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Start-up and Shutdown Protocol for Natural Gas-fired Power Stations with CO_2 Capture

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START-UP AND SHUTDOWN PROTOCOL FOR NATURAL GAS-FIRED POWER STATIONS WITH CO_2 CAPTURE

Key Messages

- In modern power grids, a power plant with CO_2 capture will be required to operate as a low-carbon, flexible, dispatchable power generator. A recent IEAGHG study[1] showed it is possible to achieve net-zero CO_2 emissions[2] from coal-fired and gas-fired power generation by employing higher capture rates and, in the case of coal-fired generation, by employing a mix of capture rates and biomass.
- With increased penetration of intermittent renewables, however, greater load-following is likely and a rise in the frequency of start-up/shutdown (SUSD) cycles would be expected. If it transpired that frequent SUSD cycles resulted in appreciable CO_2 emissions, it could undermine the value proposition of including modern, flexible, dispatchable fossil fuel power generation assets in the grid even though CCUS applied to them could enhance energy security and grid resilience.
- Limited work to-date has focused on the impact of start-up and shutdown of CO_2 capture plants, particularly with respect to the time required and the fugitive CO_2 emissions arising. This study broadens understanding of the process dynamics during start-up and shutdown, identifying key factors that impact CO_2 capture performance and operability associated with a natural gas-fired combined heat and power[3] (CHP) plant.
- To optimise CO_2 capture performance during start-up and shutdown, factors shown to be important include the solvent inventory volume, the initial start-up temperature (cold vs hot) and the timing of steam availability.
- Using a larger solvent inventory can be beneficial in terms of maximising the cumulative CO_2 capture rate from start-up, through steady state operation and shutdown. While the effect of solvent inventory volume is negligible for hot start-ups, there is significant improvement in cumulative CO_2 capture in the case of cold start-ups.
- Overall, hot start-ups showed a significantly higher cumulative CO_2 capture rate and lower specific reboiler duty compared to cold start-ups. With a low start-up solvent loading (0.05–0.11 mol CO_2/mol amine), high online CO_2 capture rates of 98–99% were achieved during start-up, occurring immediately after the introduction of flue gas to the system. The ability to sustain these high CO_2 capture rates depends on the volume of the solvent inventory, the amine concentration, the starting solvent CO_2 loading, and the timing of steam supply to the reboiler.
- Results indicate the importance of timely steam supply during start-up. Any delay in steam supply to the capture plant significantly reduces the cumulative CO_2 capture rate, thereby greatly increasing the residual CO_2 emissions. Start-up with preheating was shown to be a potentially valuable approach. Under specific operating conditions,

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[1] IEAGHG, "Towards zero emissions CCS from power stations using higher capture rates or biomass", 2019/02, March 2019.

[2] Net zero power generation is achieved when the concentration of CO_2 emitted to the atmosphere is the same as the CO_2 concentration in the incoming air, i.e., all fuel-derived CO_2 is captured.

[3] A combined heat and power (or cogeneration) plant consists essentially of a heat engine or power station to generate electricity and useful heat at the same time.

preheating can provide higher cumulative CO_2 capture rates during start-up of the capture plant, thereby minimising the residual CO_2 emissions. To maximise the value of preheating, a higher flow rate of steam supply can heat the system much faster, but the duration of preheating must be optimised to minimise residual CO_2 emissions associated with steam energy.

- Measures applied during hot start-up, such as high preheating and lower solvent loading, were shown to markedly improve capture performance. For example, a cumulative CO_2 capture rate of 98.8% was achieved compared to the lower cumulative CO_2 capture rates of between 90.0 to 90.3% using "conventional" hot start-up protocols. However, the specific reboiler duty was higher with the improved measures, at 5.58 MJ/kg CO_2, compared to values of 3.76–4.03 MJ/kg CO_2 (depending on solvent inventory volume) for the conventional start-up tests.
- In the context of a net-zero energy system, the need for operational flexibility will rise. Hence, the ability to maximise the CO_2 capture rate during start-up and shutdown would be highly valuable as it will reduce residual CO_2 emissions from power plants, thus easing the need for carbon offsets from CO_2 removal technologies, e.g., bioenergy with CCS, or direct air capture.
- The evaluation has helped identify novel operational strategies that can minimise both the time taken for start-up and shutdown and the CO_2 emissions associated with these operations.
- Finally, it should be noted that, while the detailed performance metrics, measurements and observations were plant, scale and solvent specific, the high-level insights drawn from this work should remain broadly applicable.

Background to the study

Since the adoption of the Paris Agreement in 2015 many major economies and international organisations have committed to bring their greenhouse gas emissions to net zero by mid-century or thereabouts. By reducing CO_2 emissions from fossil fuel-based power generation, CCUS will have an important role to play in the transition to a low-carbon global economy. To play its full role, however, CCUS will eventually need to reduce CO_2 emissions from fossil-based generation to net zero.

In modern power grids, the power plant with CO_2 capture will be required to operate as a low-carbon, flexible, dispatchable power generator. It will also provide the heavy rotating equipment, via steam turbines and gas turbines, which provides the inertia to stabilise system frequency. However, with increased penetration of intermittent renewables, greater load-following is likely and a rise in the frequency of SUSD cycles would be expected. If it transpired that frequent SUSD cycles resulted in appreciable CO_2 emissions, it could undermine the value proposition of CCUS as a flexible, low carbon solution for power generation and other hard-to-abate industrial sector assets.

It is possible to achieve net-zero CO_2 emissions from coal-fired and gas-fired power generation by employing higher capture rates and/or biomass[1]. The widely assumed cap of 90% capture rate was exposed as an artificial limit. The study revealed no technical barriers to increasing capture rates well beyond 90% in the three classic capture routes (post-, pre- and oxyfuel combustion) and with the broad suite of CO_2 capture technologies currently available or under development. For coal-fired power stations, the option of using biomass co-combustion (10%

biomass) combined with a standard post-combustion capture process (with 90% CO_2 capture rate) was shown to be a lower cost option to achieve zero emissions, though dependent on the region of deployment.

Integrating higher shares of intermittent renewable energy (e.g., wind and solar power) into an electricity system presents major operational challenges. While intermittent renewable sources benefit from a near-zero short-run marginal cost and near-zero carbon footprint, the true system cost of accommodating them in the power grid can be significant. To balance their intermittency and ensure electricity demands are met, energy technologies that can provide flexible, dispatchable electricity to the system will be required[4]. In this context, thermal power plants with CCS will likely have an important role in providing affordable, dispatchable, low carbon capacity, maintaining security of supply, and enabling the expansion of other low-carbon sources.

Whilst the value of flexible CCS has been demonstrated in previous studies, there has been limited work to-date that focuses on the impact of start-up and shutdown on CO_2 capture plants, particularly with respect to the time required and the fugitive CO_2 emissions arising. With increasing penetration of intermittent renewable energy, these SUSD cycles will become increasingly frequent. Consequently, the potential for fugitive emissions must be quantified and minimised. Work is therefore necessary to develop an understanding of the process dynamics during start-up and shutdown so that the key factors that impact CO_2 capture performance and operability may be identified.

Scope of Work

The aim of this study was to examine the time required for start-up and shutdown of the CO_2 capture process, the CO_2 emissions emitted and the potential for performance improvements. This involved conducting a series of SUSD tests at the Technology Centre Mongstad (TCM) CO_2 capture facility in Mongstad, Norway. The TCM plant is an industrial-scale post-combustion absorption plant, adjacent to an Equinor oil refinery. The plant uses amine-based solvents to capture CO_2 from a natural gas-fired CHP plant (Figure I), as used in this study, though it may also be configured to process a gas slipstream from the refinery residue fluid catalytic cracker (RFCC). A detailed analysis of the plant data was carried out to develop an understanding around the SUSD dynamic behaviour.

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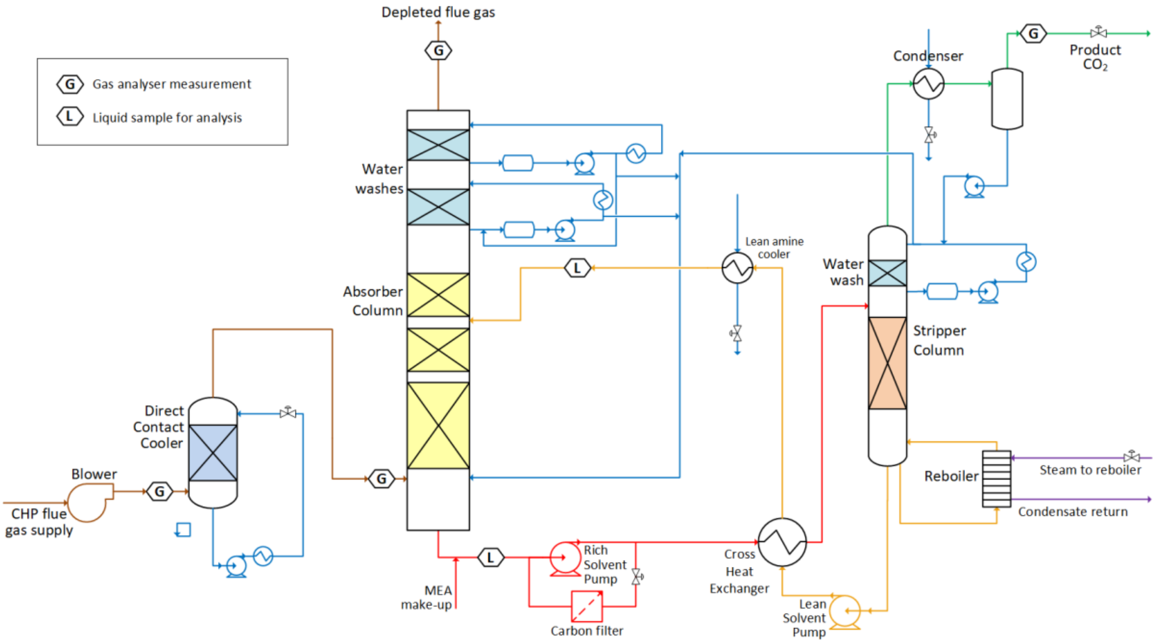
[4] IEAGHG, “Beyond LCOE: Value of technologies in different generation and grid scenarios”, 2020/11, August 2020.

Figure I: Process flow diagram of the configuration used at TCM (with much of the P&ID[5] detail omitted).



Key factors investigated include:

- Flexible operation using an advanced solvent, CESAR-1[6], a blended amine consisting of AMP[7] (26–27 wt%) and PZ[8] (10–13 wt%); as most pilot plant work on flexible operation has focused on MEA-based absorption, further work on the flexibility of systems using advanced solvents is required.
- Comparing cold start-up performance with hot start-ups to demonstrate the effect of the starting temperature.
- Combined effect of start-up and shutdown on overall performance.
- Effect of using different solvent inventory volumes, 53 m^3 versus 42 m^3, which is sufficient to illustrate differences in process dynamics and identify any potential benefits.
- Timing of steam availability on start-up time; different tests were conducted to demonstrate the impact of steam introduced:
    i. Before the start of flue gas flow by preheating with an auxiliary boiler;
    ii. At the same time as the start of flue gas flow; and
    iii. After the start of flue gas flow, i.e., delayed steam supply when steam extraction is unavailable.
- Effect of solvent CO_2 loading on the start-up performance.

The objective was to demonstrate the influence of these factors on the capture performance in the context of five conventional SUSD protocols (two cold start-ups and three hot start-ups), plus showing the results from four “improved” SUSD protocols, e.g., the effect of preheating

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[5] P&ID = Piping and instrumentation diagram.

[6] CESAR – named after the acronym for **CO_2** **E**nhanced **S**eparation **A**nd **R**ecovery, the title of a project funded under the European Commission’s Framework FP7 Programme, February 2007 – May 2011.

[7] 2-amino-2-methyl-1-propanol (AMP)

[8] Piperazine (PZ)

before start-up, lower CO_2 loading and higher amine flow on hot and cold start-ups. This work is important as it helps identify potential measures that can provide substantial reductions in CO_2 emissions, time requirements and energy demand during start-up and shutdown.

Given the context discussed above, the impact of SUSD cycles on emissions at both the technology and system level will be investigated. The study will combine dynamic modelling with an analysis of experience from actual plant testing.

Strategies for operating systems with both firm and intermittent generators will be considered. An increasing penetration of intermittent renewable technologies will, in most cases, lead to reduced output from the more traditional generators. However, there may be circumstances, from a carbon perspective, from a cost perspective or simply from the perspective of grid stability, where it may be more effective not to shut down the capture plant or to turn it down to a level where the system becomes less efficient.

Findings of the Study

The test campaigns at TCM using CESAR-1 examined different start-up and shutdown operating modes in a CO_2 capture process. The tests were designed to simulate SUSD conditions in the context of CCS with gas fired CCGT.

Cold start-up refers to a start-up that is performed after a lengthy downtime, e.g., down for more than eight hours, where the reboiler bottom temperature has cooled to “ambient” conditions of 25–30°C. Hot start-up refers to a start-up after a shorter downtime, e.g., <8 hours, where the reboiler bottom temperature was ~90°C. For all cases of shutdown, the same procedure was implemented, with the only difference being the solvent inventory volume. To ensure the plant starts with solvent that is sufficiently low in CO_2 loading, i.e., “leaned out”, steam continues to be supplied to the reboiler during shutdown after the flue gas has been turned off. Steam is turned off once all the solvent reaches the target CO_2 loading (of ≤ 0.2 mol CO_2/mol amine), which represents the end of shutdown. By the end of shutdown, all the solvent will have a low CO_2 loading for two reasons:

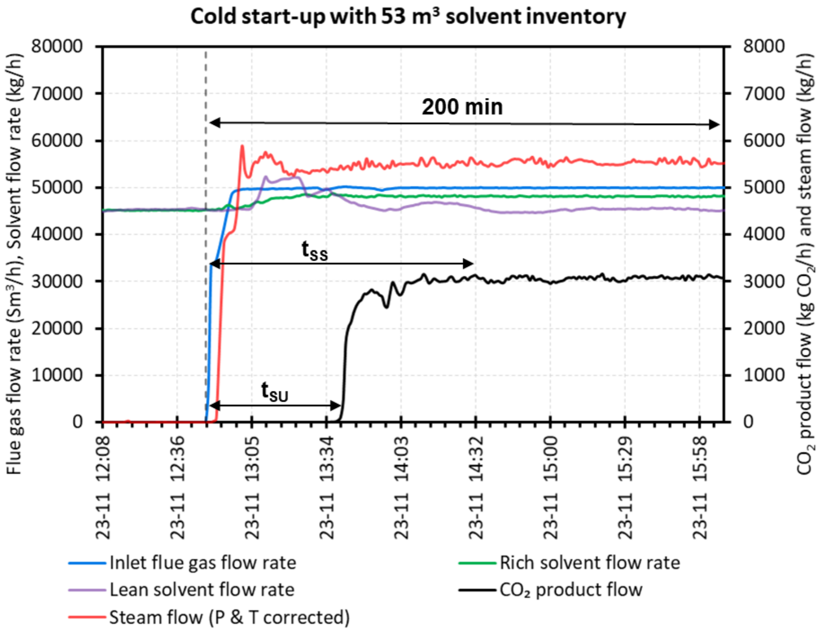
(i) It prevents precipitation during plant downtime, which can occur if CESAR-1 is rich and at low temperature,

(ii) Having lean solvent loading for the next start-up will maximise the CO_2 capture capacity.

Lean-out for non-precipitating solvents such as 30 wt% MEA would also be beneficial, but for the latter reason only.

Definitions for start-up time (t_{SU}) and time to reach steady state (t_{SS}) are illustrated in Figure II. Start-up begins when the flue gas flow starts and ends when the CO_2 product flow is first observed. Shutdown time (t_{SD}) is defined as the time from when the inlet flue gas rate begins to ramp down until the steam flow ceases completely, noting that the steam flow will continue until the entire solvent volume has been ‘leaned out’ to a specific CO_2 loading.

Figure II: Illustration to show the start-up time, t_{SU}, and the time for the system to reach steady state, t_{SS}.



CO_2 capture performance during start-up and shutdown. Table I shows that, for some tests, the solvent has a slightly different ‘start-up CO_2 loading’. For dynamic operation (e.g., load following, start-up or shutdown), while online data shows the variations in process parameters and metrics, it is difficult to benchmark performance based on transient trends. Thus, the *cumulative* capture rate and reboiler duty are also calculated over the scenario timeframe, which offer a better indication of the impact of dynamic operation on overall plant performance.

To minimise any bias associated with differences in feed CO_2 content, the analysis focused specifically on the dynamic region of data. The main dynamic trends occur within the time between start of the flue gas flow and the moment steady state of CO_2 product is achieved, i.e., t_{SS}. This was 82 minutes for the first dataset showing the effect of solvent inventory, and 85 minutes for the dataset demonstrating the effects of preheating. The performance over 200 minutes was also evaluated to establish whether the impact of changes in t_{SU} influences steady-state performance.

Table I: Comparison of the cold and hot start-up tests in terms of start-up time (t_{SU}) and the time it takes for the system to reach steady state (t_{SS}).

Start-up type	Conditions	Start-up time: time when CO_2 product flow starts, t_{SU} (min)	Time when CO_2 product flow reaches steady state, t_{SS} (min)
Cold start-up	53 m^3 inventory, start loading 0.10–0.11 mol CO_2/mol amine	47	82
	42 m^3 inventory, start loading 0.08–0.09 mol CO_2/mol amine	47	69
Hot start-up	53 m^3 inventory, start loading 0.08–0.09 mol CO_2/mol amine	22	40
	42 m^3 inventory, start loading 0.08–0.09 mol CO_2/mol amine	19	42
	42 m^3 inventory with delayed steam supply, start loading 0.08–0.09 mol CO_2/mol amine	45	63

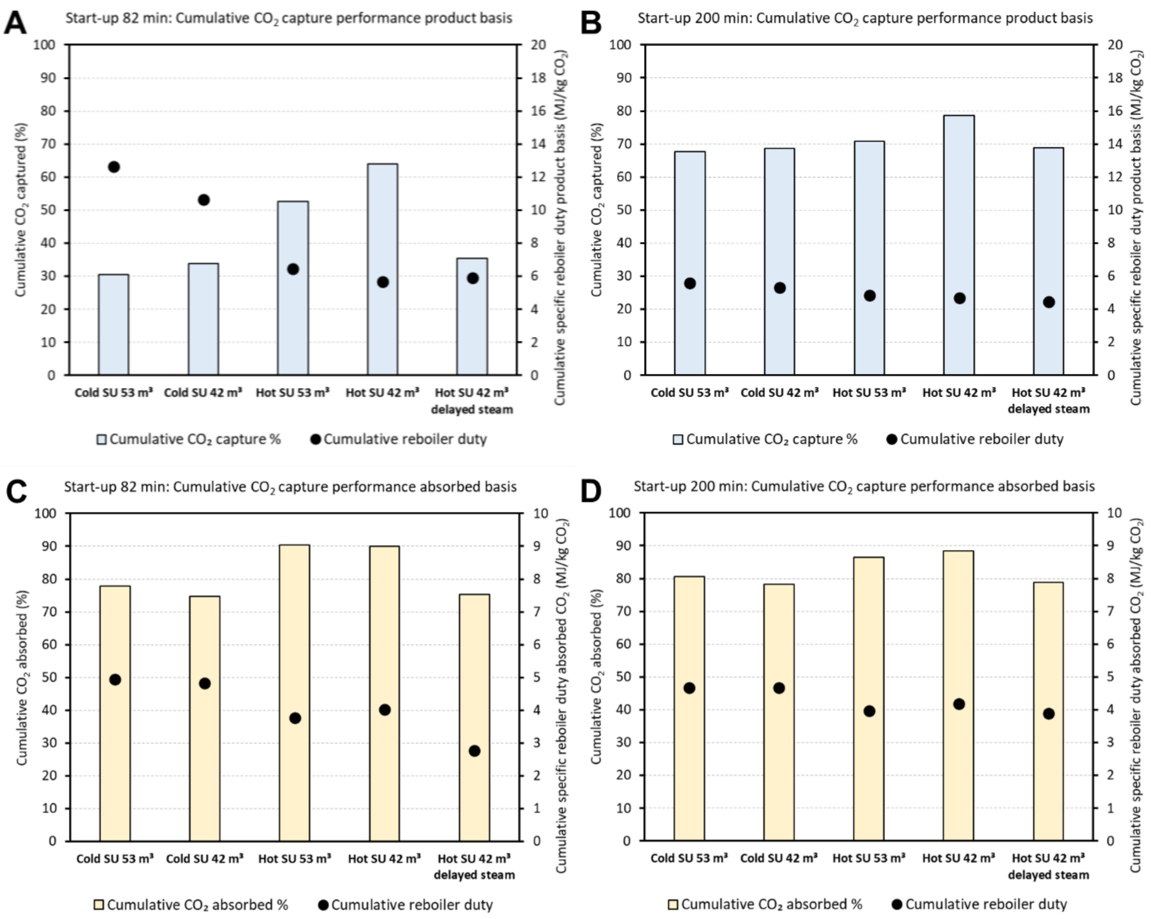
Figure III below shows the cumulative CO_2 capture rate and specific reboiler duty based on the product CO_2 and absorbed CO_2, calculated over an 82 min and 200 min period. The product CO_2 basis uses the amount of CO_2 exiting the stripper section as a proportion of the feed CO_2, providing a reflection of the process dynamics as it accounts for the solvent circulation time (i.e., observed differences are due to the solvent travel time from the absorber to the stripper). The absorbed CO_2 basis calculates the cumulative capture rate from the difference in CO_2 concentration of the inlet and outlet gas streams of the absorber column. It represents the proportion of CO_2 directly captured from the feed flue gas in the absorber, hence it provides a better indication of the residual CO_2 emissions from the process.

Cold start-up vs hot start-up. As shown in Table I, cold starts typically take longer than hot start-ups to reach steady state conditions. This is mainly due to the initial temperatures during cold start-up (at 25–30°C) being significantly lower than for hot start-up (at ~90°C). Cold start-ups take more time to heat the stripper/reboiler to the target temperature.

Cold start-ups cumulatively capture a lower percentage of incoming CO_2 and have higher specific reboiler duty compared to hot start-ups. For a start-up period of 82 minutes in a system with 53 m^3 of inventory, a cold start-up cumulatively captured 78% on an absorbed CO_2 basis, whereas a hot start-up cumulatively captured 90% – a difference of 12 percentage-points. The 200 min start-up results show the effect of including steady state operation. The cumulative CO_2 capture rate over 200 min for hot start-up is greater than for a cold start-up, although the difference is slightly smaller compared to the 82 min results (Figure III and Table II).

Effect of solvent inventory volume. For cold start-up, a smaller inventory will reduce the time required to stabilise the plant and will slightly reduce energy requirements. A larger solvent inventory will provide higher cumulative CO_2 capture rates and would therefore reduce the residual CO_2 emissions. With a larger solvent volume at start-up, more lean solvent is available to capture CO_2 as the plant heats up.

Figure III: Cumulative start-up performance over 82 minutes compared with 200 minutes for different solvent inventory volumes, 42 m^3 and 53 m^3.



Note: The effect of delayed steam supply by 20 min is shown for one hot start-up with 42 m^3. Cumulative CO_2 capture rate and cumulative specific reboiler duty are calculated based on product CO_2 (A & B) and absorbed CO_2 (C & D).

Table II: Cumulative CO_2 capture performance of start-up (82 min) and shutdown scenarios, without auxiliary boiler emissions.

	Product CO_2 basis		Absorbed CO_2 basis	
82 min start-up (SU), duration of shutdown (SD) varies	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)
Cold SU 53 m^3	12.64	30.5	4.95	77.8
Cold SU 42 m^3	10.64	33.9	4.83	74.7
Hot SU 53 m^3	6.46	52.6	3.76	90.3
Hot SU 42 m^3	5.66	64.0	4.03	90.0
Hot SU 42 m^3 delayed steam	5.91	35.4	2.77	75.3
SD 53 m^3	5.63	939	62.73	84.3
SD 42 m^3	6.49	840	61.07	89.2
SD 42 m^3	6.40	1016	72.84	89.3

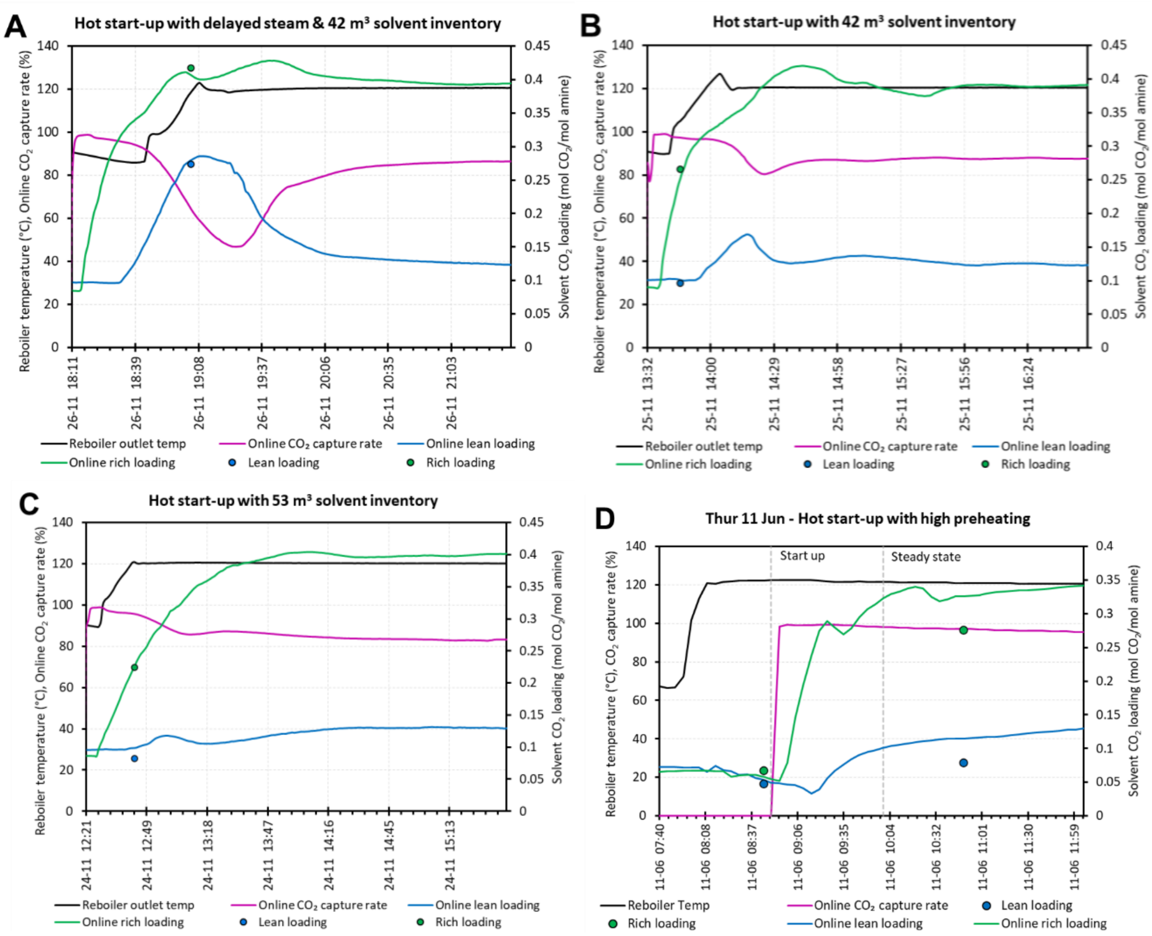
In the cases of hot start-up (Table II), the two solvent inventory cases, 42 m^3 and 53 m^3, had similar cumulative CO_2 capture rates over 82 min of 90% (absorbed CO_2 basis), while the cumulative specific reboiler duty, on a MJ/kg absorbed CO_2 basis, is slightly higher for the smaller inventory case. The steady state online CO_2 capture rate of the 42 m^3 test was higher

(88%) than that for the 53 m^3 case (83%), as shown in Figure IV. This observed difference in cumulative CO_2 capture rate over the 200 min period, however, was due to different flue gas CO_2 content for the two tests – if the flue gas CO_2 content was the same, the inventory volume size would have had a negligible effect on the residual CO_2 emissions.

Aside from the potential reduction in solvent consumption costs with the smaller inventory systems, the results indicate possible technical benefits for hot start-up performance as well. A smaller inventory volume will reduce the solvent circulation time and the effects of solvent regeneration are observed on a faster time scale. Therefore, over a given period, the smaller inventory system generates more product CO_2 (absolute terms) and, hence, a higher CO_2 capture rate (on a product basis) is observed in (A) of Figure III. Consequently, the smaller inventory system has a lower specific reboiler duty on a product basis (MJ/kg product CO_2).

Effect of delayed steam supply. A prioritisation on power generation during start-up could mean steam extraction was not available, which would delay the steam supply to the CO_2 capture plant. A hot start-up using 42 m^3 inventory with steam availability delayed by 20 minutes was found to reduce the CO_2 capture performance of the plant.

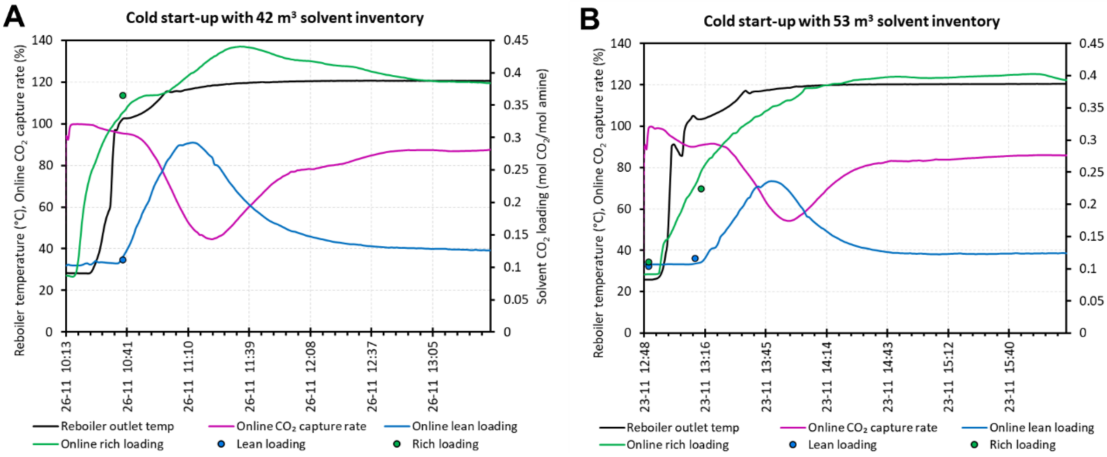
Figure IV: Results from a hot start-up with a 20 min delay steam supply (A), steam supplied at the same time as flue gas with 42 m^3 solvent inventory (B) and 53 m^3 solvent inventory (C), as well as hot start-up with an early steam supply, i.e., high preheat, and 45 m^3 solvent inventory (D).



A delay in steam supply increases the time required to heat the reboiler, resulting in a start-up time similar to that for a cold start-up (Figure V). Although delaying steam availability reduced the specific reboiler duty, the cumulative CO_2 capture rate (on both an absorbed and product

CO_2 basis) decreased significantly compared to normal hot start-up. Hence, making steam available for the CO_2 capture plant as early as possible is critical to maximise the CO_2 capture rates and minimise residual CO_2 emissions during start-up.

Figure V: Results from a cold start-up.



Combined performance of start-up with shutdown. The performance characteristics of start-up are different to those for shutdown. At the beginning of a new start-up, the solvent inventory is lean. As the plant stabilises and reaches steady state, the liquid on the absorber side is CO_2-rich, and CO_2-lean on the stripper side, i.e., the solvent temporarily stores CO_2. As the plant transitions into the shutdown phase, steam continues to be supplied even after flue gas flow stops. This enables leaning out of the solvent to a target loading (equivalent to the start-up loading) and releases a significant amount of product CO_2, i.e., the "stored" CO_2 in the system. To illustrate the impact of a SUSD cycle, we evaluated the combined SUSD performance in terms of cumulative capture rate (product CO_2 basis) and specific reboiler duty.

For start-up alone (82 min), the capture rate on a product basis is relatively low (Figure III and Table II). However, owing to the high amount of product during the shutdown phase, the combined performance of start-up and shutdown delivers a much higher capture rate, as shown in Tables III and IV.

Typically, for steady state operation, it is assumed that the steam supply is provided through steam extraction from the power plant steam cycle. However, during start-up and shutdown, the need for an auxiliary boiler to supply steam to the capture plant has been considered as steam extraction from the power plant is unavailable. We assume that a cold start-up requires steam from the auxiliary boiler for 60 min, a hot start-up requires it for 20 min, and it is used for the duration of shutdown. The CO_2 emissions associated with using a natural gas-fired auxiliary boiler was calculated for each scenario.

CO_2 emissions from the auxiliary boiler can have a major effect on the SUSD performance, increasing the cumulative specific reboiler duty and reducing the cumulative CO_2 capture rate. The cold SUSD case (82 min) using an inventory of 53 m^3 shows that the use of an auxiliary boiler reduces the cumulative CO_2 capture rate from 80% to 53% and increases specific reboiler duty from 8.2 to 12.4 GJ/t_{CO2}. For a hot start-up, the downturn in performance associated with the auxiliary boiler is smaller. Once the auxiliary boiler emissions are accounted for, a normal hot start-up and shutdown is able to achieve relatively high capture rates of 81% and 83% for inventories of 53 m^3 and 42 m^3, respectively.

Using the larger solvent inventory (53 m^3), a combined cold start-up (82 min) and shutdown provided a higher cumulative CO_2 capture. When the solvent inventory was increased from 42 m^3 to 53 m^3, the cumulative CO_2 capture would increase by 9.2–13.7%-points, depending on the role of the auxiliary boiler. A larger solvent inventory also led to a very small reduction in specific reboiler duty. In contrast, for a hot start-up with shutdown, the increase in solvent inventory from 42 m^3 to 53 m^3 had an almost negligible impact on capture performance.

Normal operation would typically include start-up, plant stabilisation, steady state operation and shutdown. Cumulative performance over 200 minutes is used to illustrate the effect of start-up and shutdown, combined with steady state operation. At steady state, the average online CO_2 capture rate was 83–88% (as illustrated in Figures IV and V). Thus, the cumulative CO_2 capture rates calculated over the longer 200 min period move closer to the performance values achieved during steady state.

Table III: Cumulative CO_2 capture performance of 82 minutes start-up combined with shutdown, showing the effect of CO_2 emissions from a gas-fired auxiliary boiler.

Product CO_2 basis	Without an auxiliary boiler		With an auxiliary boiler for shutdown*		With an auxiliary boiler for SU & SD*	
82 min start-up (SU) combined with shutdown (SD)	Cumulative specific reboiler duty (GJ/t CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (GJ/t CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (GJ/t CO_2)	Cumulative CO_2 captured (%)
Cold SU 53 m^3 & SD	8.15	80.0	9.95	65.6	12.42	52.5
Cold SU 42 m^3 & SD	8.51	66.3	10.18	55.5	13.04	43.3
Hot SU 53 m^3 & SD	6.06	97.3	7.02	83.9	7.26	81.2
Hot SU 42 m^3 & SD	5.94	96.5	6.73	85.3	6.93	82.9
Hot SU 42 m^3 delayed steam & SD	6.17	67.7	7.35	56.8	7.35	56.8

Note: Assumes that a cold start-up requires the auxiliary boiler for 60 min and a hot start-up requires it for 20 min, plus it is used for the duration of shutdown.

Importantly, the cumulative capture rates over 200 min, which account for auxiliary boiler emissions (Table IV), are highest for the hot start-up cases, reaching 82–86%. Capture rates are lower for both the cold start-up cases (72–76%) and the hot start-up case with delayed steam availability (77%). The longer analysis timeframe also lowers the cumulative specific reboiler duty to 4.8–6.4 GJ/tCO_2, depending on the scenario.

In both the 82 min and 200 min cases, delaying steam supply by 20 min before start-up was highly detrimental to the CO_2 capture performance. Although a lower specific reboiler duty was observed, the cumulative CO_2 capture rate was reduced by 26.0–28.9%-points compared to the normal hot start-up using the same solvent inventory volume. Of all the cases studied, the hot start-up with delayed steam had the lowest cumulative CO_2 capture rate. To minimise residual CO_2 emissions, it is clear that steam needs to be available from start-up of the CO_2 capture plant.

In all cases, using a natural gas-fired auxiliary boiler, i.e., using fossil energy, to supply steam during start-up and shutdown significantly reduced the overall CO_2 capture rate and increased the specific reboiler duty. In contrast, the scenarios *without an auxiliary boiler* represent the situation where steam is supplied via zero carbon intensity energy. Therefore, to maximise the cumulative CO_2 capture rate, the energy used during start-up and shutdown must exhibit a low-carbon intensity (e.g., via renewable energy). This becomes increasingly important in energy systems with frequent SUSD cycles, especially in the context of net-zero GHG emission targets.

Table IV: Cumulative CO_2 capture performance of 200 minutes start-up combined with shutdown, showing the effect of CO_2 emissions from a gas-fired auxiliary boiler.

Product CO_2 basis	Without an auxiliary boiler		With an auxiliary boiler for shutdown*		With an auxiliary boiler for SU & SD*	
200 min start-up (SU) combined with shutdown (SD)	Cumulative specific reboiler duty (GJ/t CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (GJ/t CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (GJ/t CO_2)	Cumulative CO_2 captured (%)
Cold SU 53 m^3 & SD	**5.59**	**86.9**	**5.99**	**81.1**	**6.41**	**75.8**
Cold SU 42 m^3 & SD	**5.52**	**81.1**	**5.83**	**76.8**	**6.23**	**71.9**
Hot SU 53 m^3 & SD	**5.02**	**88.6**	**5.35**	**83.1**	**5.42**	**82.0**
Hot SU 42 m^3 & SD	**4.97**	**91.3**	**5.22**	**86.9**	**5.28**	**85.9**
Hot SU 42 m^3 delayed steam & SD	**4.78**	**81.1**	**5.05**	**76.8**	**5.05**	**76.8**

Note: Assumes that a cold start-up requires the auxiliary boiler for 60 min and a hot start-up requires it for 20 min, plus it is used for the duration of shutdown.

Proposed improvement strategy: Effect of preheating on the start-up performance. The effect of preheating was demonstrated via the tests summarised in Table V. The tests compare capture rates and reboiler duties for cold and hot start-ups (with a preheating steam flow rate of 2,500 kg/h) and a hot start-up (with a higher preheating steam flow of 5,000 kg/h).

Table V: Time when the CO_2 product flow rate begins (t_{SU}) and when steady state conditions are reached (t_{SS}) after the flue gas flow starts in minutes.

Label	Start-up type	Conditions	Start-up time: time when CO_2 product flow starts, t_{SU} (min)	Time when CO_2 product flow reaches steady state, t_{SS} (min)
Cold SU (1)	Cold start-up with preheat steam flow of 2500 kg/h	**9 June:** Preheat using 45 m^3 inventory Start-up loading: 0.07–0.08 mol CO_2/mol amine	20	70
Cold SU (2)	Cold start-up with preheat steam flow of 2,500 kg/h, vol adjusted	**12 June:** Preheat, adjustment from 41.5 to 45 m^3 inventory Due to the increased volume, the average solvent concentration for this test was reduced to 23.0 wt% AMP 9.4 wt% PZ Start-up loading 0.05 mol CO_2/mol amine	10	85
Hot SU (1)	Hot start-up with preheat steam flow of 2500 kg/h	**10 June:** Preheat using 45 m^3 inventory Start-up loading 0.10 mol CO_2/mol amine	15	60
Hot SU (2)	Hot start-up with high preheat steam flow of 5,000 kg/h	**11 June:** High preheat start-up using 45 m^3 inventory Start-up loading 0.05–0.07 mol CO_2/mol amine	15	70

Note: These tests were carried out during the June 2020 campaign using CESAR-1 and had slightly different starting conditions. Average solvent concentration based on laboratory analysis of the solvent samples: 25.5 wt% AMP and 10.5 wt% PZ.

As shown in Tables VI and VII, the hot start-up with the high preheating showed the highest cumulative capture rate compared with tests using the lower preheating steam flow. As the two cold start-up tests had the same preheating steam flow, the cumulative CO_2 capture rates based on absorbed CO_2 were similar (97–98%).

Higher preheating results in a higher cumulative capture rate on a product CO_2 basis (i.e., hot start-up cases). This indicates the use of higher preheating rates before start-up allows the capture plant to reach the steady state flow of product CO_2 in a shorter timeframe, making the capture plant more responsive to the requirements of the CO_2 compression and transport system.[9]

Table VI: Effect of preheating on start-up performance in terms of the cumulative CO_2 capture rate, calculated on a product CO_2 basis and absorbed CO_2 basis, and specific reboiler duty (SRD) over 85 minutes.

85-minute start-up	Preheat steam flow rate (kg/h)	Product CO_2 basis		Absorbed CO_2 basis		Absorbed CO_2 basis, accounting preheating CO_2 emissions	
		Cumulative SRD (MJ/kg CO_2)	Cumulative CO_2 captured	Cumulative SRD (MJ/kg CO_2)	Cumulative CO_2 captured	Cumulative SRD (MJ/kg CO_2)	Cumulative CO_2 captured
Cold SU (1) with preheat	2500	10.71	65.9	7.25	97.4	8.57	82.3
Cold SU (2) with preheat	2500	10.03	60.6	6.22	97.6	7.06	86.0
Hot SU with preheat	2500	8.37	62.9	5.48	96.0	6.01	87.5
Hot SU with **high** preheat	5000	9.64	77.0	7.52	98.8	8.78	84.6
Hot SU with **high** preheat, **corrected preheat time**	5000	7.16	77.0	5.58	98.8	5.86	94.1

Note: The cumulative residual CO_2 emissions is the difference between the supply CO_2 and the absorbed CO_2. Preheat auxiliary boiler emissions assumed an emissions factor of 50 kg CO_2/GJ.

Although the cumulative CO_2 capture rate improves, higher preheating also increases the steam energy demand. Thus, the effect of preheating whilst accounting for the CO_2 emissions associated with this additional energy requirement is also considered. Once the CO_2 emissions due to preheating have been accounted for, the cumulative CO_2 capture rates based (absorbed CO_2 basis) reduce substantially from 96–99% down to 85–88%. However, as the high preheating case was supplying an excess of energy, the reboiler temperature reached its target value within 30 min, meaning there was around 40 minutes of excess preheating. To provide a better representation of this high preheating case, the preheating energy and CO_2 emissions were recalculated based on the preheat energy used over the 30 min, plus the additional 85 or 200 minutes of operation after flue gas flow begins. Compared to the low preheating cases, the high preheating test calculated with the corrected preheat time (for the 85-minute case) has a

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[9] When flexible operation of the capture plant is being implemented, the stripper conditions should remain within the operating limits of the compressor. The transport of CO_2 via pipeline will also need to meet certain specifications, including an operating pressure envelope along the pipeline, CO_2 purity requirements, and the velocity limits. Pressure boosting stations may also be included in the design of some CO_2 transport and storage systems to ensure flow remains within the operating pressure envelope.

considerably higher cumulative CO_2 capture rate of 94.1% and lower specific reboiler duty (SRD) 5.86 MJ/kg CO_2.

Table VII: Effect of preheating on start-up performance in terms of the cumulative CO_2 capture rate, calculated on a product CO_2 basis and absorbed CO_2 basis, and specific reboiler duty (SRD) over 200 minutes.

200-minute start-up	Preheat steam flow rate (kg/h)	Product CO_2 basis		Absorbed CO_2 basis		Absorbed CO_2 basis, accounting preheating CO_2 emissions	
		Cumulative SRD (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative SRD (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative SRD (MJ/kg CO_2)	Cumulative CO_2 captured (%)
Cold SU (1) with preheat	2500	5.86	85.3	5.27	94.9	5.61	89.1
Cold SU (2) with preheat	2500	5.53	84.2	4.86	95.7	5.11	91.0
Hot SU with preheat	2500	5.26	78.5	4.35	94.9	4.51	91.5
Hot SU with **high** preheat	5000	5.73	89.1	5.24	97.5	5.54	92.2
Hot SU with **high** preheat, with **corrected preheat time**	5000	4.93	89.1	4.51	97.5	4.59	95.7

Note: The cumulative residual CO_2 emissions is the difference between the supply CO_2 and the absorbed CO_2. Preheat auxiliary boiler emissions assumed an emissions factor of 50 kg CO_2/GJ.

The different operating conditions (e.g., amine concentration and flow rate) are some key contributing factors to the higher capture rates in the June 2020 tests. The solvent inventory tests (previous section) used solvent with lower amine concentrations of 24.4 wt% AMP and 8.7 wt% PZ. In contrast, the preheating tests used solvent with slightly higher concentrations of 25.5 wt% AMP and 10.5 wt% PZ, which resulted in a greater proportion of CO_2 being absorbed. The higher amine concentrations as well as higher amine flow rates for the preheating tests achieved higher steady state online CO_2 capture rates of 92.4–95.5% compared to the solvent inventory tests (83–88%). The optimised operating conditions at steady state were also contributing factors to the higher cumulative CO_2 capture rates achieved during the preheating tests.

Expert Review Comments

Detailed comments were received from several reviewers, all of which were addressed by the authors. Overall, the study was warmly welcomed as a timely addition to the collection of IEAGHG studies covering the operational performance of power plants with CO_2 capture.

Many comments hinged on the fact that that detailed performance metrics, measurements and observations would be plant, scale and solvent specific. While the authors recognised this, they pointed out that the high-level insights drawn from this work would remain broadly applicable. Furthermore, they recommended that, when applying these high-level insights in practice, a degree of pre-testing would be advisable for the collection of project-specific data.

For example, as the physical properties (e.g., CO_2 absorption capacity, heat of absorption) of different solvents have a strong influence on their overall capture performance, it would not be possible to make quantitative conclusions without doing a similar technical study with different solvents. For each solvent type, the set-point/target conditions would differ for optimal process performance to be achieved, e.g., achieve high capture rates and minimise reboiler duty.

Some reviewers made suggestions for further work connected to the study and even suggested the potential for future collaboration.

Conclusions and Recommendations

The potential for performance improvements during start-up and shutdown of CO_2 capture processes in power plants was examined. A series of SUSD tests was conducted at the TCM CO_2 capture facility in Norway that captures CO_2 from a natural gas-fired CHP plant. Due to the highly dynamic nature of SUSD operations, a bespoke method of analysis was developed to evaluate their performance. The results have led to an improved understanding of the process dynamics and capture performance during the SUSD operations. The evaluation has helped identify novel operational strategies that can minimise both the time taken for start-up and shutdown and the CO_2 emissions associated with these operations.

Key factors have been identified that influence the dynamics and performance of the CO_2 capture plant during start-up and shutdown. Performance was evaluated in terms of time requirements, amine and ammonia emissions, cumulative CO_2 capture rate and the energy consumption. The key factors that were investigated in this study include:

- Flexible operation using an advanced solvent CESAR-1.
- Comparing cold start-up performance with hot start-ups.
- Combined effect of start-up and shutdown on overall performance.
- Effect of using different solvent inventory volumes, 53 m^3 versus 42 m^3.
- Timing of steam availability on start-up time, different tests were conducted to show steam introduced before (i.e., preheating), at same time and delayed steam supply, i.e., steam flow starting after flue gas flow.
- Effect of solvent CO_2 loading on the capture performance during plant start-up.

The tests presented in this report are specific for plant operation with CESAR-1 solvent. Although the absolute numbers of the performance metrics and measurements may differ for power plants and capture plants of different scales or for different capture solvents, e.g., MEA, it is expected that the general high-level insights from this work should remain valid. Importantly, over the course of all the tests with CESAR-1, emissions of amine and ammonia were well below the acceptable thresholds specified by TCM engineers and relevant environmental emission standards. Therefore, no environmental concerns associated with amine or ammonia emissions for CO_2 capture plants using CESAR-1 are anticipated.

Cold start-ups required twice as much time to reach steady state compared to hot start-ups. A cold start-up with 53 m^3 of inventory requires 82 min to reach steady state, whereas a hot start-up with the same inventory volume only requires 40 min to reach steady state. The use of a larger solvent inventory volume in the system increased the time required for the system to reach steady state after start-up and increased the shutdown time. Delaying the steam supply during start-up was found to increase the start-up time – for example, a 20-min delay in steam supply increased the start-up time by ~20 minutes.

As it includes the time required to lean-out the solvent to a low target concentration, the shutdown time is a function of the solvent volume and the steam supply. Shutdown with the larger 53 m^3 solvent inventory required more time as a greater volume of solvent was being regenerated (leaned out). Consequently, shutdown with the larger inventory also required more steam energy on a MJ basis compared with that required for a smaller inventory.

However, a large amount of product CO_2 is recovered during shutdown through the solvent lean-out operation, i.e., 1,476–2,274 kg CO_2, depending on the inventory volume. When considering the cumulative capture of the start-up together with shutdown, the large amount of shutdown CO_2 product counterbalances the CO_2 emissions associated with start-up. This hypothesis was tested by evaluating the combined performance of both start-up and shutdown. Although the capture rate (on an absorbed CO_2 basis) was preferred for the analysis of start-up alone, capture rate on a product CO_2 basis is a more meaningful metric for benchmarking SUSD scenarios. The combined performance of start-up (calculated over 82 min and 200 min) and shutdown confirmed that using a larger solvent inventory is highly beneficial for cold start-up in terms of maximising the cumulative CO_2 capture rate (on a product CO_2 basis). However, in the case of hot start-ups, solvent inventory volume had an almost negligible effect on cumulative CO_2 capture. Hot start-up was found to have significantly higher cumulative CO_2 capture rate and lower specific reboiler duty compared to cold start-ups.

The study demonstrates that the optimal CO_2 capture performance during start-up and shutdown of the plant needs to balance several factors. Namely, that solvent inventory volume, initial temperature (cold vs hot) and timing of steam availability (preheating vs steam & flue gas at the same time vs delayed steam) are the key factors that influence the time required for and capture performance during start-up and shutdown. The preheating tests demonstrated start-up protocols that combined several improvements to achieve high cumulative CO_2 capture rates (on an absorbed CO_2 basis) of 96–99% over 85 min, whereas conventional start-ups only achieved 75–90% (function of start-up type and solvent inventory volume). Furthermore, optimising operating conditions such as slightly higher amine concentration, higher liquid-to-gas ratio and lower start-up solvent loading can help maximise the cumulative CO_2 capture rate.

Owing to the low start-up solvent loading (0.05–0.11 mol CO_2/mol amine), for all cold and hot start-up tests alike, the initial online CO_2 capture rate started at high levels of 98–99%, which were achieved immediately following the introduction of flue gas flow to the system. The ability to sustain these high CO_2 capture rates depended on the actual starting solvent CO_2 loading, the volume of the solvent inventory, the amine concentration, and the timing of steam supply to the reboiler. The results demonstrated the importance of timely steam supply during start-up. Any delay in steam supply to the capture plant reboiler significantly reduced the cumulative CO_2 capture rate, thereby increasing the residual CO_2 emissions.

On the other hand, start-up with preheating was shown to be a potentially valuable approach. Preheating provided higher cumulative CO_2 capture rates during start-up of the capture plant, thereby minimising the residual CO_2 emissions. To maximise the value of preheating, a higher flow rate of steam could heat the system faster. Importantly, the timing of steam supply was crucial to prevent excessive preheating and to minimise auxiliary boiler CO_2 emissions. In this study preheating was explored using a natural gas-fired auxiliary boiler. Results showed that the value of preheating would diminish if the preheating rate were insufficient (i.e., steam supply flow rate too low), or poorly timed (i.e., excess preheating). Using preheating energy with lower carbon intensity would further reduce residual CO_2 emissions of the process and provide higher cumulative CO_2 capture rates. Supplying energy for preheating will likely come at a cost, e.g., the cost of installing an auxiliary boiler, fuel cost. However, in the context of net-zero emissions targets, the advantage of potentially achieving higher CO_2 capture rates by preheating before start-up could outweigh the cost.

The results obtained provide valuable insights around the potential implications of start-up and shutdown at a process scale. Key measures shown to improve performance include:

- Hot start-ups provided significantly higher cumulative CO_2 capture rates and lower specific reboiler duty compared to cold start-ups. Hot start-ups also reached steady state much quicker than cold start-ups (around half the time).
- A larger solvent inventory will help maximise the cumulative CO_2 capture rate during cold start-up.
- Using a larger solvent inventory is also advantageous during shutdown as it increases the amount of product CO_2 recovered through the solvent lean-out step. In the case of cold start-up, it improves the cumulative CO_2 capture rate of combined start-up and shutdown. In contrast, the effect of solvent inventory volume in the case of hot start-ups was negligible.
- Process operating conditions shown to increase the cumulative CO_2 capture rate, i.e., "improved" start-up protocols, include preheating immediately prior to start-up, lower start-up CO_2 loading of solvent, higher amine concentration and higher liquid-to-gas ratio (e.g., increasing the amine flow rate).
- Higher rates of preheating significantly reduced the start-up time, with the reboiler reaching set-point temperature in 30 min instead of 100 min. This demonstrates value in having an auxiliary boiler for the provision of a preheating steam supply.

The "improved" hot start-up protocols with high preheating increased the cumulative CO_2 capture rate (on an absorbed CO_2 basis) to 98.8%, which resulted in a specific reboiler duty of 5.58 MJ/kg CO_2, calculated over 85 min, without accounting for (fossil-fired) auxiliary boiler CO_2 emissions. The "conventional" hot start-up protocols achieved lower cumulative CO_2 capture rates of between 90.0 to 90.3%, based on absorbed CO_2 and calculated over 82 min. The conventional start-up tests achieved lower specific reboiler duty of 4.03 and 3.76 MJ/kg CO_2 with solvent inventories of 42 m^3 and 53 m^3, respectively. This was mainly attributed to not using preheating energy for start-up and having lower amine flow rates (i.e., decreased sensible heat).

While the "improved" protocols can provide cumulative CO_2 capture rates of up to 99%, there will be trade-offs, and specific reboiler energy requirements may also increase, e.g., higher preheating energy or increased sensible heat with higher solvent flow. In the context of net-zero emission targets, the ability to maximise the CO_2 capture rate could be significant; it reduces the residual CO_2 emissions, thereby alleviating the demand for carbon offsets via CO_2 removal technologies, e.g., bioenergy with CCS, or direct air capture. [Another key contribution of this work is the comprehensive dataset of SUSD results from the TCM plant, which can be used as data input for process model validation and systems scale modelling.]

Suggestions for further work

There is much further R&D and future work in this area that might be explored. Suggestions include:

- The impact of different process configurations and process control systems that could improve plant flexibility and SUSD performance, e.g., via process modelling.
- Solvent inventory volume was shown be an important factor in this work, however, this is based on TCM plant configuration. Future work should investigate the effect of varying equipment capacities and the liquid hold-up volume (e.g., absorber column sump, reboiler sump, condenser reflux drum) on the start-up time and capture performance. For example, the impact of using parallel absorbers of different sizes, or the effect of oversizing the stripper or reboiler to achieve more efficient solvent regeneration.
- The effect of different solvent types on CO_2 capture plant flexibility and SUSD performance.
- The importance of the timely steam supply during start-up has been highlighted and the provision of an auxiliary boiler identified as a solution to satisfy this need. However, there may be other potential sources of readily available steam and it is proposed that alternative sources of steam, including non-GHG emitting solutions, such as novel energy storage devices, should be explored.
- The plant data from this study provides input specifications for model development and techno-economic analysis of different SUSD scenarios. A techno-economic analysis of start-up and shutdown will provide insight into the cost implications of different strategies and flexibility improvements. For example, compared to a hot/cold SUSD cycle, would it be more cost effective to operate at minimum loads and ramp up as required?
- The effect of power plant operation and flexibility (e.g., turndown ratio, ramp rate, shutdown procedure) on the SUSD strategy of CCS plant operation, i.e., upstream system. The dynamic interactions between the power plant and the CCS plant need to be explored further, e.g., to develop strategies to deal with changes on the power plant side which causes flue gas variations in flow rate or concentration (CO_2, O_2 or contaminants).
- The impact of start-up and shutdown in power plants with CCS on downstream processes (e.g., CO_2 compression).
- The effect of start-up and shutdown at a systems scale in the context of a national electricity grid. This could potentially demonstrate whether SUSD CO_2 emissions will impact the ability to achieve national scale net-zero emissions targets.
- This study explores strategies for shutdown of the capture plant in the case of planned shutdowns. Future work may explore strategies and protocols for shutdown of the capture plant in the case of forced outages.

Start-up and shutdown protocol for power stations with CO_2 capture

IEAGHG Report

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Abbreviations

AIT	Applied Instrument Technologies
AMP	2-amino-2-methyl-1-propanol
ASU	air separation unit
CC	combine cycle
CCGT	combined cycle gas turbine
CCC	CO_2 capture and compression
CCS	CO_2 capture and storage
CESAR	CO_2 Enhanced Separation and Recovery (the name of an EU project)
CHP	combined heat and power
conc	concentration
DCC	direct contact cooler
deNO$_X$	flue gas denitrification
EDA	ethylenediamine
FG	flue gas
FPZ	N-formyl piperazine
FTIR	Fourier transform infrared
GJ	gigajoule
GT	gas turbine
HRSG	heat recovery steam generator
HSS	heat stable salts
HX	heat exchanger
ID	induced draft
IGCC	integrated gasification combined cycle
IP	intermediate pressure
LCOE	levelised cost of electricity
L/G	liquid-to-gas ratio
LP	low pressure
MEA	monoethanolamine
MJ	megajoule
MW	megawatt
NDIR	non-dispersive infrared

NGCC	natural gas combined cycle
O&M	operational and maintenance
OPZ	2-oxopiperazine
P	pressure
PACT	Pilot-scale Advanced Capture Technology
P&ID	piping and instrumentation diagram
ppmv	parts per million volume
PZ	piperazine
RCC	refinery catalytic cracker
RFCC	refinery residue fluid catalytic cracker
SCR	selective catalytic reduction
SD	shutdown
SRD	specific reboiler duty
SSE	Scottish and Southern Electricity
ST	steam turbine
SU	start-up
SUSD	start-up and shutdown
t	tonne
T	temperature
TCM	Technology Centre Mongstad
TIC	total inorganic carbon
TOC	total organic carbon
t_{SS}	start-up time
t_{SU}	shutdown time
UKCCSRC	UK Carbon Capture and Storage Research Centre
VOC	volatile organic compounds
vol	volume
WWSI	Western Wind and Solar Integration Study

Executive Summary

Background and scope of study

Integrating higher shares of intermittent renewable energy (e.g., wind and solar power) into an electricity system presents major operational challenges. To balance this intermittency and ensure electricity demands are met, energy technologies that can provide flexibility to the system will be required, e.g., dispatchable energy storage technologies such as batteries, or pumped hydroelectricity storage. In particular, thermal power plants with carbon capture and storage (CCS) will likely have an important role in providing affordable dispatchable low carbon capacity, maintaining security of supply, and enabling the expansion of other low-carbon sources. Whilst the value of flexible CCS has been demonstrated in a number of previous studies, there has been limited work to-date which focuses on the start-up and shutdown of CCS in power plants, particularly with respect to the time required and the fugitive CO_2 emissions. This is particularly important with increasing penetration of intermittent renewable energy as these start-up/shut-down cycles will become increasingly frequent, thus the potential for fugitive emissions must be quantified and minimised. Further work is therefore necessary to develop an understanding of the process dynamics during start-up and shutdown in order to identify the key factors that will impact CO_2 capture performance and operability.

Therefore, the aim of this study is to examine the potential for performance improvements during the start-up and shutdown of a CO_2 capture process in a power plant. This involved conducting a series of start-up and shutdown tests at the TCM CO_2 capture facility in Norway. The TCM plant is an industrial-scale post-combustion absorption plant that is located in Mongstad, Norway, adjacent to the Equinor oil refinery. The plant uses amine-based solvents to capture CO_2 from a natural gas-fired CHP plant, and it can also be configured to process a gas slipstream from the refinery residue fluid catalytic cracker (RFCC). In this study, the CHP flue gas was used, and a detailed analysis of the plant data was carried out to develop an understanding around the start-up and shutdown (SUSD) dynamic behaviour. This has provided valuable insights around key factors and operation strategies that could help minimise disruption and CO_2 emissions during start-up and shutdown of CO_2 capture in a power plant. The key factors that were investigated in this study include:

- Flexible operation using an advanced solvent CESAR-1; most pilot plant work on flexible operation has focused on MEA-based absorption, and further work on the flexibility of systems using advanced solvents is required.
- Comparing cold start-up performance with hot start-ups to demonstrate the effect of the starting temperature.
- Combined effect of start-up and shutdown on overall performance.
- Effect of using different solvent inventory volumes, 53 m^3 versus 42 m^3, which is significant enough to illustrate a difference in process dynamics and identify any potential benefits.
- Timing of steam availability on start-up time, different tests were conducted to show steam introduced (i) before, i.e., preheating with an auxiliary boiler, (ii) at the same time, and (iii) after the start of flue gas flow, i.e., delayed steam supply when steam extraction is unavailable.
- Effect of solvent CO_2 loading on the start-up performance.

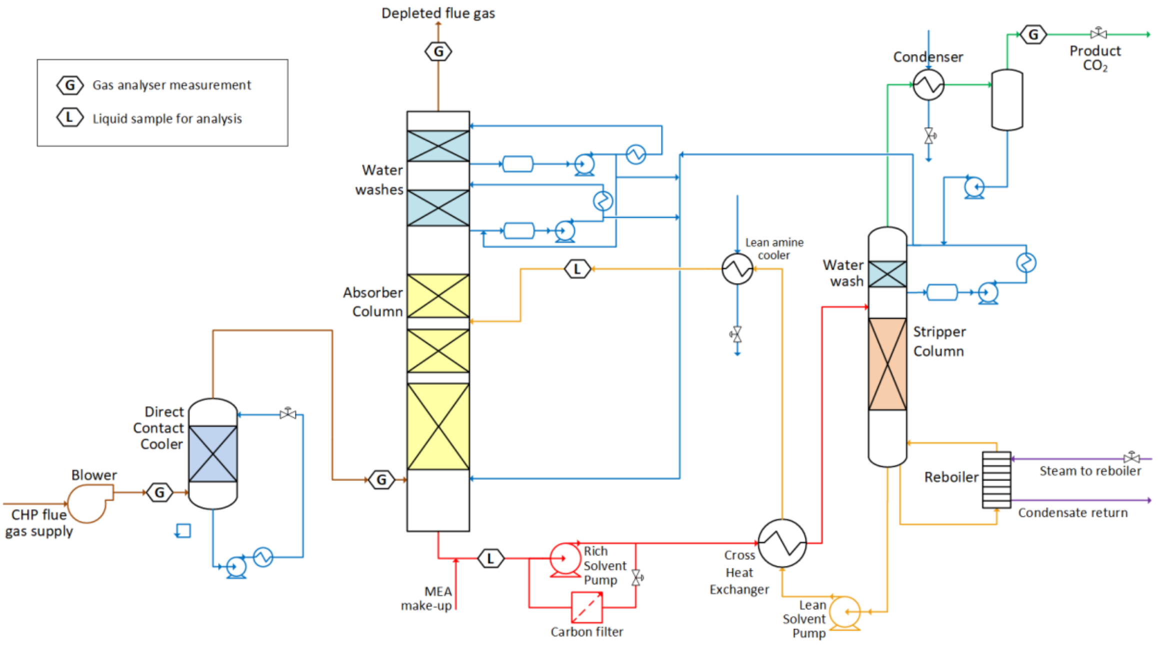

Figure i: Process flow diagram of the configuration used at TCM for the start-up and shutdown tests. The plant captured CO_2 from the combined heat and power (CHP) flue gas using CESAR-1 solvent. In this configuration, SUSD tests used 18 m of packing height, the CHP direct contact cooler and the larger stripper column (RFCC unit). Some key process control loops are shown, however, much of the P&ID detail is omitted.

The objective was to demonstrate the influence of these factors on the capture performance in the context of five conventional start-ups and shutdown protocols (two cold start-ups, three hot start-ups), also showing the results for four “improved” start-up and shutdown protocols, e.g., the effect of preheating before start-up, lower CO_2 loading and higher amine flow on hot and cold start-ups. This work is important as it helps identify potential protocol measures which can provide substantial reductions in CO_2 emissions, time requirements and energy demand for start-up and shutdown protocols.

CO_2 capture performance during start-up and shutdown

The test campaigns at Technology Centre Mongstad (TCM) using CESAR-1 examined different start-up and shutdown (SUSD) operating modes in a CO_2 capture process. The tests were designed to simulate SUSD conditions in the context of CCS with gas fired CCGT. The cold start-up corresponds to a start-up that is performed after a long downtime, e.g., shut for >8 hours, where the reboiler bottom temperature has cooled to “ambient” conditions of 25–30°C. The hot start-up simulates a start-up after a short downtime, e.g., <8 hours, where the reboiler bottom temperature was ~90°C. For all cases of shutdown, the same procedure was implemented, with the only difference being the solvent inventory volume. To ensure the plant starts with solvent that is sufficiently low in CO_2 loading, shutdown continues to supply steam to the reboiler even after the flue gas was turned off to “lean out” the solvent. Steam is turned off once all of the solvent reaches the required target CO_2 loading, which represents the end of shutdown. By the end of shutdown, all of the solvent will have lean loading of ≤ 0.2 mol CO_2/mol amine for two reasons: (i) prevents precipitation during plant downtime, which can occur if CESAR-1 is rich and low temperature, (ii) having lean solvent loading for the next start-up will maximise the CO_2 capture capacity. Lean out for non-precipitating solvents such as 30 wt% MEA would also be beneficial for the latter reason only. Table i shows some of the tests have a slightly different “start-up CO_2 loading” for the solvent.

Table i: Comparison of the cold and hot start-up tests in terms of start-up time (t_{SU}) and the time it takes for the system to reach steady state (t_{SS}).

Start-up type	Conditions	Start-up time: time when CO_2 product flow starts, t_{SU} (min)	Time when CO_2 product flow reaches steady state, t_{SS} (min)
Cold start-up	53 m^3 inventory, start loading 0.10–0.11 mol CO_2/mol amine	47	82
	42 m^3 inventory, start loading 0.08–0.09 mol CO_2/mol amine	47	69
Hot start-up	53 m^3 inventory, start loading 0.08–0.09 mol CO_2/mol amine	22	40
	42 m^3 inventory, start loading 0.08–0.09 mol CO_2/mol amine	19	42
	42 m^3 inventory with delayed steam supply, start loading 0.08–0.09 mol CO_2/mol amine	45	63

For dynamic operation (e.g., load following, start-up or shutdown), the online data illustrates the variations in process parameters and metrics, however, it is difficult to benchmark the performance of these scenarios based on transient trends. Thus, the *cumulative* capture rate and reboiler duty is also calculated over the scenario timeframe, which provides a better indication of the impact of dynamic operation measures on the overall plant performance. To minimise any bias associated with differences in feed CO_2 content, the analysis focused specifically on the dynamic region of data. The main dynamic trends occur within the time between start-up of the flue gas and the moment steady state of CO_2 product is achieved, i.e., t_{SS} (time to reach steady state). This was 82 minutes for the first dataset showing the effect of solvent inventory, and 85 minutes for the dataset demonstrating the effects of preheating. The performance over 200 minutes was also evaluated as this will demonstrate whether the impact of start-up changes is sufficiently significant to influence steady state performance.

Figure ii below shows the cumulative CO_2 capture rate and specific reboiler duty based on the absorbed CO_2 and product CO_2, calculated over an 82 min and 200 min period. The product CO_2 basis uses the amount of CO_2 exiting the stripper section as a proportion of the feed CO_2. The product basis performance metrics provide a reflection of the process dynamics as it accounts for the solvent circulation time (i.e., observed differences are due to the solvent travel time from the absorber to the stripper). Alternatively, the cumulative capture rate on an absorbed CO_2 basis is calculated from the difference in CO_2 concentration of the inlet and outlet gas streams of the absorber column. It represents the proportion of CO_2 directly captured from the feed flue gas in the absorber, hence it provides a better indication of the residual CO_2 emissions from the process.

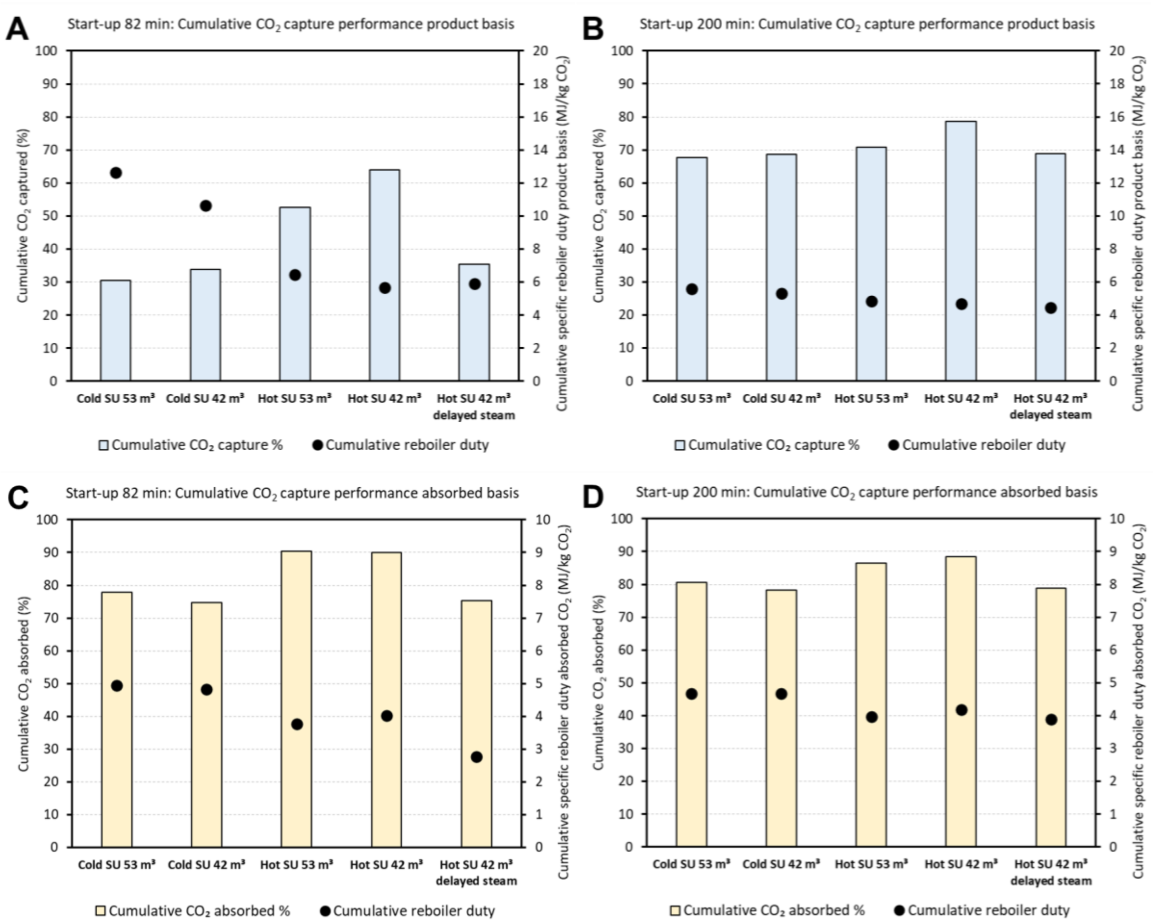

Figure ii: Cumulative start-up (SU) performance over 82 minutes compared against 200 minutes (indicated by the labels) for different solvent inventory volumes, 42 m^3 and 53 m^3, also the effect of delayed steam supply by 20 min is shown for one hot start-up with 42 m^3. Cumulative CO_2 capture rate and cumulative specific reboiler duty are calculated based on (A & B) product CO_2 and (C & D) absorbed CO_2.

Table ii: Cumulative CO_2 capture performance of start-up (82 min) and shutdown scenarios, without auxiliary boiler emissions.

	Product CO_2 basis		Absorbed CO_2 basis	
82 min start-up (SU), duration of shutdown (SD) varies	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)
Cold SU 53 m^3	12.64	30.5	4.95	77.8
Cold SU 42 m^3	10.64	33.9	4.83	74.7
Hot SU 53 m^3	6.46	52.6	3.76	90.3
Hot SU 42 m^3	5.66	64.0	4.03	90.0
Hot SU 42 m^3 delayed steam	5.91	35.4	2.77	75.3
SD 53 m^3	5.63	939	62.73	84.3
SD 42 m^3	6.49	840	61.07	89.2
SD 42 m^3	6.40	1016	72.84	89.3

Cold start-up vs hot start-up

As shown in Table i, cold starts typically take longer to start-up and reach steady state conditions compared to hot start-ups. This is mainly due to the lower starting temperatures during cold start-up (25–30°C) compared to hot start-up (~90°C). Consequently, the cold start-ups require more time to heat the stripper/reboiler to the target temperatures.

Cold start-ups cumulatively captured a lower percentage of incoming CO_2 and have higher specific reboiler duty compared to hot start-ups. For a start-up period of 82 minutes in a system with 53 m^3 of inventory, a cold start-up cumulatively captured 78% on an absorbed CO_2 basis, whereas a hot start-up cumulatively captured 90%–a difference of 12%. The 200 min start-up results show the effect of including steady state operation. The cumulative CO_2 capture rate over 200 min for hot start-up is greater than cold start-ups, although the difference is slightly smaller compared to the 82 min results (Figure ii and Table ii).

Effect of solvent inventory volume

For cold start-up, a smaller inventory will reduce the time required to stabilise the plant and will slightly reduce energy requirements. A larger solvent inventory will provide higher cumulative CO_2 capture rates, and thus would reduce the residual CO_2 emissions. With a larger solvent volume at start-up, more lean solvent is available to capture CO_2 as the plant heats up.

In the case of hot start-ups, the two solvent inventory cases, 42 m^3 and 53 m^3, had similar cumulative CO_2 capture rates over 82 min of 90% (absorbed CO_2 basis), shown in Table ii. The cumulative specific reboiler duty on a MJ/kg absorbed CO_2 basis is slightly higher for the smaller inventory case. The observed difference in cumulative CO_2 capture rate over the 200 min period is due to different flue gas CO_2 content for the two tests. The steady state online CO_2 capture rate of the 42 m^3 test was higher (88%) compared to the 53 m^3 case (83%), as illustrated in Figure iii when the online capture rate reaches a stable constant. If flue gas CO_2 content was the same, the inventory volume size would have a negligible effect on the residual CO_2 emissions during hot start-up.

Aside from the potential reduction in solvent consumption costs with the smaller inventory systems, the results indicate possible technical benefits for hot start-up performance as well. A smaller inventory volume will reduce the solvent circulation time and the effects of solvent regeneration are observed on a faster time scale. Therefore, for a given time period, the smaller inventory system generates more product CO_2 (absolute terms), and thus, a higher product basis CO_2 capture rate is observed in (A) of Figure ii. Consequently, the smaller inventory system has a lower specific reboiler duty on a product basis (MJ/kg product CO_2).

Effect of delayed steam supply

The prioritisation of power generation during start-up could mean steam extraction is not available, which would delay the steam supply to the CO_2 capture plant. A hot start-up using 42 m^3 inventory was demonstrated with 20 minutes of delayed steam availability, which was found to reduce the CO_2 capture performance of the plant. Firstly, delayed steam supply increased the time required to heat the reboiler, resulting in a start-up time similar to a cold start-up. Although delaying steam availability reduced the specific reboiler duty, the cumulative CO_2 capture rate (both absorbed and product CO_2 basis) decreased significantly compared to the normal hot start-up. Hence, making steam available for the CO_2 capture plant as early as possible is critical to maximise the CO_2 capture rates and minimise residual CO_2 emissions during start-up.

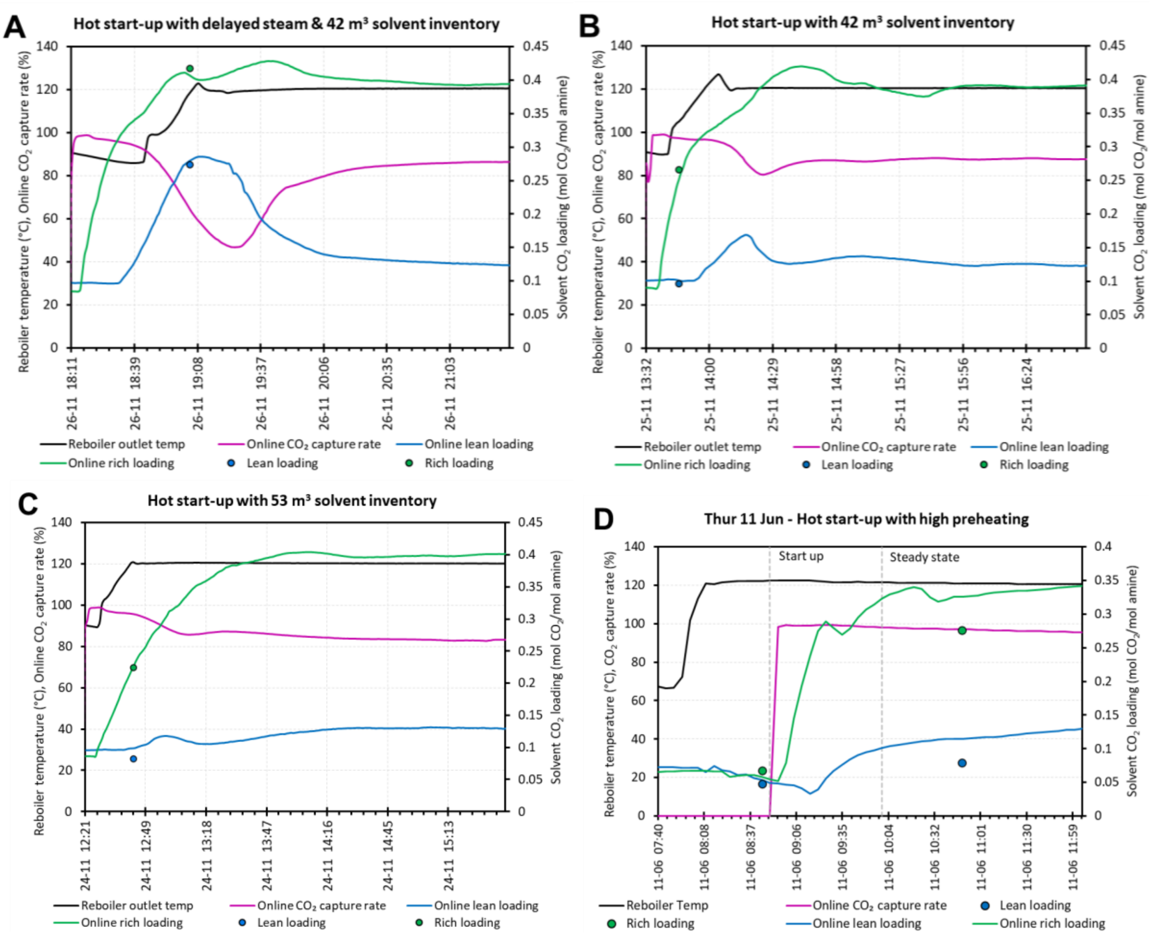

Figure iii: Online CO₂ capture rate (purple), lean CO₂ loading (blue) and rich CO₂ loading (green) during hot start-up with a 20 min delay steam supply (A), steam supplied at the same time as flue gas with 42 m^3 solvent inventory (B) and 53 m^3 solvent inventory (C), as well as hot start-up with early steam supply, i.e., high preheat, and 45 m^3 solvent inventory (D).

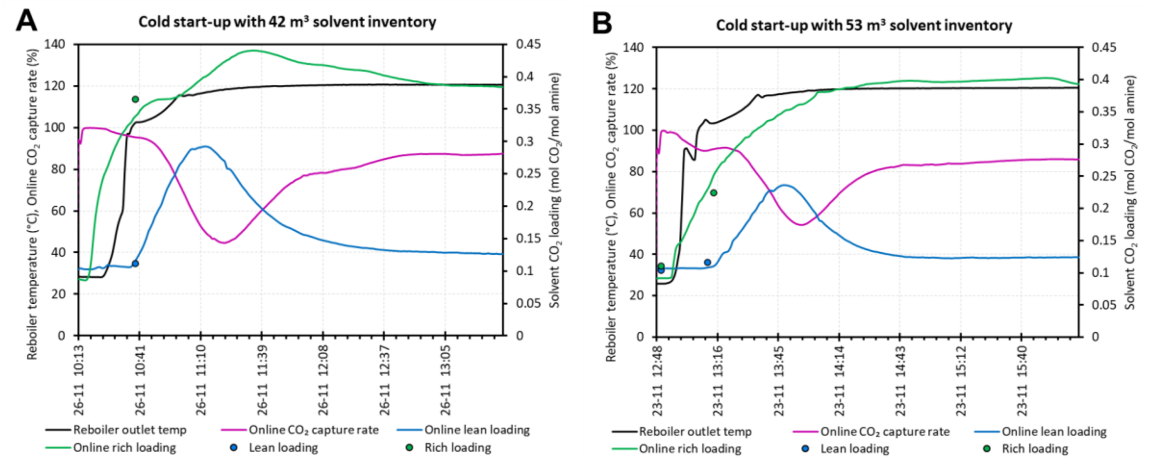

Figure iv: Online CO₂ capture rate (purple), lean CO₂ loading (blue line & points) and rich CO₂ loading (green line and points) during hot start-up with a 20 min delay steam supply (A), steam supplied at the same time with 42 m^3 solvent inventory (B) and 53 m^3 solvent inventory (C), as well as hot start-up with early steam supply, i.e., high preheat, and 45 m^3 solvent inventory (D). The CO₂ loading of the lean/rich solvent is shown as both online measurements (green and blue lines) and manual measurements (titration) plotted as blue and green points.

Combined performance of start-up with shutdown

The performance characteristics of start-up are different to shutdown when analysed separately. The solvent inventory is lean at the beginning of a new start-up. As the plant stabilises and reaches steady state, the liquid on the absorber side is CO_2-rich, and CO_2-lean on the stripper side, i.e., temporarily stores CO_2. As the plant transitions into the shutdown phase, steam supply continues even after flue gas flow stops. Thus, this enables leaning out of the solvent to a target loading (the start-up loading) and releases a significant amount of product CO_2, i.e., the "stored" CO_2 in the system. To illustrate the impact of a start-up and shutdown cycle, we evaluated the combined start-up and shutdown performance in terms of cumulative capture rate (product CO_2 basis) and specific reboiler duty.

For analysis of start-up alone (82 min), the capture rate on a product basis is relatively low (Figure ii and Table ii). However, owing the high amount of product during the shutdown phase, calculating the combine performance of start-up with shutdown has a much higher capture rate as shown in Tables iii and iv.

Typically for steady state operation, it is assumed that the steam supply is provided through steam extraction from the power plant steam cycle. However, during start-up and shutdown, we consider the need for an auxiliary boiler to supply steam to the capture plant as steam extraction from the power plant is unavailable. We assume that a cold start-up requires the auxiliary boiler for 60 min and hot start-up requires it for 20 min and it is used for the duration of shutdown. The CO_2 emissions associated with using a natural gas fired auxiliary boiler was calculated for each scenario.

The auxiliary boiler CO_2 emissions can have a major effect on the start-up and shutdown performance, increasing the cumulative specific reboiler duty and reducing the cumulative CO_2 capture rate. The cold start-up and shutdown case using 53 m^3 of inventory shows that the use of an auxiliary boiler for start-up and shutdown reduces the 82 min cumulative CO_2 capture rate from 80% to 53% and increases specific reboiler duty from 8.2 to 12.4 GJ/t_{CO2}. The degree of performance reduction associated with the auxiliary boiler is smaller in the case of hot start-ups. Thus, once auxiliary boiler emissions are accounted for, normal hot start-up and shutdown is able to achieve relatively high capture rates of 81% and 83% with 53 m^3 and 42 m^3 of inventory, respectively.

In the case of the 82 min start-up results, using the larger 53 m^3 solvent inventory provided higher cumulative CO_2 capture for cold start-ups with shutdown. When solvent inventory increased from 42 m^3 to 53 m^3, the cumulative CO_2 capture would increase by 9.3-13.7% points, depending on the auxiliary boiler calculation scenario. Larger solvent inventory also provided a very small reduction in specific reboiler duty. In contrast, for hot start-up with shutdown, the increase in solvent inventory from 42 to 53 m^3 had an almost negligible impact on capture performance.

Normal operation would typically include start-up, plant stabilisation, steady state operation and shutdown. The cumulative performance for 200 minutes of start-up with shutdown are used to illustrate the effect of start-up and shutdown combined with normal steady state operation. At steady state, the average online CO_2 capture rate was 83–88% (illustrated in Figures iii and iv). Thus, the cumulative CO_2 capture rates calculated over the longer 200 min start-up period move closer to the performance values achieved during steady state. Importantly, the cumulative capture rates over 200 min which account for auxiliary boiler emissions (Table iv) are highest for the normal hot start-up cases reaching 82–86%, with capture rates being lower for the cold start-ups (72–76%) or for hot start-up with delayed steam availability (77%). The longer analysis timeframe also lowers the cumulative specific reboiler duty to 4.8–6.4 GJ/tCO_2, depending on the scenario.

*Table iii: Cumulative CO_2 capture performance of 82 minutes start-up combined with shutdown, showing the effect of CO_2 emissions from a gas-fired auxiliary boiler. * Assumes that a cold start-up requires the auxiliary boiler for 60 min and hot start-up requires it for 20 min and it is used for the duration of shutdown.*

Product CO_2 basis	Without an auxiliary boiler		With an auxiliary boiler for shutdown*		With an auxiliary boiler for SU & SD*	
82 min start-up (SU) combined with shutdown (SD)	Cumulative specific reboiler duty (GJ/t CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (GJ/t CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (GJ/t CO_2)	Cumulative CO_2 captured (%)
Cold SU 53 m^3 & SD	**8.15**	**80.0**	**9.95**	**65.6**	**12.42**	**52.5**
Cold SU 42 m^3 & SD	**8.51**	**66.3**	**10.18**	**55.5**	**13.04**	**43.3**
Hot SU 53 m^3 & SD	**6.06**	**97.3**	**7.02**	**83.9**	**7.26**	**81.2**
Hot SU 42 m^3 & SD	**5.94**	**96.5**	**6.73**	**85.3**	**6.93**	**82.9**
Hot SU 42 m^3 delayed steam & SD	**6.17**	**67.7**	**7.35**	**56.8**	**7.35**	**56.8**

*Table iv: Cumulative CO_2 capture performance of 200 minutes start-up combined with shutdown, showing the effect of CO_2 emissions from a gas-fired auxiliary boiler. * Assumes that a cold start-up requires the auxiliary boiler for 60 min and hot start-up requires it for 20 min and it is used for the duration of shutdown.*

Product CO_2 basis	Without an auxiliary boiler		With an auxiliary boiler for shutdown*		With an auxiliary boiler for SU & SD*	
200 min start-up (SU) combined with shutdown (SD)	Cumulative specific reboiler duty (GJ/t CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (GJ/t CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (GJ/t CO_2)	Cumulative CO_2 captured (%)
Cold SU 53 m^3 & SD	**5.59**	**86.9**	**5.99**	**81.1**	**6.41**	**75.8**
Cold SU 42 m^3 & SD	**5.52**	**81.1**	**5.83**	**76.8**	**6.23**	**71.9**
Hot SU 53 m^3 & SD	**5.02**	**88.6**	**5.35**	**83.1**	**5.42**	**82.0**
Hot SU 42 m^3 & SD	**4.97**	**91.3**	**5.22**	**86.9**	**5.28**	**85.9**
Hot SU 42 m^3 delayed steam & SD	**4.78**	**81.1**	**5.05**	**76.8**	**5.05**	**76.8**

In both the 82 min and 200 min start-up cases, delaying steam supply by 20 min during start-up was highly detrimental to the CO_2 capture performance. Although a lower specific reboiler duty was observed, the cumulative CO_2 capture rate reduced by 26.0–28.9% points compared to the normal hot start-up using the same solvent inventory volume. Of all the cases studied, the hot start-up with delayed steam has the lowest cumulative CO_2 capture rate. To minimise residual CO_2 emissions, steam needs to be available for start-up of the CO_2 capture plant as soon as possible.

In all cases, using a natural gas fired auxiliary boiler, i.e., fossil fuel energy, to supply steam during start-up and shutdown significantly reduced the overall CO_2 capture rate and increased the specific reboiler duty. In contrast, the scenarios *without an auxiliary boiler* represent the situation where steam is supplied via zero carbon intensity energy. Therefore, to maximise the cumulative CO_2 capture rate, it is essential that energy used during start-up and shutdown has low carbon intensity (e.g., renewable energy). This becomes increasingly important in energy systems with frequent start-up and shutdown cycles, especially in the context of net-zero GHG emission targets.

Proposed improvement strategy: Effect of preheating on the start-up performance

The effect of preheating was demonstrated with the tests summarised in Table v, which compares start-ups with preheating at steam flow rate of 2500 kg/h against hot start-up with high preheating at steam flow of 5000 kg/h. As shown in Tables vi and vii, the hot start-up with high preheating had the highest cumulative capture rate compared to the other tests using lower preheating steam flow. The two cold start-up tests had the same preheating steam flow, consequently, the cumulative CO_2 capture rates based on absorbed CO_2 were similar (97–98%).

Higher preheating results in a higher cumulative capture rate on a product CO_2 basis (i.e., hot start-up cases). This indicates the use of higher preheating rates before start-up allows the capture plant to reach the steady state flow of product CO_2 in a shorter timeframe, making the capture plant more responsive to the requirements of the CO_2 compression and transport system.[a]

Table v: Time when the CO_2 product flow rate begins (t_{SU}) and when steady state conditions are reached (t_{SS}) after the flue gas flow starts in minutes. These tests were carried out during the June 2020 campaign using CESAR-1 and had slightly different starting conditions. Average solvent concentration based on laboratory analysis of the solvent samples: 25.5 wt% AMP 10.5 wt% PZ.

Label	Start-up type	Conditions	Start-up time: time when CO_2 product flow starts, t_{SU} (min)	Time when CO_2 product flow reaches steady state, t_{SS} (min)
Cold SU (1)	Cold start-up with preheat steam flow of 2500 kg/h	**9 June:** Preheat using 45 m^3 inventory Start-up loading: 0.07–0.08 mol CO_2/mol amine	20	70
Cold SU (2)	Cold start-up with preheat steam flow of 2500 kg/h, vol adjust	**12 June:** Preheat, adjustment from 41.5 to 45 m^3 inventory Due to the increased volume, the average solvent concentration for this test reduced down to 23.0 wt% AMP 9.4 wt% PZ Start-up loading 0.05 mol CO_2/mol amine	10	85
Hot SU (1)	Hot start-up with preheat steam flow of 2500 kg/h	**10 June:** Preheat using 45 m^3 inventory Start-up loading 0.10 mol CO_2/mol amine	15	60
Hot SU (2)	Hot start-up with high preheat steam flow of 5000 kg/h	**11 June:** High preheat start-up using 45 m^3 inventory Start-up loading 0.05–0.07 mol CO_2/mol amine	15	70

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[a] When flexible operation of the capture plant is being implemented, the stripper conditions should remain within the operating limits of the compressor.[1] The transport of CO_2 via pipeline will also need to meet certain specifications, including an operating pressure envelope along the pipeline, CO_2 purity requirements, and the velocity limits. Pressure boosting stations may also be included in the design of some CO_2 transport and storage systems to ensure flow remains within the operating pressure envelope.[2, 3]

Table vi: Effect of preheating on start-up performance in terms of the cumulative CO_2 capture rate and specific reboiler duty (SRD) over 85 minutes is calculated on a product CO_2 basis and absorbed CO_2 basis. The cumulative residual CO_2 emissions is the difference between the supply CO_2 and the absorbed CO_2. Preheat auxiliary boiler emissions assumed an emissions factor of 50 kg CO_2/GJ.

85 min start-up only	Preheat steam flow rate (kg/h)	Product CO_2 basis		Absorbed CO_2 basis		Absorbed CO_2 basis, accounting preheating CO_2 emissions	
		Cumulative SRD (MJ/kg CO_2)	Cumulative CO_2 captured	Cumulative SRD (MJ/kg CO_2)	Cumulative CO_2 captured	Cumulative SRD (MJ/kg CO_2)	Cumulative CO_2 captured
Cold SU (1) with preheat	2500	10.71	65.9	7.25	97.4	8.57	82.3
Cold SU (2) with preheat	2500	10.03	60.6	6.22	97.6	7.06	86.0
Hot SU with preheat	2500	8.37	62.9	5.48	96.0	6.01	87.5
Hot SU with **high** preheat	5000	9.64	77.0	7.52	98.8	8.78	84.6
Hot SU with **high** preheat, **corrected preheat time**	5000	7.16	77.0	5.58	98.8	5.86	94.1

Table vii: Effect of preheating on start-up performance in terms of the cumulative CO_2 capture rate and specific reboiler duty (SRD) over 200 minutes is calculated on a product CO_2 basis and absorbed CO_2 basis. The cumulative residual CO_2 emissions is the difference between the supply CO_2 and the absorbed CO_2. Preheat auxiliary boiler emissions assumed an emissions factor of 50 kg CO_2/GJ.

200 min start-up only	Preheat steam flow rate (kg/h)	Product CO_2 basis		Absorbed CO_2 basis		Absorbed CO_2 basis, accounting preheating CO_2 emissions	
		Cumulative SRD (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative SRD (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative SRD (MJ/kg CO_2)	Cumulative CO_2 captured (%)
Cold SU (1) with preheat	2500	5.86	85.3	5.27	94.9	5.61	89.1
Cold SU (2) with preheat	2500	5.53	84.2	4.86	95.7	5.11	91.0
Hot SU with preheat	2500	5.26	78.5	4.35	94.9	4.51	91.5
Hot SU with **high** preheat	5000	5.73	89.1	5.24	97.5	5.54	92.2
Hot SU with **high** preheat, with **corrected preheat time**	5000	4.93	89.1	4.51	97.5	4.59	95.7

Although cumulative CO_2 capture rate improves, there is also an increase in steam energy demand. Thus, we also consider the effect of preheating whilst also accounting for the CO_2 emissions associated with this additional energy requirement. Once the preheating CO_2 emissions have been accounted for, cumulative CO_2 capture rates based on absorbed CO_2 substantially reduced from 96–99% down to 82–88%. However, the high preheating case was supplying an excess of energy. The reboiler temperature reached the target value within 30 min and there was approximately 40 minutes of excess preheating. To provide a better representation of this high preheating case, the preheating energy and CO_2 emissions were recalculated based on the preheat energy used over the 30 min, plus the additional 85 or 200 minutes of operation after flue gas flow begins. Compared to the low preheating cases, the high preheating test calculated with the corrected preheat time has a considerably higher cumulative CO_2 capture rate of 94.1% and lower specific reboiler duty (SRD) 5.86 MJ/kg CO_2.

The different operating conditions (e.g., amine concentration and flow rate) are some key contributing factors to the higher capture rates in the June 2020 tests. The solvent inventory tests (previous section) used solvent with lower amine concentrations of 24.4 wt% AMP and 8.7 wt% PZ. In contrast, the preheating tests used solvent with slightly higher concentrations of 25.5 wt% AMP and 10.5 wt% PZ, which resulted in a greater proportion of CO_2 being absorbed. The higher amine concentration as well as greater amine flow rates for the preheating tests achieved a higher steady state online CO_2 capture rates of 92.4–95.5% compared to the solvent inventory tests (83–88%). The optimised operating conditions at steady state were also contributing factors to the higher cumulative CO_2 capture rates achieved during the preheating tests.

Conclusions

Summary of potential measures to improve start-up and shutdown performance

The optimal CO_2 capture performance during start-up and shutdown of the plant needs to balance several factors: solvent inventory volume, initial temperature (cold vs hot) and timing of steam availability (preheating vs steam & flue gas at the same time vs delayed steam). This study demonstrates that these are key factors that influence the time requirements and capture performance during start-up and shutdown of a CO_2 capture plant.

Using a larger solvent inventory is beneficial overall in terms of maximising the cumulative CO_2 capture rate (i.e., Table iii, scenario without an auxiliary boiler). The improvement in cumulative CO_2 capture is greatest in the case of cold start-ups, but the effect of solvent inventory volume is negligible with hot start-ups. Hot start-up had significantly higher cumulative CO_2 capture rate and lower specific reboiler duty compared to cold start-ups. Owing to the low start-up solvent loading (0.05–0.11 mol CO_2/mol amine, as shown in Tables i and v) used for these cold and hot start-up tests, high online CO_2 capture rates of 98–99% were achieved initially, occurring immediately after the introduction of flue gas to the system (purple lines in Figure iii below). The ability to sustain these high CO_2 capture rates depends on the volume of the solvent inventory, amine concentration, starting solvent CO_2 loading, and the timing of steam supply to the reboiler.

The results indicate the importance of timely steam supply during start-up. Any delay in steam supply to the capture plant significantly reduces the cumulative CO_2 capture rate, thereby greatly increasing the residual CO_2 emissions. Start-up with preheating was shown to be a potentially valuable approach. Under specific operating conditions, preheating can provide higher cumulative CO_2 capture rates during start-up of the capture plant, thereby minimising the residual CO_2 emissions. To maximise the value of preheating, a higher flow rate of steam supply can heat the system much faster, but the duration of preheating needs to be optimised to minimise residual CO_2 emissions associated with steam energy.

Using improvement measures (e.g., high preheating, lower solvent loading) for hot start-up protocols increased the cumulative CO_2 capture rate to 98.8% (absorbed CO_2 basis), with specific reboiler duty at 5.58 MJ/kg CO_2, calculated over 85 min, not accounting for auxiliary boiler CO_2 emissions. The "conventional" hot start-up protocols achieved lower cumulative CO_2 capture rate of between 90.0 to 90.3% (Table ii), based on absorbed CO_2 and calculated over 82 min. However, conventional start-up tests achieved lower specific reboiler duty of 3.76–4.03 MJ/kg CO_2, depending on solvent inventory volume, due to the protocols not using preheating and having lower amine flow rates (reduces sensible heat).

In the context of a net-zero energy system, there will be a rising need for flexibility. Hence, the ability to maximise the CO_2 capture rate during start-up and shutdown would be highly valuable as it will reduce residual CO_2 emissions from power plants, thus easing the need for carbon offsets from CO_2 removal technologies, e.g., bioenergy with CCS, or direct air capture. Another key contribution of this work is a comprehensive dataset of start-up and shutdown results from the TCM plant, which can be useful for process model validation and systems scale modelling of power plants with CCS.

Recommendations for further work

Further R&D and future work in this area could explore the following:

- The impact of different process configurations and process control systems that could improve plant flexibility and SUSD performance, e.g., via process modelling.
- Solvent inventory volume was shown be an important factor in this work, however, this is based on TCM plant configuration. Future work should investigate the effect of varying equipment capacities and the liquid hold-up volume (e.g., absorber column sump, reboiler sump, condenser reflux drum) on the start-up time and capture performance. For example, the impact of using parallel absorbers of different sizes, or the effect of oversizing the stripper or reboiler to achieve more efficient solvent regeneration.
- The effect of different solvent types on CO_2 capture plant flexibility and SUSD performance.
- The plant data from this study provides input specifications for model development and techno-economic analysis of different start-up and shutdown scenarios. A techno-economic analysis of SUSD will provide insight into the cost implications of different strategies and flexibility improvements. For example, compared to a hot/cold SUSD cycle, would it be more cost effective to operate at minimum loads and ramp up as required?
- Effect of power plant operation and flexibility (e.g., turndown ratio, ramp rate, shutdown procedure) on the SUSD strategy of CCS plant operation, i.e., upstream system. The dynamic interactions between the power plant and the CCS plant need to be explored further, e.g., to develop strategies to deal with changes on the power plant side which causes flue gas variations in flow rate or concentration (CO_2, O_2 or contaminants).
- The impact of SUSD in power plants with CCS on downstream processes (e.g., CO_2 compression).
- The effect of start-up and shutdown at a systems scale in the context of a national electricity grid. This could potentially demonstrate whether SUSD CO_2 emissions will impact the ability to achieve national scale net-zero emissions targets.

1 Study Objectives

Future energy systems will require higher levels of intermittent renewable power to meet CO_2 emissions reduction targets. However, the integration of large shares of intermittent renewable energy (e.g., wind, solar photovoltaics) into an electricity system presents major operational challenges.[4, 5] The transition to a net-zero energy system by 2050 will require significant increase in system flexibility (e.g., batteries, pumped hydroelectricity storage).[6] Thermal power plants with carbon capture and storage (CCS) will have the important role of providing affordable dispatchable low carbon capacity, maintaining security of supply and enabling the expansion of other low-carbon sources.[7-11]

There are many challenges with start-up and shutdown (SUSD) of power plants with CO_2 capture. As the power plant starts up, there is a period when steam is unavailable to the CO_2 capture process as extraction from power plant's steam cycle is not possible. Consequently, the degree of CO_2 capture will decrease, and the CO_2 emissions will likely increase during SUSD.[12, 13] The duration of delay before steam extraction can occur will depend on the power plant type (e.g., coal or natural gas) and whether a cold or hot start-up is being carried out. This also directly influences the time required to SUSD and the associated CO_2 emissions. With higher penetration of intermittent renewables, an increase in the frequency of SUSD cycles is expected.[14, 15] Consequently, if the CO_2 emissions increase considerably during SUSD, this could undermine the value proposition of CCS as a flexible, low carbon asset.

The value of flexible CCS has been demonstrated in a number of previous studies[7, 16-19] however, there is limited work to-date which focuses on the specific question of fugitive emissions associated with the SUSD of CCS power plants.[20] It is therefore essential that we investigate the impact of start-up and shutdown of power plants with CCS in terms of the CO_2 capture performance and operability.

The objective of this study is to examine the potential for performance improvement during the start-up and shutdown of the CO_2 capture plant through first identifying key factors that influence performance. Following this, novel process strategies were implemented to demonstrate improved start-up and shutdown performance. We perform a detailed analysis of the process performance during the start-up and shutdown of an industrial-scale CO_2 capture process. This work is necessary to understand SUSD dynamic behaviour, which will enable the design of novel operation strategies that will help minimise disruption and CO_2 emissions during start-up and shutdown of the power-CCS plant.

The report is divided into the following sections:

Section 2 provides a review of the existing literature on SUSD of power plants with CCS to provide an overview of current understanding. This literature review is used to help identify key techno-economic factors and process constraints that will influence performance during start-up and shutdown cycles of power-CCS, for instance the CO_2 emissions, start-up and shutdown times, and potential cost implications. The flexibility and the SUSD protocol for different power plants is relatively well characterised due to comprehensive understanding of power plants and operating experience. In contrast, information on the SUSD of CO_2 capture plants is limited, hence, further investigation is required.

Section 3 presents a detailed technical analysis of start-up and shutdown performance in amine-based CO_2 capture plants. Over 2020, 9 different start-up and shutdown tests were carried out at the TCM CO_2 capture facility. The results from the TCM CO_2 capture facility will be used to quantify the effects of different start-up and shutdown strategies, comparing the performance of some new approaches with conventional methods. Environmental factors will also be considered, thus, the effect of SUSD on the emissions of amine and ammonia[b] will be assessed. The time required to start-up or shutdown a capture plant will influence its ability to provide dispatchable electricity in an energy system. If the CO_2 emissions or energy requirements associated with start-up and shutdown increase considerably, higher frequency of start-up and shutdown could undermine the value of CCS. Therefore, it is important to analyse the following key performance indicators, which include the time/duration of the start-up and shutdown, the cumulative CO_2 emissions, the cumulative CO_2 capture rate, and the energy requirements. The performance of start-up will be analysed independently of shutdown, before evaluating the combined effect of both start-up and shutdown.

In Section 4, key recommendations will be formulated for operating procedures and strategies that will minimise the start-up and shut-down times of a capture plant, whilst also minimising CO_2 emissions, as well as amines and ammonia emissions.

2 Overview of flexibility of power plants with CCS

2.1 Flexibility of different technologies

2.1.1 Comparison of technologies

To coordinate the balance between electricity demand and CO_2 emissions reduction, technology providers need to ensure that power-CCS plants are capable of flexible operation.[16] Importantly, there will be a trade-off between the flexibility, cost and efficiency. From a systems perspective, the ability to ramp the power-CCS plant up and down at higher rates and operate at lower minimum load could provide greater system flexibility.

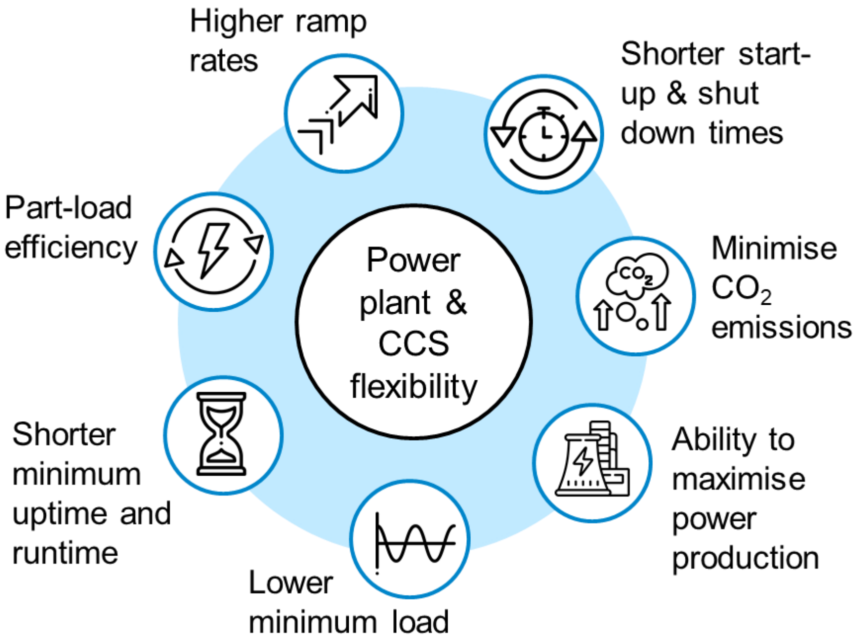

Figure 1: Key characteristics that influence the flexibility of power plants with CCS. Greater system flexibility can improve the economic performance; however, it is important to minimise/reduce CO_2 emissions.

Some of the key characteristics that need to be improved in order to increase the flexibility of power plants with CCS are summarised in Figure 1. Unabated thermal power stations

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[b] Ammonia is one of the main oxidative degradation products of some amines such as monoethanolamine (MEA) and 2-amino-2-methyl-1-propanol (AMP).

are recognised to be capable of operating flexibly in a load following manner to match electricity demand.[21-23] However, the integration of CCS will likely impose additional constraints on flexibility in terms of turndown, start-up, shutdown and ability for fast load changes of a power plant.[24]

Although there is a wide range of technologies for CO_2 capture, the impact of start-up and shutdown has only been studied in the context of more mature CO_2 capture technologies. In regards to flexible operation of CCS, the focus has mainly been on amine-based post-combustion CO_2 capture processes in coal and natural gas power plants,[20, 24-27] but there has also been some work on integrated gasification combined cycle[24] and oxy-combustion technologies.[24, 28, 29] The effects of CCS integration on key flexibility characteristics for these types of power plant are summarised in Table 2.

Post-combustion CO_2 absorption pilot plants require several hours (~3 hours) to reach steady state from a cold start-up.[25] Cold start-up of coal-fired power plants takes 4-10 hours,[23, 24] therefore, coal-CCS plants have long start-up times (~9 hours).[20] In contrast, cold start-up times of conventional combined cycle gas turbine (CCGT) power plants can range between 2–4 hours,[23, 24, 30] with gas turbines only needing <0.1 h to start-up.[31] Therefore, CCGT power plants with CCS may be better suited for flexible operation, owing to the short start-up times and faster ramp rates of CCGT. Whilst there is good understanding of power plant design and operation, the flexibility of the CCS equipment remains a major engineering challenge.

Integrated gasification combined cycle (IGCC) power plants have very limited flexibility compared to the other power plant technologies. The cold start-up of an IGCC can take up to 80–90 hours, and hot start-up of the gasification requiring 6–8 hours.[24] Although, the IGCC gasification has some ramping capabilities, IGCC is not suitable for flexible operation, owing to its high minimum load and very slow start-up times.

For oxy-combustion power plants, flexibility constraints are primarily imposed by the air separation unit (ASU), which can achieve ramp rates of up to 3%/min, and has minimum operating loads of 70% for the ASU compressor and 40–50% for the ASU cold box.[24] Hence, the minimum turndown of oxy-combustion power plants is typically limited to 50%. The start-up time of an ASU will depend on the duration of downtime after the unit has been shut down. As shown in Table 1, the hot start-up of an ASU may require 1–8 hours,[32] and a cold start-up could take as long as 36 hours.

Table 1: Typical start-up time of an air separation unit (ASU), which includes the time needed to achieve the required oxygen purity. Reproduced from IEAGHG [32]

Initial condition	**Start-up time (hours)**
After defrost	36
After 24 hours shutdown	6–8
After 16 hours shutdown	4–6
After 8 hours shutdown	3–5
Less than 1 hour shutdown	Less than 1 hour

Table 2: Flexibility characteristics of different types of power plants with and without CCS. Adapted from Domenichini, et al. [24] *and updated.*[23, 30, 33] *The minimum technical environmental load is the minimum condition that still meets the environmental limits, e.g., NO_X and CO emissions. Unavailable data = "–"*

	Natural gas CCGT		**Ultra-supercritical pulverised coal**		**Integrated gasification combined cycle**		**Oxy-combustion ultra-supercritical coal**	
	Power plant	**With CCS**	**Power plant**	**With CCS**	**IGCC**	**With CCS**	**Air-firing mode**	**Oxy-firing mode**
Turn down or minimum load (% $P_{nominal}$)	Low load operation: 15–25% CC load (10–20% GT load) Min. environmental load: 40–50% CC net power output (30–50% GT load) With flexibility improvements, CCGT min load 20–40%[30]	Post-combustion unit min. load: 30% CO_2 compressor min. efficient load: 70%	Min. boiler load: 25–40% With flexibility improvements, min load 10–20%[30]	Post-combustion unit min. load: 30% CO_2 compressor min. efficient load: 70%	Min. environmental GT Load: 60–70% of full power output. Process unit/air separation unit (ASU) cold box min. load: 50% ASU compressor min. load: 70%	CO_2 compressor min. efficient load: 70%	Min. boiler load: 25–30%	ASU cold box min. load: 40–50% ASU compressor min. efficient load: 70% CO_2 compressor min. efficient load: 70% Min. turndown of oxy power plant is typically not lower than 50%
Cycling capability: start up to full load	Hot start-up: 30–55 min Warm start-up: 60–120 min Cold start-up: 120–240 min	Regenerator preheating time • hot start-up: 1–2 h • warm start-up: 3–4 h	Very hot start-up: < 1h Hot start-up: 1–3 h Warm start-up: 3–5 h Cold start-up: 5–10 h	Regenerator preheating time • hot start-up: 1–2 h • warm start-up: 3–4 h	Cold start-up: 80–90 h Gasification hot start-up: 6–8 h ASU hot start-up: 6 h	Same as plant without CCS	Very hot start-up: < 1h Hot start-up: 1.5–2.5 h Warm start-up: 3–5 h Cold start-up: 6–7 h	Start-up in air-firing mode, ASU start-up completed in approx. 36 h
Ramp rates	35–50 MW/minute max Hot start-up load change rate: • 0–40% GT load: 3–5%/min • HRSG pressure: 1–2%/min • 40–85% GT load: 4–6%/min • 85–100% GT load: 2–3%/min Conventional CCGT can ramp 2–8%/min and the GT can ramp 8–15%/min[22]	Depends on key factors of CCS design: pump & blower capacities, solvent inventory volume and process control system.	• 30–50% load: 2–3% per min • 50–90% load: 4–8% per min • 90–100% load: 3–5% per min	Depends on key factors of CCS design: pump & blower capacities, solvent inventory volume and process control system.	Gasification ramp rate: 3–5%/min ASU ramp rate: 3%/min	Same as plant without CCS	30–50% load: 2–3%/min 50–90% load: 4–8%/min 90–100% load: 3–5%/min	ASU ramp rate: 3%/min The capability to switch to air-firing mode could decouple the power plant from the ASU and improve flexibility.[29, 32]
Part load efficiency	Approx. constant efficiency down to 85% of GT load 2–3 percentage points less @ 60% CC load 52–57% @ 100% load 47–51% @ 50% load	Same as plant without CCS.	Subcritical boiler: 4 percentage points less @ 75% load Supercritical boiler: 2 percentage points less @ 75% load Hard-coal systems 43% @ 100% load 40% @ 50% load Lignite systems 40% @ 100% load 35% @ 50% load	Same as plant without CCS.	Gross electrical efficiency: 2 percentage points less @ 70% CC load	Same as plant without CCS	Subcritical boiler: -4 percentage point @ 75% load Supercritical boiler: -2 percentage point @ 75% load	Same as plant in air-firing mode
Min uptime	4 h	–	8 h	–	–	–	8 h	–
Min downtime	2 h	–	4 h	–	7 h	–	4 h	–

The start-up of an oxy-combustion power plant requires some degree of process flexibility. There are two types of start-ups for oxy-combustion power plants:

- Oxygen-firing mode start-up which uses CO_2 to establish gas recirculation,
- Air-firing mode start-up uses air for combustion whilst the ASU reaches the required temperature.[32]

The storage of oxygen has also been shown to improve the flexibility of ASU operation in IGCC and oxy-combustion systems.[13] These approaches help decouple the start-up of the ASU from the start-up of the power plant. However, due to the long start-up time of the ASU, it is typically not feasible to shut down the ASU cold box.[13]

2.1.2 Technical and economic challenges with start-up and shutdown

In electricity systems with increasing levels of intermittent renewables, power plants will need to cycle more frequently. There are some key objectives to improve flexibility of power plants in order meet these cycling requirements, these are summarised in Table 3.

Table 3: Key objectives to improve the flexibility of power plants. Source IRENA [30]

Shorter start-up time	With shorter start-up times, the plant can quickly reach full load. Rapid start-up significantly improves the operational flexibility of a plant.
Lower start-up costs	Costs associated with the start-ups include more frequent maintenance and additional fuel consumption.
Lower minimum load	Operating thermal plants at lower loads increases the bandwidth of their operation, increasing flexibility.
Improved part-load efficiency	Most thermal power plants experience a drastic reduction in their fuel efficiency at low loads, and therefore improving this is an important element of increasing flexibility.
Higher ramp rate	The rate at which a plant can change its net power during operation is defined as the ramp rate. With higher ramp rates, the plant can quickly alter its production in line with system needs.
Shorter minimum uptime and runtime	Reducing the minimum time that the plant must be kept running after start-up, or remain closed after shutdown, allows a plant to react more rapidly

The previous section identified the types of power plants that could potentially satisfy these criteria for flexibility. Ultra-supercritical pulverised coal and oxy-combustion systems have moderate flexibility. However, natural gas CCGT with CCS have the greatest potential for flexible operation, with the lowest minimum load, shorter start-up times and the capability to ramp up and down (Table 2). Whilst shutdown and start-up of natural gas CCGT power plants on an occasional basis is feasible, frequent cycling of power plants will likely encounter technical and economic challenges.

Start-up and shutdown of power plants causes major temperature changes, i.e., thermal cycling, within the system. Thermal cycling of the components within a power plant can lead to fatigue, creep, and fatigue-creep interaction, which increases the need for maintenance and repair. Frequent start-up and shutdown reduces the power generation efficiency and increases “wear and tear” of components,[34, 35] consequently leading to higher fuel and operation and maintenance costs.[14, 36] The “wear and tear” costs can vary with plant design, plant age, operation, maintenance and repair history.[31, 36, 37] Thus, the cost of cycling is specific to a given plant (as illustrated in Figure 2).[36] The start-up, running and fixed operational and maintenance (O&M) costs for different power plant technologies are summarised in Table 4.

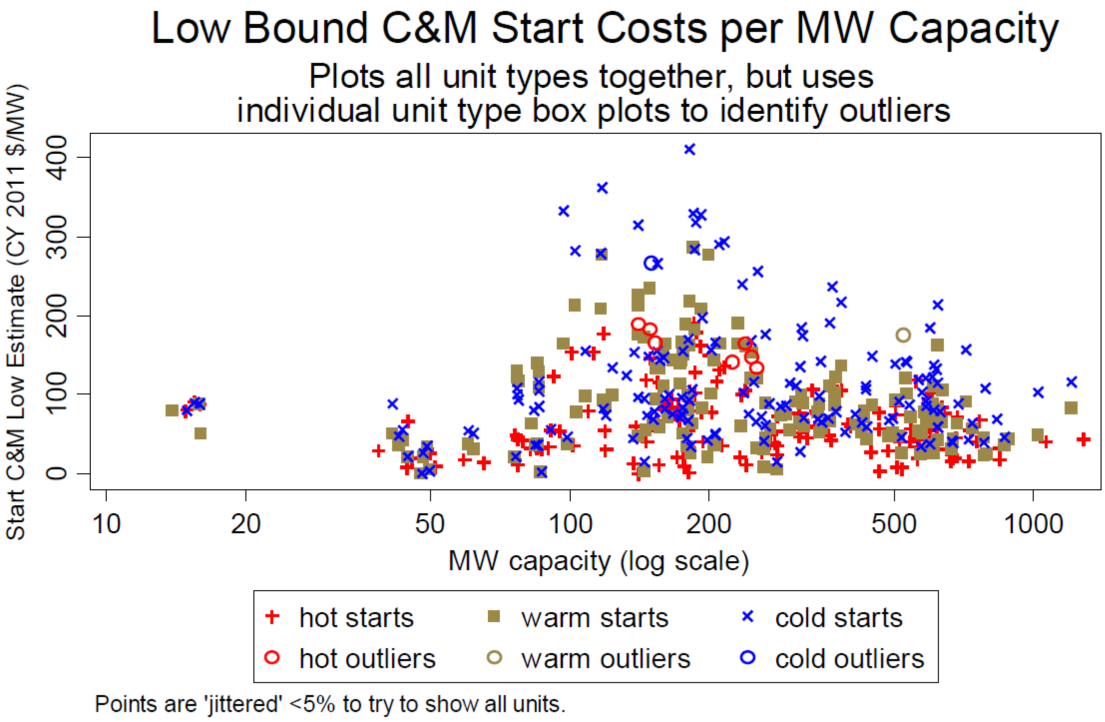

Figure 2: Distribution of low bound capital and maintenance start-up costs per MW capacity for the power plants (without CCS) considered in the Western Wind and Solar Integration Study (WWSI). Cycling costs vary due to power plant design, vintage, age, operation, and maintenance procedure/history. Figure from Kumar, et al. [36]

Table 4: Start-up, running and fixed operational and maintenance (O&M) costs. Converted from EUR, assuming an exchange rate of 1 EUR = 0.86 GBP. Data from IEA [33]

	Natural gas CCGT	**Supercritical pulverised coal**	**Coal IGCC**
Start-up cost (£/MW)	Hot 21.4–42.9 Warm 25.7–85.7 Cold 25.7–85.7	Hot 34.3–42.9 Warm 60.0–85.7 Cold 68.6–94.3	15.4
Running costs (£/MWh)	0.77–0.81	2.3–2.9	5.1
Fixed O&M (£/MW per year)	21.4	34.3	42.9

Table 5: Typical start-up and shutdown costs of coal and natural gas power plants. Converted from USD, assuming an exchange rate of 1 USD = 0.73 GBP. Data from Xu, et al. [38]

	Natural gas	Coal
Start-up costs ($/MW per start)	14.6–109.8	73.2–183.0
Shutdown costs ($/MW per shutdown)	1.5–11.0	7.3–18.3

The degree of wear and tear associated with thermal cycling is a function of the temperature change. As shown in Figure 3, the magnitude of the temperature change varies with different types of start-ups and shutdown. The largest changes in temperature occur with cold-start up and warm start-up. The changes in temperature for shutdown and hot start-up is significantly lower, whereas load following has the lowest temperature change. Consequently, cold start-ups typically have higher capital and maintenance cost, compared to warm and hot start-ups.[36] Figures 4 to 6 illustrate the cost of start-up, and show costs reducing with decreasing temperature change.

Operating the power plant more flexibly reduces the capacity factor of the unit as it will operate at low loads more frequently.[31] Consequently, the levelised cost of electricity (LCOE) will increase.[30] However, from an electricity systems perspective, the economic benefit of flexible operation is significantly high enough that associated costs will likely be negligible.[7, 16, 30]

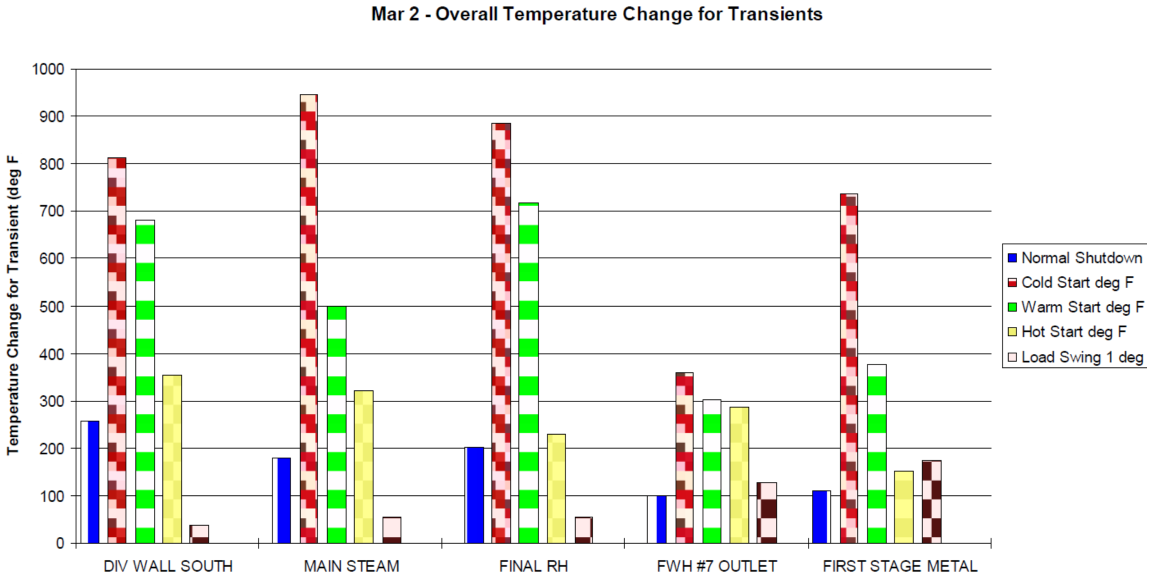

Figure 3: Example of maximum temperature change for components in the power plant (division wall south, main steam, final reheat, feed water heater #7 outlet and first stage attemperators metal). Figure from Kumar, et al. [36]

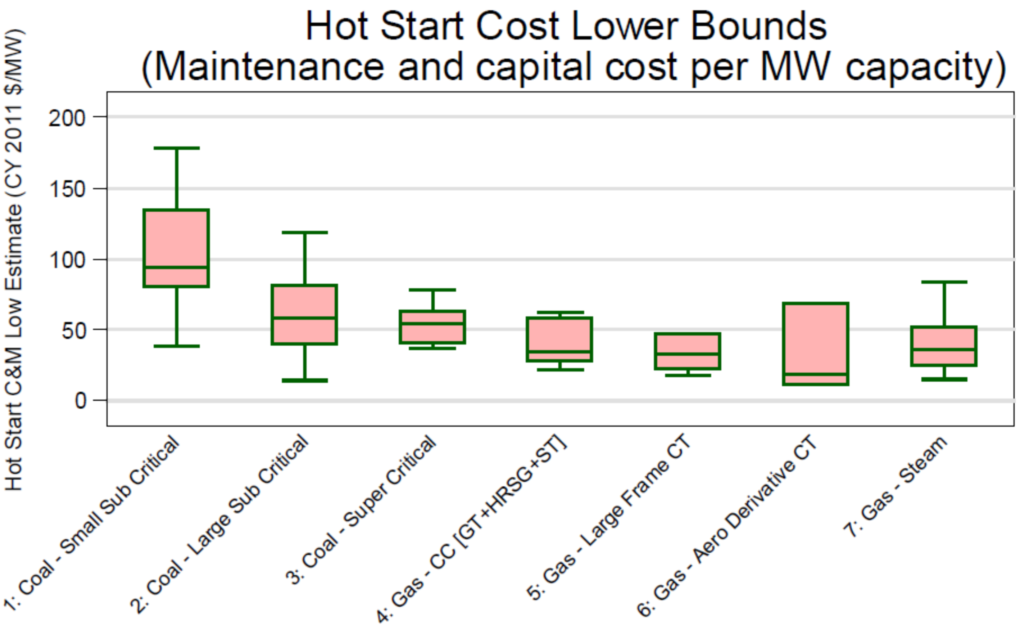

Figure 4: Hot start-up capital and maintenance cost per MW capacity for different power plants. Costs are lower bound estimates excluding outliers. Figure from Kumar, et al. [36]

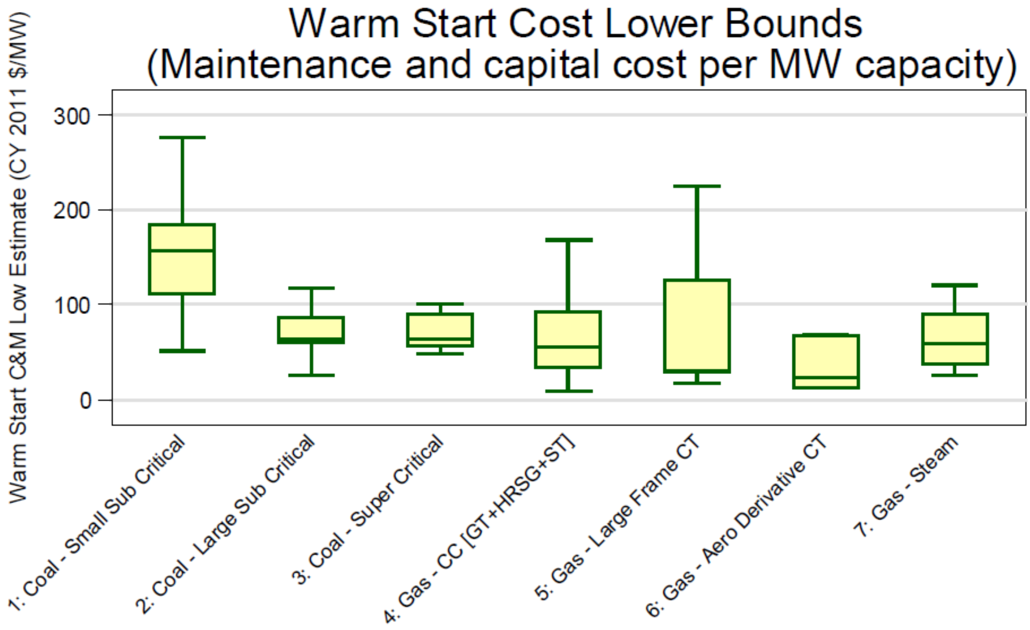

Figure 5: Warm start-up capital and maintenance cost per MW capacity for different power plants. Costs are lower bound estimates excluding outliers. Figure from Kumar, et al. [36]

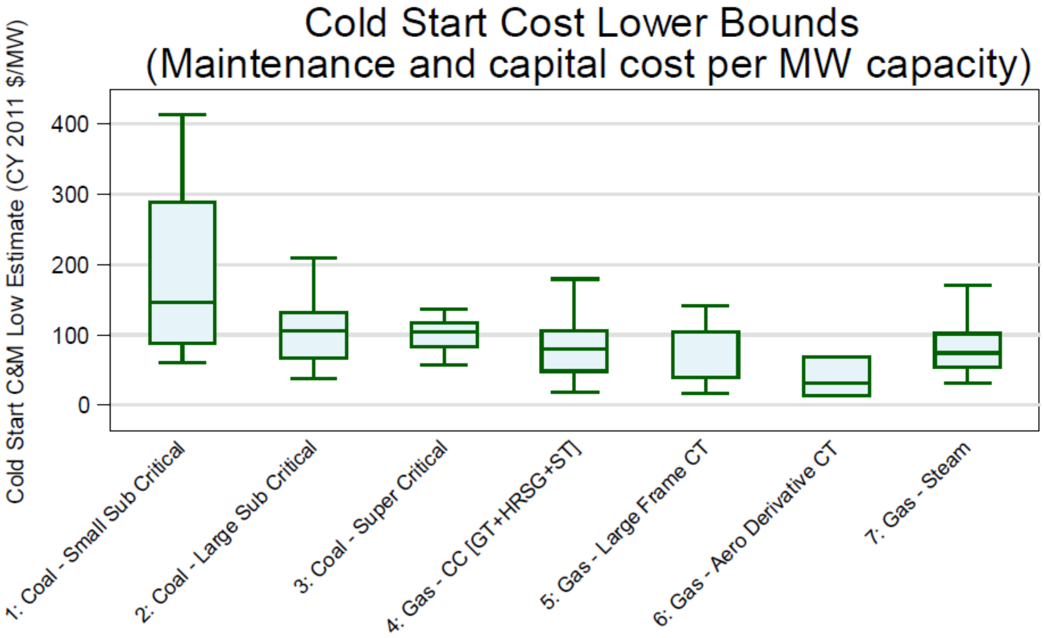

Figure 6: Cold start-up capital and maintenance cost per MW capacity for different power plants. Costs are lower bound estimates excluding outliers. Figure from Kumar, et al. [36]

The emissions of contaminants such as NO_X, CO, SO_2, and particulate matter from the power plant can be higher during start-up and shutdown compared to steady state conditions. The level of emissions and degree of increase will depend on the fuel being used, the type of power plant and the air pollution control measures in place. Upon start-up, the air-to-fuel ratio is not at optimal levels, as a consequence, incomplete combustion can result in increased emissions of CO and volatile organic compounds (VOC).[39] In the case of SO_2 emissions during start-up, the level of emissions varies from plant to plant and only apply to coal-fired power plants. The amount of SO_2 emitted is generally a function of the fuel sulphur composition and the fuel consumption.[39] During start-up of the power plant, NO_X emissions can increase compared to normal operation level due to the temperature of the selective catalytic reduction (SCR) system not being high enough to activate the SCR. Similarly, NO_X emissions can increase during power plant shutdown when the temperature drops below the SCR activation temperature.[39] As shown by Table 6, NO_X emissions are generally lower for natural gas-fired power plants compared to coal-fired plants.[14] However, due to stringent legislation around NO_X emissions globally, flue gas denitrification (deNO_X) such as SCR would still be required for natural gas-fired turbines.[40]

The integration of the power plant with a CO_2 capture process should reduce the emissions of most of these contaminants. To prevent amine degradation, some of these contaminants will need to be removed from the flue gas prior to the CO_2 capture process. Furthermore, the absorption process not only removes CO_2, it will also “scrub” other contaminants from the flue gas.[41]

Table 6: Heat input and NO_X & SO_2 emissions per megawatt of capacity for the start-up of different power plants. Adapted from Lew, et al. [14]

	Heat input (GJ/MW)	NO_X (kg/MW)	SO_2 (kg/MW)
Coal (all)	12.028	1.14	1.77
Gas combined cycle	2.532	0.38	–
Gas combustion turbine	4.009	0.27	–
Gas steam	9.812	-0.01	–

Solvent regeneration in the CO_2 capture process requires a supply of heat. The heat source typically used is steam extracted from between the intermediate pressure (IP) and low pressure (LP) turbine of the power plant steam cycle.[13, 20, 42] During normal operation, e.g., steady state conditions, steam extraction will reduce the electricity output from the power plant. An evaluation of the dynamics in natural gas CCGT plants during part-load operation demonstrates that fluctuations in the steam extraction valve has no impact on the power generation as most of the total power output is generated by the gas turbine (69–73% of the total).[43] In contrast, steam extraction from power plants dominated by the steam cycle performance, e.g., pulverised fuel fired power plants, would have a greater impact on power generation and the dynamics of the integrated system.[43]

The timing and amount of steam supply are critical factors that dictate the performance during start-up of a CO_2 capture plant.[25] The CO_2 capture process requires steam as soon as possible in order to minimise the start-up time and residual CO_2 emissions. However, steam extraction from the steam cycle during start-up and shutdown of the power plant will not be available immediately.[44] Consequently, the competing start-up priorities of the two plants will be a challenge from an operating perspective. Based on a conventional configuration for a natural gas CCGT plant with CCS, the time at which steam extraction is first available for start-up was estimated to be around 25 minutes for hot start-up, and 60 minutes for cold start-up.[44] These times are based on a standard configuration without considering potential optimisation for improving start-up performance. Therefore, faster steam extraction times could be possible through measures that enable “fast-starting”,[44] for example, optimisation of the steam cycle design,[45, 46] preheating with an auxiliary boiler.[13] Alternatively, solvent storage tanks with a fresh supply of lean solvent could be used to improve capture performance during dynamic operation.[13, 47] However, these types of process modifications will incur a cost.[13, 44]

2.2 Post-combustion capture – key SUSD process parameters

Post-combustion absorption-based capture technology is the most mature CO_2 capture technology for power plant applications.[48] Thus, this study focusses on start-up and shutdown in the context of power plants with post-combustion capture technology.

The dynamics of the post-combustion capture plant are governed by factors that influence time in the system: (i) the time required to transport material, and (ii) the time to transfer heat. These factors are typically a function of the equipment capacities and size. However, the design of the process control system can also have a significant impact on the process dynamics of the CO_2 capture plant. Previous studies have shown that process control which is typically designed for steady state operation can significantly restrict flexibility of pilot/demonstration plants.[49, 50]

The factors associated with transport of material that strongly influence the dynamics of an absorption capture plant include:[43, 49, 51, 52]

(i) **Volumetric capacity of the plant:** total volume of equipment, vessels, and piping, which dictates the residence time in each component of the system.
(ii) **Total volume of solvent inventory:** for example, the TCM is designed to be flexible, and the solvent inventory of the system can vary between 38–50 m^3. The volume of solvent used will depend on the minimum and maximum constraints of the process. The minimum requirement is the amount of inventory that provides adequate operation of the equipment (e.g., minimum flow capacity of the pumps, wetting of the packing in the column), whereas the maximum inventory is constrained by the equipment capacity and operability requirements.
(iii) **Transport delay:** introduced by the heat exchangers and piping; this is the time required to transport the solvent from one unit in the system to the next.
(iv) **Solvent circulation time:** time for solvent to circulate once through the system, which is a function of the liquid flow rate and volumetric liquid capacity of each equipment/unit, as well of additional transport delay.

Rotating equipment (e.g., blower, pumps, or compressor) have negligible influence on the dynamics of the system. Pumps can be turned on within seconds, with solvent flow rate taking minutes to stabilise (depending on plant size). Although chemical equilibrium and reaction kinetics have a minor impact on the operability of the capture plant, there is some impact on the CO_2 absorption performance, i.e., capture rate and the absorber column temperature profile.[43]

During start-up, the temperature of the reboiler and stripper column needs time to build up and reach the required temperatures (e.g., around 120°C for CESAR-1 or MEA). Therefore, heat transfer effects are a major constraint on the start-up of a CO_2 capture plant,[43, 49, 50] particularly with respect to cold start-ups. However, once the stripper section had reached the required temperature, thermal equilibrium has an insignificant impact on the dynamic behaviour.[43]

2.3 Start-up and shutdown

2.3.1 Cold start-up

A cold start-up is performed after a *long* downtime (shut for >8 hours), following a normal shutdown sequence (e.g., section 5.2.7). Once the system shifts to cooled conditions, (e.g., stripper bottom temperature <65°C and overall solvent loop cools to ambient temperature), a cold start-up may be performed if the CCGT power plant is already running and the capture equipment is still filled, vented and ready for restart. Once an outdoor plant operator verifies the manual valves and performs the equipment line up check, the control room operator can initiate the normal start-up sequence.

In this study, cold start-up will be carried out when the stripper bottom temperature and solvent loop has cooled to 20–35°C, i.e., ambient conditions. Active cooling of the plant will be required to achieve these low temperatures in between tests.

2.3.2 Hot start-up

Hot start-up is performed after a *short* downtime (i.e., shut <8 hours), following a normal shutdown sequence (e.g., section 5.2.7). As the CO_2 capture plant remains at high temperature, a hot start-up may be performed if the CCGT power plant is already running and the equipment is already filled, vented and ready for restart. The overall start-up time is shortened significantly as many of the start-up sequence steps may already be satisfied (e.g., steps 1–8 and 13 of section 5.2.2). The operator/automatic sequencer checks each step in the order of the start-up sequence, continuing to the next step until the entire sequence is completed.

2.3.3 Start-up of the integrated CCGT power plant with CCS

The start-up of the CO_2 capture unit can take several hours (depending on plant size and solvent volume) and is slower than the CCGT power plant (CCGT start-up times shown in Table 2). Hot start-up can be performed after a short downtime (e.g., <8 hours) whilst the CCGT power plant is already running. If the CCGT power plant remains running after a longer downtime of the capture plant (e.g., >8 hours and when the capture plant shifts to shutdown conditions), a warm start-up will be performed instead.[53, 54] The time to start up a large CO_2 capture plant after boiler ignition can take 2 hours for a hot start-up, or up to 4 hours for a warm start-up.[13] If the duration of downtime is sufficient for the capture plant to cool completely, a cold start-up of the capture plant will require up to half a day to reach full operation from the cold standby state. To reduce the start-up time, a small heater or auxiliary boiler could be used to provide preheating of the stripper section during the start-up procedure.[13, 21]

2.3.4 Normal shutdown (planned)

In this work, the objective is to develop strategies that make shutdown of a power-CCS system more efficient, improving its flexibility/dispatchability in the context of an electricity grid. Therefore, extended shutdown[c] or emergency shutdown are outside the scope of this work.[d] This study will only investigate improvement strategies for planned normal shutdown procedures, e.g., commercial plant shutdown sequence is provided in Appendix A, section 5.

The shutdown of a commercial scale CO_2 capture facility can also require several hours. Figure 7 shows the shutdown of Boundary Dam can take up to 4 hours depending on the initial process settings. Table 35 shows the shutdown protocol for a commercial scale capture plant. The main limiting steps in this table include:

- Reducing the flue gas flow rate from the operational steady state set-point[e] to zero flow. This is achieved by gradually reducing the blower speed (white line in Figure 7).
- Depressurising the stripper and reflux drum (done slowly by opening vent valve).
- Circulating amine flow until the stripper bottom temperature cools to be below 65°C.

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[c] A planned shutdown for an extended period of >24 hours. To prevent oxidative degradation of the amine, the amine is manually drained from the absorbers to the amine waste sump and forwarded to the lean amine storage tank.

[d] Plants will have systems in place to deal with emergency shutdowns (e.g., unplanned shutdown to deal with instability, or a trip), which safely shut down the plant to protect workers and equipment during upset or abnormal operating conditions.[53]

[e] Set-point is the target value which a controller attempts to maintain the process variable.

- Redistributing liquid to minimise levels in absorber, flash drum, stripper & reflux drum.
- Recirculate amine to allow CO_2 to off gas, which takes approximately 1 hour and minimises gas pockets at restart.

Delay in carrying out these steps will result in a longer shutdown time. Therefore, it is important they are completed efficiently to minimise the duration of shutdown. For example, by increasing the rate of cooling the stripper bottom temperature, which may vary with seasonal changes in ambient temperature (e.g., winter vs summer). However, the duration of some steps will be subject to equipment constraints, e.g., the rate of stripper/reflux drum depressurisation is a function of the venting valve size, or the blower design.

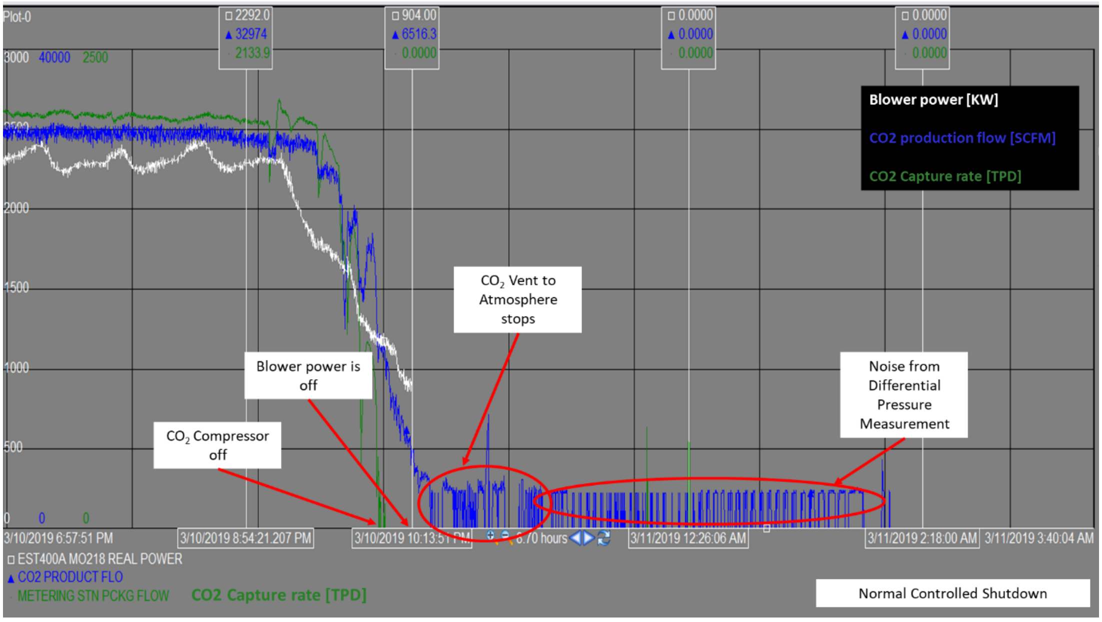

Figure 7: Example of shutdown at the Boundary Dam CO_2 capture plant. Source: International CCS Knowledge Centre, Canada.[55]

2.4 Pilot plant and demonstration tests of start-up and shutdown

The concept of flexible operation of CCS was first proposed as a means of providing grid support to complement a high proportion of renewable generation.[56, 57] Since the concept was introduced, there has been a significant body of work focused on understanding the role and value of flexible CCS operation, predominantly via modelling at a process scale and energy systems scale.[8, 16, 18, 42, 51, 58, 59] Although the study of flexible operation of post-combustion capture plants has mostly been limited to process modelling,[51] there is an increasing number of pilot plant and demonstration studies.[12, 26, 49, 50, 60-64]

An overview of the studies on flexible operation of CO_2 capture that involve experimental work with pilot and demonstration plants is summarised in Table 7. These studies have provided valuable insight into the characterisation of the process dynamics during flexible operation, which has helped improve our understanding. Furthermore, enabling improved representation of the technology in process and system models. A range of different flexible operation strategies (e.g., load following, solvent storage, time-varying solvent regeneration) have now been demonstrated experimentally (Table 7), with the majority using MEA solvent and recent studies using CESAR-1 solvent, an aqueous blend of 2-amino-2-methyl-1-propanol (AMP) and piperazine (PZ). Therefore, this body of work has been essential in illustrating the feasibility of flexible operation in CO_2 capture plants. Some of these studies have also provided valuable experimental plant data to inform future work, as indicated in Table 7.

Table 7: Summary of experimental studies testing dynamic operation of post-combustion CO_2 capture in pilot and demonstration plants, adapted from Bui, et al. [61]. Plant data availability for modelling purposes indicated as yes/no.

Reference	**Location**	**CO_2 capture capacity**	**Flue gas source**	**Operation scenarios**	**Plant data**
Faber et al. (2011)[63]	Esbjerg pilot plant, DONG Energy Esbjergværket power plant, Denmark	1 tCO_2/day using MEA solvent	Coal-fired power station	Plant operated in open-loop control to minimise effect of control loops. The following scenarios were tested: (i) decrease/increase step-change of flue gas flow rate, (ii) decrease/increase step change of steam flow rate to the reboiler, (iii) decrease/increase solvent flow rate, (iv) simultaneous decrease/increase of flue gas flow rate, steam flow rate and solvent flow rate.	No
Mangiaracina, et al. (2014)[64]	Brindisi pilot plant, ENEL Federico II coal power plant, Italy	50 tCO_2/day using 30 wt% MEA	Coal-fired power station	Pilot plant campaign of six weeks, where the following tests were completed: (i) solvent storage cycle – effect of storage tanks, (ii) maximum speed stripping – highest solvent flow rate and steam flow rate, (iii) stripping from cold start – rich solvent produced, plant shut-down and cooled, then attempted to regenerate from cold start, (iv) super lean solvent production & capture performance – effect of over stripping the solvent.	No
de Koeijer, et al. (2014)[62]	CO_2 Technology Centre Mongstad (TCM), Norway	80 tCO_2/day (CHP mode) using 30 wt% MEA	Combined heat and power plant (CHP): flue gas CO_2 content of 3.4–3.6 mol%	Two transient cases were presented: (i) Controlled stop and restart of flue gas and steam flow rate, with a period of no flue gas flow and recirculation flow maintained. (ii) Sudden stop of inlet exhaust gas blower and rapid restart with constant steam flow and solvent flow. Studied impact on MEA and NH_3 emissions from absorber, also CO_2 product flow rate and temperature.	No
Bui, et al. (2016)[60]	CSIRO PCC pilot plant at AGL Loy Yang A power station, Australia	0.48 tCO_2/day using MEA solvent	Brown coal-fired power station	The test campaign studied the effect of successive step-changes to: (i) flue gas flow rate, (ii) solvent flow rate, and (iii) steam flow rate to the reboiler. The study analysed the effect on the absorber/stripper temperature profile, CO_2 concentration of the lean and rich solvent, CO_2 removal rate and reboiler heat duty.	Yes
Tait, et al. (2016)[26]	Pilot-scale facilities of Sulzer Chemtech in Winterthur, Switzerland	0.17 tCO_2/day using 30 wt% MEA	Synthetic flue gas composed of N_2 and CO_2. For this test, 4.3 vol% CO_2 content was used to represent NGCC exhaust.	Five dynamic scenarios representative of NGCC operation with CO_2 capture: (i) gas turbine shutdown, (ii) gas turbine start-up, (iii) maximise power output by decoupling capture plant, (iv) maximise power output by decoupling the reboiler steam only, and (v) rapid increase of reboiler steam flow rate (200% baseload flow).	Yes

Table 6 (continued): Summary of experimental studies testing dynamic operation of post-combustion CO_2 capture in pilot and demonstration plants, adapted from Bui, et al. [61]. Plant data availability for modelling purposes indicated as yes/no.

Reference	Location	CO_2 capture capacity	Flue gas source	Operation scenarios	Plant data
Tait, et al. (2018)[12]	UKCCSRC PACT CO_2 capture pilot plant, University of Sheffield, United Kingdom	1 tCO_2/day using 30 wt% MEA	Synthetic flue gas from air and CO_2. Inlet gas CO_2 content was 12 vol% (simulates exhaust from coal-fired power plant).	The scenarios were designed to represent dynamic operation in a supercritical coal-fired power plant with post-combustion capture: (i) generation plant shut-down, (ii) generation plant start-up (tested two options), (iii) partial load stripping (reduce hot water flow to reboiler), (iv) capture bypass by decoupling hot water flow, (v) capture plant ramping, and (v) control capture efficiency using online solvent measurements.	Yes
Montañés, et al. (2018)[50]	CO_2 Technology Centre Mongstad (TCM), Norway	80 tCO_2/day (CHP mode) using 30 wt% MEA	Combined heat and power plant (CHP): flue gas CO_2 content of ~4 vol% (wet)	Tests on open-loop performance were conducted first. This involved implementing single step-changes to the flue gas flow rate and solvent flow rate. The second phase studied the performance of decentralised control structures, different tests were carried to: (i) control L/G ratio and stripper bottom temperature, and (ii) control capture rate.	No
Bui, et al. (2020)[49]	CO_2 Technology Centre Mongstad (TCM), Norway	80 tCO_2/day (CHP mode) using 30 wt% MEA	Combined heat and power plant (CHP): flue gas CO_2 content of ~4 vol% (wet)	Demonstrated feasibility of three flexible operation scenarios: (i) effect of steam flow rate – successive step changes of steam flow, (ii) time-varying solvent regeneration – alternates between two regimes of operation, where "peak" mode (higher flue gas flow, lowest steam flow) focuses on storing CO_2 in the solvent, and "off-peak" mode focuses on solvent regeneration of the solvent (reduced flue gas flow and highest steam flow). (iii) variable ramp rate – demonstrate the maximum achievable ramp rates in the TCM capture plant (i.e., an indicator of plant flexibility).	Yes
Moser, et al. (2020)[65]	RWE Power plant in Niederaussem, Germany	7.2 tCO_2/day using 30 wt% MEA	Flue gas CO_2 content of 14.2 vol% (dry basis), sourced from an advanced lignite-fired power plant of 965 MW_e net capacity and $43\%_{LHV}$ efficiency.	The test campaign evaluates the impact of dynamic operation on emissions, water wash efficiency and energy performance. The availability of the pilot plant was >97% during the 13,000 hours of testing, where CO_2 capture rate was kept constant at 90%, capturing 3240 tCO_2.The dynamic operation involved changing solvent flow rates in response to solvent degradation and power plant outages. (i) Due to solvent degradation over the test campaign, capture capacity is lost, thus, solvent flow rate was increased from 4000 kg/h up to 6000 kg/h to maintain the 90% capture rate. (ii) During short power plant-related stops and interruptions, flue gas flow rate stopped, but solvent circulation was maintained at reduced temperature (100°C+) to keep the capture plant in "hot mode" during the test operation.	No

Table 6 (continued): Summary of experimental studies testing dynamic operation of post-combustion CO_2 capture in pilot and demonstration plants, adapted from Bui, et al. [61]. Plant data availability for modelling purposes indicated as yes/no.

Reference	**Location**	**CO_2 capture capacity**	**Flue gas source**	**Operation scenarios**	**Plant data**
Moser et al. (2021)[66-68]	RWE Power plant in Niederaussem, Germany	7.2 tCO_2/day using CESAR1 26.74 wt% AMP and 12.92 wt% PZ.	Flue gas CO_2 content of 15.2 vol% (dry basis), sourced from an advanced raw lignite-fired power plant of 965 MW_e net capacity.	The results are from an 18-month test with aqueous AMP/PZ solvent, investigating solvent management and plant emissions. Solvent degradation and emissions were monitored for continuous operation, operating at different: (i) CO_2 capture rates: 90, 95 and 98%, (ii) Number of active absorber beds: four (total 16 m packing height) and three (12 m packing height), (iii) Position of solvent intercooling at the absorber: low and high, (iv) Desorber/stripper pressure: 1.5 and 1.75 bar(a).	No

The pilot and demonstration plant testing done to date provides certainty around the ability of the CO_2 capture plant to operate flexibly. We now understand that the flexibility of a CO_2 capture plant is generally sufficient for load following of a power plant (both coal and gas systems).[49, 64, 69] Also, high CO_2 capture rates during flexible operation can be achieved by coordinating CO_2 capture with the load changes, thereby minimising residual CO_2 emissions.[49]

Of the flexible operation test campaigns in literature, only two have examined the effect of start-up and shutdown.[12, 26] These were carried out in small scale amine-based CO_2 capture pilot plants: (i) Sulzer pilot in Switzerland which captures 0.17 t_{CO2}/day,[26] and (ii) the UKCCSRC PACT pilot in the UK which capture 1 t_{CO2}/day.[12] Further work is needed to understand the key process bottlenecks limiting flexibility during start-up and shutdown of a large-scale CO_2 capture process integrated with a CCGT power plant.

2.5 Key factors to consider for SUSD – potential improvements

A recent modelling study by Marx-Schubach and Schmitz [20] evaluated the impact of key process parameters on the start-up time and *instantaneous* capture rate of a CO_2 capture plant. They report that reduction to the start-up time of a CO_2 capture process could be achieved with the following measures:

1) Minimising the total solvent inventory volume,
2) Increasing the solvent flow circulation rate,
    - This increase amine emissions, thus for this study, solvent flow rate is kept low.
3) Increasing steam flow rate to the reboiler,
4) Supplying the steam to the reboiler as soon as it is available (any delay increases start-up time),
5) Switching on solvent pumps as late as possible (whilst ensuring enough time for adequate solvent mixing).

For (1) & (2), these both influence the time required for liquid distribution, mixing, and wetting of the packing. Factors (3) & (4) influence the heat transfer rate, i.e., reaching required stripper/reboiler temperature faster/slower. For (5), circulating fresh solvent too early on will cause a drop in the reboiler temperature, thereby resulting in a longer start up time. To minimise the start-up time, the solvent pumps should be switched on as late as possible (whilst still satisfying the mixing constraint). Although these measures can reduce the start-up time, the impact on the cumulative CO_2 emissions and amine emissions has not yet been explored. In the context of net zero emissions policy, such emissions will need to be minimised.[20]

Instead of just modifying the operation procedure, plant modifications can also improve start-up and shutdown performance. However, modifying the process configuration or using additional equipment would incur a cost. Thus, it is important to consider whether the performance improvement is sufficient to justify any additional costs.

The time scale of turning on pumps is relatively fast compared to the heat transfer required to bring the reboiler/stripper up to temperature, e.g., 120°C for CESAR-1 or MEA.[43] Therefore, measures that reduce time required for heating could improve the start-up performance for CO_2 absorption plants. Two approaches have been proposed.

Solvent storage has been proposed as a measure to overcome the heat transfer constraint and avoid the need for preheating of the reboiler/stripper.[13] By having a large supply of lean amine available upon start-up, the plant is able to capture CO_2 whilst the stripper section is heating up. However, this approach introduces an additional volume of solvent to the inventory, which will increase the solvent regeneration demand, thus requiring a larger stripper and steam energy. The larger equipment and additional solvent inventory in the main circuit will also affect the process dynamics of the system,[52] potentially buffering the response time of the plant to process changes.[43, 60]

Another approach proposes the use a small heater, such as an auxiliary boiler, to provide preheating of the stripper section during start up. Preheating of the plant was shown to reduce the overall start-up time and prevented the need to store additional lean solvent.[13, 44]

The following section presents a demonstration study carried out in an industrial scale post-combustion capture plant. The aim was to understand the effects of start-up and shutdown on the performance of a CO_2 capture plant. The analysis helped identify key factors and potential process modifications that could provide improvements to the performance of the capture plant during start-up and shutdown, e.g., reduced CO_2 emissions and minimise time required to start-up/shutdown.

3 Assessing process-scale SUSD performance for power-CCS

3.1 Objectives for the start-up and shutdown tests

The test campaigns at Technology Centre Mongstad (TCM) examined different start-up and shutdown (SUSD) operating modes in a CO_2 capture process, which were performed in the context of CCS with gas-CCGT. This study will examine the potential for performance improvement during the start-up and shutdown of the CO_2 capture plant. Importantly, this work will include emissions monitoring and analysis of CO_2 emissions and volatile organic compounds, e.g., PZ, AMP, or amine degradation products (including ammonia).

The cold start-up simulates a start-up after a long downtime, where the reboiler bottom temperature has cooled to “ambient” conditions of 25–30°C. The hot start-up simulates a start-up after a short downtime, where the reboiler bottom temperature was ~90 °C. For all cases of shutdown, the same procedure was implemented. To ensure the plant starts with a solvent that meets the CO_2 loading requirement (i.e., low CO_2 loading), steam continued to flow after the flue gas was turned off to lean out the solvent to a target loading. By the end of shutdown, the entire volume of CESAR-1 solvent has low CO_2 loading (i.e., ≤ 0.2 mol CO_2/mol amine). This step is required for two reasons: (i) prevents precipitation during plant downtime, which can occur if CESAR-1 is rich and low temperature, (ii) having lean solvent loading for the next start-up will maximise the CO_2 capture capacity. Although the former reason does not apply to non-precipitating solvents such as 30 wt% MEA, the second reason would still apply, thus shutdown lean out and start-up with low CO_2 loading solvent will be needed to minimise residual CO_2 emissions during start-up (also done in commercial-scale systems[53, 54]).

In comparing the differences between cold start-up, hot start-up and shutdown performance, the study will also investigate the following factors:

- Flexible operation using an advanced solvent CESAR-1; most pilot plant work on flexible operation have previously focused on MEA-based absorption.
- Timing of steam availability on start-up time, different tests were conducted to show effect of steam introduced before, at same time and after the start of flue gas flow.
- Effect of solvent CO_2 loading on the capture performance upon the start-up of the plant.
- Effect of using different solvent inventory volumes, 53 m^3 versus 42 m^3.

Understanding the impact of these key factors will help in the development of improved start-up and shutdown strategies. Therefore, there are two sections to the study, comparing the conventional and “improved” methods for start-up and shutdown.

Conventional start-up & shutdown: The TCM test campaign in November 2020 examined the following operating modes (also conducted in the context of CCS with gas-CCGT). These scenarios represent “conventional” operation with the use of different solvent inventories:

1) Cold start-up and normal shutdown with 53 m^3 solvent inventory
2) Cold start-up and normal shutdown with 42 m^3 solvent inventory
3) Hot start-up and normal shutdown with 53 m^3 solvent inventory
4) Hot start-up and normal shutdown with 42 m^3 solvent inventory
5) Hot start-up with delayed steam supply and 42 m^3 solvent inventory

Improved start-up: The TCM test campaign in June 2020 examined the effect of preheating before start-up using a solvent inventory of 45 m^3 in the context of CCS with gas-CCGT. These tests simulate the effect of “preheating” with an auxiliary boiler by introducing the steam for a period of time before the flue gas begins Additionally, start-up CO_2 solvent loading for these tests was lower compared to the November tests (shown in Table 13 and Table 28).

1) Cold start-up with low preheating and normal shutdown
2) Hot start-up with low preheating and normal shutdown
3) Hot start-up with high preheating and normal shutdown
4) Cold start-up with varying solvent inventory volume and normal shutdown
    - Note, solvent volume was reduced to 41.5 m^3 at first, but water was added to the system, consequently the inventory volume increased to 45 m^3 and the amine concentration reduced.

3.2 Technology Centre Mongstad CO_2 capture test facility

The Technology Centre Mongstad (TCM) test facility is located in Mongstad, Norway, adjacent to the Equinor oil refinery. The TCM amine-based absorption plant is designed to capture CO_2 from different feed flue gases and has a flexible plant configuration (e.g. adjustable absorber packing height, two stripper column sizes).[70, 71] The natural gas-fired combined heat and power (CHP) plant uses a combined cycle gas turbine (CCGT) and the CO_2 composition of the exhaust gas is typically 3.5–4.3 mol%, full composition in Table 8. When the TCM plant operates with CHP flue gas at the volumetric capacity of 60,000 Sm^3/h,[f] it captures around 80 tonnes CO_2/day.[71] An alternative configuration processes a slipstream with 13 mol% CO_2 composition from the refinery residue fluid catalytic cracker (RFCC), and has a capture capacity of 200 tonnes CO_2/day.[71, 72] It is also possible to vary the CO_2 concentration of the feed gas between 2.5% and 15%, either by exhaust gas recirculation, i.e., recirculating the dry CO_2 product upstream of the direct contact cooler (8% CO_2),[71, 73] or by air dilution of the RFCC gas.[72] To accommodate the different flue gas CO_2 concentrations, the TCM plant has two direct contact coolers (DCC) and two stripper column units with different dimensions (CHP or RFCC modes). The RFCC configuration uses larger columns for the DCC and stripper compared to the CHP configuration in order to treat flue gas streams with higher CO_2 content (>4 mol%).[71] The two stripper columns can operate independently of each other, with the unused stripper potentially being used as buffer solvent storage capacity, i.e., to adjust the volume of solvent inventory. The process configuration of the CHP system is shown in Figure 8, and the operating range of some key parameters are summarised in Table 10.

Table 8: Composition of the flue gas from the natural gas-fired combined heat and power (CHP) plant at TCM, showing the typical average and the range for the composition after the DCC unit.

Flue gas component	Typical composition (mol%)	Composition range (mol%)
N_2	78.6	71.6–78.6
CO_2	3.6	3.5–4.3
H_2O	2.5	2.5–6.3
O_2	14.4	12.5–14.4
Ar	0.9	0.9–1.0

The induced draft (ID) blower used to supply flue gas to the system has an output capacity of up to 70,000 Sm^3/h. The direct contact cooler initially quenches, cools and pre-scrubs the flue gas through counter-current contact with water. The flue gas enters the bottom of the absorber column and lean solvent flows counter-currently from the top, which then absorbs CO_2 from the flue gas. The rectangular absorber column has cross-sectional measurements of 3.55m×2m with a total height of 62 m and is constructed from polypropylene-lined concrete. There are three beds of packing in the lower section of the absorber column with three possible packing heights, 12 m, 18m or 24m (12m+6m+6m), and three inlet points along the height of the column. For the CESAR-1 tests in this work, 18 m of packing was used to be consistent with previous CESAR-1 baseline experiments. The flue gas flows upwards and passes

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[f] S denotes standard conditions of 1 atm and 15°C.

through the water washes in the upper section of the absorber column. The cold water wash scrubs the flue gas to: (i) maintain a closed water balance by condensing out the water vapour in the flue gas before it exits the system, (ii) minimise solvent loss by reducing solvent entrainment, i.e., loss of solvent droplets, particularly with high gas flows, and (iii) reduce the concentration of volatile organic compounds in the depleted flue gas, this includes vapour phase amine or amine degradation products (e.g. ammonia, formaldehyde, acetone, acetaldehyde).[74g] The characteristics of the packing in the plant as summarised in Table 9. The CO_2-depleted flue gas exits the top of the absorber column and rich solvent exits the bottom of the column. In the cross-heat exchanger, this rich solvent is heated by a counter current stream of hot lean solvent.

The TCM plant also has the option of using a cold rich solvent bypass – a portion of the rich stream bypasses the cross-heat exchanger and is added directly to the top of the stripper. The low temperature bypass stream condenses water out of the hot gases leaving the top of the stripper. This prevents the escape of energy (i.e., heat of vaporisation energy) from the stripper column by transferring it into the cool bypass solvent, thus, reducing the reboiler duty. Another benefit is that the bypass causes a flow imbalance between the streams in the cross heat exchanger, increasing the temperature driving force so that the hot rich solvent entering the stripper achieves a higher temperature.[75]

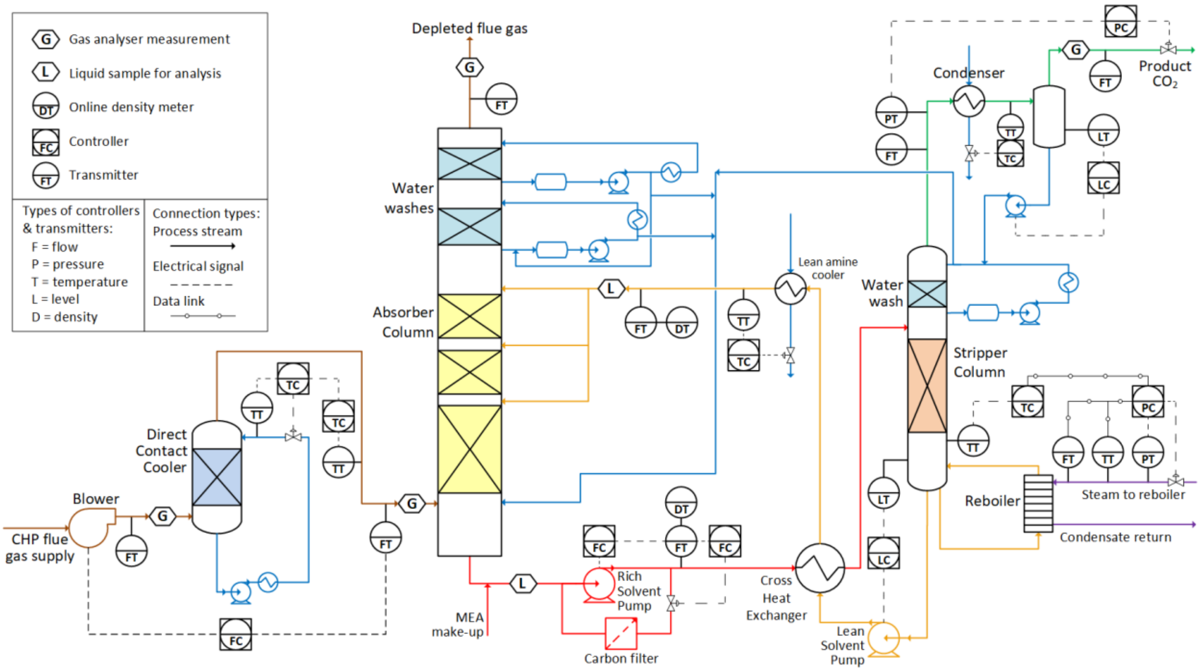

Figure 8: Process flow diagram of the amine-based CO_2 capture process at TCM. The plant has variable packing height, two DCC and two stripper columns which can be configured to process flue gas from either the combined heat and power (CHP) plant or refinery residue fluid catalytic cracker (RFCC) unit. Some key process control loops are shown, however, much of the P&ID detail is omitted.

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[g] However, the loss of amine from the plant via emissions is typically insignificant compared to loss through amine degradation.

Table 9: Column specifications of the absorber and RFCC stripper at the TCM CO_2 capture plant.[49, 70, 71, 73, 76] *Other dimensions and details described in the Appendix B.*

	Absorber	**RFCC stripper**
Geometry	Rectangular	Cylindrical
Total height (m)	62	30
Cross sectional area (m^2)	3.55 m × 2 m	3.8
Diameter (m)	–	2.2
Packing type	Flexipac 2X structured	Flexipac 2X structured
Packing height (m)	18	8
Vendor	Koch Glitsch	Koch Glitsch
Material of packing	Stainless steel	Stainless steel
Surface area (m^2/m^3)	225	225
Void fraction	0.97	0.97
Sump volume (m^3)	8.1	2.3
	Absorber wash section	**Stripper wash section**
Packing height (m)	6	1.6
Packing type	Flexipac 2Y HC structured	Flexipac 2Y HC structured
Packing vendor	Koch Glitsch	Koch Glitsch
Material of packing	Stainless steel	Stainless steel
Full load capacity of water wash (t/h)	50 or 60	Not in use for this study
Reboiler type	–	Shell & tube thermosiphon reboiler

The main stream of rich solvent from the absorber is then directed to one of the two stripper columns. Both strippers have a height of 30 m and a thermosiphon reboiler, with selection typically being based on the flue gas CO_2 content and the fluid hydraulic effects. The smaller CHP stripper has a diameter of 1.3 m and is designed for <6 vol% CO_2 flue gas, e.g., from the CHP plant. The larger RFCC stripper has a diameter of 2.2m and can be used with >4 vol% CO_2 content gas. Steam at 140–160 °C is supplied to the reboiler, resulting in reboiler temperatures of between 110–125 °C. Rich solvent flows downwards from the top of the stripper column, and the heat enables desorption of CO_2 from the solvent, which then generates a CO_2 product (exits top) and a lean solvent stream (exits bottom). The lean solvent goes to the cross-heat exchanger, where it is cooled by lower temperature rich amine (from absorber), and further cooled at the absorber inlet by a lean amine cooler. The CO_2 product exiting the stripper goes to the condenser and reflux drum, which removes entrained droplets, before being sent to the CO_2 stack.[50, 71, 77]

*Table 10: The operational ranges for various parameters.[49, 78] The ID flue gas blower has an output capacity of up to 70,000 Sm³/h [71]. DCC = direct contact cooler, L/G = liquid-to-gas. *Typically operated at CO_2 capture percentages between 85–95%. These ranges reflect the target set-point[h] conditions over the different SUSD tests. CHP flue gas was used with the RFCC stripper and a solvent consisting of piperazine and AMP (CESAR-1). used with the RFCC stripper/reboiler.*

Parameter	**Unit**	**Range**
Flue gas flow rate	Sm^3/h	30,000–60,000
Flue gas temperature (after DCC)	°C	20–50
Flue gas CO_2 concentration	vol%	3.2–4.2 (CHP mode) 11.0–13.0 (RFCC mode) 2.5–15.0 (achieved by recirculating air or CO_2)
Lean solvent flow rate	kg/h	28,200–60,100
Lean solvent temperature	°C	20–45
L/G ratio	kg liquid/kg gas	0.5–2.5
CO_2 capture rate*	%	14–97
CESAR-1 solvent concentration	wt%	26–27 PZ 9.5–13 AMP
Absorber packing height	m	12–24
RFCC stripper bottom pressure	Bar_a	1.6–2.6
RFCC steam temperature	°C	140–160
RFCC reboiler temperature	°C	110–128
RFCC reboiler heating rate	MJ/h	5,500–17,000
Steam flow rate for stable operation of RFCC stripper reboiler	kg/h	2500–7400

3.3 Experimental measurements and data processing

Previous contributions provide details on the measurement instruments used to monitor stream conditions and composition, as well as details on the analysis of measurement accuracy, bias and precision, including the quantification of uncertainty and error.[49, 70, 71, 77-80] The use of online and continuous data is particularly important for tests that involve dynamic or flexible operation as the transient behaviour of the plant will need to be analysed. Some measurements may be prone to noise or instability under certain conditions at specific locations. Typically, noisy plant data would need to undergo noise reduction first before being used for further analysis. Depending on the nature of the noise, approaches include using readings from an adjacent transmitter (if available) or applying a noise smoothing filter with data processing software. The details associated with this protocol are available in Bui, et al.[49]

Measurements of temperature, pressure and flow rate are available throughout the plant and are logged (for this test, every 30 seconds). Gas phase composition is monitored with the use of multiple gas measurement systems, and combined, these ensure data continuity and provide a means to evaluate measurement uncertainty. For further information on gas composition precision and uncertainty, refer to Faramarzi, et al. [79] Two Gasmet Fourier transform infrared (FTIR) and one Applied Instrument Technologies (AIT) FTIR gas analysers

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[h] Set-point is the target value at which a controller attempts to maintain the process variable. Process parameters can be maintained at the set-point value automatically with a controller. However, some process parameters may require manual adjustment by the plant operator to a maintain operation at the set-point or target value.

supply continuous measurements of CO_2, H_2O, NH_3, NO, NO_2, SO_2, CH_2O, C_2H_4O, MEA, PZ and AMP. The gas chromatograph (GC) measures the composition of CO_2, O_2, N_2, H_2O.[i] The five non-dispersive infrared (NDIR) are used for CO_2 content: two at the absorber inlet (low and high gas CO_2 concentration), two at the absorber outlet and one analysing the CO_2 product. A trace O_2 analyser measures O_2 concentration in the CO_2 product.[79] Combining these different measurements provides detailed gas phase composition at three locations – absorber gas inlet (bottom), absorber gas outlet (top), product CO_2 at the top gas outlet of the stripper, shown in Figure 8.

The temperature profiles in the absorber and stripper columns are important indicators of plant performance, providing some insight into dynamics of the columns during transient conditions. Temperature profiles can also be used for process model validation, an important step during the development of dynamic models. The TCM CO_2 capture plant has four temperature transmitters distributed radially at each metre along the height of the absorber column, resulting in a total of 96 temperature sensors, providing more detail for temperature profiles. Along the 8 m height of the stripper column, there are 28 temperature sensors in total, four for every 1.14m of packing. The temperature at a given height of the profile is shown as a median of the 4 sensors with whiskers to indicate the minimum and maximum. Temperature representation in this format (i.e., min–median–max) provides a quantitative indication of variability and uncertainty in the experimental data.[49, 61] This approach is distinct to most pilot plants, which typically have only one temperature transmitter at a given column height.

3.4 Development of the correlation for online CO_2 loading

The ability to monitor transient behaviour in the liquid phase is essential for dynamic tests.[26, 60] At the TCM plant, the lean and rich CO_2 loading of the solvent is measured using two approaches: (i) manual off-line titration, total inorganic carbon (TIC) and total organic carbon (TOC) of solvent samples collected periodically, and (ii) continuous online method using the density meters and a CO_2 loading correlation.

Off-line method: Samples of the solvent are manually collected at the inlet (lean) and outlet (rich) liquid streams of the absorber. Chemical liquid analysis of these samples provides solvent composition, including CO_2 loading and PZ/AMP concentration. The laboratory can only accommodate a limited number of chemical samples for analysis per day. Thus, lean and rich samples are taken at key time periods from the solvent sampling locations in Figure 8 are prioritised for chemical analysis. These manual lean/rich loading measurements are typically plotted as points as a function of time, which is recorded when the sample is taken. Importantly, the number of lean and rich samples needs to be sufficient to describe the dynamic trends, which is critical for the development of an accurate online CO_2 loading correlation.

Online CO_2 loading correlation method: The CO_2 loading of amine solution is typically a function of the solution density and temperature.[81] Thus, it is possible to develop a data-driven surrogate correlation from known inputs (density meter and temperature readings) and a known output (CO_2 loading from the laboratory analysis). Each CO_2 loading data point from the laboratory analysis is matched against the corresponding readings with the same timestamp for solvent density and temperature. It is essential that the online density and temperature meters considered are proximal to the location of the manual solvent sampling points. This creates a dataset consisting of CO_2 loading, density, and temperature, including

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[i] Gasmet FTIR analysers are located at the flue gas absorber outlet and CO_2 product stream, whereas the AIT FTIR is located at the flue gas absorber inlet. These three gas streams are also analysed by the GC.

data from both the lean inlet and rich outlet of the absorber. A software called ALAMO[82,j] is used to generate a data-driven correlation that predicts the online CO_2 loading based on online density meter and temperature readings (Figure 11).

As density is related to composition, the developed correlation is only valid for tests that use the same solvent composition, i.e., solvent type, amine concentration, degradation products with or without oxygen scavenger. A new correlation is developed for tests using different compositions of CESAR-1. For the test campaigns in this report, we developed the following online CO_2 loading correlations (Equation 1 and 2):

June 2020 using CESAR-1 blend 27 wt% AMP + 13 wt% PZ:

$$CO_2\ loading = 1.91536 \times \ln(\rho) + 1.2737 \times 10^{-5} \times T^3 - 12777.46572 \times \left(\frac{T}{\rho}\right)^3 - 13.22016 \qquad \textbf{(1)}$$

November 2020 using CESAR-1 blend 26 wt% AMP + 9.5 wt% PZ:

$$CO_2\ loading = -2.3799 \times 10^{-3} \times \rho + 7.8367 \times 10^{-2} \times ln(T) + 2.1084 \times 10^{-9} \times \rho^3 \qquad \textbf{(2)}$$

where the CO_2 loading is in units of mol CO_2/mol amine, ρ is density in kg/m^3 and T is solvent temperature in °C.

The input density and temperature data used to generate the online CO_2 loading correlation is shown in the left column of Figure 9 (hot start-ups) and Figure 10 (cold start-ups), whereas the right column shows the off-line and online CO_2 loading. The online CO_2 loading is continuous data (blue and green), whereas the circular points correspond to chemical analysis measurements at specific solvent sampling times. There are periods of downtime after the flue gas is turned off, where the temperature gradually decreases, and the solvent density increases accordingly. As the flue gas flow is zero, the off-line measurements indicate that CO_2 loading remains approximately constant. Therefore, it was important that the surrogate loading correlations developed for this work had constant CO_2 loading during periods of plant downtime, e.g., (C) & (D) in Figure 9 and Figure 10.

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[j] ALAMO is a software tool designed to generate algebraic models of simulations, experiments, or other black-box systems. Surrogate correlations can be “built” by choosing a combination of functions, including exponential, logarithmic, linear, sine, cosine, or polynomial functions.[82]

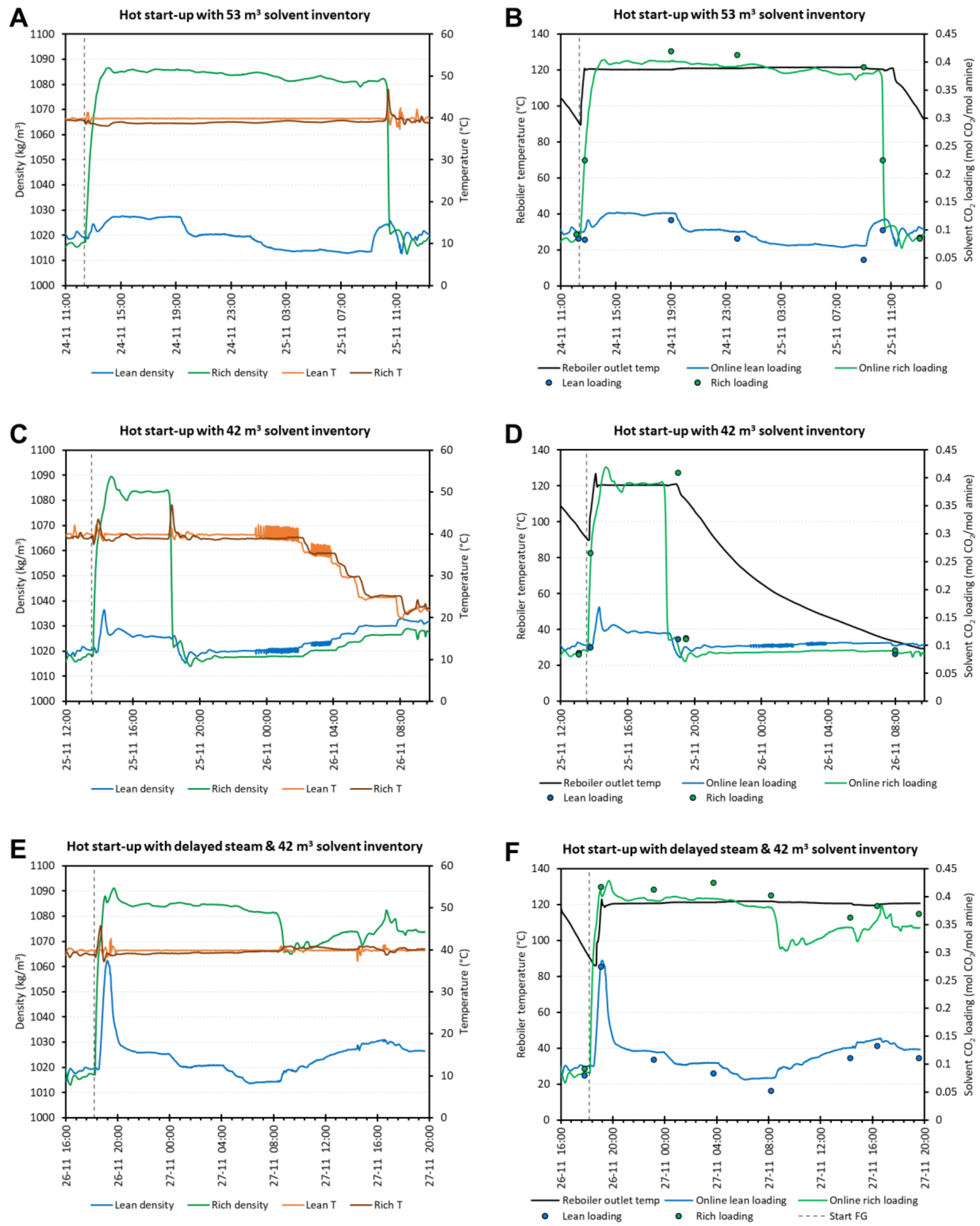


Figure 9: Hot start-up and shutdown results: Online measurements of solvent density and temperature (A, C, E) and laboratory analysis of CO_2 loading measured from solvent samples were used to develop the correlation for online solvent CO_2 loading. This correlation predicts CO_2 loading from online density and temperature readings (B, D, F).

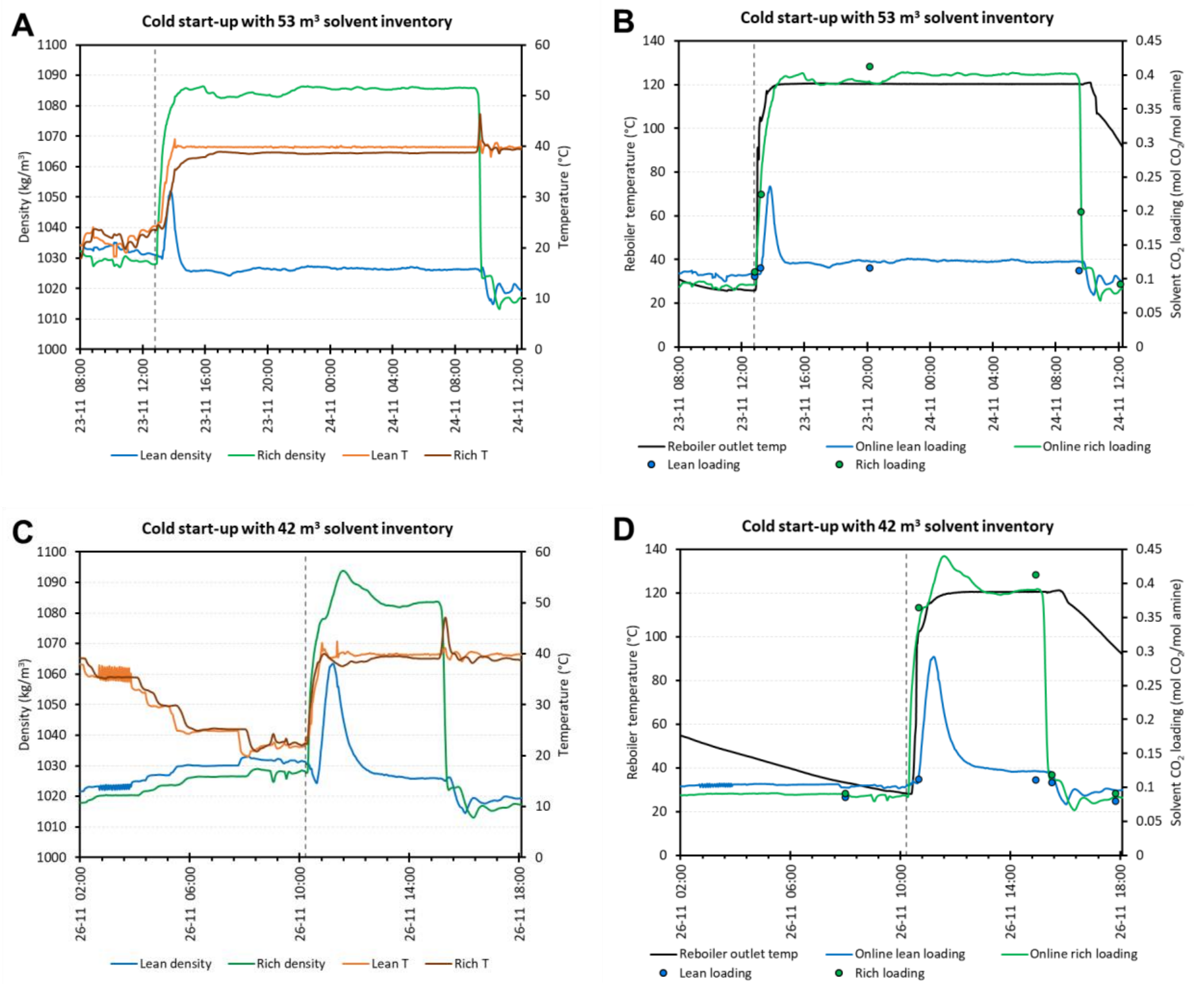
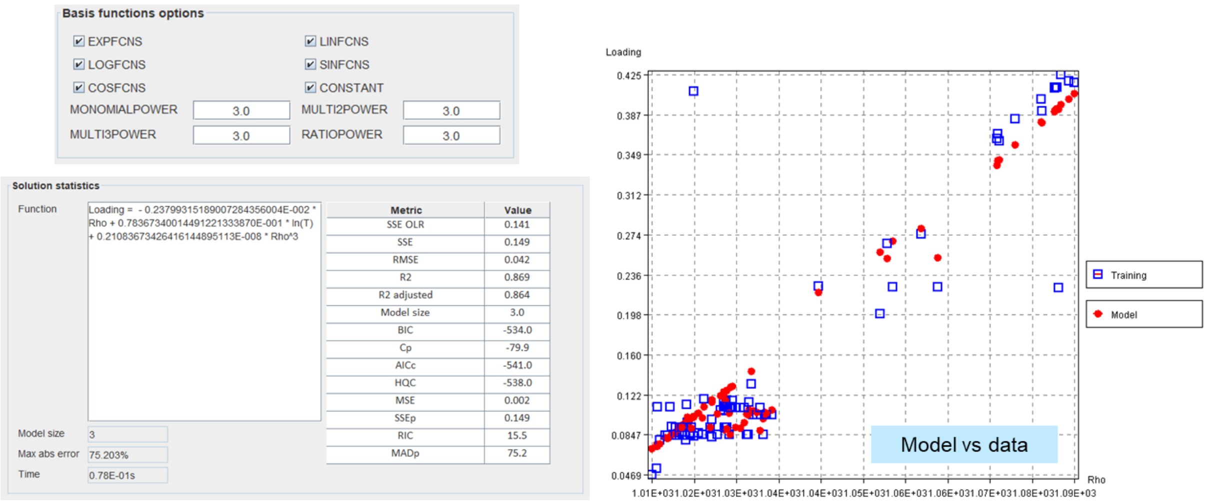


Figure 10: Cold start-up and shutdown results: Online measurements of solvent density and temperature (A, C) and laboratory analysis of CO_2 loading measured from solvent samples were used to develop the correlation for online solvent CO_2 loading. This correlation predicts CO_2 loading from online density and temperature readings (B, D).


Basis functions options

☑ EXPFCNS
☑ LOGFCNS
☑ COSFCNS
☑ LINFCNS
☑ SINFCNS
☑ CONSTANT

MONOMIALPOWER	3.0	MULTI2POWER	3.0
MULTI3POWER	3.0	RATIOPOWER	3.0

Solution statistics

Function: Loading = - 0.23799315189007284356004E-002 * Rho + 0.78367340014491221333870E-001 * ln(T) + 0.21083673426416144895113E-008 * Rho^3

Model size: 3
Max abs error: 75.203%
Time: 0.78E-01s

Metric	Value
SSE OLR	0.141
SSE	0.149
RMSE	0.042
R2	0.869
R2 adjusted	0.864
Model size	3.0
BIC	-534.0
Cp	-79.9
AICc	-541.0
HQC	-538.0
MSE	0.002
SSEp	0.149
RIC	15.5
MADp	75.2

Figure 11: ALAMO is used to develop the correlations for online CO_2 loading. This shows the model fitting for the correlation developed from the November 2020 TCM data.

3.5 Flexible operation and start-up and shutdown tests

During normal steady state conditions, the process control system enables automatic operation of the TCM capture plant. Dynamic or flexible operation of the TCM capture plant can involve steps that cannot be automated within the existing process control system, which is designed for steady state operation. Manual operation to adjust some process parameters will be needed during certain flexibility tests. For example, manual operation of the flue gas blower to achieve higher ramp rates as described in Bui, et al. [49] Similarly, many of the steps for the start-up and shutdown tests at TCM required manual operation of the plant. However, we recognise that in commercial-scale plants, start-up and shutdown protocols will mostly be automated through the process control system which will carry out an automatic sequence.[53] Examples of start-up and shutdown operation procedures for commercial scale systems have been provided in Appendix A. We have used these examples and findings from published literature as well as expertise from technology operators at TCM and SSE Thermal to develop our SUSD procedures.

For the different tests at TCM, the "conventional" operating procedures will be implemented, as well as different proposed improved methods. The set-point conditions for key process parameters are summarised in Table 11. The study examined the potential for performance improvement during the start-up and shutdown of the CO_2 capture plant, analysing the impact of the following considerations:

- **Total amine inventory volume:** Two different solvent inventory volumes will be tested, 42 m^3 and 53 m^3; this is adjusted using the CHP stripper as buffer storage capacity. This will demonstrate the effect of solvent inventory volume on the dynamic performance.
- **Steam supply:** Examine the effect of steam flow rate to the reboiler, and the impact of delaying the supply of steam at start-up (i.e., based on timing of steam availability).
- **Solvent loading:** The initial lean solvent loading is a key factor in dictating the CO_2 emissions during start-up. For CO_2 absorption with CESAR-1, the optimal lean loading is typically between 0.1–0.2 mol CO_2/mol amine,[83-85] depending on the L/G and target capture rate. Storing solvent with this lower lean loading upon shutdown can help minimise the CO_2 emissions during the start-up period.[k]

For safety reasons, start-up and shutdown tests could only be carried out during the day-time due to the large number of process changes required for these tests. A test day will begin with the start-up procedure. This is followed by a period of stabilisation and steady state operation. Although there were steam step changes to increase the capture rate on some of the test days (Figure 14), steam flow rate was restored to the original level and stabilised before carrying out the shutdown. This was to ensure consistency and reproducibility of the results for the shutdown tests. The test day finished with a shutdown procedure and then there was a downtime period overnight.

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[k] For a solvent inventory of 40.7–40.8 m^3 at TCM, the total solvent circulation time at lean solvent flow of 62 300 kg/h is 41.4 min, and at 37 500 kg/h flow rate takes 71.4 min.[50]

Table 11: The target set-point conditions used for the June and November 2020 start-up and shutdown test campaigns at the TCM CO_2 capture plant. CHP flue gas was used with the RFCC stripper and a solvent consisting of piperazine and AMP (CESAR-1). The use of the rich solvent bypass helps reduce the reboiler duty.

	June 2020	**November 2020**
Solvent inventory	45 m^3	42 m^3 & 53 m^3
CHP flue gas flow rate (Sm^3/h)	50,000	50,000
Lean solvent flow (kg/h)	57,000	45,000
Total rich solvent flow (kg/h)	61,000	48,000
Uses rich solvent bypass configuration?	Yes 12,000 kg/h	No
L/G ratio (kg liquid/Sm^3 gas)	1.14	0.9
Feed flue gas CO_2 concentration (vol%)	3.5–3.8	3.6–4.1
Feed flue gas O_2 concentration (vol%)	12.5–13.4	13.8–14.8
Feed flue gas H_2O concentration (vol%)	6.3	5.3–5.4
Absorber flue gas inlet temperature (°C)	38	35
Absorber lean solvent inlet temperature (°C)	40	40
Stripper rich solvent inlet temperature (°C)	111–114	112–117
Stripper bottom pressure (barg)	0.97	0.95–0.96
Steam flow rate (kg/h)	5100	5500
Reboiler temperature (°C)	120.3	120.3–120.7
CESAR-1 PZ/AMP concentration (wt%) *Note: Lab measurements differ slightly*	27 wt% AMP 13 wt% PZ	26 wt% AMP 9.5 wt% PZ
Start-up solvent loading titration (mol_{CO2}/mol_{amine})	0.05–0.10	0.08–0.11
Steady state lean loading titration (mol_{CO2}/mol_{amine})	0.132–0.155	0.108–0.117
Steady state lean loading online (mol_{CO2}/mol_{amine})	0.128–0.151	0.124–0.129
Steady state rich loading titration (mol_{CO2}/mol_{amine})	0.354–0.381	0.409–0.419
Steady state rich loading online (mol_{CO2}/mol_{amine})	0.336–0.357	0.387–0.399
CO_2 capture rate, product basis (%)	97–99%	83–91%
CO_2 capture rate, absorbed CO_2 basis (%)	92–96%	84–88%
Steady state SRD (MJ/kg CO_2), product basis	3.70	4.07–4.24
Steady state SRD (MJ/kg CO_2), absorbed CO_2 basis	3.73	4.23–4.37

3.6 Operating experience and test design considerations

There were some important process considerations that were incorporated into the design of the SUSD tests. These were essential to ensure stability of the plant during operation and maintain consistency in the tests results. These considerations are described below.

Amine concentration & water balance: To ensure amine concentration remains constant, the water balance will need to be regulated carefully. Amine concentration is measured through manual titration of amine samples in the laboratory. After solvent samples are collected, laboratory analysis of liquid samples is conducted. Depending on when the sample is taken (and lab capacity), the timing of the analysis will vary, e.g., 6am samples can be analysed on the same day, whereas samples taken after 3pm will be analysed the next day. For same day testing, the lab is limited to 3 samples per day. However, if the results are not time sensitive (i.e., non-urgent), additional samples can be analysed but would require multiple days to acquire results.

Stabilisation and steady state: Depending on the process parameter, it can take up to 1-2 hours for the plant to stabilise and reach set-point conditions, and it may take an additional 2–3 hours to reach steady state. The time to stabilise and regain steady state depends on the magnitude of the change and the process parameter. After process parameter changes, there is usually a stabilisation period of at least 3–5 hours before samples are collected to ensure homogeneous solvent composition, i.e., adequate mixing.

Solvent conditions during downtime: When using CESAR-1 in the capture plant, the CO_2 lean loading of the entire solvent inventory must be reduced to ≤ 0.2 mol CO_2/mol amine before the plant is shut down to prevent precipitation when the plant cools down. Precipitation of AMP/PZ blends can occur at both very high and low CO_2 loading, and in combination with other process parameters[86-89] such as AMP/PZ concentration ratio[88] and low solvent temperatures of 20–22°C.[86, 88] During shutdown, TCM operators typically “lean out” the solvent (i.e., reduce CO_2 loading) to reach a target density of 1020–1030 kg/m^3, which is approximately 0.1–0.2 mol CO_2/mol amine. In some of the shutdown tests at TCM, the amine pumps were also turned off, and the solvent would remain in the same location upon the point of amine pump shutdown, e.g., in vessels, columns, piping. Unlike other pilot plants, the solvent is not redistributed to lean storage tanks during downtime. Alternatively, some shutdown tests did not turn off the amine pumps, meaning amine circulation continued throughout the downtime period, i.e., when flue gas flow rate is zero in Figure 14. Constant amine circulation was necessary for two reasons: (i) to actively cool the plant and reduce the temperature in preparation for the next start-up test, and (ii) to mitigate leaking from a gasket on one of the heat exchangers.[l] Amine circulation needs to be completely stable before the flue gas flow or steam flow can be introduced to the system. This allows time for even distribution of the solvent liquid through the absorber, ensuring that the packing is properly wetted before the flue gas enter (better absorption due to improved contact between gas and liquid). Therefore, turning amine pumps off upon shutdown will impose additional time requirements for the start-up procedure. Continual amine circulation during downtime, can reduce the duration of the start-up procedure.

Cooling of the plant before start-up: Compared to pilot plants, the TCM plant has a low surface area to volume ratio. Consequently, the TCM capture plant can retain heat relatively well once the plant is turned off, owing to the insulation and the larger plant size. Depending on the start-up temperature required, there are two modes of cooling used during plant downtime: (i) passive cooling, or (ii) active cooling. For “passive cooling”, there is no solvent circulation during downtime, resulting in a temperature decrease of around 15°C every 24 hours in the stripper section. Thus, passive cooling overnight (e.g., 8 hours) would only reduce the stripper/reboiler temperature by ~5°C. To reduce the temperature further, “active cooling” was used to cool the plant faster and achieve the required target temperature for the next start-up. During downtime, circulation of the amine (i.e., lean/rich pumps on) and using the lean amine cooler (provides overall cooling of the system) increased the cooling rate of

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[l] The exact cause of the leak was unclear. It was not due to mechanical damage, but likely either a change in the properties of the gasket material or thermal expansion/contraction. There was more leaking from the gasket during cold start-ups compare to hot start-up, which suggested that major shifts in temperature from cold to hot could be the cause. There was also more leaking with start-ups that required starting of the amine pumps.

the plant. By actively cooling, the rate of temperature decrease in the stripper section is roughly 20°C per hour.[m] For example, to prepare for a cold start-up, around 6 to 8 hours of active cooling would be needed to reduce the stripper bottom temperature to 20–30°C.

3.7 Conventional start-up & shutdown: Effect of solvent inventory

3.7.1 Amine & ammonia emissions during start-up and shutdown

Solvent management measures are usually necessary to control and reduce solvent degradation and emissions, which decreases solvent consumption/loss and minimises negative effects on plant operability or on the environment.[41, 72, 90-92] The plant emissions and the water wash samples are monitored to ensure the levels of accumulated impurities are below the threshold limits.[72] The rate of solvent consumption, types of degradation products formed and effects on plant operation vary with different amines.

At TCM, there are several key indicators of amine degradation which are monitored and used to regulate degradation products below the acceptable threshold. The solvent should be clear and transparent, similar to water, and any change in colour is an indicator of the presence of solvent degradation products or dissolved metal ions. However, some colour change from clear to yellow/brown is acceptable as long as plant operation is maintained within the solvent thresholds specified by TCM and the Norwegian Environmental Agency.[93] The emissions and discharge permit granted to TCM in 2011 by the Norwegian Environmental Agency (Miljødirektoratet) specifies regulatory levels for amines, alkylamines, ammonia, aldehydes and other flue-gas related species, both in immediate concentration levels as well as permitted annual levels and environment deposition concentrations.[94, 95] The TCM permit limits the emissions of total amines to 6 ppmv as a daily average or 2.8 t per year, and also provides different limits for each amine class, i.e., primary, secondary and tertiary amines.[93, 94] The details of the regulatory levels for emissions according to the permit is outlined in Table 38 of Appendix B.

In an MEA-based test campaign at TCM,[72] the acceptable solvent thresholds were developed, which include: (i) solvent mass balance (water + amines + CO_2) maintained at levels above 95 wt%, (ii) heat stable salts (HSS) regulated to be below 1.5 wt%, (iii) thermal degradation products (D-mix) below 3 wt%, (iv) metal Fe^{2+}/Fe^{3+} below 5 ppmw, and (v) average ammonia emissions concentration kept below 5 ppmv. If the system exceeds any of these threshold limits significantly, then thermal reclaiming will be required to reduce solvent degradation products to acceptable levels. Moreover, if ammonia emissions are above 5 ppmv, the combination of an oxygen scavenger to inhibit degradation and thermal reclaiming may need to be considered.[72] By operating within these solvent thresholds, plant operators can ensure that environmental regulatory emission limits are being met.[93, 94]

There are different solvent management approaches employed at TCM, in addition to oxygen scavengers and slipstream or batch thermal reclaiming, the plant also has an activated charcoal filter and when RFCC flue gas is processed, the Brownian Diffusion filter is used to remove particulates.[72] Also, the absorber water wash sections have been found to be highly effective at reducing amine and ammonia emissions at TCM.[93] Better solvent management was found to provide a significant reduction in solvent consumption, and shown to decrease consumption from 1.6 down to 0.2 kg MEA per t_{CO2}.[72] A study of CESAR-1 solvent at TCM found the average total amine loss to be 0.16 kg amine per t_{CO2}. Most of the solvent loss can be attributed the degradation of PZ that occurs in the presence of NO_2, which forms

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[m] Based on TCM data observations, which showed a reduction in temperature from 50°C to 30°C after 60 min of active cooling.

nitrosamines. This highlights the importance of flue gas pre-treatment to remove NO_X prior to amine absorption.[96]

Experiments show that oxidative degradation of MEA is much faster than AMP/PZ,[96] whereas oxidative degradation of AMP/PZ has been noted to occur faster in the blend compared to PZ on its own. The most dominant degradation product is ammonia, with other significant degradation products including ethylenediamine (EDA), N-formyl piperazine (FPZ), and 2-oxopiperazine (OPZ).[97, 98] Thus, the main gaseous degradation product emitted from the capture plant is ammonia (NH_3), and measurements of ammonia at the absorber outlet can be used as an indicator of AMP/PZ degradation.[97] As PZ is a secondary amine, one key concern is the emissions of PZ into the atmosphere as secondary amines have the potential to form stable nitrosamines, which are considered to be carcinogens and are harmful. Therefore, monitoring the concentration of the amines (AMP and PZ) and ammonia at the gas outlet of the absorber is critical (shown in Figure 12).

For different start-up and shutdown tests in Figure 12, the PZ concentration was below the detection level across all tests carried out, whereas AMP was detected at very low levels of between 0.01–0.45 ppmv. This demonstrates the effectiveness of the absorber water wash sections, hence there is very low risk of amine emissions. However, a sudden spike in ammonia emissions is observed upon start-up of the plant. Gaseous ammonia formed from amine degradation is present in the depleted gas stream and as it passes through the water wash section, ammonia is dissolved in the water wash solution. Thus, the water wash section typically contains higher amounts of ammonia compared to other sections of the plant. Some of this ammonia is released at start-up.

Whilst the plant is off during the overnight downtime period, the system cools to lower temperatures. Upon start-up, the temperature change in the absorber and water wash cause a transient increase of ammonia in the depleted gas stream, i.e., the sudden spike. The largest increase of up to 31.2 ppmv in ammonia concentration occurs with the cold start-up using 42 m^3 solvent inventory, whereas the smallest increase occurs with a hot start-up using 53 m^3 solvent inventory (9.8 ppmv of ammonia). Thus, the degree of temperature change in the absorber (i.e., cold vs hot start-up) and solvent inventory volumes will influence ammonia emission at start-up. However, once the spike occurs, the ammonia concentration decreases below the threshold to steady state levels of 1.9–3.6 ppmv as the system stabilises.

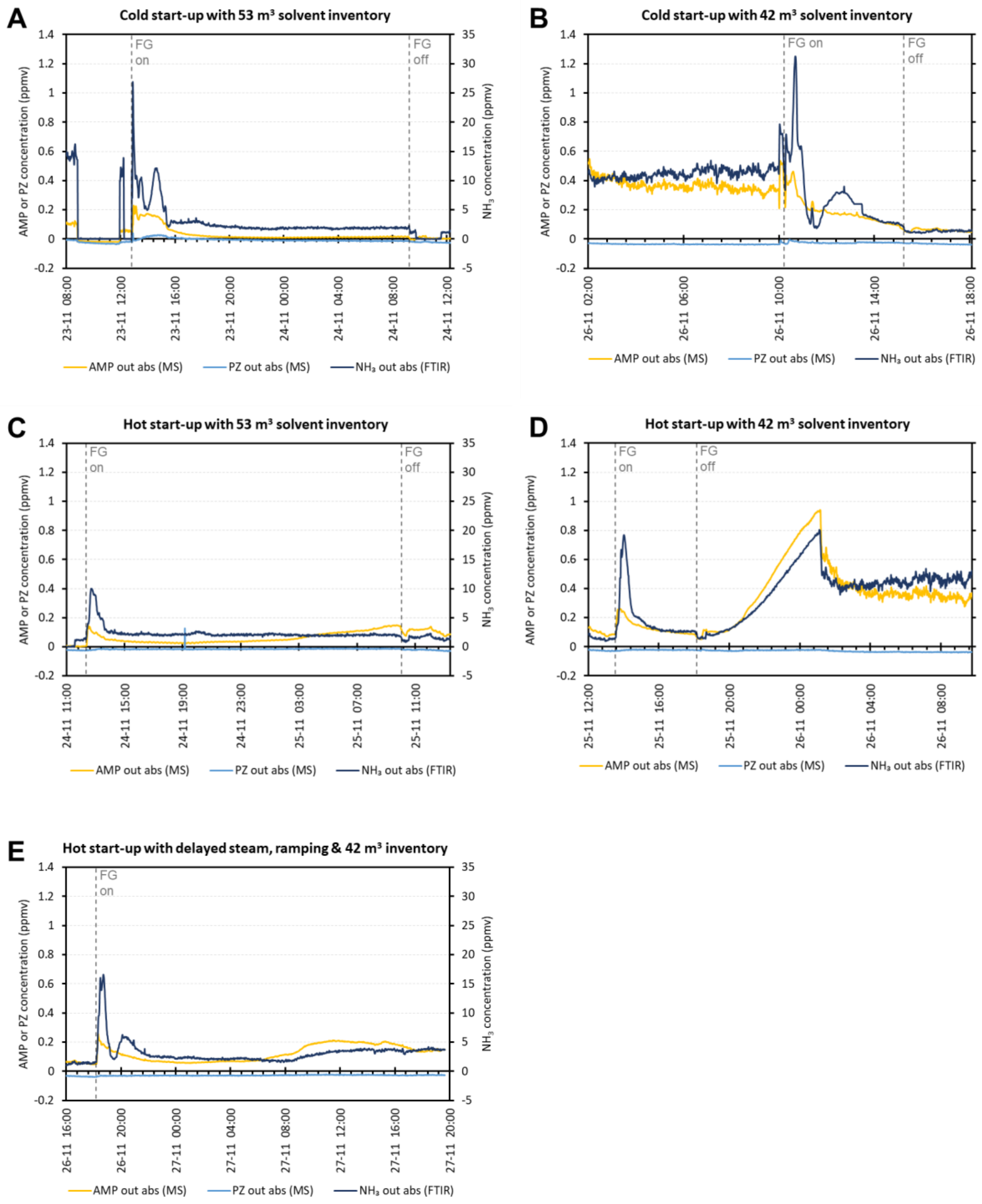

Figure 12: Ammonia (NH_3), piperazine (PZ) and AMP amine concentration at the outlet gas of the absorber column during cold start-up (A & B), hot start-up (C, D & E) and shutdown with different solvent inventories, 42 m^3 vs 53 m^3. The hot start-up with a 20 min delay in steam is shown in (E), but there was no shutdown on this day. The first vertical dashed lines indicate when flue gas was turned on, and second line is when flue gas is turned off.

3.7.2 Defining start-up & shutdown to evaluate performance

For this study, the analysis needs to focus on the two distinct phases of interest (Figure 13):

Start-up begins when the flue gas flow starts. However, performance will depend on the test protocol, namely, the timing of steam flow availability. Different scenarios include: (i) preheating of the system which will introduce steam before flue gas, (ii) conventional start-up with flue gas and steam starting at the same time, or (iii) delayed steam availability which starts after the flue gas flow. Thus, to ensure comparability of the results, the tests should be consistent in terms of starting conditions and steady state set-point process parameters. For instance, the whole volume of solvent needs to be at a uniform low CO_2 loading before start-up, also tests should target the same set-point temperatures and flow rates.

Shutdown begins when the flue gas blower begins to ramp down and continues until the steam flow is turned off completely. For the shutdown protocol at TCM, the entire solvent volume in the system is “leaned out” to a target solvent density, which corresponds to a specific CO_2 loading. Hence at the end of shutdown, the entire solvent volume will have a uniform CO_2 loading, and is ready for the next start-up test.

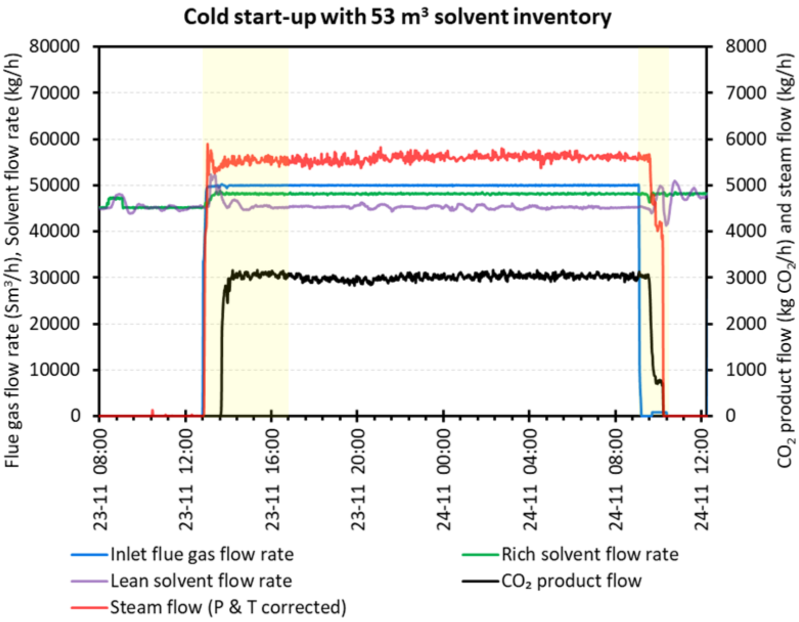

Figure 13: The two key periods that will be analysed in this study will be start-up and shutdown, which are both highlighted in yellow.

These phases will be analysed independently to better identify how specific factors (e.g., solvent inventory) will influence the performance of each phase. This approach can help identify any potential trade-offs in performance, highlight any strategies that improve the performance for only one phase (e.g., either start-up or shutdown), or strategies that are detrimental to performance.

3.7.3 Start-up and shutdown times

The process dynamics of absorption-based systems are a function of the volumetric capacity of the plant, i.e., the total available volume/capacity of equipment, vessels and piping. This volumetric plant capacity has a direct effect on the other characteristics of flexibility, this includes the total volume of solvent inventory, residence time for the different units, total solvent circulation time and transport delay associated with piping and heat exchangers.[43, 49, 50] Given its importance to the dynamics of the process, the effect of solvent inventory volume was demonstrated by conducting both cold and hot start-ups with two different inventory volumes, 42 m^3 to 53 m^3. As there is no dedicated lean amine buffer tank at the TCM plant, the CHP stripper column, which was not in operation during these tests, was used to store the adjustment volume of 11 m^3 solvent.

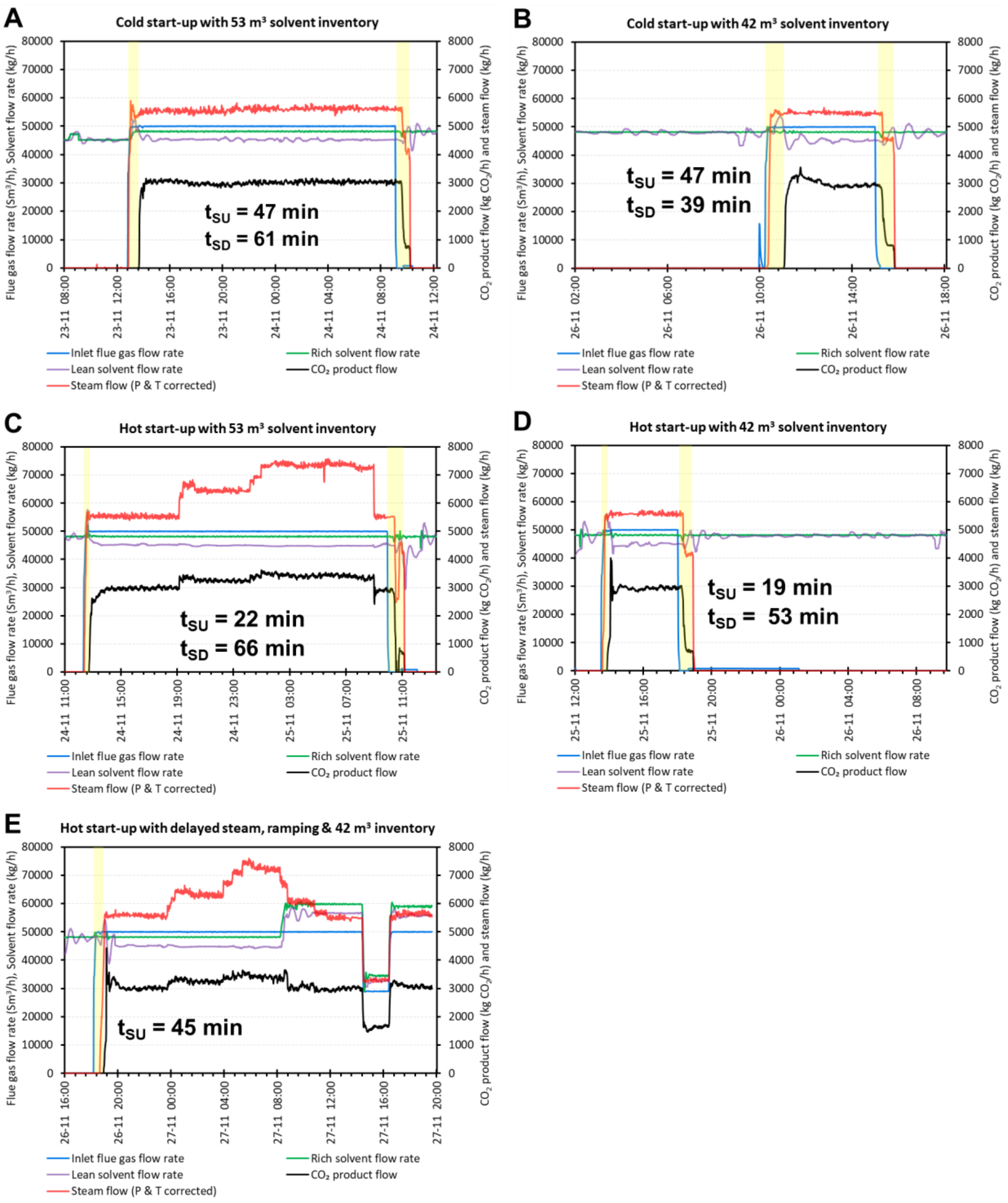

Figure 14: Time required for cold start-up (A & B) and hot start-up (C & D) and the shutdown when using different solvent inventories, i.e., 42 m^3 vs 53 m^3. The start-up time, t_{SU}, is defined as the time between when flue gas enters the system (blue line) until CO_2 product flow begins (black line). The t_{SU} is greater with cold start-up cases and when the steam availability is delayed by 20 min for a hot start-up (E). The t_{SD} is the shutdown time, which is the period between the flue gas being turned off and time steam is turned off.

The volume of inventory has an almost negligible effect on the start-up time of the plant (t_{SU}), i.e., duration of time from when flue gas is introduced until CO_2 product flow begins. Figure 14 shows that the two inventory volumes have comparable times for cold start-ups (47 min), whereas hot start-up may take 19 to 22 min, with the slightly shorter time achieved with the smaller 42 m^3 inventory.

The starting temperature and availability of heat will have a greater impact on the start-up time of the capture plant. For a cold start-up of the CO_2 capture plant, the reboiler temperature is around 20–35°C. In contrast, a hot start-up begins with the reboiler bottom temperature at 70-90°C. Consequently, the cold start-up requires a factor of 2.1–2.5 more time to reach the set-point reboiler temperature. During a hot start-up, delaying the availability of steam by 20 min will also increase the start-up time from 19–22 min to 45 min.

For shutdown of the TCM plant, the same procedure was implemented. To ensure the next plant start-up has the required CO_2 loading, the supply of steam continues after the flue gas flow is zero to “lean out” the solvent to a target CO_2 loading. The shutdown time, t_{SD}, is defined as the period from when the flue gas is turned off until steam supply is turned off. The shutdown time will be a function of the solvent volume and the target solvent density, which is directly related to the CO_2 loading. Shutdown time is also a function of amine solvent flow rate; however, solvent flow rate was kept constant for each SUSD test campaign. Figure 14 shows that the shutdown time is longer when operating the plant with a larger solvent inventory.

The effect of different start-up and shutdown methods on the CO_2 capture rate and residual CO_2 emissions will be quantified in the following section.

3.7.4 Start-up performance

3.7.4.1 Online CO_2 capture rate under dynamic conditions

For the absorption capture process (Figure 15), the flow rate of CO_2 in a specific stream is typically calculated by multiplying the flow rate of the stream by the CO_2 composition measurement. The CO_2-containing streams associated with the calculation of CO_2 capture rate include:

- Feed flue gas is the “supply CO_2” stream (input)
- Product CO_2 is the stream exiting the stripper (output)
- Residual emissions of CO_2 in the depleted flue gas stream (output).

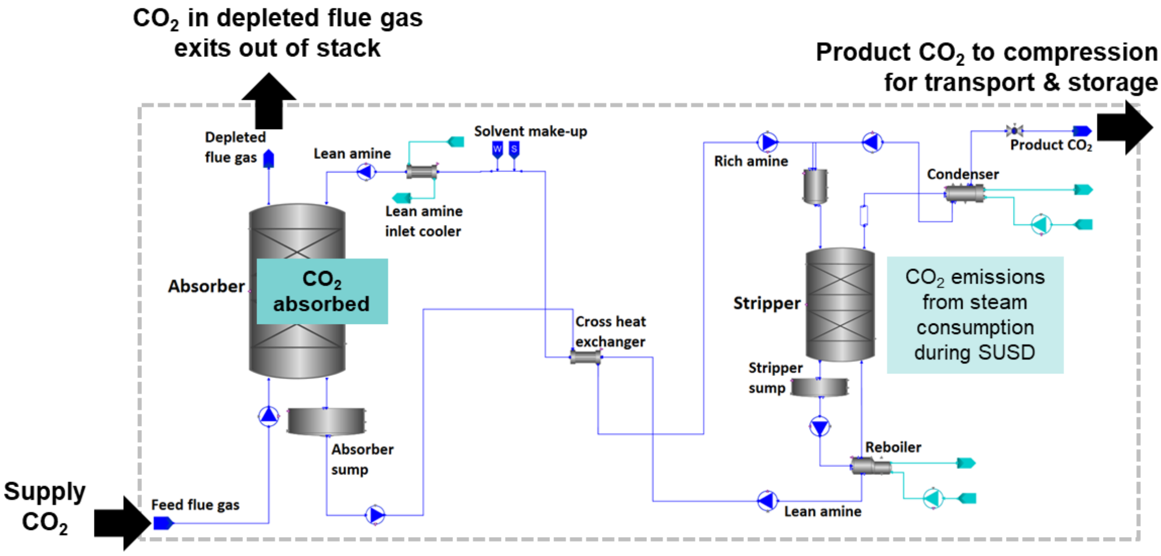

Figure 15: Stream flows of CO_2 in an absorption system. The main CO_2 flows used to calculate the CO_2 capture rate include the supply CO_2 (in the feed flue gas), CO_2 in the depleted flue gas, product CO_2 (exiting the stripper).

The CO_2 capture rate % quantifies the proportion of CO_2 that is captured from the feed flue gas. Under steady state conditions, the online measurements of CO_2 compositions and stream flow rates are used in these calculation methods, providing the "online" or instantaneous CO_2 capture performance (summarised in Table 12).

Table 12: Methods for calculating online CO_2 capture rate at the TCM capture facility. Adapted from Hamborg, et al. [71]*, Faramarzi, et al.* [79] *and Hume, et al.* [99]*. For dynamic conditions, the CO_2 capture rate is calculated via this online/instantaneous metric, but the cumulative capture rate is also determined, i.e., using cumulative amounts of CO_2 over a duration of time. Methods 1 and 2 are on a product CO_2 basis. Methods 3 and 4 rely on absorber side measurements.*

CO_2 capture rate method	**Description**	**Formula**
Method 1	Ratio of the CO_2 product flow to the CO_2 flow in the flue gas supply, referred to as the ***CO_2 capture rate, product basis***.	$= \frac{\mathrm{CO_2\ (product)}}{\mathrm{CO_2\ (supply)}}$
Method 2	Ratio of the CO_2 product flow to the sum of the CO_2 product flow and CO_2 flow in the depleted flue gas	$= \frac{\mathrm{CO_2\ (product)}}{\mathrm{CO_2\ (product)} + \mathrm{CO_2\ (depleted)}}$
Method 3	Ratio of the difference between the CO_2 flow in the flue gas supply and the CO_2 in the depleted flue gas to the CO_2 flow in the flue gas supply	$= \frac{\mathrm{CO_2\ (supply)} - \mathrm{CO_2\ (depleted)}}{\mathrm{CO_2\ (supply)}}$
Method 4	The proportion of CO_2 absorbed from the feed flue gas is equal to one minus the ratio of the depleted flue gas CO_2 concentration to the flue gas supply CO_2 concentration. We use this to calculate the amount of "absorbed CO_2", which is used to determine the ***absorber side cumulative CO_2 capture rate***.	$= \frac{I_{CO_2} - O_{CO_2}}{I_{CO_2}}$ Where O_{CO_2} = CO_2 concentration of depleted flue gas, dry basis I_{CO_2} = CO_2 concentration of supply flue gas, dry basis

Direct plant measurements of CO_2 composition and flow rate for the feed and product gas streams can be used for the capture rate calculations. However, at the time of this study, the flow rate measurements of the depleted flue gas stream at TCM were not reliable, consequently, the CO_2 flow rate for the depleted stream could not be calculated directly. Thus, it was not possible to use Methods 2 and 3 in this work. Furthermore, method 1 cannot be calculated on an online basis in the case of start-up and shutdown tests. Method 1 becomes invalid at times when flue gas feed flow is zero, e.g., during the start-up region when supply CO_2 is zero and dividing by zero is not possible. The stripper section can still generate product CO_2 if at the correct temperature even when flue gas feed is zero.

For the calculation of online CO_2 capture rate, only Method 4 is able to provide continuous data under start-up and shutdown conditions. Figure 16 shows the dynamic trends of "online CO_2 capture rate" derived from Method 4. This represents the absorbed CO_2 as a percentage of the supply CO_2 in the feed flue gas. It is equal to one minus the ratio of the depleted flue gas CO_2 composition to the flue gas supply CO_2 composition.

Small variations in the CO_2 content of the flue gas were observable on some of the test days, for instance (A) and (E) in Figure 16. There is an observable change in the online CO_2 capture rate in response to these small changes in CO_2 concentration. For the cold start-up with 53 m^3 of solvent inventory, the inlet CO_2 concentration increased from 3.9% to 4.2%, which reduced the online CO_2 capture rate from 87% to 83%.[n] Thus, for comparability purposes, it was important to have relatively constant flue gas CO_2 content. However, the performance of the

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[n] If the L/G ratio and solvent concentration remains the same, the amount of amine available to absorb CO_2 is also the same. Thus, even if the inlet CO_2 concentration increases, the absolute amount of CO_2 that is absorbed remains the same. However, this will mean that the capture rate percentage of absorbed CO_2 will decrease.

CHP plant is beyond the control of the TCM capture plant operators. If observed early, it was possible for the TCM operators to readjust the CO_2 content of the feed gas by either recirculating a small fraction of the CO_2 product or diluting with air.

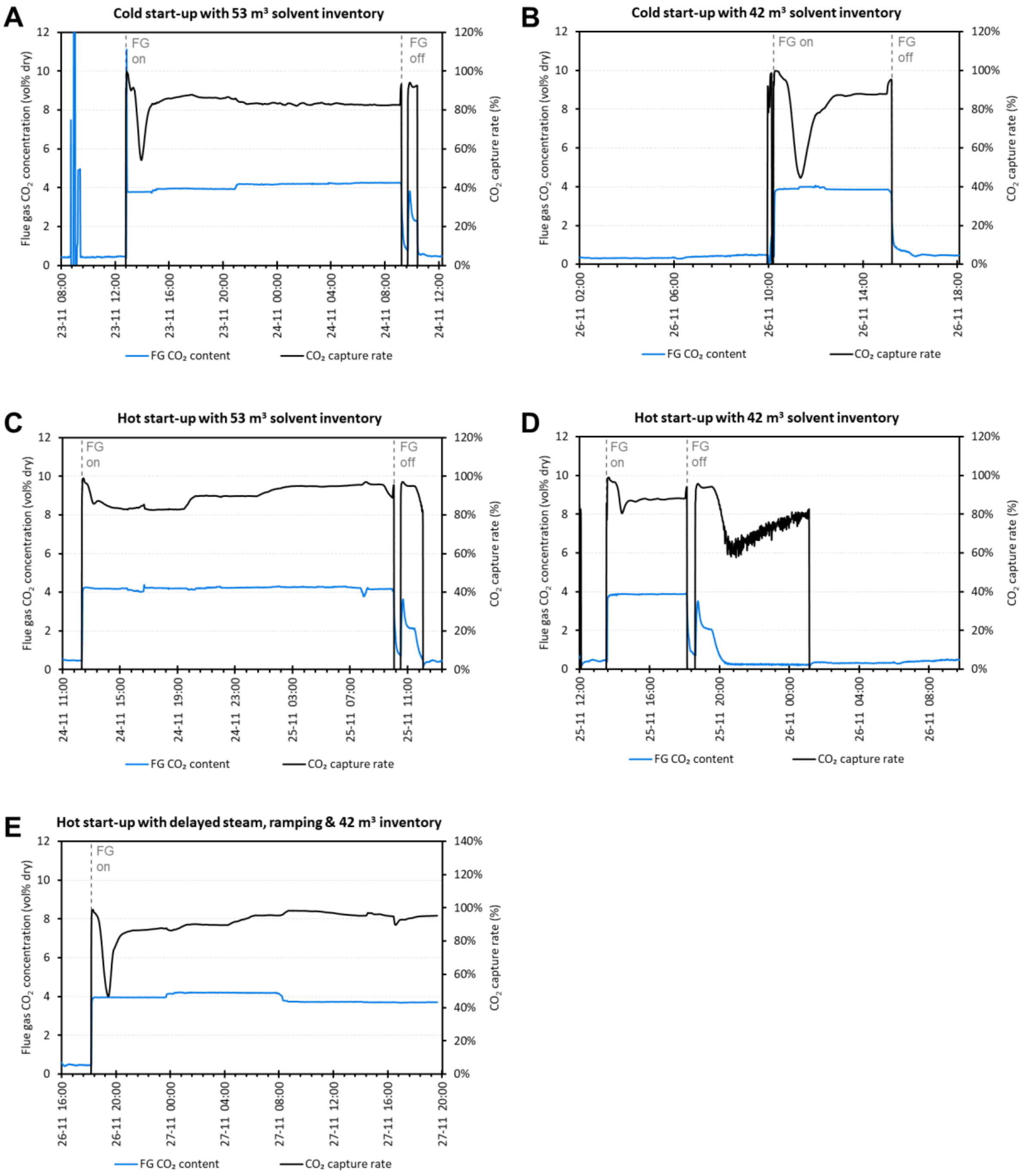

Figure 16: The flue gas CO_2 content (blue line) and online CO_2 capture rate (black line) during cold start-up (A & B), hot start-up (C, D & E) and shutdown with different solvent inventories, 42 m^3 vs 53 m^3. The hot start-up with a 20 min delay in steam is shown in (E), but there was no shutdown on this day. The first vertical dashed lines indicate when flue gas was turned on, and second line is when flue gas is turned off.

The analysis of capture performance during dynamic operation also requires the calculation of the *cumulative* CO_2 capture rate. Although the online data illustrates variations in trends, it is difficult to benchmark the performance for dynamic operation scenarios, e.g., flexible operation, start-up or shutdown. The cumulative capture performance, evaluated over the scenario timeframe, provides a better indication of the impact of dynamic operation on the overall plant performance. The changes in feed flue gas CO_2 concentration can also have an impact on the cumulative capture rate. Thus, we developed measures to reduce this effect and ensure comparability. The results for cumulative CO_2 capture rate are presented and discussed later in section 3.7.4.5.

3.7.4.2 Identifying a suitable period for the analysis of performance

Temperature (e.g., hot vs cold start-up) and the availability of steam are the main constraints of start-up time (t_{SU}) during the initial phase before CO_2 product is generated (shown in section 3.7.3). However, once the reboiler reaches the target temperature, conditions will continue to be dynamic as the system is still stabilising to reach a new steady state (when CO_2 product flow or the online CO_2 capture rate are constant). As illustrated by Figure 17, the time required for the system to reach steady state is denoted by t_{SS}. Table 13 shows that during cold start-ups, a smaller solvent inventory volume reduces the time required to reach steady state. However, similar to t_{SU}, significantly lower t_{SS} is achieved with hot start-ups compared to cold start-ups, with negligible effects from inventory volume. The hot start-up time is mainly impacted by the delay in steam availability.

The results in Table 13 indicate that start-up time (t_{SU}) is a function of the initial temperature of the system and the heating rate of the stripper section. Thus, observed differences in t_{SU} arise when comparing cold vs hot start-ups, and when steam supply is delayed. On the other hand, the time to reach steady (t_{SS}) provides an indication of the time required for the system to stabilise, which is a function of the solvent inventory volume and solvent flow rate (constant here). The temperature also has an observable impact on the time to reach steady state as shown by the time difference when steam supply is delayed.

As it was important to isolate the effects of either change in solvent inventory or steam availability, the same start-up procedure and consistent process conditions were also used across the different tests. In general, the TCM plant is designed to ensure consistency and reproducibility of results; it is relatively well insulated and controlled, hence ambient conditions (e.g., temperature) have little influence on the results.

The evaluation of cumulative performance during start-up and shutdown scenarios should be calculated over the same period of time to ensure comparability across the results for each scenario. One approach was to choose an arbitrary period, e.g., 200 min, to conduct the calculations. However, using a period of 200 minutes would include the start-up period as well as an extended period of steady state data (Figure 17), which can make it difficult to specifically compare the start-up performance. Steady state performance at the set-point conditions for these tests provided CO_2 capture rates of between 83–88%. Therefore, with steady state data included in the analysis of start-up, the data is skewed, becoming similar to steady state performance. To demonstrate this effect, the performance was calculated over 200 minutes. The dynamic behaviour of plant start-up is also illustrated for the first 200 min (Figure 18 to Figure 22).

The CO_2 content of the flue gas exiting the CHP plant can vary slightly on some of the test days (Figure 16). Similar to the effects of including steady state data, changes to feed flue gas CO_2 content have the potential to affect the analysis of capture performance. The degree of impact on the cumulative CO_2 capture rate will depend on when the variation occurs and the duration of the analysis period. If the analysis focuses specifically on the dynamic region of data, any bias from feed CO_2 content changes can be minimised. The time between start-up of the flue gas and the moment steady state is achieved is the dynamic period for each start-up; this is t_{SS} in Table 13. The longest t_{SS} of 82 min in Table 13 corresponds to the cold start-up with the larger solvent inventory of 53 m^3. Hence, performance was analysed over 82 min as this was sufficient in duration to capture the main start-up dynamics for all scenarios.

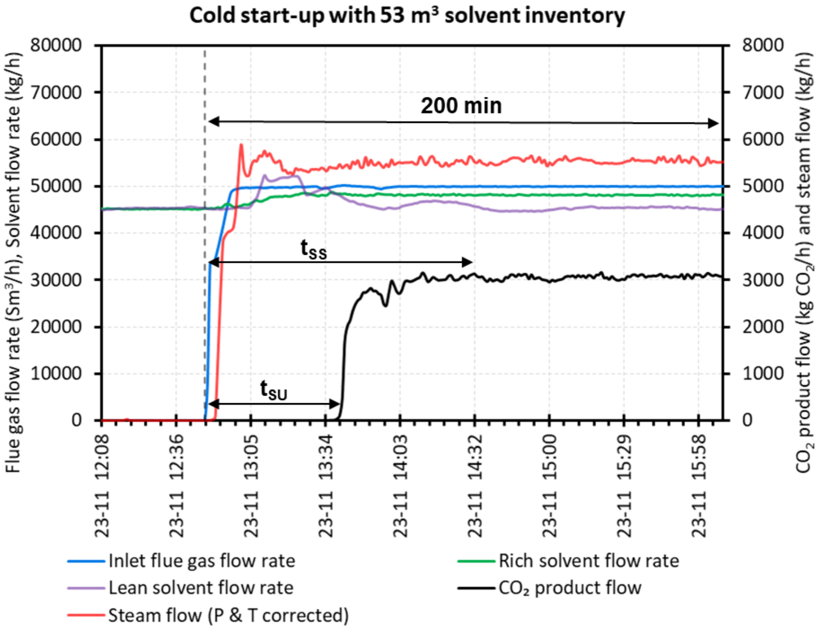

Figure 17: There are different time periods to consider when analysing the performance of start-up and shutdown in the capture plant. The start-up time, t_{SU}, is defined as the time between when flue gas enters the system (blue line) until CO_2 product flow begins (black line). The time required for the system to reach steady state is t_{SS}, e.g., this may be 40–82 min depending on the scenario. If an extended period is considered, e.g., 200 min, steady state conditions will influence the results, thus, making it difficult to specifically benchmark the start-up performance.

Table 13: Time when the CO_2 product flow rate begins (t_{SU}) and when steady state conditions are reached (t_{SS}) after the flue gas flow starts in minutes. These tests were carried out during the November 2020 campaign. Average solvent concentration based on laboratory analysis of the solvent samples: 24.4 wt% AMP 8.7 wt% PZ.

Start-up type	Conditions	Start-up time: time when CO_2 product flow starts, t_{SU} (min)	Time when CO_2 product flow reaches steady state, t_{SS} (min)
Cold start-up	53 m^3 inventory, start loading 0.10–0.11 mol CO_2/mol amine	47	82
	42 m^3 inventory, start loading 0.08–0.09 mol CO_2/mol amine	47	69
Hot start-up	53 m^3 inventory, start loading 0.08–0.09 mol CO_2/mol amine	22	40
	42 m^3 inventory, start loading 0.08–0.09 mol CO_2/mol amine	19	42
	42 m^3 inventory with delayed steam supply, start loading 0.08–0.09 mol CO_2/mol amine	45	63

3.7.4.3 Dynamic behaviour during cold start-up

The process behaviour during 200 min of cold start-up with 53 m^3 and 42 m^3 solvent inventory volumes is illustrated in Figure 18. Importantly, to isolate the effects of solvent inventory on the dynamic plant behaviour, the same start-up protocol and set-point conditions were used, e.g., the same target flow rates and temperatures. Although relatively constant, there are small observable changes in the feed flue gas CO_2 content. This causes minor variations of 100–300 kg/h in the supply CO_2 stream,[o] however, the impact on the online CO_2 capture rate and absorbed CO_2 flow is almost negligible.

As discussed in section 3.6, the total volume of CESAR-1 needs to be regenerated to a CO_2 loading of ≤ 0.2 mol CO_2/mol amine before shut-down to prevent precipitation when the solvent cools. Although this requires additional time and energy during shutdown, having a large inventory of lean solvent for plant start-up will provide significant improvements to the CO_2 capture performance. As Figure 18 shows, all the solvent has a CO_2 loading of 0.087-0.110 mol CO_2/mol amine at the beginning of start-up. Once flue gas enters the absorber, the low CO_2 loading of the solvent provides high CO_2 absorption capacity, thus, enabling a very high online CO_2 capture rate initially of 98.9–99.9%. From the beginning of a cold start-up, the reboiler and stripper needs time to heat up and reach the target temperature, consequently, the solvent is not being regenerated and the CO_2 loading gradually increases. This reduces the rate of absorbed CO_2, and there is a significant decrease in online CO_2 capture rate.

As shown in (C)–(F) of Figure 18, the cold start-up with 53 m^3 inventory has an initial small decrease in online CO_2 capture rate to ~90%, before decreasing further to a minimum of 54.2%. Once the reboiler temperature reaches ~118.7°C, the lean solvent loading reduces from 0.235 to 0.124 mol CO_2/mol amine, which results in a final steady state online capture rate of 86.0%. In the 42 m^3 case, the online CO_2 capture rate decreases to a minimum of 44.6%. The reboiler temperature only needs to increase to 117.2°C before the lean solvent loading begins to decrease from 0.292 to 0.126 mol CO_2/mol amine, with the steady state online capture rate reaching 87.6%. In both cases, the final steady state reboiler temperature reaches 120.3–120.7°C. These results demonstrate that cold start-up can benefit significantly from using larger solvent inventories as the plant can sustain higher CO_2 capture rates for longer. This potentially reduces residual CO_2 emissions whilst the plant heats during cold start-ups.

The rich solvent density and loading are measured at the absorber sump outlet (Figure 8). A comparison of (C) and (D) in Figure 18 shows that solvent inventory volume has an observable effect on the dynamics of the rich solvent loading. The gradient of the online rich CO_2 loading for the smaller 42 m^3 inventory case has a steeper increase compared to the 53 m^3 case. As the liquid level in the absorber sump is significantly lower with 42 m^3 of inventory compared to 53 m^3 (Figure 19), the rich solvent will reach the exit of the absorber sump faster. When the smaller solvent inventory is used, the measured rate of change in rich CO_2 loading is much quicker and appears to be more responsive. In contrast, using a larger 53 m^3 of inventory acts as a buffer, thus the changes in rich CO_2 loading are more gradual before reaching a stable steady state loading.

The temperature profiles (Figure 20) in the absorber and stripper columns are useful performance indicators. As the CO_2 absorption reaction is exothermic, a temperature increase inside the absorber indicates some degree of CO_2 absorption within that section of packing. This creates a temperature bulge or curved shape in the middle section of the column temperature profile.

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[o] For example, the supply CO_2 stream in (E) Figure 18 changes from 3593 kg/h initially, before decreasing to 3283 kg/h and then reaching 3398 kg/h.

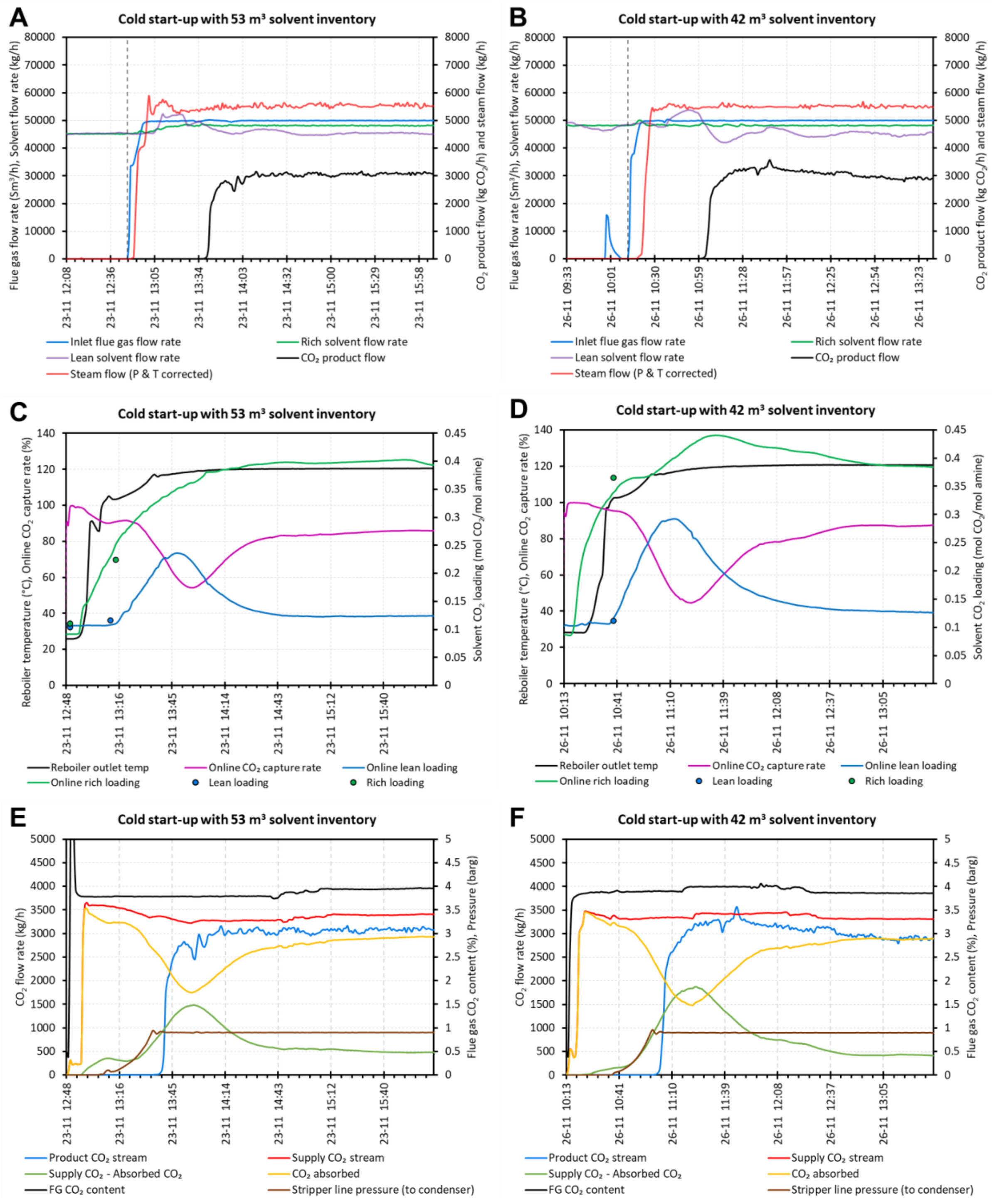

Figure 18: Process changes for a 200-minute time period for a cold start-up with 53 m^3 solvent inventory (A, C & E) and a cold start-up with 42 m^3 solvent inventory (B, D & F).

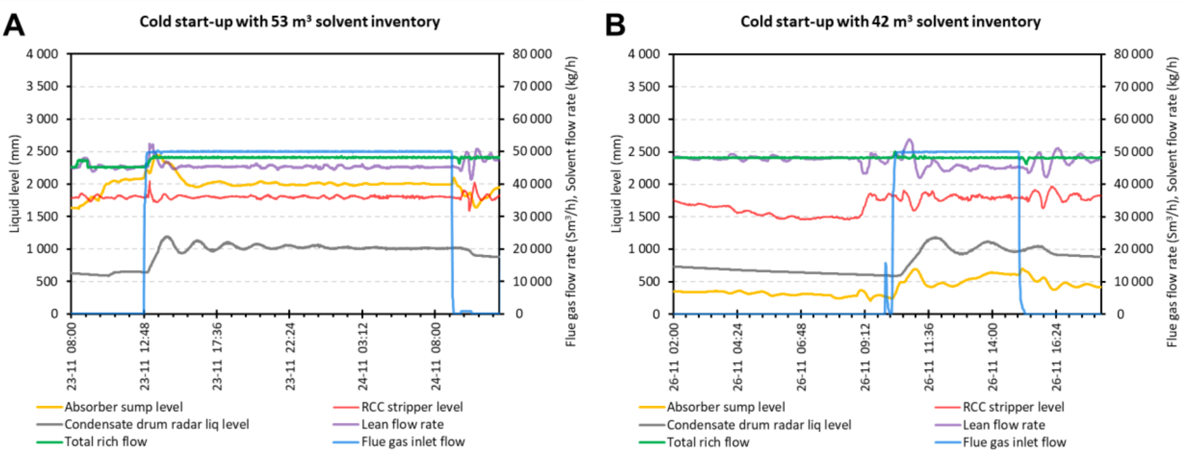

Figure 19: The change in liquid level during the cold start-ups with shutdown for the tests using 53 m^3 solvent inventory (A) and 42 m^3 solvent inventory (B). Using different solvent inventory in the TCM plant mainly affects the liquid level in the absorber sump, whereas the stripper liquid level in both cases is similar.

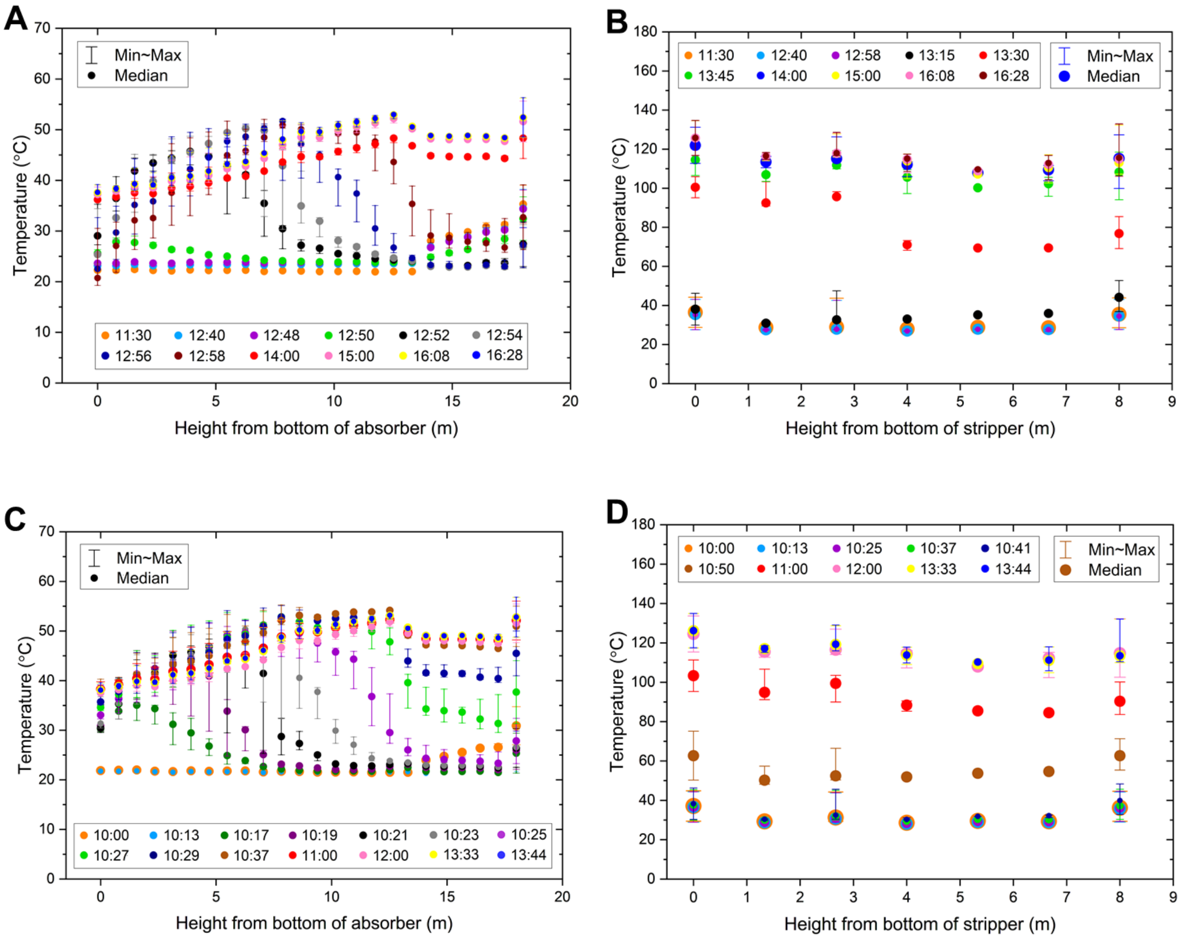

Figure 20: Absorber (left) and stripper (right) temperature profiles for a cold start-up with 53 m^3 solvent inventory (A & B) and 42 m^3 solvent inventory (C & D). For the cold start-up with 53 m^3 inventory (A & B), flue gas flow starts at 12:48, the set-point conditions are reached around 13:08 and product CO_2 flow rate reaches steady state at 14:10. For the cold start-up with 42 m^3 inventory (C & D), flue gas flow starts at 10:13, set-point conditions are reached around 10:24 and product CO_2 flow rate reaches steady state at 11:22.

The shape of the absorber temperature profiles provides an indication of the level of CO_2 absorption, and can help explain the overall CO_2 capture performance of the plant. The key process factors that determine the profile shape and location of the temperature bulge include the flue gas CO_2 content, liquid-to-gas (L/G) ratio, solvent properties (e.g., heat of absorption) and packing height. If the L/G ratio decreases, the temperature bulge will typically shift closer to the top of the absorber column. The temperature bulge also shifts to the top of the absorber with increased packing height, or higher flue gas CO_2 concentration.[100]

As shown in Figure 20 (A) and (C), when the plant is switched off, there is no flue gas feed to the system, thus no absorption of CO_2. Therefore, the absorber temperature profile is flat without a temperature bulge and starts at 22°C. As flue gas enter the absorber at the base of the column, a small temperature bulge forms at the base of the column, indicating some degree of CO_2 absorption at this initial phase of start-up. From the moment the flue gas blower is started, it will take time before the flue gas flow rate reaches the final set-point value, e.g., 20 min for the cold start-up with 53 m^3 inventory, or 11 min with the cold start with 42 m^3.[p] Owing to the faster increase in flue gas flow rate for the 42 m^3 system compared to 53 m^3, a slightly more prominent temperature bulge was observed for the first temperature profile after starting the flue gas. As the flue gas flow rate increased towards the final set-point value, the L/G ratio instantaneously decreased, and the temperature bulge shifted to the top of the column (shown for every two minutes). Once the system reached steady state, the temperature profile shifted towards higher temperatures with a small temperature bulge in the middle.

The stripper column has a flat horizontal temperature profile, as shown by Figure 20 (B) and (D), and initially starts at 30–40°C. Observing the shift in stripper temperature over the start-up period can help identify the time at which the column reaches stable steady state conditions. The changes in stripper temperature occur on a slower time scale compared to the absorber, as the dynamics will be dictated by the heat capacity of the equipment and fluid, whereas absorber temperature is a function of the degree of CO_2 absorption (driven by the L/G ratio and reaction). Over the start-up period, the stripper profile gradually shifts upwards to higher temperatures before reaching the steady state conditions at around 120°C.

3.7.4.4 Dynamic behaviour during hot start-up

Figures 21 and 22 illustrate the process behaviour for 200 min during hot start-ups with 53 m^3 and 42 m^3 of solvent inventory. Although similar start-up procedures were used for both hot and cold start-up tests, the key difference was the initial temperature of the system. For hot start-ups, the initial reboiler outlet temperature was at ~90 °C, whereas cold start-ups had an initial reboiler temperature of 25–30 °C. Compared to the cold start-up results, hot start-up has significantly different dynamic behaviour.

Figure 21 shows that the online lean and rich solvent loading starts at 0.084–0.112 mol CO_2/mol amine. Owing to the low CO_2 loading, very high initial online CO_2 capture rates of 98.8–99.8% are achieved. Unlike the cold start-up, the online CO_2 capture rate only reduces slightly, before levelling off to steady state conditions once the reboiler outlet temperature reaches 120.5°C (for normal hot start-ups in Figure 21).

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[p] It is important to note that flue gas flow rate is ramped independently of solvent flowrate and is not a function of solvent inventory volume. For each key process parameter, i.e., flue gas flow, steam flow and amine solvent flow rate, the test plan was to change each of these at the same ramp rate across every start-up test. As some process parameters such as the flue gas and steam flow were ramped manually, this resulted in some variability in ramp rates. All start-up tests had the same flue gas ramp rate, and reached the flue gas set-point value within ~20 min. However, the one exception was the cold start-up with 42 m^3 inventory, which was ramped a bit quicker than planned so reached the set-point flow rate within 11 min.

In the case of the hot start-up with 53 m^3 of inventory, there is a sufficiently large volume of “fresh” solvent in the system to meet the CO_2 capture demands whilst the reboiler is still heating up. The lean solvent loading only increases marginally from 0.096 to 0.117 mol CO_2/mol amine, decreasing the online CO_2 capture rate to the minimum of 85.8%. Subsequently, the system stabilises to steady state conditions with lean loading reaching 0.130 mol CO_2/mol and online CO_2 capture rate is 83%.

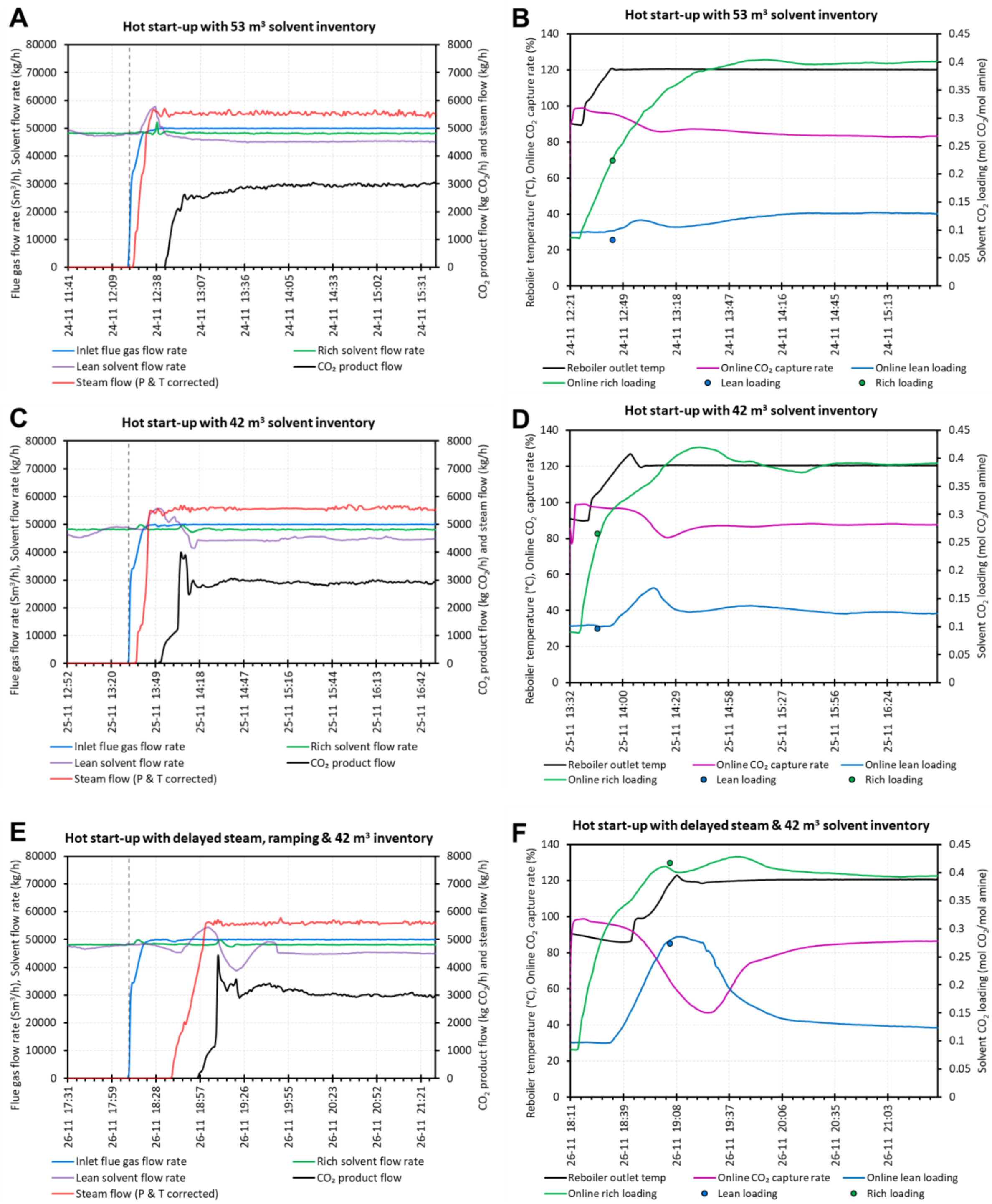

Figure 21: Process changes for a 200-minute time period for a hot start-up with 53 m^3 solvent inventory (A & B), hot start-up with 42 m^3 solvent inventory (C & D). A hot start-up with a 20-minute delay in steam supply (E & F) was tested with 42 m^3 solvent inventory.

Compared to the 53 m^3 case, hot start-up with 42 m^3 had a greater increase in lean loading from 0.101 to 0.169 mol CO_2/mol amine, resulting in a decrease of online CO_2 capture rate to a minimum of 80.5%. Once the reboiler reaches the target temperature, the conditions stabilise to the final steady state with 0.123–0.125 mol CO_2/mol lean loading and online CO_2 capture rate 88%.

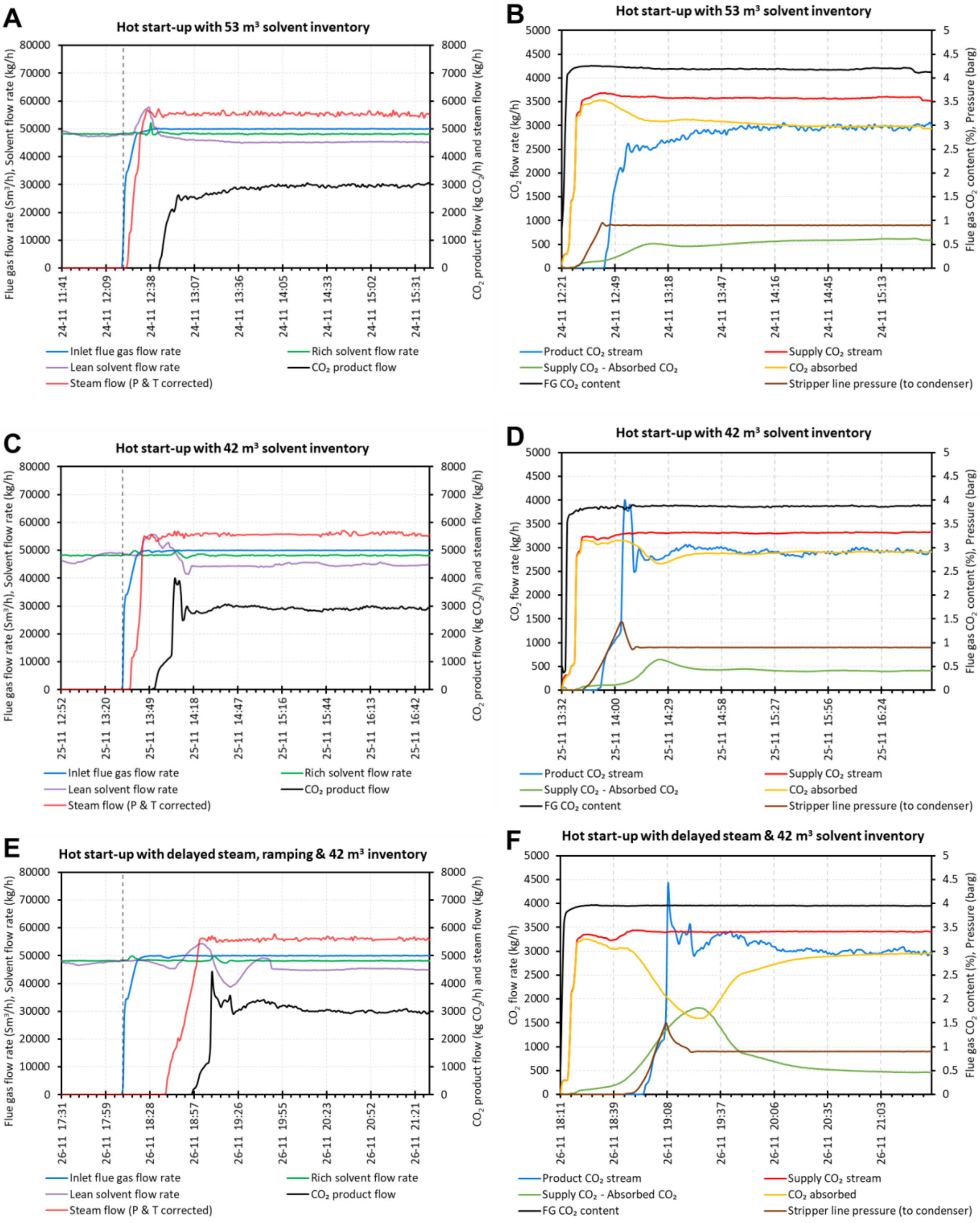

Figure 22: Process changes for a 200-minute time period for a hot start-up with 53 m^3 solvent inventory (A & B), hot start-up with 42 m^3 solvent inventory (C & D) and a hot start-up with a 20-minute delay in steam supply (E & F).

Figure 21 (E) and (F) shows the effect of delaying steam supply by 20 minutes for a hot start-up using 42 m^3 of inventory. By delaying the supply of heat to the reboiler, this increases the start-up time as the reboiler will take longer to reach the target temperature required for solvent regeneration. The dynamic behaviour of the online lean loading is very similar to the cold start-up with 42 m^3 of solvent case, however, when steam is delayed, there is a wider maximum peak for lean CO_2 loading. When the steam supply is delayed, the online CO_2 capture rate reduces to the minimum of 46.8%. As the reboiler temperature approaches 120°C, the lean solvent loading begins to decrease from 0.286 to 0.123 mol CO_2/mol amine, with the steady state online capture rate reaching 86%. These results show that any delay in steam supply significantly reduces the capture performance during start-up.

Although a hot start-up with 42 m^3 had a greater initial decrease in CO_2 capture rate, the steady state capture rate was higher (88%) compared to the 53 m^3 case (83%). Figure 16 shows that during steady state operation, slight decreases in inlet flue gas CO_2 concentration will increase the online CO_2 capture rate, the converse also applies. Therefore, the difference in steady state capture performance can be attributed to the variation in flue gas CO_2 concentration, which was 4.2 vol% of CO_2 for the 53 m^3 case, and slightly lower at 3.9 vol% for the 42 m^3 test (shown in Figure 22). The hot start-up with the delayed steam supply using 42 m^3 of inventory also had different flue gas CO_2 content at 4.0 vol%, which resulted in a steady state capture rate of 86% that was in between the other cases. This highlights the importance of maintaining a similar flue gas CO_2 content across tests to ensure comparability of online data. However, as this study is focused on comparing the *cumulative* capture performance over a very short timeframe (i.e., 82 min) for the most dynamic region of operation, the impact of variations in flue gas CO_2 content on the comparability of cases should almost be negligible.

The dynamic behaviour of the rich CO_2 loading during hot start-up is essentially the same as the observations for cold start-up. Similar to cold start-up, solvent inventory volume has an observable effect on the rich loading, with the 42 m^3 inventory tests having a steeper gradient compared to the 53 m^3 case. Using a smaller solvent inventory reduces the liquid volume in the absorber sump (e.g., Figure 19), thus the changes in rich loading are observed at a faster rate. The changes in rich loading for the 53 m^3 case occur at a slower rate due the larger volume, which buffers the response.

Figure 22 (D) and (F) shows the stripper line pressure (brown curve) increasing to a peak before stabilising to steady state conditions. This peak in stripper line pressure coincides with a spike in the CO_2 product flow rate (blue line). This phenomenon only occurred with the two 42 m^3 tests. This behaviour is caused by a delay in switching the stripper valve from manual operation to automatic control. Consequently, pressure builds up in the stripper, causing the CO_2 product to suddenly discharge and there is an observable overshoot. There are no anomalies observed in the steam supply flow rate or online CO_2 capture rate, therefore, the overall cumulative CO_2 capture performance would not be impacted in any way.

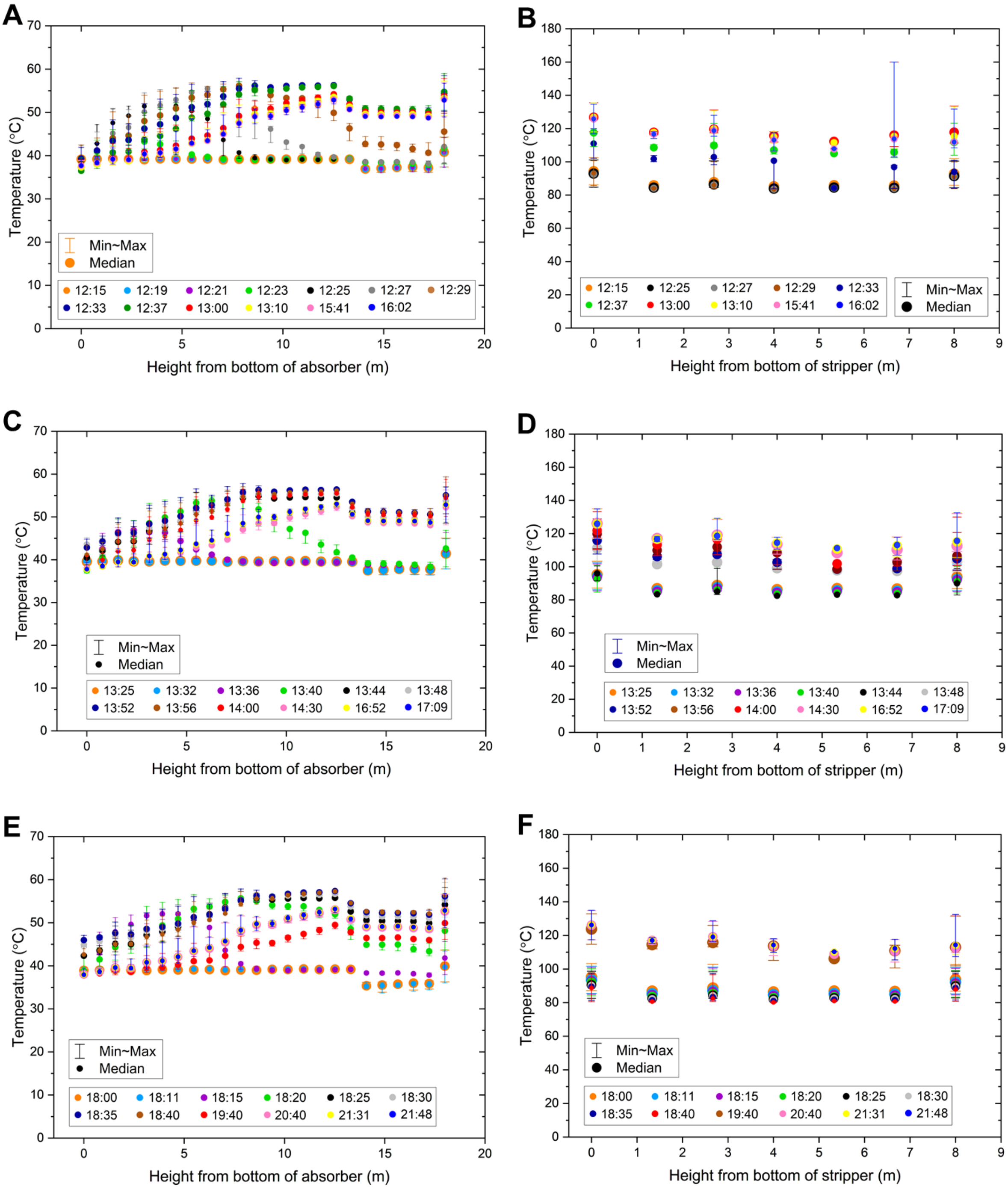

Figure 23: Absorber (left) and stripper (right) temperature profiles for a hot start-up with 53 m^3 solvent inventory (A & B), hot start-up with 42 m^3 solvent inventory (C & D), and hot start up with delay steam supply and 42 m^3 solvent inventory (E & F). For the hot start-up with 53 m^3 inventory (A & B), the flue gas flow starts at 12:21, set-point conditions are reached around 12:42 and the product CO_2 flow rate reaches steady state at 13:01. For the-hot start up with 42 m^3 inventory (C & D), the flue gas flow starts at 13:32, set-point conditions are reached around 13:49 and product CO_2 flow rate reaches steady state at 14:14. For the hot start-up with delayed steam supply, the flue gas flow starts at 18:11, set-point conditions are reached at 18:28 and product CO_2 flow rate reaches steady state at 19:14.

The absorber and stripper temperature profiles for hot start-up are illustrated in Figure 23. For the hot start-up tests, the initial temperature profiles begin at higher temperatures compared to the cold start-up tests. The general direction in which the temperature profiles shift is very similar to the observation for cold start up (described in section 3.7.4.3).

The initial temperature inside the absorber column ranged between 39–40°C just before start-up commenced. The flue gas enters the base of the absorber and a small temperature bulge forms in the T profile, which indicates there is some level of CO_2 absorption. The time it takes for the flue gas flow rate to reach the final set-point value after the blower is turned on is 21 min for the hot start-up with 53 m^3 inventory, 17 min for hot start with 42 m^3, and 17 min for a hot start with delayed steam supply and 42 m^3 inventory.

In general, the solvent inventory volume did not have a significant impact on the CO_2 capture performance during hot start-up, which is distinct from the observations for cold start-up. However, the delay of steam supply was shown to have a negative impact, reducing the CO_2 capture performance of the hot start-up significantly. A quantitative comparison of the capture performance for the three hot start-up tests is presented in section 3.7.4.5, where the cumulative capture and energy performance is evaluated.

3.7.4.5 Comparison of cumulative CO_2 capture performance for start-up

Under dynamic conditions, the flow rate and composition measurements are transient, making time an important factor. To describe the overall plant performance over a specified duration of time, the *cumulative CO_2 capture rate* is also calculated using the cumulative amounts of CO_2 on a mass basis, i.e., instantaneous/online gas flow rate multiplied by CO_2 concentration and cumulatively added over the time period. The time period used to analyse cumulative performance metrics is particularly critical. The method used to select a suitable timeframe which encapsulates the dynamic behaviour of interest is outlined in section 3.7.4.2.

In this section, the performance was analysed for the duration of 82 min. It was determined that this period contained the main start-up dynamics for all scenarios (section 3.7.4.2). We also calculate the performance over 200 min. This includes an extended period of steady state operation, which can skew the results as the higher capture rates at steady state will “cancel out” the effects of start-up. Although the 200 min results do not represent true “start-up” performance, these results will help demonstrate whether the start-up improvement is significant enough to benefit the overall long-term performance. For instance, some start-up “improvements” will have an impact in the short-term performance, however, this impact could be negligible once the steady state operation period is considered. Moreover, the overall impact will also depend on the number of start-up and shutdown cycles.[101, 102]

The main cumulative metrics include: (i) cumulative CO_2 capture rate on a product basis, and (ii) cumulative CO_2 capture rate, absorber side, (iii) cumulative specific reboiler duty (SRD) on a product basis, and (iv) cumulative specific reboiler duty on an absorbed CO_2 basis.

$$\text{Cumulative CO}_2\text{ capture rate, product basis} = \frac{\text{Cumulative product CO}_2\text{ (kg)}}{\text{Cumulative supply CO}_2\text{ (kg)}} \times 100\% \qquad \textbf{(3)}$$

The cumulative CO_2 capture rate on a product basis (Equation 3) is influenced by the solvent circulation time, which is a function of the volume of solvent inventory, the solvent flow rate and plant configuration, as shown by the examples in Table 14. Due to the time required to circulate solvent from one location to another, a delay is observed from the time flue gas flow starts until CO_2 product flow begins (Figure 14). Hence, the CO_2 capture rate on a product basis is strongly influenced by the time period used to perform the calculation. This metric does not provide an indication of the residual emissions from the plant as it does not account for the CO_2 exiting via the depleted flue gas stream. Instead, the CO_2 capture rate on a product basis simply represents the proportion of the feed CO_2 that is sent to compression for CO_2 transport and storage.

Table 14: Comparison of process characteristics for different test facilities. The process dynamics of amine absorption systems is influenced by the plant scale (i.e., size) and the volume of solvent inventory. The solvent circulation time provides some indication of the flexibility in a given system. Note: TCM plant is designed to have greater flexibility, the volume of solvent inventory can vary across a wide range depending on operation mode.

	UKCCSRC PACT pilot plant	**Brindisi CO_2 capture plant**		**TCM CO_2 capture plant**	
CO_2 capture capacity (t_{CO2}/day)	1	60		80–200	
Volume solvent inventory (m^3)	0.470	61		38.2–40.8	
Solvent circulation time (min)	36	105	146	41	71
Corresponding solvent flow rate (m^3/h)	1	35	25	58	34

$$\text{Cumulative CO}_2\text{ capture rate, absorber side} = \frac{\text{Cumulative absorbed CO}_2\text{ (kg)}}{\text{Cumulative supply CO}_2\text{ (kg)}} \times 100\% \tag{4}$$

Equation 4 is the indicator for the amount of CO_2 cumulatively absorbed by the solvent represented as a percentage of the total supply CO_2. The cumulative absorbed CO_2 is the online CO_2 capture rate (method 4 in Table 12) multiplied by the supply CO_2 flow rate, calculated cumulatively over the specified time period. The percentage of the supply CO_2 that is emitted as residual emissions is Equation 5:

$$\begin{aligned}&\%\text{ Cumulative residual CO}_2\text{ emissions}\\ &\qquad = 100\% - \text{Cumulative CO}_2\text{ capture rate, absorber side}\end{aligned} \tag{5}$$

The specific reboiler duty was also calculated based on cumulative metrics of steam energy, product CO_2 (Equation 6) and absorbed CO_2 (Equation 7).

$$\text{Cumulative specific reboiler duty, product basis} = \frac{\text{Cumulative steam energy (MJ)}}{\text{Cumulative product CO}_2\text{ (kg CO}_2\text{)}} \tag{6}$$

$$\text{Cumulative specific reboiler duty, absorbed CO}_2 = \frac{\text{Cumulative steam energy (MJ)}}{\text{Cumulative absorbed CO}_2\text{ (kg CO}_2\text{)}} \tag{7}$$

These cumulative performance metrics were evaluated, and the results provided in Tables 15–18. The trends for cumulative CO_2 capture rate during start-up are illustrated in Figures 32 and 41 for the November 2020 and June 2020 test campaigns, respectively. We can quantitatively compare the performance of hot and cold start-up, as well as understand the quantitative impact of solvent inventory and delayed steam supply.

Product basis vs absorbed CO_2 basis: Which is more important for SUSD?

As observed in the previous sections, the dynamics of the absorption column are driven by the L/G ratio (e.g., gas flow rate) and reaction, whereas the stripper dynamics is mainly dictated by the heat capacity of the equipment and fluid. The process dynamics of the stripper section is slower than the absorption section, and the behaviour occurs over a longer timescale. Whilst the absorption of CO_2 is relatively immediate, there will be a delay before CO_2 product is generated on the stripper side. Consequently, if we only consider the initial 82 min of start-up operation, which is the most dynamic region, the cumulative amount of CO_2 absorbed will always be greater than the cumulative CO_2 product. Hence, the cumulative CO_2 capture rate on a product basis (Table 15) generally has lower values compared to the cumulative CO_2 capture rate based on absorbed CO_2 (Table 17). Conversely, the cumulative specific reboiler duty is higher when calculated on a product CO_2 basis compared to absorbed CO_2.

Under steady state operation, the CO_2 capture rate calculated on a product basis is comparable to the CO_2 capture rate based on absorbed CO_2, and the two metrics can be used interchangeably. However, under highly dynamic conditions, the values for these two metrics differ significantly. In the context of start-up and shutdown operation, the amount of residual CO_2 emissions from the process is of greater concern as this is the CO_2 released into the atmosphere. The residual CO_2 emissions are directly related to the amount of absorbed CO_2. Therefore, we will focus on the insights from the results of cumulative performance based on the *absorbed* CO_2, i.e., the results in Table 17, Table 18 and Figure 24 (C) & (D). For specific reboiler duty, it is still important to consider this on the basis of absorbed CO_2 as well as product CO_2. The key general observations are summarised below.

Cold start-up: Large versus small solvent inventory

The cold start-up using the larger 53 m^3 of inventory required more reboiler steam energy on a MJ basis compared to the 42 m^3 case, and consequently, it had slightly higher specific reboiler duty. Another benefit of the smaller 42 m^3 inventory system for cold start-ups is a reduction in the time required to reach steady state, 69 min compared to 82 min in the 53 m^3 system (Table 13). However, the cumulative CO_2 capture rate (absorbed CO_2 basis) over 82 min with the 53 m^3 inventory is higher at 77.8% compared to the 42 m^3 case, which only captured 74.7 %. When considering a 200 min period, the cumulative CO_2 capture rate for the larger 53 m^3 solvent inventory still exceeds that of the 42 m^3 system.

For cold start-ups, a smaller inventory may help reduce stabilisation time and slightly reduce energy requirements. However, a larger solvent inventory will provide higher cumulative CO_2 capture rates, and thus would reduce the residual CO_2 emissions.

Hot start-up: Large versus small solvent inventory

For the hot start-up cases, the two solvent inventory cases had very similar cumulative CO_2 capture rate (absorbed CO_2 basis) over 82 min, with 42 m^3 capturing 90.0% and 53 m^3 capturing 90.3%. As less CO_2 is absorbed (kg amount in Table 17) in the 42 m^3 case, the cumulative specific reboiler duty on a MJ/kg absorbed CO_2 basis is slightly higher. Hot start-up with the larger 53 m^3 inventory absorbs much more CO_2 (Tables 17 and 18), which leads to much lower cumulative specific reboiler. As Figure 21 shows, the 53 m^3 system has more low loading solvent available upon start-up, providing a buffering effect so that the lean loading can stay relatively constant, whereas the 42 m^3 system exhibits a small increase in lean loading which reduces the total amount of absorbed CO_2.

As discussed in section 3.7.4.4, the steady state capture rate of the 42 m^3 test was higher (88%) compared to the 53 m^3 case (83%) due to the difference in flue gas CO_2 content. When a longer 200 min period was considered for the cumulative CO_2 capture rate, the smaller inventory 42 m^3 system captured more CO_2 at 88.5%, compared to the 53 m^3 test which achieved 86.4% capture rate. Therefore, assuming the same flue gas CO_2 content and plant configuration, the inventory volume size has very little impact on the residual CO_2 emissions during hot start-up.

Aside from the potential reduction in solvent consumption costs with the smaller inventory systems, the results indicate possible technical benefits for hot start-up performance as well. Over 82 minutes, the cumulative CO_2 capture rate on a *product CO_2 basis* is 64% for the smaller 42 m^3 system, capturing more CO_2 than the 53 m^3 system at 53%. With the smaller inventory volume, there is a shorter solvent circulation time, and the effects of solvent regeneration are observed on a faster time scale. Therefore, for a given time period, the smaller inventory system will generate more product CO_2 and a higher product basis CO_2 capture rate is observed. Consequently, the smaller inventory system has a lower specific reboiler duty on a product basis (MJ/kg product CO_2). Note, this is just a reflection of the process dynamics, and not an indicator of the CO_2 emissions from the plant. For CO_2 capture performance, the CO_2 capture rate % on an absorbed CO_2 basis provides a better indication of the residual CO_2 emissions.

Effect of steam availability

The impact of steam availability on the performance was evaluated for hot start-up using 42 m^3 solvent inventory. Delaying steam availability by 20 minutes had a clear impact on the CO_2 capture performance of the plant. Delaying the steam supply increases the time required to heat the reboiler, meaning the start-up time (t_{SU}) increases from 19 to 45 min, and the time to reach steady state (t_{SS}) increases from 42 to 63 min. Although delaying steam availability reduced the specific reboiler duty, the 82 min cumulative CO_2 capture rate based on absorbed CO_2 decreased to 78.8% compared to the normal hot start-up which cumulatively captured 88.5%. The impact was even greater in the case of cumulative CO_2 capture rate on a product basis, with delayed steam reducing product basis capture rate to 35.4% from 64.0% for the normal hot start-up. Hence, making steam available for the CO_2 capture plant as early as possible is critical to maximise the CO_2 capture rate and minimise residual CO_2 emissions during start-up.

Cold start-up versus hot start-up

Cold start-ups take significantly longer to reach steady state conditions compared to hot start-ups. For a system using 53 m^3 of inventory, the time required before CO_2 product flow reached steady state (t_{SS}) was 82 min for a cold start-up, and 40 min for a hot start-up. Similarly, the time before CO_2 product flow begins (t_{SU}) is also longer in the case of cold start-ups, which can take up to 47 min, whereas hot start-ups only take 19–22 min (Table 13). As shown earlier, a large decrease in the online CO_2 capture rate occurs with cold-start-ups (C & D Figure 18), however, this does not occur for hot start-up scenarios (B & D Figure 21). Consequently, the cold start-ups cumulatively captured less CO_2 and have higher specific reboiler duty compared to hot start-ups, both on a product CO_2 basis and absorbed CO_2 basis. For a start-up period of 82 minutes in a system with 53 m^3 of inventory, a cold start-up cumulatively captured 78% (absorbed CO_2 basis), whereas a hot start-up cumulatively captured 90%–a difference of 12%. When considering the smaller inventory system and the capture rate on a product CO_2 basis, the difference in capture rate between cold vs hot becomes even greater (~30%). The 82 min cumulative capture rate on a product basis for 42 m^3 inventory system is 34% for the cold start-up, and 64% with the hot start-up.

Table 15: Product CO_2 basis calculations of cumulative capture rate and specific reboiler duty over 82 minutes. This is calculated from the cumulative amounts of CO_2 in the different streams and the cumulative steam energy. The cumulative residual CO_2 emissions is the difference between the supply CO_2 and the absorbed CO_2.

Start-up conditions	Cumulative amount of CO_2 over 82 min period (kg)				Steam energy (MJ)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured, product CO_2 basis (%)
	Supply CO_2	Product CO_2	Absorbed CO_2	Supply – Absorbed			
Cold SU 53 m^3	4197.7	1278.6	3266.1	931.6	16156.2	**12.64**	**30.5**
Cold SU 42 m^3	4271.4	1447.6	3190.6	1080.8	15409.9	**10.64**	**33.9**
Hot SU 53 m^3	4559.1	2396.3	4116.3	442.8	15477.9	**6.46**	**52.6**
Hot SU 42 m^3	4105.5	2628.2	3692.9	412.7	14874.9	**5.66**	**64.0**
Hot SU 42 m^3 delayed steam	4280.0	1514.5	3224.6	1055.4	8944.6	**5.91**	**35.4**

Table 16: Product CO_2 basis calculations of cumulative capture rate and specific reboiler duty over 200 minutes. This is calculated from the cumulative amounts of CO_2 in the different streams and the cumulative steam energy. The cumulative residual CO_2 emissions is the difference between the supply CO_2 and the absorbed CO_2.

Start-up conditions	Cumulative amount of CO_2 over 200 min period (kg)				Steam energy (MJ)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured, product CO_2 basis (%)
	Supply CO_2	Product CO_2	Absorbed CO_2	Supply – Absorbed			
Cold SU 53 m^3	10779.9	7302.0	8698.1	2081.8	40714.3	**5.58**	**67.7**
Cold SU 42 m^3	10888.4	7473.5	8530.5	2357.9	39868.0	**5.33**	**68.6**
Hot SU 53 m^3	11595.7	8209.1	10022.2	1573.6	39817.7	**4.85**	**70.8**
Hot SU 42 m^3	10622.2	8358.6	9394.8	1227.4	39296.5	**4.70**	**78.7**
Hot SU 42 m^3 delayed steam	10985.3	7553.3	8656.6	2328.7	33662.7	**4.46**	**68.8**

Table 17: Absorbed CO_2 basis calculations of cumulative CO_2 capture rate and specific reboiler duty over 82 minutes. This is calculated from the cumulative amounts of CO_2 in the different streams and the cumulative steam energy. The cumulative residual CO_2 emissions is the difference between the supply CO_2 and the absorbed CO_2.

Start-up conditions	Cumulative amount of CO_2 over 82 min period (kg)				Steam energy (MJ)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured, absorbed CO_2 basis (%)
	Supply CO_2	Product CO_2	Absorbed CO_2	Supply – Absorbed			
Cold SU 53 m^3	4197.7	1278.6	3266.1	931.6	16156.2	**4.95**	**77.8**
Cold SU 42 m^3	4271.4	1447.6	3190.6	1080.8	15409.9	**4.83**	**74.7**
Hot SU 53 m^3	4559.1	2396.3	4116.3	442.8	15477.9	**3.76**	**90.3**
Hot SU 42 m^3	4105.5	2628.2	3692.9	412.7	14874.9	**4.03**	**90.0**
Hot SU 42 m^3 delayed steam	4280.0	1514.5	3224.6	1055.4	8944.6	**2.77**	**75.3**

Table 18: Absorbed CO_2 basis calculations of cumulative CO_2 capture rate and specific reboiler duty over 200 minutes. This is calculated from the cumulative amounts of CO_2 in the different streams and the cumulative steam energy. The cumulative residual CO_2 emissions is the difference between the supply CO_2 and the absorbed CO_2.

Start-up conditions	Cumulative amount of CO_2 over 200 min period (kg)				Steam energy (MJ)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured, absorbed CO_2 basis (%)
	Supply CO_2	Product CO_2	Absorbed CO_2	Supply – Absorbed			
Cold SU 53 m^3	10779.9	7302.0	8698.1	2081.8	40714.3	**4.68**	**80.7**
Cold SU 42 m^3	10888.4	7473.5	8530.5	2357.9	39868.0	**4.67**	**78.3**
Hot SU 53 m^3	11595.7	8209.1	10022.2	1573.6	39817.7	**3.97**	**86.4**
Hot SU 42 m^3	10622.2	8358.6	9394.8	1227.4	39296.5	**4.18**	**88.5**
Hot SU 42 m^3 delayed steam	10985.3	7553.3	8656.6	2328.7	33662.7	**3.89**	**78.8**

The difference between the CO_2 capture rate for hot and cold start-ups becomes smaller once steady state operation is considered, however, hot start-up still captured more CO_2 than cold start-up. This effect is illustrated in the 200 min cumulative performance results. The difference between the cumulative capture rate on an absorbed CO_2 basis for hot and cold start-up ranges from 6–10%. For product basis cumulative capture rate over 200 min, the difference between hot and cold start up is 3–10%.

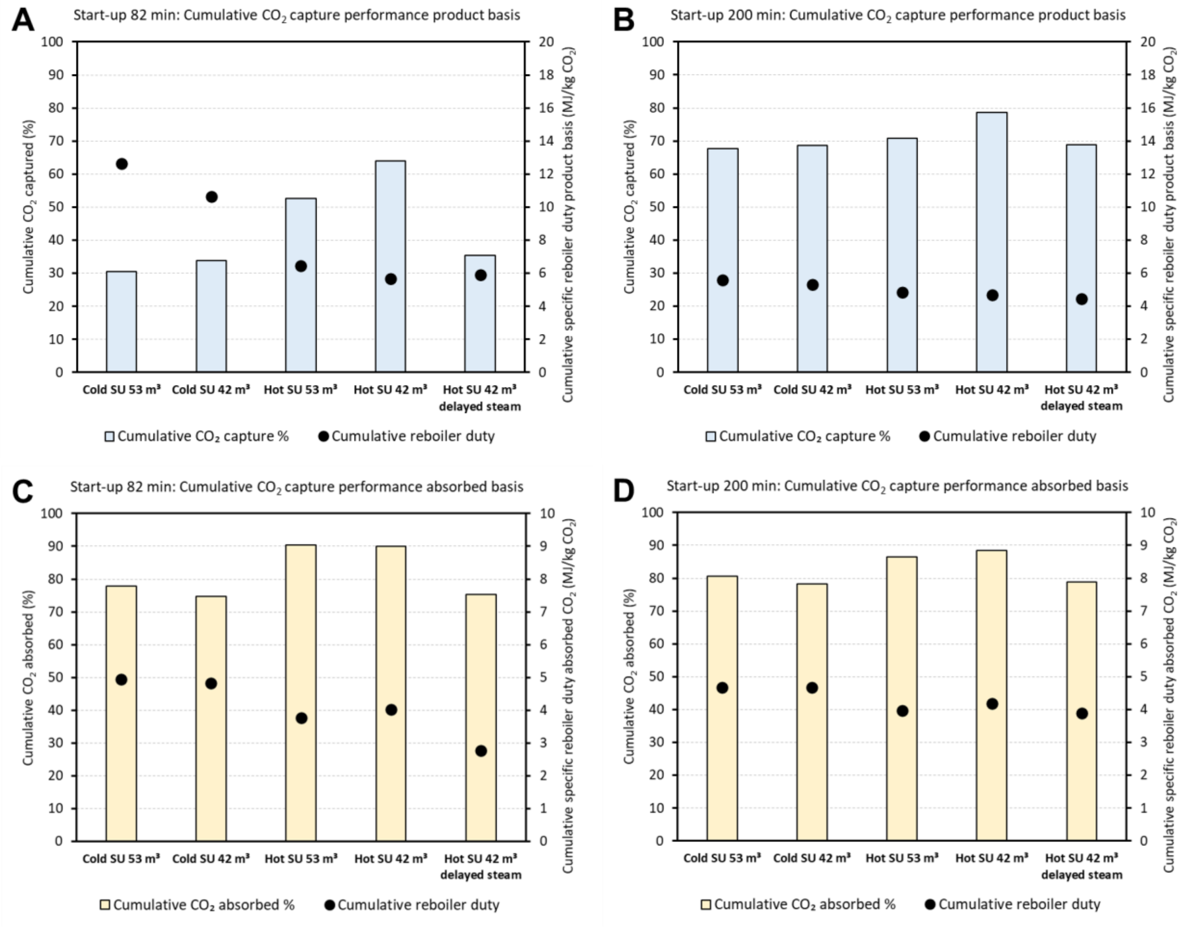

Figure 24: Cumulative CO_2 capture rate and reboiler duty calculated based on the cumulative amounts of product CO_2 (A & B) and absorbed CO_2 (C & D). The numbers are from the Tables 15 to 18.

3.7.5 Shutdown performance: Effect of solvent inventory volume

The shutdown tests summarised in Table 19 demonstrate the effect of using 53 m^3 and 42 m^3 inventory volumes on shutdown performance, including shutdown time, CO_2 emissions and energy requirements. The case called “SD 53 m^3 (2) volume adjusted” is not comparable with the others due to the sudden CO_2 product decrease, which corresponds to the volume adjustment from 53 to 42 m^3 that occurs midway through the shutdown (Figure 27). Hence, this case was omitted from the performance evaluation. The similarity in the dynamic trends across the remaining shutdown cases in Figure 26 and Figure 27 (i.e., SD 53 m^3 (1), SD 42 m^3 (1), SD 42 m^3 (2)) indicates these tests are comparable.

*Table 19: Calculations of cumulative amounts of CO_2, energy and specific reboiler duty over the shutdown period. *This shutdown included an inventory volume adjustment from 53 m^3 to 42 m^3, consequently, less product CO_2 is generated compared to SD 53 m^3 (1). This case cannot be used for comparison of performance.*

Shutdown scenario	Shut-down time, t_{SD} (min)	Cumulative amount of CO_2 over time period (kg)					Steam energy (MJ)	Cumulative specific reboiler duty, product basis (MJ/kg CO_2)
		Supply CO_2	Product CO_2	Absorbed CO_2	Supply – Absorbed	Supply – Product		
SD 53 m^3 (1)	61	242.2	2273.9	204.2	38.0	-2031.6	12810.5	5.63
SD 53 m^3 (2) volume adjusted*	66	302.5	2037.4	272.2	30.3	-1734.9	12742.5	6.25
SD 42 m^3 (1)	53	179.4	1506.8	160.1	19.3	-1327.4	9778.2	6.49
SD 42 m^3 (2)	39	145.3	1476.1	129.8	15.6	-1330.8	9452.2	6.40

The shutdown time is a function of the solvent volume and the steam supply. The shutdown required more time with the larger 53 m^3 solvent inventory as a greater volume of solvent is being processed in the stripper section, assuming constant amine flow rate. The shutdown with the larger 53 m^3 inventory also requires more steam energy on a MJ basis to lean out the solvent volume compared to the shutdown tests with 42 m^3 inventory. However, the shutdown with 53 m^3 of solvent recovers significantly more product CO_2 (2274 kg CO_2) than the 42 m^3 tests (1476–1507 kg CO_2). Thus, the shutdown test with 53 m^3 inventory has a lower specific reboiler duty (5.63 MJ/kg CO_2) in comparison with the 42 m^3 tests (6.40–6.49 MJ/kg CO_2).

During shutdown, the amount of cumulative supply CO_2 is quite low as no flue gas is being fed into the system. However, a large amount of product CO_2 is recovered during shutdown through the solvent lean out step, i.e., 1476–2274 kg CO_2, depending on the inventory volume. This CO_2 product could potentially counterbalance most, or possibly all, of the CO_2 emissions associated with start-up. To test this hypothesis, the following section analyses the combined performance of both start-up and shutdown together.

Figure 25 illustrates the effect of shutdown on the temperature inside the absorber and stripper columns. A comparison of the 53 m^3 shutdown test with one of the 42 m^3 tests shows that the dynamic behaviour for the column temperature profiles is essentially the same. As the flue gas ramps down, the absorber temperature bulge shifts from the middle towards the bottom of the absorber column. Once the flue gas is completely off, the absorber temperature profile becomes flat and horizontal, indicating there is no more CO_2 absorption. The stripper temperature profile remains constant until the steam flow rate is turned off once shutdown finishes. An observable decrease in the stripper temperature begins around one hour after steam is switched off.

In Figure 26 (F), there is a discrepancy between online rich loading and the lab measurement point. The time used for the loading correlation plots are dictated by the clock settings of the instrumentation and control system. In contrast, the solvent loading points are plotted from times manually recorded by the plant operators when the solvent samples were taken. This can lead to the occasional mismatch in the timestamps between the online and manual readings of CO_2 loading, as observed in Figure 26 (F).

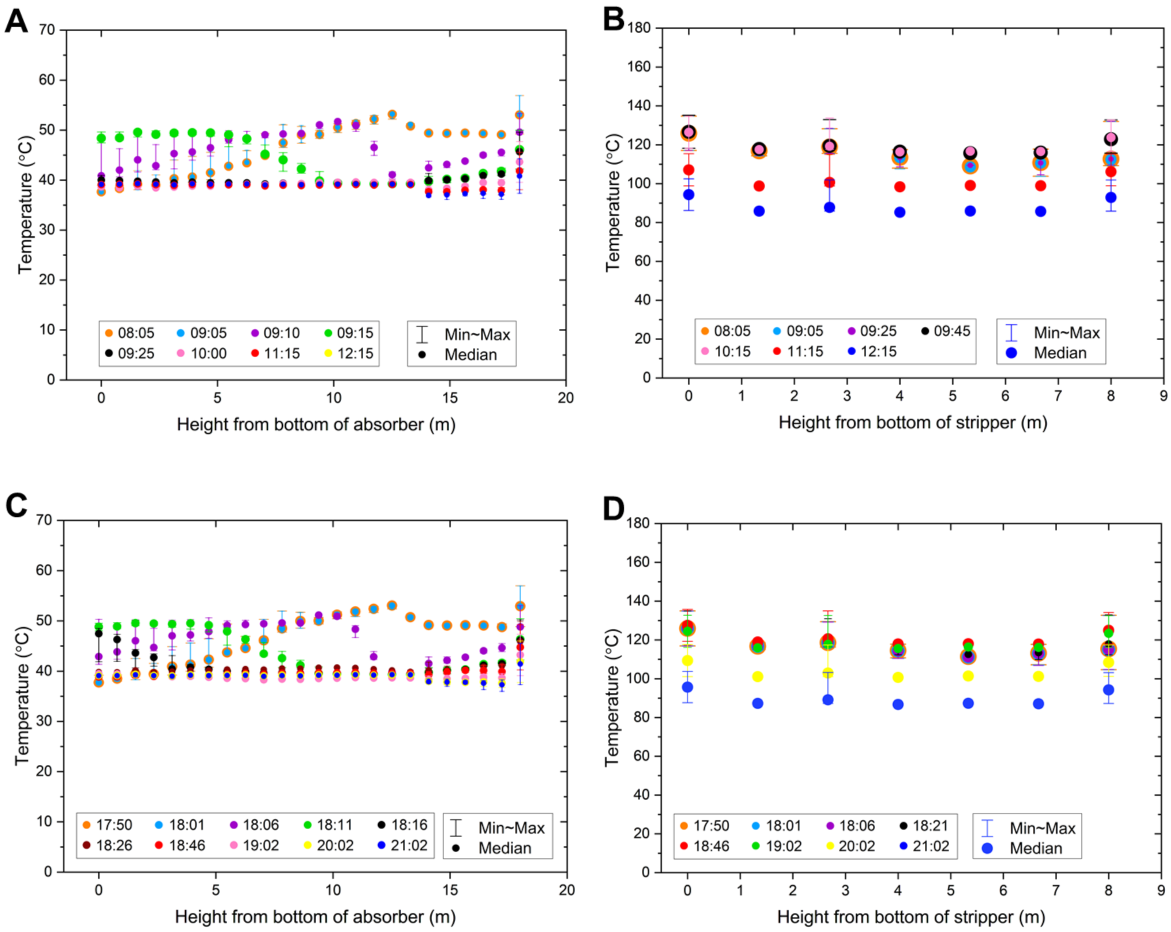

Figure 25: Absorber (left) and stripper (right) temperature profiles for shutdown. For the 53 m^3 solvent inventory case (A & B), flue gas flow begins to turn off around 09:05 and the steam is shut off around 10:15. For the 42 m^3 inventory case (C & D), flue gas flow starts to turn off around 18:01 and the steam is shut off at 19:02.

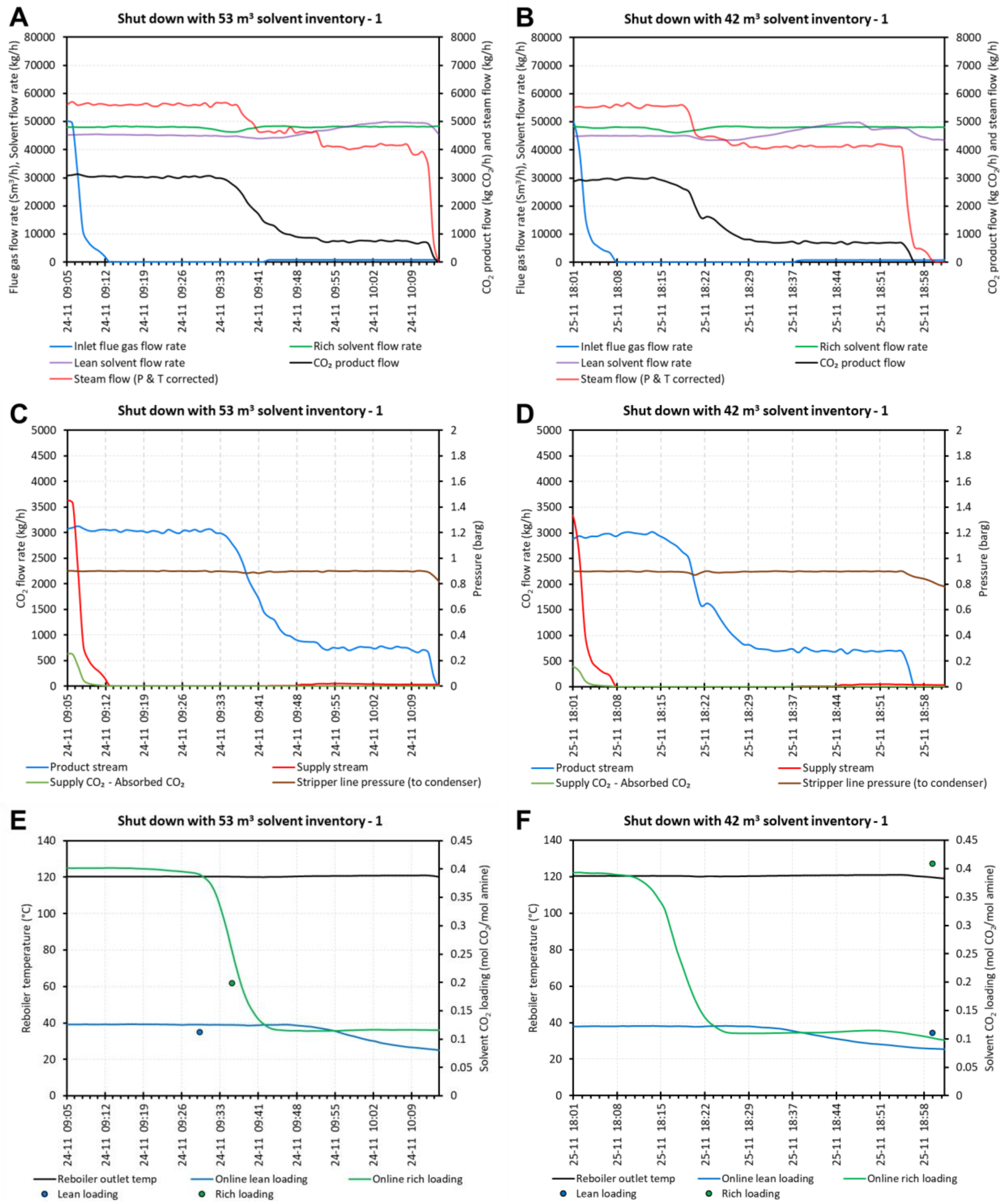

Figure 26: Process changes for the shutdown of the plant using different solvent inventory volumes of 53 m^3 (A, C & E) and 42 m^3 (B, D & F), which correspond to SD 53 m^3 (1) and SD 42 m^3 (1) in Table 19, respectively.

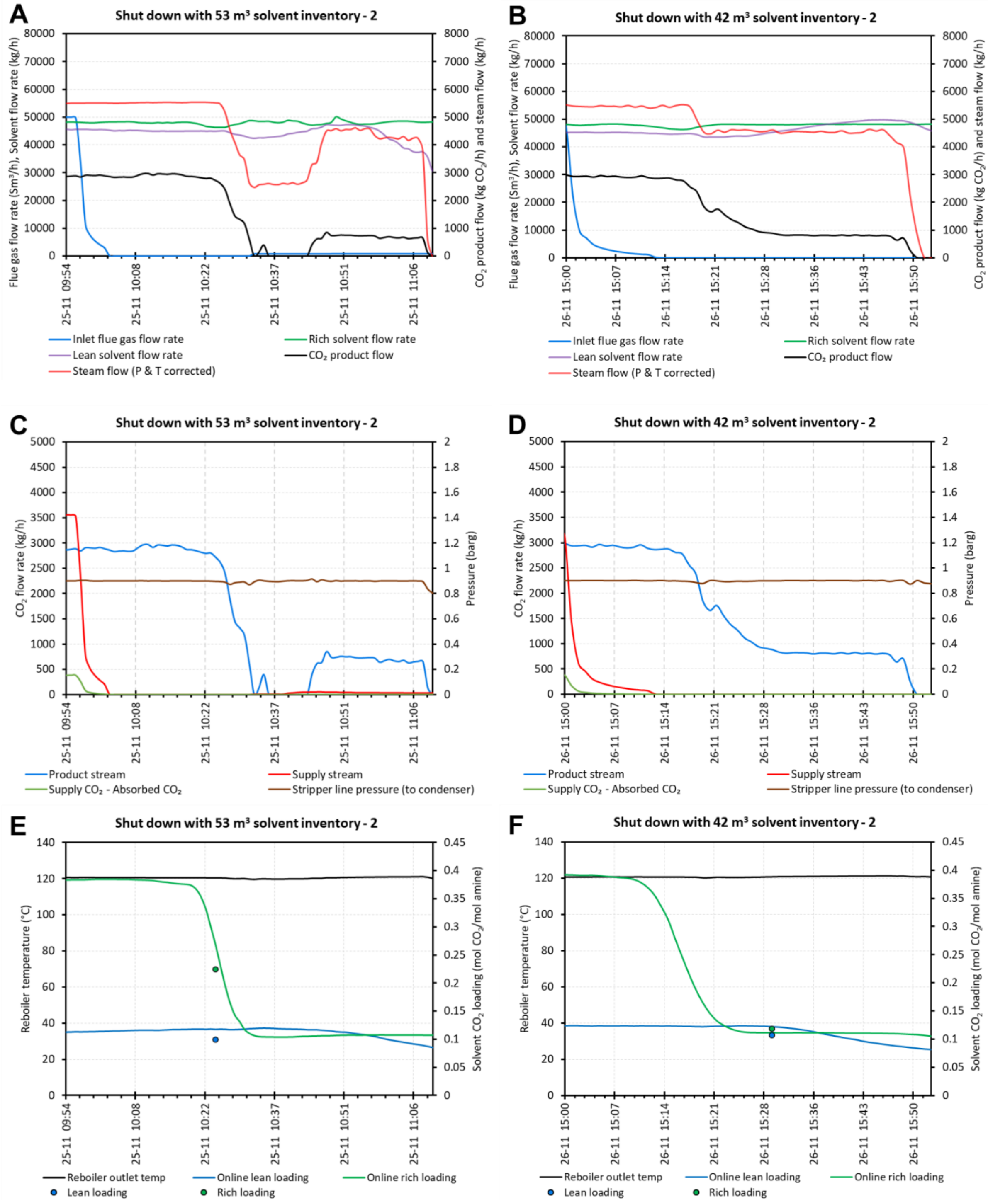

Figure 27: Process changes for the shutdown of the plant using different solvent inventory volumes for SD 53 m^3 (2) and SD 42 m^3 (2) in Table 19, which corresponds to A, C & E and B, D & F, respectively.

3.7.6 Combined performance of start-up and shutdown periods

3.7.6.1 Accounting for CO_2 emissions from an auxiliary boiler

The CO_2 capture plant requires steam for solvent regeneration, supplied from steam extraction between the IP and LP turbines of the power plant steam cycle.[20, 42] Steam extraction from the power plant is possible during steady state operation at full load, but is not possible during start-up and shutdown of the power plant. Alternatively, an auxiliary boiler or dedicated CHP plant could be used to supply steam to the capture plant during periods when steam extraction from the power plant is unavailable. However, the use of an auxiliary boiler or CHP plant will have an associated CO_2 emissions penalty.[q]

In this section, we assume a natural gas or heat/steam emission factor of 50 kg CO_2/GJ[103] to calculate the CO_2 emissions associated with the use of an auxiliary boiler for the following instances:

- Upon start-up of a power plant with CO_2 capture, there is a delay in steam supply which is estimated to be around 20 min for hot start-ups, and 60 min for cold start-ups.[44]
- During shutdown, steam is required to "lean out" the solvent for a period of time. However, as this occurs after the power plant has shut down, the supply of shutdown steam for solvent lean out will likely come from an auxiliary boiler.

The combined performance of start-up (SU) & shutdown (SD) is evaluated using Equations 8 to 13 under the following scenarios:

1) Performance <u>without</u> an auxiliary boiler

Product CO_2 basis

$$\text{SUSD Reboiler duty (MJ/kg CO}_2\text{)} = \frac{\text{SU steam energy (MJ)} + \text{SD steam energy (MJ)}}{\text{SU product CO}_2\text{ (kg)} + \text{SD product CO}_2\text{ (kg)}} \tag{8}$$

$$\text{SUSD CO}_2\text{ capture (\%)} = \frac{\text{SU product CO}_2\text{ (kg)} + \text{SD product CO}_2}{\text{SU supply CO}_2\text{ (kg)} + \text{SD supply CO}_2\text{ (kg)}} \times 100\% \tag{9}$$

Absorbed CO_2 basis

$$\text{SUSD Reboiler duty (MJ/kg CO}_2\text{)} = \frac{\text{SU steam energy (MJ)} + \text{SD steam energy (MJ)}}{\text{SU absorbed CO}_2\text{ (kg)} + \text{SD absorbed CO}_2\text{ (kg)}} \tag{10}$$

$$\text{SUSD CO}_2\text{ capture (\%)} = \frac{\text{SU absorbed CO}_2\text{ (kg)} + \text{SD absorbed CO}_2}{\text{SU supply CO}_2\text{ (kg)} + \text{SD supply CO}_2\text{ (kg)}} \times 100\% \tag{11}$$

2) Performance <u>with</u> an auxiliary boiler for <u>shutdown</u>

Product CO_2 basis

$$\text{SUSD Reboiler duty (MJ/kg CO}_2\text{)} = \frac{\text{SU steam energy (MJ)} + \text{SD steam energy (MJ)}}{\text{SU product CO}_2\text{ (kg)} + \text{SD [product CO}_2\text{ (kg)} - \text{auxiliary boiler CO}_2\text{ (kg)]}} \tag{12}$$

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[q] There will likely be a cost penalty as well, however, the evaluation of cost was outside the scope of this study.

$$\text{SUSD CO}_2\text{ capture (\%)} = \frac{\text{SU product CO}_2\text{ (kg)} + \text{SD [product CO}_2\text{ (kg)} - \text{auxiliary boiler CO}_2\text{ (kg)]}}{\text{SU supply CO}_2\text{ (kg)} + \text{SD supply CO}_2\text{ (kg)}} \times 100\% \quad \textbf{(13)}$$

Absorbed CO_2 basis

$$\text{SUSD Reboiler duty (MJ/kg CO}_2\text{)} = \frac{\text{SU steam energy (MJ)} + \text{SD steam energy (MJ)}}{\text{SU absorbed CO}_2\text{ (kg)} + \text{SD [absorbed CO}_2\text{ (kg)} - \text{auxiliary boiler CO}_2\text{ (kg)]}} \quad \textbf{(14)}$$

$$\text{SUSD CO}_2\text{ capture (\%)} = \frac{\text{SU absorbed CO}_2\text{ (kg)} + \text{SD [absorbed CO}_2\text{ (kg)} - \text{auxiliary boiler CO}_2\text{ (kg)]}}{\text{SU supply CO}_2\text{ (kg)} + \text{SD supply CO}_2\text{ (kg)}} \times 100\% \quad \textbf{(15)}$$

3) Performance <u>with</u> an auxiliary (aux) boiler for <u>start-up and shutdown</u>

Product CO_2 basis

$$\text{SUSD Reboiler duty (MJ/kg CO}_2\text{)} = \frac{\text{SU steam energy (MJ)} + \text{SD steam energy (MJ)}}{\text{SU [product CO}_2\text{ (kg)} - \text{aux boiler CO}_2\text{ (kg)]} + \text{SD [product CO}_2\text{ (kg)} - \text{aux boiler CO}_2\text{ (kg)]}} \quad \textbf{(16)}$$

$$\text{SUSD CO}_2\text{ capture (\%)} = \frac{\text{SU [product CO}_2\text{ (kg)} - \text{aux boiler CO}_2\text{ (kg)]} + \text{SD [product CO}_2\text{ (kg)} - \text{aux boiler CO}_2\text{ (kg)]}}{\text{SU supply CO}_2\text{ (kg)} + \text{SD supply CO}_2\text{ (kg)}} \times 100\% \quad \textbf{(17)}$$

Absorbed CO_2 basis

$$\text{SUSD Reboiler duty (MJ/kg CO}_2\text{)} = \frac{\text{SU steam energy (MJ)} + \text{SD steam energy (MJ)}}{\text{SU [absorbed CO}_2\text{ (kg)} - \text{aux boiler CO}_2\text{ (kg)]} + \text{SD [absorbed CO}_2\text{ (kg)} - \text{aux boiler CO}_2\text{ (kg)]}} \quad \textbf{(18)}$$

$$\text{SUSD CO}_2\text{ capture (\%)} = \frac{\text{SU [absorbed CO}_2\text{ (kg)} - \text{aux boiler CO}_2\text{ (kg)]} + \text{SD[absorbed CO}_2\text{ (kg)} - \text{aux boiler CO}_2\text{ (kg)]}}{\text{SU supply CO}_2\text{ (kg)} + \text{SD supply CO}_2\text{ (kg)}} \times 100\% \quad \textbf{(19)}$$

3.7.6.2 Performance: Combined start-up 82 min and shutdown

The performance characteristics of start-up are different to shutdown as demonstrated in Table 21. The volume of solvent inventory is lean at the beginning of each new start-up. This lean solvent has the capacity to temporarily "store" CO_2 in the system. As the plant reaches steady state, the liquid on the absorber side is CO_2-rich, and CO_2-lean on the stripper side. As the plant transitions into the shutdown phase, leaning out of the solvent to a target loading (the start-up loading) releases a significant amount of product CO_2, i.e., the "stored" CO_2 in the system. The cumulative amounts of CO_2 corresponding to periods of 82 min start-up with the relevant shutdown and auxiliary boiler emissions are presented in Table 20. The capture performance of start-up and shutdown was evaluated separately in sections 3.7.4 and 3.7.5

(summarised in Tables 21 and 25). However, in this section, we evaluate the **combined** start-up (SU) and shutdown (SD) performance on a product CO_2 basis (Table 22) and absorbed CO_2 basis (Table 23), illustrating the impact of one start-up and shutdown cycle.

Table 20: Cumulative amount of CO_2 over 82 min in the supply and product streams, and the absorbed CO_2. The difference between supply and absorbed CO_2 corresponds to the cumulative amount of residual CO_2 emitted over 82 min. The CO_2 emissions for an auxiliary boiler to supply steam energy is based on the assumptions that a cold start-up requires the auxiliary boiler for 60 min and hot start-up requires it for 20 min. Auxiliary boiler emissions assumed an emissions factor of 50 kg CO_2/GJ. For hot SU 42 m^3 20 min delayed steam, no steam was provided for 20 min, thus auxiliary boiler emissions are zero.

82 min start-up (SU) and shut-down (SD) varied duration	Cumulative amount of CO_2 over time period (kg)					Cumulative CO_2 emissions associated with SU/SD steam energy (kg) = auxiliary boiler CO_2
	Supply CO_2	Product CO_2	Absorbed CO_2	Supply – Absorbed	Supply – Product	
Cold SU 53 m^3	4197.7	1278.6	3266.1	931.6	2919.1	**579.0**
Cold SU 42 m^3	4271.4	1447.6	3190.6	1080.8	2823.7	**539.0**
Hot SU 53 m^3	4559.1	2396.3	4116.3	442.8	2162.8	**132.7**
Hot SU 42 m^3	4105.5	2628.2	3692.9	412.7	1477.4	**102.7**
Hot SU 42 m^3 delayed steam	4280.0	1514.5	3224.6	1055.4	2765.5	**0.0**
SD 53 m^3	242.2	2273.9	204.2	38.0	-2031.6	**640.5**
SD 42 m^3	302.5	2037.4	272.2	30.3	-1327.4	**488.9**
SD 53 m^3	179.4	1506.8	160.1	19.3	-1330.8	**472.6**
SD 42 m^3	145.3	1476.1	129.8	15.6	-1329.1	**480.8**

Table 21: Cumulative CO_2 capture performance of start-up (82 min) and shutdown scenarios, without auxiliary boiler emissions.

	Product CO_2 basis		Absorbed CO_2 basis	
82 min start-up (SU), duration of shutdown (SD) varies	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)
Cold SU 53 m^3	12.64	30.5	4.95	77.8
Cold SU 42 m^3	10.64	33.9	4.83	74.7
Hot SU 53 m^3	6.46	52.6	3.76	90.3
Hot SU 42 m^3	5.66	64.0	4.03	90.0
Hot SU 42 m^3 delayed steam	5.91	35.4	2.77	75.3
SD 53 m^3	5.63	939	62.73	84.3
SD 42 m^3	6.49	840	61.07	89.2
SD 42 m^3	6.40	1016	72.84	89.3

Combined SUSD: Comparison of product CO_2 basis vs absorbed CO_2 basis

One main observation of the combined SUSD performance (Tables 22 and 23) is that the CO_2 capture rate on a product CO_2 basis is generally higher compared to absorbed basis – this is the case for most of the SUSD scenarios. The exception being the scenario with cold SU 42 m^3 & SD, where the absorbed basis capture rate is higher than the product basis. The observed trends of the two CO_2 capture rate metrics are driven by the different proportions of supply CO_2, absorbed CO_2 and product CO_2.

The capture rate metric used to benchmark the different scenarios needs to be representative of both the start-up and shutdown phases of operation. To explain the difference between the capture rate methods, we will first consider the performance of the cold start-up and shutdown with 53 m^3 inventory individually. As shown in Table 20:

- Cold start-up over 82 min had 1279 kg product CO_2, 3266 kg absorbed and 4198 kg supply.
- Shutdown with the same inventory generated significantly more product CO_2 than absorbed CO_2 and had very low supply CO_2, i.e., 2274 kg product, 204 kg absorbed and 242 kg supply.

For the start-up period only, the capture rate on an absorbed CO_2 basis is much higher (77.8%) than the product basis (30.5%). In contrast, the capture rate on an absorbed basis for shutdown alone was 84.3%, whereas the product basis capture was 939% owing to the product CO_2 being over 9 times more than the supply CO_2. Importantly, there is very low supply CO_2 during shutdown compared to the very high amounts of product CO_2. When combining start-up performance with shutdown, the low amounts of product CO_2 during start-up is counterbalanced by the very high amounts of product CO_2 during shutdown. Although the product basis capture rate for start-up alone was only 30.5%, the combined SUSD capture rate was 80.0% (i.e., Table 22, cold SU 53 m^3 & SD without an auxiliary boiler). Therefore, the product basis capture rate can be used to benchmark the combined SUSD scenarios.

In contrast, capture rate on an absorbed basis is an unsuitable metric for combined SUSD performance. Owing to the small supply CO_2, shutdown has a very small amount of absorbed CO_2, hence, the combined SUSD capture rate on an absorbed basis is similar to that of start-up alone:

- Cold start-up alone with 53 m^3 inventory captures 77.8% on an absorbed basis,
- Cold SU & SD with 53 m^3 inventory captures 78.2% on an absorbed basis.

Similarly, for 42 m^3 solvent inventory, the capture rate on an absorbed basis of the combined cold SU & SD is almost the same as cold start-up alone:

- Cold start-up alone with 42 m^3 inventory captures 74.7% absorbed basis,
- Cold SU & SD with 42 m^3 inventory capture 75.2% absorbed basis.

As demonstrated here, the two capture rate metrics (absorbed vs product CO_2) serve different purposes and should be used for specific phases of operation, e.g., just for start-up alone, or combined SUSD performance. The recommended cumulative CO_2 capture rate metrics for:

- **Start-up alone or shutdown alone:** should consider both product CO_2 and absorbed CO_2 metrics of capture rate; both relevant to demonstrate the desorption/stripper performance and residual emissions (exiting absorber), respectively.
- **Combined start-up and shutdown:** capture rate on a product basis provides an indication of the stripper side performance and is more relevant to shutdown. Thus, capture rate on a product basis is a more meaningful metric for benchmarking of the SUSD scenarios.

As this section is focused on benchmarking the *combined* SUSD scenarios, the cumulative product basis capture rate is the preferred performance metric.

Table 22: Cumulative CO_2 capture performance on a ***product CO_2 basis*** *for start-up over 82 minutes combined with the shutdown. The use of an auxiliary boiler may result in additional CO_2 emissions (refer to Table 20). The cumulative specific reboiler duty and cumulative CO_2 captured are calculated assuming start-up and shutdown with and without an auxiliary boiler. As there were two SD tests using 42 m^3, both a mean value and a range in brackets are provided*

Product CO_2 basis	Without an auxiliary boiler		With an auxiliary boiler for shutdown*		With an auxiliary boiler for SU & SD*	
82 min start-up (SU) combined with shutdown (SD)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)
Cold SU 53 m^3 & SD	**8.15**	**80.0**	**9.95**	**65.6**	**12.42**	**52.5**
Cold SU 42 m^3 & SD	**8.51** (8.50–8.53)	**66.3** (66.2–66.4)	**10.18** (10.14–10.22)	**55.5** (55.4–55.5)	**13.04** (13.00–13.07)	**43.3** (43.3–43.3)
Hot SU 53 m^3 & SD	**6.06**	**97.3**	**7.02**	**83.9**	**7.26**	**81.2**
Hot SU 42 m^3 & SD	**5.94** (5.93–5.96)	**96.5** (96.5–96.6)	**6.73** (6.70–6.76)	**85.3** (85.1–85.4)	**6.93** (6.89–6.96)	**82.9** (82.7–83.0)
Hot SU 42 m^3 delayed steam & SD	**6.17** (6.15–6.20)	**67.7** (67.6–67.8)	**7.35** (7.31–7.39)	**56.8** (56.8–56.9)	**7.35** (7.31–7.39)	**56.8** (56.8–56.9)

*Assumes that a cold start-up requires the auxiliary boiler for 60 min, hot start-up requires it for 20 min, and the auxiliary boiler is used for the duration of shutdown.

Table 23: Cumulative CO_2 capture performance on an ***absorbed CO_2 basis*** *for start-up over 82 minutes combined with the shutdown. The use of an auxiliary boiler may result in additional CO_2 emissions (refer to Table 20). The cumulative specific reboiler duty and cumulative CO_2 captured are calculated assuming start-up and shutdown with and without an auxiliary boiler. As there were two SD tests using 42 m^3, both a mean value and a range in brackets are provided*

Absorbed CO_2 basis	Without an auxiliary boiler		With an auxiliary boiler for shutdown*		With an auxiliary boiler for SU & SD*	
82 min start-up (SU) combined with shutdown (SD)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)
Cold SU 53 m^3 & SD	**8.35**	**78.2**	**10.24**	**63.7**	**12.87**	**50.7**
Cold SU 42 m^3 & SD	**7.50** (7.49–7.52)	**75.2** (75.2–75.3)	**8.77** (8.73–8.80)	**64.4** (64.3–64.5)	**10.81** (10.77–10.84)	**52.2** (52.2–52.3)
Hot SU 53 m^3 & SD	**6.55**	**90.0.**	**7.69**	**76.6**	**7.97**	**73.9**
Hot SU 42 m^3 & SD	**6.38** (6.36–6.40)	**89.9** (89.9–89.9)	**7.30** (7.26–7.33)	**78.7** (78.5–78.8)	**7.53** (7.49–7.56)	**76.3** (76.1–76.4)
Hot SU 42 m^3 delayed steam & SD	**5.51** (5.48–5.53)	**75.9** (75.8–75.9)	**6.42** (6.38–6.47)	**65.0** (64.9–65.1)	**6.42** (6.38–6.47)	**65.0** (64.9–65.1)

Effect of solvent inventory volume and auxiliary boiler emissions

The capture rate on a product basis for start-up alone is relatively low. The cumulative capture rate improves considerable when evaluating start-up *combined* with shutdown. As shown, using the 42 m^3 inventory for a cold start-up alone has a capture rate on a product basis of 33.9% (Table 21), whereas combined SU & SD performance captures 66.3% on a product basis (Table 22). For the 53 m^3 system, the capture rate (product basis) during cold start-up alone was only 30.5%, whereas combined cold SU & SD achieved 80.0% capture rate (product basis). The degree of capture rate improvement is much more significant for the larger 53 m^3 inventory system compared to 42 m^3. This is due to the lower amount of product CO_2 recovered during shutdown with 42 m^3 of inventory (1445 kg product CO_2) compared to 53 m^3 (2274 kg product CO_2). A similar degree of capture rate improvement is observed when combining hot start-up with shutdown, with the 53 m^3 system exhibiting a higher degree of capture rate increase.

The auxiliary boiler CO_2 emissions can have a major impact on the start-up and shutdown performance, increasing the cumulative specific reboiler duty and reducing the cumulative CO_2 capture rate. The degree of impact will vary with the type of start-up (hot vs cold) and the solvent inventory volume (Table 22). Depending on the availability of steam from the power plant, the periods requiring an auxiliary boiler can vary and may be needed for shutdown only or both start-up and shutdown. For example, the cold start-up and shutdown case using 53 m^3 of inventory shows that the use of an auxiliary boiler for start-up (i.e., 60 min) and shutdown reduces the cumulative CO_2 capture rate from 80.0% to 52.5%, and increases specific reboiler duty from 8.15 to 12.42 GJ/t_{CO2} product basis. By accounting for the CO_2 emissions from the auxiliary boiler, the overall amount of CO_2 captured is reduced, which decreases the cumulative CO_2 capture rate and increases the specific reboiler duty (Equations 8 to 13). The degree of performance reduction associated with the auxiliary boiler is smaller in the case of hot start-ups. Accounting for auxiliary boiler emissions reduces product basis capture rate by 13.7–16.1% in the case of hot start-ups, whereas cold start-up capture rate reduces by 23.0–27.5%.

For cold start-ups with shutdown, increasing solvent inventory from 42 m^3 to 53 m^3 increased the CO_2 capture rate (product basis) by 9.3–13.7% points, depending on the auxiliary boiler calculation scenario (Table 22). The larger solvent inventory also provided a small reduction in specific reboiler duty. For hot start-up with shutdown, the increase in solvent inventory from 42 to 53 m^3 has an almost negligible impact on capture performance. The auxiliary boiler CO_2 emissions, which are a function of solvent volume and start-up type, have a greater impact on the overall capture performance. Once auxiliary boiler use is accounted for, hot start-up and shutdown with the smaller 42 m^3 solvent inventory is observed to have *slightly* better performance.

Effect of delayed steam availability

As expected, delaying the availability of steam by 20 min during start-up can be detrimental to the CO_2 capture performance. Although the hot start-up with delayed steam case has the lowest specific reboiler duty on an absorbed basis, it has the higher reboiler duty on a product basis. Importantly, the cumulative CO_2 capture rate (product basis) reduced significantly by 26.0–28.9% points compared to the normal hot start-up using the same solvent inventory volume. Of all the cases studied, the hot start-up with delayed steam has the lowest cumulative CO_2 capture rate. The highest capture rates are achieved by cases using hot start-up or the larger solvent inventory 53 m^3.

3.7.6.3 Performance: Start-up 200 min and shutdown together

The analysis over 200 min demonstrates the effect of the steady state period on the overall capture performance. Also, this will provide an indication of how start-up and shutdown improvements will impact the performance when considering time periods closer to normal operation, i.e., a complete cycle of start-up, stabilisation, steady state to shutdown.

The cumulative amounts of CO_2 corresponding to 200 min of start-up with the relevant shutdown and auxiliary boiler emissions are provided in Table 24. These amounts of CO_2 were used to evaluate the combined SUSD cumulative performance on a product and absorbed CO_2 basis (Tables 26 and 27, respectively). The absorbed basis capture rate for start-up alone (Table 25) and combined SUSD (Table 27) are almost the same value. Therefore, as discussed previously, the product basis cumulative capture rate should be used to benchmark the combined SUSD performance.

At steady state operation, the average online CO_2 capture rate was 83–88%. When considering the longer 200 min start-up analysis period, the cumulative CO_2 capture rate moves closer to the online capture rate at steady state. Compared to the 82 min SUSD results, the longer 200 min timeframe for SUSD analysis and lowers the cumulative specific reboiler duty significantly. Without an auxiliary boiler, the specific reboiler duty across the 200 min SU with SD scenarios ranged between 4.8–5.6 MJ/kg CO_2 (product basis), whereas the 82 min SU with SD was 5.9–8.5 MJ/kg CO_2 (product basis).

Whilst the absolute numbers of the 200 min results may differ, the general trends (e.g., 53 m^3 vs 42 m^3, and cold vs hot start-up vs delayed steam) are essentially the same as the 82 min results. For example, the larger solvent inventory improves the performance of cold start-ups but may reduce performance during hot start-ups. The main difference is that the CO_2 capture performance over the 200 min is influenced by steady state data, thus, leading to lower specific reboiler duty and cumulative CO_2 capture rates closer to steady state values, i.e., Table 26.

Evidently, the impact of the auxiliary boiler CO_2 emissions will diminish with longer analysis periods (e.g., 82 min vs 200 min). Accounting for auxiliary boiler emissions decreased the capture rate for hot start-ups by 5.4–6.5%, whereas capture of the cold start-ups decreased by 9.2–11.1%, i.e., only half the percentage reduction compared to the 82 min SUSD analysis.

Table 24: Cumulative amount of CO_2 over 200 min in the supply and product streams, and the absorbed CO_2. The difference between supply and absorbed CO_2 corresponds to the cumulative amount of residual CO_2 emitted over 200 min. The CO_2 emissions for an auxiliary boiler to supply steam energy is based on the assumptions that a cold start-up requires the auxiliary boiler for 60 min and hot start-up requires it for 20 min. Auxiliary boiler emissions assumed an emissions factor of 50 kg CO_2/GJ. For hot SU 42 m^3 20 min delayed steam, no steam was provided for 20 min, thus auxiliary boiler emissions are zero.

200 min start-up (SU) and shut-down (SD) varied duration	Cumulative amount of CO_2 over time period (kg)					Cumulative CO_2 emissions associated with SU/SD steam energy (kg) = auxiliary boiler CO_2
	Supply CO_2	Product CO_2	Absorbed CO_2	Supply – Absorbed	Supply – Product	
Cold SU 53 m^3	10779.9	7302.0	8698.1	2081.8	3477.9	**579.0**
Cold SU 42 m^3	10888.4	7473.5	8530.5	2357.9	3414.9	**539.0**
Hot SU 53 m^3	11595.7	8209.1	10022.2	1573.6	3386.6	**132.7**
Hot SU 42 m^3	10622.2	8358.6	9394.8	1227.4	2263.6	**102.7**
Hot SU 42 m^3 delayed steam	10985.3	7553.3	8656.6	2328.7	3432.0	**0.0**
SD 53 m^3	242.2	2273.9	204.2	38.0	-2031.6	**640.5**
SD 42 m^3	302.5	2037.4	272.2	30.3	-1327.4	**488.9**
SD 53 m^3	179.4	1506.8	160.1	19.3	-1330.8	**472.6**
SD 42 m^3	145.3	1476.1	129.8	15.6	-1329.1	**480.8**

Table 25: Cumulative CO_2 capture performance of start-up (200 min) and shutdown scenarios, without auxiliary boiler emissions.

	Product CO_2 basis		Absorbed CO_2 basis	
200 min start-up (SU), duration of shutdown (SD) varies	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)
Cold SU 53 m^3	5.58	67.7	4.68	80.7
Cold SU 42 m^3	5.33	68.6	4.67	78.3
Hot SU 53 m^3	4.85	70.8	3.97	86.4
Hot SU 42 m^3	4.70	78.7	4.18	88.5
Hot SU 42 m^3 delayed steam	4.46	68.8	3.89	78.8
SD 53 m^3	5.63	939	62.73	84.3
SD 42 m^3	6.49	840	61.07	89.2
SD 42 m^3	6.40	1016	72.84	89.3

Table 26: Cumulative CO_2 capture performance on a ***product CO_2 basis*** *for start-up over 200 minutes combined with the shutdown. The use of an auxiliary boiler may result in additional CO_2 emissions (refer to Table 24). The cumulative specific reboiler duty and cumulative CO_2 captured are calculated assuming start-up and shutdown (i) without an auxiliary boiler, (ii) with an auxiliary boiler for shutdown, and (iii) with an auxiliary boiler for both start-up and shutdown. As there were two SD tests using 42 m^3, both a mean value and a range in brackets are provided.*

Product CO_2 basis	Without an auxiliary boiler		With an auxiliary boiler for shutdown*		With an auxiliary boiler for SU & SD*	
200 min start-up (SU) combined with shutdown (SD)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)
Cold SU 53 m^3 & SD	**5.59**	**86.9**	**5.99**	**81.1**	**6.41**	**75.8**
Cold SU 42 m^3 & SD	**5.52** (5.51–5.53)	**81.1** (81.1–81.1)	**5.83** (5.82–5.85)	**76.8** (76.7–76.8)	**6.23** (6.21–6.24)	**71.9** (71.9–71.9)
Hot SU 53 m^3 & SD	**5.02**	**88.6**	**5.35**	**83.1**	**5.42**	**82.02**
Hot SU 42 m^3 & SD	**4.97** (4.96–4.97)	**91.3** (91.3–91.3)	**5.22** (5.21–5.23)	**86.9** (86.8–87.0)	**5.28** (5.26–5.29)	**85.9** (85.9–86.0)
Hot SU 42 m^3 delayed steam & SD	**4.78** (4.77–4.79)	**81.1** (81.1–81.2)	**5.05** (5.04–5.07)	**76.8** (76.8–76.9)	**5.05** (5.04–5.07)	**76.8** (76.8–76.9)

*Assumes that a cold start-up requires the auxiliary boiler for 60 min, hot start-up requires it for 20 min, and the auxiliary boiler is used for the duration of shutdown.

Table 27: Cumulative CO_2 capture performance on an ***absorbed CO_2 basis*** *for start-up over 200 minutes combined with the shutdown. The use of an auxiliary boiler may result in additional CO_2 emissions (refer to Table 24). The cumulative specific reboiler duty and cumulative CO_2 captured are calculated assuming start-up and shutdown (i) without an auxiliary boiler, (ii) with an auxiliary boiler for shutdown, and (iii) with an auxiliary boiler for both start-up and shutdown. As there were two SD tests using 42 m^3, both a mean value and a range in brackets are provided.*

Absorbed CO_2 basis	Without an auxiliary boiler		With an auxiliary boiler for shutdown*		With an auxiliary boiler for SU & SD*	
200 min start-up (SU) combined with shutdown (SD)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative specific reboiler duty (MJ/kg CO_2)	Cumulative CO_2 captured (%)
Cold SU 53 m^3 & SD	**6.01**	**80.8**	**6.48**	**75.0**	**6.97**	**69.7**
Cold SU 42 m^3 & SD	**5.70** (5.69–5.71)	**78.5** (78.5–78.5)	**6.04** (6.02–6.05)	**74.2** (74.1–74.2)	**6.46** (6.45–6.48)	**69.3** (69.2–69.3)
Hot SU 53 m^3 & SD	**5.15**	**86.4**	**5.49**	**81.0**	**5.57**	**79.9**
Hot SU 42 m^3 & SD	**5.13** (5.12–5.14)	**88.5** (88.5–88.5)	**5.40** (5.39–5.41)	**84.0** (83.9–84.1)	**5.46** (5.45–5.48)	**83.1** (83.0–83.1)
Hot SU 42 m^3 delayed steam & SD	**4.92** (4.91–4.93)	**79.0** (78.9–79.0)	**5.20** (5.19–5.22)	**74.6** (74.6–74.7)	**5.20** (5.19–5.22)	**74.6** (74.6–74.7)

*Assumes that a cold start-up requires the auxiliary boiler for 60 min, hot start-up requires it for 20 min, and the auxiliary boiler is used for the duration of shutdown.

3.7.7 Exploring strategies to improve SUSD performance

The shutdown performance is a function of the solvent inventory and the target CO_2 loading (set for the solvent leaning out step). The process operating decisions for the shutdown procedure are typically dictated by the performance requirements of start-up and steady state (e.g., need to achieve a certain capture rate). As shown in Table 21, depending on the type of start-up, the capture rates on a product CO_2 basis ranged between 30.5–64.0%, whereas shutdown scenarios achieved 84.3–90.0% (absorbed CO_2 basis) and has very low residual emissions. Given that the lowest cumulative capture rates occur during the initial start-up phase, there is strong potential for further performance improvement during the start-up phase. Hence, the development of strategies that focus on improving **start-up** capture performance should be the key priority.

The next section with discuss different strategies that can be used to improve the SUSD performance of an amine-based CO_2 capture plant. The process strategies include optimising process operating conditions and low/high preheating of the plant during start-up.

3.8 Effect of preheating & operating conditions on start-up

In June 2020, tests simulating “improved” start-up and shutdown in the context of CCS with gas-CCGT were conducted at the TCM CO_2 capture plant (Table 28). Constant solvent inventory of 45 m^3 was used for four different start-up and shutdown tests; results provided in Appendix D. As these tests used a similar shutdown procedure with the November 2020 tests in the previous section, we will only focus on examining the start-up results for the June 2020-tests, which show the effect of preheating on start-up performance.

Similar to the method used in Section 3.7.4.2, we select the greatest t_{SS} of 85 min to conduct the cumulative CO_2 capture performance for each test. Additionally, the performance over 200 minutes will also be evaluated to demonstrate whether the impact of start-up changes will be significant enough to impact steady state performance.

Table 28: Time when the CO_2 product flow rate begins (t_{SU}) and when steady state conditions are reached (t_{SS}) after the flue gas flow starts in minutes. These tests were carried out during the June 2020 campaign using CESAR-1 and had slightly different starting conditions. Average solvent concentration based on laboratory analysis of the solvent samples: 25.5 wt% AMP 10.5 wt% PZ.

Label	Start-up type	Conditions	Start-up time: time when CO_2 product flow starts, t_{SU} (min)	Time when CO_2 product flow reaches steady state, t_{SS} (min)
Cold SU (1)	Cold start-up with preheat steam flow of 2500 kg/h	**9 June:** Preheat using 45 m^3 inventory Start-up loading: 0.07–0.08 mol CO_2/mol amine	20	70
Cold SU (2)	Cold start-up with preheat steam flow of 2500 kg/h, vol adjust	**12 June:** Preheat, adjustment from 41.5 to 45 m^3 inventory Due to the increased volume, the average solvent concentration for this test reduced down to 23.0 wt% AMP 9.4 wt% PZ Start-up loading 0.05 mol CO_2/mol amine	10	85
Hot SU (1)	Hot start-up with preheat steam flow of 2500 kg/h	**10 June:** Preheat using 45 m^3 inventory Start-up loading 0.10 mol CO_2/mol amine	15	60
Hot SU (2)	Hot start-up with high preheat steam flow of 5000 kg/h	**11 June:** High preheat start-up using 45 m^3 inventory Start-up loading 0.05–0.07 mol CO_2/mol amine	15	70

3.8.1 Impact of operating conditions on start-up capture performance

The main difference between the June and November 2020 test campaigns is the timing of steam availability. In November 2020, the start-up tests introduced steam at the same time as the flue gas flow rate, with one demonstrating a 20 min delay in steam – these tests are considered “normal” start-ups. In contrast, the June 2020 test results in this section demonstrate the effect of supplying steam ***before*** flue gas flow starts, which demonstrates the effect of "preheating", e.g., with an auxiliary boiler. Unlike the November 2020 tests where the amine pumps remained on for the entire week, the start-up protocol for the June 2020 tests also involved start-up of the amine pumps. Consequently, the amine flow rates fluctuate during the initial period of start-up as the liquid flow stabilises (Figures 28 and 29).

As shown in Table 11, the plant conditions such as amine flow rates, amine composition, start-up CO_2 loading and inventory volume for the June 2020 tests differ from the November tests. These process parameters will have a direct impact on the CO_2 capture of the process. A combination of factors could be contributing to the difference between start-up performance across the June and November tests. Therefore, it would be difficult to attribute the difference in performance to a single factor. However, within the set of June tests, it is possible to observe the impact of preheating on the start-up performance (e.g., capture rate, start-up time).

The different operating conditions (e.g., amine concentration and flow rate) are some key contributing factors to the higher capture rates in the June 2020 tests. The solvent used for tests in the previous section had lower concentrations of 24.4 wt% AMP and 8.7 wt% PZ. In contrast, the preheating tests used solvent with slightly higher concentrations of 25.5 wt% AMP and 10.5 wt% PZ, which resulted in a greater proportion of CO_2 being absorbed. This is illustrated through comparing with (B)/(D) of Figure 22 with (E)/(F) of Figure 29, which corresponds to low and high amine concentration, respectively. The system with the higher amine concentration has a smaller difference between the supply CO_2 (red line) and absorbed CO_2 (yellow line). Another factor that could increase the amount of CO_2 captured is the higher amine flow rate. These two factors resulted in higher steady state online CO_2 capture rates of 92.4–95.5% for the preheating tests, whereas the steady state capture rates for the November tests reached 83–88%. These operating parameters will mainly influence the steady state capture performance, and the rate of change in the data. Consequently, this impacts the comparability of the June 2020 cumulative capture rates against the November dataset. Thus, we focus on observing the difference in dynamic behaviour rather than making a quantitative comparison.

As shown by Figures 28 and 29, the start-ups with preheating have distinctively different dynamic behaviour compared to "normal" start-up (e.g., Figure 18). For the preheating tests in both the cold and hot start-ups cases, high online CO_2 capture rates of 98.8–99.3% were achieved immediately after the flue gas flow begins, owing to the low start-up solvent loading (0.05–0.10 mol CO_2/ mol amine). This behaviour was also observed in tests without preheating. However, tests that employed preheating allowed the CO_2 capture rate to remain constant without any decline, this is due to the reboiler being near the set-point temperature when flue gas is introduced. In contrast, without preheating, the online CO_2 capture rate would decline gradually before increasing again, e.g., Figure 18 (C) & (D).

As shown in Tables 29 and 30, regardless of the time period, the preheating tests achieved significantly higher cumulative CO_2 capture rates of 95–99% for *absorbed CO_2 basis* compared to the November tests (75–90% in Tables 17 & 18). This can be attributed to the combination of preheating before start-up, which avoids the decline in online capture rate, as well as using process conditions that achieve higher capture rates, e.g., higher amine concentration and amine flow rate.

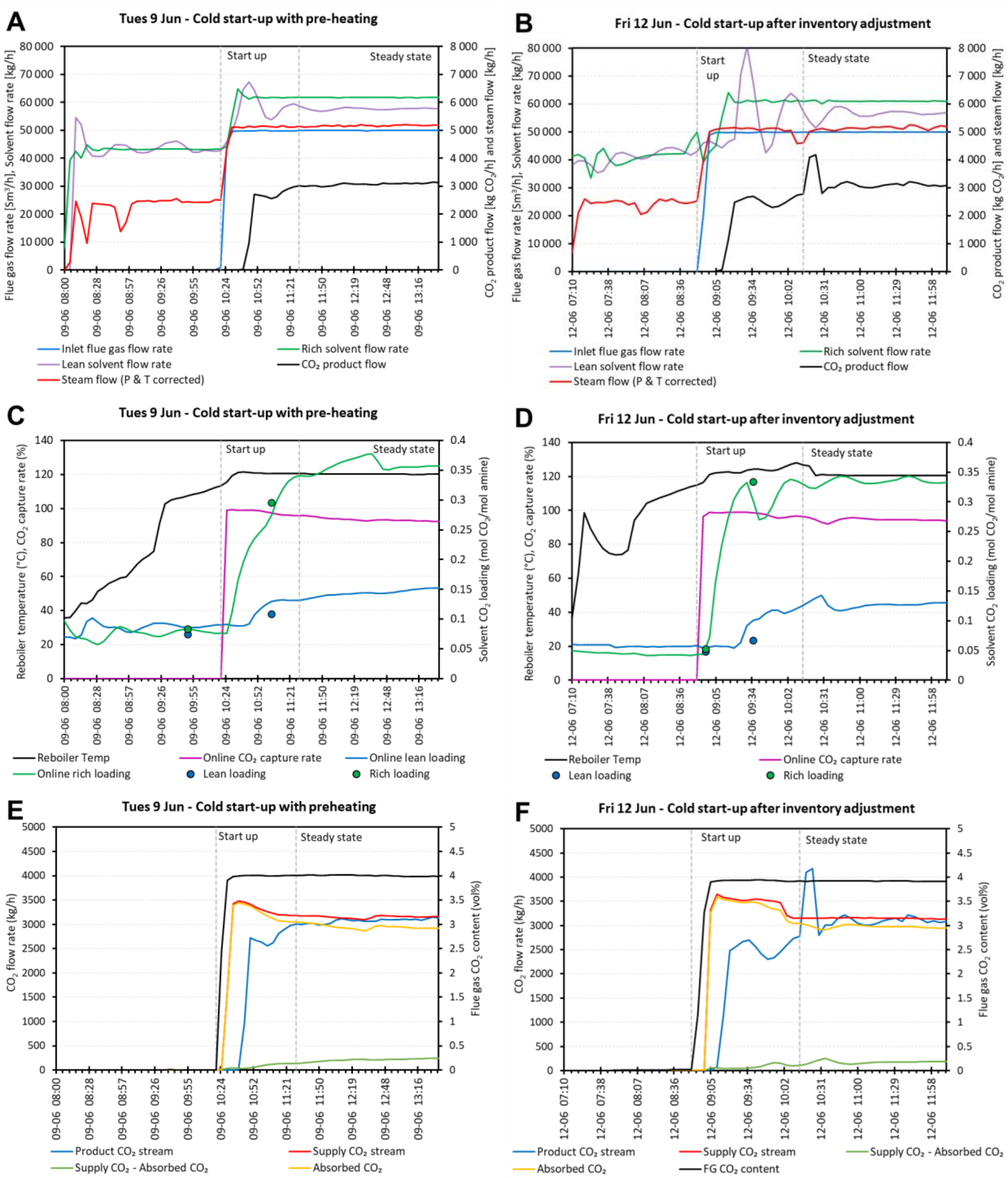
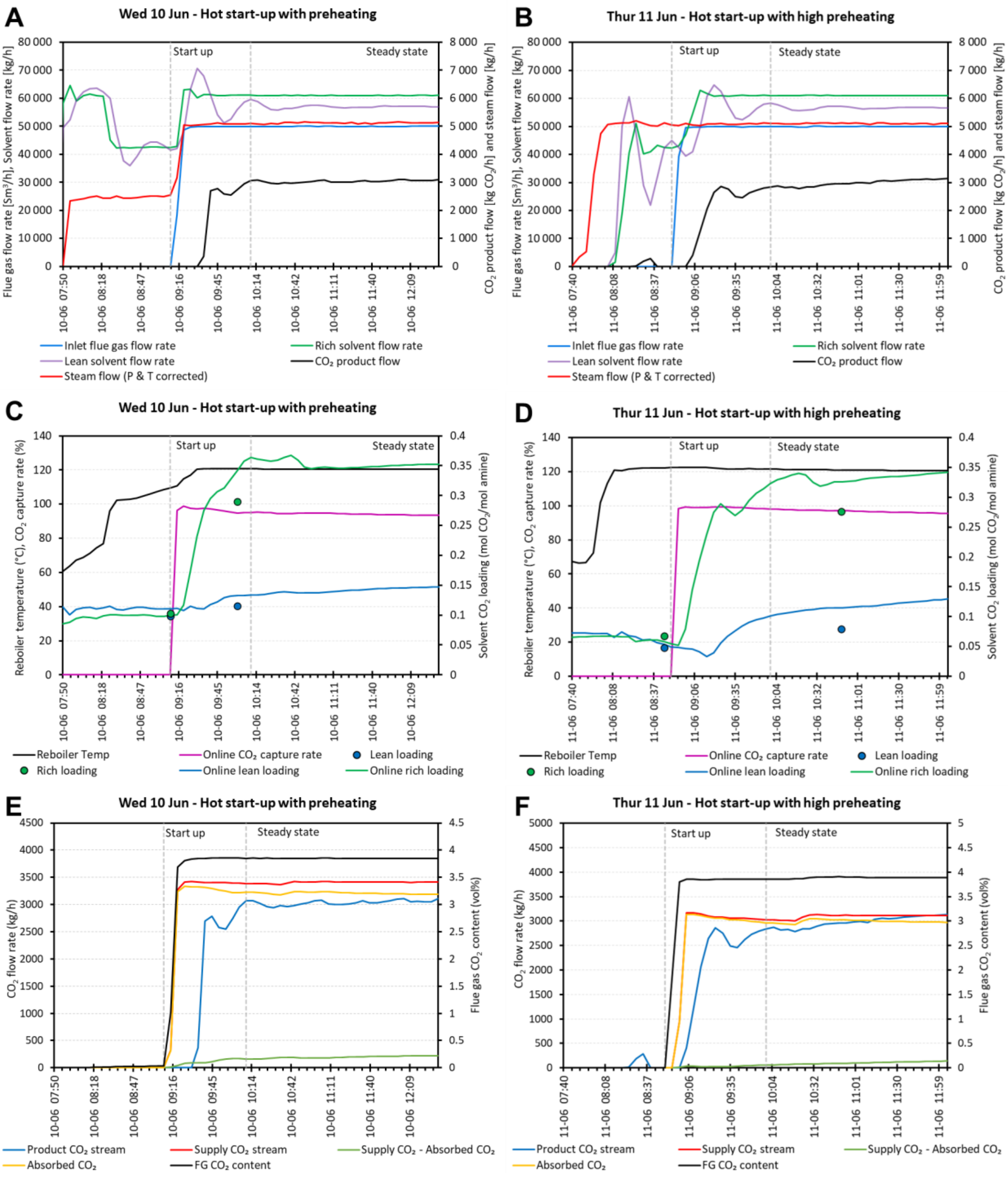


Figure 28: Process changes for cold start-up using 45 m^3 solvent inventory with preheating, i.e., starting the steam flow before the flue gas. The period shown begins at the time steam flow starts plus an additional 200 minutes after the flue gas enters. The cold start-up on 9 June 2020 (A, C & E) had constant inventory volume. However, the cold start-up on 12 June 2020 (B, D & F) started with 41.5 m^3 of solvent inventory, and water was gradually added to the system until the inventory was 45 m^3 – this diluted the Ceasar-1 concentration slightly.



A Wed 10 Jun - Hot start-up with preheating

B Thur 11 Jun - Hot start-up with high preheating

C Wed 10 Jun - Hot start-up with preheating

D Thur 11 Jun - Hot start-up with high preheating

E Wed 10 Jun - Hot start-up with preheating

F Thur 11 Jun - Hot start-up with high preheating

Figure 29: Process changes for hot start-up using 45 m^3 solvent inventory with preheating, i.e., starting the steam flow before the flue gas. The period shown begins at the time steam flow starts plus an additional 200 minute after the flue gas enters. The hot start-up on 10 June 2020 (A, C & E) started with 2500 kg/h steam flow for preheating. The hot start-up on 11 June 2020 (B, D & F) started with 5000 kg/h steam flow for preheating, i.e., referred to as the "hot start-up with high preheat".

Table 29: Effect of preheating on start-up performance, refer to Table 28 for start-up conditions. The cumulative capture rate and specific reboiler duty (SRD) over 85 minutes is calculated on a product CO_2 basis and absorbed CO_2 basis. The cumulative residual CO_2 emissions is the difference between the supply CO_2 and the absorbed CO_2. Preheat auxiliary boiler emissions assumed an emissions factor of 50 kg CO_2/GJ.

Start-up conditions with preheating	Inlet FG CO_2 conc vol%	Cumulative CO_2 over preheat time + 85 min after flue gas flow starts (kg)				Total steam energy (preheat + SU) (MJ)	Preheat steam energy, e.g., from auxiliary boiler (MJ)	Cumulative preheating CO_2 emissions (kg)	**Product CO_2 basis**		**Absorbed CO_2 basis**		**Absorbed CO_2 basis, accounting preheating CO_2 emissions**	
		Supply CO_2	Product CO_2	Absorbed CO_2	Supply – Absorbed				Cumulative SRD (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative SRD (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative SRD (MJ/kg CO_2)	Cumulative CO_2 captured (%)
Cold SU (1)	4.0	3841.2	2532.4	3741.1	100.1	27110.8	11568.1	578.4	10.71	65.9	7.25	97.4	8.57	82.3
Cold SU (2)	3.9	4186.7	2534.9	4086.9	99.7	25429.4	9694.0	484.7	10.03	60.6	6.22	97.6	7.06	86.0
Hot SU (1)	3.8	4405.3	2768.6	4229.9	175.4	23174.5	7493.5	374.7	8.37	62.9	5.48	96.0	6.01	87.5
Hot SU (2)	3.9	3543.1	2726.8	3499.4	43.7	26299.4	10053.4	502.7	9.64	77.0	7.52	98.8	8.78	84.6
Hot SU (2) corrected preheat time	3.9	3543.1	2726.8	3499.4	43.7	19532.0	3285.9	164.3	7.16	77.0	5.58	98.8	5.86	94.1

Table 30: Effect of preheating on start-up performance, refer to Table 28 for start-up conditions. The cumulative capture rate and specific reboiler duty (SRD) over 200 minutes is calculated on a product CO_2 basis and absorbed CO_2 basis. The cumulative residual CO_2 emissions is the difference between the supply CO_2 and the absorbed CO_2. Preheat auxiliary boiler emissions assumed an emissions factor of 50 kg CO_2/GJ.

Start-up conditions with preheating	Inlet FG CO_2 conc vol%	Cumulative CO_2 over preheat time + 200 min after flue gas flow starts (kg)				Total steam energy (preheat + SU) (MJ)	Preheat steam energy, e.g., from auxiliary boiler (MJ)	Cumulative preheating CO_2 emissions (kg)	**Product CO_2 basis**		**Absorbed CO_2 basis**		**Absorbed CO_2 basis, accounting preheating CO_2 emissions**	
		Supply CO_2	Product CO_2	Absorbed CO_2	Supply – Absorbed				Cumulative SRD (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative SRD (MJ/kg CO_2)	Cumulative CO_2 captured (%)	Cumulative SRD (MJ/kg CO_2)	Cumulative CO_2 captured (%)
Cold SU (1)	4.0	9877.2	8428.9	9378.4	498.8	49384.3	11568.1	578.4	5.86	85.3	5.27	94.9	5.61	89.1
Cold SU (2)	3.9	10227.5	8607.3	9791.6	435.9	47574.3	9694.0	484.7	5.53	84.2	4.86	95.7	5.11	91.0
Hot SU (1)	3.8	10944.9	8594.8	10385.1	559.8	45186.3	7493.5	374.7	5.26	78.5	4.35	94.9	4.51	91.5
Hot SU (2)	3.9	9490.9	8458.9	9250.0	240.9	48441.1	10053.4	502.7	5.73	89.1	5.24	97.5	5.54	92.2
Hot SU (2) corrected preheat time	3.9	9490.9	8458.9	9250.0	240.9	41673.6	3285.9	164.3	4.93	89.1	4.51	97.5	4.59	95.7

3.8.2 High preheating vs. low preheating

The degree of preheating had a negligible effect on the start-up time. As shown in Table 28, the hot start-up cases with low preheating, Hot SU (1), and high preheating, Hot SU (2), had comparable start-up times (t_{SU}). As discussed earlier, the start-up time, i.e., when CO_2 flow begins, is a function of the solvent circulation time, which in turn, is directly related to the solvent inventory volume and amine flow rate. The June 2020 tests used a higher amine flow rate with a medium inventory volume compared to November, thus, the June tests have shorter start-up times (Table 28 vs. Table 13).

However, there is an observable relationship between the preheating steam flow rate and the time at which the reboiler reaches set-point temperature. The two cold start-ups (Figure 28) and the hot start-up (C in Figure 29) used a lower steam flow rate of 2500 kg/h for preheating, and thus, had a gradual increase in reboiler temperature. Even when the flue gas flow rate started, the reboiler temperature had not quite reached the set-point temperature, i.e., ~120°C. A comparison of the two hot start-up results show that using 2500 kg/h of preheating steam required up to 100 minutes to reach 120.5°C (from 07:50 to 09:30), whereas using 5000 kg/h of steam for preheating reached 121.0°C in 30 minutes (07:40 to 08:10). Increased preheating steam flow appears to provide a higher cumulative CO_2 capture rate on the basis of product CO_2, with capture rate increasing from 63% to 77% for the 85 min start-up calculation, as shown in Table 29. If steady state operation is considered in the calculation (Table 30 and Figure 41), the cumulative product basis capture rate is still 10% higher for the high preheating case compared to low preheating, i.e., 89% and 79%, respectively. In general, the preheating tests resulted in higher cumulative capture rate on a *product basis* (Table 29 and Table 30) compared to tests without preheating (Table 15 and Table 16).

The use of higher preheating rates before start-up of the CO_2 capture plant can be advantageous, especially when considering interactions of the capture plant with downstream processes. It provides the capture plant the ability to supply higher amounts of product CO_2 in a shorter timeframe, which means the capture plant can be more responsive to the requirements of the CO_2 compression and transport system.

3.8.3 Preheating energy requirements & accounting for CO_2 emissions

The Hot SU (2) test with high preheating also had higher the cumulative capture rate on an absorbed CO_2 basis of 99% compared to low preheating (96%). The cold start-up tests both used the same preheating steam flow rate, and thus, had similar cumulative CO_2 capture rates based on absorbed CO_2.

Although the cumulative CO_2 capture rates may improve when preheating is used before start-up, there is an increase in steam energy demand. Steam extraction from the power plant steam cycle will not be available during the preheating phase of the capture plant start-up. Consequently, an auxiliary boiler or CHP plant will be needed to provide steam for preheating, which will incur a CO_2 emissions penalty. Tables 29 and 30 show the start-up performance for the preheating tests, accounting for the CO_2 emissions associated with the preheating energy.

The cumulative CO_2 capture rates based on absorbed CO_2 substantially decrease once the preheating CO_2 emissions have been accounted for, reducing from 96–99% down to 82–88%. Therefore, the value of preheating could diminish when the energy that is used has high carbon intensity. Here, we assumed a natural gas-fired auxiliary boiler, thus, to minimise the residual CO_2 emissions of the system, preheating energy with low carbon intensity should be considered. Whilst the cumulative capture rates for these cases appear low, it is also important to observe the increasing trend in reboiler temperature to see if there was an excess of preheating. If so, the cumulative CO_2 capture performance can be adjusted accordingly.

There was one case of excess preheating. As shown in Figure 29 (D), the reboiler temperature reached set-point relatively quickly, i.e., within 30 minutes after 5000 kg/h of steam was supplied at 07:50. This indicates that the preheating energy supplied before flue gas was introduced between 08:10 and 08:50 was not required, thus representing approximately 40 minutes of *excess preheating*. This reduces the cumulative capture performance. To provide a better representation of the cumulative performance for the high preheating case, i.e., Hot SU (2), the preheating energy and CO_2 emissions were recalculated based on the energy used to get the reboiler temperature to the target set-point (i.e., energy used in the first 30 min), plus the additional 85 minutes of operation after flue gas flow begins. Compared to the low preheating cases, the high preheating test calculated with the adjusted/corrected preheat time has considerably higher cumulative CO_2 capture rate of 94.1% and lower SRD 5.86 MJ/kg CO_2.

The cumulative specific reboiler duties for the normal start-up tests *without preheating* were considerably lower at 3.76–4.95 MJ/ kg CO_2, calculated based on absorbed CO_2 over 82 min. For the start-up tests using preheating, the 85 min cumulative specific reboiler duties based on absorbed CO_2 were between 5.48–7.52 MJ/kg CO_2. The SRD increased slightly once the CO_2 emissions from the auxiliary boiler used for preheating are accounted for.

4 Conclusions

The objective of this study was to examine the potential for performance improvement during start-up and shutdown of CO_2 capture processes in power plants. We conducted a series of start-up and shutdown tests at the TCM CO_2 capture facility in Norway, an industrial-scale absorption plant that captures CO_2 from a natural gas-fired CHP plant. Due to the highly dynamic nature of the start-up and shutdown plant data, a unique analysis method was developed to evaluate SUSD performance for this study. The results have improved our understanding of SUSD behaviour, including the process dynamics and the effects on capture performance. This evaluation helped identify novel operation strategies that can minimise time requirements and CO_2 emissions associated with start-up and shutdown of power plants with CCS.

The evaluation has identified key factors that influence the dynamics and performance of the CO_2 capture plant during start-up and shutdown. We evaluate the performance in terms of time requirements, amine and ammonia emissions, cumulative CO_2 capture rate and the energy consumption. The key factors that were investigated in this study include:

- Flexible operation using an advanced solvent CESAR-1.
- Comparing cold start-up performance with hot start-ups.
- Combined effect of start-up and shutdown on overall performance.
- Effect of using different solvent inventory volumes, 53 m^3 versus 42 m^3.
- Timing of steam availability on start-up time, different tests were conducted to show steam introduced before (i.e., preheating), at same time and delayed steam supply, i.e., steam flow starting after flue gas flow.
- Effect of solvent CO_2 loading on the capture performance during plant start-up.

The tests presented in this report are specific for plant operation with CESAR-1 solvent, which is a blended amine consisting of AMP (26–27 wt%) and PZ (10–13 wt%). Although the absolute numbers of the performance metrics and measurements may differ for power plants and capture plants of different scale or different capture solvents, e.g., MEA, it is expected that the general high-level insights from this work should be applicable to facilities of different scales. Furthermore, over the course of all the tests with CESAR-1, the emissions of amine and ammonia were well below the acceptable thresholds specified by TCM engineers[72] (refer to Section 3.7.1), and thus meets environmental emission standards.[93, 94] Therefore, we do not anticipate any environmental concerns associated with amine or ammonia emissions for CO_2 capture plants using CESAR-1 (i.e., AMP + PZ).

Cold start-ups required twice as much time to reach steady state compared to hot start-ups. A cold start-up with 53 m^3 of inventory requires 82 min to reach steady state, whereas a hot start-up with the same inventory volume only requires 40 min to reach steady state. The use of a larger solvent inventory volume in the system increased the time required for the system to reach steady state after start-up, it also increased the shutdown time. Delaying the steam supply during start-up by a given time period was found to increase the start-up time by that equivalent timeframe. For example, a 20 min delay in steam supply increased the start-up time (t_{SU}) and time to reach steady state (t_{SS}) by ~20 minutes.

The shutdown time is a function of the solvent volume and the steam supply. The shutdown with the larger 53 m^3 solvent inventory required more time as a greater volume of solvent is being regenerated. Consequently, shutdown with the larger inventory also required more steam energy on a MJ basis to lean out the solvent compared to shutdown with a smaller inventory. However, a large amount of product CO_2 is recovered during shutdown through the solvent lean out step, i.e., 1476–2274 kg CO_2, depending on the inventory volume. When considering the cumulative capture of the start-up together with shutdown, this large amount of shutdown CO_2 product counterbalances the CO_2 emissions associated with start-up.

To test this hypothesis, the combined performance of both start-up and shutdown was also evaluated. Although absorbed based capture rate was preferred for the analysis of start-up alone, in the case of combined SUSD performance, capture rate on a product CO_2 basis is a more meaningful metric for benchmarking SUSD scenarios. The combined performance of start-up (calculated over 82 min and 200 min) with shutdown confirmed that using a larger solvent inventory is highly beneficial for cold start-up in terms of maximising the cumulative CO_2 capture rate (product basis). However, solvent inventory volume has an almost negligible effect on cumulative CO_2 capture in the case of hot start-ups. Hot start-up was found to have significantly higher cumulative CO_2 capture rate and lower specific reboiler duty compared to cold start-ups.

As this study demonstrates, the optimal CO_2 capture performance during start-up and shutdown of the plant needs to balance several factors. Namely, solvent inventory volume, initial temperature (cold vs hot) and timing of steam availability (preheating vs steam & flue gas at the same time vs delayed steam) are the key factors that influence the time requirements and capture performance during start-up and shutdown. The preheating tests demonstrated start-up protocols that combined several improvements to achieve high cumulative CO_2 capture rates of 96–99% based on absorbed CO_2 over 85 min, whereas conventional start-ups only achieving 75–90% capture on an absorbed CO_2 basis (function of start-up type and solvent inventory volume). Furthermore, optimising the operating conditions such as slightly higher amine concentration, higher L/G ratio and lower start-up solvent loading can help maximise the cumulative CO_2 capture rate.

Owing to the low start-up solvent loading (0.05–0.11 mol CO_2/ mol amine) for all of the cold and hot start-up tests, the initial online CO_2 capture rate started at high levels of 98–99%, which were achieved immediately after the introduction of flue gas flow to the system. The ability to sustain these high CO_2 capture rates depends on the volume of the solvent inventory, amine concentration, starting solvent CO_2 loading, and the timing of steam supply to the reboiler. The results indicate the importance of timely steam supply during start-up. Any delay in steam supply to the capture plant significantly reduces the cumulative CO_2 capture rate, thereby increasing the residual CO_2 emissions.

Conversely, start-up with preheating was shown to be a potentially valuable approach. Under specific operating conditions, preheating can provide higher cumulative CO_2 capture rates during start-up of the capture plant, thereby minimising the residual CO_2 emissions. To maximise the value of preheating, a higher flow rate of steam supply can heat the system faster. Also, the timing of steam supply is crucial to prevent excess preheating and minimise auxiliary boiler CO_2 emissions. In this study we assumed a natural gas fired auxiliary boiler. The results show that the value of preheating would diminish if the preheating rate was insufficient (i.e., steam supply is too low), or poorly timed (i.e., excess preheating). Using preheating energy with lower carbon intensity would further reduce residual CO_2 emissions of the process and provide higher cumulative CO_2 capture rates. The decision to supply energy for preheating will likely come at a cost, e.g., to install an auxiliary boiler, fuel cost. However, in the context of net-zero emissions targets, the advantage of potentially achieving higher CO_2 capture rates by preheating before start-up could outweigh the cost.

These results provide valuable insights around the potential implications of start-up and shutdown at a process scale. This study provides data that characterises the performance of a power plant with CCS during cold start-up, hot start-up and shutdown. The results provide quantitative data around the fugitive CO_2 emissions and time requirements for each operating mode, also demonstrating the impact of measures that can enhance performance. The effect of varying solvent inventory volume and potential operational improvements have been identified. In summary, the key measures shown to improve performance include:

- Hot start-ups provided significantly higher cumulative CO_2 capture rates and lower specific reboiler duty compared to cold start-ups. Also, hot start-ups reached steady state much quicker than cold starts (around half the time).
- A larger solvent inventory will help maximise the cumulative CO_2 capture rate during cold start-ups.
- Using a larger solvent inventory with shutdown is also advantageous as it increases the amount of product CO_2 recovered through the solvent lean out step. In the case of cold start-up, this improves the cumulative CO_2 capture rate when calculating the combined performance of start-up and shutdown together. In contrast, the effect of solvent inventory volume on hot start-ups was negligible.
- For the "improved" start-up protocols, the process operating conditions shown to increase the cumulative CO_2 capture rate include preheating just before start-up, lower start-up CO_2 loading, higher amine concentration and higher L/G ratio (e.g., increasing amine flow rate).
- Higher rates of preheating significantly reduced the start-up time, with the reboiler reaching set-point temperature in 30 min instead of 100 min. This demonstrates the value in having an auxiliary boiler for preheating just before start-up.

The "improved" hot start-up protocols with high preheating increased the cumulative CO_2 capture rate (absorbed CO_2 basis) to 98.8%, which resulted in a specific reboiler duty of 5.58 MJ/kg CO_2, calculated over 85 min without accounting for auxiliary boiler CO_2 emissions. The "conventional" hot start-up protocols achieved lower cumulative CO_2 capture rates of between 90.0 to 90.3%, based on absorbed CO_2 and calculated over 82 min. The conventional start-up tests achieved lower specific reboiler duty of 4.03 and 3.76 MJ/kg CO_2 with solvent inventory of 42 m^3 and 53 m^3, respectively. This was mainly attributed to not using preheating energy for start-up and having lower amine flow rates (i.e., decreased sensible heat).

We demonstrate that start-up improvement measures can provide higher cumulative CO_2 capture rates of up to 99%, however, there will be trade-offs, and specific reboiler energy requirements may also increase, e.g., preheating energy, or increased sensible heat with higher solvent flow. In the context of net-zero emission targets, the ability to maximise the CO_2 capture rate could be significantly valuable as it reduces the residual CO_2 emissions, thereby alleviating the demand for carbon offsets via CO_2 removal technologies, e.g., bioenergy with CCS, or direct air capture. Another key contribution of this work is the comprehensive dataset of start-up and shutdown results from the TCM plant, which can be used as data input for process model validation and systems scale modelling.

Further R&D work in this area could explore the impact of different process configurations, solvent selection and process control systems that could improve plant flexibility and SUSD performance from both technical and cost perspectives, e.g., via process modelling which evaluates techno-economic performance of different SUSD scenarios. A potential study investigating the effect of varying equipment capacities on the performance during SUSD could be valuable. For example, the impact of using parallel absorbers of different sizes, or the effect of oversizing the stripper or reboiler to achieve more efficient solvent regeneration. Future demonstration testing that shows the power plant side of operation would also be useful since power plant operation and flexibility (e.g., turndown ratio, ramp rate, shutdown procedure) will also affect the SUSD strategy of the CCS plant. The dynamic interactions between the power plant and the CCS plant should be explored further. For example, during start-up and shutdown, variations in the flue gas (e.g., concentration of CO_2, O_2 and contaminants) from the power plant would likely have an impact on how the CCS plant should respond and the strategies employed to improve SUSD performance. The impact of SUSD in power plants with CCS on downstream processes (e.g., CO_2 compression) should also be considered. Other future work could also investigate the effect of start-up and shutdown at a systems scale in the context of a national electricity grid. This could potentially demonstrate whether SUSD CO_2 emissions will impact the ability to achieve national scale net-zero emissions targets.

5 Appendix A: Start-up and shutdown of commercial plants

The operating and maintenance philosophy of commercial scale CO_2 capture facilities have been published; these projects include:

- Kårstø CCS project at a gas fired CCGT power plant in Norway [54]
- Peterhead CCS project at gas-fired CCGT power station in the UK [104]
- Shand CCS project at a coal-fired power plant in Canada.[105]

The reports on the Peterhead project focus on describing the operation and maintenance of the CO_2 transport and storage equipment. However, the documentation published does not provide information on the operating and maintenance philosophy for the CO_2 capture unit.[104]

The start-up and shutdown procedures for the Shand and Kårstø CO_2 capture facilities are provided below. These procedures operate the CO_2 capture plant and considers the connections with upstream and downstream systems, i.e., the CCGT power plant and CO_2 compression, respectively.

5.1 Shand CO_2 capture plant

Table 31 provides an overview of the start-up procedure developed by MHI for the Shand CCS facility. The time required by the CO_2 capture system to reach full operation from the cold standby state (Step 1) would be up to half a day, whereas only several hours is required from the hot standby state (step 4). These start-up timeframes would also apply to stop and restart of the plant, e.g., restart after a trip.

Table 31: Typical start-up procedure for the Shand CO_2 capture facility provided by MHI, reproduced from International CCS Knowledge Centre [105].

Step	Task	Description
1	Start: Cold standby	• All utilities except steam are available • All equipment is ready for start-up • All process units are filled with required liquids
2	CO_2 capture unit initialisation	• Start absorbent solution circulation • Start trim FGD system[r]
3	CO_2 capture unit steam supply	• Supply steam to the reboilers and heat up the absorbent solution
4	Hot standby	• Capture island is now in hot standby mode
5	Flue gas diversion/introduction	• Introduce flue gas into the system • Start caustic soda makeup pump • Manually load the CO_2 capture unit to 50%
6	CO_2 capture unit operations	• Normal operation of the CO_2 capture unit begins at this point
7	CO_2 compression unit	• Start CO_2 compressor • Compress CO_2 and discharge into pipeline • Load capture facility up to 100%

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[r] Needed for coal flue gas applications to remove SO_X & NO_X and prevent solvent degradation.

5.2 Kårstø CO_2 capture facility

The following tables present operating procedures for first start-up, hot start-up, cold start-up and planned shutdown of the proposed Kårstø CO_2 capture and compression (CCC) facility in Norway (integrated with a gas fired CCGT power plant).[54] These tables have been reproduced from the feed study by Bechtel [53, 54].

5.2.1 Flue gas diversion from the power plant to capture plant

The diversion of flue gas from the CCGT stack to the CO_2 capture unit is done in a manner that does not impact the power plant operation. A duct directs flue gas from the base of an existing stack to the CO_2 capture plant. A pair of shut-off dampers are installed at this location to isolate the duct from the main stack when the capture plant is shut down. During normal operation of the capture plant, these shut-off dampers are fully open, and the existing stack damper is closed. The stack damper motor operator is replaced with a modulating pneumatic operator. Closing the stack damper diverts 100% of the flue gas into the CO_2 capture plant. The stack damper is modulated during start-up and shutdown, or when the capture plant is operated at reduced capacity.

Two blowers operating in parallel draw flue gas through the duct to the CO_2 capture plant. Control of the flue gas is important to ensure precise pressure control on the duct. This is necessary to avoid any negative effects on power plant operation and to prevent air ingress into the CO_2 capture plant through the stack opening.

5.2.2 General start-up sequence of the automatic sequencer

The plant can be started manually or via the automatic sequence. For automatic start-up, the sequence is initiated by the operator, and the sequencer guides the system through unit start-up until the admission of flue gas.

1) Makeup is added to the absorber and stripper bottom levels, water wash chimney tray, condensate blowdown tank, and compressor steam generators as needed.
2) Seawater pumps are started
3) The auxiliary boiler start sequence is initiated.
4) The LP steam line is warmed via the drain line until the minimum required superheat is reached. Steam is then admitted to the reboiler, and the drain valve is closed.
5) The reflux and stripper are brought to operating pressure, and reflux flow is established.
6) The lean amine, rich amine, and flash drum pumps are started in recirculation mode.
7) Minimum lean/rich amine flow is established. At this point, CO_2 loading in the rich amine flow is minimal due to zero flue gas flow through the absorbers.
8) The wash water pump is started, and wash water flow is established.
9) The compressor is started at minimum speed in recirculation mode.
10) The CCC Plant isolation dampers are opened – located within the flue gas ductwork connecting the HRSG stack to the blower before the absorber.
11) The flue gas blower for the first absorber is started at minimum speed.
12) The CO_2 master output gradually increases from zero, admitting flue gas to the first absorber.
    - At first, the blower damper controls flow until it reaches maximum throttling position, at which point it goes open and the blower speed increases to take more flue gas flow.
    - The HRSG stack damper is modulated to maintain steady pressure in the HRSG/CCC Plant duct.
    - Lean amine flow to the absorber is controlled by the CO_2 master.
    - Steam to the reboiler increases as amine flow increases.

  - At first, the stripper reflux drum pressure control valve keeps constant pressure in the stripper. As CO_2 flow increases, the pressure control valve fully opens, and the compressor speed is used to control constant stripper pressure.

13) The CO_2 master output is fixed to a minimum load until the CO_2 product system has been filled and started and the pipeline has been filled and is in service.
    - As CO_2 begins to fill the surge drum, air vents from opened motor-operated valves located on the CO_2 product send-out pumps and on the piping upstream of the CO_2 product control valve.
    - Once the system is vented, the motor-operated valves close and a CO_2 product send-out pump starts.
    - Flow to the CO_2 pipeline is strictly controlled until the pressure in the pipeline approaches operating pressure (details to be determined during final design with input from outside the battery limit).
14) The CO_2 master output begins to increase again.
15) After the first absorber takes approximately 50% of the combustion turbine exhaust flow, the second absorber is started in the same sequence as outlined above. The HRSG stack damper goes fully closed during this step.
16) Once the unit has stabilized, the CO_2 master is released for fully automatic control.
17) Flow is established through the carbon filter package after the system is fully stabilized.
18) Semi-lean amine[s] flow to the absorber is controlled in proportion to the rich amine flow.

5.2.3 First start-up

The first start-up of the CCC process is needed after the system is completely drained and requires additional manual steps.

Table 32: Operating protocol for the first start-up of the Kårstø CO_2 capture project in Norway. Reproduced and adapted from Bechtel [53, 54].

First start-up	
1	Operators must verify manual valve and equipment line up.
2	Charge the amine storage tank with monoethanolamine (MEA). An amine solution at the nominal/specification concentration (e.g., 30 wt%) may need to be created if insufficient level exists in the lean amine solvent storage tank. The tank is filled with process water and then concentrated amine added until MEA solution is at the nominal concentration. A grab sample is taken and manually injected into the online gas chromatograph to confirm the proper amine concentration.
3	The lean/semi-lean/rich amine system piping and pumps are filled and vented using the 30 wt% amine solution and a lean amine solvent fill pump.
4	Establish recirculation flow through the lean and rich amine flow paths.
5	Establish sea water cooling flow through the cooling system. The seawater system piping may not be completely full if it was drained. The system should be filled in a controlled manner to preclude water hammer.
6	The wash water system piping and pumps are filled and vented using process water and an absorber makeup water pump.
7	The stripper reflux system piping and pumps are filled and vented using process water and an absorber makeup water pump.
8	Allow time for the amine solution to increase and build its temperature.

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[s] A portion of rich amine is diverted, heated and flashed. This amine is partially regenerated to create semi-lean amine, which is returned directly to the absorber. Semi-lean amine is injected partway through the absorber column packing to absorb part of the CO_2 from the flue gas. This system can be bypassed, and the plant can run using only lean amine.

9	Once the amine temperature in the stripper section reaches the set-point temperature, initiate the start of the ID fans and begin to close the damper in the CCGT power plant stack.
10	Initiate flue gas temperature control.
11	Allow CO_2 capture process to approach steady state, monitoring CO_2 flow through exit valve to the absorber stack outlet.
12	As the CO_2 builds up, start the CO_2 compressor.
13	Initiate the transfer of CO_2 to the CO_2 compressor suction drum, removing any liquid from the feed to the compressor.
14	Initiate CO_2 send-out pumps once CO_2 liquid level is established in the CO_2 surge tank. The CO_2 product send-out system piping and pumps are filled and vented as determined during final design with input from outside the battery limit.
15	Balance and tune control loops to stabilise levels, flows and total amount of CO_2 stripped

Some additional considerations for the automatic sequencing tasks are as follows:

- The 35% amine makeup to the unit is more than normal. The condensate blowdown tank fills to ensure an adequate water supply for the LP steam desuperheater until the system reaches equilibrium. Condensate may be rejected until the initial fill from the process water system is rejected back to the process water surge tank.
- The auxiliary boiler drum may not be full. It is recommended that the operator fill the drum prior to starting; however, the automatic sequencer performs this task if not already done.

5.2.4 Start-up after short downtime – Hot start up

The simplified hot start-up procedure is outlined in the following table.

Table 33: Operating protocol for a hot start-up of the Kårstø CO_2 capture project in Norway. Hot start-up can be performed after a short downtime when the CCGT power plant is already running. Reproduced from Bechtel [54].

Hot start-up	
1	Establish sea water cooling flow through the cooling system
2	Steam is then admitted to the reboiler, and the drain valve is closed.
3	The reflux and stripper are brought to operating pressure, and reflux flow is established.
4	Establish recirculation flow through the lean and rich amine flow paths
5	Initiate start of the ID fans and begin to close damper in the CCGT power plant stack.
6	Allow CO_2 capture process to approach steady state, monitoring CO_2 flow through exit valve to the absorber stack outlet.
7	Initiate flue gas temperature control.
8	As the CO_2 builds up, start the CO_2 compressor.
9	Initiate the transfer of CO_2 to the CO_2 compressor suction drum, removing any liquid from the feed to the compressor.
10	Initiate CO_2 send-out pumps once CO_2 liquid level is established in the CO_2 surge tank.

5.2.5 Start-up after long downtime – Cold start-up

The simplified cold start-up procedure is outlined in the following table.

Table 34: Operating protocol for a cold start-up of the Kårstø CO_2 capture project in Norway. Cold start-up will be performed after a longer downtime when there is a shift to shutdown conditions, however, the CCGT power plant will already be running. Reproduced and adapted from Bechtel [53, 54].

Cold start-up	
1	Operators to verify manual valve and equipment line up. Open dampers as necessary (open shut-off dampers which isolate flue gas ductwork from main stack).
2	Transfer amine from the lean amine storage tank to fill the absorber column sumps (if sumps have been emptied to the lean amine tank).
3	Establish recirculation flow through the lean and rich amine flow paths.
4	Establish sea water cooling flow through the cooling system.
5	Steam is admitted to the reboiler, and the drain valve is closed.
6	Allow time for the amine solution to increase and build its temperature.
7	Once the amine temperature in the stripper section reaches the set-point temperature, initiate the start of the ID fans and begin to close the damper in the CCGT power plant stack.
8	Initiate flue gas temperature control.
9	Allow CO_2 capture process to approach steady state, monitoring CO_2 flow through exit valve to the absorber stack outlet.
10	As the CO_2 builds up, start the CO_2 compressor.
11	Initiate the transfer of CO_2 to the CO_2 compressor suction drum, removing any liquid from the feed to the compressor.
12	Initiate CO_2 send-out pumps once CO_2 liquid level is established in the CO_2 surge tank.

5.2.6 Restart following a trip

In most cases, after diagnosing and troubleshooting the cause of the trip, the operator can restart the CO_2 capture unit using the start-up sequencer.

5.2.7 Planned normal shutdown

The plant can be shut down manually or via the automatic sequence. For automatic shutdown, the sequence is initiated by the operator, and the sequencer guides the system through unit shutdown.

Table 35: Operating protocol for the shutdown of the Kårstø CO_2 capture project in Norway. This procedure is for a planned shutdown of the capture plant for short duration <24 hours and follows the shutdown of the CCGT power plant. It applies to cases of CCGT power plant shutdown between 6 and 24 hours. Reproduced and adapted from Bechtel [53, 54].

Shutdown	
1	Open damper in the CCGT power plant. CO_2 master automatic control is deactivated, and flue gas flow is slowly reduced to zero, at first by reducing blower speed and then by the blower damper. One absorber is shut down at a time. The HRSG stack damper opens to maintain a stable pressure in the HRSG and CCC Plant duct.
2	HP steam to the reclaimer is shut down (if in operation).
3	LP steam to the reboiler is shut down after the CO_2 in the rich amine has been removed.
4	The auxiliary boiler is shut down.
5	Semi-lean amine flow is stopped.

6	The reflux and stripper are slowly depressurised. Vent valves on the knockout and feed drums remain closed. Vent valve on the reflux drum opens.
7	The compressor is stopped several minutes after CO_2 production stops.
8	Flow is circulated until the stripper bottom temperature drops below 65 °C.
9	Flow through the carbon filter package is stopped.
10	Absorber, flash drum, stripper bottom, and reflux drum levels are decreased to minimum level by rejecting amine to the lean amine solvent storage tank (TK-102).
11	The wash water pump is stopped.
12	The reflux pump is stopped.
13	Allow amine to recirculate for approximately 1 hour to allow CO_2 to off gas and minimise pockets at restart.
14	The lean and rich amine pumps are stopped.
15	The CCC Plant isolation dampers are closed – located within the flue gas ductwork connecting the HRSG stack to the blower before the absorber.
16	The seawater pumps are stopped manually after the operator confirms that all equipment is shut down and there are no further cooling requirements.

5.2.8 Extended shutdown

For planned extended shutdown of >24 hours, the amine is manually drained from the absorbers to the amine waste sump and then transferred to the lean amine storage tank to minimise oxidative degradation of the amine.

To restart the plant, follow the procedure for the start-up after longer downtime.

6 Appendix B: TCM plant specifications

Additional information about the plant specifications is provided in this section.

Table 36: Specifications of the two direct contact coolers (DCC) used to cool the flue gas before it enters the absorber column.

Specification	**CHP DCC**	**RFCC DCC**
Diameter, m	3	2.7
Total height, m	16	16
Packing height, m	3.1	3
Packing type	Flexipac 3X structured	Intalox Snowflake random
Vendor	Koch Glitsch	Koch Glitsch
Material	Stainless steel	Polypropylene

Table 37: Specifications of the absorber and the two stripper types (CHP and RFCC). In this study, the RFCC stripper was used.

Specification	**Absorber**	**Stripper CHP**	**Stripper RFCC**
Geometry	Rectangular	Cylindrical	Cylindrical
Construction	Concrete & polypropylene-lined	Stainless steel	Stainless steel
Total height, m	62	30	30
Cross-sectional area, m^2 (m x m)	7.1 (3.55m x 2m)	1.33	3.80
Diameter, m	–	1.3	2.2
Number of packing sections	Upper: 2 water wash Lower: 3 absorption sections (each has a separate lean amine inlet)	Upper: 1 water wash Lower: 1 desorption	Upper: 1 water wash Lower: 1 desorption
Packing height of each absorption (or desorption) section, m	12 m + 6 m = 18 m (6 m of unused absorber packing)	8	8
Packing height of each water wash section, m	3, 3 (total 6 m)	1.6	1.6
Water wash full load capacity, t/h	50, 60	–	–
Sump height, m	3		
Reboiler type	–	Thermosiphon Plate and frame HX	Thermosiphon Shell and tube HX

Table 38: Regulatory levels for air emissions as specified by the TCM emissions and discharge permit, which can be either an immediate concentration level (average of operating time) or cumulative annual levels. Note that ammonia limits for the chilled ammonia process and amine absorption plant differ. The limit of each amine group (i.e., primary, secondary and tertiary) is based on the different risks of nitrosamines and nitramines formation for each amine type. Table reproduced from Maree, et al. [94]

Emissions component	Source of emissions	Limit # (concentration)	Limit + (extended period) tonnes/year
Ammonia (NH_3)	Amine absorption process	100 ppmv	6
Total amines =	Amine absorption process	6 ppmv average per test campaign 15 ppmv max allowed concentration	2.8
Aldehydes	Amine absorption process	Max allowed flow limit of 1 g/s	3

Daily average limit as an average for 90% of operating time.
+ Cumulative limit annually.
= The sum of amines (e.g., primary, secondary, tertiary) shall not exceed the total amount of amines. Maximum extended period limits will not exceed the values for the individual amine groups. Limit for total amines applies to CESAR-1 (PZ is a cyclic diamine and AMP is a sterically hindered amine).

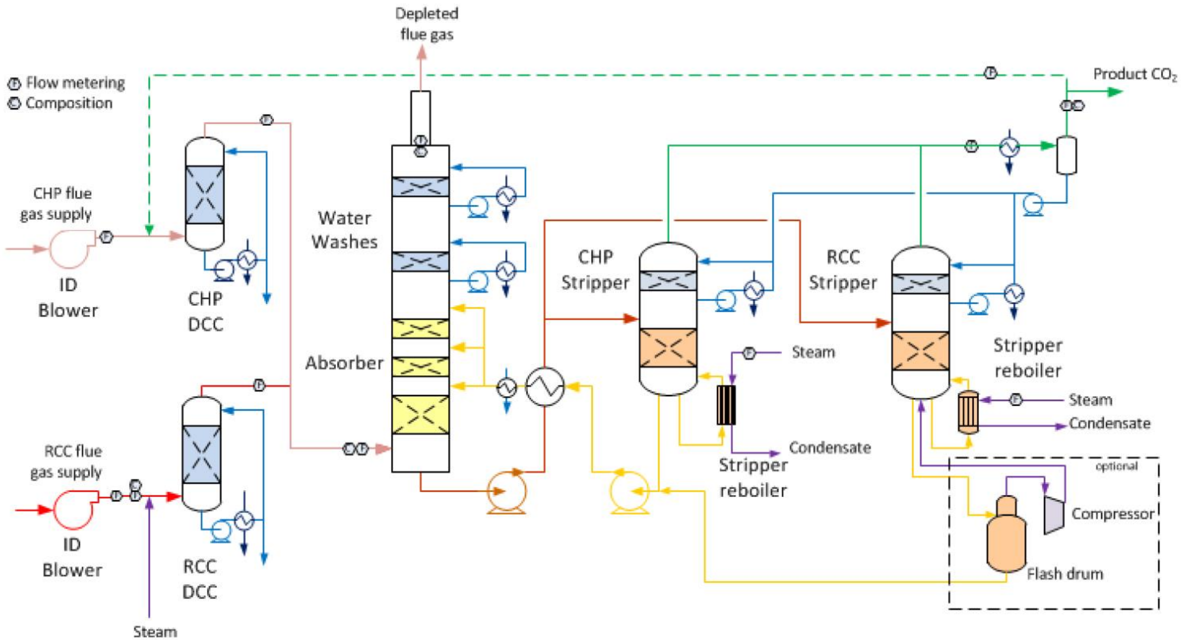

Figure 30: Process flow diagram of the amine-based CO_2 capture process at TCM. The plant has variable packing height, two DCC and two stripper columns. Depending on the flue gas composition, the capture plant can use either the combined heat and power (CHP) configuration, or the refinery residue fluid catalytic cracker (RFCC) configuration. [71, 77, 78, 106].

7 Appendix C: Normal start-up and shutdown tests, November 2020 – Effect of solvent inventory 42 m^3 vs 53 m^3

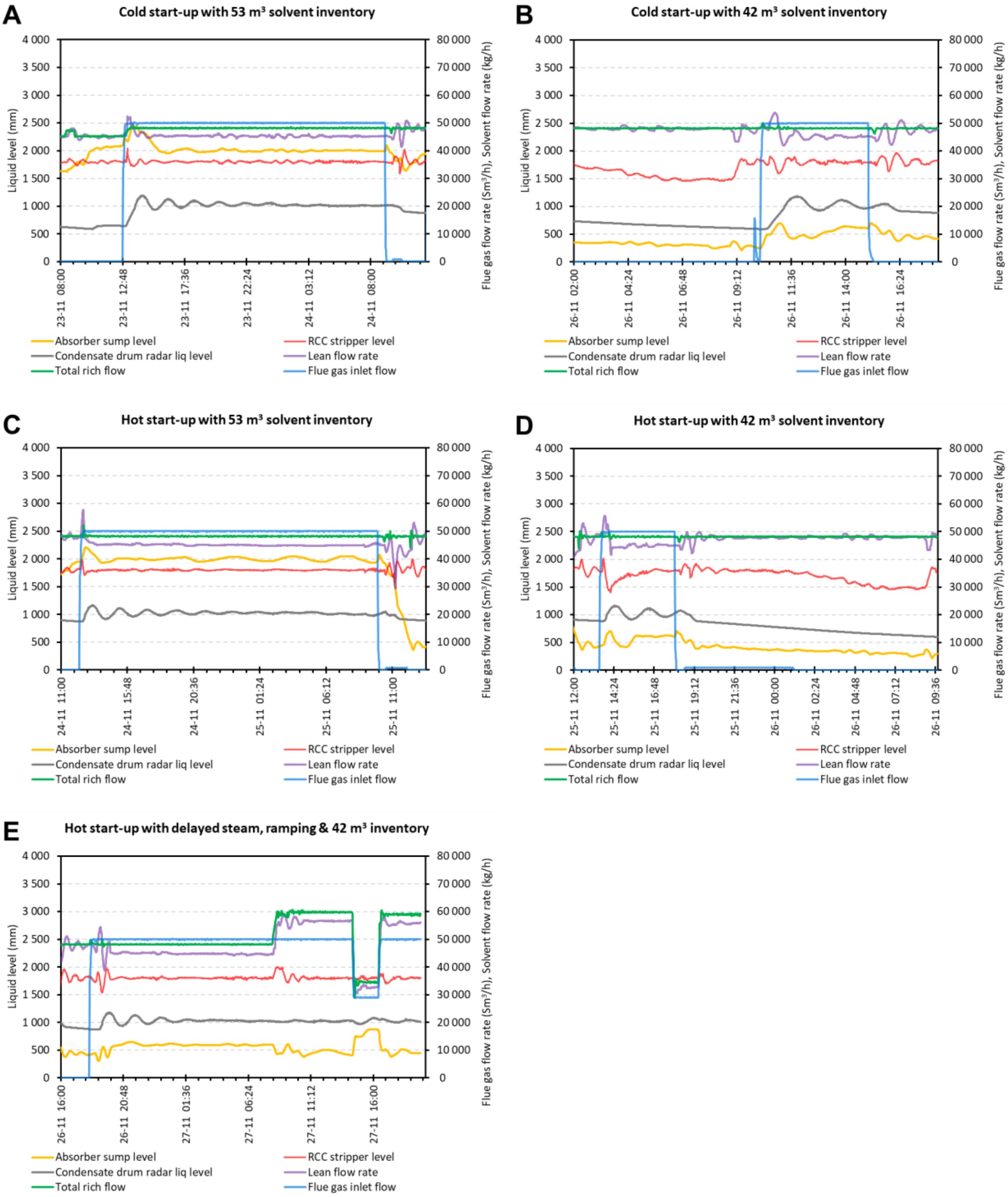

Figure 31: The change in liquid level during the cold and hot start-ups with shutdown for the tests using 53 m^3 solvent inventory (A, C) and 42 m^3 solvent inventory (B, D, E). Using different solvent inventory in the TCM plant mainly affects the liquid level in the absorber sump, whereas the stripper liquid level in both cases is similar.

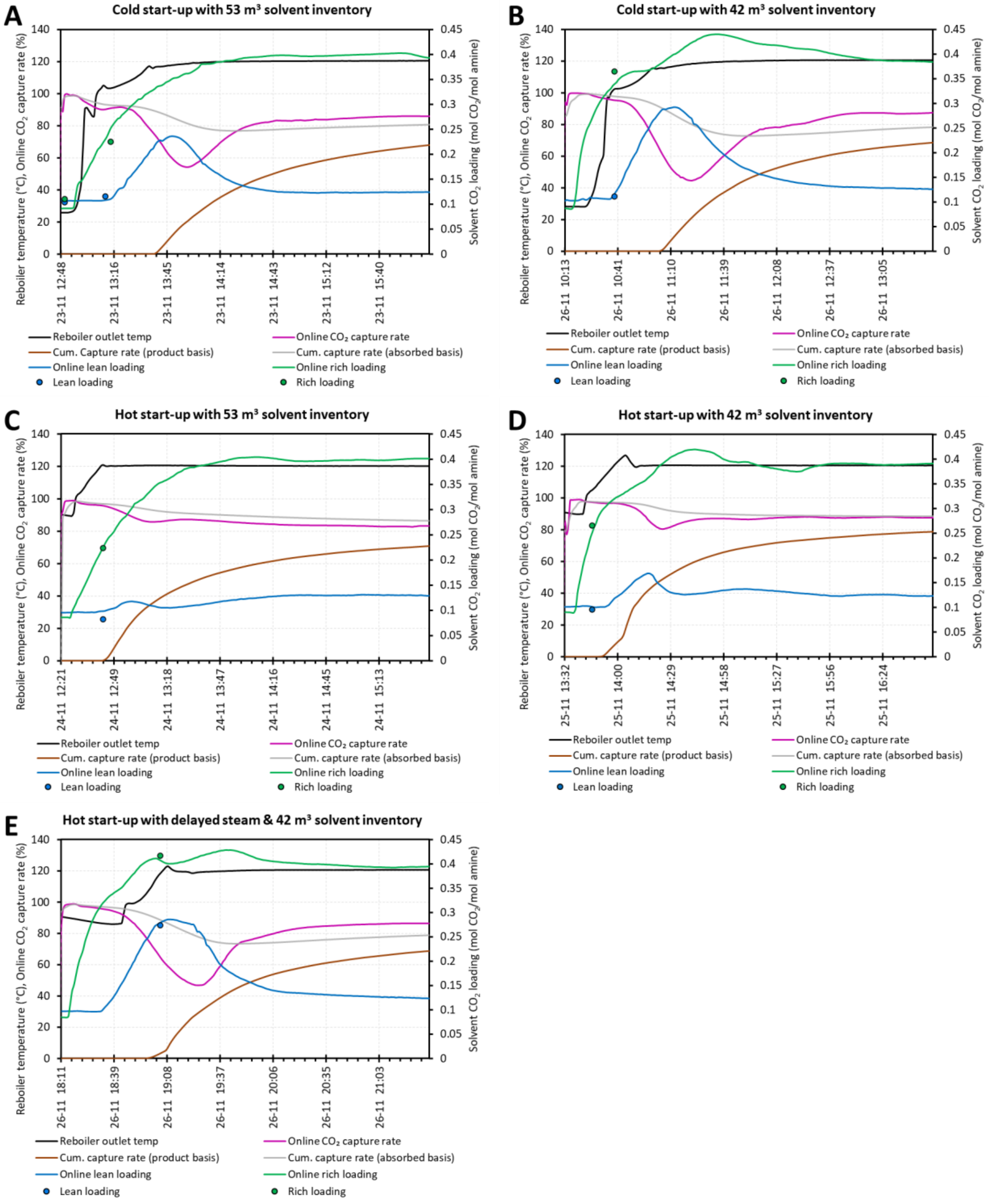

Figure 32: Solvent loading and CO_2 capture rate changes during cold start-up (A & B), hot start-up (C, D & E) and shutdown with different solvent inventories, 42 m^3 vs 53 m^3. The hot start-up with a 20 min delay in steam is shown in (E), but there was no shutdown on this day. The period shown begins at the time flue gas flow starts plus an additional 200 minute. Online capture rate and cumulative capture rates (product CO_2 basis and absorbed CO_2 basis) are shown.

8 Appendix D: Start-up and shutdown tests in June 2020 – Effect of preheating

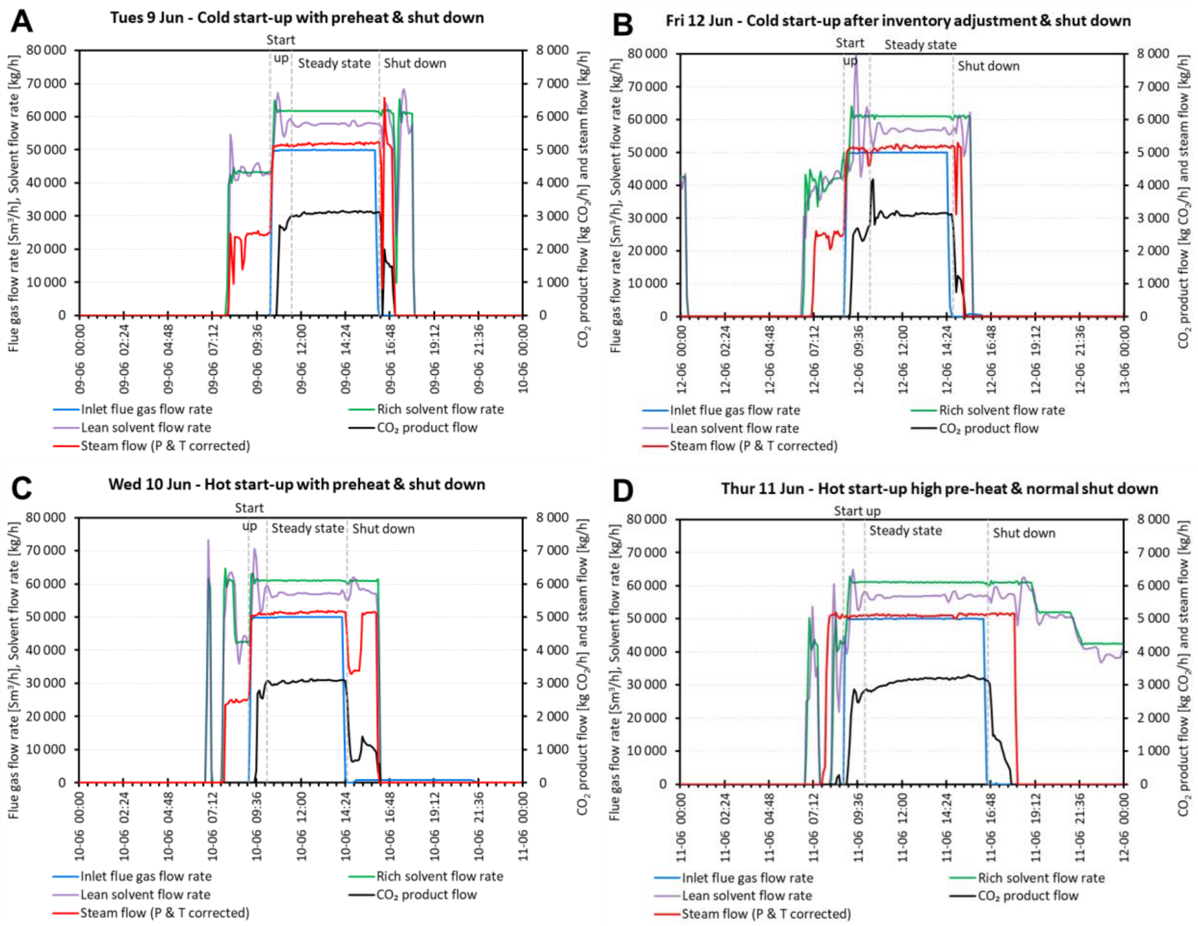

Figure 33: Process changes during the start-up and shutdown tests in June 2020. Summary of the process conditions found in Table 11. (A) and (B) correspond to cold start-up tests with preheating. (C) Hot start-up with preheat and (D) is a hot start-up with high preheating.

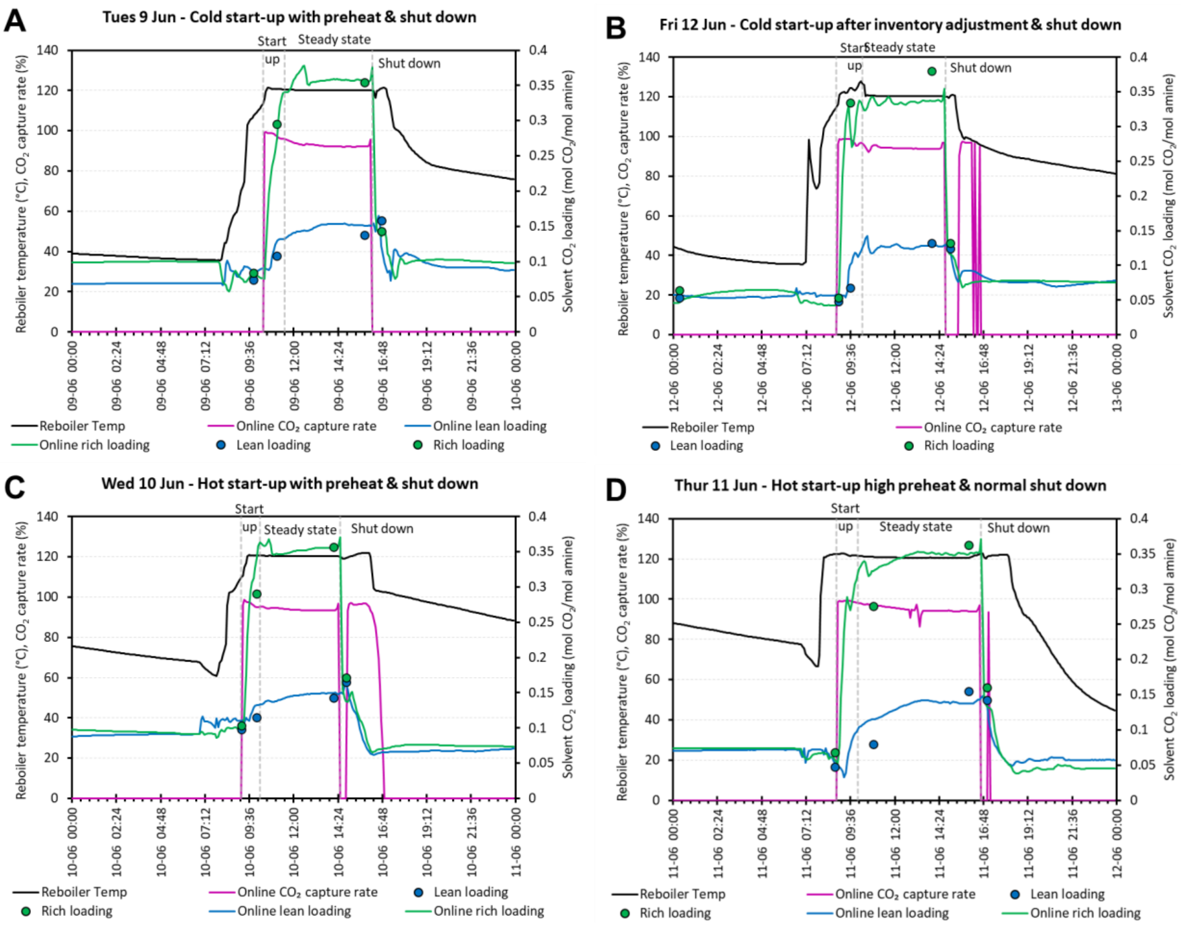

Figure 34: Solvent CO2 loading and reboiler temperature during the start-up and shutdown tests in June 2020. Summary of the process conditions found in Table 10. (A) and (B) correspond to cold start-up tests with preheating. (C) Hot start-up with preheat and (D) is a hot start-up with high preheating.

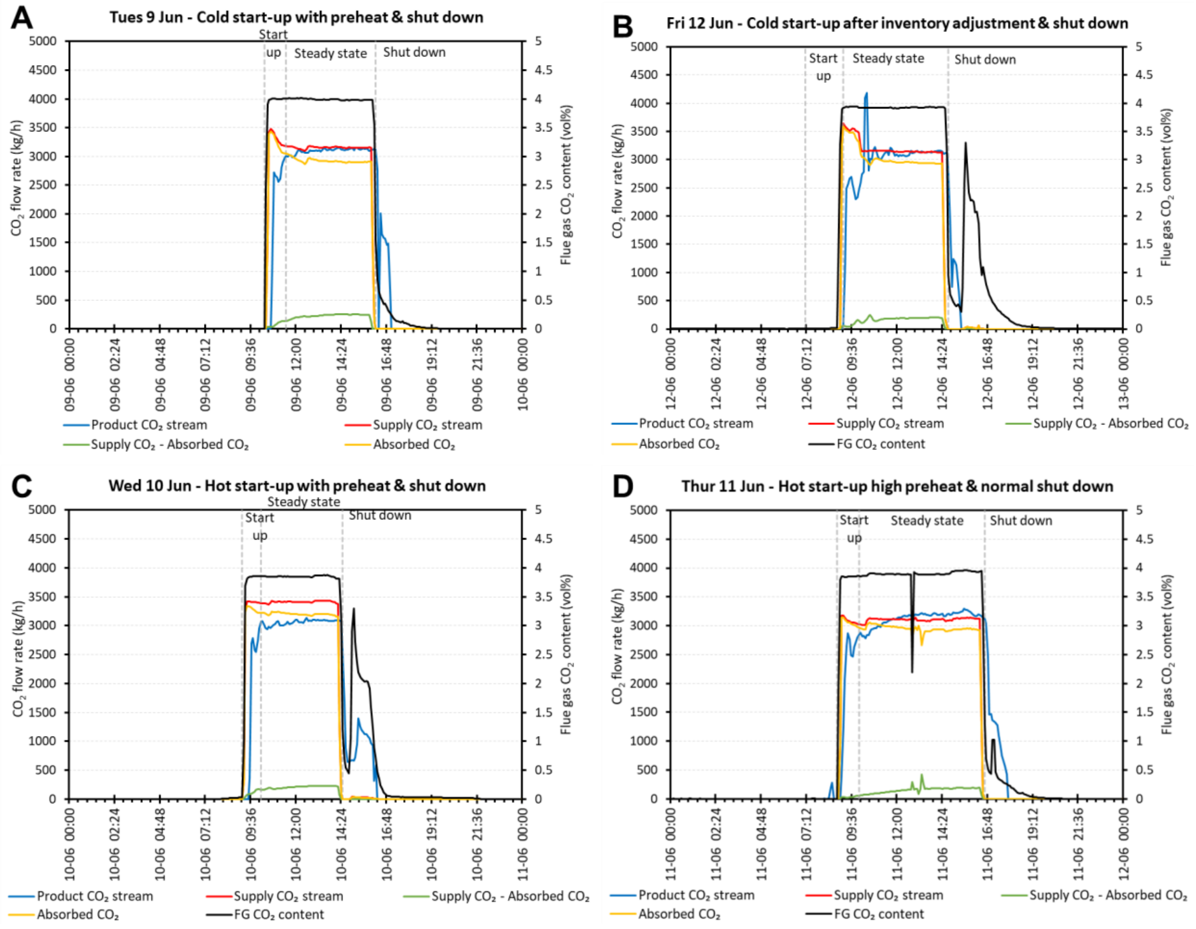

Figure 35: Streams of CO_2 flow and the flue gas CO_2 content during the start-up and shutdown tests in June 2020. Summary of the process conditions found in Table 10. (A) and (B) correspond to cold start-up tests with preheating. (C) Hot start-up with preheat and (D) is a hot start-up with high preheating.

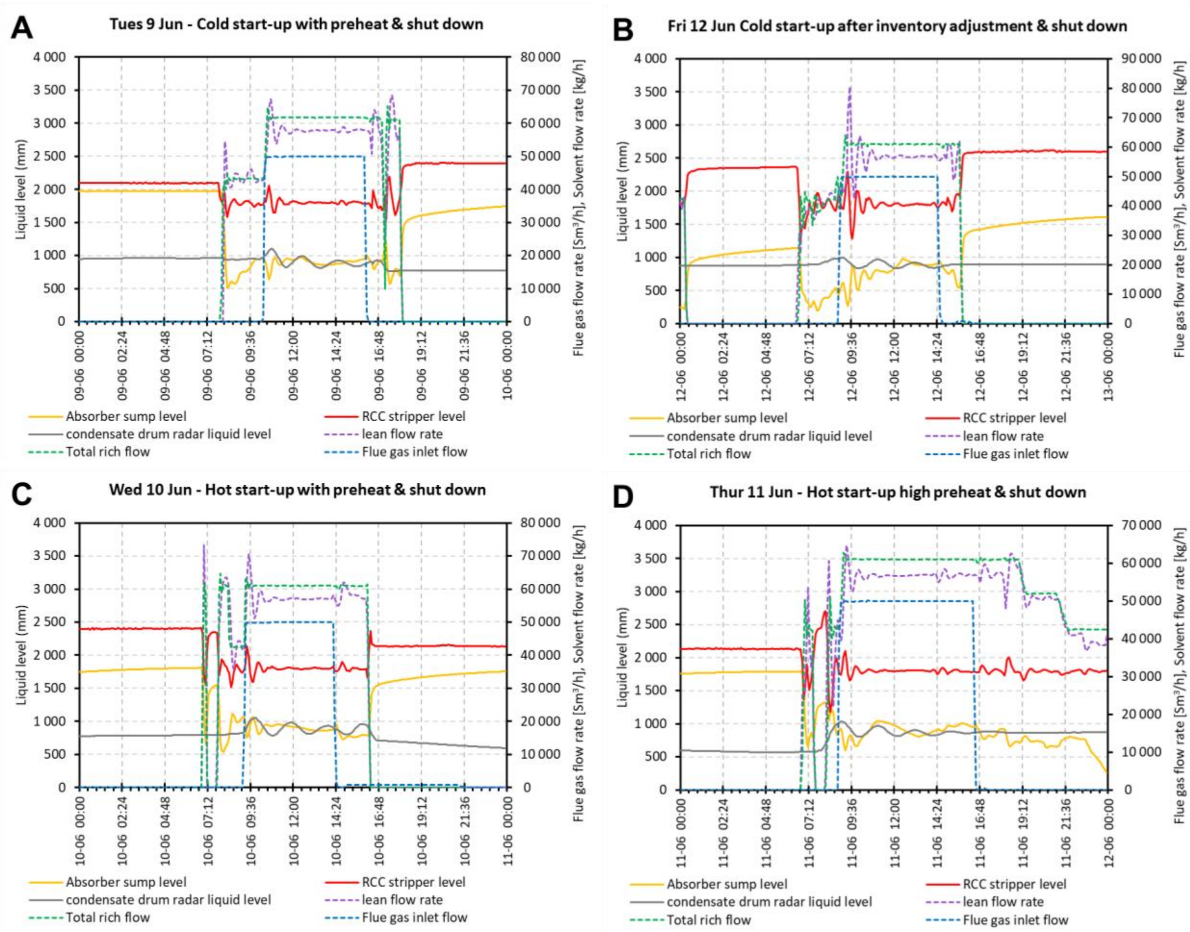

Figure 36: Process changes, with the corresponding levels in the absorber and RFCC stripper during the start-up and shutdown tests in June 2020. Summary of the process conditions found in Table 11. (A) and (B) correspond to cold start-up tests with preheating. (C) Hot start-up with preheat and (D) is a hot start-up with high preheating.

Cold start-ups with preheating and shutdown

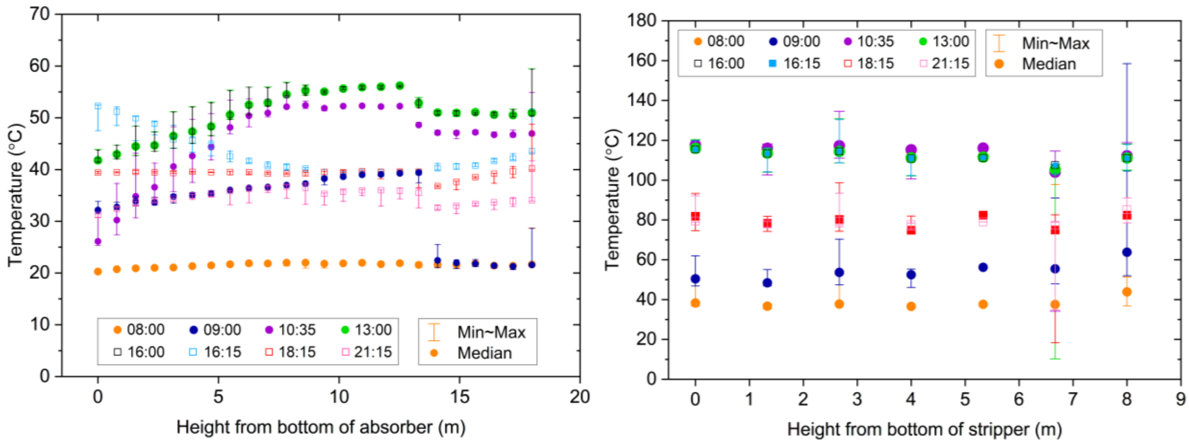

Figure 37: Absorber (left) and stripper (right) temperature profiles for a cold start-up with preheating and normal shutdown using 45 m^3 solvent inventory on Tuesday 9 June 2020. The flue gas flow starts at 10:20, set-point conditions are reached around 10:35 and product CO₂ flow rate reaches steady state at 11:30. For shutdown, flue gas flow starts to turn off around 16:05 and the steam is shut off at 16:15.

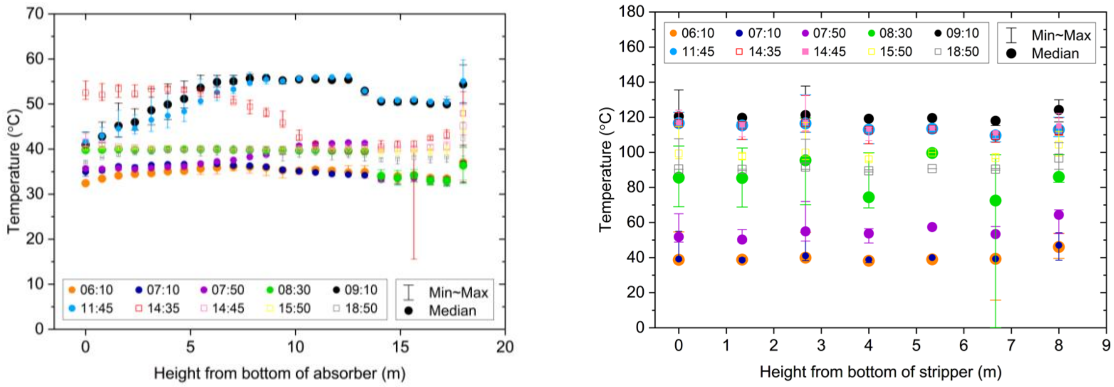

Figure 38: Absorber (left) and stripper (right) temperature profiles for a cold start-up with high preheating and normal shutdown using 45 m^3 solvent inventory on Friday 12 June 2020. The flue gas flow starts at 08:50, set-point conditions are reached around 09:30 and product CO₂ flow rate reaches steady state at 11:00. For shutdown, flue gas flow starts to turn off around 14:30 and the steam is shut off at 15:20.

Hot start-up with preheating and shutdown

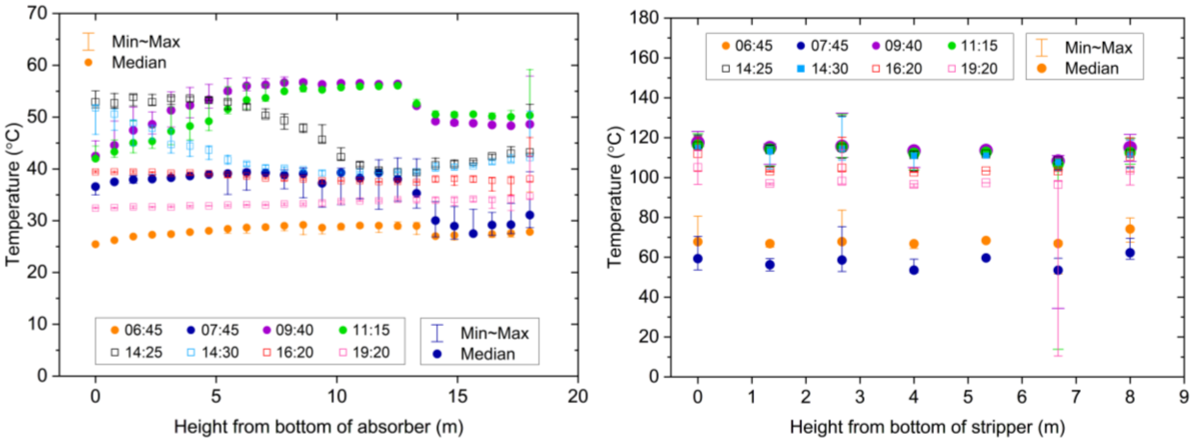

Figure 39: Absorber (left) and stripper (right) temperature profiles for a hot start-up with preheating and normal shutdown using 45 m^3 solvent inventory on Wednesday 10 June 2020. The flue gas flow starts at 09:10, set-point conditions are reached around 09:45 and product CO_2 flow rate reaches steady state at 10:10. For shutdown, flue gas flow starts to turn off around 14:20 and the steam is shut off at 16:15.

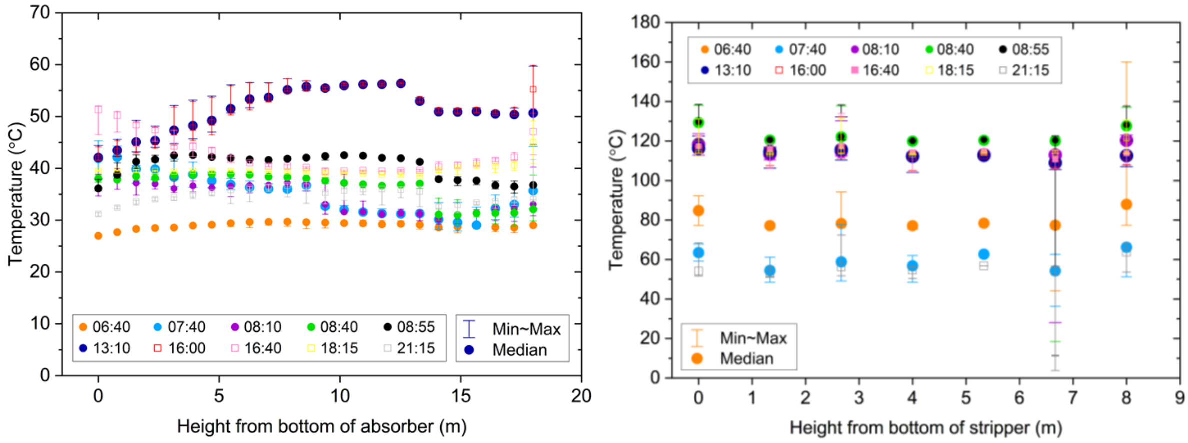

Figure 40: Absorber (left) and stripper (right) temperature profiles for a hot start-up with high preheating and normal shutdown using 45 m^3 solvent inventory on Thursday 11 June 2020. The flue gas flow starts at 08:50, set-point conditions are reached around 09:10 and product CO_2 flow rate reaches steady state at 10:00. For shutdown, flue gas flow starts to turn off around 16:30 and the steam is shut off at 18:15.

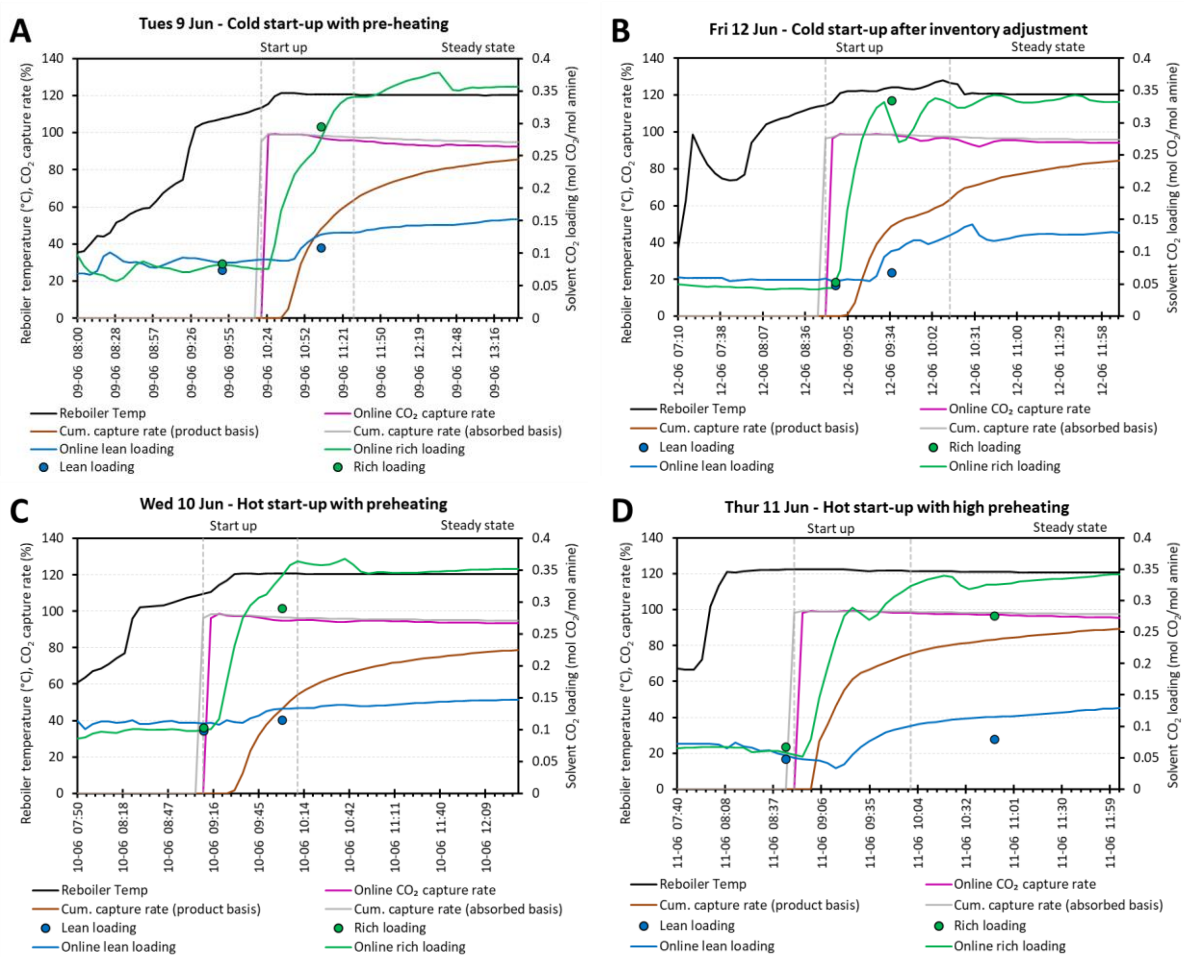

Figure 41: Solvent loading and CO_2 capture rate changes during the start-up and shutdown tests in June 2020. The period shown begins at the time steam flow starts plus an additional 200 minute after the flue gas enters. Online capture rate and cumulative capture rates (product CO_2 basis and absorbed CO_2 basis) are shown. Summary of the process conditions Table 11. (A) and (B) correspond to cold start-up tests with preheating. (C) Hot start-up with preheat and (D) is a hot start-up with high preheating.

9 References

1. T. Spitz, A. González Díaz, H. Chalmers and M. Lucquiaud, *International Journal of Greenhouse Gas Control*, 2019, **88**, 92-108.
2. T. M. Spitz, University of Edinburgh, 2019.
3. T. Spitz, V. Avagyan, F. Ascui, A. R. W. Bruce, H. Chalmers and M. Lucquiaud, *International Journal of Greenhouse Gas Control*, 2018, **74**, 296–311.
4. C. F. Heuberger and N. Mac Dowell, *Joule*, 2018, **2**, 367–370.
5. S. Ludig, M. Haller and N. Bauer, *Energy Procedia*, 2010, **4**, 2580–2587.
6. IEA, *Net Zero by 2050: A Roadmap for the Global Energy Sector*, International Energy Agency, https://www.iea.org/reports/net-zero-by-2050, 2021.
7. IEAGHG, *Valuing Flexibility in CCS Power Plants, Technical Report 2017-09*, International Energy Agency Greenhouse Gas R&D Programme (IEAGHG), London, United Kingdom, 2017.
8. N. Mac Dowell and I. Staffell, *International Journal of Greenhouse Gas Control*, 2016, **48, Part 2**, 327–344.
9. National Grid, *Future Energy Scenarios*, Warwick, UK, http://fes.nationalgrid.com/fes-document/, 2019.
10. Committee on Climate Change, *Net zero - The UK's contribution to stopping global warming*, https://www.theccc.org.uk/wp-content/uploads/2019/05/Net-Zero-The-UKs-contribution-to-stopping-global-warming.pdf, London, UK, 2019.
11. IEA, *The role of CCUS in low-carbon power systems*, International Energy Agency, France, https://iea.blob.core.windows.net/assets/ccdcb6b3-f6dd-4f9a-98c3-8366f4671427/The_role_of_CCUS_in_low-carbon_power_systems.pdf, 2020.
12. P. Tait, B. Buschle, K. Milkowski, M. Akram, M. Pourkashanian and M. Lucquiaud, *International Journal of Greenhouse Gas Control*, 2018, **71**, 253–277.
13. IEAGHG, *Operating flexibility of power plants with CCS, Report 2012/6*, United Kingdom, 2012.
14. D. Lew, G. Brinkman, N. Kumar, P. Besuner, D. Agan and S. Lefton, *Impacts of wind and solar on fossil-fueled generators (Paper No. NREL/CP-5500-53504)*, National Renewable Energy Laboratory (NREL), United States, IEEE Power and Energy Society General Meeting San Diego, California, 22–26 July, 2012, 2012.
15. NREL, *Western Wind and Solar Integration Study*, National Renewable Energy Laboratory, United States, https://www.nrel.gov/grid/wwsis.html, 2014.
16. C. F. Heuberger, I. Staffell, N. Shah and N. Mac Dowell, *Energy & Environmental Science*, 2016, **9**, 2497–2510.
17. E. Mechleri, P. S. Fennell and N. Mac Dowell, *International Journal of Greenhouse Gas Control*, 2017, **59**, 24–39.
18. A. M. Abdilahi, M. W. Mustafa, S. Y. Abujarad and M. Mustapha, *Renewable and Sustainable Energy Reviews*, 2018, **81**, 3101-3110.
19. S. M. Cohen, G. T. Rochelle and M. E. Webber, *International Journal of Greenhouse Gas Control*, 2012, **8**, 180–195.
20. T. Marx-Schubach and G. Schmitz, *International Journal of Greenhouse Gas Control*, 2019, **87**, 44–57.
21. N. Ceccarelli, M. van Leeuwen, T. Wolf, P. van Leeuwen, R. van der Vaart, W. Maas and A. Ramos, 12th International Conference on Greenhouse Gas Control Technologies (GHGT-12), Austin, Texas, USA, 2014.
22. J. Hentschel, U. a. Babić and H. Spliethoff, *Energy Reports*, 2016, **2**, 40–47.
23. M. A. Gonzalez-Salazar, T. Kirsten and L. Prchlik, *Renewable and Sustainable Energy Reviews*, 2018, **82**, 1497–1513.
24. R. Domenichini, L. Mancuso, N. Ferrari and J. Davison, *Energy Procedia*, 2013, **37**, 2727–2737.
25. T. Marx-Schubach and G. Schmitz, *Industrial & Engineering Chemistry Research*, 2018, **57**, 16751–16762.
26. P. Tait, B. Buschle, I. Ausner, P. Valluri, M. Wehrli and M. Lucquiaud, *International Journal of Greenhouse Gas Control*, 2016, **48, Part 2**, 216–233.
27. J. Gaspar, J. B. Jorgensen and P. L. Fosbol, *IFAC-PapersOnLine*, 2015, **48**, 580–585.
28. B. Jin, M. Su, H. Zhao and C. Zheng, *Energy Conversion and Management*, 2015, **106**, 782-792.
29. IEAGHG, *Oxy combustion processes for CO_2 capture from power plant, Report number 2005/9*, IEA Greenhouse Gas R&D Programme, https://ieaghg.org/docs/General_Docs/Reports/Report%202005-9%20oxycombustion.pdf, 2005.

30. IRENA, *Innovation Landscape Brief: Flexibility in Conventional Power Plants*, International Renewable Energy Agency, Abu Dhabi, 2019.
31. M. Wiatros-Motyka, *Power plant design and management for unit cycling, Report CCC/295*, IEA Clean Coal Centre, London, United Kingdom, 2019.
32. IEAGHG, *Oxy-combustion turbine power plants, Report 2015/05*, https://ieaghg.org/docs/General_Docs/Reports/2015-05.pdf, 2015.
33. IEA, *Status of Power System Transformation - Advanced Power Plant Flexibility*, International Energy Agency, https://www.sipotra.it/wp-content/uploads/2019/02/Status-of-Power-System-Transformation.-Advanced-Power-Plant-Flexibility-2018-Technical-Annexes.pdf, 2018.
34. J. Rúa, R. Agromayor, M. Hillestad and L. O. Nord, *Applied Thermal Engineering*, 2020, **170**, 114858.
35. J. Rúa and L. O. Nord, *Applied Energy*, 2020, **265**, 114820.
36. N. Kumar, P. Besuner, S. Lefton, D. Agan and D. Hilleman, *Power Plant Cycling Costs*, National Renewable Energy Laboratory (NREL), California, United States, https://www.nrel.gov/grid/wwsis.html, 2012.
37. D. Neshumayev, L. Rummel, A. Konist, A. Ots and T. Parve, *Applied Energy*, 2018, **224**, 124–135.
38. T. Xu, A. B. Birchfield, K. M. Gegner, K. S. Shetye and T. J. Overbye, *Proceedings of the 50th Hawaii International Conference on System Sciences*, 2017, 3123-3129.
39. J. Obaid, A. Ramadan, A. Elkamel and W. Anderson, *Energies*, 2017, **10**, 179.
40. J. L. Sorrels, D. D. Randall, K. S. Schaffner and C. R. Fry, *Chapter 2: Selective Catalytic Reduction, in Section 4 - NO_X Controls, EPA Air Pollution Control Cost Manual*, United States Environmental Protection Agency, https://www.epa.gov/sites/default/files/2017-12/documents/scrcostmanualchapter7thedition_2016revisions2017.pdf, 2019.
41. CSIRO, *Environmental Impacts of Amine-based CO_2 Post Combustion Capture (PCC) Process*, https://www.globalccsinstitute.com/archive/hub/publications/169153/process-modelling-amine-based-post-combustion-capture-plant.pdf, 2012.
42. E. Sanchez Fernandez, M. Sanchez del Rio, H. Chalmers, P. Khakharia, E. L. V. Goetheer, J. Gibbins and M. Lucquiaud, *International Journal of Greenhouse Gas Control*, 2016, **48, Part 2**, 275–289.
43. J. Rúa, M. Bui, L. O. Nord and N. Mac Dowell, *International Journal of Greenhouse Gas Control*, 2020, **95**, 102984.
44. BEIS, *Start up and shut down times of power carbon capture, usage and storage (CCUS) facilities, BEIS research paper number 2020/031*, Department for Business, Energy & Industrial Strategy, United Kingdom, https://www.gov.uk/government/publications/start-up-and-shut-down-times-of-power-carbon-capture-usage-and-storage-ccus-facilities, 2020.
45. M. Lucquiaud and J. Gibbins, 10th International Conference on Greenhouse Gas Control Technologies (GHGT-10), Amsterdam, The Netherlands, 2010.
46. L. M. Romeo, S. Espatolero and I. Bolea, *International Journal of Greenhouse Gas Control*, 2008, **2**, 563–570.
47. S. M. Cohen, M. E. Webber and G. T. Rochelle, in *Proceedings from ASME International Mechanical Engineering Congress and Exposition (IMECE)*, The American Society of Mechanical Engineers (ASME), Texas, United States, PARTS A AND B edn., 2012, vol. 6, pp. 581–593.
48. M. Bui, C. S. Adjiman, A. Bardow, E. J. Anthony, A. Boston, S. Brown, P. S. Fennell, S. Fuss, A. Galindo, L. A. Hackett, J. P. Hallett, H. J. Herzog, G. Jackson, J. Kemper, S. Krevor, G. C. Maitland, M. Matuszewski, I. S. Metcalfe, C. Petit, G. Puxty, J. Reimer, D. M. Reiner, E. S. Rubin, S. A. Scott, N. Shah, B. Smit, J. P. M. Trusler, P. Webley, J. Wilcox and N. Mac Dowell, *Energy & Environmental Science*, 2018, **11**, 1062–1176.
49. M. Bui, N. E. Flø, T. de Cazenove and N. Mac Dowell, *International Journal of Greenhouse Gas Control*, 2020, **93**, 102879.
50. R. M. Montañés, N. E. Flø and L. O. Nord, *International Journal of Greenhouse Gas Control*, 2018, **73**, 42–59.
51. M. Bui, I. Gunawan, V. Verheyen, P. Feron, E. Meuleman and S. Adeloju, *Computers & Chemical Engineering*, 2014, **61**, 245–265.
52. M. Bui and N. Mac Dowell, *Proceedings of the 15th Greenhouse Gas Control Technologies Conference, 15-18 March 2021*, 2021, Available at SSRN: http://dx.doi.org/10.2139/ssrn.3820843.
53. Bechtel, *CO_2 capture facility at Kårstø, Norway - Front-End Engineering and Design (FEED) Study Report. 320-CCC FEED Study*, Bechtel Power Corporation, https://ukccsrc.ac.uk/wp-

content/uploads/2020/03/8.5-x-11-Full-Karsto-FEED-Study-Report-Redacted-Updated_OCR-1.pdf, 2009.

54. Bechtel, *Operating and Maintenance Philosophy - CO_2 capture facility, Kårstø, Norway*, Bechtel Power Corporation, https://ukccsrc.ac.uk/wp-content/uploads/2020/03/Operating-and-Maintenance-Philosophy-25474-000-517-U07G-00001r001v2_0.pdf, 2009.
55. C. Bruce, *Email correspondence - Start-up/shut-down cycles of Boundary Dam*, International CCS Knowledge Centre, Regina, Canada.
56. J. R. Gibbins and R. I. Crane, *Proceedings of the Institution of Mechanical Engineers, Part A: Journal of Power and Energy*, 2004, **218**, 231–239.
57. J. R. Gibbins and R. I. Crane, *Proceedings of the Institution of Mechanical Engineers, Part A: Journal of Power and Energy*, 2004, **218**, 551–555.
58. S. M. Cohen, G. T. Rochelle and M. E. Webber, *Journal of Energy Resources Technology*, 2010, **132**, 021003-021001–021003-021008.
59. O. Errey, H. Chalmers, M. Lucquiaud and J. Gibbins, in *12th International Conference on Greenhouse Gas Control Technologies (GHGT-12)*, Energy Procedia, Austin, Texas, USA, 2014, vol. 63, pp. 7471–7484.
60. M. Bui, I. Gunawan, V. Verheyen, P. Feron and E. Meuleman, *International Journal of Greenhouse Gas Control*, 2016, **48, Part 2**, 188–203.
61. M. Bui, P. Tait, M. Lucquiaud and N. Mac Dowell, *International Journal of Greenhouse Gas Control*, 2018, **79**, 134–153.
62. G. M. de Koeijer, K. I. Aasen and E. S. Hamborg, Abu Dhabi International Petroleum Exhibition and Conference, Society of Petroleum Engineers, Paper SPE-171873, Abu Dhabi, UAE, 2014.
63. R. Faber, M. Köpcke, O. Biede, J. N. Knudsen and J. Andersen, *Energy Procedia*, 2011, **4**, 1427–1434.
64. A. Mangiaracina, L. Zangrilli, L. Robinson, H. M. Kvamsdal and P. Van Os, *Energy Procedia*, 2014, **63**, 1617–1636.
65. P. Moser, G. Wiechers, S. Schmidt, J. Garcia Moretz-Sohn Monteiro, C. Charalambous, S. Garcia and E. Sanchez Fernandez, *International Journal of Greenhouse Gas Control*, 2020, **95**, 102945.
66. C. Charalambous, A. Saleh, M. van der Spek, G. Wiechers, P. Moser, A. Huizinga, P. Gravesteijn, J. Ros, J. Garcia Moretz-Sohn Monteiro, E. Goetheer and S. Garcia, *Proceedings of the 15th Greenhouse Gas Control Technologies Conference 15-18 March 2021*, 2021, Available at SSRN: http://dx.doi.org/10.2139/ssrn.3812299.
67. P. Moser, G. Wiechers, S. Schmidt, J. Garcia Moretz-Sohn Monteiro, E. Goetheer, C. Charalambous, A. Saleh, M. van der Spek and S. Garcia, *Proceedings of the 15th Greenhouse Gas Control Technologies Conference 15-18 March 2021*, 2021, Available at SSRN: http://dx.doi.org/10.2139/ssrn.3812132.
68. P. Moser, G. Wiechers, S. Schmidt, J. G. M.-S. Monteiro, E. Goetheer, C. Charalambous, A. Saleh, M. van der Spek and S. Garcia, *International Journal of Greenhouse Gas Control*, 2021, **109**, 103381.
69. N. E. Flø, H. M. Kvamsdal and M. Hillestad, *International Journal of Greenhouse Gas Control*, 2016, **48, Part 2**, 204-215.
70. V. Andersson, K. Wittmeyer, O. Gorset, Y. Maree and K. Sanden, *Energy Procedia*, 2013, **37**, 6348–6356.
71. E. S. Hamborg, V. Smith, T. Cents, N. Brigman, O. F. Pedersen, T. De Cazenove, M. Chhaganlal, J. K. Feste, Ø. Ullestad, H. Ulvatn, O. Gorset, I. Askestad, L. K. Gram, B. F. Fostås, M. I. Shah, A. Maxson and D. Thimsen, 12th International Conference on Greenhouse Gas Control Technologies (GHGT-12), Austin, Texas, US, 2014.
72. A. K. Morken, S. Pedersen, S. O. Nesse, N. E. Flø, K. Johnsen, J. K. Feste, T. de Cazenove, L. Faramarzi and K. Vernstad, *International Journal of Greenhouse Gas Control*, 2019, **82**, 175–183.
73. R. Montañés, N. Flø and L. Nord, *Energies*, 2017, **10**, 1527.
74. J. N. Knudsen, J. N. Jensen, P.-J. Vilhelmsen and O. Biede, *Energy Procedia*, 2009, **1**, 783–790.
75. A. Awtry and E. Meuleman, *ION Advanced Solvent CO_2 Capture Pilot Project - Final Scientific/Technical Report*, ION Engineering LLC, Boulder, CO, USA. https://www.osti.gov/servlets/purl/1484045, 2018.
76. Koch-Glitsch, *Intalox Packed Tower Systems - Structured Packing*, http://www.koch-glitsch.com/masstransfer/pages/INTALOX-PACKED-TOWER-SYSTEMS.aspx, USA, 2010.

77. D. Thimsen, A. Maxson, V. Smith, T. Cents, O. Falk-Pedersen, O. Gorset and E. S. Hamborg, 12th International Conference on Greenhouse Gas Control Technologies (GHGT-12), Austin, Texas, US, 2014.
78. N. Brigman, M. I. Shah, O. Falk-Pedersen, T. Cents, V. Smith, T. D. Cazenove, A. K. Morken, O. A. Hvidsten, M. Chhaganlal, J. K. Feste, G. Lombardo, O. M. Bade, J. Knudsen, S. C. Subramoney, B. F. Fostås, G. d. Koeijer and E. S. Hamborg, 12th International Conference on Greenhouse Gas Control Technologies (GHGT-12), Austin, Texas, US, 2014.
79. L. Faramarzi, D. Thimsen, S. Hume, A. Maxon, G. Watson, S. Pedersen, E. Gjernes, B. F. Fostås, G. Lombardo, T. Cents, A. K. Morken, M. I. Shah, T. de Cazenove and E. S. Hamborg, *Energy Procedia*, 2017, **114**, 1128–1145.
80. N. E. Flø, L. Faramarzi, F. Iversen, E. R. Kleppe, B. Graver, H. N. Bryntesen and K. Johnsen, *International Journal of Greenhouse Gas Control*, 2019, **84**, 91–110.
81. F. Seibert, E. Chen, M. Perry, S. Briggs, R. Montgomery and G. Rochelle, 10th International Conference on Greenhouse Gas Control Technologies, Amsterdam, The Netherlands, 2010.
82. A. Cozad, N. V. Sahinidis and D. C. Miller, *AIChE Journal*, 2014, **60**, 2211–2227.
83. P. Brúder, A. Grimstvedt, T. Mejdell, E. F. da Silva and H. F. Svendsen, in *Proceedings of the 2nd Annual Gas Processing Symposium*, eds. F. Benyahia and F. T. Eljack, Elsevier, Amsterdam, 2010, vol. 2, pp. 31-40.
84. S. K. Dash, A. N. Samanta and S. S. Bandyopadhyay, *International Journal of Greenhouse Gas Control*, 2014, **21**, 130–139.
85. W. Zhang, J. Chen, X. Luo and M. Wang, *International Journal of Greenhouse Gas Control*, 2017, **63**, 37–46.
86. C. Nwaoha, T. Supap, R. Idem, C. Saiwan, P. Tontiwachwuthikul, M. J. Al-Marri and A. Benamor, *Petroleum*, 2017, **3**, 10-36.
87. C. Benquet, A. B. N. Knarvik, E. Gjernes, O. A. Hvidsten, E. Romslo Kleppe and S. Akhter, *Proceedings of the 15th Greenhouse Gas Control Technologies Conference 15-18 March 2021*, 2021, Available at SSRN: http://dx.doi.org/10.2139/ssrn.3814712.
88. P. Brúder, A. Grimstvedt, T. Mejdell and H. F. Svendsen, *Chemical Engineering Science*, 2011, **66**, 6193-6198.
89. H. Li, L. Li, T. Nguyen, G. T. Rochelle and J. Chen, *Energy Procedia*, 2013, **37**, 340–352.
90. P. Khakharia, L. Brachert, J. Mertens, C. Anderlohr, A. Huizinga, E. S. Fernandez, B. Schallert, K. Schaber, T. J. H. Vlugt and E. Goetheer, *International Journal of Greenhouse Gas Control*, 2015, **34**, 63–74.
91. P. Khakharia, H. M. Kvamsdal, E. F. da Silva, T. J. H. Vlugt and E. Goetheer, *International Journal of Greenhouse Gas Control*, 2014, **28**, 57–64.
92. A. J. Reynolds, T. V. Verheyen, S. B. Adeloju, E. Meuleman and P. Feron, *Environmental Science & Technology*, 2012, **46**, 3643–3654.
93. A. K. Morken, B. Nenseter, S. Pedersen, M. Chhaganlal, J. K. Feste, R. B. Tyborgnes, Ø. Ullestad, H. Ulvatn, L. Zhu, T. Mikoviny, A. Wisthaler, T. Cents, O. M. Bade, J. Knudsen, G. de Koeijer, O. Falk-Pedersen and E. S. Hamborg, *Energy Procedia*, 2014, **63**, 6023–6038.
94. Y. Maree, S. Nepstad and G. de Koeijer, *Energy Procedia*, 2013, **37**, 6265-6272.
95. G. de Koeijer, V. R. Talstad, S. Nepstad, D. Tønnessen, O. Falk-Pedersen, Y. Maree and C. Nielsen, *International Journal of Greenhouse Gas Control*, 2013, **18**, 200-207.
96. G. Wiechers, P. Moser, C. Benquet, J. Gibbins, J. Monteiro, A. Hartono, K.-A. Solli and H. Knuutila, *Deliverable Nr. D1.2.6 Guidelines for effective solvent management*, Accelerating Low carboN Industrial Growth through CCUS (ALIGN CCUS), ACT Project, https://www.alignccus.eu/sites/default/files/[WEBSITE]%20ALIGN-CCUS%20D1.2.6%20Guidelines%20for%20effective%20solvent%20management_0.pdf, 2020.
97. T. Spietz, S. Dobras, T. Chwoła, A. Wilk, A. Krótki and L. Więcław-Solny, *International Journal of Greenhouse Gas Control*, 2020, **102**, 103155.
98. T. Wang and K.-J. Jens, *International Journal of Greenhouse Gas Control*, 2014, **24**, 98-105.
99. S. Hume, M. I. Shah, G. Lombardo, T. de Cazenove, J. K. Feste, A. Maxson and C. Benquet, *Proceedings of the 15th Greenhouse Gas Control Technologies Conference 15-18 March 2021*, 2021, Available at SSRN: http://dx.doi.org/10.2139/ssrn.3821037.
100. H. M. Kvamsdal and G. T. Rochelle, *Industrial & Engineering Chemistry Research*, 2008, **47**, 867–875.
101. W.-P. Schill, M. Pahle and C. Gambardella, *Nature Energy*, 2017, **2**, 17050.
102. W.-P. Schill, M. Pahle and C. Gambardella, *Discussion Papers, Deutsches Institut für Wirtschaftsforschung*, 2016, **1540**, https://d-nb.info/115301274X/115301234.

103. BEIS, *2019 Government greenhouse gas conversion factors for company reporting: Methodology paper for emission factors final report*, Department for Business, Energy & Industrial Strategy, https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/904215/2019-ghg-conversion-factors-methodology-v01-02.pdf, 2019.
104. BEIS, *Carbon Capture and Storage knowledge sharing: Knowledge collected from UK CCS projects*, Department for Business, Energy & Industrial Strategy, https://www.gov.uk/government/collections/carbon-capture-and-storage-knowledge-sharing#list-of-peterhead-and-white-rose-key-knowledge-deliverables, 2015.
105. International CCS Knowledge Centre, *The Shand CCS Feasibility Study, Public Report*, https://ccsknowledge.com/pub/documents/publications/Shand%20CCS%20Feasibility%20Study%20Public%20_Full%20Report_NOV2018.pdf, 2018.
106. V. Andersson, K. Wittmeyer, O. Gorset, Y. Maree and K. Sanden, 11th International Conference on Greenhouse Gas Control Technologies (GHGT-11), Kyoto, Japan, 2012.

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