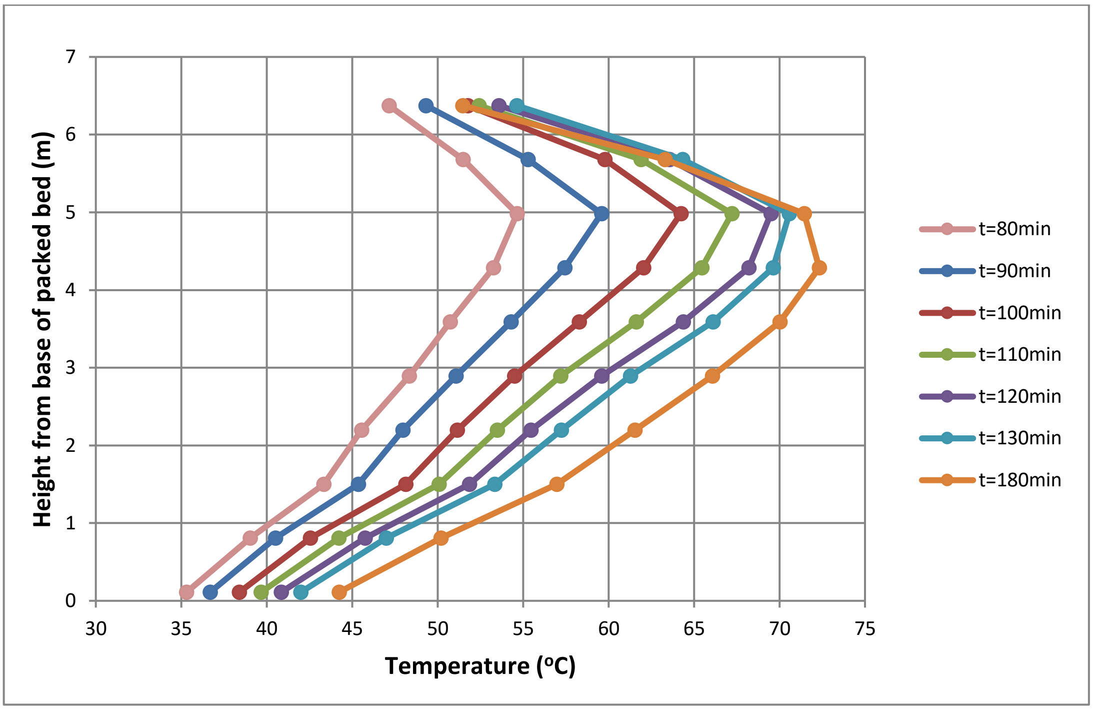


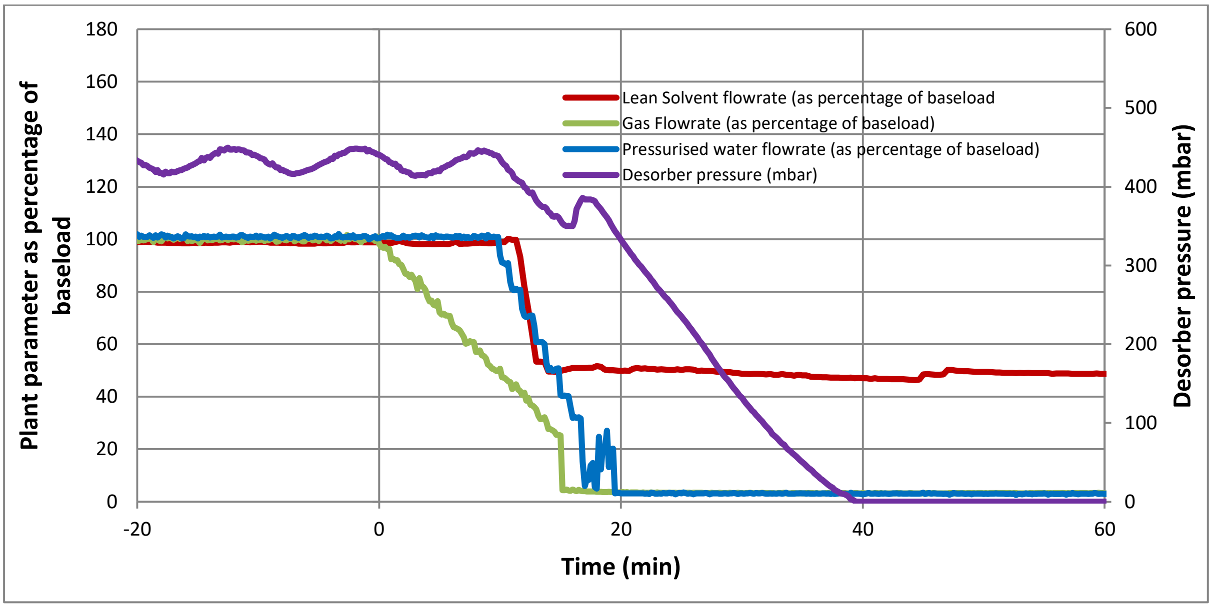
Fig. 10a Absorber temperature profile, startup scenario 1, t= -10min to t=70min
Fig. 10b Absorber temperature profile, startup scenario 1, t= 80min to t=180min

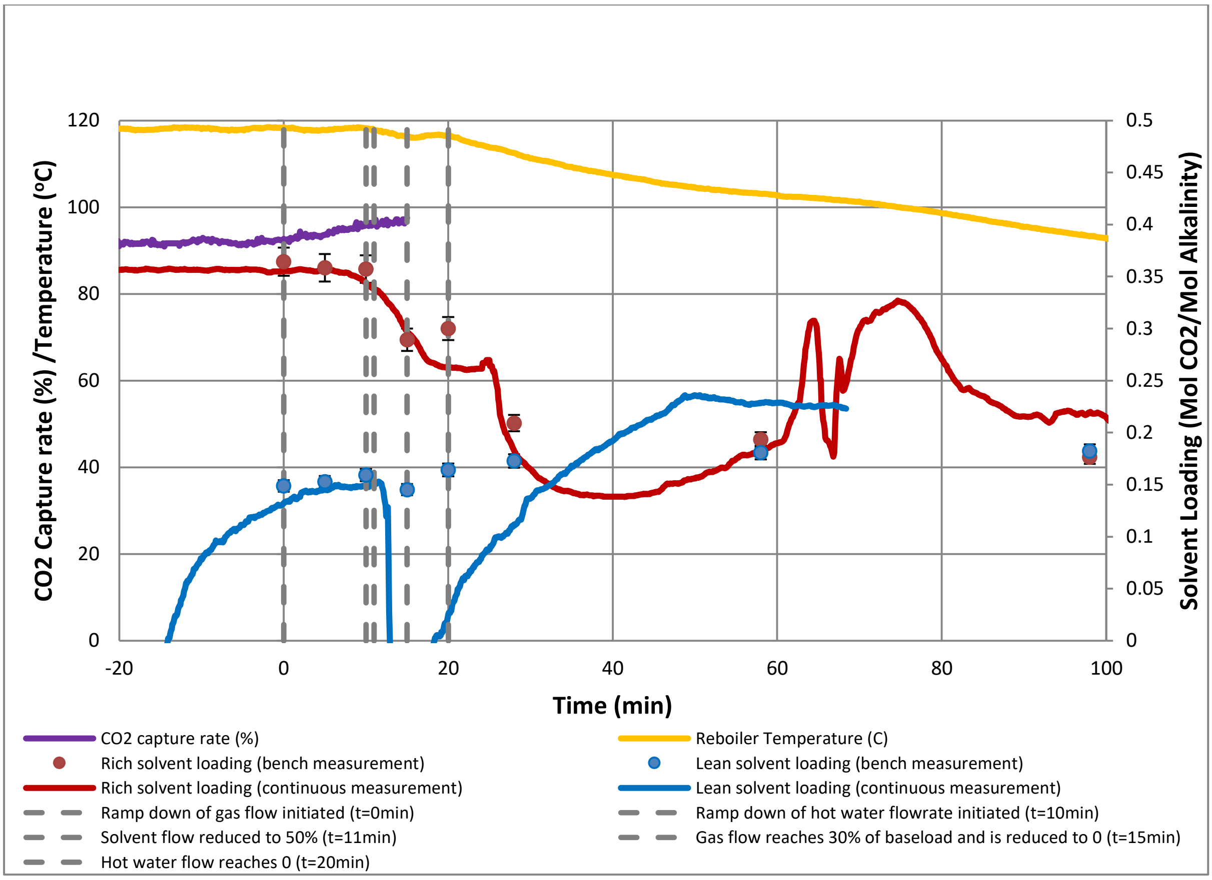
The absorber temperature bulge increases in magnitude and rises up the packed bed as the gas flow rate increases, until t=20min (fig. 10a). Just after t=20min there is a step-change in solvent flow rate from 500l/hr to 1000l/hr. This rapid increase in L/G ratio results in a larger proportion of the CO_2 being absorbed close to the gas inlet, so the temperature bulge migrates to a lower location in the packed bed. As the flow of gas continues to increase, the L/G ratio decreases and the temperature bulge moves further up the packed bed. After t=50min it begins to decrease in magnitude as the lean loading at the absorber inlet increases and the capture efficiency falls. The observed increase in the lean loading during this period is due to lower rate of desorption. Although the flow rate of the pressurised hot water is being increased, the solvent temperature in the reboiler did not achieve the temperature high enough for stripping. Because of the lower desorption rate, lean solvent leaving the reboiler and entering the absorber was at relatively higher lean loading which resulted in increased rich loading in the absorber and in return an increasing trend in lean loading until the reboiler temperature reaches operational temperature. At this point lean loading begins to decrease. Between t=70min and t=80min the capture efficiency begins to rise again, as does the magnitude of the temperature bulge until it is fully established at t=180min (fig. 10b).

4.2 Shutdown/Startup coupling 2

4.2.1 Shutdown

This shutdown scenario was carried out with similar changes in gas, liquid and hot water flow to shutdown scenario #1 (fig. 11a and 7a, respectively). Online lean and rich solvent sensors experienced stability issues prior to the initiation of this scenario. Therefore, manual solvent samples for off line analyses are taken at more regular intervals. This is to make sure that the effect of the shutdown operation on solvent loading can still be observed while online solvent measurements appear to be. A marginal increase is again observed in CO_2 capture efficiency before the flow of gas is shut down, and rich & lean solvent loadings rapidly converge and stabilise at approx. 0.18 mol CO_2/mol amine (fig. 11b). Temperature trends (fig. 11c) are similar to those of the previous shutdown operation (fig.8) with no significant differences.





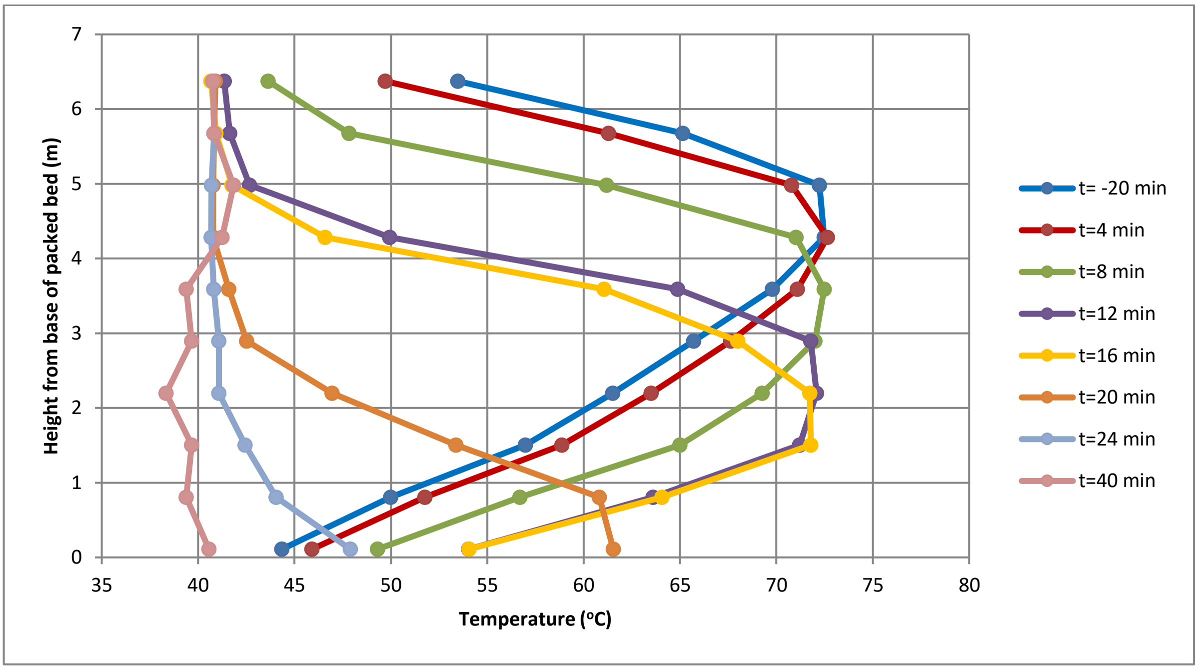


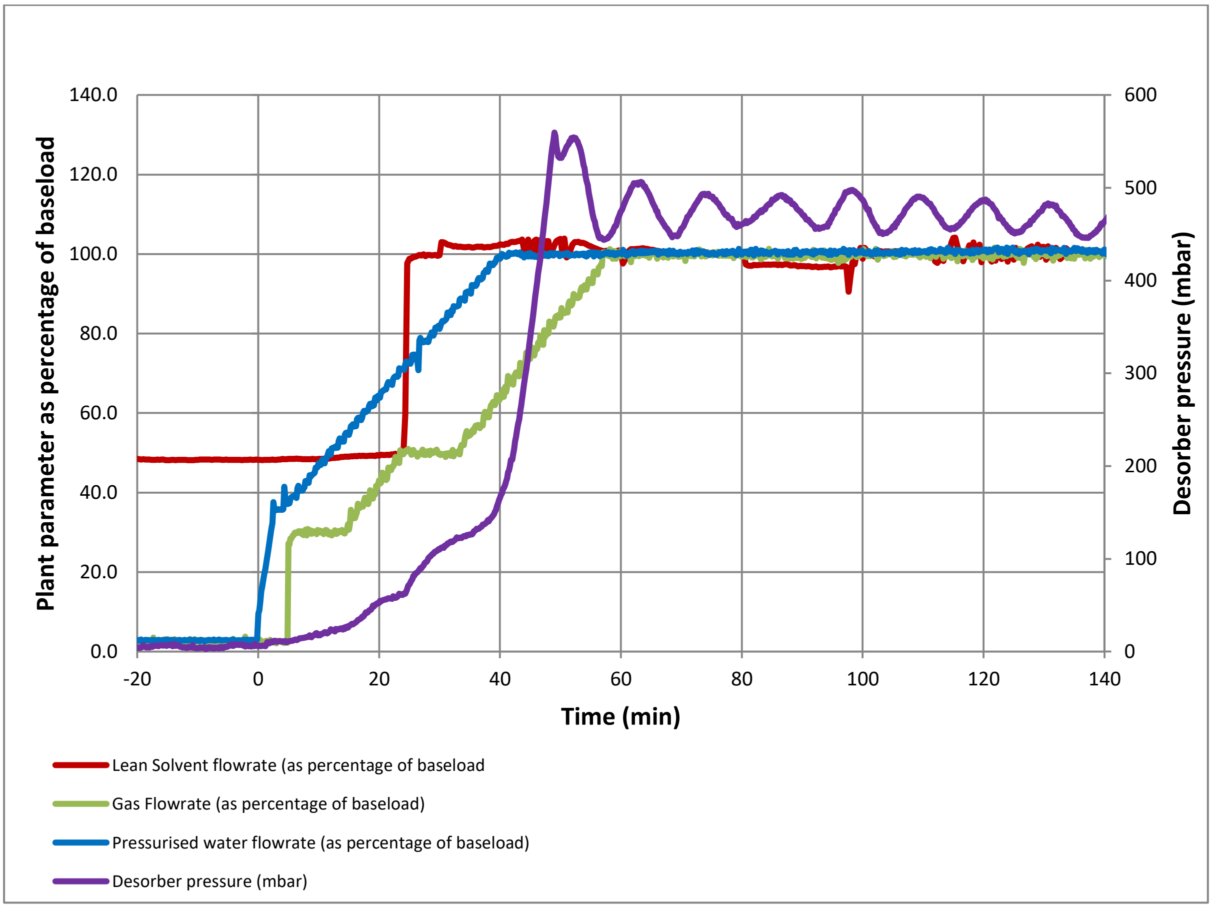
Fig. 11a. Gas, solvent hot water flow rate and desorber pressure as percentage of baseload operation, shutown scenario 2

Fig. 11b. Rich and lean solvent loading, reboiler temperature and CO_2 capture efficiency, shutdown scenario 2

Fig. 11c Absorber temperature profile, startup scenario 2, t= -20min to t=40min

4.2.2 Startup – with prioritisation of CO_2 emissions minimisation

In this scenario steam is introduced to the reboiler as soon as it becomes available instead of after 35 minutes, as was the case in the previous shutdown/startup coupling (section 4.1). This may be useful in situations where the plant operator is subject to significant emissions penalties in the case of large spikes in CO_2 emissions from a point source, or in the event of extremely high carbon price. Pressurised hot water is ramped up to 30% of baseload ($3m^3/hr$) at t=0 and is subsequently ramped up at 1.75% of baseload ($0.175m^3/hr$) per minute until it reaches $10m^3/hr$ (fig. 12a). All other flow rates remain similar to the startup scenario described in section 4.1.2.



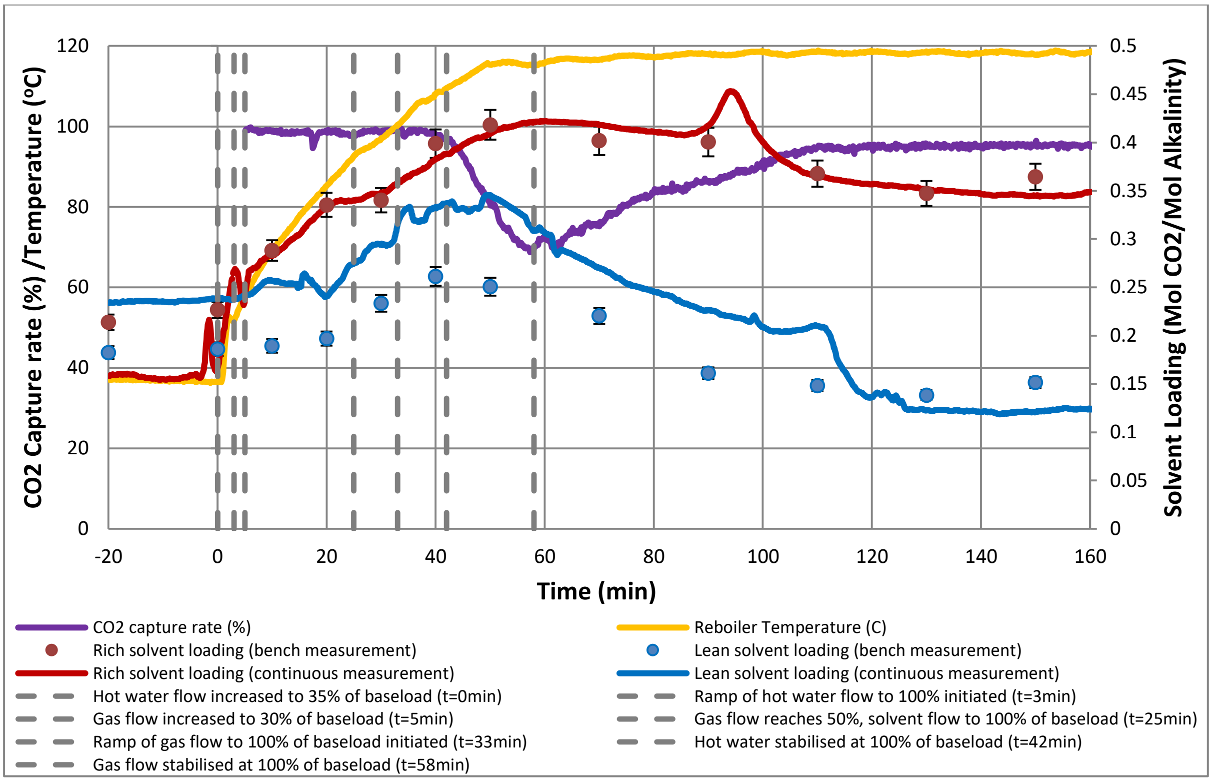


Fig. 12a. Gas, solvent hot water flow rate and desorber pressure as percentage of baseload operation, startup scenario 2

Fig. 12b. Rich and lean solvent loading, reboiler temperature and CO_2 capture efficiency, startup scenario 2

The reboiler reaches operational temperature much more rapidly than in scenario 4.1.2, so the drop-off in CO_2 capture efficiency is less sharp and reaches a minimum of approx 70% (fig. 12b) instead of 33%. If a similar approach were to be attempted during real plant startup operation, it could proceed by synchronising the turbine shaft while abstracting the maximum possible flow of steam from the IP/LP crossover, allowing the remainder to flow through the LP turbine to remove the resultant frictional heat. It may also be possible to extract additional steam from the HP turbine outlet during start-up, if maintaining a capture efficiency as close to 90% as possible were critical.

For comparison with the startup scenario described in 4.1.2 the total CO_2 emissions over the first 160mins of gas being introduced to the absorber are calculated. This length of time is selected as it is the duration required for the plant in scenario 4.1.2 to stabilise at baseload operating conditions (fig. 9b).

$$mCO_2 = \int_{0min}^{160min} \left(\frac{Q_{gas,t}}{60} \cdot \varphi_{CO2,t} \cdot \rho_{CO2,t}\right)\left(1 - \frac{\eta_{CO2,t}}{100}\right) \qquad \text{(Equation 2)}$$

mCO_2 is the total mass of CO_2 emitted, Q_{gas} is the volumetric flow rate of gas in m^3/hr, φ_{CO2} is the volume fraction of CO_2 in the gas phase, ρ_{CO2} is the density of CO_2 at the gas inlet temperature and η_{CO2} is the percentage CO_2 capture efficiency. mCO_2 for startup scenario 4.1.2 is 25.1kg. mCO_2. For startup scenario 4.2.2 is 10.3kg, a saving of 14.8kg CO_2 over the same time period.

To determine the potential effect on total daily CO_2 emissions this result is considered in the context of a coal-fired power station, equipped with CCS and operating under a two-shifting dispatch pattern. In this operating mode a hot startup is initiated at 6am, then operates at steady-state baseload with 90% capture efficiency until 10pm, for a total daily operating time of 16 hours.

Operating Scenario	Duration (mins)	Total startup CO_2 emissions (kg)	Total daily CO_2 emissions (kg)

Startup with prioritization of grid synchronization	160	25.1	79.4
Startup with prioritization of emissions minimization	160	10.3	64.6

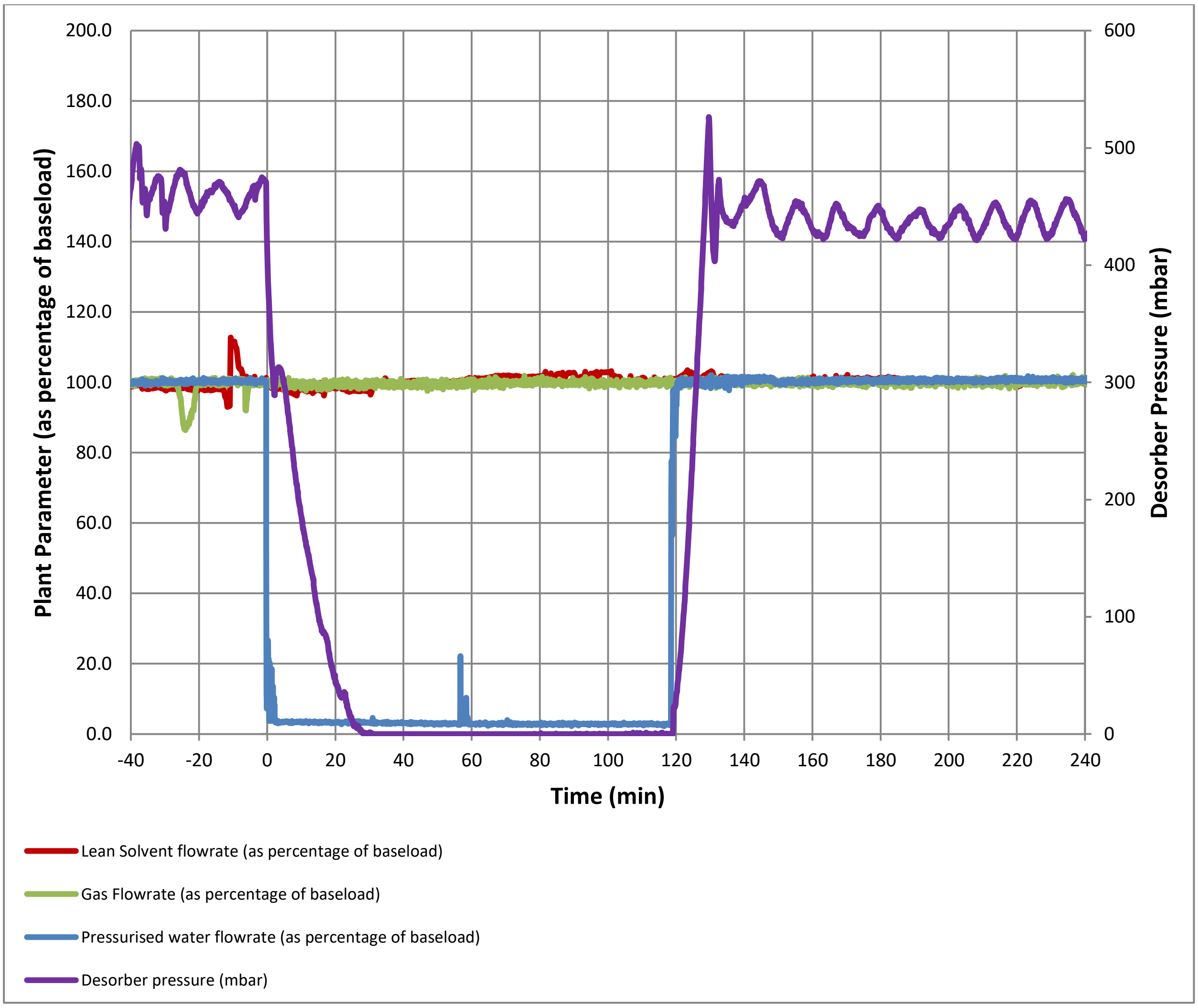
Table 3. Total CO_2 emissions in total kg per scenario

The saving of 14.8kg CO_2 during startup is approx. 18.6% of the total emissions for a day under two-shifting operation. As steam is introduced more rapidly in scenario 2 the total mass of steam used during the startup period increases by 23.6%. However, as stripping steam is extracted before the inlet of the low-pressure steam turbine the impact on overall plant energy output is likely to be small. Depending on the future emissions cost of CO_2, this analysis shows that it may be economical to implement advanced control strategies to begin capturing CO_2 as rapidly as possible during a start-up event. A comparison of two similar scenarios at large-scale via, for example, dynamic modelling would be an interesting follow-up study.

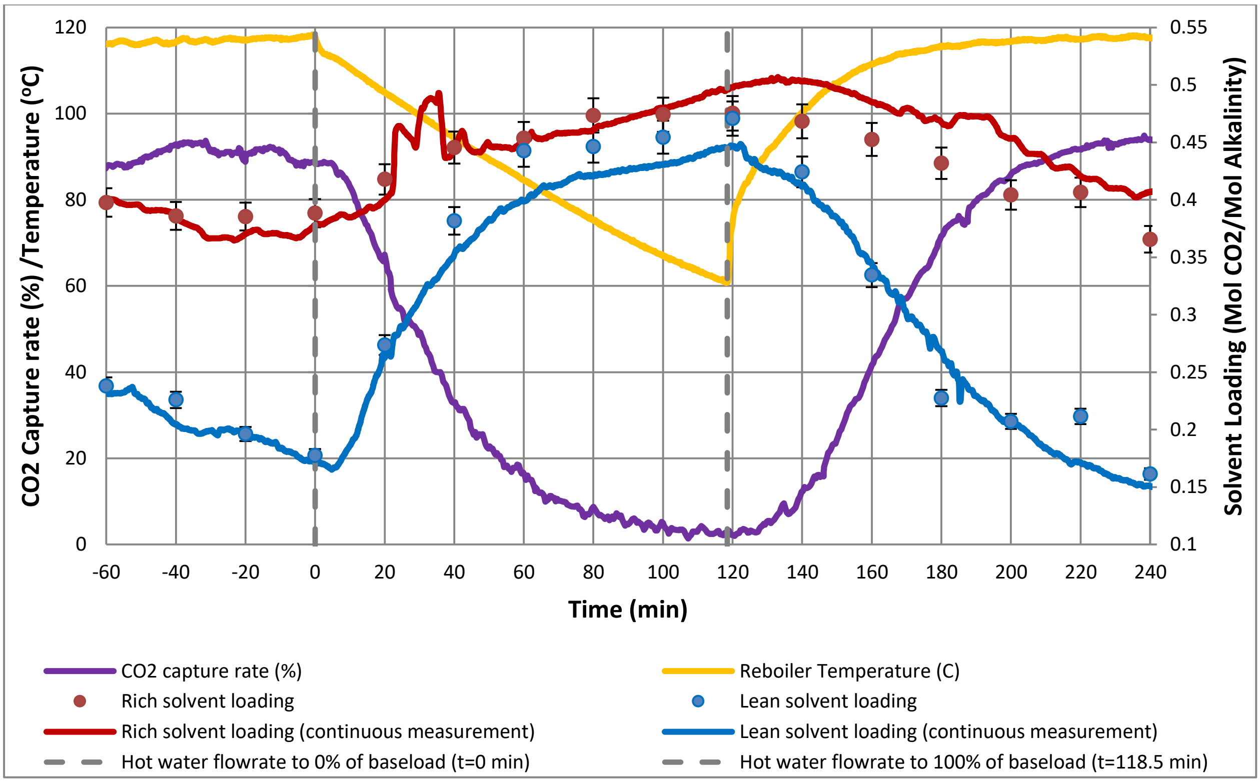
4.3 Power output maximisation via hot water decoupling – Capture Bypass scenario 1

It can be advantageous for plant operators to stop the flow of steam to the reboiler, redirecting it instead to the low-pressure steam turbine to capitalise on high electricity selling price. This scenario demonstrates how the capture plant responds to the decoupling of steam flow from the reboiler. It also provides valuable insights about plant circulation times and dynamics which prove useful for capture efficiency control using online solvent measurements (scenario 4.7).

Flow of hot water to the reboiler is switched off at t=0min (fig. 13a). The online solvent sensor detects a change in lean loading at t=5min, with the CO_2 capture efficiency responding at approximately t=8min (fig. 13b). The CO_2 capture efficiency decreases steadily as both rich and lean solvent become more concentrated in CO_2. Hot water is reintroduced to the reboiler at t=118min 30sec. The lean solvent sensor detects a reduction in lean loading around 5mins after the step-change in reboiler heat input, at t=123min 30sec. The capture efficiency responds between t=126 and 127mins. The following conclusions can be drawn based on the observation made on the plant response time to introduction of step changes. If the plant is operating at baseload solvent flow conditions and a step change is introduced in hot water flow, a change in lean online solvent measurement appears after 5mins, and a change in capture efficiency appears after around 8mins (table 4).



200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
600
500
400
300
200
100
0
-40
-20
0
20
40
60
80
100
120
140
160
180
200
220
240
Plant Parameter (as percentage of baseload)
Desorber Pressure (mbar)
Time (min)
Lean Solvent flowrate (as percentage of baseload)
Gas Flowrate (as percentage of baseload)
Pressurised water flowrate (as percentage of baseload)
Desorber pressure (mbar)



120
100
80
60
40
20
0
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
-60
-40
-20
0
20
40
60
80
100
120
140
160
180
200
220
240
CO2 Capture rate (%) /Temperature (°C)
Solvent Loading (Mol CO2/Mol Alkalinity)
Time (min)
CO2 capture rate (%)
Reboiler Temperature (C)
Rich solvent loading
Lean solvent loading
Rich solvent loading (continuous measurement)
Lean solvent loading (continuous measurement)
Hot water flowrate to 0% of baseload (t=0 min)
Hot water flowrate to 100% of baseload (t=118.5 min)

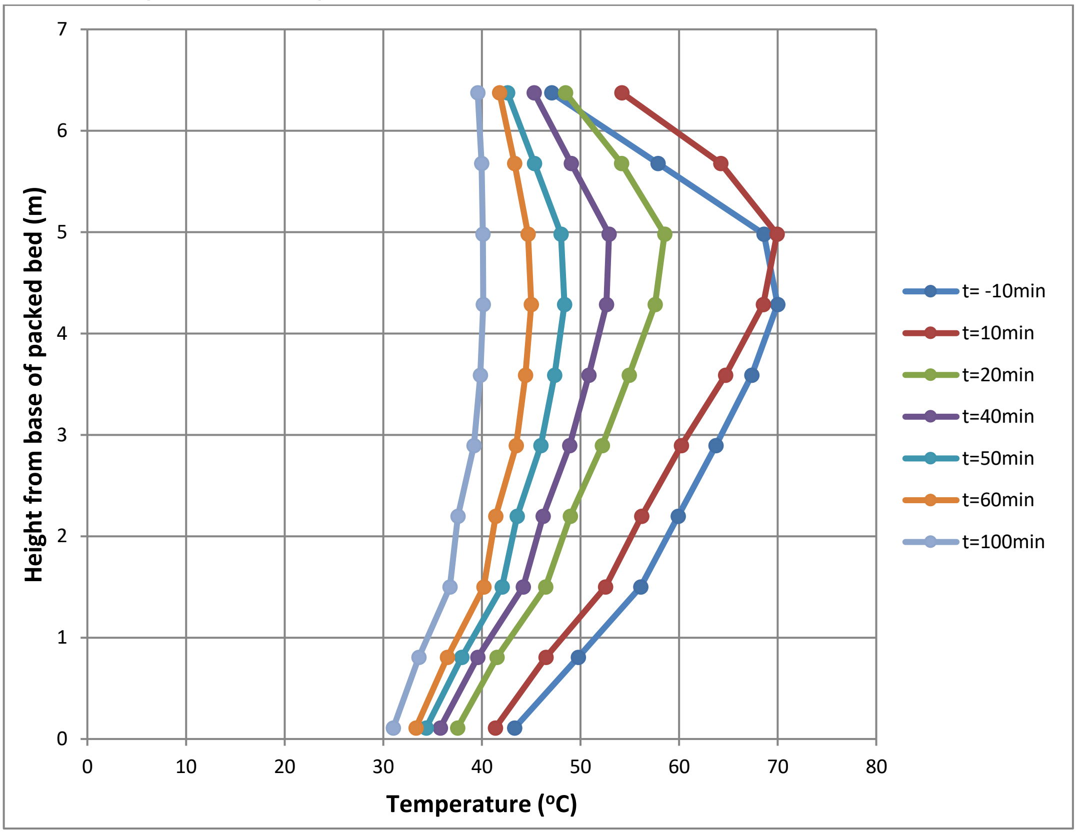
Fig. 13a. Gas, solvent hot water flow rate and desorber pressure as percentage of baseload operation, capture bypass scenario 1

Fig. 13b. Rich and lean solvent loading, reboiler temperature and CO_2 capture efficiency, capture bypass scenario 1

Event	Cause of event	Approximate elapsed time since hot water flow is reintroduced (min)
Hot water flow increased from $0m^3/hr$ to $10m^3/hr$	Step-change in setpoint from operator.	0
Response in online lean loading measurement	Solvent which is leaner as a result of hot water step-change reaches the lean online solvent sensor.	5
Response in CO_2 capture efficiency	Leaner solvent reaches the absorber inlet.	8

Table 4. Response of plant parameters to reintroduction of reboiler heat input

The absorber temperature profile gradually decreases in magnitude along with the capture efficiency (fig. 14a). When the flow of hot water is reintroduced to the reboiler at 118min 30sec the capture efficiency increases and the absorber temperature increases in magnitude until the plant reaches steady state, baseload operating conditions (fig. 14b).



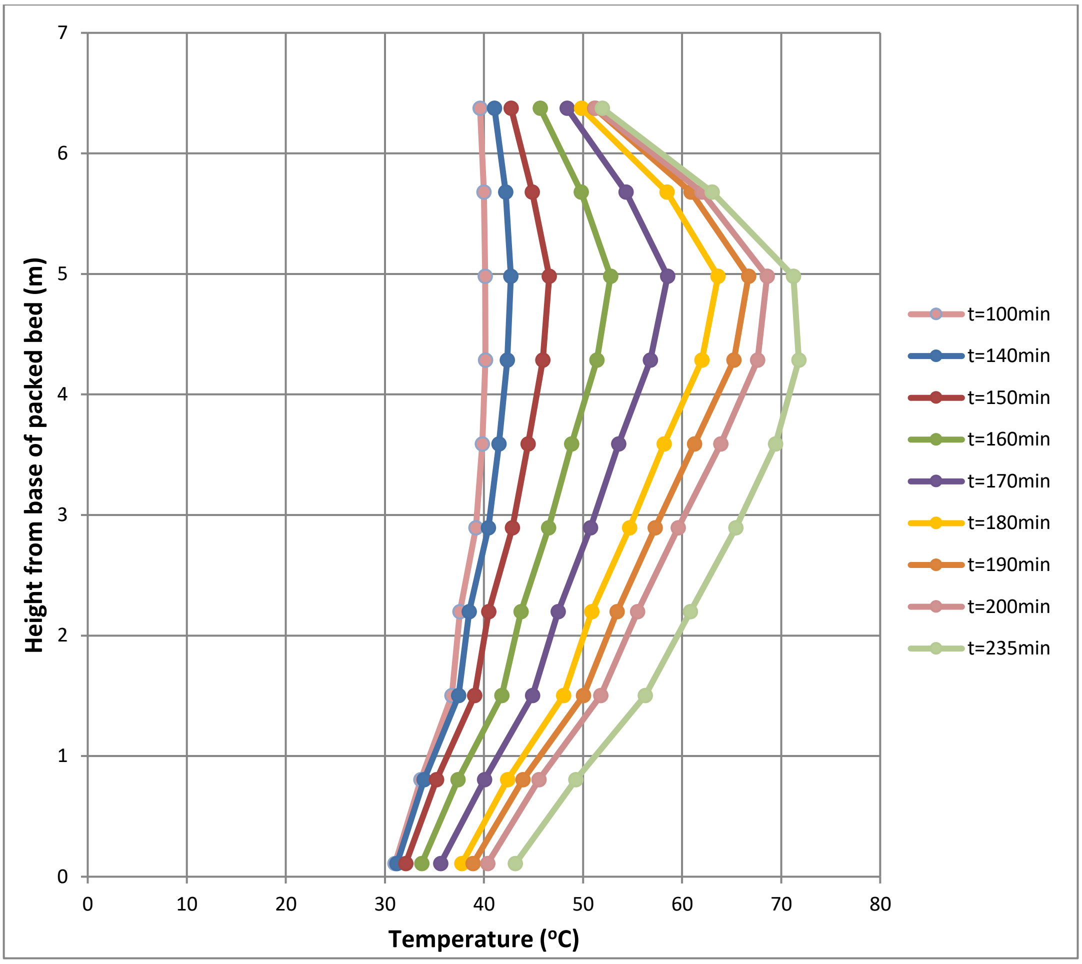


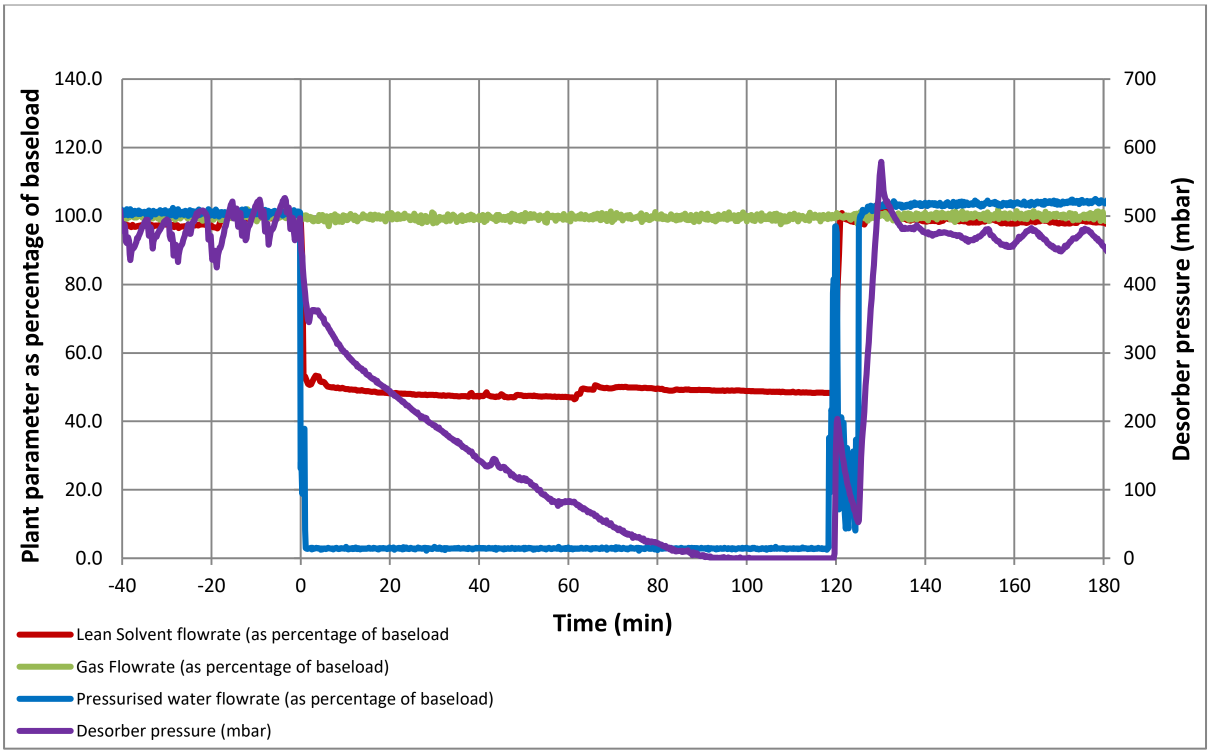
Fig. 14a. Absorber temperature profile, capture bypass scenario 1, t= -10min to t=100min

Fig. 14b. Absorber temperature profile, capture bypass scenario 1, t= 100min to t=235min

4.4 Power output maximisation via hot water decoupling, solvent flow reduced by 50% - Capture bypass scenario 2

This scenario is similar to the previous hot water decoupling event (section 4.3), but the flow of solvent to the absorber is reduced to 50% in addition to the reduction of hot water flow to zero. In a real CO_2 capture plant, this would reduce both the power consumption of the pumps and the booster fan, via reduction of the pressure drop across the absorber.

Hot water flow to the reboiler is both reduced to zero and solvent flow is reduced to 50% of baseload at t=0min (fig. 15a). Due to the rapid decrease in L/G flow ratio the capture efficiency is reduced almost immediately, reaching 60% within 4 minutes (fig. 15b). Capture efficiency continues to decrease over the course of the hot water decoupling event. At t=118min the flow of solvent and hot water are both increased to 100% of baseload, but due to an error with the Labview control system the hot water flow is not stabilised at baseload until t=125min (fig. 15a). CO_2 capture efficiency begins to increase noticeably at around t=130mins, the plant response being slower than in scenario 4.3 due to the error with hot water flow stabilisation at t=118min.



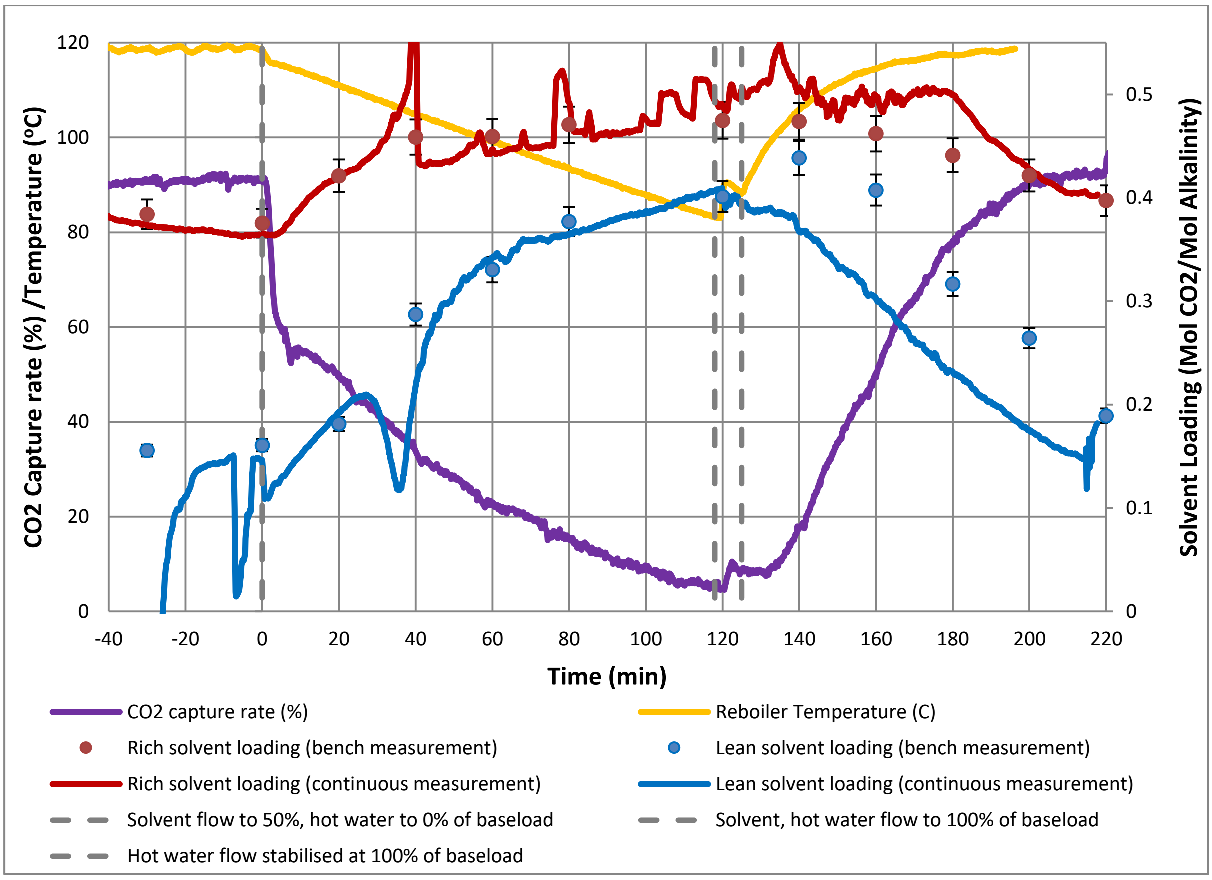


Fig. 15a. Gas, solvent hot water flow rate and desorber pressure as percentage of baseload operation, power output maximisation event 2.

Fig. 15b. Rich and lean solvent loading, reboiler temperature and CO_2 capture efficiency, power output maximisation event 2

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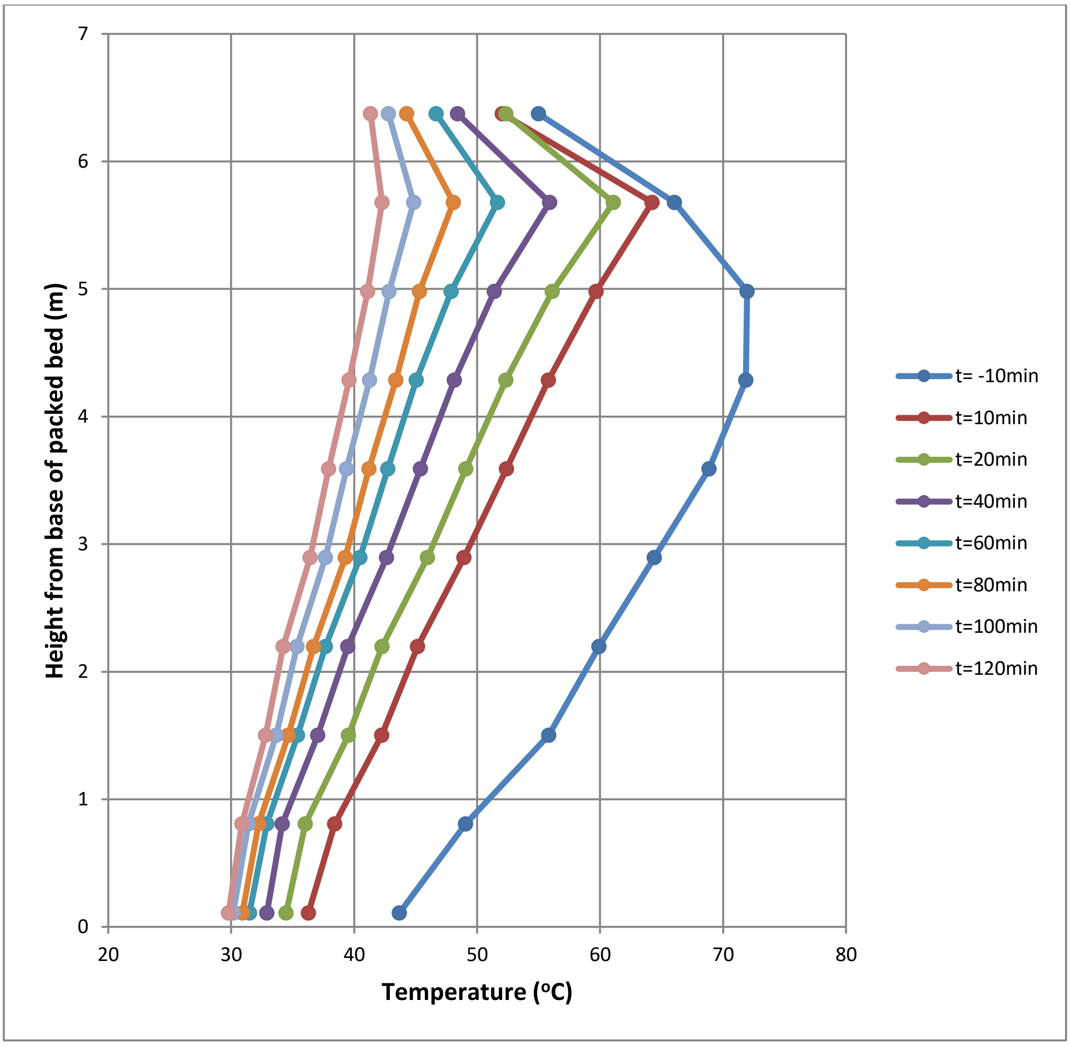


Height from base of packed bed (m)
Temperature (°C)
0
1
2
3
4
5
6
7
20
30
40
50
60
70
80
t= -10min
t=10min
t=20min
t=40min
t=60min
t=80min
t=100min
t=120min

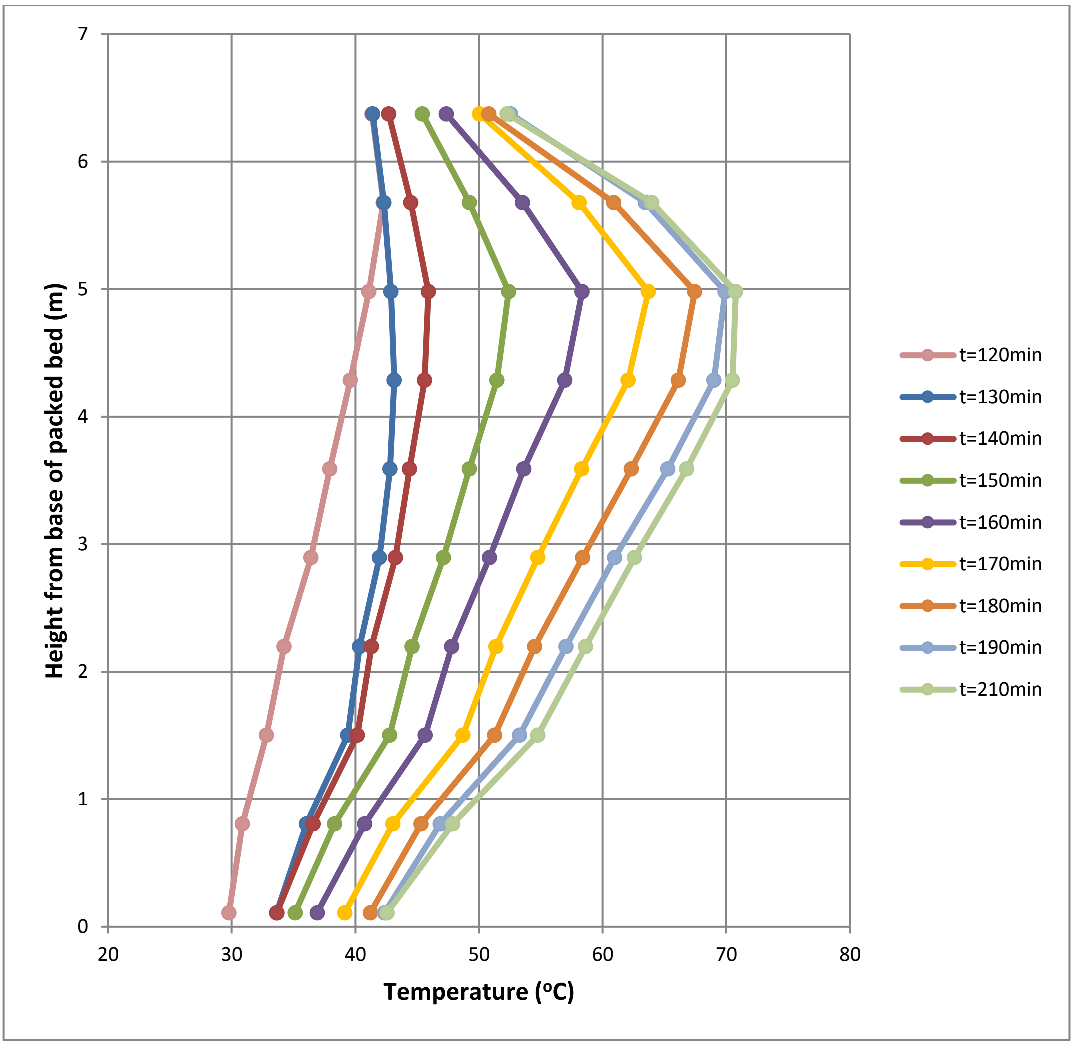


Fig. 16a. Absorber temperature profile, capture bypass scenario 2, t= -10min to t=120min
Fig. 16b. Absorber temperature profile, capture bypass scenario 2, t= 120min to t=210min

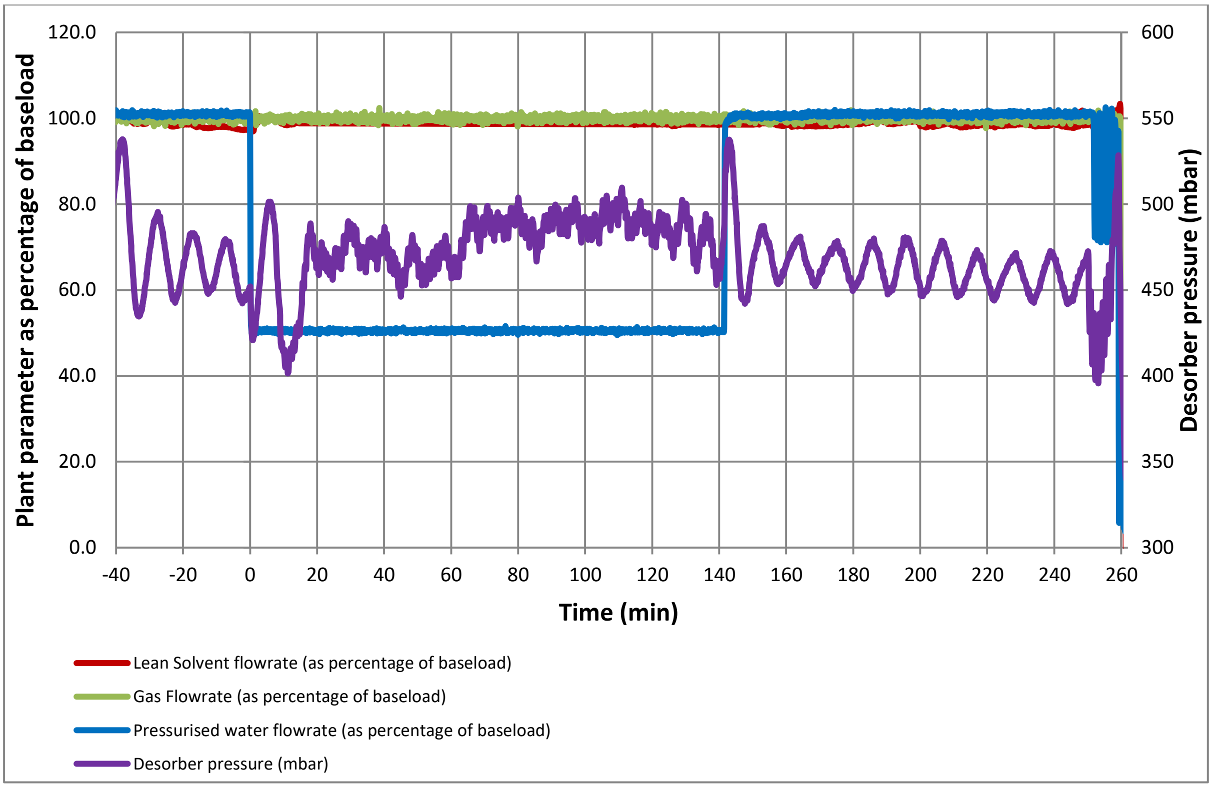
In comparison to the scenario 4.3 the absorber temperature profile follows a roughly similar trajectory although the initial decrease in the magnitude of the temperature bulge is more rapid due to the reduced solvent flow rate and hence, reduced capture efficiency (fig. 16a).

4.5 Frequency response via hot water flow reduction

Coal-fired power stations can enhance their flexibility via the addition of post-combustion capture, which allows them to rapidly increase (or reduce) plant output via redirection of steam flow from the reboiler to the low pressure steam turbine (Lucquiaud, 2009; Haines and Davison, 2014). In this scenario the flow of hot water to the reboiler is reduced by 50% at t=0 (fig. 17a). All other plant flow rates remain at baseload throughout. A decrease in CO_2 capture efficiency is observed over the course of t=20min to t=100min, stabilising at around 75% (fig. 17b). This results in an 8°C decrease in absorber temperature bulge magnitude over this time period (fig. 18a).

At t=141min the flow of hot water to the reboiler is increased to 100% of baseload (fig. 17a). A response in capture efficiency is observed at approx. t=149min which is consistent with the plant response observed in scenario 4.3. The capture efficiency requires 70mins to increase to its original value, stabilising at around 93% at t=210min. The absorber temperature bulge increases to its original magnitude as the capture efficiency increases (fig. 18b).

The rich solvent online measurement is in close agreement with bench titration measurements, but the lean online measurement suffers from severe measurement instability until approx. t=122min.



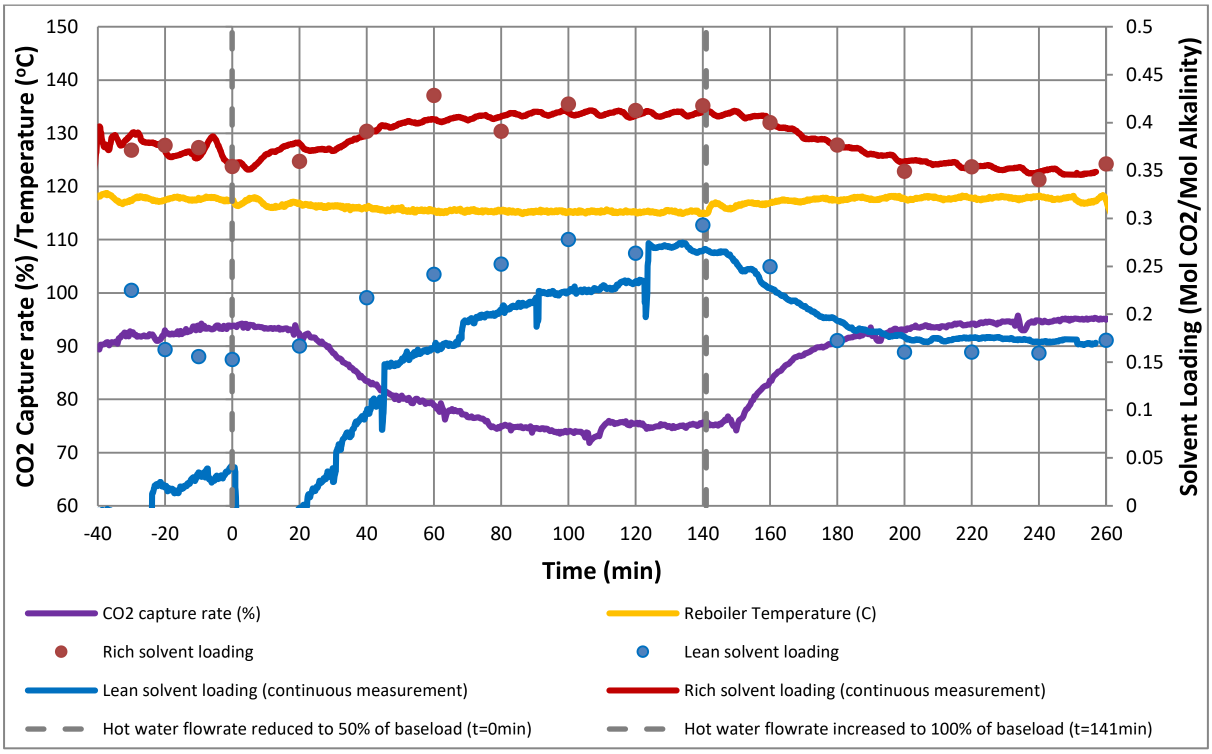
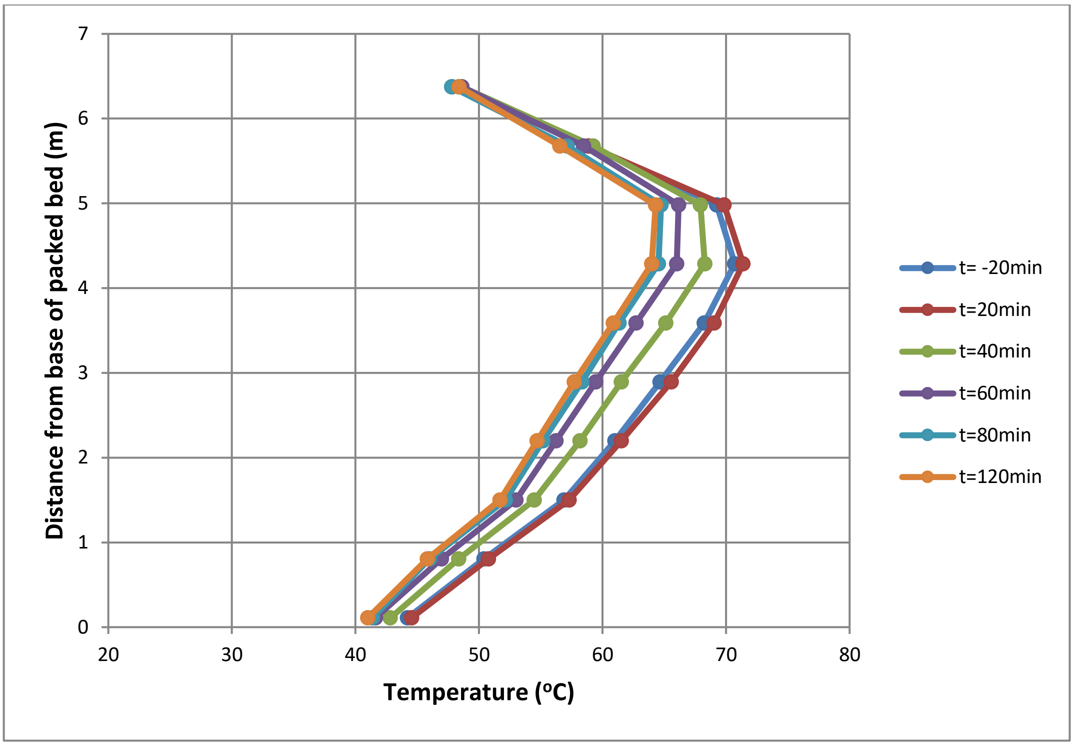


Fig. 17a. Gas, solvent hot water flow rate and desorber pressure as percentage of baseload operation, frequency response scenario

Fig. 17b. Rich and lean solvent loading, reboiler temperature and CO_2 capture efficiency, frequency response scenario



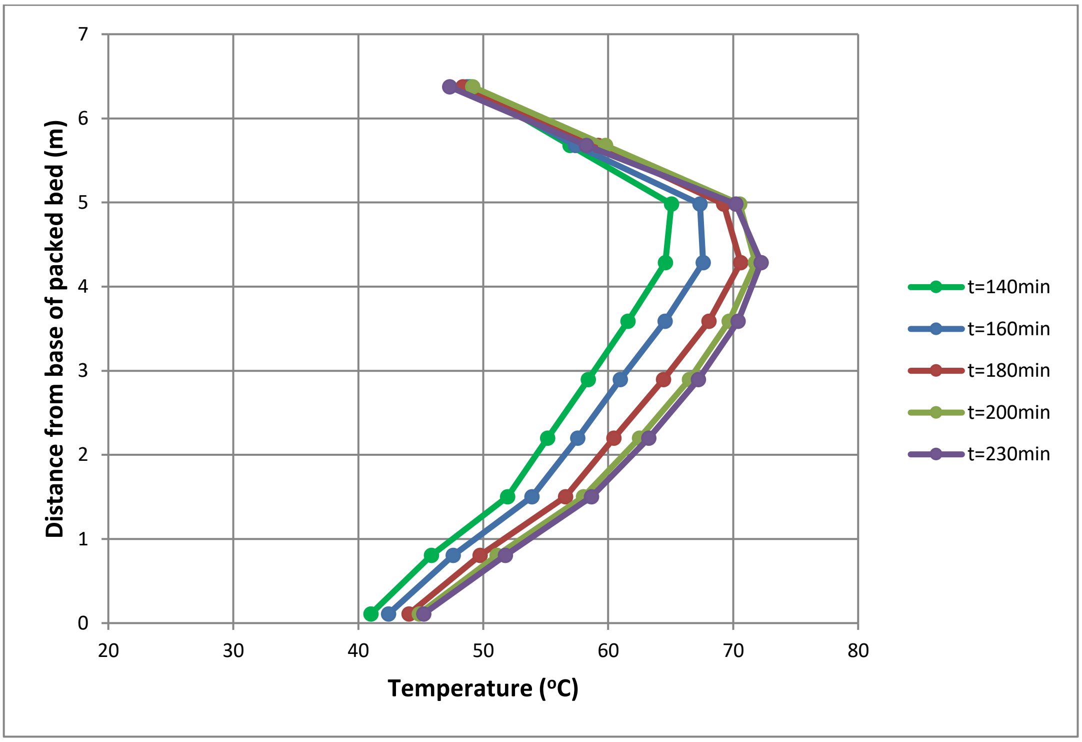


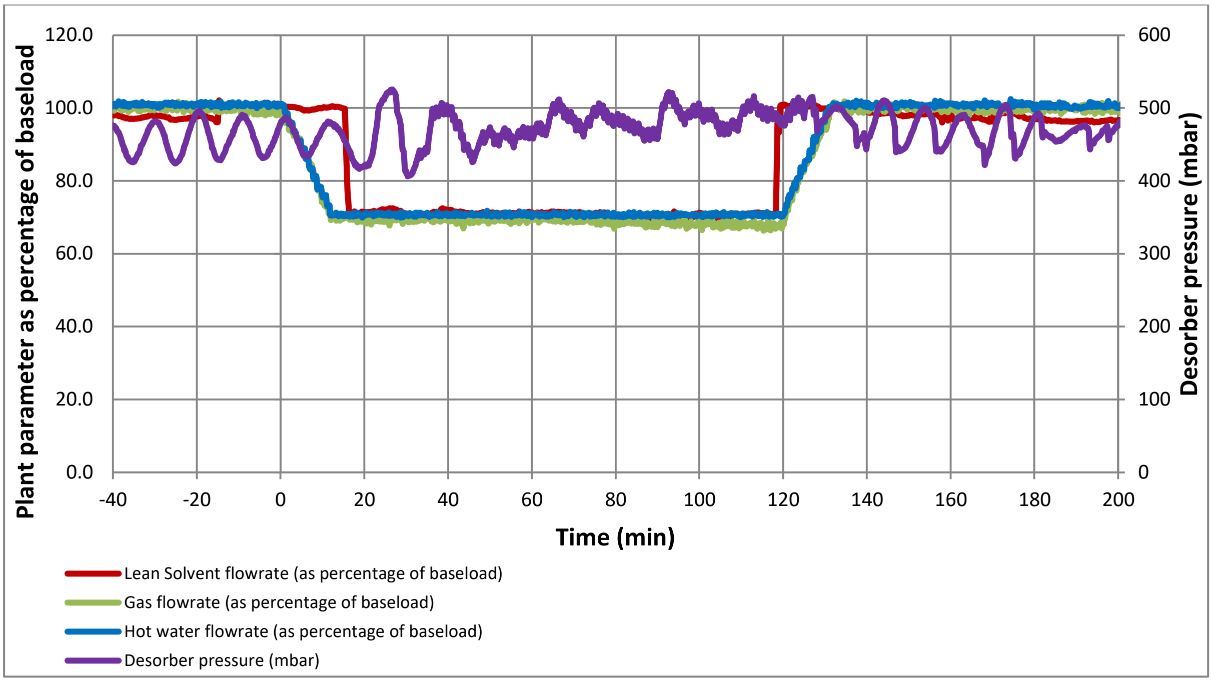
Fig. 18a. Absorber temperature profile, frequency response scenario, t= -10min to t=100min
Fig. 18b. Absorber temperature profile, frequency response scenario, t= -100min to t=235min

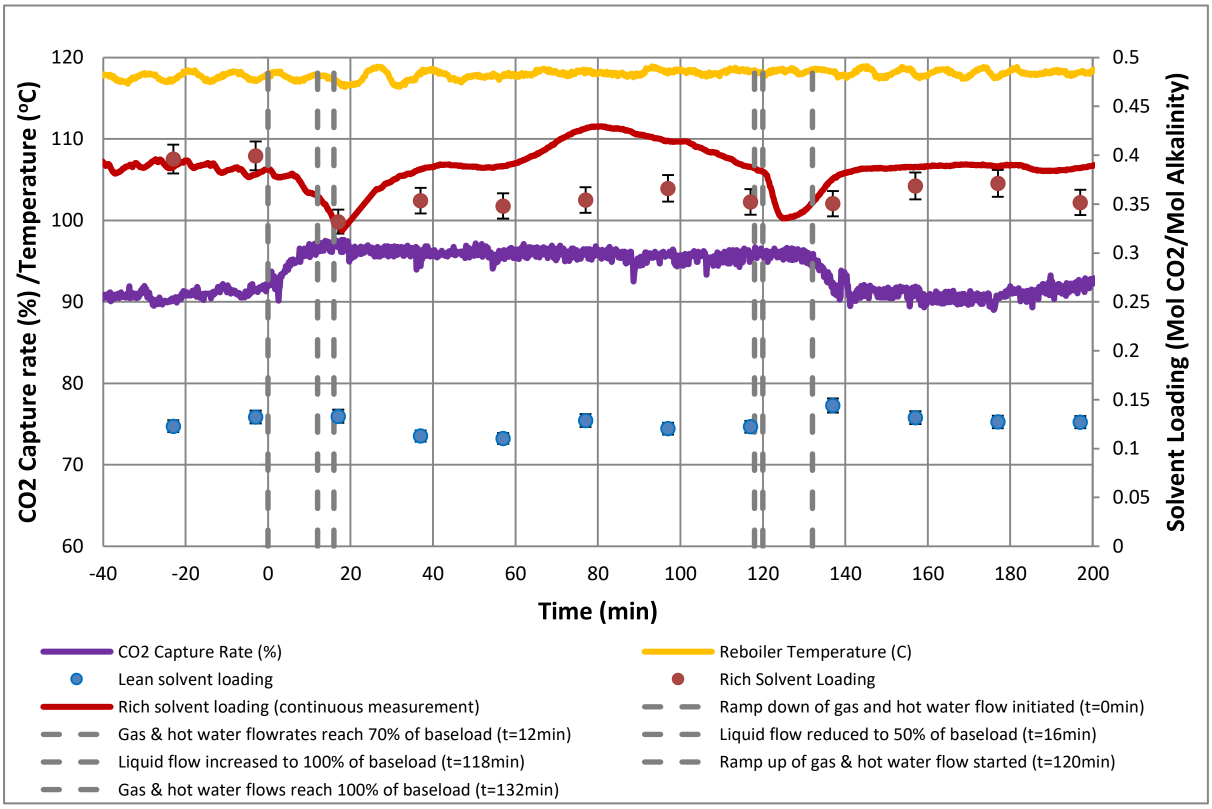
4.6 Capture plant ramping

With increasing contribution to an electricity generation portfolio from intermittent renewable sources it is likely that some coal-fired power stations will operate in a load-following regime for a significant proportion of their operational lifetime. This scenario simulates the capture plant reducing its output from baseload to 70%, then ramping back up to baseload after 2 hours. Gas flow is ramped down at 2.5% of baseload ($5m^3/hr$) per minute to represent a coal unit cycling rate of 2.5% of its output per minute (DECC, 2014). Hot water flow is also ramped down at 2.5% of baseload ($0.25m^3/hr$) per minute (fig. 19a). Once gas and hot water flows have been stabilised at 70% of baseload at t=12min a step-change in solvent flow from 100% to 70% of baseload (1000l/hr to 700l/hr) is made to keep the L/G ratio constant for as much of the operation as possible.

At t=119min the flow of solvent is increased to 100% of baseload operating conditions (1000l/hr) in anticipation of the gas and hot water ramp operation. At t=120min, gas and hot water flow are both ramped up at a rate of 2.5% of baseload per minute, then stabilised at baseload at t=132min (fig. 19a).

A slight increase in CO_2 capture efficiency from 90% to 96% is observed while the plant is operating at 70% capacity. This is the opposite of what is observed in the simulation of Mac Dowell and Shah (2015), who report a small decrease. The reason for this becomes clear if the gas and liquid flow rate during the load-following operation are inspected closely (fig. 19c). In the modelling study, the L/G flow ratio and both lean and rich loading are kept constant throughout. Due to the imperfect control system of the pilot plant, for a significant proportion of the real operation the L/G ratio is greater than at baseload, with liquid flow varying between 71-72% and gas flow at around 68-69%. The lean solvent loading also appears to decrease slightly over the duration of the event which may account for the higher capture efficiency during t=78-93min, when the L/G ratio is almost the same as at baseload flow conditions (fig. 19b). However, the change is small (around 0.01-0.02 mol/mol) and there is some variation in titration measurements both at baseload and during the ramping operation (titration points at t=-23min, t=77min). In the absence of accurate continuous lean loading measurements it is not possible to come to definitive conclusions about how this factor affects the capture efficiency.


Plant parameter as percentage of baseload
Desorber pressure (mbar)
Time (min)
Lean Solvent flowrate (as percentage of baseload)
Gas flowrate (as percentage of baseload)
Hot water flowrate (as percentage of baseload)
Desorber pressure (mbar)


CO2 Capture rate (%) /Temperature (°C)
Solvent Loading (Mol CO2/Mol Alkalinity)
Time (min)
CO2 Capture Rate (%)
Lean solvent loading
Rich solvent loading (continuous measurement)
Gas & hot water flowrates reach 70% of baseload (t=12min)
Liquid flow increased to 100% of baseload (t=118min)
Gas & hot water flows reach 100% of baseload (t=132min)
Reboiler Temperature (C)
Rich Solvent Loading
Ramp down of gas and hot water flow initiated (t=0min)
Liquid flow reduced to 50% of baseload (t=16min)
Ramp up of gas & hot water flow started (t=120min)

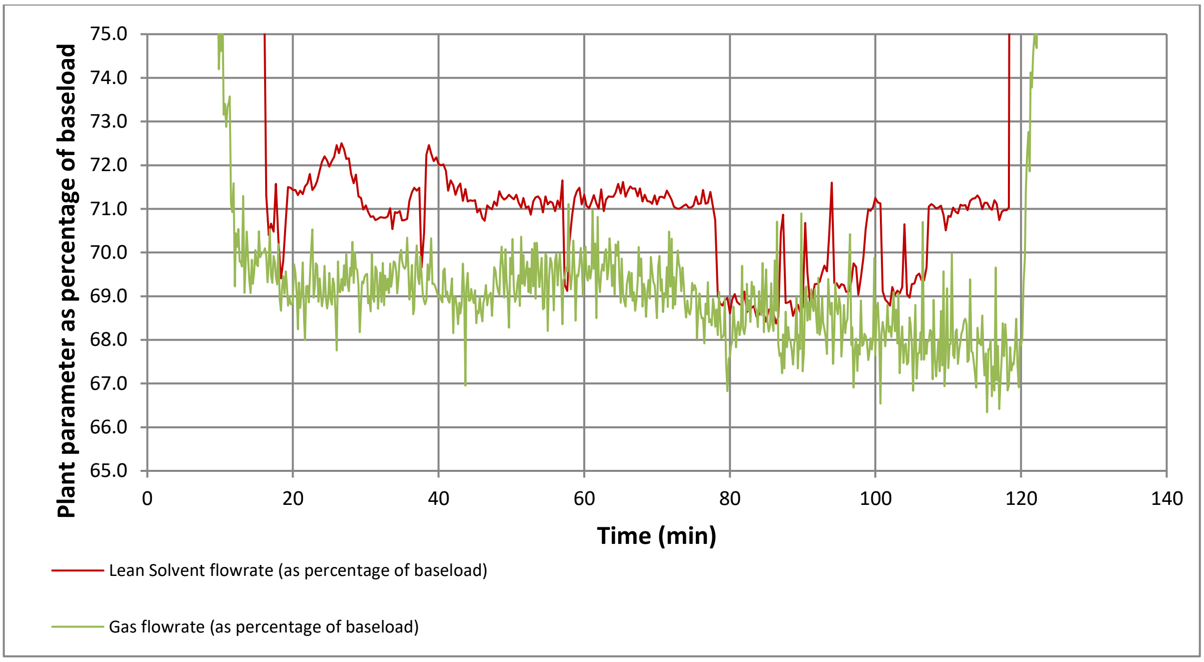


Fig. 19a. Gas, solvent hot water flow rate and desorber pressure as percentage of baseload operation, load following scenario

Fig. 19b. Rich and lean solvent loading, reboiler temperature and CO_2 capture efficiency, load following scenario

Fig. 19c Gas and solvent flow rate as percentage of baseload operation, load following scenario

The temperature bulge increases in magnitude slightly as a result of the increased capture efficiency and moves down the packed bed, indicating that a relatively higher proportion of CO_2 is being absorbed per unit of solvent at the absorber inlet (fig. 20). Once the plant is stabilised at baseload flow conditions after t=132min the capture efficiency decreases back to around 90%, as the L/G ratio returns to 5l/m^3.

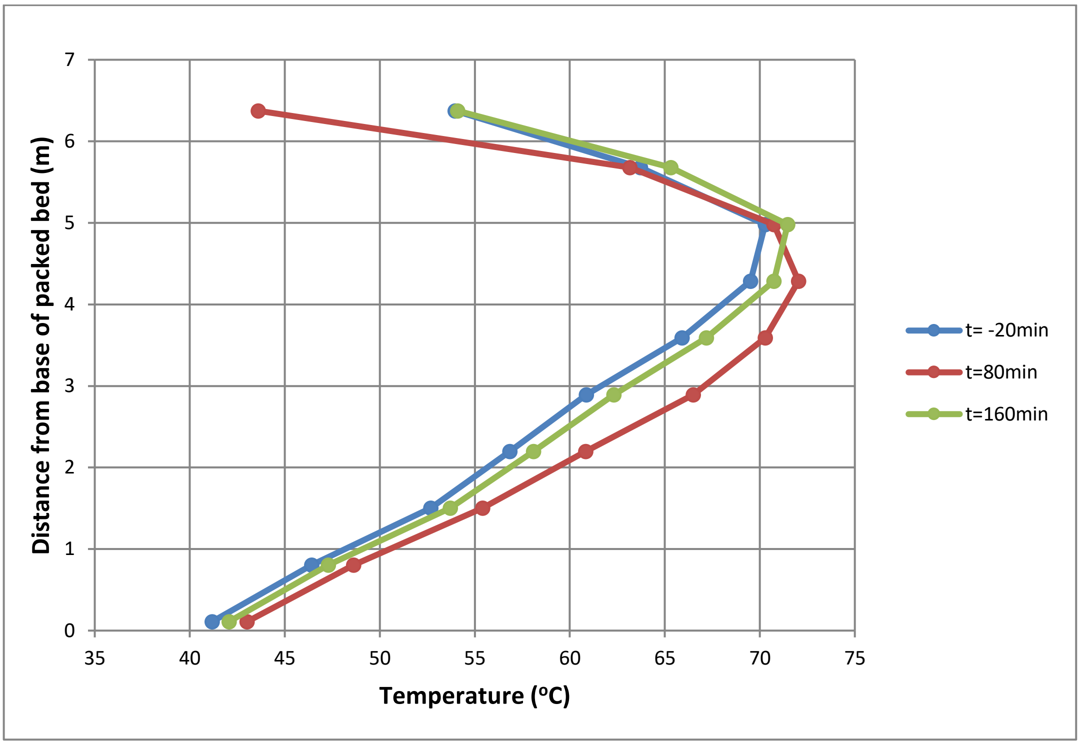


Fig. 20 Absorber temperature profile, load following scenario

There remains scope for the implementation of flexible load-following operations by using strategies such flue gas venting, varying degrees of solvent regeneration and solvent storage. The idea is to maximise the electricity available for export during peak selling times, while maintaining an average level of CO_2 capture close to 90% over the course of a single day (Enaasen et al, 2016; Mac Dowell & Shah, 2015). These could be investigated in future pilot-scale test campaigns on flexible CCS.

4.7 Real-time control using online solvent measurement

In this scenario, control of the plant in real-time using online solvent measurements is demonstrated. It has already been demonstrated (section 4.3) that at baseload solvent and gas flow rates, a response in lean loading online measurement is observed approx. 5min after a step-change change in reboiler heat input. The CO_2 capture efficiency responds after a further 3min (see table 5).

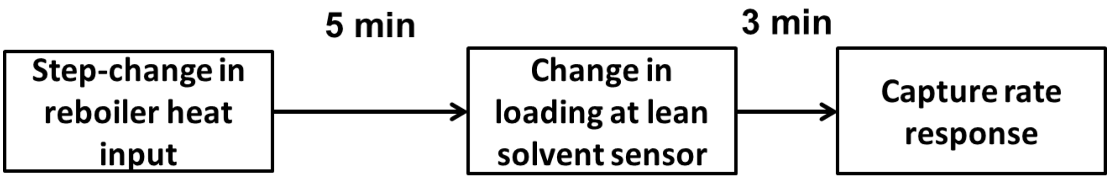


Fig. 21 Capture efficiency and lean solvent response times at baseload solvent flow conditions

This knowledge can be used to estimate the lean solvent loading which will result in a desired capture efficiency by observing plant trends from previous scenarios. For the purpose of demonstration, a capture efficiency of 30% was selected. In scenario 4.3 the capture efficiency reaches 30% at t=44min, this allows ample time for the rate of change in lean CO_2 solvent loading to be estimated and recalculated if necessary.

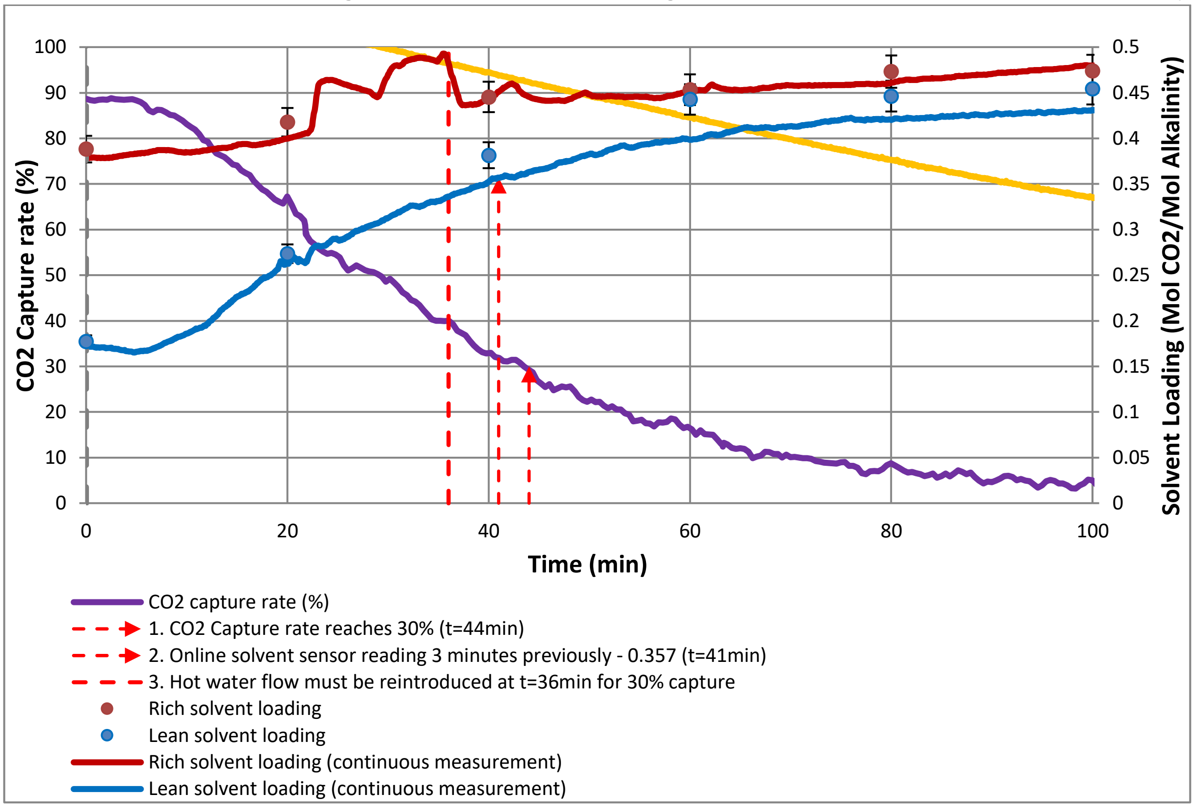


Fig. 22 Section of data between t=0 and t=100min from scenario 4.3

With reference to a section of data from scenario 4.3 (fig. 22) and table 4, it is possible to retroactively calculate when the flow of hot water to the reboiler should be reintroduced using the time at which the CO_2 capture efficiency reaches 30%.

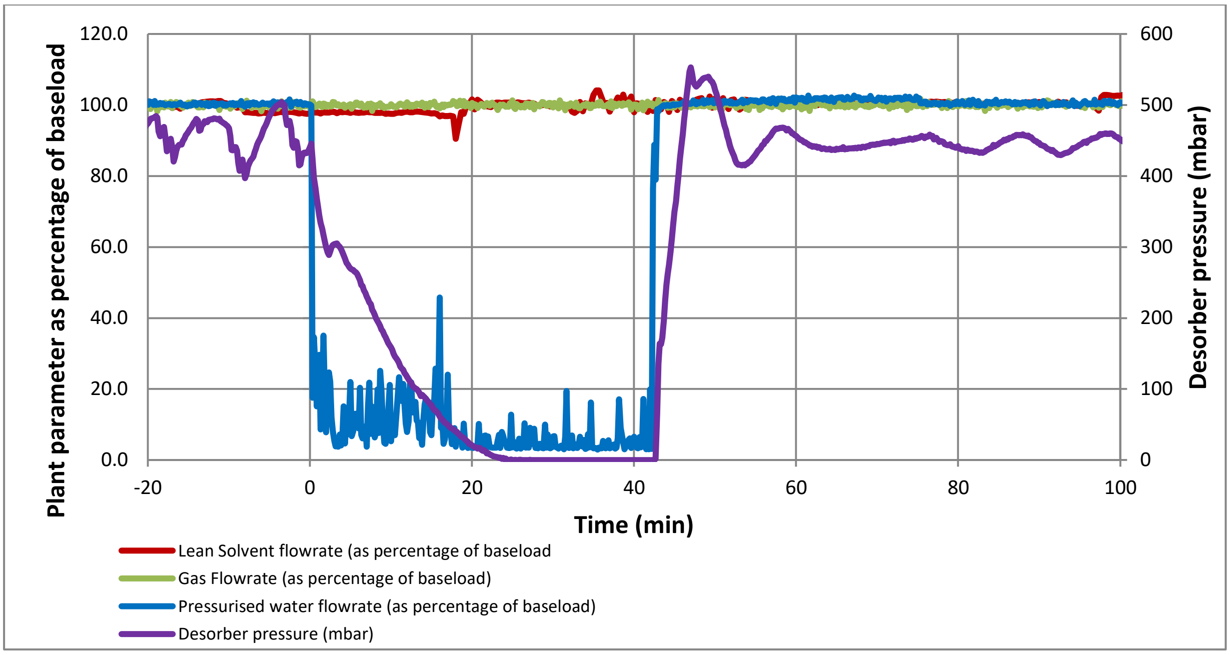
1. CO_2 capture efficiency reaches 30% at t=44min.

2. The solvent loading which corresponds to 30% capture passes through the lean solvent loading analyser 3 minutes previously, at t=41min. At this time, lean loading is 0.357 mol MEA/mol CO_2.
3. To achieve a maximum solvent loading of 0.357 mol MEA/mol CO_2 and hence a CO_2 capture efficiency of 30% the flow of hot water to the reboiler must be reintroduced 5 minutes before (2.), at t=36min.

The lean loading can be used to control the plant by calculating the rate of change of lean solvent based on current trends and predicting its value in 5 minutes time. If this value exceeds the "target" lean loading of 0.357mol CO_2/mol MEA the flow of hot water to the reboiler should be restarted. A simple Boolean expression for the method in more general terms could look as follows:

$$If\ \left(\alpha_{current} + \left(\Delta t_{desorber-sensor} * \frac{\Delta\alpha}{\Delta t}\right) > \alpha_{target}\right) Then \quad \text{(Equation 3)}$$
$$(PV = 0)$$
$$Else(PV = 1)$$

Where $\alpha_{current}$ is the current online lean loading measurement, $\Delta t_{desorber-sensor}$ is the time delay between making a change in reboiler heat input and a response being observed in lean loading measurement, $\frac{\Delta\alpha}{\Delta t}$ is the lean loading's rate of change (based on t=15min – t=25min in this case) and α_{target} is the previously-determined "target" lean loading. PV refers to the position of the hot water bypass valve, 0 being completely open (all flow goes through the bypass), 1 being completely closed (all flow goes to the reboiler).
This is a fairly rudimentary method of lean loading and capture efficiency prediction. It could be improved by taking into account dependencies on current plant temperatures (especially in the absorber), variations in nominal amine concentration and planned changes in solvent flow rate. In future studies, rich online solvent measurements could also be used as a predictor of how the rate of change in lean loading will vary in the future. As the response of the lean loading upon reboiler shutdown is non-linear the rate of change should be recalculated at regular intervals. This would require more plant data to be acquired than is practical in the limited experimental time available, but future control efforts should consider these dependencies and attempt to integrate the method with the plant control system.
Hot water flow to the reboiler is reduced to zero at t=0min (fig. 23a). The capture plant has no continuous capture efficiency measurement as absorber gas inlet and outlet CO_2 concentrations are recorded on separate FTIR machines, so plant control is dependent entirely on lean solvent measurements and the prediction method. It is predicted that the loading will reach the target of 0.357 mol CO_2/mol MEA at t=46min, so the flow of hot water is redirected to the reboiler at t=41min. The plant operator and PID controlled bypass valve require additional time to respond, and the flow of hot water to the reboiler requires time to stabilise. In retrospect, this could have been compensated for. The hot water reaches its baseload operating flowrate at approximately t=43min.



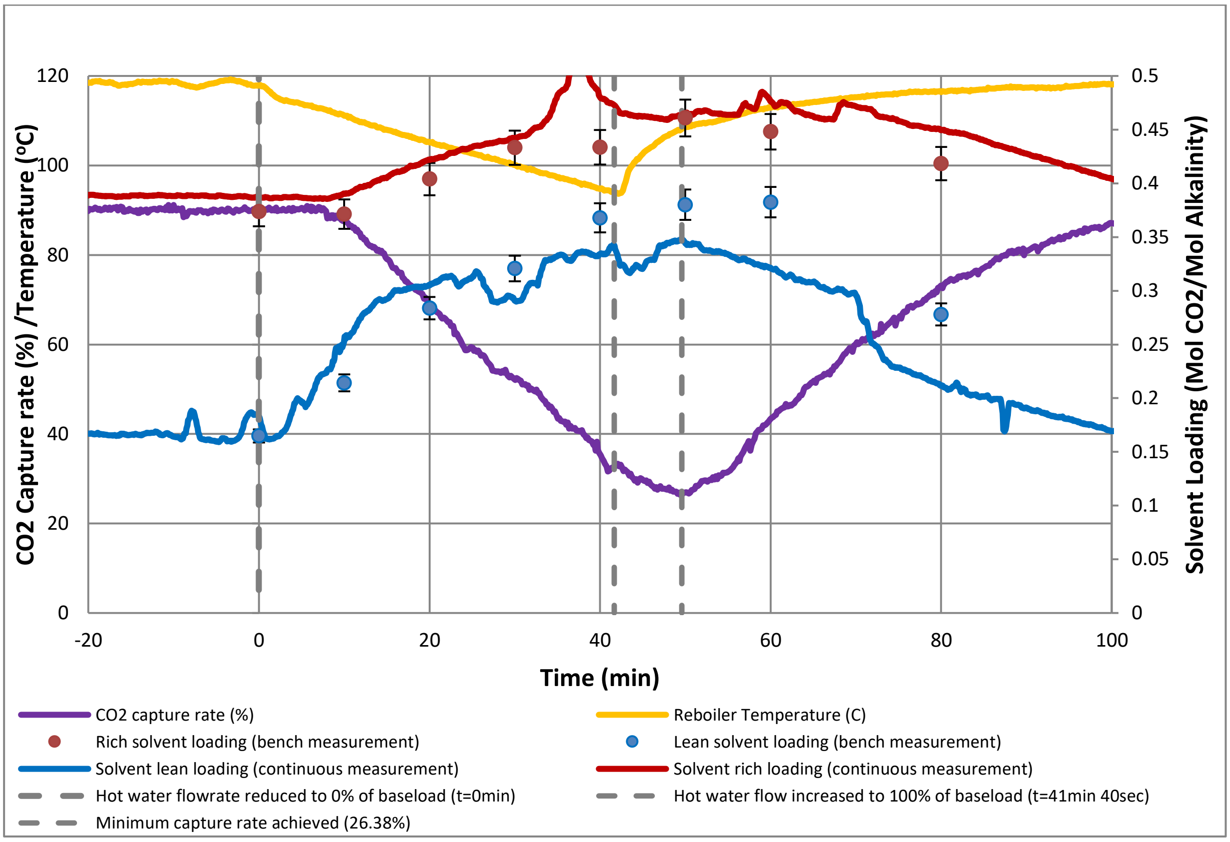


Fig. 23a. Gas, solvent hot water flow rate and desorber pressure as percentage of baseload operation, real time control with online solvent measurement

Fig. 23b. Rich and lean solvent loading, reboiler temperature and CO_2 capture efficiency, real time control via online solvent measurement

The target minimum capture efficiency is 30% and the actual capture efficiency achieved is 26.4%, displaying that while plant control using continuous online solvent measurements is possible there remains scope for improvement (Fig.23b). The rate of change of lean loading is estimated using the values at t=15 and t=25min. Titration measurements suggest that this resulted in an underestimation of $\Delta\alpha/\Delta t$, leading to the optimum time for reintroduction of hot water being overshot. A comparison between the values of Δα/Δt as predicted by continuous measurement and by bench titration is provided in table 6. Although there is no titration point measurement at t=15min or t=25min an estimate can be made via linear interpolation of the surrounding data points.

Lean loading data points used	Loading at t=15min	Loading at t=25min	Δα/Δt	Predicted time to reach target lean loading	Predicted time to reintroduce hot water flow
Continuous measurement	0.292	0.313	0.0021	t = 46min	t = 41min
Interpolation of bench measurement	0.249	0.302	0.0053	t = 35min	t = 30min

Table 6. Comparison of Δα/Δt based on continuous measurements and interpolation of titration data

Assuming that linear interpolation provides a sensible value of lean loading, the flow of hot water should have been reintroduced approximately 11 minutes earlier during the experiment (figs 23a, b). The reasons for the significantly higher solvent loading at t=15min shown in table 6 can be explained by comparing the trends in nominal amine concentration for the online sensor and bench measurements (fig.24).

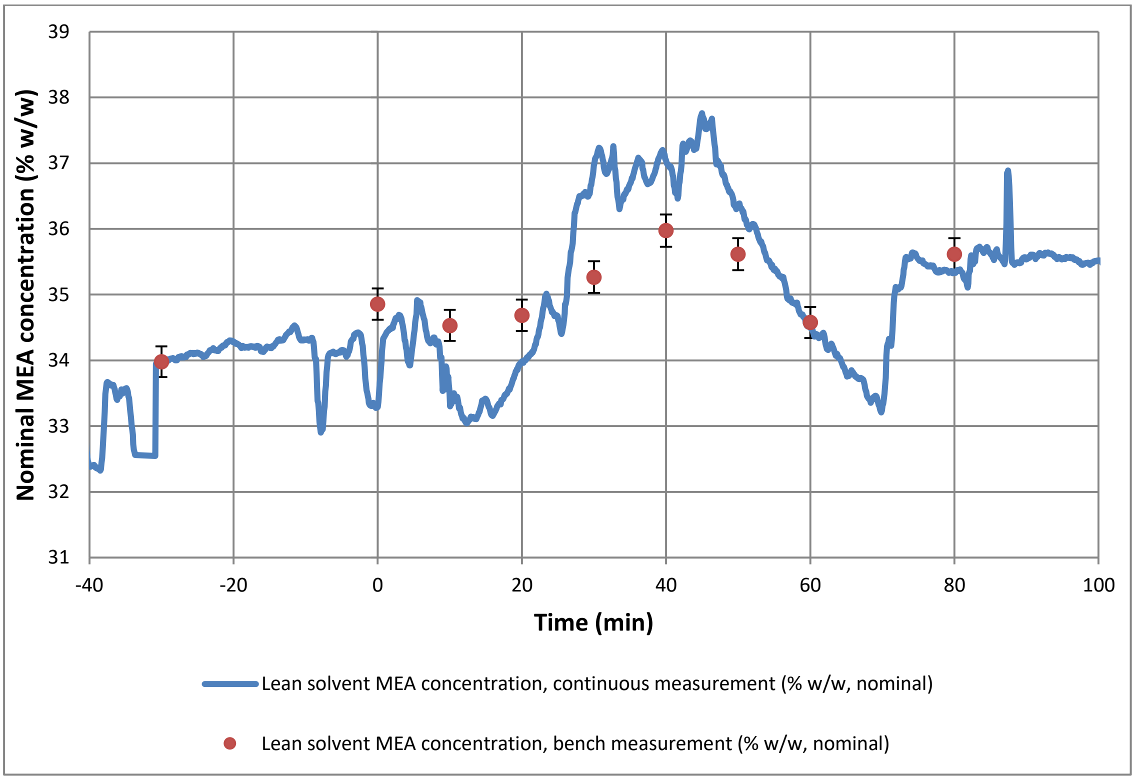


Fig. 24 Continuous measurements of nominal amine concentration compared with titrations

The data shows that the lean solvent sensor under-estimates nominal solvent amine concentration at t=15min. Lean loading at t=15min is overestimated in comparison with bench titration measurements, accounting for the low value of Δα/Δt calculated during the experiment (table 6). Due to the non-linearity of the CO_2 capture efficiency response a more robust method of achieving a target capture efficiency would be to recalculate Δα/Δt at regular intervals using Labview or similar control software, so it can be used as a control variable in scenarios which are more complex and relevant to real plant operation than a simple steam decoupling. The algorithm used by the online sensor to calculate lean loading could also be improved. The measured values of lean loading using online measurement techniques (such as the one described in the article) can be translated into rate of change of lean loading (Δα/Δt) which can be fed into a PLC/labview code or any other process plant control software as a control variable. The live data of the control variable coming from the plant then can be used to predictively control the plant.

Nevertheless, given the non-ideal operating environment and basic prediction method the sensor performed sufficiently well to achieve a minimum CO_2 capture efficiency within 4% of the target. To our knowledge, this is the first implementation of PCC plant control combined with in-situ online loading measurements reported in the public domain. It opens the door for the development of fit-for-purpose control strategy tools for dynamic operation, with further work focusing on the improvement of sensor performance and refinement of the prediction method.

5. Conclusions and Key Findings

Six flexible operating scenarios which could be encountered by operators of PCC as applied to coal-fired power plant are demonstrated. Via comparison of different methodologies for plant start-up, rapid introduction of steam to the reboiler is found to provide CO_2 emissions savings equivalent to 18.6% of the total daily emissions for a similar plant operating in a two-shifting dispatch pattern with 90% capture following startup (Table 3). Differences in plant construction are found to have a direct effect on solvent circulation times and as a result, how the plant reacts to dynamic operations. In contrast to the absorption/desorption facility described in Tait et al. (2016) which has a desorber outlet to absorber inlet solvent circulation time of 15-25mins, the PACT pilot facility used in this work has a circulation time of approx. 8mins. Changes in capture efficiency are observed after a relatively short period of time after making changes to reboiler heat input at the PACT pilot, but the increase or decrease is gradual and no significant additional fluctuations are observed following the initial return to baseload flow conditions, as the solvent becomes more rapidly mixed in the large desorber tank and sump. Steady state data and full datasets from these six dynamic tests are available via open access as supplementary material to this paper, for the potential validation of dynamic models. Tables of information which detail plant dimensions and packing types are also provided.

A final dynamic operating scenario demonstrates plant control uses real-time measurement of solvent loading to attempt to hit a "target" CO_2 capture efficiency following a steam shutdown event. A capture efficiency of 26.4% is achieved for a target of 30%. While not possible during this campaign due to time constraints, the next immediate steps for development of CO_2 capture efficiency control using online solvent measurements are as follows:

- Write Labview code (or other control software) which allows the existing prediction method to be implemented programmatically, with rate of change in solvent loading ($\Delta\alpha/\Delta t$) being recalculated on a regular basis.
- Refine the sensor algorithm which calculates solvent loading to make measurements more reliable, accurate and less prone to instability. Additional studies at pilot-facilities and large-scale commercial CCS plants which are not published at the time of writing show considerable improvements in sensor stability, and consistent close agreement with offline measurements. These results are to be presented at the GHGT-14 conference.
- Continue to develop knowledge of plant hydrodynamics so that the prediction method can be scaled to account for changes in solvent flow rate.

Achievement of these objectives at the UKCCSRC PACT amine pilot can form a basis for the development of an enhanced plant control system, which uses continuous solvent measurements as control variables to maintain plant parameters within pre-defined boundaries. Differences in plant construction are found to significantly affect response to dynamic operation, so a step-by-step methodology for the development of similar control systems at other plants is likely to be a useful tool.

Solvent working capacity as a potential control variable was discussed by Tait et al. (2016) but it is now obvious that this is too simplistic an approach. Discrete knowledge of plant hydrodynamics, response times based on current plant conditions, knowledge of upcoming changes in generation plant output and continuous monitoring of rich and lean solvent loading will be required to optimise operation. Advanced process control system architectures such as Model-predictive control (MPC) and fuzzy logic control applied to the control of post-combustion capture are a promising alternative to single input-single output

PID or cascading-PID control systems in maintaining plant operation within environmental, economic and operational boundaries via active control of solvent flow, desorber pressure and reboiler energy input (Luu et al., 2015; Mechleri, 2015). The successful demonstration of the sensor represents a significant practical step toward combining online solvent measurements with novel control strategiues to optimise plant operation.

To summarise, the key findings of this work are:

- Six dynamic pilot-scale datasets are generated and provided as supplementary material to this work for the potential validation of dynamic plant models.
- Two plant startup modes are implemented at pilot-scale.
    - Startup method 1: The low pressure steam turbine is powered up before stripping steam is sent to the reboiler.
    - Startup method 2: Low pressure steam is immediately introduced to the reboiler as soon as it becomes available.

  Total CO_2 emissions during startup are 25.1kg for method 1 and 10.3kg for method 2, a saving of 14.8kg. To quantify these potential savings, the case of a two-shifting coal plant which initiates a hot startup at 6am, operates with 90% capture efficiency for the rest of the day and shuts down at 10pm is considered. Total residual CO_2 emissions for a plant of this scale over the 16hr period are 79.4kg with startup method 1, and 64.6kg with startup method 2. This represents a potential 18.6% reduction in daily emissions, at the cost of increased low-pressure steam consumption during startup.
- A steam shutdown event is used to determine response times critical plant response times, with the intent of using continuous online solvent measurements as an input parameter for the control of CO_2 capture efficiency.
- In the final dynamic scenario, we demonstrate the use of an online solvent sensor combined with knowledge of plant response times to achieve an arbitrarily chosen “target” capture efficiency following a steam shutdown event. For a target of 30%, a minimum capture efficiency of 26.4% is achieved.

Acknowledgement

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Glossary of Terms

Cp – Specific heat capacity (J/kg.K)
m – Mass flow rate (kg/s)
Q_{reb} – Reboiler heat duty (GJ/tCO_2)
T – Temperature (^oC)
t – Time (min)
α – Solvent CO_2 loading (mol CO_2/mol alkalinity)
η – CO_2 capture efficiency (%, mass basis)
ρ – Density (kg/m^3)
φ – Volume fraction

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