**Research Article**

**Pilot testing of CO\textsubscript{2} capture from a coal-fired power plant—Part 2: Results from 1-MWe pilot tests**

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**Abstract**

Using a 1-MWe slipstream pilot plant, solid-sorbent-based post-combustion CO\textsubscript{2} capture was tested at a coal-fired power plant. Results from pilot testing were used to develop a preliminary full-scale commercial design. The sorbent selected for pilot-scale evaluation during this project consisted of an ion-exchange resin that incorporated amines covalently bonded to the substrate. A unique temperature-swing-absorption (TSA) process was developed that incorporated a three-stage fluidized-bed adsorber integrated with a single-stage fluidized-bed regenerator. Overall, following start-up and commissioning challenges that are often associated with first-of-a-kind pilots, the pilot plant operated as designed and expected, with a few key exceptions. The two primary exceptions were associated with: (i) handling characteristics of the sorbent, which were sufficiently different at operating temperature than at ambient temperature when design specifications were established with lab-scale testing; and (ii) CO\textsubscript{2} adsorption in the transport line between the regenerator and adsorber that preloaded the sorbent with CO\textsubscript{2} prior to entering the adsorber. Results from the pilot programme demonstrate that solid-sorbent-based post-combustion capture can be utilized to achieve 90\% CO\textsubscript{2} capture from coal-fired power plants.

**Graphical Abstract**

**Keywords:** CO\textsubscript{2} capture; coal-fired power plant; CCS; solid sorbent; temperature-swing adsorption
Introduction

Capturing and geologically storing the carbon dioxide from point-source emitters may be one of the best options for controlling anthropogenic CO₂ emissions. Commercially available post-combustion processes for CO₂ capture from flue gas utilize an aqueous amine solvent, often monoethanolamine (MEA), to react with the CO₂ at low temperature and then release it in a purified form at a higher temperature. Because the solvent is in an aqueous medium, there is an energy penalty associated with solvent-based temperature-swing processes. For example, studies have shown that aqueous MEA for 90% CO₂ capture from a retrofit coal-fired power plant can reduce the thermal efficiency by approximately 20% and cost $60 per ton of CO₂ removed [1]. Much of this cost is associated with the heat of vaporization of water that is incurred when releasing the purified CO₂ in the heating/regeneration step. Most of the energy penalty associated with heating and cooling the solution can be recovered in a solvent-based system through a heat exchanger, but the heat of vaporization is non-recoverable.

In addition to potential cost savings, interest in solid sorbents is further motivated by environmental concerns associated with solvent technologies. In particular, a significant concern is the volatile emissions of amines. At the expected regeneration temperature, the vapour pressure of 3.5 M aqueous MEA is approximately 0.5 kPa [2]. Emissions of amines could be a significant environmental concern for aqueous CO₂-capture systems. Another environmental consideration is related to potential spills. If the sorbent used in a solid-sorbent-based process were to spill either in transport or at the power plant, neither the sorbent nor the amine will leach into the soil and the sorbent can be readily cleaned up without serious environmental consequences. Inadvertent leaks from systems using aqueous solutions are more difficult to contain and represent greater environmental risks. Finally, concerns exist that aqueous solutions that are regenerated and reused within a CO₂-capture system may concentrate heavy metals such as selenium or mercury, potentially leading to an issue with hazardous waste or supplemental wastewater treatment costs. By using a solid sorbent rather than water-based solvents, concentrating water-soluble contaminants may be avoided.

Solid sorbents can be used in a process that utilizes a temperature swing, referred to as the temperature-swing-adsorption (TSA) process. A temperature-swing process that utilizes solids has the potential to reduce the energy penalty associated with the post-combustion CO₂-capture process.

This paper and its companion Part 1 [3] present results from a project sponsored by the US Department of Energy (DOE) and supported by industrial groups, in which the viability of solid sorbents for CO₂ capture was assessed [4]. The project investigated the use of solid sorbents in a temperature-swing process for CO₂ capture as a means to significantly reduce costs associated with post-combustion CO₂ capture. A preliminary techno-economic analysis showed that levelized cost of electricity (LCOE) of the solid-sorbent process was within 10% of the costs typically associated with MEA systems [5]. An integrated development effort was used in which sorbent properties were co-developed with a suitable process.

In Part 1 of this work [3], properties of the sorbent to be used in the 1-MWe pilot-scale validation were measured using laboratory or bench-scale equipment under simulated-process conditions. Adsorption–desorption cycling of the sorbents in the laboratory using simulated-process gas provided confidence that the sorbent could be used in the 1-MWe pilot-scale tests for proof-of-concept validation. The results from a bench-scale, trickle-down reactor as well as from laboratory thermogravimetric analysis (TGA) tests suggested that the adsorption kinetics were very fast. Under typical cycling conditions, the rate of desorption was faster than the rate of adsorption, which has implications for the design of the adsorption and regeneration stages. The measured moisture uptake of the sorbent was affected by both the moisture concentration in the gas and the temperature. From this information, the delta moisture loading was estimated under the process conditions of the pilot unit. Laboratory testing showed that exposure of the sorbent to air or to gas with 6% O₂ at elevated temperatures reduced the CO₂ working capacity of the sorbent. Thus, the use of CO₂-lean flue gas, which contains residual O₂ as a carrier gas between the regeneration vessel and the adsorption vessel could lead to a loss of sorbent capacity. The heat-transfer coefficient of the sorbent, measured in a bench-scale fluidized bed, was higher than the original design value. This allowed a reduction in the overall height of the 1-MWe pilot adsorber, which reduced material, fabrication and installation costs.

In order to optimize the capital and operating costs of a process that achieves 90% post-combustion CO₂ capture, the process must be designed by taking into account the sorbent properties. A review of reactor-design options was conducted at the onset of the project [6]. Reactor types considered and the outcome of the design consideration are shown in Table 1. A summary of the selection process is included after the table.

Some reactor designs were quickly and easily removed from consideration. For example, an entrained reactor was eliminated because the CO₂ loading would be limited due to the CO₂ partial pressure at the reactor exit at the design goal of 90% CO₂ capture. Specifically, at 90% capture for a plant with 15% CO₂ in the flue gas operating at sea level, the CO₂ partial pressure would be 15 kPa at the inlet of the reactor and 1.5 kPa at the outlet of the reactor. Because the gas entrains the sorbent, CO₂ loading will be limited to equilibrium conditions at the reactor exit, or a CO₂ partial pressure of 1.5 kPa. Assuming an adsorption temperature of 40°C, a regeneration temperature of 120°C and the laboratory isotherms reported for the selected sorbent
in Part 1 of this paper [3], the working capacity in an entrained reactor would be approximately 1.5 g CO₂/100 g of sorbent, which is lower than the reported working capacity of aqueous MEA [7, 9].

True countercurrent flow, such as a trickle-down reactor in which solids are introduced at the top of a column and gas is introduced at the bottom, would result in the loaded sorbent exiting the reactor at inlet-gas conditions. Although the equilibrium loading under ideal conditions would be maximized, this reactor design was also eliminated as an option when considering the complexities associated with scale-up to a full-scale power plant. Novel packing structures would be required to maintain good sorbent distribution and effective gas/solids mixing and heat-transfer surface area to maintain proper operating temperatures as the sorbent was exothermically reacting with CO₂. In a fluidized-bed reactor, a multibed design can be used to approach countercurrent equilibrium conditions and increase the loading on the sorbent. Due to the exothermic reaction between the sorbent and CO₂ in the gas, a significant heat-transfer surface area is required to operate a TSA-based CO₂-capture process to prevent rapid quenching of the reaction due to increased temperature. The exact amount of heat-transfer surface area depends on the reactor type. Widely known empirical correlations were utilized during this project to estimate the heat-transfer coefficients for moving beds and fluidized beds. Because this is an order-of-magnitude estimate, it was assumed that the estimate applied to both fixed beds and tightly packed moving beds because the mechanisms of heat transfer are largely similar. The ratio of the overall heat-transfer coefficient for fixed/moving beds and fluidized beds can be observed from the data collected by Xavier et al. [8, 9]. As the gas velocity increases, the heat-transfer coefficient in the fixed bed slowly increases. More surface area for cooling would be required in a system operating with a higher heat-transfer coefficient. The overall heat-transfer coefficient in a bubbling fluidized bed is superior to that of other reactor types and that translates into a lower surface area. Due to the optimal equilibrium loading conditions and lower heat-transfer surface-area requirements, a bubbling fluidized bed was selected as the optimal reactor type for this project.

The conceptual design for the selected process used a three-stage fluidized bed for adsorption and a single fluidized bed for regeneration. A separate paper describes the characteristics of the sorbent selected for testing [3]. In this paper, we present and discuss the detailed design of the 1-MWe pilot-scale reactor and results from pilot testing at a coal-fired power plant.

1 Methods and materials

The design for the pilot was established based upon high-level laboratory results, including physical modelling and characteristics of the single ion-exchange resin sorbent selected for this project. The sorbent is described in more detail in a previous paper [3].

The host power plant burned sub-bituminous coal and had typical air-pollution-control equipment: selective catalytic reduction, cold-side electrostatic precipitator (ESP) and wet flue-gas desulphurization (FGD). The pilot was designed to treat a slipstream gas-flow rate of 51 m³/min of flue gas (actual conditions) extracted from the host plant downstream of the FGD unit at a temperature averaging 57°C. The design gas-flow rate corresponds to generation of approximately 1 MWe from coal. A conceptual sketch of the pilot showing the main components and measurement locations is shown in Fig. 1.

A slipstream of flue gas from the outlet of the host plant’s wet FGD passed through a polishing scrubber that reduced sulphur dioxide (SO₂) concentrations in the incoming flue gas to the design specification of <1 ppmv to minimize the formation of heat-stable salts that would create a loss of amine functionality. The temperature of the flue gas increased within the scrubber due to the heat of the reaction of the SO₂ with the scrubber’s 20% caustic solution. A built-in water/slurry cooler utilizing a plate-and-frame heat exchanger reduced the gas to a scrubber-exit temperature of 40°C.

A blower was installed after the scrubber to provide sufficient pressure to overcome the pressure drop of the capture system and allow flue gas to pass through the carbon-capture equipment and return it via ductwork back to the original stack. The pilot was designed to operate with a blower back pressure and differential pressure of 50 and 53 kPa, respectively. The pressure drop of the

Table 1: Reactor designs considered for the pilot programme

| Reactor design | Description |
|----------------|-------------|
| Entrained flow | Sorbent simultaneously reacts and is conveyed using the flue gas in the adsorber and (most likely) by a mixture of CO₂ and H₂O in the regenerator |
| Trickle-down   | Sorbent with significant mobility (i.e. not packed) flows countercurrent to gas |
| Moving bed     | Densely packed sorbent moves in the opposite direction to the gas while the gas can flow either countercurrent or across the sorbent |
| Fixed bed      | Stationary systems with internal heat transfer |
| Fluidized bed  | A series of fluidized beds in the bubbling regime where the gas moves upwards while the sorbent enters at the top bed and leaves the adsorber in the bottom bed. This design was chosen due to the optimal equilibrium loading conditions and lower heat-transfer surface-area requirements, as described below |

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system was due in part to the bed density, bed depth, pressure drop across the distribution plates at each stage and pressure drops through the cyclones and bag houses. As a result of the flue-gas compression, the flue-gas temperature increased. As the flue gas was compressed within the blower, the temperature increased by approximately 50°C. Immediately following the blower was a water-cooled shell and tube heat exchanger to reduce the temperature of the flue gas to the reactor inlet temperature of 40°C.

Flue gas entered the base of a three-stage fluidized bed after exiting the flue-gas cooler. Flue gas entered the bottom of the lower bed and proceeded upwards at sufficient velocity to fluidize the sorbent. Above each bed, there was a disengagement zone allowing gravity to carry most of the sorbent back into the bed immediately below the zone. Flue gas flowed through a distribution plate and into the next fluidization stage until the low-CO₂ gas exited the top of the adsorber.

Adsorber-operating parameters could be varied to influence the overall system performance. Key variables include:

- adsorption temperature;
- bed height in each of the staged fluidized beds;
- flue-gas volume into the adsorber;
- sorbent-circulation rate.

Densely packed CO₂-loaded sorbent exited the bottom of the pilot adsorber through a dip leg and slide-gate valve and was conveyed to the top of the regenerator using ~2.2 m³/min (standard conditions) of CO₂ from the CO₂-product stream. Flue-gas introduction into the regenerator was minimized by maintaining dense-phase conditions in the adsorber-exit dip leg. Sorbent exited the regenerator via an overflow pipe, thus the adsorber-outlet valve controlled the rate at which the sorbent circulated within the system. The sorbent mass flow rate range ranged from 0 to 15 000 kg/h.

CO₂-deficient flue gas exited the adsorber through a two-stage cyclone. As the flue gas tangentially entered the cyclones, any entrained sorbent particles were carried to the walls and exited the bottom of the cyclones through dip legs and were then returned to the adsorber. This cyclone pair was designed to remove particulate from the gas stream at 99.99% efficiency within the designated sorbent-particle-size distribution. Flue gas exited through the top of the cyclones and into a pulse-jet fabric filter to remove very fine sorbent that may have been damaged through attrition as well as any sorbent that may be carried through the cyclones during an upset in operation.

The regenerator consisted of a single-stage fluidized bed. A steam-fed condensing heat exchanger within the regenerator was used to heat the sorbent to the required regeneration temperature of 120°C. Indirect heating allowed better control of the system to prevent hot spots and potential damage to the sorbent as a result of exposure to high temperatures. The temperature of the regenerator could be controlled, affecting the equilibrium CO₂ loading on the regenerated sorbent. Upon heating, CO₂ was released from the sorbent and exited the regenerator through a two-stage cyclone and a small fabric filter similar to the arrangement at the flue-gas exit of the adsorber described previously. Some of the CO₂ was recycled to use as regenerator fluidization gas. In a commercial application, the balance of CO₂ would be transferred to a compression plant, while, in the pilot unit, the off-gas was returned to the plant stack.

The level of sorbent in the regenerator was not varied because the design incorporated an overflow pipe to remove sorbent. The regenerator was designed so that sorbent passing through the overflow was conveyed to a cyclone at...
the top of the adsorber using approximately 8.3 standard m³/min of 120°C CO₂. This cyclone should effectively separate the heated regenerated sorbent from the conveying CO₂. The sorbent exiting the cyclone would then enter the top of the adsorber through a densely packed dip leg to minimize the amount of CO₂ introduced into the scrubbed gas stream. As will be noted in the ‘Results’ section, the material-handling characteristics of the heated sorbent changed enough from the unheated sorbent to cause actual operations to deviate from design. The conveying CO₂ was routed to the inlet of the cyclone pair at the exit of the regenerator.

The 1-MWe pilot was instrumented to allow detailed analysis of temperatures, pressures, gas-flow rates, CO₂ concentrations and moisture levels throughout the system. Gas analysers were utilized to measure the gas at the adsorber inlet, outlet and the regenerator outlet; these sampling points allowed a mass balance to be calculated. These sampling locations are shown in Fig. 1. CO₂, O₂, SO₂, CO, NO and NO₃ were sampled in all locations marked. Intermittent H₂O measurements were taken at locations 2, 3, 4 and 5.

The percentage of CO₂ removal across the system was calculated as

\[
\text{Mass of CO}_2 \text{ in} - \text{Mass of CO}_2 \text{ out} \over \text{Mass of CO}_2 \text{ in}
\]

The mass of CO₂ in was calculated based upon the CO₂ measured in the flue-gas inlet at location 1. The mass of CO₂ out was calculated based upon flue-gas measurements in location 4, the adsorber outlet. The working capacity of the sorbent was calculated based upon the calculated sorbent mass circulation rate of the sorbent and the mass of CO₂ removed from the gas.

The sorbent-circulation rate was not measured directly due to challenges in measuring the flow of solids in the system. Sorbent circulation was calculated during testing using two pressure taps located in the vertical pipe at the outlet of the regenerator using the Darcy–Weisbach equation [10]:

\[
\Delta p/L = \lambda \rho u^2 / 2D
\]

where \( \Delta p/L \) is the pressure drop per unit length in the vessel, \( \lambda \) is the Darcy friction factor, \( \rho \) is the fluid density, \( u \) is the mean flow velocity and \( D \) is the hydraulic diameter of the vessel.

The equation can be rearranged to yield density and, since the density of the sorbent is much greater than that of the gas, this value can be used along with the measured gas flow to determine the sorbent flow rate.

Samples of the sorbent were collected throughout the duration of the 1-MWe pilot testing. Sorbent samples from different locations were analysed periodically and tested in the laboratory to assess whether any degradation had occurred and to monitor any uptake of the eight metals (arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver) classified as one of the ‘D’-listed wastes by the US Environmental Protection Agency under the Resource and Recovery Act (RCRA). Sorbent was collected from the adsorber and the regenerator.

2 Results

The goal of the parametric tests was to identify the optimal operating conditions for 90% CO₂ removal. Pilot testing reported herein was defined as Round 1 and Round 2 Parametric Testing. Parametric testing periods were planned to determine the sensitivity to flow and temperature and collect design details critical for scale-up. Most of the parametric testing periods were spent with operators working to maintain stable operation and struggling with challenges associated with the material-handling characteristics of the hot sorbent in a system designed using handling characteristics of cool sorbent. Specifically, the sorbent did not flow through the system as well at the higher operating temperatures.

During Round 1 of the parametric testing, CO₂ removal was much lower than expected based upon the calculated sorbent-circulation rate. However, on-site operators noted several indicators that, during some periods of operation, the cyclone designed to separate hot, regenerated sorbent from the CO₂ conveying gas became partially plugged, causing sorbent to exit the cyclone with the gas and be returned to the regenerator rather than dropping into the adsorber. This scenario would result in lower-than-expected CO₂ removal because a portion of the sorbent was not participating in CO₂ capture. This created uncertainty in the data analysis, because the fraction of sorbent recirculating to the regenerator could not be measured. Further discussion of this issue is included below.

2.1 Achieving stable operation

A fluidized-bed system is a dynamic system that requires careful controls for smooth operation. Prior to initiating parametric testing, stable sorbent circulation was achieved in the presence of flue gas, but without heating the regenerator. Upon increasing the sorbent temperature in the regenerator, sorbent-handling characteristics changed. These changes were not anticipated or thoroughly assessed during pilot-design activities and caused significant heated sorbent material-handling issues associated with the regenerator sorbent-exit cyclone and dip leg. Because the cyclone and dip-leg assemblies were not designed using proper material-handling considerations, pilot operations were challenging.

A sketch of the regenerator components including the transport line delivering CO₂-lean sorbent to the gas/solids separation cyclone dropping CO₂-rich sorbent into the top bed of the adsorber and the CO₂ gas exit on the regenerator and CO₂-sorbent fines cyclone pair is shown in Fig. 2 for reference. For clarity, note that the transport line delivering CO₂-rich sorbent from the bottom adsorber bed...
to the regenerator has been omitted. Please refer to Fig. 1 for the entire assembly.

During normal operation, sorbent should exit the regenerator through an overflow pipe and be conveyed upward to a cyclone using clean CO$_2$ taken from downstream of the CO$_2$ baghouse filter. This cyclone was designed to separate regenerated sorbent from the carrier gas, allowing CO$_2$-lean sorbent to exit the bottom of the cyclone and drop into the adsorber, and clean CO$_2$ exiting the top of the cyclone to be combined with CO$_2$ exiting the regenerator. However, when the sorbent was hot, sorbent in the cyclone exit could agglomerate, causing the exit to become partially plugged and sorbent to exit the top of the cyclone with the carrier gas rather than dropping into the adsorber. This sorbent could then drop back into the top of the regenerator or be carried into the cyclone pair designed to separate sorbent fines from relatively pure CO$_2$ gas.

Sorbent flow to the adsorber was measured using pressure taps located in the vertical pipe at the sorbent discharge of the regenerator and upstream of the CO$_2$-lean-sorbent cyclone (see Fig. 2). If sorbent was exiting the CO$_2$-lean-sorbent return cyclone (shown on the left of Fig. 2), the measured sorbent flow would not represent the actual sorbent flow into the adsorber. Specifically, the instrumentation would indicate higher sorbent flow into the adsorber than was actually occurring.

Although no direct measurements were possible to confirm that sorbent was periodically carried out of the CO$_2$-lean-sorbent separation cyclone with the carrier gas, indirect evidence was provided by the presence of large amounts of sorbent periodically clogging the CO$_2$-sorbent fine cyclone pair and subsequent sorbent backflowing into the CO$_2$ baghouse filter shown previously in Fig. 1.

2.2 Analysis and discussion of pilot results

During Round 2 of the parametric testing, fine-tuning of the regenerator-outlet CO$_2$-fluidization valves and careful operation to prevent sorbent bridging in the CO$_2$-lean-sorbent return cyclone were required to achieve CO$_2$-removal levels about 40%. Analysis of the raw data for the two distinct time periods and data sets, pre and post valve adjustment (see Table S1 in the online Supplementary Data) reveals significant changes in some of the results, which supports the hypothesis of sorbent carryover with the carrier gas out of the CO$_2$-lean cyclone and the associated reduced sorbent delivery into the adsorber during periods prior to operational adjustments.

Operating conditions compared to design conditions during the second round of parametric testing are presented in Table S2 in the online Supplementary Data. The regenerator was maintained at nominally 120°C, the design operation conditions, but dropped below this point periodically. The flow rate of flue gas through the
adsorber was varied between 10.2 and 45.3 actual m³/min throughout the period. The design condition for the pilot was 51.2 actual m³/min. The circulation rate of sorbent when hot, it was difficult to maintain the sorbent flow above about 9100 kg/h.

The results indicate that >90% of the CO₂ removal was achievable during some test conditions, particularly at low flue-gas (adsorber) flow rates. At gas flows of 22.7 actual m³/min or above, the CO₂ removal was typically below 50%.

Results from testing indicated that the overall pilot performance and the calculated capacity of the sorbent were much lower than expected. Data collected during Round 2 parametric testing were further analysed to determine trends. Due to periods of unstable operation, the data set was scrubbed for analysis to remove data corresponding to the conditions below.

- Calibration points generated during calibration of:
  - CO₂ analyser at adsorber inlet;
  - CO₂ analyser at adsorber outlet;
  - CO₂ analyser at regenerator outlet.
- Data generated during:
  - manual moisture measurement at CO₂-gas-sampling locations;
  - filter blow-backs at CO₂-gas-sampling locations;
  - regenerator temperatures <104°C;
  - other corrupt data as indicated by O₂ measurements in excess of 10% at CO₂-gas-sampling locations.

A plot of the CO₂ capture compared to the ratio of the sorbent-circulation rate/CO₂ mass flow for a range of flue-gas flow rates through the adsorber is presented in Fig. 3. For illustration, a line showing the CO₂ capture by a sorbent with a CO₂ delta loading across the adsorber of 5.4 g CO₂/100 g sorbent is included in the figure. Note that, because the units on the x-axis in the figure represent the sorbent-to-CO₂ mass ratio, 100% CO₂ capture is expected at a sorbent-to-CO₂ ratio of 18.5 at a delta loading of 5.4 g CO₂/100 g sorbent working capacity. Results indicating >5.4 g CO₂/100 g (5.4%) sorbent working capacity would fall to the left of the line shown in the graph. Thus, it is clear from the data shown that 5.4 g CO₂/100 g sorbent working capacity is the effective maximum delta CO₂ loading across the adsorber that the sorbent demonstrated during pilot operation.

An analysis of pilot-test results was conducted to determine key factors that were limiting the delta CO₂ loading on the sorbent across the adsorber and the CO₂-removal potential of the pilot. Several of the factors are discussed in the following paragraphs.

2.2.1 Sorbent stability
The TGA measurements performed on samples of sorbent taken from the pilot after Round 1 testing to assess the CO₂-capture performance indicated that no significant change in CO₂ capacity had resulted due to exposure to flue gas and system operation. During Round 1, the pilot experienced an upset condition when the temperature of the regenerator was initially increased to the design temperature. The system was operated with the flue gas for several days at 40°C to establish stable operation prior to this, however.

For the TGA measurement, the sorbent was exposed to 100% CO₂ at 120°C at first and subsequently CO₂ adsorption was assessed at temperatures in the range 120–40°C under 15% CO₂ in N₂. Details of these results are shown in Fig. 4.

Three sorbent samples were analysed using the TGA to determine whether there was any sorbent degradation after exposure to flue gas in the pilot. The samples were: Sorbent A (as-received), Sorbent B (sample taken from initial pilot testing) and Sorbent C (sample taken from pilot 2 months after Sorbent B).
initial pilot testing) and Sorbent C (sample taken from pilot testing 2 months after Sorbent B). The results indicated that the samples collected during Round 1 of testing did not show a substantial reduction in CO₂ working capacity between regeneration (120°C, 100% CO₂) and adsorption (40°C, 15% CO₂) conditions when compared to the as-received sorbent. Results of the particle-size analyses also showed no change in particle-size distribution from unused material.

The TGA analysis was again performed on sorbent taken from the pilot after 23 days of continuous operation, in addition to cycling in flue gas without regeneration for nominally 2 weeks during Round 1 parametric testing. This TGA analysis also indicated that there was no significant change in the CO₂ working capacity when compared to the as-received sorbent. During the TGA test, the sorbent was again exposed to 100% CO₂ at 120°C at first and subsequently CO₂ adsorption was assessed at temperatures in the range 120–40°C under 15% CO₂ in N₂. The TGA weight-versus-time trend for the stepwise temperature test is shown in Fig. 5.

Laboratory data from TGA testing suggested that the equilibrium working capacity of the sorbent under conditions present at the inlet and outlet of the adsorber in the pilot should approach 7 g CO₂/100 g sorbent. The CO₂ delta loading of the sorbent based on CO₂ measurements at the inlet and outlet of the adsorber compared to the mass flow of sorbent indicated that the working capacity within this portion of the system was 5.4 g CO₂/100 g sorbent (5.4%). Since laboratory data on sorbent removed from the system indicated that the equilibrium working capacity of the sorbent between the regenerator-outlet conditions and the adsorber-outlet conditions were relatively unchanged from the sorbent prior to field testing, it is likely that there was another explanation for the limited CO₂ working capacity calculated from pilot testing. Two potential explanations are non-equilibrium conditions at the exit of the adsorber and loading the sorbent with CO₂ prior to entering the adsorber. These two potential causes are discussed further in subsequent sections.

2.2.2 Preloading with CO₂ prior to adsorber
The most likely cause of the constrained working capacity is associated with the conveying gas used to transport sorbent from the regenerator to the adsorber. The conceptual design approach was to use CO₂-lean flue gas to minimize the adsorption of CO₂ onto the regenerated sorbent. Because of the risk of oxidation of amines at elevated temperatures in the presence of oxygen, a last-minute design change was made prior to pilot testing to use oxygen-free gas. Rather than using nitrogen, which would have required adding a large nitrogen generator and other design changes in the pilot that may not be feasible at full scale, a decision was made to use CO₂-rich gas from the outlet of the regenerator blower at the outlet of the CO₂ baghouse filter as the conveying gas. See Figs 1 and 2 for details on the locations of the components. Although the risk of CO₂ uptake was noted, the risk was initially discounted because of the misconception that the nominal 2 seconds of residence time during sorbent conveying was not sufficient to result in significant CO₂ adsorption in the transport line.

The regenerator blower-outlet temperature at the regenerator fluidizing and carrier lift gas location was nominally 75°C, well below the regeneration temperature of 120°C. The cooled blower-exit CO₂ was used as the carrier gas to transport the regenerated sorbent from the regenerator outlet to the adsorber. The average carrier gas flow was 8.2 standard m³/min. The stream was 80–90% CO₂, which results in nominally 816 kg/h CO₂ in the carrier gas. Based on the sorbent isotherms presented in Part 1 of this paper [3], at 75°C and 80 kPa partial pressure, the sorbent loading is at equilibrium at around 8.5 g CO₂/100 g sorbent (note that this is total loading, not working capacity).

Although insufficient time was available while the sorbent was transported from the regenerator to the adsorber to reach equilibrium, laboratory results suggests that even a few seconds could result in significant CO₂ uptake. Results from trickle-down reactor testing in the laboratory [3] indicated that <2 seconds was sufficient for the sorbent to adsorb 2.6 g CO₂/100 g sorbent at 40°C from a gas stream with 12.5% CO₂. Additionally, a thermocouple that was installed in the dip leg below the cyclone designed to separate returning sorbent from the carrier gas indicated that the sorbent had cooled to 63°C prior to entering the adsorber.

Referring again to the sorbent isotherms suggests the information shown in Table 2. If the sorbent did not adsorb any CO₂ from the transport line prior to entering the adsorber vessel, these laboratory results indicate that sorbent could absorb an additional 7.02 g CO₂/100 g sorbent from the flue gas. However, if the sorbent removed some
CO₂ from the carrier gas between the regenerator and the adsorber, the amount of CO₂ that could be removed from flue gas in the adsorber would be lower. Recall that, from Fig. 3, the maximum sorbent delta loading in the adsorber calculated from pilot testing was limited to 5.4 g CO₂/100 g sorbent. The overall working capacity between the regenerator outlet and adsorber outlet matches the laboratory-predicted 7.0 g CO₂/100 g sorbent when the sorbent reaches 1.6 g CO₂/100 g sorbent at the exit of the transport line and an additional 5.4 g CO₂/100 g sorbent while in the adsorber.

Using heated CO₂ or oxygen-free flue gas to convey sorbent from the regenerator to the adsorber should mitigate adsorption in the conveying line because adsorption of CO₂ decreases with increasing temperature, as illustrated in Fig. 5. Unfortunately, challenges with pilot operation and subsequent limitations in funding prevented testing of this hypothesis.

### 2.2.3 Computational modelling

A model was developed to better understand the potential impact of CO₂ adsorption in the transport line between the regenerator and adsorber, and the resulting impacts on pilot performance. A sketch of the three-stage reactor, showing key model inputs (in blue) and select calculated parameters, is shown in Fig. 6. The simplified model assumed isothermal conditions in the adsorber at 40°C and system pressures that were consistent with both the design conditions and operation. A curve fit of the 40°C sorbent isotherms from laboratory testing for the range of partial pressure expected in the adsorber was incorporated into the model, where

\[
\text{CO}_2 \text{ loading} = 0.57\ln(P, \text{MPa}) + 15.56, \quad R^2 = 0.99 \tag{3}
\]

The flue-gas flow rate, inlet CO₂ concentration and sorbent-recirculation rate were independent variables in the model. Data from pilot testing were used to calibrate the model for the amount of CO₂ that entered the adsorber with the return sorbent. As noted previously, the equilibrium loading was based on the TGA analysis at the conditions in the transport line between the regenerator and the adsorber being nominally 75°C and 80% to 90% CO₂. At 75°C and 80-kPa partial pressure, the loading is 8.5 g CO₂/100 g sorbent (note that this is total loading, not working capacity).

Outputs of the model compared to the pilot results are presented in Table 3. As shown in the table, if the sorbent loading entering the adsorber is consistent for all conditions at 6.3 g CO₂/100 g sorbent, which is below the equilibrium loading for conditions in the transport line, the model output for CO₂ removal across the adsorber is in good agreement with actual pilot-test results (see Cases 2–4 in the table). For Case 1, the sorbent-circulation rate was near the limit of stable pilot operations. The low-measured CO₂ removal in the pilot compared to model results suggests that a portion of the sorbent was recirculating back into the regenerator through the CO₂-lean-sorbent cyclone, as discussed previously.

Two additional model runs are shown in Table 3. Case 5 shows the pilot-design conditions for the adsorber flow rate and the sorbent-circulation rate with the additional CO₂ added to the transport gas. Case 5b shows the design conditions without additional CO₂ collected in the transport line. The model predicts >90% CO₂ removal at the pilot-design conditions with the sorbent if the CO₂ addition in the transport line is eliminated. These data are shown with the pilot results graphically in Fig. 7. There are no pilot results for Case 5 because, as previously discussed, there were handling issues associated with the sorbent at elevated temperatures that prevented operation at design flow rates. Physical modifications to the CO₂-lean-sorbent cyclone and dip leg at the outlet of the regenerator would be required to accommodate issues associated with handling hot sorbent.

Complete characterization of each bed in the adsorber using field measurements was not possible due to sampling issues. Occasional spot checks could be performed with a portable CO₂ analyser within the disengaging space between the bottom and middle beds and between the middle and top beds. These spot checks indicated that ≤80% of the capture occurred in the top bed; however, the data are questionable, as the analysers sampled through an extraction system that could have had a pressure slightly higher than ambient and that did not cool the gas sample. Given the questionable nature of these readings and the fact that they were not continuous, it was not practical to determine a mass balance around each bed from actual measurements. The model developed does provide insights, however.

When the sorbent-recirculation rate compared to CO₂ entering the system is low, more CO₂ is captured in the top bed because the sorbent approaches capacity before cascading into lower beds. As the sorbent/CO₂ ratio increases, the fraction of CO₂ captured in the top bed approaches zero because the CO₂ captured in the gas is adsorbed by the excessive sorbent prior to reaching the top bed. Furthermore, the model suggests that, as the CO₂ removal increases, the benefit of three stages versus two stages declines because most of the removal is occurring in the lower two beds. These results are shown in Fig. 8 for both the case with CO₂ in the transport gas from the regenerator to the adsorber contributing to the loading on the sorbent and for the case where no additional CO₂ from the transport gas is adsorbed by the sorbent.

| Location                  | Temperature (°C) | Equilibrium CO₂ loading (g CO₂/100 g sorbent) |
|---------------------------|------------------|-----------------------------------------------|
| Regenerator exit          | 120              | 3.45                                          |
| Adsorber exit             | 40               | 10.47                                         |
| Delta loading             |                  | 7.02                                          |
| (adsorber—Regen)         |                  |                                               |
Additional analysis was conducted using the model in conjunction with the pilot data to estimate the influence of sorbent-residence time in the adsorber, or sorbent kinetics, on sorbent-adsorption capacity. Fig. 9 presents the delta CO₂ capacity across the adsorber as a function of residence time in the adsorber for several model cases and corresponding experimental results. The CO₂/Sorb values shown in the legend represent the ratio of CO₂ in the flue gas entering the system to the sorbent-circulation rate in g CO₂/100 g sorbent. This is the inverse of the sorbent-circulation rate presented previously as Sorb/CO₂ (kg/kg) multiplied by 100 for easier comparison to the delta capacity in this figure. For the experimental results, the amount of CO₂ captured in the adsorber, or delta capacity across the absorber, was estimated using the total capture across the entire system and the estimated CO₂ recaptured in the sorbent transport line between the regenerator and stage 3 of the adsorber.

For all cases, there does not appear to be a correlation between sorbent-residence time and the delta capacity of the sorbent. Specifically, when the flue gas CO₂/Sorb ratio (legend values) was in excess of 5.4 g CO₂/100 g sorbent, the maximum delta loading from pilot testing as discussed in Fig. 3, the delta capacity on the sorbent was relatively high. When the CO₂/Sorb ratio was lower, the delta loading was limited by excess sorbent. It should be noted that, for the lowest CO₂/Sorb case (CO₂/Sorb = 2.4), the CO₂ capture measured across the pilot was 88% at 15 minutes of residence time in the adsorber. This supports the hypothesis that adsorption was not limited by residence time in the adsorber.
2.3 Analysis of solids and liquids

The as-produced sorbent selected for use in this project is considered non-hazardous by the OSHA Hazard Communication Standard. Throughout the operation, the pilot samples were extracted from the system and analysed for eight RCRA metals (arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver) to monitor for any accumulation that could lead to reclassification of the used material. The results of this testing show that no significant accumulation occurred and that the majority of the monitored constituents were below the recordable limit of the testing method.

Total liquid discharge of the system was monitored for total suspended solids, HEM (oil and grease), as well as RCRA metals. The total discharge was the combined discharge of the SO₂ scrubber blowdown, the flue-gas-cooler condensate, CO₂-cooler condensate, as well as the steam condensate. Results from this testing also indicated that no significant accumulation occurred and that the majority of the monitored constituents were below the recordable limit of the testing method. Pilot testing indicates that no special consideration for process waste is required.

2.4 Techno-economic analysis

Two high-level techno-economic assessments (TEAs) were completed: one prior to pilot testing using the design conditions and one following pilot testing using data collected during the 20-hour, 90% CO₂ capture test. The reader is referred to [4, 5] for detailed TEA results. Based on the results from pilot testing and extrapolations using the computational operating model for conditions where adsorption of CO₂ in the transport line between the regenerator and adsorber was mitigated, the TEA utilizing pilot-design parameters conducted prior to testing is valid. For this case, the sorbent-based CO₂ capture resulted in lower cost of electricity increases (as compared to the base case) than the benchmark Econamine-based CO₂ capture. Specifically, the preliminary estimates indicate that a PC plant featuring the solid-sorbent process evaluated during this project could lead to improved economic viability as well as a greater technical performance than that of the MEA process published in the DOE Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity, Rev. 2 [2]. The cost of electricity (COE) is lowered by 3% and the net plant efficiency is increased by 13% for the initial study [5].

Conversely, if data from the 20-hour, 90% capture test is utilized for the TEA, solid sorbents are not competitive with the Econamine because, during these tests, the sorbent capacity was partially utilized by CO₂ in the gas carrying the regenerated sorbent to the adsorption
module, as previously discussed. Thus, the amount of sorbent required for 90% capture of emitted CO$_2$ was unrepresentative.

A comparison of the key economic considerations between the Econamine-based process and the solid-sorbent-based process shows that:

- Capital costs, fuel costs and CO$_2$ transport, storage and monitoring (TS&M) costs of the sorbent-based process were lower than those of the MEA case, respectively. Specifically, to generate 550 MWnet with 90% CO$_2$ capture, the gross power plant was smaller when sorbent-based CO$_2$ capture was used due to the lower thermal input required to operate the CO$_2$-capture facility.
- The operating and maintenance (O&M) costs of the sorbent-based CO$_2$-capture process were estimated to be higher than those of the MEA process, mostly as a result of a high sorbent cost and consumption for an initial fill.
- The electricity requirement for the compression of CO$_2$ is significant for both aqueous amine and sorbent-based CO$_2$ capture. However, because the gross power plant with sorbent-based capture is smaller, less CO$_2$ must be compressed and the related costs are nominally lower.
- The COE and LCOE of the sorbent-based process were lower than those of the aqueous MEA system due to lower capital costs, fuel costs and CO$_2$ TS&M costs, offsetting higher O&M costs.

In addition to costs, there are also environmental benefits for the sorbent-based CO$_2$ capture. For example:

- The coal supply to the PC plant is linearly related to the power-plant gross thermal output. Because the gross thermal output for the power plant with sorbent-based CO$_2$ capture is estimated at nominally 11% less than that for the Econamine process, less coal is burned and thus less Hg, SO$_x$, SO$_3$, NOx, etc. are created.
- Similarly, the raw water consumption of the power plant with the solid-based process is 20% lower than that of the Econamine process. This can be attributed to the fact that the gross power plant is smaller when the sorbent-based CO$_2$-capture process is implemented. Because water is likely to become an increasingly scarce resource in the future, lower water consumption could play an important role in the CO$_2$-capture technology-selection process.
- A significant environmental concern is related to the volatile emissions of amines. At the regeneration temperature of 120°C, the vapour pressure of 3.5 M aqueous MEA is approximately 0.5 kPa; emissions of amines could be a significant environmental concern for aqueous CO$_2$-capture systems. Although the sorbent has been degraded in the laboratory using excessively high temperatures, no measurable volatile emissions were recorded using a mass spectrometer and no degradation of sorbent exposed to flue-gas and temperature cycles was noted from sorbent samples removed from the pilot. It is possible that the amine
on the selected sorbent remains covalently attached to the surface of the substrate even when being converted to urea, heat-stable salts or being otherwise degraded.

- Solid-waste disposal in the sorbent-based process was determined to be non-hazardous as a result of EPA Method 1311 screening which indicated that heavy metals including mercury and selenium were not concentrated in the sorbent. As a result, no special handling or additional costs or equipment was determined to be necessary for sorbent disposal. Thus, if Sorbent BN were to spill either in transport or at the power plant, unlike an aqueous solution, the sorbent will not seep into the soil. The sorbent could more easily be cleaned up without serious environmental consequences. The sorbent is not considered hazardous by the OSHA Hazard Communication Standard; thus, waste disposal should be in accordance with the plant’s local environmental controls.

3 Conclusions

Overall, following start-up and commissioning challenges that are often associated with first-of-a-kind pilots, the pilot plant operated as designed and expected, with a few key exceptions. The two primary exceptions were associated with the handling characteristics of the hot sorbent that were outside of design specifications, which were collected at ambient temperature, and CO₂ adsorption in the transport line between the regenerator and adsorber. As a result, no special handling or additional costs or equipment was determined to be necessary for sorbent disposal. Thus, if Sorbent BN were to spill either in transport or at the power plant, unlike an aqueous solution, the sorbent will not seep into the soil. The sorbent could more easily be cleaned up without serious environmental consequences. The sorbent is not considered hazardous by the OSHA Hazard Communication Standard; thus, waste disposal should be in accordance with the plant’s local environmental controls.

4 Nomenclature

| Symbol | Meaning |
|--------|---------|
| D      | Hydraulic diameter of reaction vessel, m |
| Λ      | Darcy friction factor |
| L      | Length of reaction vessel, m |
| P      | Density of flue gas, kg/m³ |
| P      | Pressure, bar |
| V      | Mean gas-flow velocity, m/s |

Supplementary Data

Supplementary data is available at Clean Energy online.

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Conflict of Interest

None declared.

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