Final Report

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Sorbent Based Post-Combustion CO_2 Slipstream Testing

Final Report

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Executive Summary

TDA Research, Inc. is developing a new CO_2 sorbent (alkalized alumina) technology for post-combustion CO_2 capture. In this DOE sponsored project (DE-FE0012870), TDA constructed a pilot-scale skid, which was installed and tested at National Carbon Capture Center (NCCC). It was designed to process coal derived flue gas equivalent to 0.5 MW_e of power generation. The pilot test data shows that TDA's process can achieve 90% capture rate and 95% CO_2 purity (the performance target) for both coal and natural gas (NG) flue gases. The techno-economic analysis (TEA) for a 550-MW_e supercritical coal fired power plant with CO_2 capture shows that the capture cost for TDA's process is \$34.9/tonne CO_2 captured, which meets DOE's goal of \$40/tonne and is 17.1% less than the DOE baseline Case 12 (an amine solvent technology).

TDA's process is based on a low-cost alkalized alumina sorbent that absorbs and desorbs CO_2 at about the same temperature (140°C). The major reaction is $M \cdot H_2O + CO_2 \rightleftharpoons M \cdot CO_2 + H_2O$, in which M represents the sorbent. In adsorption step, CO_2 displaces H_2O from the sorbent as the forward reaction; in regeneration step, H_2O displaces CO_2 from the sorbent as the reverse reaction, which is displacement desorption. The reaction heat of this reaction is also low. In our case, the sorbent is regenerated without a temperature-swing or pressure-swing process. TDA's process is a nearly isothermal operation at ambient pressure. We expect the cost of the sorbent to be \$2~3/kg at commercial scale.

For a coal fired power plant, the simplified flow diagram is shown in Figure 1. The CO_2 in flue gas is adsorbed in the capture unit. Steam enters the capture unit to regenerate the sorbent by displacing the CO_2 from the sorbent. High purity CO_2 product is obtained at the steam outlet after the moisture is condensed. In the optimized process, strip air is fed into the capture unit to further regenerate the sorbent. The strip air contains a small amount of CO_2 at the outlet and is mixed with the rest of the incoming combustion air, thereby increasing the CO_2% in the flue gas at the boiler outlet. Higher CO_2% in flue gas is favorable for the adsorption kinetics. Unlike a thermal swing process, the steam is used to displace the CO_2 absorbed by the sorbent, not as a heat source.

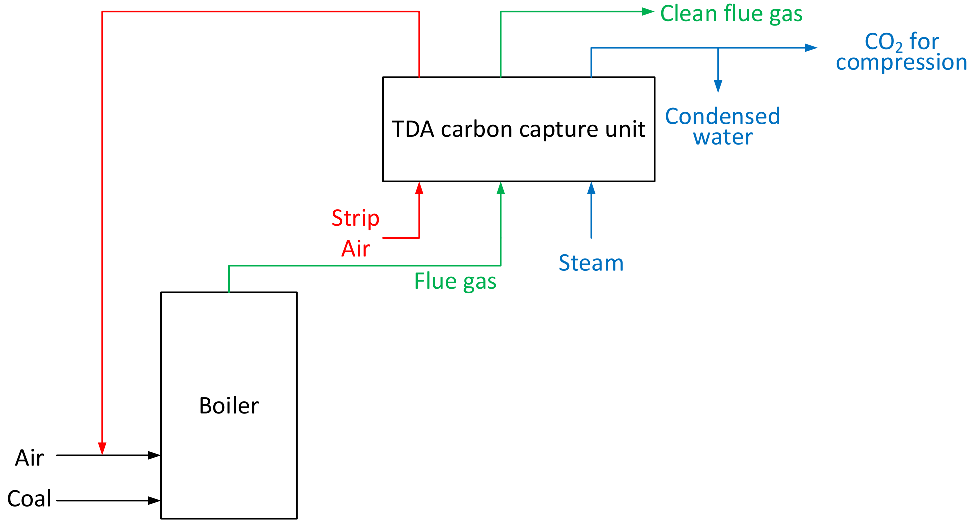


Figure 1. Simplified flow diagram of TDA's CO_2 capture process

For our unique isothermal operation, fixed bed reactors are the most economic option for the process. No costly sorbent transfer step is needed. By controlling the flow paths, we operate 10 reactors to simulate a moving-bed process. The flue gas goes through the beds in parallel to reduce the pressure drop. The steam flows in series to make the full use of it.

At the beginning of the project, University of California, Irvine (UCI) carried out a preliminary TEA, which was based on experimental data collected under a previous project (DE-NT0005497). Three cases were analyzed. Case 1 used natural gas to heat the flue gas before entering the capture unit, which was not economical for carbon capture. Thus, both Cases 2 and 3 used the boiler feed water to heat the flue gas. Case 2 studied the operating conditions needed to achieve \$40/tonne CO_2 captured. In Case 3, the capture unit used 12 beds, increased from 8 beds in previous design. Our bench-scale tests showed 12-bed system consumed less regeneration steam. The capture cost for Case 3 was \$37.8/tonne, meeting DOE's goal of \$40/tonne.

TDA ran tests in the bench-scale apparatus (Figure 2) to study the optimized process design. Adsorption was run in parallel among beds, and regeneration was run in series. New process steps, including air purge, steam saver, and breakthrough recycle, were identified and then tested in experiments. The flow mode containing air purge and steam saver had the best performance. We found the break-through recycle was not worth the added capital and operating cost for this more complex system. The number of beds was reduced from 12 to 10 as well.

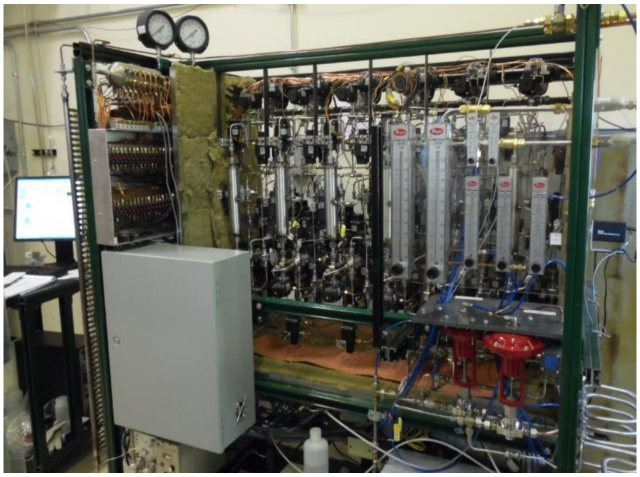


Figure 2. TDA Multiple fixed bed bench-scale apparatus

After the number of beds and flow mode were finalized, TDA started the detailed design of the pilot unit. A comprehensive stream table for a typical run in the pilot test was calculated. The sorbent reactors, sorbent trailers, service unit and instrument unit were designed based on our process and subjected to the constraints of the test site at the NCCC. The 3d model of the pilot unit was shown in Figure 3. It took the space of three semi-truck trailers. The two sorbent trailers, housing 5 reactors each, were on the outside. Each reactor contained about 1.75 m^3 of sorbent. The service and instrument trailer, containing blowers, heaters, flow meters and instruments, etc., was located in the middle. A Process Hazard Analysis was conducted and safety features were added to address hazard issues. The construction cost for the pilot unit was estimated as \$2.03 million, not including TDA labor or General and Administrative Expenses.

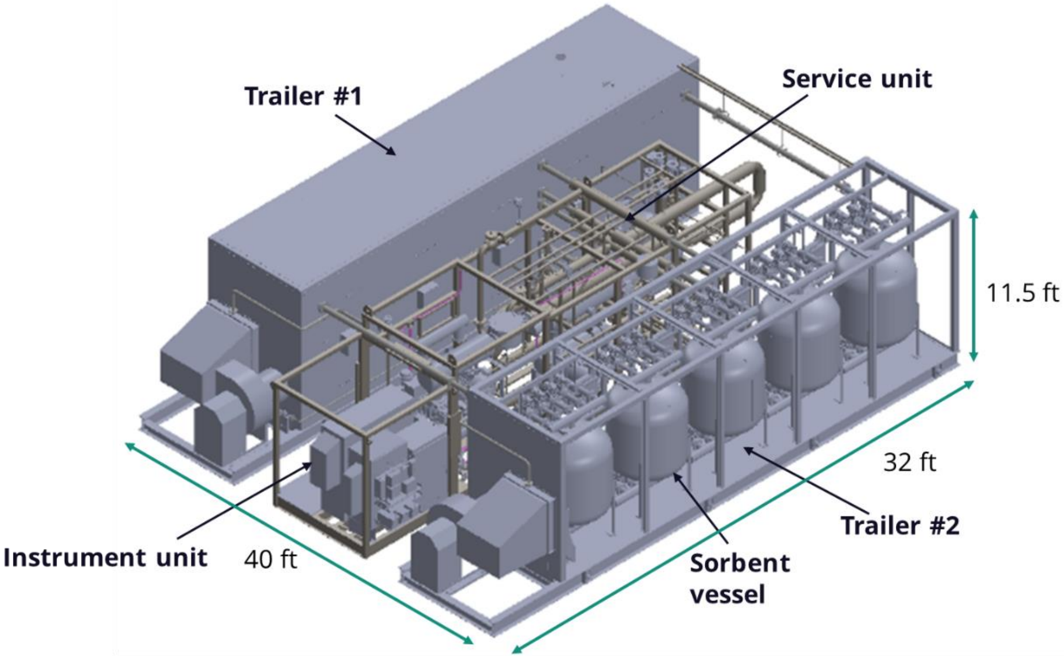


Figure 3. 3d model of TDA's pilot unit

TDA’s design went through a series of engineering reviews, and was determined to comply the safety requirements from NCCC. The pilot unit was constructed at Spring Fabrication Inc. in Colorado Springs, CO, and TDA’s team routinely visited to check the initial progress, and then worked at Springs Fabrication alongside their workers during final assembly and check-out. The construction was complete in September, 2017. The Factory Acceptance Testing was conducted in early October, 2017.

Two rounds of sorbent scale-up were conducted to finalize the sorbent production process. In the first round, TDA’s sorbent manufacturing partner produced the 4 different sorbents, which were modified from existing commercial sorbents. Single bed test results for these 4 sorbents were OK, but the 10-bed test results were not. The second round scale-up production was based on the recipe of the best TDA sorbent. 3 samples were made and they had small difference on the recipes. The performance of Batch 1 was excellent and the Batch 1 recipe was chosen for the large-scale production. TDA’s partner produced the 15-ton sorbent in its plant and shipped the sorbent to NCCC.

In the 4th quarter of 2017, the pilot skids were installed at NCCC and the pilot sorbent was loaded. TDA later found the sorbent was manufactured incorrectly at the factory of TDA’s partner. Lab tests showed the sorbent had good performance initially, but its long-term stability was not acceptable. Further characterization tests determined the sorbent contained unreacted raw materials, which led to the lack of stability. In order to remedy the as-received sorbent, TDA worked with our partner to develop a process to reprocess the sorbent. The original sorbent was extracted from the 10 pilot reactors and reprocessed in 2018. Due to unavoidable volume loss in the sorbent reprocessing, only 8 reactors (beds 3-10) were filled with reprocessed sorbent. Beds 1 and 2 were loaded with Dynocel, which is based on a commercial sorbent, but modified using a process developed at TDA that improves its performance.

To hydrate the fresh sorbent as a pre-treatment step, TDA developed a procedure to flow hot humid air though the bed where the H_2O% gradually increased from 0.4 mol% to 100 mol%.

This procedure controlled the temperature rise of the sorbent during the exothermic hydration in the reactors.

The 2019 pilot test showed significant benefits of the purge and steam saver steps that we had added to TDA's process. 90% capture and 95% CO_2 purity were achieved for both coal and simulated NG flue gases (diluted from coal flue gas). The test was stopped in October 2019 due to a plant outage. In late January 2020, we found the sorbent had changed into a different form and had much lower capture capacity than the sorbent before the 3.5-month shut-down, and we suspected that the moisture in the reactor changed the sorbent.

The compromised sorbent was extracted and fresh sorbent was loaded in the second quarter of 2021. Beds 1-5 were loaded with Dynocel, and Beds 6-10 with Chlorocel (a commercial sorbent). Although neither of two sorbents were as good as the TDA sorbent developed in the lab, they were the best available options based on the budget and manufacturer's schedule. The pilot test in 2021 went very well, with few interruptions. The skid successfully met the performance target for flue gas with CO_2% in the range of 4~11%. The long-term test data was summarized in Table 1. The flue gas was supplied by a coal boiler from July 22nd until August 30th, 2021. From August 31st to October 20th, 2021, flue gas was supplied by a natural gas boiler. For coal flue gas, the system reached performance target when processing up to 0.62 MW flue gas, showing a capacity that was 24% higher than design capacity. The strip air flow was designed to be 0.25 of that of the flue gas. The test data showed the strip/flue ratio can be reduced to as little as 0.18, which saves the power consumption for the strip air blower. The test was concluded in October 2021. After the 3-month test, the Dynocel sorbent still maintained 91% capture capacity and the degradation had stopped. The degradation for Chlorocel was much worse (as expected), since it was not designed for use as a long-term carbon capture sorbent, but was the only available sorbent when we wanted to replace the previous sorbent.

Table 1. TDA skid performance in long-term test

Date	Flue gas SV, 1/hr	CO_2% (wet) in flue gas	Capture rate	Purity
8/25/2021	261	10.9	90.9%	99.2%
9/2/2021	268	4.0	90.4%	99.7%
9/9/2021	264	4.2	93.5%	95.0%
9/23/2021	268	4.2	90.6%	96.3%
9/29/2021	258	4.2	90.2%	99.2%
10/4/2021	260	9.0	90.8%	97.9%
10/12/2021	265	8.9	90.7%	97.2%

After the pilot test, XRD measurements were done for the cycled sorbents. Both Dawsonite and Boehmite were seen in cycled Dynocel and Chlorocel. Recalcination of Dynocel converted it back to the same phase as the fresh Dynocel as shown from the XRD data. The recalcined Dynocel restored some CO_2 capacity, but not as high as a fresh one.

Our Environmental, Health and Safety Risk Assessment showed the sorbent production and pilot operation do not pose any environmental risk to local communities. NCCC ran analyses for the cycled sorbents and did not detect any sulfur and heavy metals. Thus, the sorbents were disposed as non-hazard material. The pilot unit was decommissioned in May 2022. The sorbent trailers were scrapped in Alabama, and the service unit and instrument unit were shipped back to TDA.

Since we changed the system from 12 beds to 10 beds, five new cases were run for the final TEA. The TEA results for Cases 4-8 are shown in Table 2. Cases 4-7 were based on the bench-scale test. Case 4 was the baseline for the 10-bed system. Heat integration approaches were applied in the capture unit to Cases 5 and 6, in order to increase plant efficiency. Case 5 had higher plant efficiency than Case 4, but at a price of high capital cost. Case 6 achieved higher plant efficiency and had less increase on the capital cost, so the capture cost was about the same as Case 4. In addition, the cost of avoided CO_2 for Case 6 was less than Case 4. Thus, the heat integration in Case 6 was worth doing. The capture rate for Case 7 was reduced to 80%, while the process design was the same as Case 6. The CO_2 capture cost of Case 7 was 4% lower than Case 6. Reducing the capture rate from 90% to 80% didn't save significantly. Case 8 incorporated the pilot test data and used the same process as Case 6 with 90% capture. Pilot test showed the sorbent could process more flue gas than the designed case, had less pressure drop than calculation from the empirical equation, and used less strip air. Thus, the capture cost for Case 8 was less than Case 6. The capture cost for Case 8 is 17.1% less than DOE Case 12 (an amine based solvent process). The cost saving is mainly from the higher plant efficiency and lower capital cost. TDA's process consumes less auxiliary power than DOE Case 12.

Table 2. The TEA results for the Cases 4-8

CASE NO.	DOE 12	4	5	6	7	8
Description		TDA – Air Stripping W/O BTR	Same as Case 4 except Raw CO2 Compressor as Heat Pump	Same as Case 4 except additional Stripped Air Heat Recovery	Same as Case 6 except Lower Carbon Capture & Steam Use	Same as Case 6 except Lower Steam Use
Carbon Captured, %	90	90	90	90	80	90
Steam Turbine Power, KWe	662,800	658,848	663,702	658,448	647,171	654,485
Total Auxiliary Consumption, KWe	112,830	108,848	113,702	108,448	97,171	104,485
Net Power Output, KWe	550,000	550,000	550,000	550,000	550,000	550,000
Net plant efficiency (HHV), %	28.4	29.85	29.94	29.96	31.66	30.25
As-received coal feed, kg/h	256,652	244,481	243,692	243,575	230,486	241,215
Natural Gas Feed, kg/h	0	0	0	0	0	0
Raw Water Withdrawal, m^3/min	38.1	33.1	32.9	32.9	29.6	32.4
1st year cost of electricity (COE) w/o CO_2 TS&M, $/MWh, 2007$	100.9	94.6	94.9	94.5	87.8	92.2
1st year CO2 capture cost w/o TS&M, $/tonne, 2007$	42.1	37.00	37.51	37.02	35.57	34.90
1st year CO2 avoided cost w/o TS&M, $/tonne, 2007$	61	51.28	51.79	51.09	47.96	47.65
1st year CO2 avoided cost with TS&M, $/tonne, 2007$	75.2	65.14	65.60	64.89	61.45	61.30

To extend the sorbent longevity, TDA explored reprocessing methods to restore the Batch 1 sorbent performance after long term service in the lab. The sorbent was calcined after observable degradation was seen in the bench-scale test. We first ran the calcination at 538 ^{o}C in January, 2022. For the second recalcination in June, 2022, the temperature was set at 380 ^{o}C. Before the recalcination, the sorbent lost 8.5% capacity from fresh after about 1250-hour run. After both recalcinations, the sorbent restored its performance as the fresh sorbent and ran for about 1250 hours. This reprocessing frequency is acceptable for a commercial sorbent. Calcination at 380 ^{o}C can be done in situ, without extracting the sorbent.

TDA believed it is the inappropriate calcination step in the large-scale sorbent production caused that the pilot sorbent to be inferior to the Batch 1 sorbent manufactured in our lab-scale equipment. The sorbent manufactured at our partner was actually calcined at a temperature lower than what we did in the lab, even though the set points for temperature were the same. To reproduce Batch 1 at intermediate-scale, TDA carried out the production in the lab with similar equipment to large-scale production. A rotary calciner, which can run continuously, was used in the final calcination. Multiple batches of sorbents were made, and they all have better or close performance to Batch 1. Thus, we are confident that we can reproduce Batch 1 properly if a large-scale production is needed again.

1. Introduction

Even with the rapid growth of renewable energies, coal and natural gas still accounted for 60% of U.S. electric power generation in 2021 [1]. With such high dependence on fossil fuels in power sector, carbon capture and storage from point sources is a critical and practical approach to achieve the ambitious goal for a carbon-pollution-free power sector by 2035.

The carbon capture technologies under development include pre-combustion capture, post-combustion capture and oxy-combustion. In pre-combustion capture, the fossil fuel is partially oxidized to generate CO, then CO reacts with steam to produce H_2. H_2 can be used as fuel, and CO_2 is captured by techniques before combustion taking place. In oxy-combustion, O_2 is separated from air and supplied to the combustor, so the flue gas mainly contains CO_2 and H_2O. CO_2 is separated by condensing the steam. In post-combustion capture, low concentration of CO_2 (4-15%) in the flue gas is enriched to 95+% purity by various technologies, including solvent, sorbent, membrane and hybrid process. Solvent based post-combustion process is the most mature technology, even though its cost and energy penalty are very high. R&D efforts are needed to develop technologies to minimize the capture cost.

The fundamental reason that post-combustion CO_2 removal, compression and sequestration is expensive and consumes a large amount of energy and capital is that the power plant flue gas is at ambient pressure and the CO_2 is diluted with N_2 (there is only 10 to 15 mol% CO_2 in the flue gas). As a result, any successful carbon capture technology must be able to concentrate the CO_2 to 95% purity, so that it can be compressed by a factor of 150 for subsequent sequestration. There is a minimum theoretical energy requirement to recover 90% of the dilute CO_2 in the flue gas (i.e. concentrate it from 10% to 100%) and then to compress it to 2,200 psig, which corresponds to 9.46% of the plant output. The minimum power loss to concentrate CO_2 in the flue gas to pure CO_2 at 1 atm is 3.05% and compression to 2,200 psia adds another 6.41%. Assuming an additional 4% penalty for transportation and sequestration, CO_2 capture will reduce the plant output by a minimum of 13.46%. For example, for a 433.7 MW_e power plant this would reduce the power plant output to 375.3 MW_e. Any inefficiency in the CO_2 removal system will further increase this energy penalty. Therefore, our objective is to come as close as possible to the theoretical minimum energy requirement with our process.

2. TDA's Sorbent Post Combustion CO_2 Capture Process

TDA's process is based on an alkalized alumina sorbent that removes CO_2 via an adsorption reaction that has a low heat of desorption. The sorbent is very low in cost, and can be regenerated without temperature-swing or pressure-swing via steam regeneration (low pressure, 140°C superheated steam). The major reaction is $M{\cdot}H_2O + CO_2 \rightleftharpoons M{\cdot}CO_2 + H_2O$, in which M represents the sorbent. In adsorption step, CO_2 displaces H_2O from the sorbent as it adsorbs in the forward reaction; in the regeneration step, H_2O displaces CO_2 from the sorbent in the reverse reaction. TDA's process is a nearly isothermal operation running at ambient pressure. We expect the cost of the sorbent to be $2~3/kg at commercial scale.

For a coal fired power plant, the simplified flow diagram is shown in Figure 4. The CO_2 in flue gas is adsorbed in the capture unit. Steam enters the capture unit to regenerate the sorbent by displacing the CO_2 from the sorbent. High purity CO_2 product is obtained at the steam outlet after the moisture is condensed. In the optimized process, strip air is fed into the capture unit to further regenerate the sorbent as shown in Figure 4. The strip air contains CO_2 at the outlet and is mixed with the rest of the incoming combustion air, thereby increasing the CO_2% in the flue gas at the boiler outlet. Higher CO_2% in flue gas is favorable for the adsorption kinetics. Unlike a thermal swing process, the steam is used to displace the CO_2 absorbed by the sorbent, not as a heat source.

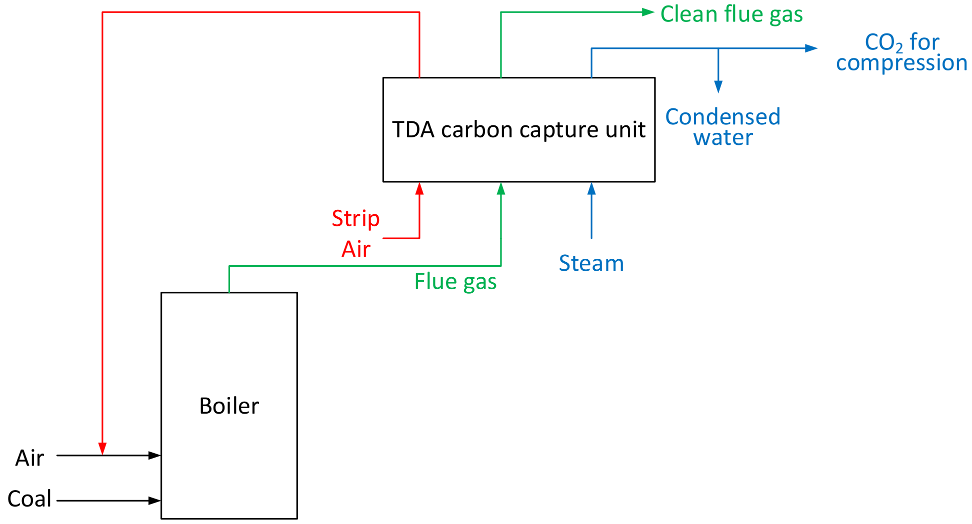


Figure 4. Simplified flow diagram of TDA's CO_2 capture process

Ten reactors are used in the capture unit, and each reactor alternates between the adsorption and desorption modes using valves at the top and bottom of the reactors. The flow pattern, developed to minimize the steam consumption to capture per tonne of CO_2, is shown in Figure 5. The flue gas flows in parallel among the absorbers and the steam flows in series among the regenerators. The steam saver step routes the wet purge strip outlet (that contains steam and CO_2) to the bed that just completed the adsorption cycle to push out inert void gas (e.g. N_2, O_2. etc.) before steam is brought in for actual regeneration. This increased steam efficiency is achieved by moving steam from the wettest bed in the cycle to the driest; it also increases regeneration purity by purging the inert diluents. A divert step is used to increase the CO_2 purity in the product by purging the residual gas from the void space within the reactor at the beginning of regeneration. This gas flows out to the strip outlet line. A strip step further regenerates the sorbent after the steam regeneration by "stripping" any remaining CO_2 off the sorbent with dry air. As a result, the overall sorbent CO_2 loading increases.

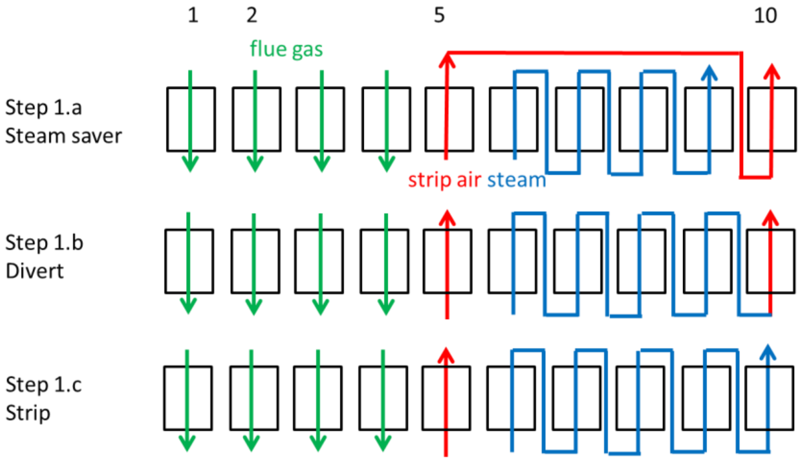


Figure 5. The flow pattern of a 10-bed operation with steam saver

We used a simple fixed axial-flow bed as the reactor. Unlike a moving bed, there is no attrition issue in our system. The capital cost for fixed bed is also less.

3. Project Objectives

The overall goal of the slipstream testing project is to evaluate TDA's sorbent-based CO_2 capture technology under realistic conditions in continuous long-term operation at the 0.5 MW_e scale, in order to collect the data necessary for scale-up the process to a larger plant. The objective during the first budget period was to design the pilot-scale demonstration plant for slipstream testing at the NCCC, and to prepare a detailed Techno-Economic Analysis (TEA) to establish the merit of the recipient's approach for meeting the DOE performance goals of 90% CO_2 capture with 95% purity at a cost of $40/tonne captured. The objective of the second budget period was to finalize the design and then fabricate and build the pilot plant. This included construction of the adsorption/desorption beds and all ancillary equipment, such as heat exchangers, blowers, etc. The goal of the third budget period is to demonstrate the pilot-scale process at the NCCC, processing a 0.5 MW_e slipstream of flue gas from the Wilsonville power plant. The amount of flue gas equivalent to 0.5 MW_e is nominally 5,400 lb/hr, or about 1100 SCFM. Results from the slipstream testing were used to evaluate the effectiveness and economics of the new technology. Based on the pilot testing results, as well as equipment and sorbent cost estimates, we updated the Techno-Economic Analysis to accurately estimate the cost of CO_2 removal, based on DOE/NETL's Cost Guidelines. We also finalized the EH&S assessment. Finally, the data from the pilot plant test was used to develop recommendations for the next level of scale up.

4. Results

In this section, the results from the whole project were reported chronologically. Budget Period 1 is from February 2014 to February 2016; Budget Period 2 is from March 2016 to January 2018; Budget Period 3 is from February 2018 to July 2022. Sections 4.1-4.4 are results from BP1.

4.1 Preliminary Techno-Economic Analysis

We completed the Preliminary Techno-Economic Analysis (TEA) on Nov, 11, 2014 for an initial case (Case 1); the analysis was based on experimental data collected previously under contract DE-NT0005497, which from ran from Nov 2008 through August 2013. The analysis was carried out by University of California, Irvine (UCI). Two more cases were analyzed later and completed on Jan 22, 2016. The UCI analysis showed that the improved process based on recent experimental results in the 12-bed bench-scale apparatus has a CO_2 capture cost of $37.8/tonne. Thus, the preliminary TEA showed that TDA's CO_2 capture technology meets DOE's goal of less than $40/tonne CO_2 captured.

UCI carried out the preliminary TEA per the DOE requirements as outlined in our contract. UCI followed the analysis method documented in the NETL report "Cost and Performance Baseline for Fossil Energy Plants - Volume 1: Bituminous Coal and Natural Gas to Electricity (Rev 2, November 2010)," with economic updates from the report "Updated Costs (June 2011 Basis) for Selected Bituminous Baseline Cases." Post-combustion capture technology analyses followed Case 12, a super-critical pulverized coal (PC) case with CO_2 capture by a solvent technology. The economic analysis followed NETL Quality Guidelines. They set up a detailed process design and simulation using Aspen-Plus software to perform necessary material and energy balances. UCI integrated TDA's CO_2 capture process with a nominal 550 MW_e supercritical greenfield power plant. UCI prepared general process flow diagrams identifying all major process equipment and/or subsystems, material and energy balances, and completed tables showing major stream compositions, temperatures, pressures and flow rates. They estimated the overall plant performance, taking into account the power generators, steam extraction and plant auxiliary loads. UCI determined the installed plant cost estimate (AACE Class 4), capital requirement and levelized cost of electricity. The results were compared with the currently available state of the art amine-based CO_2 capture technology.

A summary of the preliminary technical economic analysis is presented in Table 3. The three TDA cases are compared to CO_2 capture by Amine (DOE Case 12). The cost is expressed in 2007 $.

Table 3.Comparison of TDA's Sorbent-based CO2 capture process with Amine capture.

CO_2 Capture Technology	**No Capture Case 11**	**Amine Capture Case 12**	**TDA Case 1**	**TDA Case 2**	**TDA Case 3**
Carbon Captured,%	0	90	90	90	90
Steam Turbine Power, KWe	580,400	662,800	643,413	639,263	658,313
Total Auxiliary Consumption, KWe	30,410	112,830	93,443	89,263	108,003
Net Power Output, KWe	550	550	550	550	550
% Net Plan Efficiency, HHV	39.3	28.4	29.68	31.61	29.56
As-received coal feed, kg/h	185,759	256,652	234,514	230,817	246,884
Natural Gas Feed, kg/h	0	0	5,864	0	0
Raw Water Withdrawal, m^3/min	20.1	38.1	35.7	30.4	33.9
1 rst year cost of electricity (COE), $/MWh $2007	58.9	100.9	99.8	94.4	95.7
1 rst year CO_2 capture cost w/o TS&M, $/tonne $2007	-	42.1	44.1	40.0	37.8
1 rst year CO_2 avoided cost w/o TS&M, $/tonne	-	61	58	50	53
1 rst year CO_2 avoided cost TS&M, $/tonne	-	75.2	71.8	63	67

The cost of CO_2 captured/tonne was calculated as shown below (Matuszewski, 2014):

$$\text{Cost of CO}_2\text{ captured} = \frac{COE_{with\ CC} - COE_{without\ CC}}{\text{CO}_2\text{ captured}}$$

The avoided cost was also calculated as an additional metric for comparison. The cost of CO_2 avoided is calculated analogously to above as follows:

$$\text{Cost of CO}_2\text{ avoided } = \frac{COE_{with\ CC} - COE_{without\ CC}}{\text{CO}_2\text{ avoided}}$$

Three cases were analyzed in Budget Period 1. The assumptions for each case are as follows:

Case 1: Natural Gas Heated Flue Gas and 2013 experimental data

This case was based on previous experimental data collected under completed contract DE-NT0005497. In TDA's process the CO_2 capture occurs at elevated temperature. In Case 1 we used natural gas to preheat the flue gas to the operating temperature of our carbon capture process (from 68 ^oC to 165 ^oC). The flue gas leaving the flue gas desulfurizer (FGD) unit is boosted in pressure using a booster fan and then natural gas is combusted and directly introduced into the flue gas to preheat it to the required temperature of 165°C (328°F) for adsorption before it enters TDA's unit. The steam required to regenerate the sorbent is extracted from the steam turbine at 1.172 bar (17 psia). The CO_2 regenerated, along with the accompanying steam is cooled in a heat exchanger while recovering heat for preheating boiler feed water (BFW) for the steam cycle. Additional heat for preheating the BFW is recovered from the decarbonized flue gas leaving the adsorber unit. The CO_2 stream is then cooled against cooling water before it is compressed to the final pressure in an intercooled compressor. The use of natural gas in Case 1 and its price of $6.55/MM Btu HHV (per DOE guidelines), which was valid for 2007, significantly increased the cost of electricity. Under this scenario (mainly due to the use of NG to heat the flue), the cost of CO_2 captured was $44.1 and $58 per tonne. This shows marginal improvement compared to the amine system ($42.1 and $61 per tonne, respectively). Thus, NG was not used to preheat the flue gas in the following cases.

Case 2: BFW Heated Flue Gas and goal performance metrics

In Case 2, we assumed the flue gas was heated using boiler feed water (BFW, coal derived heat). We also based the sorbent bed operation on performance goals metrics for the CO_2 capture process. Our purpose was to determine what process changes and/or process improvements were required to meet the DOE CO_2 Capture goal of $40/tonne captured. In this process the flue gas leaving the FGD unit is boosted in pressure using a booster fan and then preheated against BFW in a heat exchanger to the required temperature of 140°C (284°F) for adsorption before it enters TDA's unit. Steam required for regeneration is extracted from the steam turbine at 1.172 bar (17 psia). The CO_2 regenerated along with the accompanying steam is cooled in a heat exchanger while recovering heat for preheating BFW for the steam cycle. Additional heat for preheating the BFW is recovered from the decarbonized flue gas leaving the adsorber unit. The CO_2 stream is then cooled against cooling water before it is compressed to the final pressure in an intercooled compressor. Eliminating the use of NG at $6.55/MM Btu HHV significantly improves the overall economics. This Case 2 process just meets DOE goal of $40/tonne CO_2 captured. The CO_2 capture avoided cost is $50/tonne CO_2 avoided without TS&M.

Case 3: BFW heated flue gas and 2015 experimental data

In Case 3, we again used BFW to heat the flue gas to temperature. We based the sorbent bed performance on 2015 experimental data from the improved process developed in Budget Period 1. This experimental data was collected after we optimized the process flow pattern to include 12 beds (our previous designs had only 8 beds). The experimental data was a little better than what we calculated for Case 2. In short, UCI economics showed that the TDA process as demonstrated experimentally in the bench-scale apparatus is able to meet the DOE CO_2 capture target of $40/tonne captured.

Case 3 is based on 2015 experiment data on the optimized lab-scale 12-bed version of TDA's CO_2 capture process. This case includes the optimized air purge and recycle steps identified in the experimental work under Task 3 Pilot Plant Design Optimization. (This flow pattern is discussed in Section 4.2 and shown in Figure 8.) Our experimental data was able to match the space velocity (SV) assumed in the Case 2 performance goal case and still achieve 90% capture. The experimental case had 23% more regeneration steam than the idealized case, however, it was still very favorable. The Case 3 process, based on current bench-scale experimental data, has a CO_2 capture cost of $37.8/tonne without TS&M. The CO_2 capture avoided cost is $53/tonne CO_2 avoided.

The results of the preliminary techno-economic analysis in Table 3 suggested that TDA's sorbent based CO_2 capture process can make substantial improvements over conventional amine technology. Based on the measured performance of our bench-scale system, TDA's CO_2 capture process (Case 3 with 2015 experimental data) can meet DOE's goal of capturing CO_2 at <$40/tonne without TS&M with a cost of only $37.8/tonne. This is a 10% reduction in CO_2 capture cost compared to the amine-based CO_2 capture process. The Case 2 simulation with goal performance metrics show that the CO_2 capture avoided cost can be further reduced by decreasing the steam usage. Experiments in January 2016 had already reduced steam by 8% compared with Case 3, and further sorbent improvements had already been made by our industrial partner, so we expected further advances during the project to improve the economics of the TDA process.

4.2 Pilot Plant Design Optimization

The objective of this task was to collect the experimental data needed to properly design the pilot plant. This included conducting process optimization tests in TDA's bench-scale laboratory unit (Figure 6) with the most advanced adsorbent formulations available, and parametric testing of the recycle and purge operations to determine how much they could improve on the basic cycles. During this task we modified our bench-scale apparatus in a series of experimental steps to evaluate several process flow options. The optimized design developed in this task includes an air purge step, a steam saver step, and a breakthrough recycle to maintain high capture rates. This pilot unit was then designed around the optimized flow pattern and experimental SV for the flue gas and regeneration steam.

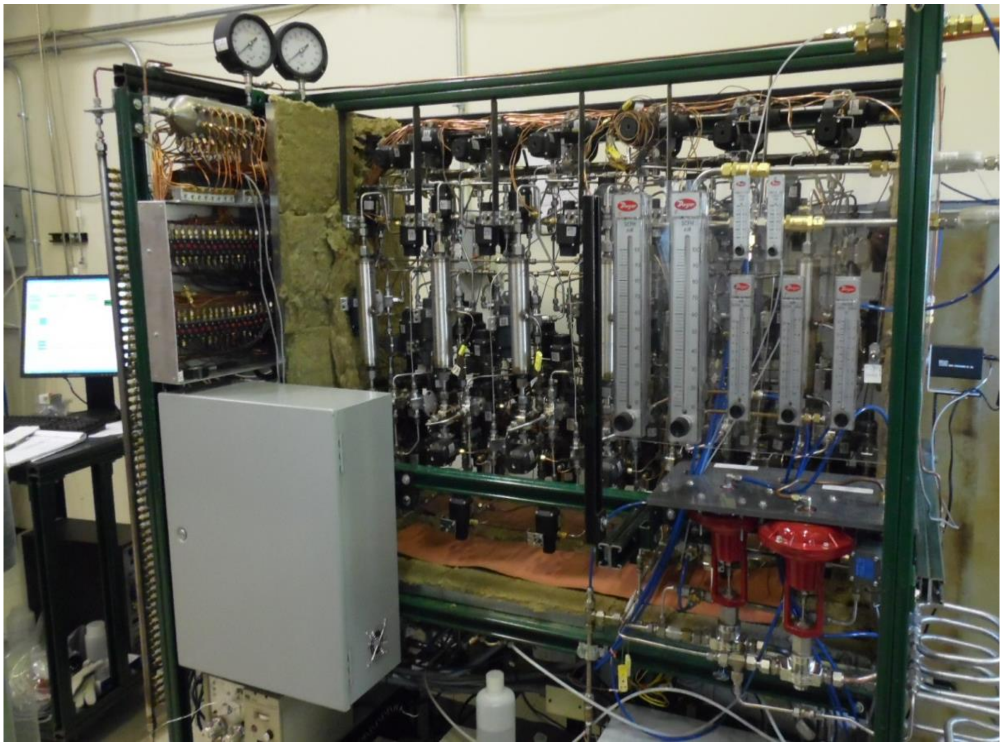


Figure 6. TDA Multiple fixed bed bench-scale apparatus

In this task we collected data to evaluate optimized process conditions and the performance of proposed recycles/purge steps. TDA's previous bench-scale apparatus had 8 beds and only a limited ability to simulate recycle options. As part of this project, we expanded our bench-scale apparatus to have 12 sorbent beds. Through a series of modifications, the new 12 bed apparatus was redesigned for improved performance and to better simulate a slip stream unit and the ultimate commercial system.

Figure 7. CO_2 Capture bench-scale (5L sorbent) apparatus with 12 bed (Two rows of 6 beds with one row of beds shown in front).

Table 4. Performance results under varying flow patterns.

Date	**12 Bed configuration**	**Flue SV (sccm/g)**	**Steam SV (sccm/g)**	**Cycle time (s)**	**Capture %**
4/3/15	Air purge+4 adsorption+steam saver+ purge+ 6 regeneration	1.78	0.98	93	88.8%
4/7/15	Air purge+5 adsorption+steam saver purge+ 5 regeneration	1.78	0.98	93	90.4%
4/15/15	SS purge + 4 adsorption + steam saver purge + 6 regeneration	1.78	0.98	93	83.7%
4/16/15	SS purge + 5 adsorption + steam saver purge + 5 regeneration	1.78	0.98	93	83.6%
4/22/15	SS purge + 5 adsorption+ SS purge/Breakthrough recycle+ 5 regeneration	1.78	0.98	93	84.8%

We evaluated many flow patterns options during the design optimization. We compared five main flow configurations (Table 4). All tests were run under the same flue flow SV (1.78 sccm/cc) and steam SV (0.98 sccm/cc). These tests evaluated several purge and recycle options and looking at using four or five beds in adsorption and more/less beds in regeneration. The best flow pattern had an air purge step after regeneration with a steam saver step after adsorption; this process had the highest capture rate and lowest steam usage.

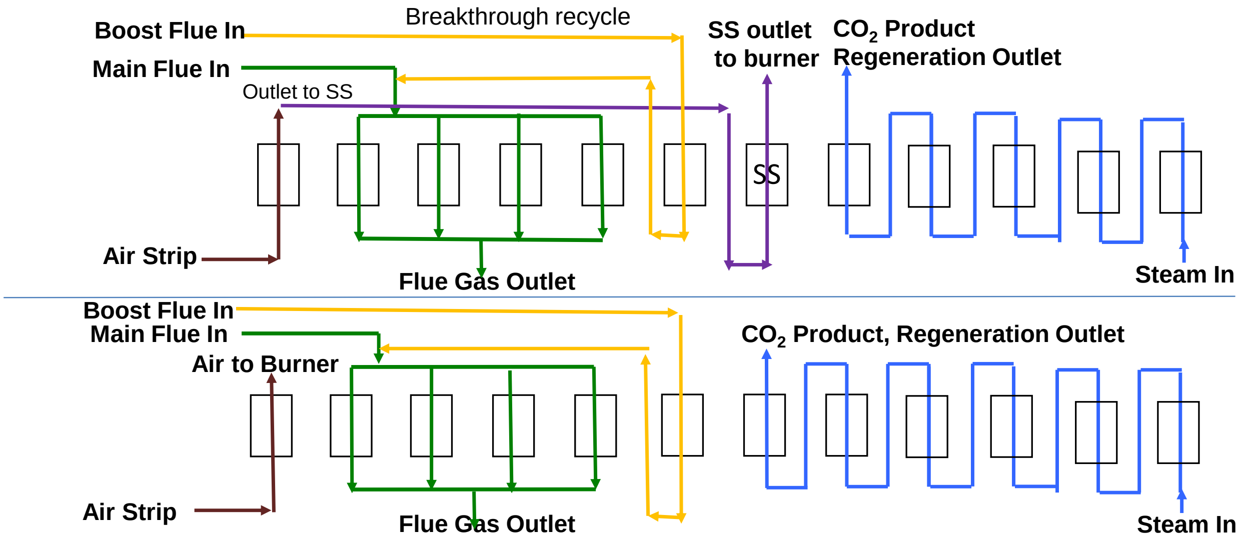


Figure 8. Air purge + Steam saver + Breakthrough Recycle flow pattern (Purge + 4 Ads+BTR + SS + 5Reg)

We determined it would be desirable to test the strip purge with steam saver and breakthrough recycle running simultaneously during the entire cycle. Thus, we further modified the apparatus to add another manifold dedicated for the breakthrough recycle so it could be simultaneously run the purge and steam saver recycle. This flow pattern is show in Figure 8. Testing was performed in the updated apparatus using the best sorbent produced to date by our industrial partner.

Table 5. Optimal performance of CO_2 capture process with preferred flow patter and most advanced adsorbent formulations. This data was used for TEA study (Case 3) and design basis for pilot unit

Date	**12 Bed configuration**	**Flue SV (sccm/g)**	**Steam SV (sccm/g)**	**Cycle time (s)**	**Capture %**
9/23/15	Air purge+4 adsorption + Breakthrough recycle+steam saver purge+ 5 regeneration (Figure 8)	2.55	1.17	97	90.9%

The simultaneous operation of the steam saver and breakthrough recycle performed better than either of the two alone. This test was run with 5.0 slpm flue flow rate (Table 5), which was 43% higher SV than experiments shown in Table 4. Further, this flow pattern had the lowest steam usage with 90% CO_2 capture. Thus, we selected this case as our design basis for the pilot unit. Further, we used this experimental data for the TEA study (Case 3) performed by UCI discussed in Section 4.1. This TEA established the economic merit of the improved process.

During Budget Period 1 we also evaluated the composition of the dry regeneration product gas to ensure that our process could meet the 95% CO_2 purity requirement. During regeneration the CO_2 is released at very high concentration after the gas in void space is pushed out of the bed. Through a series of experiments, we confirmed that if we trim off the initial plug of flue gas (mainly N_2) left in void space of the bed after adsorption and divert it from our CO_2 product, we can achieve 95% CO_2 purity without further clean up. These experiments were conducted in our single fixed bed and later confirmed in the bench-scale unit.

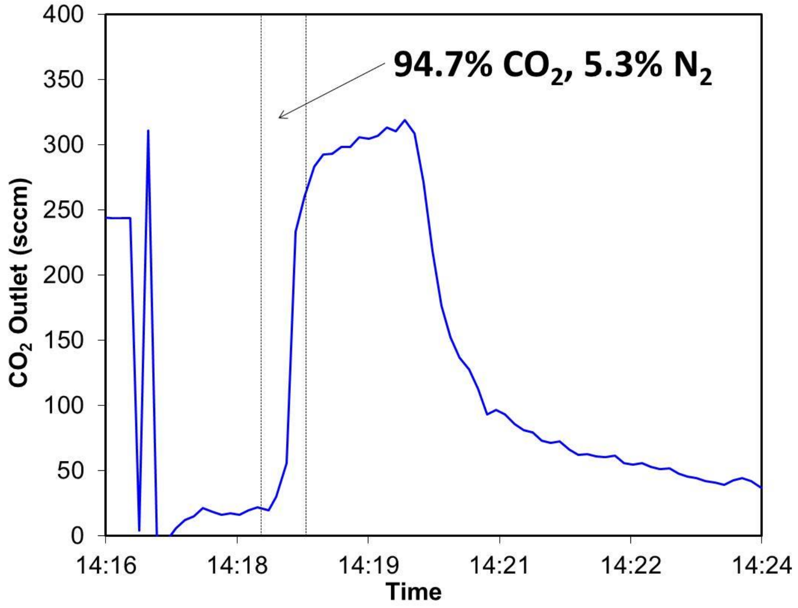


Figure 9. Dry CO2 product concentration during onset of regeneration

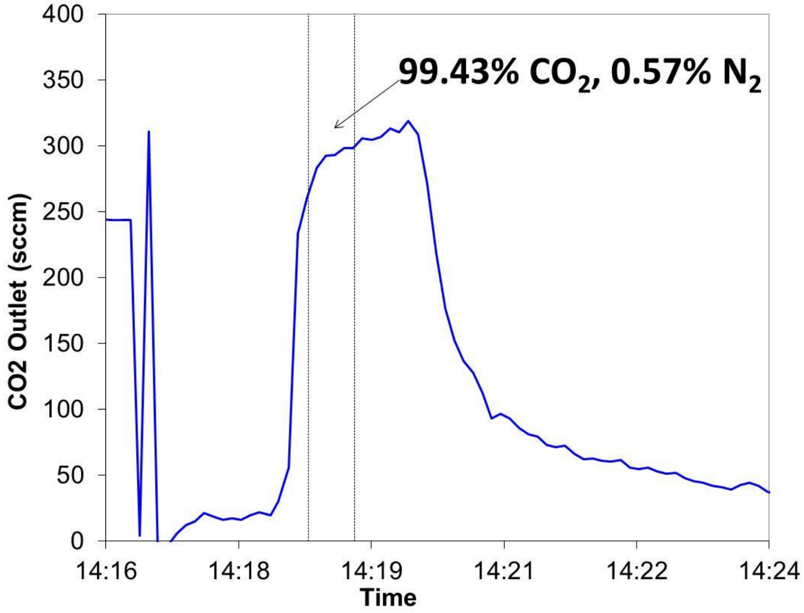


Figure 10. Dry CO2 product concentration during regeneration

This experiment was run using a GC to measure CO_2 composition in the regeneration outlet of the fixed bed. Typically, we use an online IR analyzer to measure the CO_2 concentration in the regeneration outlet. To make this measurement we add a metered flow rate of N_2 (by mass flow controller) into the dry regeneration gas outlet in order to bring the CO_2 concentration into the range of our California Analytics CO_2 online analyzer (less than 25%). By this method we can calculate the flow rate of CO_2 and achieve a good CO_2 mass balance. However, this method does not allow us to accurately calculate the amount of N_2 that could be co-adsorbed onto the sorbent, because this quantity is very small compared to the amount of N_2 added for dilution. Therefore, to further measure any co-adsorbed/desorbed N_2, we measured the regeneration gas composition by GC (during cycles where no dilution N_2 gas was added). For these cycles, we sampled the effluent at the beginning of the appearance of the CO_2 sharp peak when regeneration starts and in the regeneration peak. We analyzed the nitrogen concentration in the regeneration effluent using a SRI gas chromatograph with a Carboxen-1000 column and a TCD detector. The gas chromatogram results confirmed the concentration of nitrogen in the dried effluent is small. The concentration of nitrogen measured from gas chromatogram during the transition to regeneration at the end of pushing out the void gas was 5.3% (94.7% CO_2). Once regeneration has fully commenced the N_2 concentration is only 0.57%% N_2 (99.43% CO2). Other measurements confirmed that the N_2 levels were even lower in the tail of the regeneration peak. Based on these results we were confident that our process can achieve an average CO_2 purity of >95%. And this did later prove to be correct at larger scale.

Initially, we chose a 12-bed design and the flow pattern included strip purge, steam saver and break-through recycle. However, our preliminary sensitivity analysis showed that the addition of the break-through recycle was not worth the added capital and operating cost for this more complex system. Thus, we changed the pilot unit design to focus its operation on the most advantageous flow configuration, which includes strip purge and steam saver only (Figure 11). In addition, the process analysis showed that there is a positive trade-off with increasing SV even if it slightly increased steam usage. We are particularly interested in higher SV with the improved sorbent that was developed by our industrial partner. This material has better kinetics at higher SV. Thus, we would like to operate at higher space velocities. TDA's system (blowers, piping etc.) is designed for only 5000 lb/hr of flue gas (0.5 MW_e). Further the NCCC runs multiple tests simultaneously and more flue gas seemed unlikely to be available. Without the break-through recycle we do not need as many transition beds in the system. Thus, the most straight forward way to modify our original design to increase the SV is by reducing the number of beds from twelve beds to ten beds and making the beds 6 inches shorter. This approach allows us to tailor the pilot unit operation to the higher SV case without redesigning the pilot unit system.

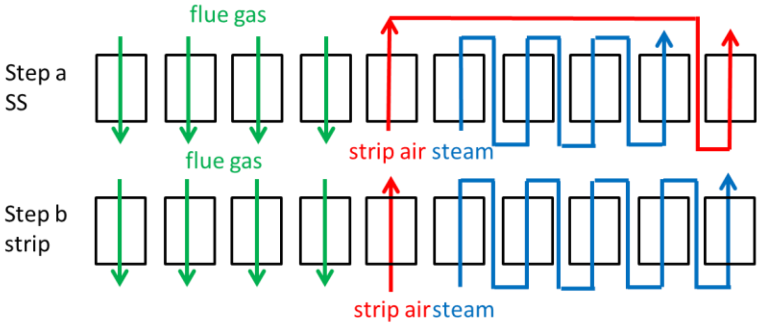


Figure 11. Flow pattern for "SS+4+5 / Strip+4+5" for 10 beds

4.3 Pilot Plant Detailed Design

TDA's process is based on an alkalized alumina sorbent that removes CO_2 via an adsorption reaction that has a low heat of desorption. The sorbent is low cost and can be regenerated without temperature-swing or pressure-swing via steam regeneration (low pressure, 140°C superheated steam). This regeneration mechanism makes our process significantly different from other solid adsorbent processes under development because of its unique, nearly isothermal operation at near ambient pressure. The TDA system is skid mounted with multiple fixed beds. The fixed beds cycle between adsorption, regeneration and purge/recycle operations. The detailed process design was conducted around the improved process flow pattern shown in section 4.2.

4.3.1 10-Bed CO_2 Capture System with Gas Conditioning Process Overview

The ten fixed beds are housed in two trailers, each holding five beds (Figure 12). These trailers have walls made from removable panels and are internally insulated. The entire structure is maintained at 140°C. Both the adsorption and regeneration processes are operated at the same temperature (~140°C) during normal operation. Each trailer is 39 x 8.5 x 11.5 feet. The trailers are connected to each other and to the utility sources through a manifold system that allows us to change the operating mode without requiring changes to the system plumbing.

In addition to the skid-mounted reactor units, the slipstream system also includes an instrument unit and a service unit. The instrument unit contain process control and analysis components, and is maintained at ambient temperature. The service unit is not be heated, but most of the major gas streams flowing through it are at the process operating conditions (~140°C), so heating is not necessary. The service unit is the main structure for connecting streams from the NCCC and Gaston plant to the reactor units containing TDA's sorbent. The service unit contains mechanical systems such as blowers, electric resistive heaters, in-line heat exchangers, condensers, water knock outs and valves (relief, pressure control and shutoff). In addition, multiple flow sensors are installed to monitor and control each gas stream. Sensors such as flow meters, thermocouples and pressure transducers are installed on each major pipe leading out to the fixed bed trailers.

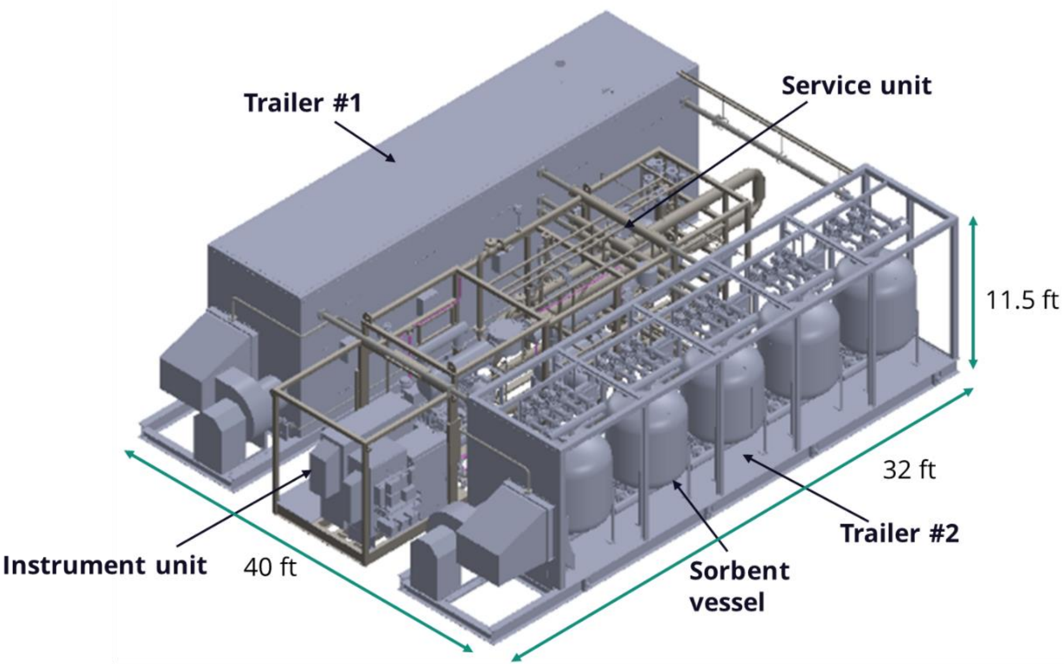


Figure 12. TDA's pilot unit as installed at NCCC. TDA’s system includes two sorbent bed trailers (Trailer #1 and Trailer #2), the service unit (which contains heat exchangers, blowers, flow metering, exhaust coolers) and the instrument unit (which contains analyzers and the Programmable Logic Controller "PLC").

Figure 13 shows the overall process flow diagram for the pilot scale system. The main process feeds include flue gas, low-pressure steam for regeneration, ambient air for purging and pressurized air for water stripping. Due to the relatively small size of the demonstration and our desire to quickly start up the unit, high-pressure steam is used to heat the reactor trailers at startup and for makeup heat during testing. Exiting the process are the adsorption flue gas effluent (with low CO_2 concentration), purge air, and the regeneration effluent with CO_2 and steam.

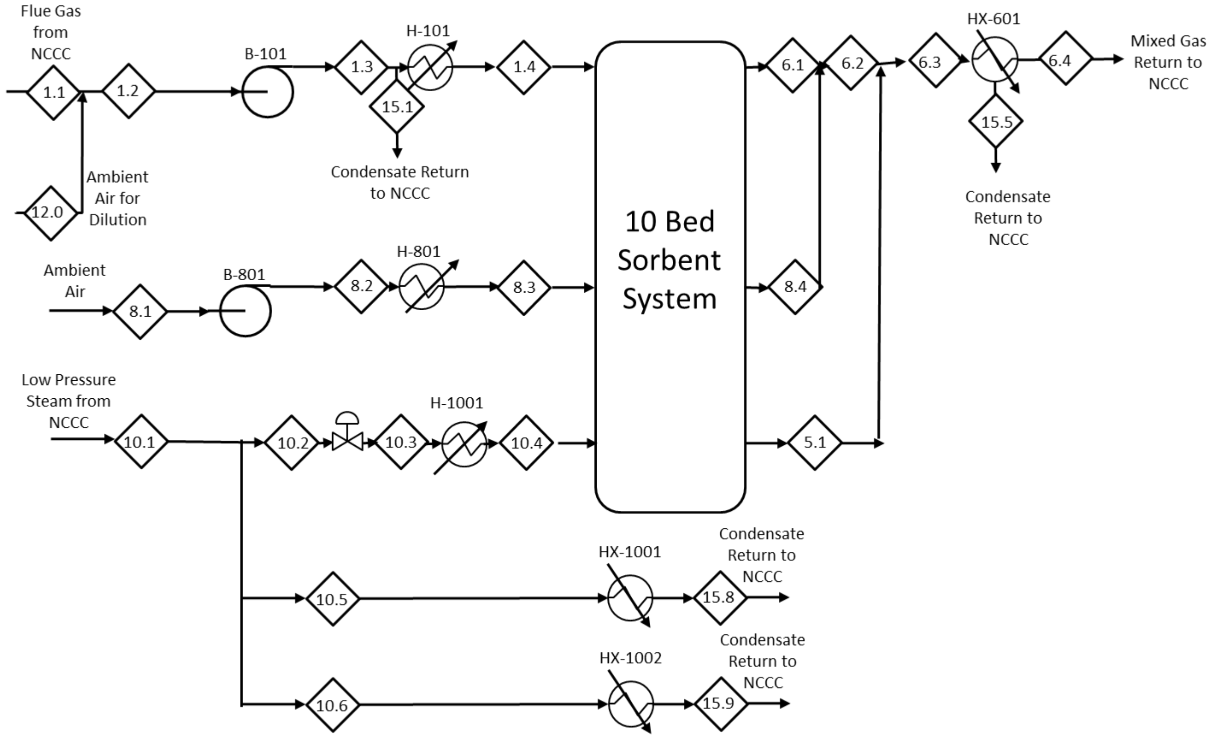


Figure 13. Overall Process Flow Diagram for pilot scale CO_2 removal system

Three streams enter the TDA pilot plant from the NCCC: 1) flue gas (from the Gaston Plant slip stream); 2) low pressure steam (~saturated, 170°C); and 3) cooling water. Additionally, compressed air at 80 psig is used by the system as a utility, for pneumatic valves and other process components. The pilot plant returns used cooling water, condensate, and a recombined gas effluent consisting of the treated flue gas, the CO_2-enriched product and the purge gas (essentially air). The recombined gas effluent stream has largely the same composition as the inlet flue gas. TDA's sorbent is comprised entirely of nonvolatile components in pellet form. The only volatile component in the carbon capture system is the steam used to regenerate the sorbent. Thus, the humidity of the effluent stream returned to the Gaston Plant may be different than the humidity of the slip flue gas stream. TDA's process includes condensing heat exchangers to reduce the humidity and temperature of this stream before it is returned.

The cooling water composition remains unchanged, as there is no direct contact with any process stream. The condensate, from both the treated flue gas and the regeneration stream, may have an acidic pH due to the presence of dissolved CO_2. This water is returned to NCCC for treatment in their existing facilities, along with the condensate from the low-pressure steam.

4.3.2 Stream Summaries and Process Flow Diagram (PFD)

Figure 13 shows the process flow diagram (PFD) for the preferred flow path operation of the 10-bed sorbent system. The coal derived flue gas enters the system. When a natural gas flue gas case needs to run, air can be added to dilute the CO_2 in the coal flue gas. (In our later tests at NCCC, a NG boiler was installed to provide NG flue gas.) The sorbent is regenerated with steam and then purged with air. In a commercial system, the air purge outlet would be recycled back to main burner. As a result, the concentration of CO_2 in the flue gas would increase.

Table 6 and Table 7 show the stream summaries for the operating condition shown in Figure 13. Table 6 shows every stream used in this operating scenario on a molar basis. Table 7 shows every stream used in this operating scenario on a mass basis.

Table 6. Stream Summary for TDA capture process, Molar Basis (System shown in Figure 13)

Stream Number		**12.0**	**1.1**	**1.2**	**1.3**	**1.4**	**6.1**	**6.2**	**6.3**	**6.4**	**10.1**	**10.2**	**10.3**	**10.4**	**10.5**	**10.6**	**5.1**	**8.1**	**8.2**	**8.3**	**8.4**
Stream Name		Supplemental Air for Startup, Shutdown & Dilution for simulated NG flue	Flue Feed	Flue Gas with Dilution (if using)	Pressure Boosted Flue Gas	Heated, Boosted Flue Gas for Absorption	Treated Flue Gas Out	Flue & Air Out Wet	Flue, Air & Reg Out Wet	Cooled Gas Return to NCCC	Low Pressure Steam from NCCC	Low Pressure Steam for Regen	Throttled Low Pressure Steam	Heated Low Pressure Steam	Heating Steam Trailer A	Heating Steam Trailer B	Steam and CO_2 Product	Purge Air	Pressure Boosted Air	Heated, Boosted Air	Air out of beds
	Mol%																				
CO_2		-	12.14%	12.14%	12.14%	12.14%	0.94%	1.80%	6.73%	9.00%	0%	0%	0%	0%	0%	0%	51.21%	0%	0%	0%	3.55%
H_2O		-	13.30%	13.30%	13.30%	13.30%	30.52%	37.16%	38.05%	17.23%	100%	100%	100%	100%	100%	100%	46.09%	0%	0%	0%	50.65%
N_2		79.30%	69.36%	69.36%	69.36%	69.36%	63.76%	54.67%	49.42%	66.03%	0%	0%	0%	0%	0%	0%	2.13%	79%	79%	79%	36.18%
O_2		20.70%	5.20%	5.20%	5.20%	5.20%	4.78%	6.37%	5.79%	7.74%	0%	0%	0%	0%	0%	0%	0.57%	21%	21%	21%	9.62%
Temperature	°C	32	71	71	129	140	140	140	60	60	176	176	121	140	176	176	152	21	121	140	140
Pressure	PSIG	0	-0.7	0	6.7	5.3	2	1.75	0.3	0	100	100	15.3	7.1	100	100	0.9	-0.6	10.1	8.2	2
Total Flow	mol/hr	25000	78693	78693	78693	78693	85610	127706	141867	106186	61134	43514	43514	43514	8810	8810	14161	19660	19660	19660	42095

Table 7. Stream Summary for TDA capture process, Mass Basis (System shown in Figure 13)

Stream Number		**12.0**	**1.1**	**1.2**	**1.3**	**1.4**	**6.1**	**6.2**	**6.3**	**6.4**	**10.1**	**10.2**	**10.3**	**10.4**	**10.5**	**10.6**	**5.1**	**8.1**	**8.2**	**8.3**	**8.4**
Stream Name		Supplemental Air for Startup, Shutdown & Dilution for simulated NG flue	Flue Feed	Flue Gas with Dilution (if using)	Pressure Boosted Flue Gas	Heated, Boosted Flue Gas for Absorption	Treated Flue Gas Out	Flue & Air Out Wet	Flue, Air & Reg Out Wet	Cooled Gas Return to NCCC	Low Pressure Steam from NCCC	Low Pressure Steam for Regen	Throttled Low Pressure Steam	Heated Low Pressure Steam	Heating Steam Trailer A	Heating Steam Trailer B	Steam and CO2 Product	Purge Air	Pressure Boosted Air	Heated, Boosted Air	Air out of beds
	Mass%																				
CO_2		0%	18.53%	18.53%	18.53%	18.53%	1.64%	3.19%	11.61%	14.12%	0%	0%	0%	0%	0%	0%	71.28%	0.0%	0.0%	0.0%	6.54%
H_2O		0%	8.31%	8.31%	8.31%	8.31%	21.74%	26.95%	26.87%	11.08%	100%	100%	100%	100%	100%	100%	26.27%	0.0%	0.0%	0.0%	38.19%
N_2		77.0%	67.38%	67.38%	67.38%	67.38%	70.58%	61.64%	54.25%	65.96%	0%	0%	0%	0%	0%	0%	1.89%	76.7%	76.7%	76.7%	42.40%
O_2		23.0%	5.77%	5.77%	5.77%	5.77%	6.05%	8.21%	7.27%	8.84%	0%	0%	0%	0%	0%	0%	0.57%	23.3%	23.3%	23.3%	12.88%
Temperature	°F	90	160	160	264	284	284	284	140	140	348	348	250	284	348	348	305	70	250	284	284
Pressure	PSIG	0	-0.7	0	6.7	5.3	2	1.75	0.3	0	100	100	15.3	7.1	100	100	0.9	-0.6	10.1	8.2	2
Total Flow	lb/hr	1,589	5,002	5,002	5002	5002	4776	6994	7981	6564	2,429	2,049	1,729	1,729	350	350	987	1,250	1,250	1,250	2218

4.3.3 Sorbent Trailers and Service Unit Design

Each sorbent bed reactor is designed to run below 15 psig, and is constructed from A36 carbon steel. The main cylinder and elliptical caps are formed from 0.25" thick material, as shown in Figure 14. The section to load sorbent has a dimension of Φ60.5” x 37.27”. It can hold 1.75 m^3 sorbent. A 1.5-inch-thick steel grating with a fine mesh screen is attached to the bottom elliptical cap and serves to suspend the sorbent bed in the main cylinder. Because we load the reactors on site, a top screen is not originally installed. However, to ensure the sorbent stays within the reactor during flow from the bottom up, a small screen is installed in the top 12" flange insert to prevent sorbent ejection. In addition, each elliptical cap has a thin, sheet-metal cone inserted (shown as the dotted lines) to cut down on vortex shedding and better shape the flow. Shutoff valve manifolds are attached at the top and bottom of each reactor to control separate process gas paths. Each of these manifolds is constructed from schedule 10 A36 carbon steel. The main pipe is 6" sch40 with several 2" & 3” pipe branches for connecting each shutoff valve. Overall, there are 10 connection points on each reactor, all serving separate process gas paths.

The flow for each cycling operation is directed into the bed through the 2” & 3” shut-off ball valves shown in Figure 15. The series steam path only has one control valve on the inlet to each vessel, the outlet from each vessel does not require a shutoff valve as the path is direct between vessels and only needs one shutoff point.

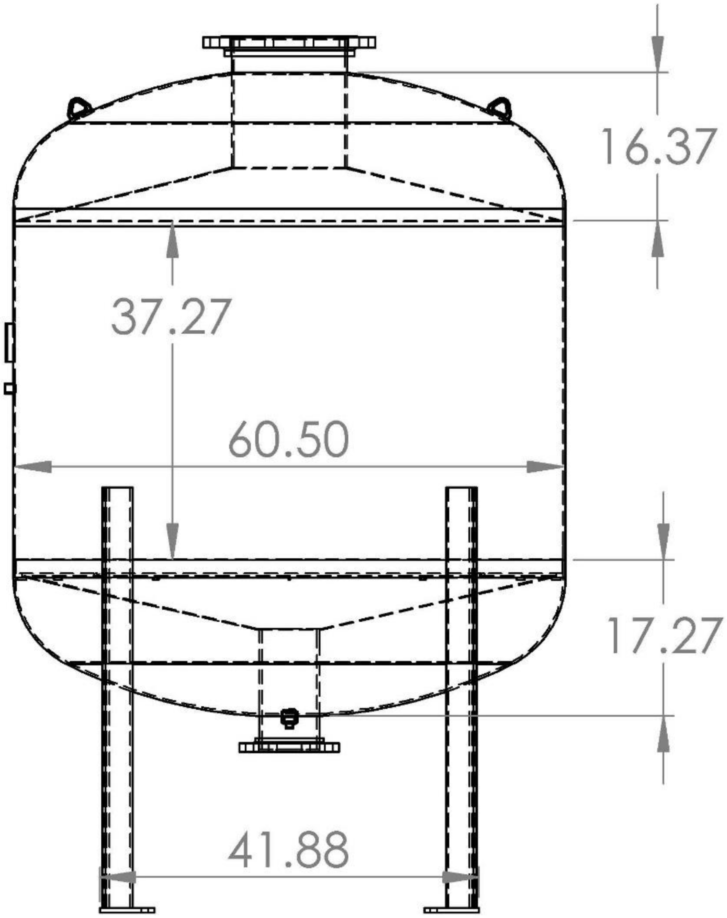


Figure 14. Drawing of the Sorbent Bed Reactor (all units in inches)

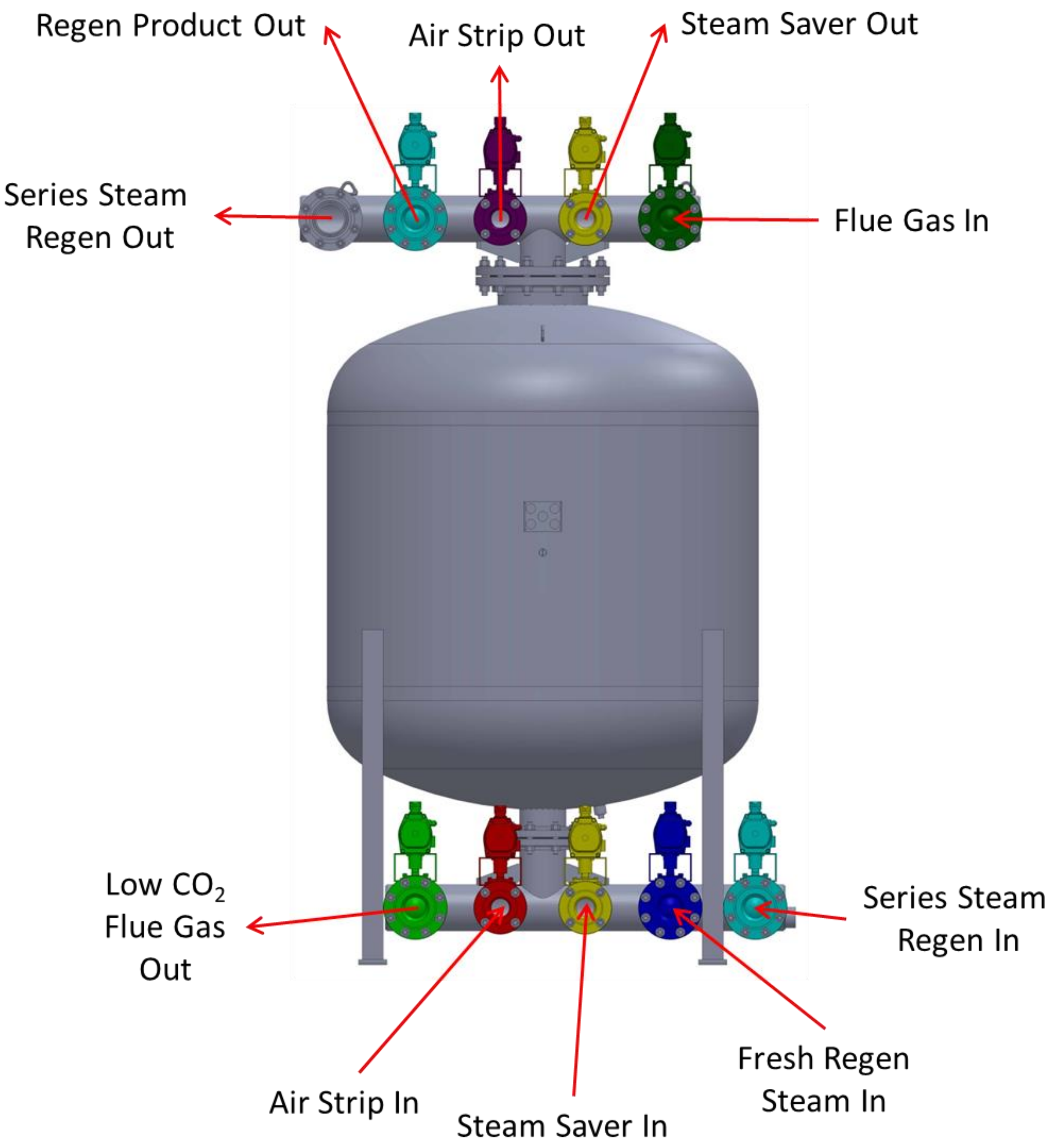


Figure 15. Sorbent bed reactor front view (process gas paths labeled)

The ten reactors are divided into two trailers which each hold five beds. The reactors and manifolding in the trailer are shown in Figure 16.The second trailer (not shown) has manifolding that is a mirror image of the first sorbent bed trailer. All leading to the middle of the trailer along its long side. This then serves as the main connection hub to the service unit skid.

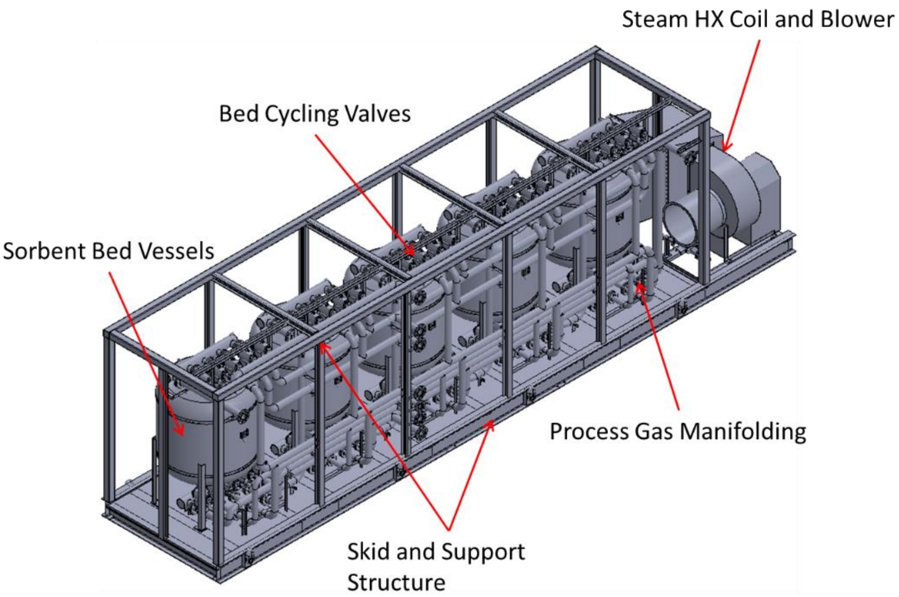


Figure 16. Isometric view of one sorbent bed trailer (8.5 ft x 40 ft), panels and insulation not shown.

The 3D model of the Service Unit Trailer is shown in Figure 17. The service unit is the main structure for connecting streams from the NCCC and Gaston plant to the reactor units containing TDA's sorbent. The service unit contains mechanical systems such as blowers, electric resistive heaters, in-line heat exchangers, condensers, water knock outs and valves (relief, pressure control and shutoff). In addition, multiple flow sensors are installed to monitor and control each gas stream. Sensors including flow meters, thermocouples and pressure transducers are installed on each major pipe leading out to the fixed bed trailers.

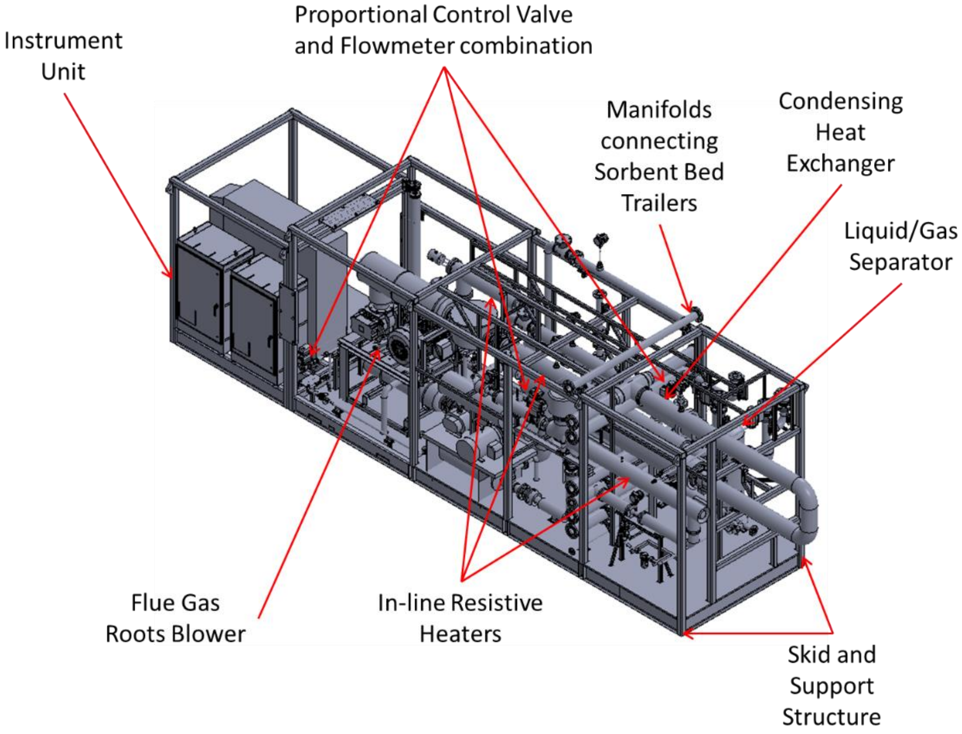


Figure 17. Isometric view of service unit skid (23 ft x 8.6 ft)

The full NCCC pilot unit layout, including the 2 sorbent bed trailers, the service unit and all interconnecting piping, is shown in Figure 18.

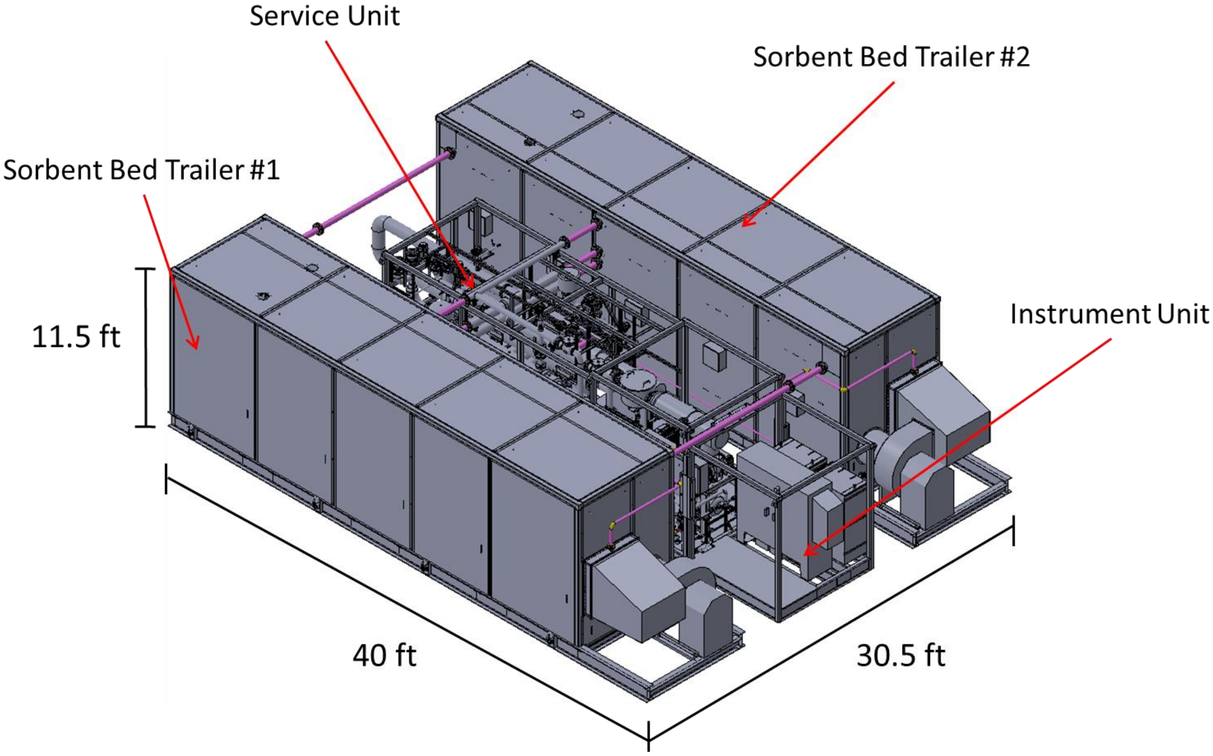


Figure 18. Isometric view of Trailer #1 and Trailer #2 and Service unit

4.3.4 Safety Features

Before finalizing the Pilot Unit's PI&Ds, TDA conducted a preliminary Hazard Review with NCCC on May 12, 2015. A detailed Failure Modes and Effect Analysis (FMEA) was also carried out at TDA to identify safety vulnerabilities and correct them in the design. A formal Process Hazard Analysis (PHA) was conducted on September 29 and 30, 2015. This review was facilitated by Process Improvement Institute, Inc. with the National Carbon Capture staff in attendance. During the PHA the HAZOP analysis technique was used to analyze the continuous flow processes. The PHA team supplemented the HAZOP analysis with the What-If? Methodology for the procedure analysis. Based on the results and insight gained from performing the hazard analysis, the PHA team identified 23 recommendations for improving process safety of the TDA's Post-Combustion CO_2 Capture Process These recommendations include items for: (1) improving or providing additional engineering controls, (2) reducing the potential for human errors through training, procedures or management system improvements and (3) performing further studies to verify that potential consequences of interest are credible and/or to determine the best method to reduce the risk associated with a consequence. These recommendations were incorporated in the pilot unit design.

4.3.5 Facilities Requirements

Facilities requirements for the process are summarized in Table 8. Overall dimensions (and foot print) are presented in Table 9. General arrangement sketches for the three units are provided in Figure 12.

Table 8. Facilities requirements.

INPUT				
Service Unit				
*Overall Power:*480VAC,~350 kW				
	Flow	**Pressure (psig)**	**Temperature (F)**	**Interconnection**
Flue gas	5000lb/hr	0.361	160	4" Pipe Connection
Low Pressure Steam	1800 lb/hr	100	338	4" Pipe Connection
High Pressure Steam	950lb/hr	420	450	0.5" Pipe Connection
Cooling Water	250 gal/m	60	90	2" Pipe Connection
Air	1250 lb/hr	Ambient	Ambient	3" Pipe Connection
Instrument Air	~0.6 SCFM	80	Ambient	0.25" Tube Connection
Trailers/reactors				
Flue Gas	5000 lb/hr	6.5	300	4" Pipe Connection
Low Pressure Steam	1800 lb/hr	14	300	4" Pipe Connection
Air	1250 lb/hr	10	300	3" Pipe Connection
Instrument Air	~2.0 SCFM	80	Ambient	0.25" Tube Connections
Instrument unit				
O2 Cylinder	10-100 SCCM	Ambient	Ambient	0.25" Tube Connection
OUTPUT				
Service Unit				
Flue gas	6000 lb/hr	>Ambient	170	4" Pipe Connection
Condensate	3000 lb/hr	Ambient	140	1" Pipe Connection
Used cooling water	250 gal/m	50	140	2" Pipe Connection

Table 9. Footprint and Weights for Pilot Scale System

Segment of System	**Length (ft)**	**Width (ft)**	**Height (ft)**	**Weight (lb) *without Sorbent***
Sorbent Bed Trailer #1	40	9	11.5	~80,000
Sorbent Bed Trailer #2	40	9	11.5	~80,000
Service Unit	23	8.6	10.8	~20,000
Instrument Unit	5	8.5	10	~2,000

4.3.6 Preliminary EH&S assessment

A preliminary EH&S study was completed on the pilot plant operation and sorbent production. The EH&S study reviewed emissions, environmental hazards, and relevant regulations. During operations of the pilot plant, all gas and water emissions are returned to the Gaston Plant for treatment (as needed) in their existing facilities which meet all regulatory requirements. At the conclusion of the test, all spent and unused sorbent are disposed of by NCCC. Prior to disposal, spent sorbent should be tested to confirm the disposal method is appropriate.

The TDA sorbent based pilot plant process does not present any significant environmental hazards. The sorbent is comprised of low hazard, primarily inorganic compounds. All are solids at ambient temperatures, and have low NFPA ratings for health, fire, and reactivity risk. Most components in sorbent are inorganic, and thus ecological persistence and degradability measures do not apply. For those components for which data is available, there is no bio-accumulative potential. For those components for which bio-accumulative potential data was not available, similar compounds are listed as safe.

The sorbent production process does not utilize any toxic or hazardous materials. The sorbent is mixed and extruded, then calcined to remove excess water and any rheology modifiers or binders used in the extruding process. This firing releases normal combustion by-products, and is exhausted in accordance with the facility's existing permits and in compliance with all applicable laws and regulations. The production process does not produce any volatile organic emissions. The most significant hazard arising from the sorbent production process is the creation of dust. During operations known or likely to create dust, such as loading/unloading sorbent containers, all personnel should wear appropriate PPE to protect against this hazard. Sorbent loading and unloading should be conducted in accordance with all relevant regulation with appropriate PPE to manage dust exposure.

4.4 Pilot Unit Construction Cost

In our last Budget Period 1 task, TDA determined the cost to build the pilot plant. This included purchasing of materials and equipment, subcontracts for fabrication of the sorbent beds and manifolding, sorbent production subcontract, sorbent loading, unloading and disposal. The estimated cost in the design report was estimated at $2.03 million. It does not include any TDA labor or General and Administrative Expenses (G&A).

One of the major costs for the pilot unit is sorbent production. TDA contacted five U.S. companies regarding the toll production of our carbon capture sorbent: BASF, Clariant, Porocel, Unicat and Tricat. Each company was given information on the lab-scale production of sorbents under a confidentially agreement. We received quotes from four of the five companies contacted. Sorbent production cost ranged from $6.5/lb to $20/lb. The pilot scale batch of 45,000 lbs is large, but still a custom order and considered a small toll production batch. However, based on discussion with several manufacturers this sorbent could be made for near $2/lb (with very large production volumes) when the technology is commercialized and installed across the power plant sector. The total cost for the sorbent production for the pilot unit is estimated at $342,500.

All the milestones in BP1 were matched. Sections 4.5-4.8 covers results from BP2.

4.5 Sorbent QA/QC

TDA worked with Porocel (Little Rock, AR) to scale up production of the carbon capture sorbent developed by TDA and our industrial collaborator. Porocel is a leading supplier of activated alumina products. They have over 35 years of experience in catalyst and sorbent manufacturing, with over 15 years of toll processing experience. They have facilities in North America, Europe, and Asia; their capabilities include extrusion, ball forming, drying, impregnation, calcination, and milling. TDA's alkalized alumina sorbent had been produced at the laboratory scale in BP1. In BP2, we worked with Porocel to scale up the sorbent and develop a production ready process. Porocel produced two rounds of sorbent samples using their industrial manufacturing equipment, in the course of which they developed a sorbent production method which reproduced TDA's laboratory samples. The sorbent for the pilot unit (13.75 tons) was scheduled to be delivered to the NCCC in early November 2017.

4.5.1 Sorbent Scale-up Work at TDA – Definition of Production Method

Initial work with Porocel focused on the recipe of the best sorbent produced to date. Because TDA's sorbent was produced in a small scale in a laboratory environment, there were some significant parameters that needed to be further defined before large scale production could begin. For instance, after extruding, sorbents prepared on a small scale were dried in a non-convection oven overnight. While this is perfectly acceptable for small batches, on a commercial scale this drying plan is neither desirable nor feasible. Commercial drying equipment is typically a belt conveyor oven, with stages set to different temperatures, with total residence times ranging from a few minutes to an hour. Consequently, determining the temperatures and residence time that sufficiently dried the extrudates is critical, and difficult to replicate on a lab scale. Thus, early in the project we collected data on the extent of dryness achieved in the laboratory production as measured by weight loss on ignition (LOI). This data allowed us to define an important sorbent production (QA/QC) parameter to be duplicated during large scale production at Porocel.

TDA's formulation is unique compared to some other alumina sorbent processes. Because of this, there was some concern about the strength of the pellets. Low strength pellets may be crushed under the weight of the sorbent over them in the pilot scale system, so it was important to verify that the sorbent made using TDA's formulation was strong enough (>1 lb/mm). We measured the crush strength on both the finished product and the intermediate pellets, and determined that TDA's sorbent would be strong enough to survive during manufacturing and service.

4.5.2 First Round Sorbent Scale-up Work at Porocel

Our next task was to have Porocel duplicate the sorbent on their commercial production equipment. Porocel prepared 4 customized alkalized alumina samples. These sorbents were

Table 10. Physical properties of customized alkalized sorbent prepared by Porocel. (BET data measured by TDA)

Sample	Batch size	Calcination temperature (°C)	Density (g/ml)	BET surface area (m^2/g)	Pore Vol (ml/g)	Pore Size (nm)
CO_2 sorbent 1 – 1/16"	0.5 L	537	0.87	113.0	0.27	9.4
CO_2 sorbent 2 – 1/16"	0.5 L	765	0.82	65.5	0.27	17
CO_2 sorbent 1 – 1/8"	5 L	538	0.79	88.1	0.26	11.4
CO_2 sorbent 2 – 1/8"	5 L	765	0.78	76.5	0.26	13.5
TDA Sorbent	5 L	538	0.62-0.75	80-145	0.36-0.53	9-11

made at two different calcination temperatures and at two different diameters. The sorbent produced in spherical balls using an existing process at Porocel. The sorbent was produced to be as similar as possible to the TDA sorbent using this process. Due to the some limitation of this process the formulation was not identical to the TDA lab sorbent. The physical properties of the samples are summarized in Table 10. Sorbent 1 and 3 are 1/16" spheres and sorbent 2 and 4 are 1/8" spheres. A photograph of one of the sorbents is shown in Figure 19.

All four Porocel sorbent samples were screened in TDA single fixed bed (300 cc) test apparatus. The single bed alternates operation between adsorption and regeneration. A picture of the single bed apparatus is shown in Figure 20. This apparatus is computer controlled for automated 24 hours operation.

Figure 19. Round 1 CO_2 sorbent produced by Porocel.

Figure 20. TDA single fixed bed sorbent testing apparatus

The four sorbent samples, which were manufactured by Porocel, were compared to a sorbent sample produced in the laboratory by our industrial partner. The Porocel sorbents had varying bulk densities. For comparison during testing, the dosages of CO_2 in adsorption and steam in regeneration per gram sorbent were held constant for each test. The flow rates of the flue gas and steam in regeneration were kept the same and the lengths of adsorption and regeneration periods were adjusted accordingly. The results are shown in Table 11.

Table 11. Single bed test results for six sorbents under coal flue gas condition (14.7% CO_2, 14.8% H_2O and 70.5% N_2)

Date	Sorbent	Bulk density (g/ml)	CO_2 volume based loading g/100 (ml)	Ads time (min)	Reg time (min)	CO_2 loading wt%	+/-
2/21/17	CO_2 sorbent 1 – 1/16”	0.81	0.82	9.0	9.0	1.01	0.00
2/20/17	CO_2 sorbent 2 – 1/16”	0.81	0.74	9.0	9.0	0.92	0.01
2/28/17	CO_2 sorbent 1 – 1/8”	0.82	0.78	9.0	9.0	0.95	0.04
2/27/17	CO_2 sorbent 2 – 1/8”	0.78	0.72	9.0	9.0	0.93	0.02
3/2/17	MC-20812	0.62	0.69	7.1	7.1	1.14	0.02

The CO_2 loadings both on weight and volume bases are reported. The Porocel sorbents performed very well on a volume loading basis. The volume loading is an important metric because it is the volume of sorbent and not the weight of the sorbent that is fixed in the pilot unit (each bed holds 1.75 m^3 of sorbent). Based on this data this sorbent approach appeared promising.

Figure 21 shows the adsorption breakthrough curves of the tested sorbents. The slopes of the Porocel produced sorbents are similar to sorbents produced by our industrial R&D partner.

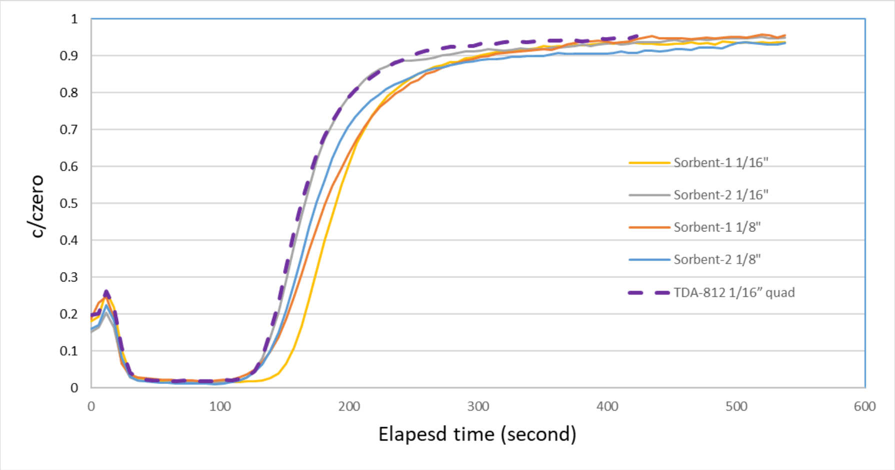


Figure 21. Adsorption breakthrough curves of the tested sorbent

Overall, the performance of the first round of sorbents’ produced by Porocel was nearly comparable to the sorbent developed by our industrial partner in the single bed tests. The CO_2 loadings of first round of sorbents are a little lower than TDA-812 sorbent, but kinetically all the sorbents looked comparable in single bed testing. After the single bed test, the Porocel sorbent was further studied in the bench scale apparatus.

The Sorbent-2 1/8” 765°C sorbent was loaded into the 10 beds unit to run bench scale tests where adsorption and regeneration operate continuously. This apparatus is shown in Figure 22. The flue gas composition was based on average flue gas composition provided by NCCC (10.2% CO_2, 13% H_2O and 76.8% N_2). The inlet flue gas flow rate was set to have the same space velocity as the pilot unit when processing 5000 lb/hr flue gas. The regeneration steam flow and cycle time were adjusted to study their influences on CO_2 capture rate. Testing was done with our optimized process cycle (SS+4+5 / Strip+4+5). This process includes using an air purge step to further strip CO_2 off the sorbent in a second regeneration step. In addition to removing CO_2, this strip air is enriched in water that is desorbed from the sorbent. The first portion of the air strip outlet runs over the sorbent bed that is in transition from adsorption to regeneration. This steam saver process reuses the steam within the process.

Figure 22. TDA Bench-scale apparatus with 10 beds for continuous adsorption and regeneration

Table 12 shows some of the key bench-scale testing results. Unfortunately, the CO_2 capture rate for the first round of sorbents was lower than for the TDA sorbent under the same process conditions. Thus, although promising in the screening tests the performance of the first round of Porocel sorbents was not sufficient when evaluated under the simulated process.

Table 12. Bench scale results for two Porocel produced sorbents (Round 1) under flue concentration conditions of DOE study Case 12 [2]

Date	Sorbent	Avg Bed Temps (°C)	CO_2 Loading, wt%	%CO_2 Capture
8/10/16	TDA Sorbent	143.1	0.82	90.6%
4/10/17	Sorbent-1 1/8”	144.7	0.38	79.1%
4/17/17	Sorbent-2 1/8”	143.4	0.50	80.5%

Because the CO_2 capture rate for the first round of sorbents is lower under the same process conditions, we worked with Porocel to make a second set of customized sorbents for further tests.

4.5.3 Second Round Sorbent Scale-up Work at Porocel

Next Porocel prepared three more sorbent samples using industrial processing equipment based recipes provided by TDA to determine performance with scale-up (Figure 23). These sorbents were extruded which allowed Porocel to more closely repeat the TDA formulation recipe. The physical properties are listed in Table 13.

Table 13. Physical properties measured by TDA of customized extrusion sorbents (Round 2 sorbent samples)

Batch number	Bulk density (g/ml)	BET Surface Area (m^2/g)	BJH Adsorption Cumulative Pore Volume of pores (cm^3/g)	Adsorption Average Pore Diameter (nm)
1	0.728	84.3	0.214	10.15
2	0.709	79.2	0.333	16.76
3	0.727	82.4	0.356	17.3

Figure 23. Round two customized extruded sorbent prepared by Porocel

The three second round sorbent samples were screened in TDA single fixed bed test apparatus. The simulated inlet flue gas contained 13.4% CO_2 and 15.2% H_2O. The duration of adsorption and regeneration was adjusted based on the sorbent density to provide the same dosage of CO_2 in each test. The test results are summarized in Table 14. Previous results for MC-20812, MC-21246 and Sorbent 2 1/8" (first round) are also listed. The performance of Batch 1 and 2 is good relative to the benchmark TDA-20812 sorbent and better than the first round sorbents.

Table 14. Single bed testing results of six sorbents (Round 2 Porocel and TDA sorbents comparison)

Date	Sorbent	adsorption time (min)	regeneration time (min)	CO_2 loading (wt%)	+/-	H_2O loading (wt%)	+/-
22-May	Batch 1	8.3	8.3	1.22	0.05	1.71	0.13
24-May	Batch 2	8.2	8.2	1.21	0.05	1.41	0.26
25-May	Batch 3	8.4	8.3	0.95	0.02	1.33	0.19
2-Mar	MC-20812	7.1	7.1	1.14	0.02	1.66	0.04
13-Apr	MC-21246	7.9	7.8	1.02	0.12	1.11	0.09
27-Feb	Sorbent-2 1/8”	9.0	9.0	0.93	0.02	1.18	0.03

Table 14 shows the CO_2 loading of Batch 3 is much lower than the other two samples. The performance of Batch 1 and 2 are roughly the same. Their performance was further investigated by the bench scale tests.

Next, the second round sorbents were loaded into the 10-bed bench-scale apparatus and we run through continuous adsorption and regeneration cycles. Early bench scale tests confirmed that Batch 3 was the lowest performing among the three customized sorbents. Further testing was therefore performed only on Batches 1 and 2.

Our optimized process cycling includes using an air purge step to further strip CO_2 off the sorbent in a deep regeneration step. In addition to removing CO_2, this strip air is enriched in water that is desorbed from the sorbent. The first portion of the air strip outlet runs over the sorbent bed that is in transition from adsorption to regeneration. This steam saver process reuses the steam within the process. The strip (S) with steam saver (SS) flow pattern (SS+4+5 / Strip+4+5) was run for Batch 1 and 2 to compare the sorbents and determine their performance under our optimized cycle. Multiple cycle times and regeneration flow rates were evaluated in this study. Table 6 summarizes the results for tests having 90% capture rate when the flue gas contains 15.7 % CO_2 and 12.6% H_2O. This higher level of CO_2 accounts for the recycle of the air strip outlet which puts CO_2 back to the burner. This simulates an actual flue gas concentration of 13.3% for both Batch 1 and Batch 2 (Case 12 in [2]). The flow rates of the flue gas and regeneration steam at 90% capture were 6.6 slpm and 3.4 slpm, respectively, which is the same space velocity as the pilot scale tests that we planned to run at NCCC. The steam saver time was adjusted to avoid regenerated CO_2 from going into strip outlet. The cycle time was adjusted to achieve 90% capture. The results for Batch 1 and Batch 2 are very similar.

Table 15. Bench scale SS+4+5 / Strip+4+5 case results for three customized extrusion samples with 15.7% CO_2 and 12.6% H_2O

Date	Batch	Steam saver time	Cycle Time	Avg Bed Temps	CO_2 loading, wt% ADS	H_2O loading wt%, REG	% CO_2 capture (with recycle)
27-May	1	10	85	141.1	0.76	1.18	89.8%
6-Jun	2	10	80	142.0	0.75	1.21	89.8%

The optimized flow pattern (SS+4+5 / Strip+4+5) was also run with the expected flue gas feed composition at NCCC for Batch 1 and 2. Steam saver time and cycle time were adjusted as described above. The flue gas has a flow rate of 6.7 slpm and contains 10.5% CO_2 and 12.8% H_2O. The steam flow rate was reduced to as low as possible. For the results reported in Table 7, 2.6 slpm steam was fed at the inlet. Below 2.6 slpm steam, the sorbent performance dropped off. Similar to the results illustrated in Table 6, the results from NCCC inlet condition runs also demonstrated Batch 1 and 2's performance was very close.

Table 7. Bench scale SS+4+5 / Strip+4+5 case results for three customized extrusion samples under NCCC inlet condition with 10.5% CO_2 and 12.8% H_2O

Date	Batch	Steam saver time (s)	Cycle Time (s)	Avg Bed Temps (°C)	CO_2 loading ADS, (wt%)	H_2O loading REG (wt%)	% CO_2 capture (with recycle)
15-Jun	1	10	115	144.7	0.69	1.24	89.9%
7-Jun	2	10	95	141.5	0.57	1.12	90.7%

4.5.4 Pilot Unit Sorbent Production Order

Porocel has significant experience in scaling up from this batch size to full scale (tons quantities), so they expected that sorbents produced in these runs would be readily reproduced in the pilot unit run. The large-scale sorbent order was placed with Porocel for the pilot unit. We ordered 15 tons of sorbent, which was scheduled to be delivered to NCCC in early November 2017. The sorbent was packaged with the amount of sorbent for one reactor split evenly into two supersacks plus additional smaller bags to top off each reactor. The sorbent was produced in Little Rock, AR and shipped to NCCC in early November 2017. We arranged with NCCC to have inside storage space for warehousing the sorbent until it was ready to be loaded into the unit.

4.6 Procurement of Components and Fabrication of Units

We worked with Springs Fabrication Inc. to prepare the fabrication drawings and construct the sorbent skid structures, manifolds and ten vessels on the sorbent trailers as well as for the service unit, which handles pre- and post-gas processing. The instrument unit and control box were built at the TDA and incorporated into the service unit. The three pilot unit skids were connected together and completed factory acceptance test (FAT) testing and cold shakedown at Springs Fabrication prior to shipment to NCCC.

4.6.1 Coordination with NCCC and Engineering Reviews and Documentation

TDA committed to comply with all the safety requirements from NCCC. We had continuous discussions with NCCC on requirements throughout BP2, and provided the following items to NCCC:

- Follow-up hazard review
- The skid lifting and rigging plan issued by AL PE
- Structural review issued by AL PE
- Foundation drawing issued by Al PE
- The sorbent loading plan
- The type of pre-made electrical connectors which would be re-connected at NCCC

Some of the documentation and Alabama PE drawings required by NCCC were not in the project management plan and therefore not in our project schedule. We still worked diligently with NCCC to provide all engineering documentation required. We were able to complete the requirements within the project budget but it did impact our timeline. Construction was put on hold several times until necessary work from an Alabama PE was completed and feedback was received from NCCC. For example, six months into BP2 NCCC requested additional review of the PI&D, a follow-up hazard review, structural and thermal analysis of the full system and PE stamped structural report. As these items were completed, and we delayed submission of the design to the fabricator to avoid potentially costly changes after equipment had entered fabrication.

In BP2, TDA provided NCCC the skid drawings, a 3-D model, P&ID, electrical diagram, operating procedure, interlock table and AL PE stamped documents for the pilot unit to be accepted on site. All safety issues were addressed and we engaged Cowles, Murphy, Glover & Associate (CMG), an Alabama licensed PE, to address additional engineering requirements. CMG was the engineer of record for the project. A few of the key parts of the pilot unit design finalization and coordination work with NCCC are discussed below.

NCCC Follow-up Hazard Review:

TDA completed its multi-level review process with the NCCC. A preliminary process hazard review with the NCCC had previously occurred on May 12, 2015 during BP1. This was a formal process hazard analysis (PHA) review conducted with an outside facilitator, Process Improvement Institute Inc., in September 2015. During BP2, a follow-up HAZOP analysis was conducted on Oct 20, 2016 (via conference call) to review the most updated P&ID, Safety Shutdowns, Interlocks, and Operating Conditions. The purpose of the hazard review meeting was to discuss any changes to the system design since the formal HAZOP review September 2015. One important change in our system was the elimination of medium pressure steam (420 psig) as part of the system to protect against heat losses in the sorbent bed trailers. TDA explained that we switched from medium pressure steam (420 psig) to low pressure steam (100 psig) for the guard heating. This change reduced the cost and complexity of the system, and allowed for better control of the system, with less chance of overheating the trailers. The updated system includes a commercial low pressure heat exchanger, multiple steam traps and drains to ensure proper and safe operation. Several lines and components were also removed to simplify the process to run only the CO_2 capture flow pattern that was identified as the most efficient.

Engineering Review and Documentation:

We hired Cowles, Murphy, Glover & Associates, an Alabama licensed PE firm, to do a structural review of the pilot unit skids and to develop a rigging and lifting plan for the skids. They analyzed the skid under lift conditions, in-service conditions with thermal effects, and wind loading. The structural analysis was conducted in the software RISA. For the thermal effects, the skid was assumed to be 330^{o}F, the maximum possible temperature that could reached based on the steam heating. The nominal operating temperature is 284^{o}F. The deflection of the structural skid under both the static and lifting case was within allowable safety factors. However, to minimize any stress on the piping and internal components, the design of the structural skid was re-optimized to further reduce deflection. The W4x13 cross I-beams were updated in the design to a W8X24 beam where the maximum deflection on the beam was only 0.033”. The lifting lugs were relocated to better distribute the load. A report on the structural analysis was completed in January 2017. NCCC asked to review the structural report and fabrication drawings prior to our releasing the skids to fabrication.

TDA partnered with Glew Engineering to review the mechanical stresses within the trailer and provide feedback on the placement of piping supports and the use of flexible lines in the system. A finite element analysis (FEA) was conducted. We studied the stress in the following locations:

the series steam pipe connections, connections at the manifold header and the nozzle on the vessel. To relieve the stress in the series steam pipe connections during the thermal expansion, flexible hoses were used next to the top valve header. A gusset was added beneath the manifold valves headers to provide extra support, particularly during shipping. The location of the pipe supports designed by TDA and Springs Fabrication were sufficient, although a few additional pipe supports were recommended by Glew Engineering.

We also worked with CMG on lifting and rigging plans for the sorbent skids. NCCC was shown a draft version of the lift plans on May 17, 2017. NCCC responded with additional concerns about particular labels and the center of gravity determined by the 3D model of the units. We worked closely with CMG and NCCC to determine the best course of action to resolve the issues. The corrected stamped lifting and rigging plans for the sorbent skids were provided to NCCC July 16, 2017. NCCC determined it would be prudent to have CMG confirm the center of gravity (CoG) with another analysis. CMG performed an additional analysis of the CoG and submitted the results to NCCC on August 8, 2017. An additional correction to the lift and rigging plans was issued on August 8, 2017. All the lift and rigging plans for this project were accepted by NCCC on August 11, 2017. Stamped and sealed hard copies of the lifting and rigging plans were delivered to NCCC on August 15, 2017.

CMG also conducted a structural review of the service unit skid design. The service unit contains the control box, instrument cabinet, power box and the equipment to support operation. The equipment includes heat exchangers, blowers, gas/liquid separator, etc. There are fourteen pipes connecting the service unit and sorbent trailers. The PE stamped structural report for the service unit was provided to NCCC. Although a stamped structural support document was not part of the NCCC project management plan, we worked diligently with NCCC to provide them with their required documentation for acceptance of our skids. After the NCCC completed their review of the service unit fabrication drawings and structural report, we finalized the design with our fabricator, Spring Fabrication. TDA released the drawings to the fabricator shop in June 2017. Because the service unit was <50,000 lbs and contained four lift lugs at the top a PE stamped rigging plan was developed for this skid, a lifting plan was not required. However, CMG issued the rigging plan for the service unit (June 29, 2017), which was subsequently submitted to NCCC (July 5, 2017).

Finally, CMG prepared foundation drawings for the three skids. The sorbent trailer skid drawings were provided to NCCC in February 2017. In May 2017, the NCCC came back with comments and changes on where NCCC propose to install the support pillars for the skids and wanted a new proposal reviewed. After going back and forth with NCCC and CMG, this issue was resolved. All the required Alabama PE stamped documents were submitted to NCCC.

4.6.2 Construction of the Sorbent Trailers

The two sorbent trailers were built at Spring Fabrication Inc. Springs Fabrication first prepared the fabrication drawings on the sorbent trailers based on TDA provided Solidworks models. TDA ordered all the valves for the sorbent trailers, which were shipped to Springs Fabrication. The two sorbent trailers are essentially identical, but one is a mirror image of the other. Both sorbent trailers were completed by June 2017. Sorbent vessels were hydro-tested separately along with all manifold piping. A chronology of the construction in shown in the following pictures.

On Dec. 9, 2016, TDA's team visited Springs Fabrication, Inc. to check the fabrication progress. Springs Fabrication, Inc. had fabricated the major parts for the sorbent vessels and the manifold pipes for the trailer, which are shown in Figure 24. Preliminary checks indicated the fabrications are within the specified tolerance.

Figure 24. Photos of finished parts at Springs Fabrication, Inc. December 9, 2016

In first quarter of 2017 after structural engineering review was completed by the AL PE, the design for the two sorbent trailers was finalized and TDA released the documents for fabrication for both units. Springs Fabrication, Inc. completed the hydraulic test for the sorbent vessels with the manifold connected. The painted sorbent vessels and manifolds were installed on trailer #1. The corresponding pneumatic valves and the long manifolds besides the vessels were put in place as well, as shown in Figure 25.

Figure 25. Photos of trailer #1 at Springs Fabrication, Inc. March 23rd, 2017

During the second quarter of 2017 TDA visited Springs Fabrication, Inc. multiple times to check the progress and coordinate with our other contractors. Pictures during the visits are shown in Figures 24-27. The construction of the two sorbent trailers was completed, as shown in Figures 26-27 by June 2017.

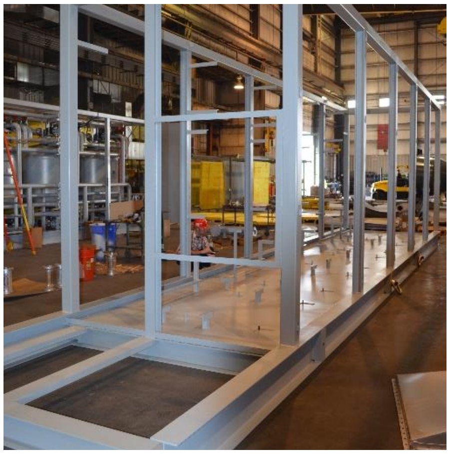


Figure 26. Photographs of the skids at Springs Fabrication, Inc. on May 8, 2017

Figure 27. Photographs of the skids at Springs Fabrication, Inc. on May 30, 2017

Figure 28. Photographs of the skids at Springs Fabrication, Inc. on June 14, 2017

Figure 29. Photographs of sorbent trailer at Springs Fabrication, Inc. on June 22, 2017

4.6.3 Construction of Instrument Unit/Electronics Cabinet

The instrument and control cabinets were constructed in house at TDA. The instrument unit holds all analytical instruments to measure the gas composition and sample conditioning equipment. The control cabinets hold the OPTO control modules and high voltage power panel for the blowers and heaters. These cabinets were fabricated at TDA and were shipped together with high voltage power cabinet to the shop of Springs Fabrication, Inc. The cabinets were mounted on the frame, shown in Figure 30. TDA engineers installed the connecting cables among the three cabinets. The control modules passed the initial check-out at startup. The units

Figure 30. Photographs of the instrument unit on August 17, 2017

were attached to the end of the service unit and where they were shipped and lifted in place as one unit.

4.6.4 Construction of the Service Unit

The last skid to be constructed was the service unit. TDA ordered all the major pieces of equipment and components for the service unit. We worked with the vendors on the selection, design and ordering of the blowers, heaters, heat exchangers, separators, flow meters, relief valves, and pneumatic valves etc. Components were shipped directly to Springs Fabrication, Inc. Spring Fabrication completed the fabrication drawings for the service unit skid by June 2017. Construction of the service unit was finished by the end of September 2017. TDA assisted in the construction of this skid (working at Springs Fabrication site) by installing thermocouples, pressure transducers, gas sample lines and heat tracing cables on service unit. Photographs documenting the construction of the service unit skids are shown in Figure 31 through Figure 33.

By mid September 2017, Springs Fabrication, Inc. had completed the assembly of service unit. Following that, TDA arranged the insulation and electrical contractors to come to continue work on the service unit. The TDA team stayed on site with the contractors to provide guidance. The insulation contractor first did the hard insulation on the pipes, and then used blankets to cover valves and equipment. The electrical contractor first built the conduits within the service unit, and then inserted the cable to each device through the conduits. At the end of September, the skids were set into the planned position in preparation for operation and FAT testing.

Figure 31. Photographs of the Service unit skid frame at Springs Fabrication, Inc. on Aug 17, 2017

Figure 32. Photographs of the Service Unit skids at Springs Fabrication, Inc. on August 25, 2017

Figure 33. Photographs of the skids at Springs Fabrication, Inc. on September 25, 2017

4.6.5 Final Skids Assembly and Factory Acceptance Testing of the Pilot Unit

FAT testing at Springs Fabrication was conducted in the beginning of October 2017. To run FAT the skids were set up in their arrangement for operation together. On September 29, 2017 the three skids were moved into position (Figure 34). The final connecting pipes between the skids were finalized based on the dimensions of the positioning. The remaining piping was completed for the service unit and the condensate lines. Electrical work and insulation were completed in the first week of October 2017. NCCC sent two persons to inspect the skids during FAT on October 11, 2017. The NCCC was satisfied with the skid construction and operation.

Figure 34. Sorbent trailers and Service unit/instrument unit skid put into position on Sept 29, 2017

We conducted FAT testing on the assembled skids at Springs Fabrication from October 5-18, 2017. During this time the system was powered using a single 480VAC power feed. All resistive heaters (inline coil style and heat trace cabling) were fully powered to ensure proper wiring and connections. Temperature rise was noted on all thermocouples tied to the heaters. All pneumatic shutoff valves on the sorbent beds were cycled fully to ensure proper fail-to-close positioning and fully open upon open signal trigger. In addition, all pneumatic and solenoid shutoff valves on the service unit trailer were cycled to ensure correct plumbing, wiring and signal allocation. The flow control valves on the service unit were calibrated and run through full open/close cycling. Both pressure boost blowers were bump checked for proper rotation. They were then run up to full speed to flow air through all piping. The reactor vessels and piping was pressure checked up to 4 psig then closed off to ensure pressure holds with no leaks in the system. Finally, sorbent bed cycling tests were performed. With the flue gas blower running, beds were cycled as they would be in the field for carbon capture. Five adsorption beds were open in parallel flowing top down from the flue gas supply lines. Five regeneration beds were open in series flowing bottom up. All beds were then rotated continually for ~ 1 hour to demonstrate uninterrupted bed cycling. Issues with signal misallocation were corrected and corrections were made to flow meters to remove background vibration noise the signal. No major problems were identified that delayed the shipment of the skids.

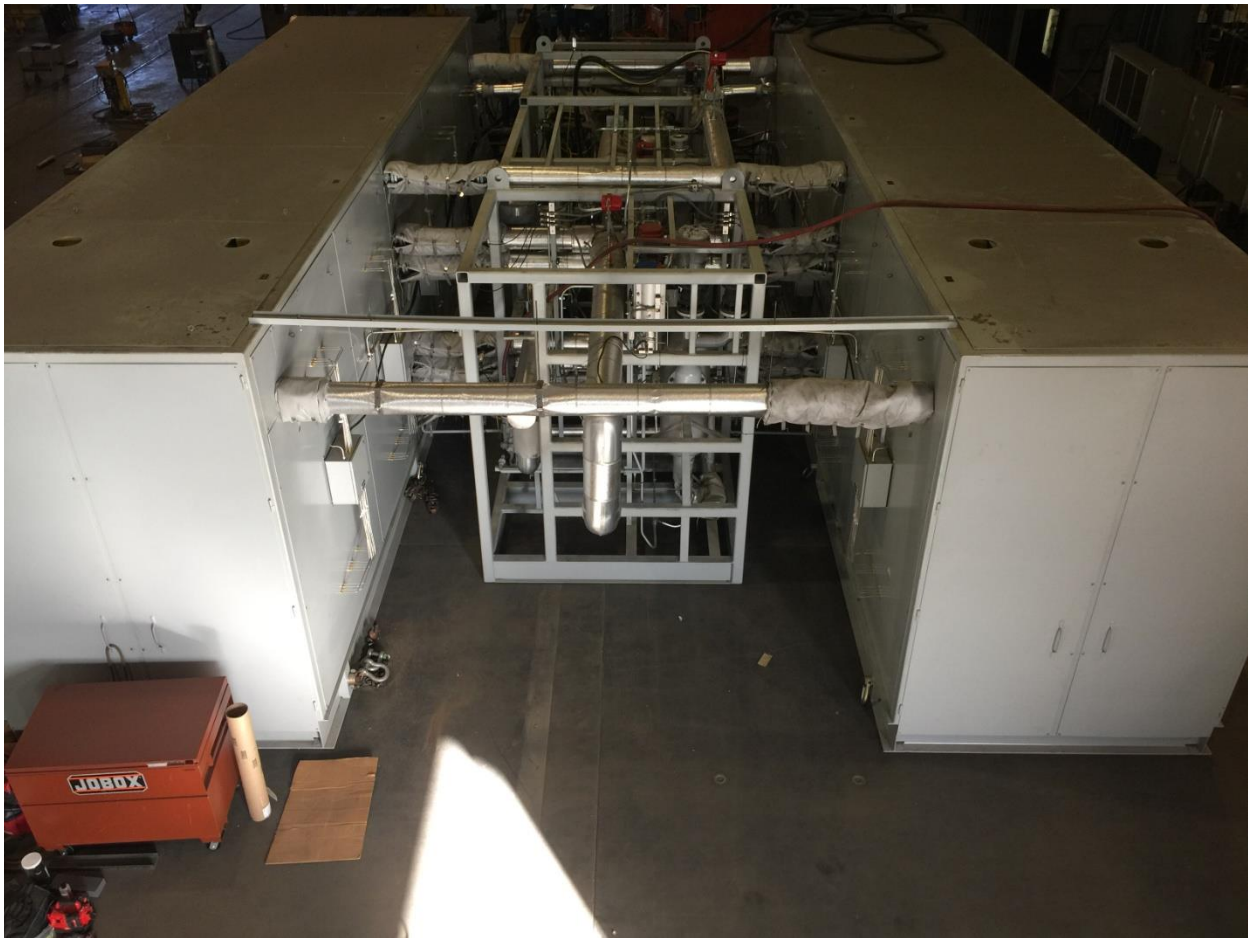


Figure 35. The whole Pilot Unit fully assembled for FAT at Springs Fabrication

4.7 Pilot Test Plan

The primary objective of the pilot unit field tests is to demonstrate the technical merits of this sorbent-based CO_2 capture process. The process should also achieve a 95+% pure CO_2 product stream (on a dry basis). A detailed test matrix was developed to meet our overall test objectives. TDA personnel have completed appropriate safety training.

During the field tests, we planned evaluate two different cycle schemes, and in each of the cycle schemes optimize the cycle parameters to achieve the following goals:

- Minimize the amount of regeneration steam used
- Maximize the flue gas flow rate through the TDA system
- Maximize the adsorption step time (cycle time) and optimize other step times
- Minimize the adsorption temperature
- Minimize purge gas flow

We would also evaluate the process under both coal derived flue gas and simulated natural gas conditions (diluted flue gas). Finally, we would demonstrate cyclic operation at steady-state using the optimized adsorption cycle scheme.

Operator Training: Start up, Operation and Shutdown procedures were prepared for the pilot unit. TDA employees also completed safety training necessary for the work at NCCC. This including Scaffolding, LockOut-Tag out, Ladder Safety, Fall prevention, energized electronics and arc flash safety, and confined space entry. TDA employees completed online training for NCCC as well. Additional training in coordination with NCCC would be conducted on site when the pilot plant is installed.

4.8 Pilot Unit Installation at NCCC

After factory acceptance testing (FAT), the units were shipped from Colorado Springs to Wilsonville, Alabama. The four trucks carried sorbent trailer 1; sorbent trailer 2; service unit/instrument unit; and connecting piping between skids and instruments that packed into individual crates for safe transport. The two sorbent trailers are oversized loads. All the trucks arrived at NCCC the week of October 23, 2017.

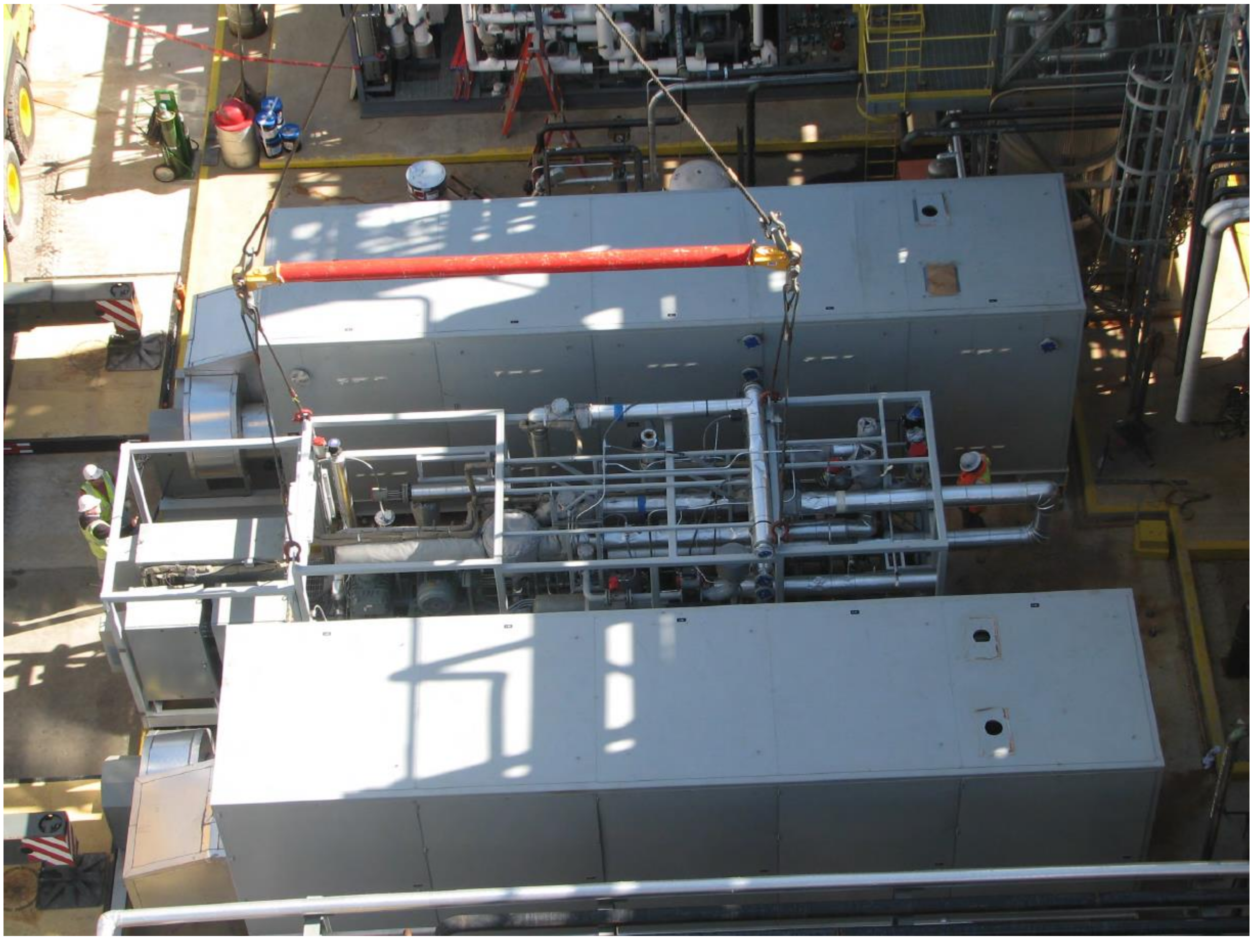


Figure 36. Installation of TDA Pilot unit on-site at NCCC

The TDA post-combustion pilot unit was installed at Pilot Bay #2 (Figure 36). TDA provided NCCC with Alabama PE stamped foundation drawing. NCCC completed the design of the skid anchoring. NCCC prepared concrete pillars for the TDA pilot unit skid. The three large skids were transported off the trucks and installed on site by crane per the stamped lifting and rigging plans as appropriate. An Alabama PE stamped rigging plan and lifting plan was prepared for the sorbent trailers. Due to its smaller size (<50,000 lbs) and that it has four lift lugs on the top, a lifting plan was not required for the service unit skid. A rigging plan was prepared for the service unit by an Alabama PE. All lifting and rigging plans had been submitted to NCCC for review and comments ahead of time.

TDA developed a procedure to load the sorbent into the reactors at NCCC. We discussed the loading plan with NCCC to get feedback on feasibility and safety. They approved our plan and would provide necessary assistance on site. Sorbent was delivered in early November and stored onsite in a warehouse. We loaded two supersacks of sorbent per each reactor plus additional smaller bags to top-off the reactors. The supersacks were lifted by a NCCC crane and sorbent were sock loaded into the ten beds.

Figure 37. Sorbent loading at NCCC

TDA had already coordinated with NCCC on the integration and tie-in of the pilot plant. The interfaces include the flue gas slip stream, regeneration steam, required utilities such as cooling water and electricity and proper venting of the exhaust gas. NCCC carried out all needed site modifications and provided all necessary tie-ins and utilities for the pilot plant. NCCC has completed the design of the steam and flue piping and has piping ready to install. We worked with NCCC for them to add heat tracing and insulation to their design to prevent condensation in the flue gas upstream of our system. The NCCC provided a relay signal to TDA's control box in order to permit operations.

All the milestones in BP2 were matched. Sections 4.9-4.18 are results from BP3.

4.9 Shake-down at NCCC

From early 2018 to early 2019, TDA conducted a series of shakedown tests to check the functionality of the skid, repair the malfunctioning components and calibrate analyzers. All the components, including blowers, heaters, analyzers, pneumatic valves, thermocouples and flow meters, were checked.

We had 2 major repairs: 1) The original installed vortex meter for steam flow didn't provide reliable readings, even after we installed a flow straightener. Thus, it was replaced by a steam meter based on differential pressure, which outputs very reliable/repeatable readings. 2) The screen at the bottom of bed 2 was broken and caused sorbent to fall into the bottom header. TDA laid additional screen on the broken section and loaded Denstone™ deltaP™ material as the bottom layer for bed 2 as a failsafe to prevent sorbent falling through again. As a result, bed 2 was comparatively under filled with sorbent.

The gas sampling system was thoroughly vetted by "snooping" each tubing connection for leaks, and ensuring there was enough chiller capacity to cool very wet gas from the process. We also went through several experiments to prove we had accurate measurements to correlate flow rate of any particular stream and concentrations of each component of said stream. This enables an accurate mass balance for the overall system and is critical to have confidence in the results.

4.10 Sorbent Produced for Pilot Test

4.10.1 As-received Sorbent

TDA evaluated the as-received pilot sorbent (a 15-ton production batch) produced by Porocel. Every sample was tested at TDA. Table 16 summarizes the CO_2 loading from individual super sacks and composites of the two lots of samples produced. The composite samples contained mixtures from multiple super sacks. Composite samples are more representative of the overall expected sorbent performance in the pilot unit. There is some variation, but the CO_2 loading was good except for Bag #2.

Table 16. CO_2 loading of the pilot unit sorbent from single bed test

Sorbent	CO_2 loading, wt%
Porocel batch 1 (previously produced scale up batch)	1.10
Pilot Unit Bag #2	0.65
Pilot Unit Bag #7	1.01
Pilot Unit Bag #8	0.85
Pilot Unit Bag #13	1.01
Pilot Unit 1030A composite	0.86
Pilot Unit 1105A composite	0.92

Looking at the adsorption kinetics for the pilot sorbent in Figure 38, the two composite samples have breakthrough curves very close to Porocel Batch 1 (previous scale-up batch) except a single supersack (Bag #2). Based on the kinetics of the composite samples (Lot 17PT-1030A and Lot PT-1105A), we expected the 10-bed test would have similar results as the Porocel Batch 1.

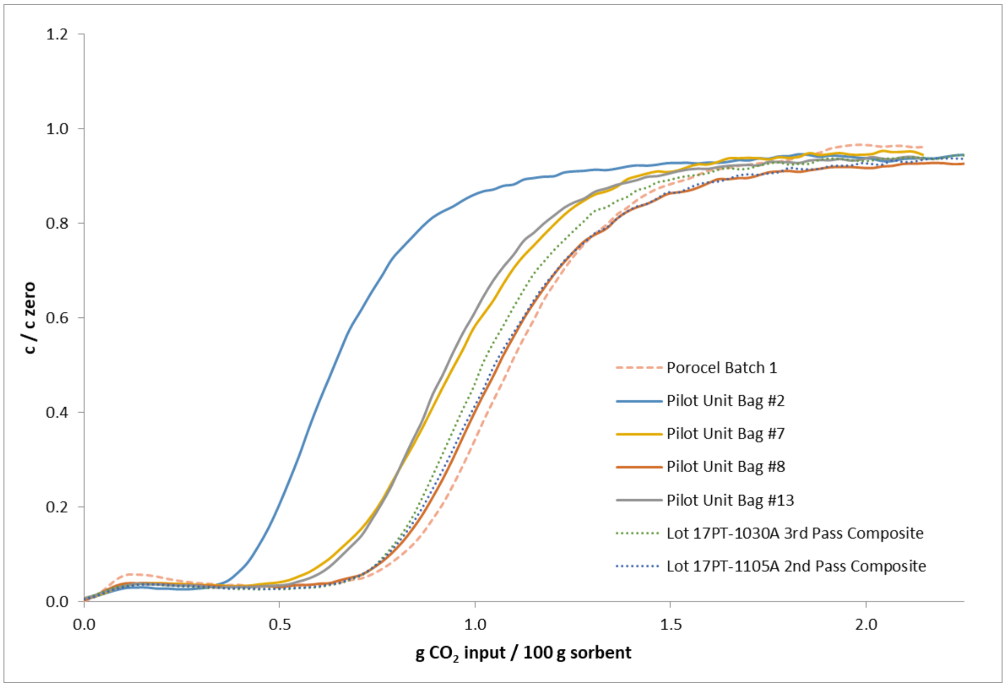


Figure 38. Adsorption breakthrough curves for pilot sorbents

After Gaston 5 plant shut down and NCCC stopped producing flue gas and steam, we took the time to run an extended cycling test of the pilot unit sorbent (Composite 1030A and 1105A) in the 10 bed bench unit test.

Although the single bed results showed the performance of pilot sorbent is close to that of Batch 1 sorbent, the pilot unit sorbent suffered from significant and unexpected degradation after cycling. In the 10-bed test, the capture rate for the pilot sorbent is much lower than Porocel Batch 1 under the same condition shown in Table 17.

Table 17. Bench scale SS+4+5 / Strip+4+5 case results for Batch 1 and pilot sorbent under Case 12 condition

Date	Sorbent	Flue gas (slpm)	Avg Bed Temps (°F)	CO_2 loading, wt%	CO_2 capture rate
5/27/2017	Batch 1	6.65	141.2	0.82	89.3%
2/7/2018	Pilot	6.70	144.4	0.31	66.0%

The cycled pilot sorbent was put back in single bed to check the loading after running in bench unit for 125 and 339 hours. Figure 39 shows the CO_2 loading for composite 1105A. The degradation of the pilot sorbent was severe, and unlike that of any sorbent we had previously tested.

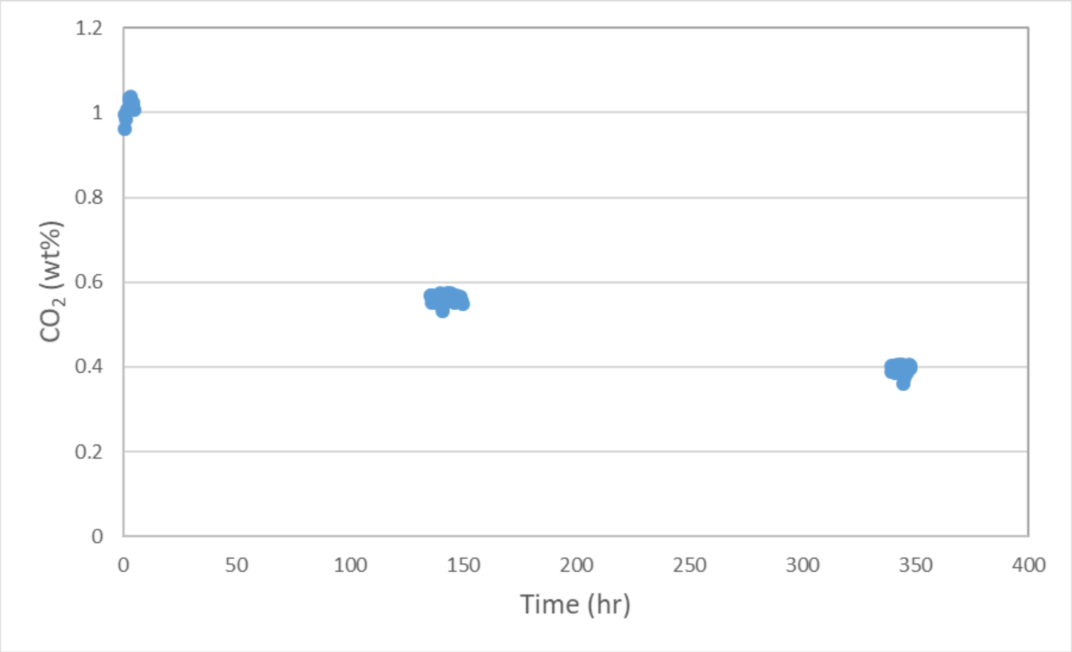


Figure 39. Degradation of the pilot sorbent composite 1105A with cycling

Further characterization testing was performed to understand what was different with the pilot unit sorbent that could cause the poor performance. One of the tests we ran was XRD to check the morphology of the material. The composite sample 1030A has significant crystallinity. This crystallinity matches the XRD of the boehmite raw materials. Figure 40 shows the XRD result for composite 1030A and Versal 250 (a raw material of the pilot sorbent). The XRD of the composite 1030A and Versal 250 have overlapping peaks observed in XRD results. Versal 250 is a boehmite alumina having crystal structure. In our sorbent production process, however, the calcination should convert the boehmite into γ-alumina. γ-alumina is amorphous. Porocel Batch 1 and all TDA laboratory sorbents are completely amorphous. Porocel Batch 1 is shown in Figure 41; note there is no boehmite peak at 14°. The pilot unit sorbent was determined to be under calcined and contains unreacted raw material. This explains the degradation, because a sorbent containing large amounts of boehmite would not be hydrothermally stable under our steam regeneration process.

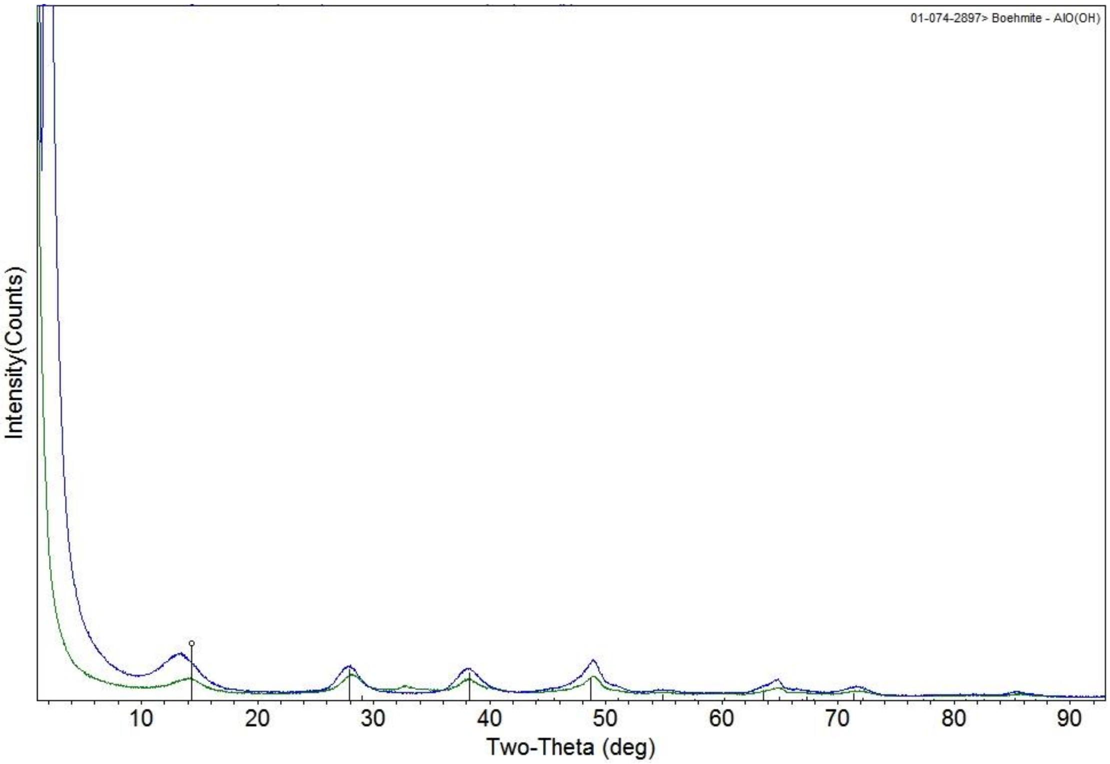


Figure 40. XRD results for pilot sorbent 1030A composite and Versal 250 (boehmite) (Green: pilot sorbent; blue: Versal 250)

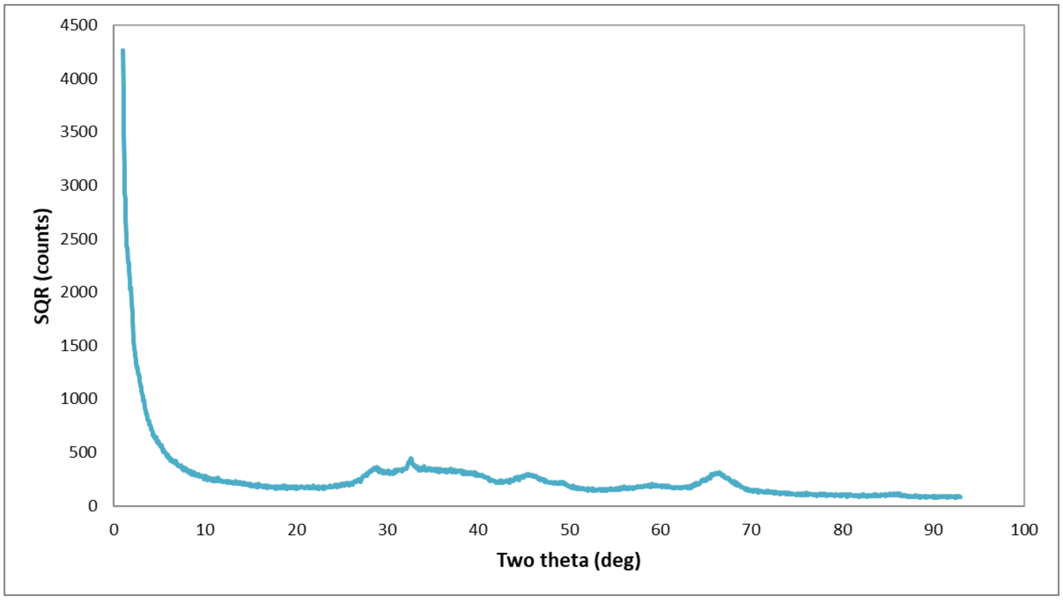


Figure 41. XRD result for Porocel Batch 1 (previous scale up batch produced by Porocel)

TDA discussed the sorbent production extensively with the pilot sorbent manufacturer, Porocel. Porocel independently confirmed the presence of boehmite in the pilot unit product in laboratory testing at their facility. The pilot unit sorbent was considered sufficiently calcined at the time based on the temperature that was reached and based on the LOI (loss on ignition). The LOI of the large batch was compared to LOI of the scale-up samples previously made by Porocel. After further discussion with Porocel it was determined however that their LOI measurements were impacted by their humidity and did not accurately measure whether the sorbent was sufficiently calcined. We then started working with Porocel to define an LOI metric that is accurate and reproducible along with XRD.

4.10.2 Sorbent Reprocessing Method Development

TDA conducted laboratory tests to develop a method to reprocess the sorbent and restore its performance. TDA hypothesized restoring full sorbent performance could be achieved by returning the material as close as possible to its pre-fired form. TDA accomplished this by reimpregnating the as-received material with water.

We looked at different method for reprocessing. Initially, sorbent was mixed by hand with a spray bottle of water, measuring the amount of water before and after impregnation to record %weight of water added. Later, in order to confirm the scalability of our process, water was added in a commercial tablet-coater mixing system using a pressurized spray bar, a form a common form of commercial processing. After the rewetted material was removed, samples were extracted for various tests, and the remainder was recalcined. This was done in two ways. Initially, sorbent was calcined in a muffle furnace with a programmed ramp rate and hold time. Later, in order to confirm scalability, a batch rotary furnace with a humid air feed was used. A continuous feed rotary oven would be used in the large-scale reprocessing. TDA's rotary furnace, while not continuously fed, served as an appropriate comparison. Again, after the calcine step was finished, several samples were extracted and the remainder was loaded into our bench scale and single bed test units. Several calcination profiles were evaluated.

Preliminary results were very promising. The next step was to vary the amount of H_2O added to correlate performance to the amount of water added. Multiple water levels were tested. Porocel was involved on a weekly basis to develop a process that was consistent with their large-scale equipment. A concern was the strength of the sorbent pellet processed with the added water. The pellet would dissolve if too much water was added. With Porocel's input, TDA determined a recipe for the best performance with the lowest sorbent loss due to the rewet processing step. Porocel also produced a sample in their laboratory under the identified reprocessing conditions. TDA then loaded and tested sorbents made both at TDA and Porocel. We also compared the results with material that had been recalcined only without water impregnation.

Figure 42 shows the CO_2 capture results of bench scale testing for several reprocessed sorbents. The original production batch of the sorbent by Porocel shows a rapid drop in performance (red diamond). The results obtained by recalcining the original sorbent is shown by the brown circles in Figure 42. Recalcining does improve the performance, but there is still a drop in capture rate as cycling continues. The green and grey squares show the capture rates for the Porocel lab batch and TDA lab batch, respectively, after the two-step reprocessing. Reimpregnating the sorbent with H_2O before recalcining increased both the overall performance and stability of the sorbent. This, method was selected for reprocessing the entire pilot unit sorbent batch.

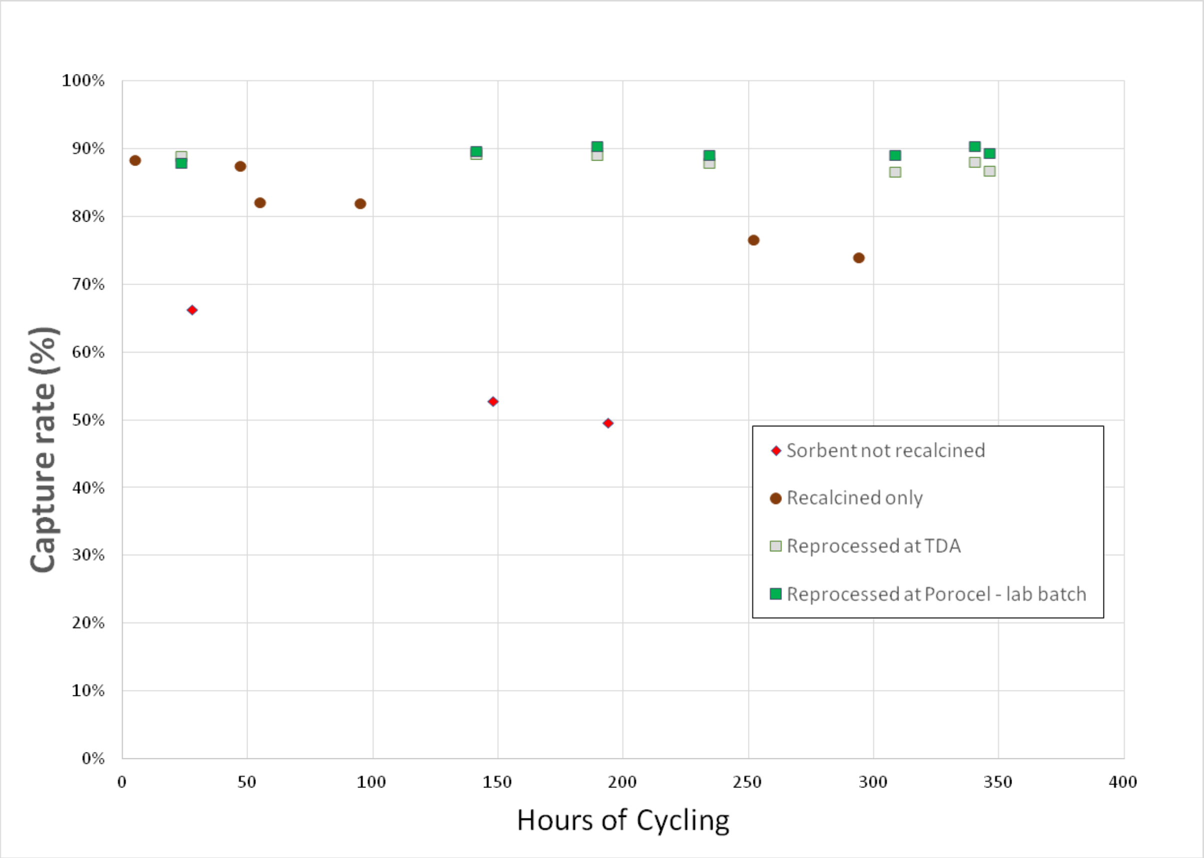


Figure 42. CO_2 capture for original sorbent and various reprocesses.

4.10.3 Sorbent Reprocessing at Porocel

The sorbent was extracted by vacuuming at NCCC in May 2018. Then, the extracted sorbent was shipped to Porocel. Reprocessing of the sorbent began on June 26, 2018. This date was the first available time that Porocel had both the impregnation and calcination equipment available. During reprocessing TDA and Porocel worked closely together to reduce attrition as much as possible. TDA sent a representative to Porocel in Little Rock, AR to monitor the setup and conditions of reprocessing the extracted sorbent. QA/QC on the reprocessed sorbent included XRD and Loss on Ignition (LOI) measurements.

A major factor in attrition control was to minimize the number of steps in the reprocessing. Each process step was directed to be Flexible Intermediate Bulk Container (FIBC) to FIBC. This means each process step would start with a supersack full of material and end with a supersack full of material. Porocel did not use elevators or lifts while processing the material. Every piece of equipment was gravity fed from a FIBC. This minimizes the losses from handling material between pieces of equipment. Our recipe for reprocessing does not require intermediate cooling or drying, and thus only three major steps were required in this large-scale process.

Our goal was to replicate the results in the lab tests but immediately scale up to our large-scale batch size. Porocel had already screened the as-received vacuum extracted sorbent using an 18 mesh screen when the TDA representative arrived. The remainder of the screened sorbent was loaded to the mixer in large batches where it was rewet with RO water. The first three bags of material had water added based on their free moisture results (surface water from exposure).

This proved to be inaccurate as the samples taken to determine free moisture varied widely (2-12%). As a result, after the third batch, TDA and Porocel agreed to add a set amount of water based on the average free moisture results from all previous samples (~6%). This streamlined the process and ultimately resulted in less loss. The material was loaded into the mixer and immediately began water impregnation. The spray bar was activated for ~seven minutes. The material continued to mix for an additional five minutes after deactivating the RO water spray.

The next step was to calcine the material after the rewet procedure. The rewet material was loaded into the calciner immediately following the rewet step. No more than two supersacks of material were loaded at a time. The material spent approximately 2.5 hours of time within the calciner. The cooler at the end of the calciner was not used as this would increase loss from the additional process step. Instead as the material emerged from the calciner, it was loaded into large steel hoppers to sit and cool at room temperature for several hours.

Once the material was cooled enough, the hopper was unloaded onto the 18 mesh screen once again to sift out any powders or fines from the reprocessing. After the screen, the finished material was loaded into a fresh super sack. A ~400cc sample was extracted from each supersack in order to perform acceptance testing at TDA. The sack was sealed, placed on a pallet and stored in the warehouse until TDA accepts the material and authorizes shipment back to the NCCC.

Porocel ran post-processing quality tests to ensure the material was properly calcined. Figure 43 shows the results from XRD testing. The black line indicates the state of the extracted sorbent as-received after initial screening. All other lines indicate the state of the sorbent after properly calcining the material. The large black peaks (as-received sorbent) indicate crystallinity which should not be in the final product. All other lines show proper conversion to an amorphous material.

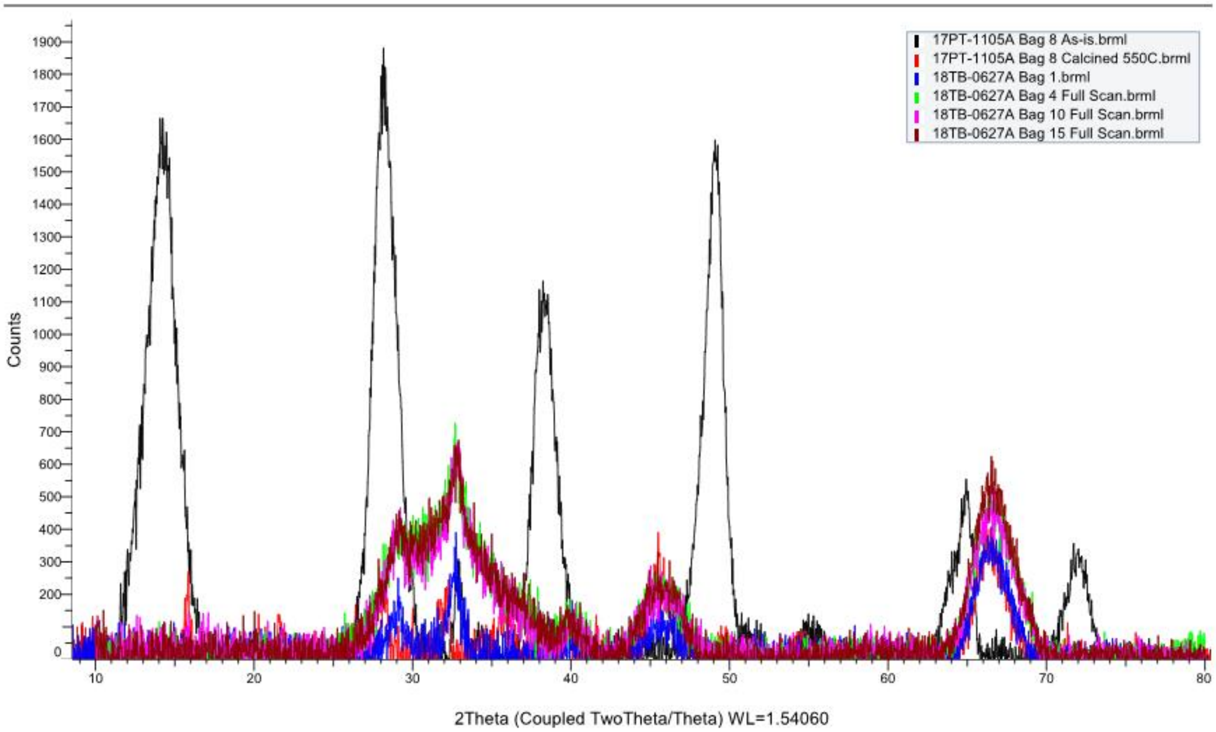


Figure 43. Porocel XRD results, as received (black) and reprocessed sorbent batches

In addition to XRD, Porocel also ran Loss on Ignition (LOI) tests on the sorbent, shown in Table 18. The target LOI for the reprocessed sorbent was < 6%; all bags were within this range. Photographs of the original processed sorbent and the sorbent after reprocessing are shown in Figure 44. One can clearly see the reprocessed sorbent is quite smaller than that from the original production lot. The reprocessed sorbent has a shorter pellet length due to breakage by the multiple handling and processing steps. In addition, the sorbent pellets also shrank in diameter during reprocessing. The diameter on ten pellets was measured with a set of calipers. The average decrease in diameter of the reprocessed pellets was ~0.004" from a starting diameter of 0.067".

Table 18. LOI Results on Reprocessed Sorbent

Bag #	Net LOI, 250-1000°C (wt%)	Compacted Bulk Density (g/cc)
1	4.9	
2	4.2	0.75
3	5.0	
4	4.3	0.79
5	4.5	
6	5.0	
7	4.6	
8	5.2	
9	5.0	
10	5.4	
11	5.2	
12	4.9	
13	5.1	
14	4.9	
15	4.6	
16	5.3	

Figure 44. a) Original processed sorbent b) Sorbent after reprocessing

Removing the sorbent and reprocessing the inevitably led to a reduction in the volume of material. The fully calcined sorbent took up less volume than the originally made material. When the material was calcined it shrunk (estimated at 8% by volume). The vacuum removal process went well but still broke up the length of the extrudates so that the sorbent compacted more (about 5 to 10% volume compaction). We also sieved the material to remove dust/fines (estimated at 5% by volume) and there were some losses due to handling in reprocessing (reimpregnation with water and recalcining, 3 to 10%). All together with volume shrinkage in calcination, compaction and handling, we had 25-30% less sorbent by volume than we started with. As a way to address this, TDA filled 2 beds with a custom modified commercial alkalized alumina made by Porocel. This material does work in our process but not as efficiently as TDA's material. This make-up sorbent was segregated into trailer #1 in vessels #1 and #2. TDA believed this was the best option as the entire system could still run and we could also independently analyze the performance of the TDA only sorbent trailer.

The total amount of sorbent produced after reprocessing by Porocel was 21,556 lbs (10.78 tons). This material filled 16 supersacks; the last supersack was 1/3 full. Porocel also produced 7,429 lb (3.7 tons) of Dynocel, which was made by calcining Chlorocel 901 1/16” sphere sorbent at 765 °C. The Dynocel materials was loaded into 5 supersacks. All supersacks were filled to TDA’s specification to a convenient weight for loading into the reactors.

4.11 Pilot Test in 2018-2020

From 2018 to 2020, pilot test was run for the reprocessed sorbent and Dynocel when the flue gas and steam at NCCC were available. The reprocessed sorbent in bed 10 was found accidentally hydrated and not active in CO_2 capture. The sorbent in bed 10 was replaced by Chlorocel 901 in August 2019. The corresponding pilot results in this period were shown below.

4.11.1 Controlled Hydration of the Sorbent

The fresh sorbent had a large capacity for steam. And adsorption of steam was very exothermic. To avoid a high temperature spike in the reactor, we developed a hydration process gradually increasing H_2O% in air from 0.4% to 100% by mol. The H_2O% at the bed inlet was only increased when the reading of H_2O% in the outlet stabilized and the temperature was stable in the reactor. The trailer temperature was reduced to 121 °C as well during this process. A high flow rate of gas is needed to remove the heat generated. Figure 45 shows the temperature history for bed 8 with controlled hydration, which remained below 166 °C. The H_2O% at the bed outlet was recorded as well. The temperature immediately spiked each time the H_2O% increased to the next step in the hydration process. The hydration for one reactor took about 8 hours.

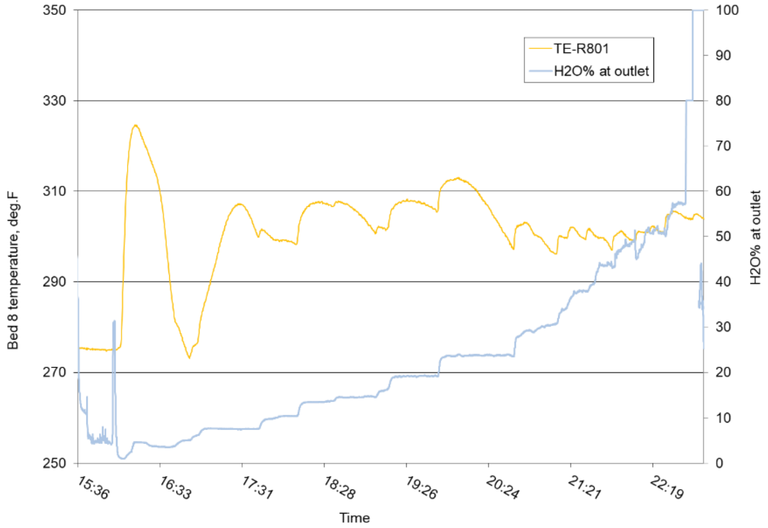


Figure 45. Temperature inside of bed 8 and H_2O% at outlet with controlled hydration (5/25/19)

4.11.2 System Functionality Test with Flue Gas

Before we ran the pilot unit through the full 10-bed operation, we tested the cycling functions step-wise through 2-bed, 3-bed and 4-bed cycling experiments. These simplified flow patterns use fewer beds, but have the same major cycle steps (adsorption and desorption) for a cycle as a 10-bed test.

4.11.2.1 2-Bed Test

At first, we ran a simple 2-bed test, in which each bed is run alternatively between adsorption and regeneration (Figure 46). The two beds filled with Dynocel sorbent (beds 1 and 2) were used first for this test. The flue gas and steam were set to flow continuously with the beds operating in swing mode. At that time, the vortex steam meter was still in use. The flow rate of steam was regulated by the control valve (% open) and determined by the Cv calibration curve of said valve. The flue gas flow rate was 684 scfm, measured by FT101 and FT102, which corresponds to 0.3 MW.

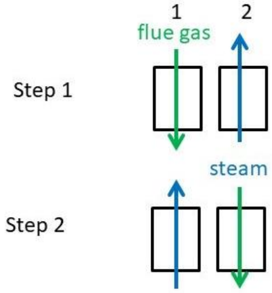


Figure 46. 2-bed flow pattern

The goal of the 2-bed run was to test the functionality of the cycling process and all service unit components. The operation was successful: the valves turned correctly when the bed status switched; the temperature in the trailer was well controlled; the heaters and cooler worked properly under PID control; analyzers responded correctly. The outlet gas composition under a steady state is shown in Figure 47 (explanation of the legend in Nomenclature). The grey vertical lines on Figure 47 indicate the change of bed status. The curves show the repeated cycling pattern under stable/repeatable operation.

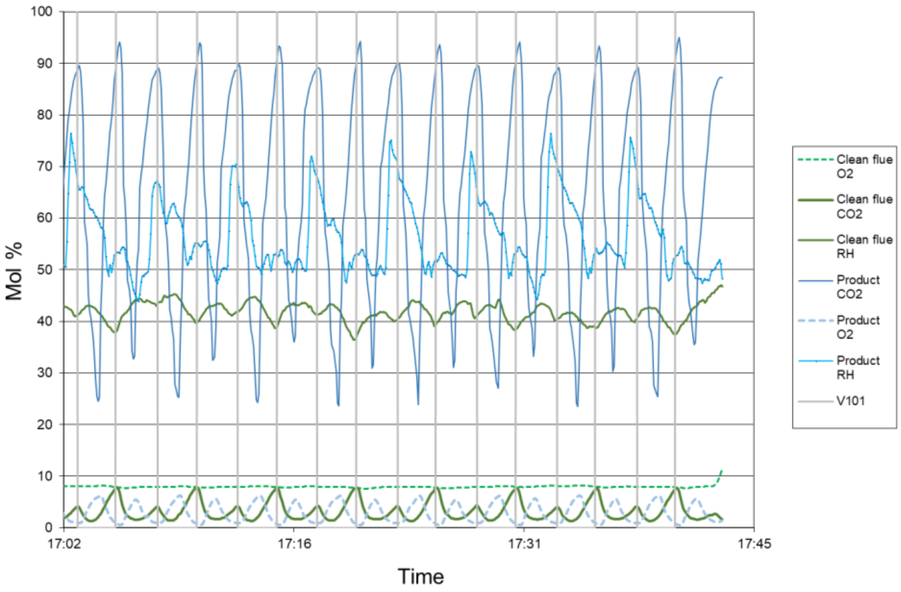


Figure 47. Outlet gas composition as a function of time with the system stabilized at a known inlet condition during 2-bed experiment on 3/18/19

It took about 4~5 cycles for the 2-bed test to reach steady state. The OPTO control program has online calculations to show the performance of the sorbent in read time. We also made a macro program in Excel for the post data processing. The CO_2 mass balance (inlet/outlet) was 91% for the steady state period in Figure 47. The cycle time and regeneration condition in the 2-bed experiments were not tuned to achieve a particular capture level. During the period shown in Figure 47, the overall capture rate was 79% with 0.58 wt% CO_2 loading for the Dynocel sorbent. Bed 2 has less sorbent because there is ~7.5 inches of Denstone inerts loaded at the bottom, resulting in a lower capture rate than bed 1. The capture rates for bed 1 and 2 were 82% and 76%, respectively. The CO_2 flow rates for the flue gas inlet and outlet and regeneration outlet are shown in Figure 48 and Figure 49.

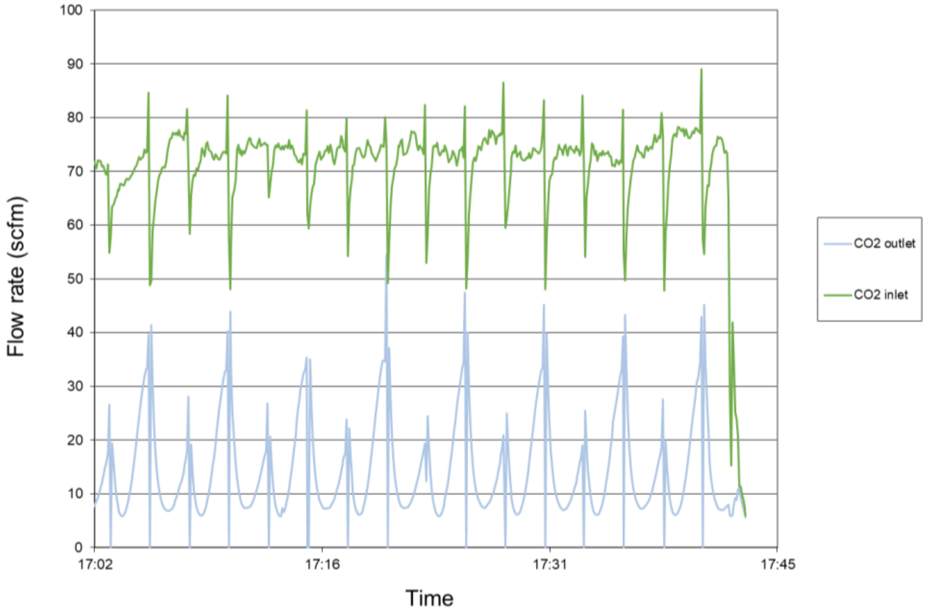


Figure 48. Flue gas inlet and outlet CO_2 flow rate on 3/18/19

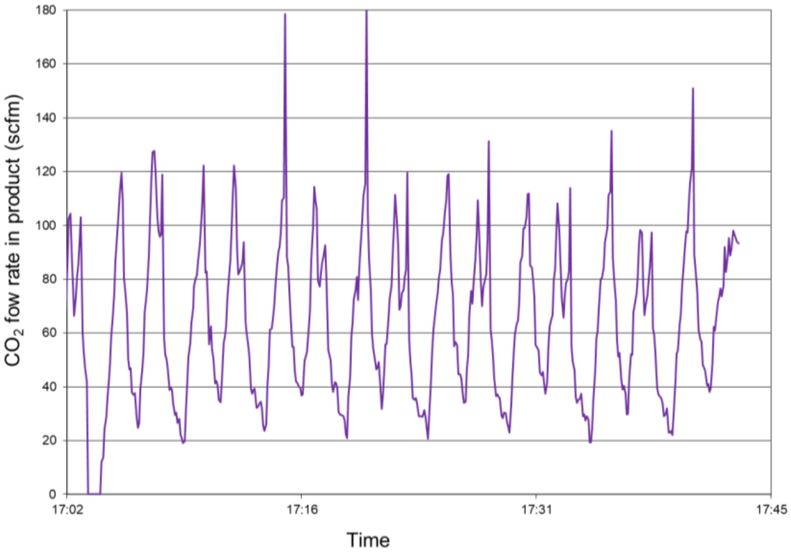


Figure 49. CO_2 flow rate at regeneration outlet on 3/18/19

Several step times were evaluated in the 2-bed test while keeping other conditions the same as 3/18/19. The capture rates are illustrated in Figure 50. As the step time is reduced from 130s, the capture rate increased slightly.

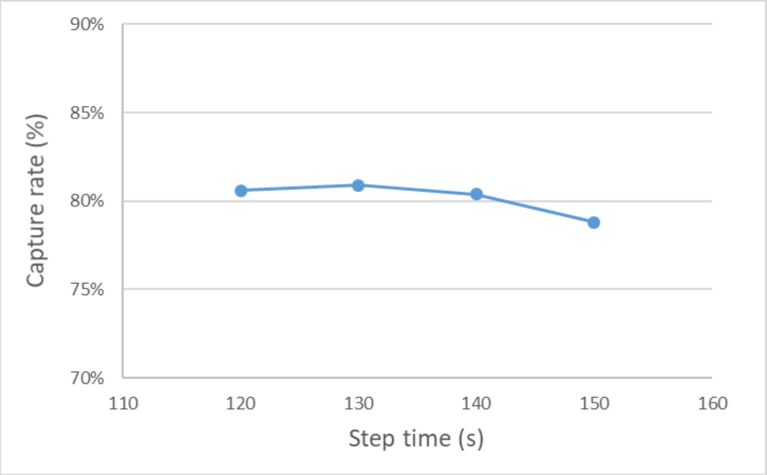


Figure 50. The effect of step time on capture rate for 2-bed test (3/21/19)

4.11.2.2 Divert Step for 2-bed Test

In our 10-bed operation, there is a divert step to increase the CO_2 purity in the product by purging the residual flue gas from the void space within the reactor at the beginning of regeneration. This gas flows out to the strip outlet line (which is recycled back to the power plant air feed in the proposed commercial application). The flow pattern for a 2-bed test with divert is shown in Figure 51. In Step 1.a, the gas from the regeneration went to the strip outlet rather than going into the product, because of the low CO_2% in that period. This step is called divert.

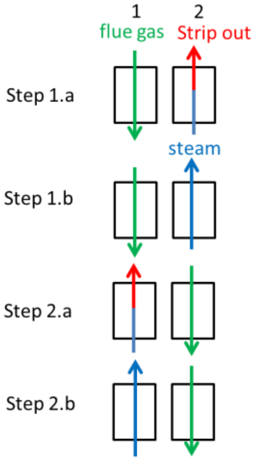
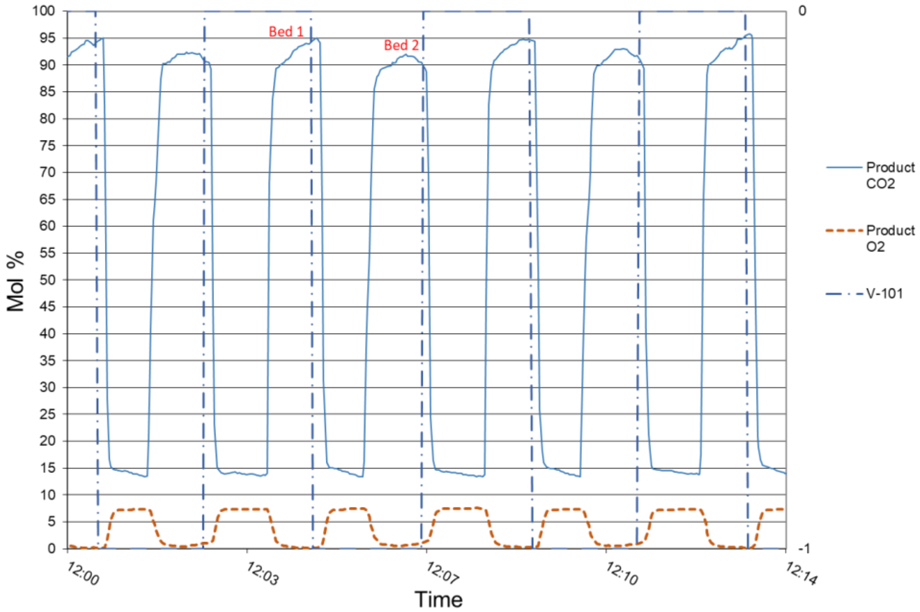
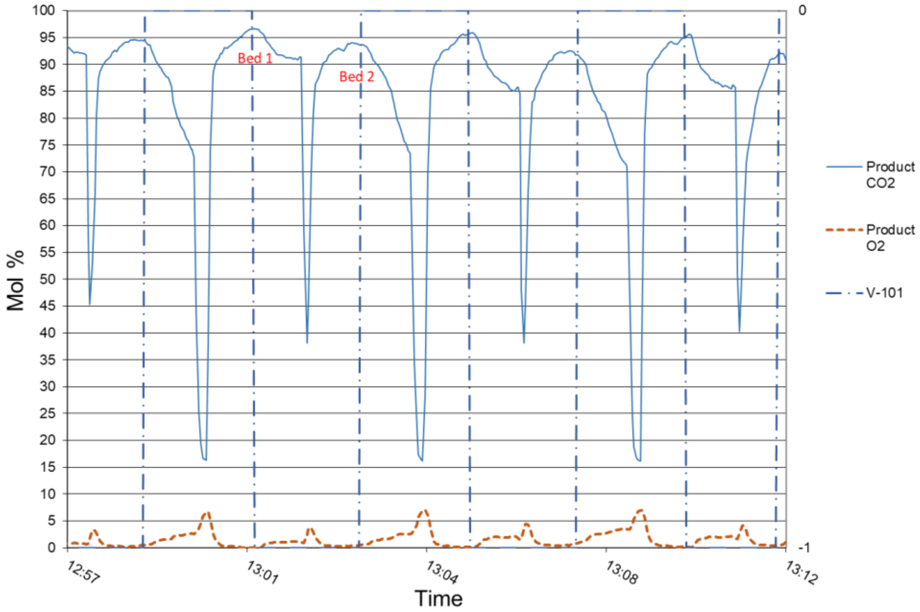


Figure 51. 2-bed operation with divert step (Step 1.a & 2.a)

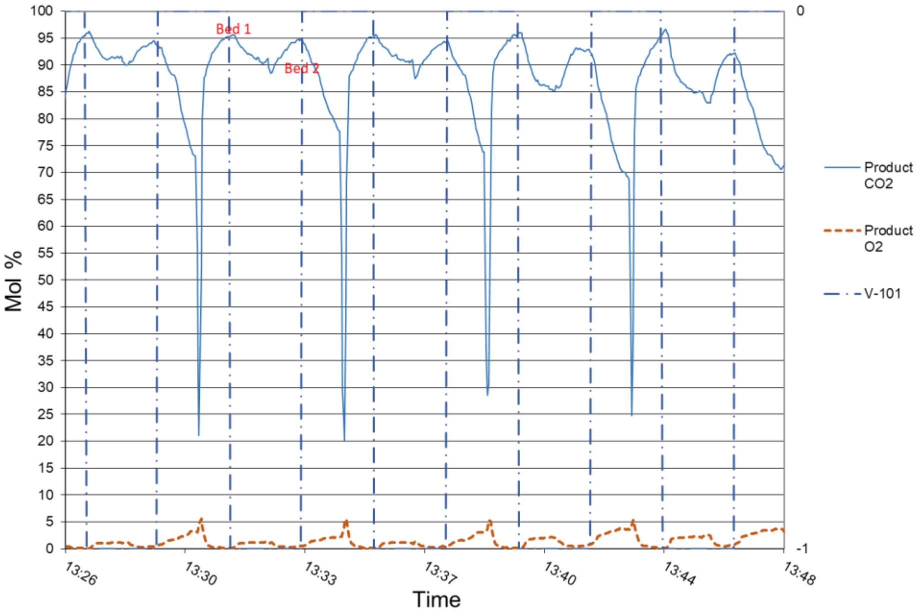
We ran the test for beds 1 and 2 without and with divert (50 s, 60 s, 70 s and 80 s) and results were shown in Figure 52A-E. The total step time was 130s. The CO_2% in the product steam is labeled Product CO2 in the legend. Without divert, there is a large drop in the CO_2% out during the regen step. Adding the divert step, the dropout was shortened, so the overall CO_2 purity in the product was improved. This can also be seen in the decrease in the O_2% in the product steam (Product O2). The impurities in the product include O_2 and N_2. Low O_2% is a confirmation of high CO_2 purity. The divert step worked as expected. In these tests, 70s divert case had the highest CO_2 purity. Diverting for 80s is too long and some high concentration CO_2 was lost to the strip outlet.



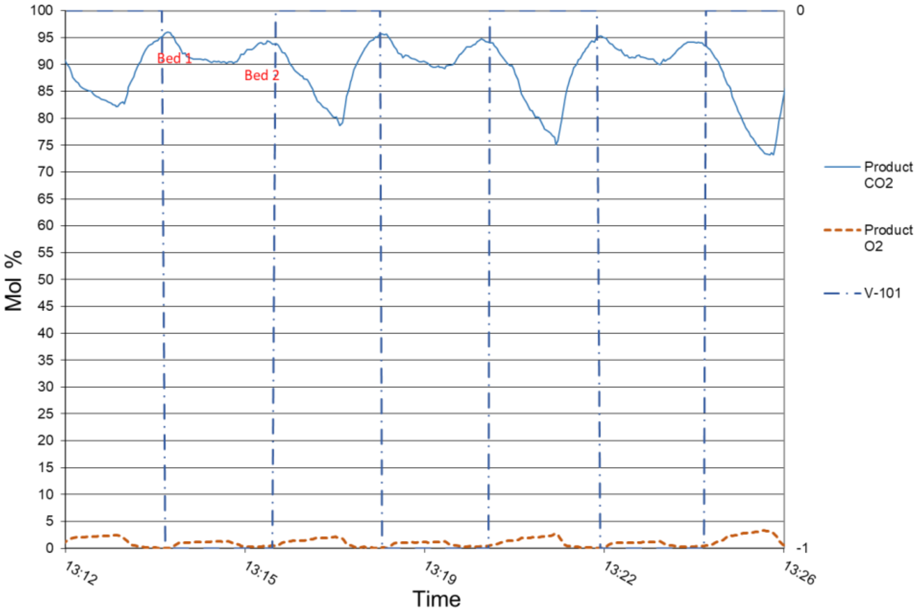
A. No divert



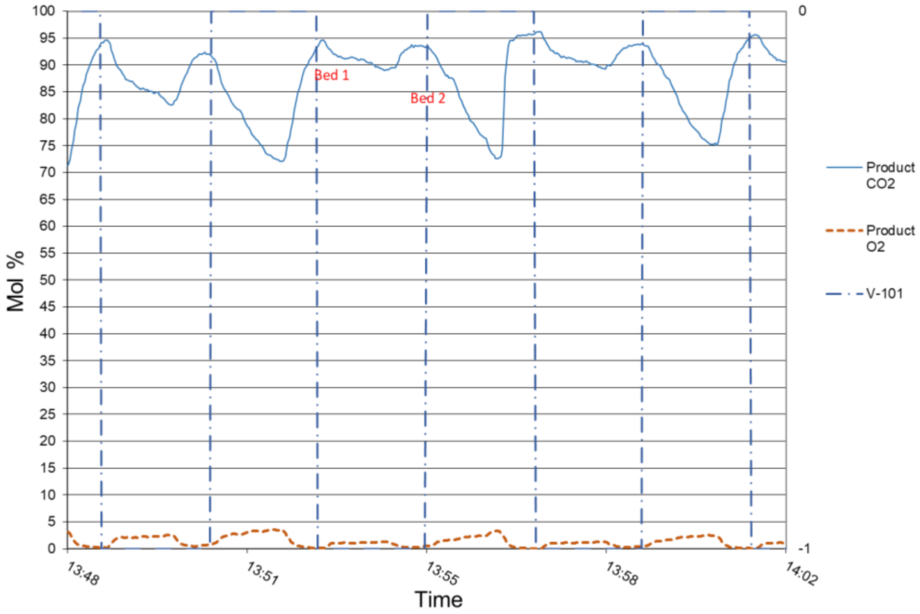
B. 50s divert



C. 60s divert



D. 70s divert



E. 80s divert

Figure 52. 2-bed divert test (4/20/19)

4.11.2.3 3-bed Test with Strip Step

Our optimized flow pattern has several additional features to maximize performance. We tested these featured one at a time to evaluate their operation and demonstrate their benefit. These tests were successful and showed the whole system’s functionality. These experiments were run at a higher space velocity for the adsorption step than is planned for the long term test and commercial cycles (since we are running only one bed in adsorption). Therefore, the apparent capture rate is not as high as would be seen in a full-scale test.

We first added the purge transition step (strip step) into a 3-bed test. The air purge step further regenerates the sorbent after the steam regeneration by "stripping" any remaining CO_2 on the sorbent with dry air. As a result, the overall sorbent CO_2 loading increases. In a commercial system the outlet stream from strip step will mix with combustion air to feed the boiler. This operation worked well. The strip step further regenerated the sorbent, so the performance improved as shown in Table 19; the A-Capture (refer to Nomenclature) rate increased from 74% to 89%. In these tests, the step time, total flue gas flow rate and steam flow rate were 130s, 683 scfm and 340 scfm, respectively. For the 3-bed case, the flow rate of the strip air was 18% of that for the flue gas, or 123 scfm.

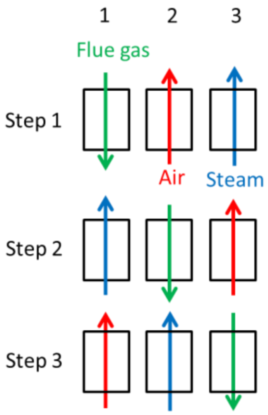


Figure 53. 3-bed test with strip

Table 19. 2-bed and 3-bed performance comparison with 0.3MW flue gas

Date	Operation	CO_2 loading, wt%	H_2O loading, wt%	A-Capture rate, %
5/1/19	2-bed (1,2)	0.48%	1.11%	74%
5/3/19	3-bed (1,2,3)	0.57%	0.98%	89%

Two sets of 3-bed tests were run on May 24, 2019 to benchmark the performance of the six beds involved and the results are shown in Table 20. Bed 6 had the highest capture rate.

Table 20. Individual bed performance from 3-bed test on 5/24/19 0.3MW flue gas

Bed	Bed Temp, °F	A-Capture rate, %
1 (Dynocel)	297	87%
2 (Dynocel)	297	73%
3	310	85%
4	327	87%
6	312	93%
9	313	91%

4.11.2.4 4-bed Test with Steam Saver (SS) Step

In our optimized flow pattern, we have a critical steam saver step to reduce the overall steam consumption. The steam saver step routes the wet purge strip outlet (that contains steam and CO_2) to the bed that just completed the adsorption cycle to push out inert void gas (e.g. N_2, O_2. etc) before steam is brought in for actual regeneration. This increased steam efficiency by moving steam from the wettest bed on the cycle to the driest and increases regeneration purity by purging the inert diluents. At least 4 beds are needed to test the functionality of the steam saver operation. We ran the 4-bed test as shown in Figure 54. Beds 1, 2, 3 and 4 were used first and there was no issue. In addition, a steam saver route was tested that included transfer piping bridging the two sorbent trailers. This was accomplished using beds 1, 2, 3, (trailer 1) and 9 (trailer 2). The pressure drop and heat tracing in the cross-over steam saver line were manageable.

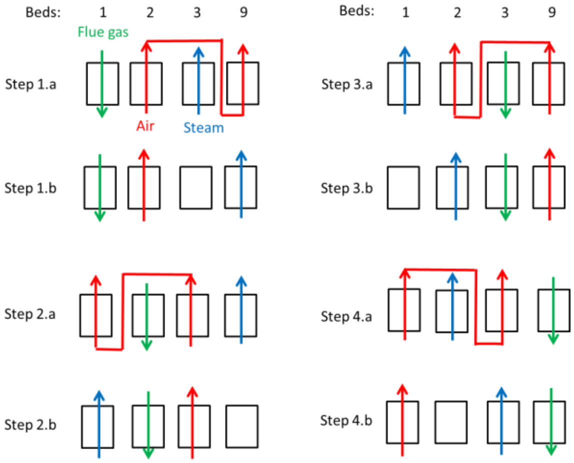


Figure 54. 4-bed test with steam saver

For the tests mentioned in Table 21, the step time, flue gas flow rate, steam flow rate and strip air flow rate were 130s, 683 scfm, 360 scfm and 123 scfm, respectively. The H_2O loading was calculated by the difference of steam going in and out of the reactor in the regeneration step. Adding steam saver step reduced the amount of H_2O the sorbent adsorbs from regeneration steam, so the H_2O loading was reduced. With the steam saver step operation, the regeneration steam inlet flow rate was reduced by 16% from 360 scfm to 304 scfm with a negligible effect on the A-Capture rate.

Table 21. 3-bed and 4-bed performance comparison with 0.3MW flue gas

Date	Test	A-Capture rate, %	CO_2 loading, wt%	H_2O loading, wt%
5/13/19	3-bed strip	87.8%	0.59%	0.94%
5/13/19	SS 20s	88.4%	0.58%	0.86%
5/13/19	SS 22s (304 scfm steam)	86.1%	0.57%	0.72%
5/13/19	SS 30s	87.3%	0.58%	0.84%

4.11.2.5 Overnight Operation

The skid was run in 2-bed mode overnight without an operator on-site on May 24, 2019 for the first time. The operation was stable. A representative "snap shot" of the data is show in Figure 55. The step time, total flue gas flow rate and steam flow rate were 130s, 672 scfm and 355 scfm, respectively.

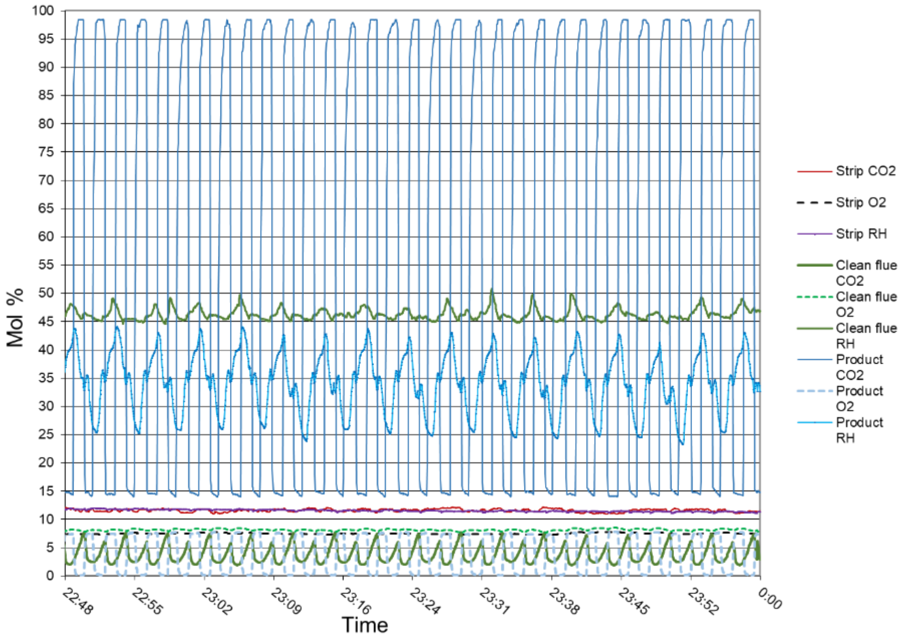


Figure 55. Representative concentration data from the overnight run on 5/24/19

The CO_2% in the inlet flue gas changes over a 24-hour period as shown in Figure 56. In the daytime, the flue gas normally has a higher CO_2% than it does in the night. This pattern was consistent and repeatable. In the post data processing, the feed CO_2% provided directly from NCCC was used for the performance calculations.

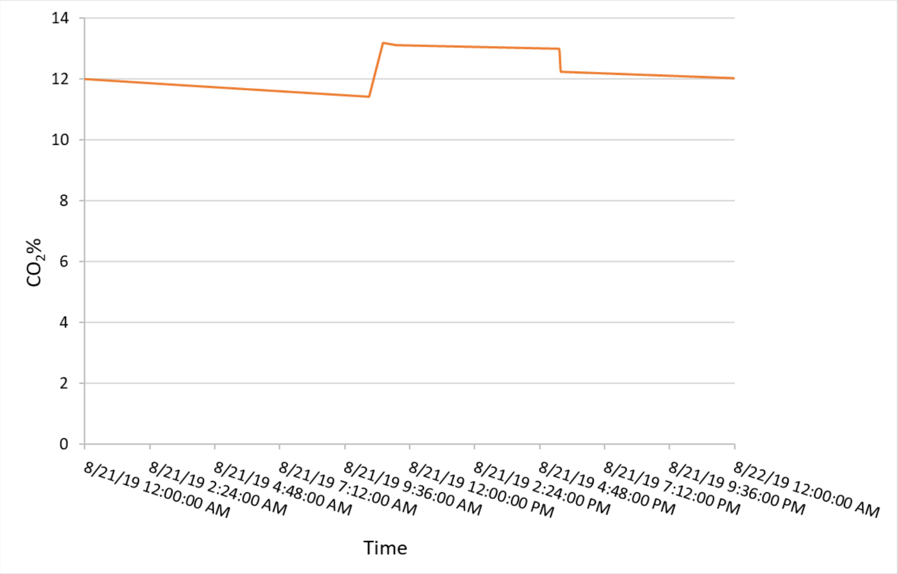


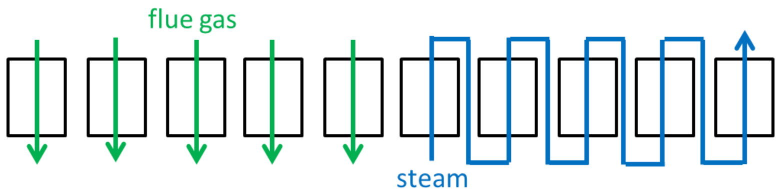
Figure 56. The CO_2% in the flue gas entering our unit for the whole day of 8/21/19

4.11.3 Benefit of Strip and Steam Saver Steps

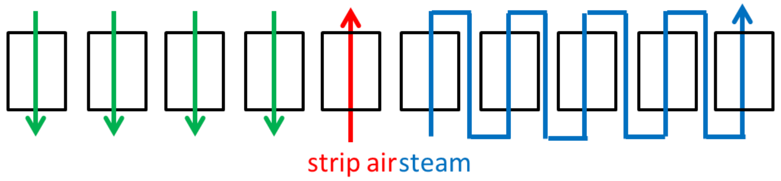
The 5+5 flow pattern was run as part of our staged start-up process since it is a simple cycle. TDA's optimized flow pattern has additional transition and regeneration steps. To demonstrate the advantage of the strip and steam saver (SS) steps, we ran excursions from the basic 5+5 mode by adding one step at a time. The three flow patterns are shown in Figure 57. The flue gas, steam and strip air (if involved) flow rates were 1085 scfm, 586 scfm and 265 scfm, respectively. The total step time is 70s. The A-Capture was used as an indicator to show the difference. Adding a strip step, the A-Capture increased about 30 percentage points. Applying the additional steam saver step gave another 10 percentage points increase in the capture. The results clearly showed the advantage of strip and SS steps of the flow pattern optimized in the bench-scale unit.

Table 22. Results of the tests showing the advantage of strip and steam saver. The flue gas, steam and strip air (if involved) flow rates were 1085 scfm, 586 scfm and 265 scfm, respectively. The total step time is 70s.

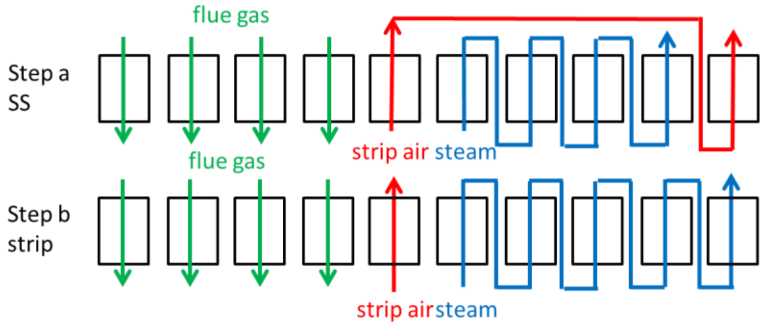
Date	Running mode	A-Capture rate, %	CO_2 loading, wt%
8/17/19	5+5	53.8%	0.32%
8/17/19	Strip only	82.4%	0.48%
8/17/19	Strip + SS 20s	92.2%	0.53%



A. 5+5



B. Strip only

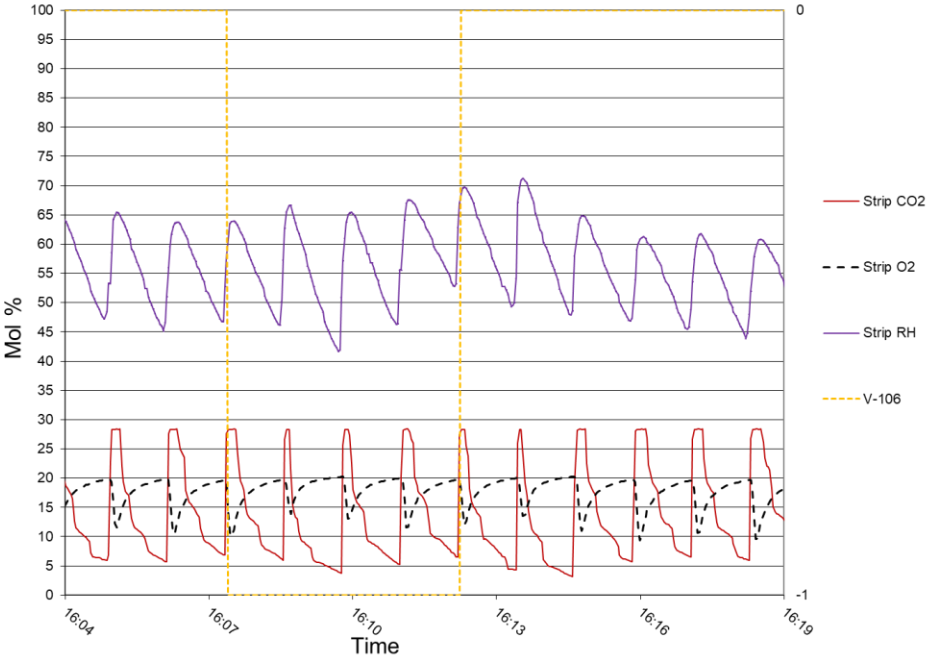


C. Strip + steam saver (SS) 20s

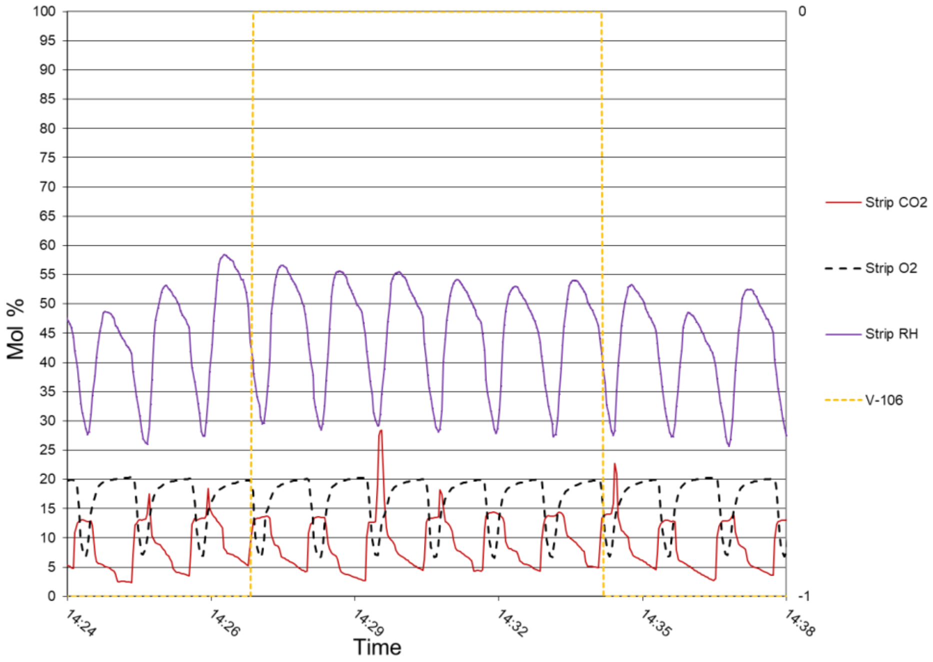
Figure 57. Flow patterns mentioned in Table 22

After the regeneration step, the beds run the strip step, where the purge gas further removed CO_2 from the sorbent bed. This step also increases steam efficiency by transferring steam from the last bed on regeneration to the next bed to start regeneration. This transfer steam was lost in the strip effluent in the Mode B process shown in Figure 57.

Then, we implemented the SS step to transfer steam from a reactor just finished regeneration (SS supplying bed) to a reactor just finished adsorption (SS receiving bed). It did this efficiently, as shown by the decrease in H_2O% in strip outlet (Figure 58). After comparing the component concentration from strip outlet for tests with and without SS, it was clear that CO_2 was recaptured by the SS receiving bed. Without SS, CO_2% in the strip outlet was over 15% in the beginning of strip step. Applying SS, CO_2% in the strip stream out dropped. Recapturing CO_2 increased the sorbent loading, leading to higher capture. When tuning the SS step, the duration can be increased as long as the peak in CO_2% out doesn't spike (breakthrough). This maximizes the recapture. The breakthrough peak can be seen in Figure 58 (red line).



A. Without SS



B. With SS

Figure 58. Component concentrations at strip outlet for cases with and without SS step (8/17/19) The flue gas, steam and strip air flow rates were 1085 scfm, 586 scfm and 265 scfm, respectively. The total step time is 70s.

4.11.4 Achieving 95+% Purity by Tuning the Divert Step Time

Since the CO_2% in the regen outlet is low in the beginning of the regeneration step, the divert step is designed to direct this portion of the regen effluent into the strip outlet (Figure 59). The purity in the regen outlet is increased.

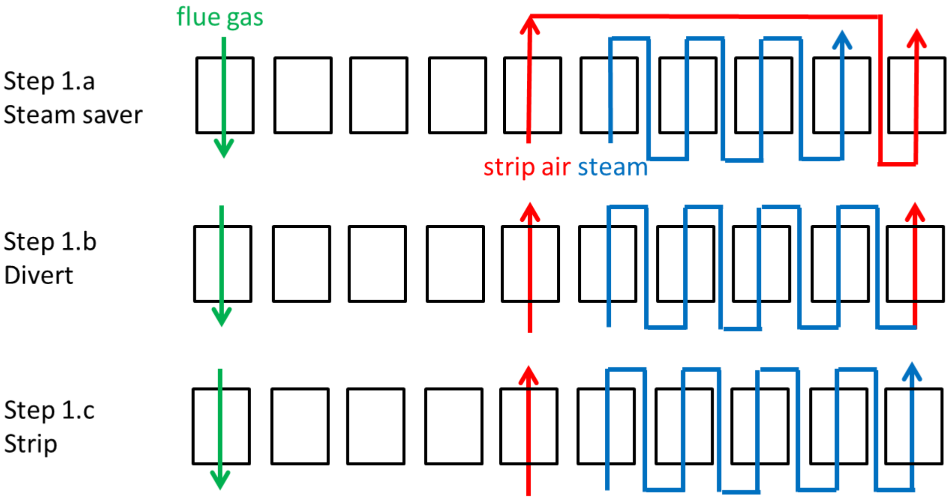
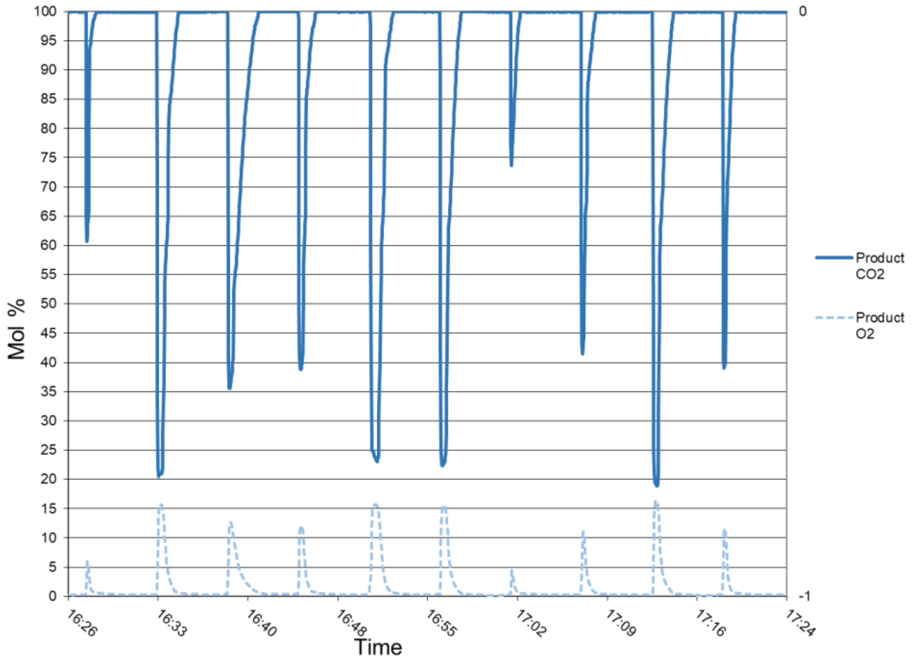
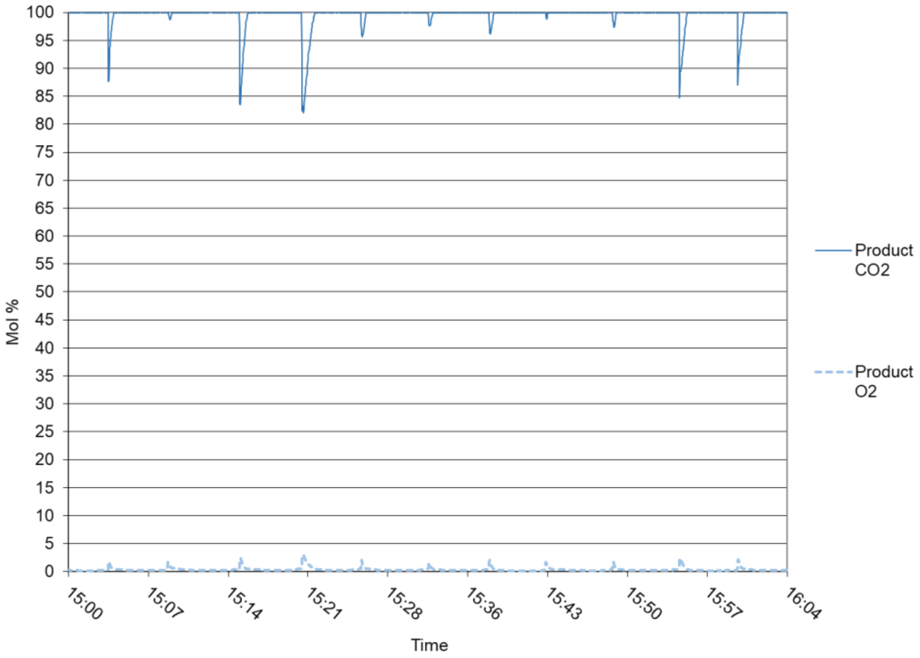


Figure 59. Flow pattern for 1+4 case with divert

In Figure 60, the “Product CO2” is the dry CO_2% in the product stream (refer to Nomenclature at end). The flue gas, steam and strip air flow rates were 273 scfm, 125 scfm and 66 scfm, respectively. The total step time was 340 s. For the short divert case, there were many deep dips on the product CO_2% curve, which dragged the overall product purity down. If the divert time was extended (140 s), a high purity was achieved (shown as in Figure 60.B. The dips in CO_2 concentration were much shallower than the short divert case (120 s). The peaks on the O_2% curve were lower as well. The CO_2 purity corresponding to the case shown in Figure 60.B was 99.4%. Thus, we can tune the divert time to reach 95% purity.



A. Short diverts (93.9% purity)



B. Long diverts (99.4% purity)

Figure 60. The effect of divert on product purity (8/21-22/19)

4.11.5 Evaluation of Individual Bed Performance: 1+4 Test

It was apparent that the sorbent in each bed performs differently even as we ran several beds together in adsorption in parallel. Because of the heterogeneity in the sorbent processing and the fact that some beds have a commercial or modified commercial alkalized alumina sorbent, we wanted a way to measure directly the performance of each bed. To do this, TDA set up the pilot unit to run in "1+4" mode by having one reactor under adsorption in a single full step. Thus, the reactors can be characterized individually. All the featured process steps were included in the 1+4 mode. Compared to a normal 10-bed operation, 3 reactors were in isolated mode, as illustrated in Figure 61. In 1+4 mode, the flue gas, steam and strip air flow rates were reduced to ¼ of the 0.5 MW case for 10-bed operation so that we maintain the same adsorption space velocity. The goal was to find the economical condition to reach 90% R-Capture (Refer to Nomenclature section), which is calculated as CO_2 in regen outlet/(CO_2 in green flue gas + CO_2 in regen outlet), and 95% product purity. Since the performance of Bed 10 was the best, all the results reported for 1+4 mode are for Bed 10.

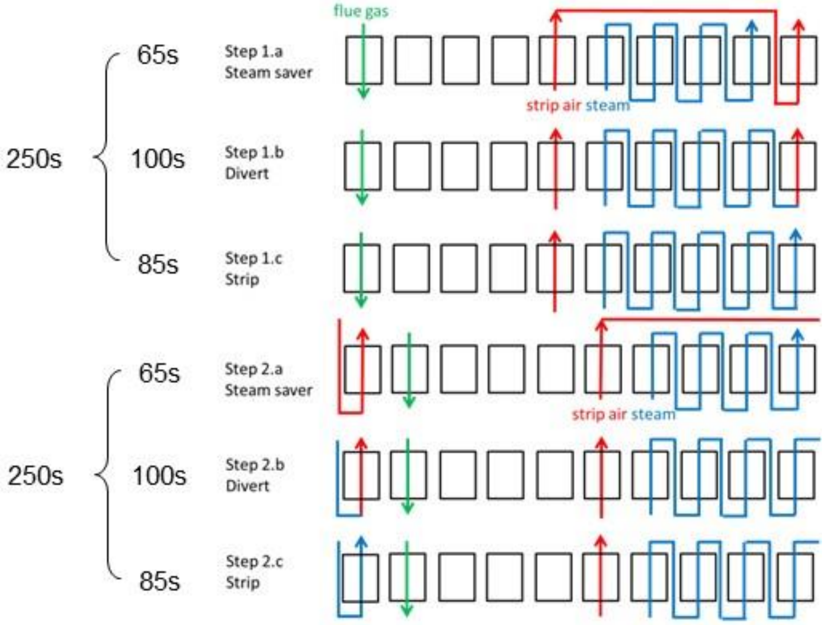


Figure 61. Flow pattern of 1+4 mode

Table 23. 1+4 Test result reaching 90% R-Capture and 95% product purity (coal derived flue gas) The flue gas, steam and strip air flow rates were 278 scfm, 148 scfm and 70 scfm, respectively.

Date	Total step, s	Steam save, s	Divert, s	Purity %	R Capture %
8/26/19	250	65	100	96.7%	90.5%

4.11.6 Comparison of Individual Sorbent Bed Performance

We evaluated how the different sorbent beds were holding up over just after we reached 1000 hours of shakedown and operation time. The stability of the sorbent looked adequate. We have determined, however, that the reprocessed sorbent, although immensely better than when it was first manufactured, is still compromised compared to the small scale batch of sorbent made by Porocel. In fact, the commercial alkalized sorbent (Chlorocel 901) we purchased is showing the best performance in our process. We know from earlier bench-scale testing however, that the small scale batch of sorbent made by Porocel with the TDA/EMRE recipe (Batch #1) was better than the Chlorocel 901. If the pilot unit sorbent were as good as the small scale Batch #1, we would have higher capture for the same steam usage than what is being measured in the pilot unit.

Over the testing period of just over 1000 hours of operation, we tracked the performance of the individual beds under 1+4 mode. The flow rates for flue gas, steam, and strip air were 280 scfm, 106 scfm and 68 scfm, respectively. The step time was 340s with SS of 50s. No divert was included. This cycle was run initially and then repeated to for comparison. It is not optimized to achieve the lowest steam usage, but it is a reasonable cycle.

Table 24. Sorbent Performance of each bed under 1+4 mode over 1000 hr operation time

	A-Capture rate for each bed									
Test hrs	1	2	3	4	5	6	7	8	9	10
	Dynocel	Dynocel	Re-processed sorbent	Re-processed sorbent	Re-processed sorbent	Re-processed sorbent	Re-processed sorbent	Re-processed sorbent	Re-processed sorbent	Chlorocel
235	85.1%	74.1%	84.5%	81.6%	82.5%	89.4%	84.7%	59.0%	81.9%	90.5%
337	82.4%	73.0%	81.2%	76.6%	77.5%	85.0%	75.4%	52.2%	83.7%	86.4%
725	83.8%	77.3%	79.4%	76.8%	75.0%	82.1%	82.7%	67.4%	78.3%	86.5%
1063	86.0%	82.4%	82.9%	81.0%	81.1%	83.0%	83.2%	72.2%	78.5%	85.9%

The results are shown in Table 24 and Figure 62. Beds 1, 6 and 10 have the highest performance among the ten beds. The performance of these beds was stable over the test period. The A-Capture rates for the best beds dropped less than 5% from hour 235 to hour 1063.

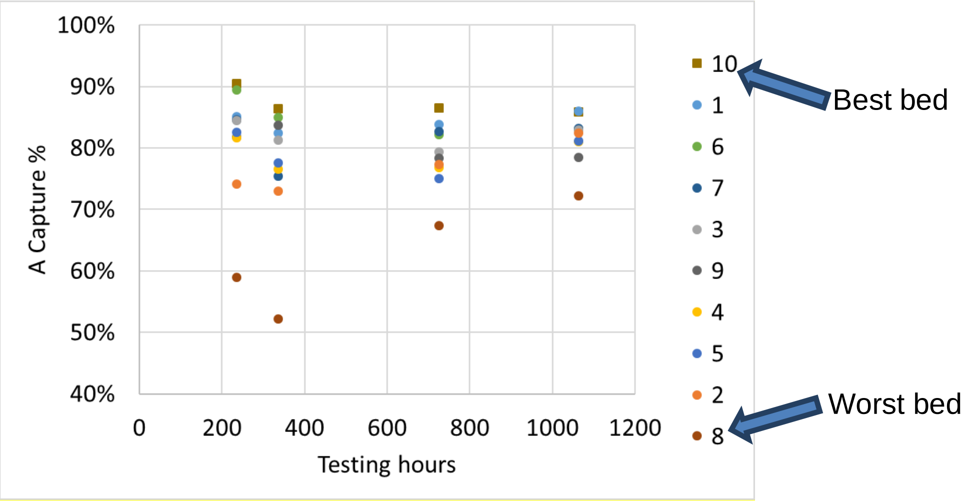


Figure 62. Sorbent Performance of each bed under 1+4 mode

Figure 63 showed clearly the difference on A-Capture rate among the 10 beds. Even the beds loaded with reprocessed sorbent had a large variation on the performance. The performance of the sorbent itself dominates the overall system performance. Underperforming beds, such as bed 8, reduce the overall capture rate for the 10-bed operation.

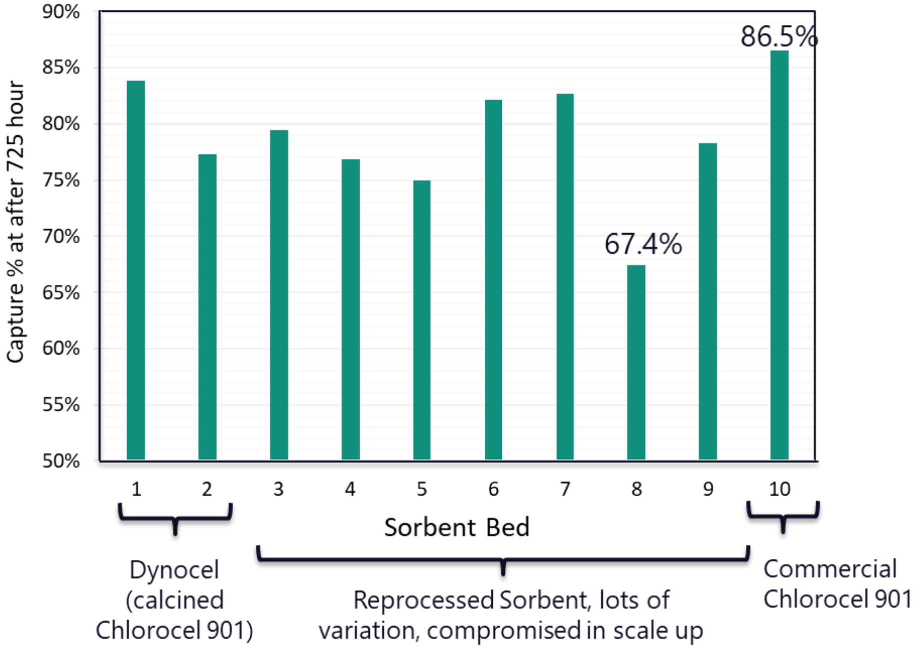


Figure 63. A-Capture rate for each bed after 725 running hours

Further, it is unexpected that Chlorocel 901 outperformed the reprocessed sorbent. Both Chlorocel 901 and a small batch of TDA sorbent scaled up at Porocel (Porocel Batch #1) were tested in TDA's bench-scale unit previously. The bench unit was designed to run 12 beds originally, though we later focused the test on 10-bed mode. The testing of Chlorocel and Porocel Batch #1 were performed under 6+6 mode under the same flow rates. The results are shown in Figure 64. After accumulating over 500 testing hours, Batch #1 still had decent A-Capture rate of 83% to 85%. In contrast, Chlorocel's performance dropped significantly in the first 200 hours from 86% to 76%. Even if there was no further degradation for Chlorocel 901, it would not be as good as Batch #1 produced by Porocel at 10 lb scale. If the pilot sorbent were as good as Batch #1, we should have much better results than what is being measured in the pilot unit where Chlorocel 901 is the strongest performing bed. The reprocessed sorbent is underperforming the Porocel Batch # 1.

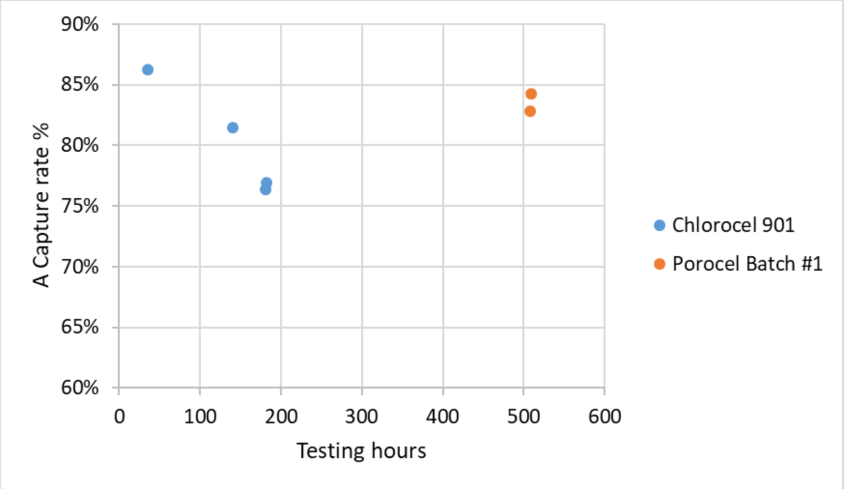


Figure 64. Bench unit 6+6 mode results for Porocel Batch #1 and Chlorocel 901

4.12 Performance Loss for Sorbent Loaded in 2018 after 3.5-month storage

The TDA team returned to NCCC in late January 2020, 3.5 months after the pilot unit was shut down on October 4, 2019. The performance of the sorbent was significantly lower than it was before the shut-down in October 2019, as shown in Table 25. The reactors were purged with air during the shut-down in 2019. Apparently, the moisture in the reactors was not fully removed, and the humidity that remained in the reactors then changed the form of the sorbent, which decreased its performance.

Table 25. Performance comparison under 5+5 flow pattern before and after 3.5-month storage

Date	Capture rate
10/4/2019	82.4%
1/29/2020	65.5%

TDA decided to replace the sorbent in the beds at NCCC due to this severe performance loss. In May 2021, all of the previous sorbent was replaced. Dynocel was loaded in beds 1-5 and Chlorocel, a commercial sorbent, was loaded in beds 6-10. Both sorbents were ~1/16" spheres. Though these two sorbents were not as good as the TDA sorbent developed in the lab, they were the best available options based on the budget and manufacturer's schedule.

As we did in 2019, the 1+4 mode (Figure 61) was run to evaluate the performance of the individual beds. This test allows a direct bed to bed comparison, since only one bed is in adsorption at a time. The inlet gas streams were 275 scfm flue gas, 150 scfm steam, and 58 scfm strip air. The results are shown in Table 26. The steam flow was increased 50% from 2019 tests to see if it would improve capture performance. Even with the additional steam, the capture was still less than in 2019. For the same steam flow rate as before (2/1/20), the capture rate was significantly lower than the data on 10/4/19. Bed 8 was the worst in 2019, and bed 10 was the best (Chlorocel-901 loaded in July 2019). In January 2020, the same trends on individual bed performance were seen. It seemed that all the beds were affected equally.

Table 26. Bed Performance (% A Capture) over time under 1+4 operation

				Dynocel		Reprocessed TDA sorbent							Chlorocel
Date	Total Hrs Operation	Flue gas scfm	Regen steam scfm	Bed 1	Bed 2	Bed 3	Bed 4	Bed 5	Bed 6	Bed 7	Bed 8	Bed 9	Bed 10
8/18/19	235	276.4	106.6	85.1	74.1	84.5	81.6	82.5	89.4	84.7	59.0	81.9	90.5
9/16/19	725	282.5	99.7	83.8	77.3	79.4	76.8	75.0	82.1	82.7	67.4	78.3	86.5
10/4/19	1063	278.5	107.3	86.0	82.4	82.9	81.0	81.1	83.0	83.2	72.2	78.5	85.9
System off/ cold													
1/27/20	1086	274.5	150.9	77.2	58.8	74.6	68.6	68.9	69.2	72.4	48.5	64.3	70.5
1/28/20	1090	239.4	151.7	82.9	64.4	80.7	75.8	75.6	77.4	80.3	53.5	70.4	77.2
1/28/20	1093	210.3	152.3	88.1	76.5	86.4	83.4	82.0	84.6	86.0	63.7	79.9	85.6
2/1/20	1101	266.6	106.2	59.3	41.8	60.2	53.5	51.9	54.5	59.8	34.9	49.6	55.1

To diagnose the compromised sorbent after 3.5-month shut-down, TDA conducted X-Ray diffraction measurements for fresh, cycled, and post-shutdown sorbents.

Figure 65 showed results of beam intensity across a 90-degree spectrum (angle of incidence of the X-Ray) for Bed 6 samples. The fresh sorbent was calcined at 550 °C and had not been exposed to steam. Thus, it had a different spectrum from the cycled sorbent. This was a TDA-developed sorbent, which is composed of base alumina plus alkali. The result for the fresh sorbent was shown in the grey line. What is notable is the difference between the sorbent cycled at TDA and sorbent cycled at NCCC and after 3.5-month shut-down. Four new peaks appeared, showing that there was a change in the composition of the material. Further, the peak shape around 65 degrees was much less intense.

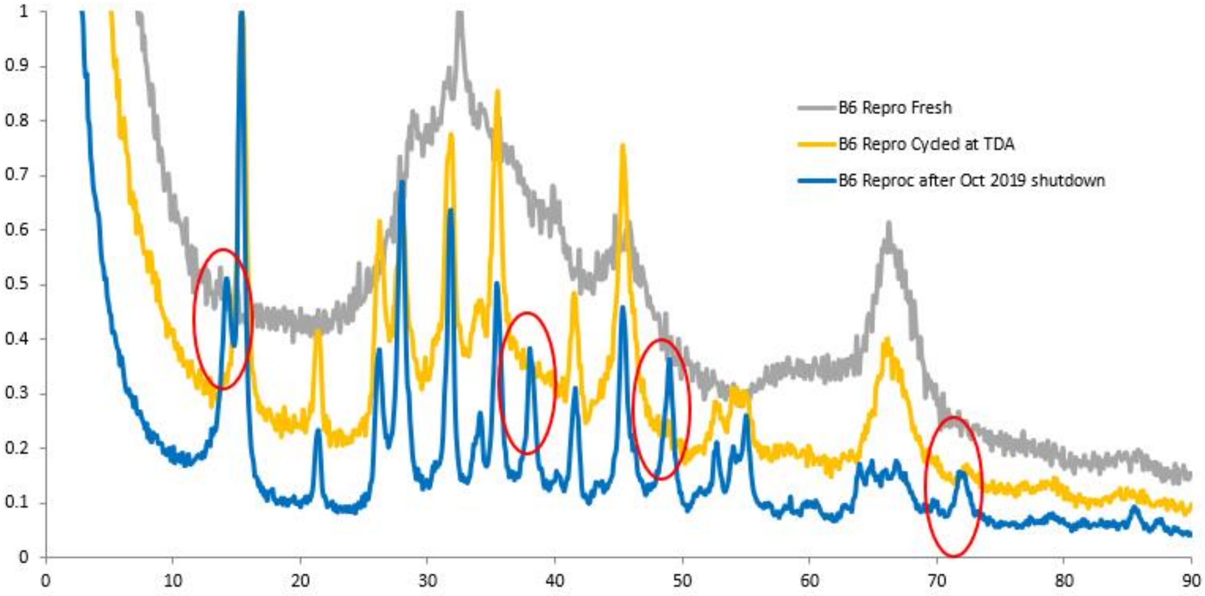


Figure 65. Bed 6 XRD plots

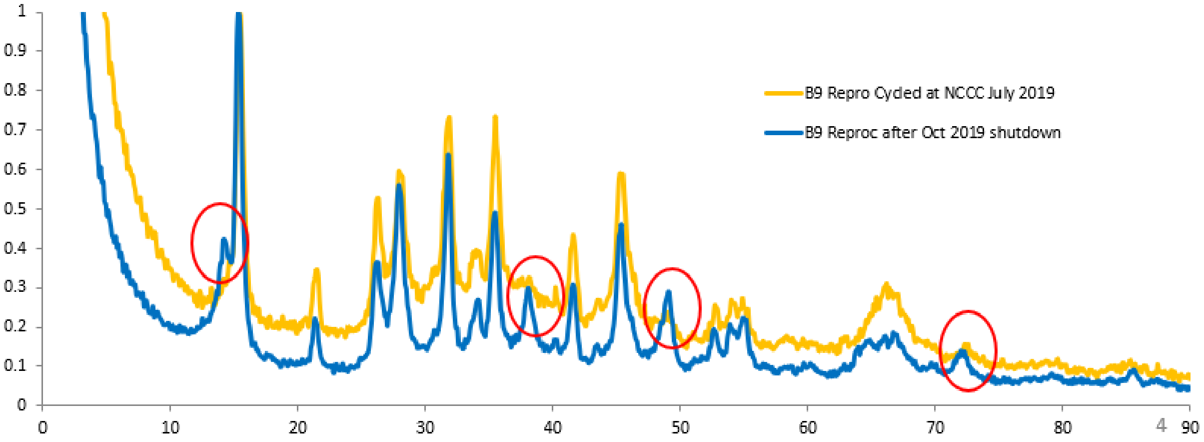


Figure 66. Bed 9 XRD plots

The XRD data for Bed 9 samples (TDA developed sorbent) are plotted in Figure 66. The same peaks as Bed 6 sorbent appeared in the post-shutdown sample. For this bed, we had previously pulled a sample at NCCC in July 2019 and we were able to run the XRD on this material taken before the Oct 2019 – Jan 2020 shutdown. This July 2019 NCCC sorbent looked very similar to the sorbent cycled at TDA; its XRD did not look like the compromised post-shutdown sorbent. Thus, it is likely that the change in composition indicated by the XRD in the post-shutdown sorbent was related to a specific degradation event and not just an effect of cycling at NCCC.

Bed 10 contained commercial Chlorocel 901 sorbent. The Bed 10 XRD result is shown in Figure 67. It had a different alumina and alkali composition, and the sorbent pellets were 2-3 mm spheres rather than 1.5 x 5 mm extrusions. Interestingly, this post shutdown sample also had the additional peaks found in the TDA formula sorbents (Beds 6 and 9). These peaks did not appear in the commercial sorbent cycled at TDA.

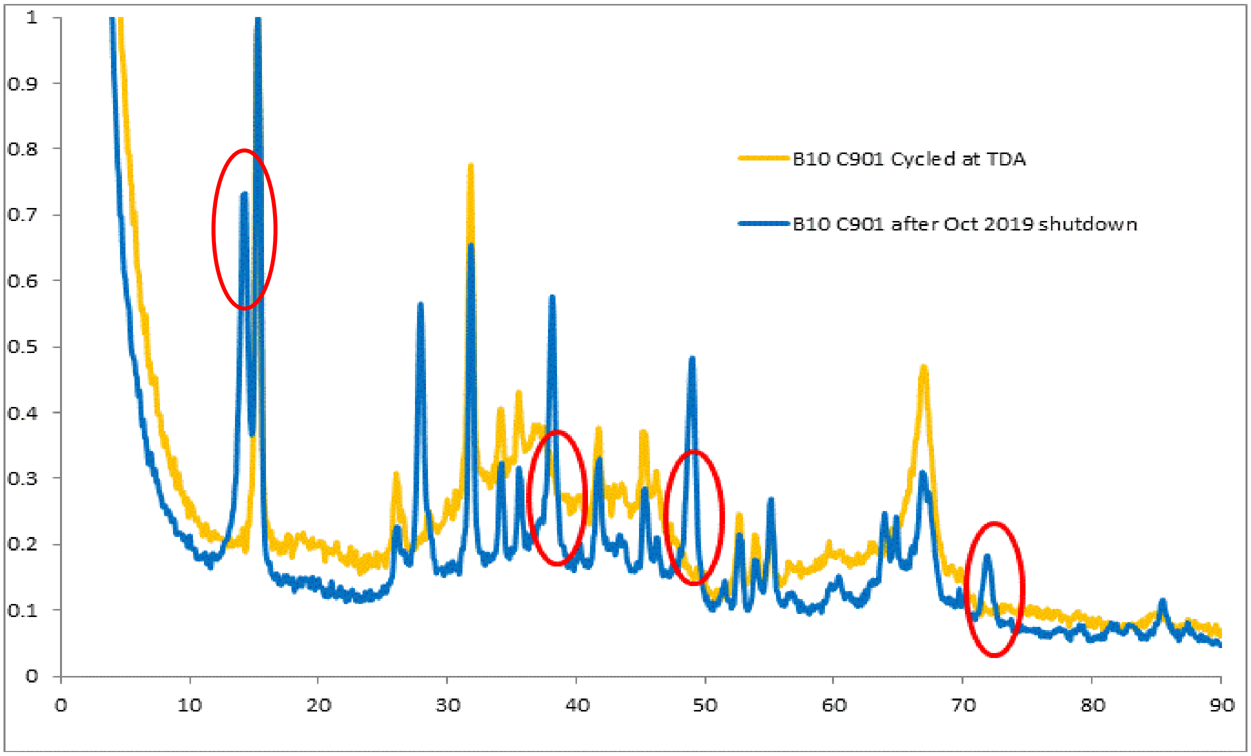


Figure 67. Bed 10 XRD plots

Analysis of the XRD results showed that phase present in the sorbent developed by TDA was Dawsonite before it was degraded significantly. After the 3.5-month shut-down, a mixture of Boehmite and Dawsonite was present. Boehmite, which is thermodynamically more stable, was formed during the long term shut-down. However, it compromised the sorbent performance. Boehmite was also formed in Chlorocel analyzed after the shut-down, which used a different alumina from the customized TDA sorbent.

4.13 Pilot Test in 2021

TDA replaced the sorbent in the beds at NCCC due to the severe performance loss. We expected the test could resume in late February 2020. We planned to replace sorbent for 5 reactors at that time. The only sorbent that could be procured quickly was commercial sorbent Chlorocel 901 from Porocel. In February 2020, eight supersacks (16,000 lbs) were purchased. One supersack was left over from July 2019 (Bed 10 replacement), and would also be used. In March 2020, NCCC was closed due to COVID-19 and our pilot test was suspended. In January 2021, TDA obtained approval from DOE to replace the sorbent in the remaining 5 reactors as well. 20,000 lbs of Dynocel was purchased in March 2021. Dynocel is produced by calcining Chlorocel at 765 °C. All of the sorbent was replaced in May 2021. Dynocel was loaded in beds 1-5 and Chlorocel was loaded in beds 6-10. Both sorbents were ~1/16" spheres. The pilot testing resumed in July 2021. We finished the parametric and long-term tests in 2021. The pilot test results are shown below.

4.13.1 Sorbent Loaded in 2021 vs. Sorbent Loaded in 2018

In the beginning, we ran the same basic 5+5 flow pattern (with the same flow rates for flue gas (1049 scfm) and steam (666 scfm) as used in 2019) was run. The performance was compared with the 5+5 case run in the beginning of the pilot tests in 2019 (Table 27). The capture rate in 2021 was higher than that from 2019. However, the previous lab data showed that the properly made TDA sorbent had better performance than Dynocel and Chlorocel. The result shown in Table 27 indicated that the reprocess we ran on the improperly manufactured sorbent in 2019 helped, but didn't fully restore the capture capacity of the sorbent designed by TDA.

Table 27. Performance comparison under 5+5 flow pattern between 2019 and 2021

Date	Sorbents in skid	Capture rate
8/13/2019	Dynocel in beds 1-2, reprocessed sorbent in beds 3-9 and Chlorocel in bed 10	83.8%
7/22/2021	Dynocel in beds 1-5 and Chlorocel in beds 6-10	87.0%

We then ran tests with the 1+4 flow mode at the same conditions (including the flow rates and step setting) to evaluate the performance of each bed. The flow rates for flue gas, steam and strip air were 275 scfm, 108 scfm and 68 scfm, respectively. The total step time was 340 s and the steam saver (SS) time was 50 s. The A capture rate results on 7/22/2021 were much higher than those on 2/1/2020, and were higher than or close to the best results in 2019. Additionally, the Chlorocel was better than the Dynocel at the beginning of the 2021 pilot test. In the first 1.5 month, we focused on tuning the unit for optimal performance of Chlorocel.

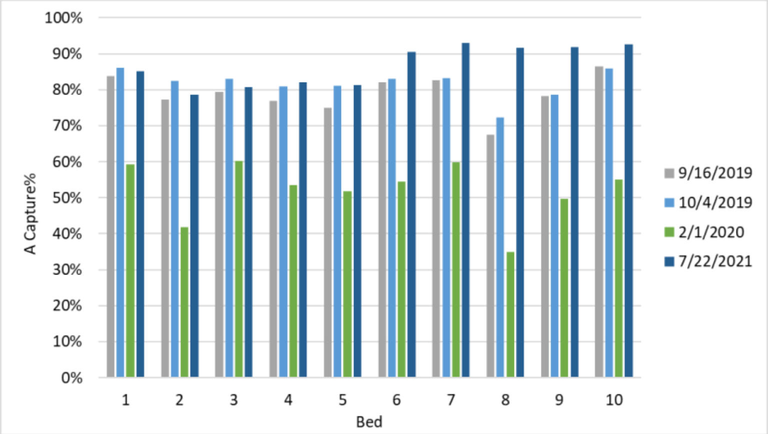
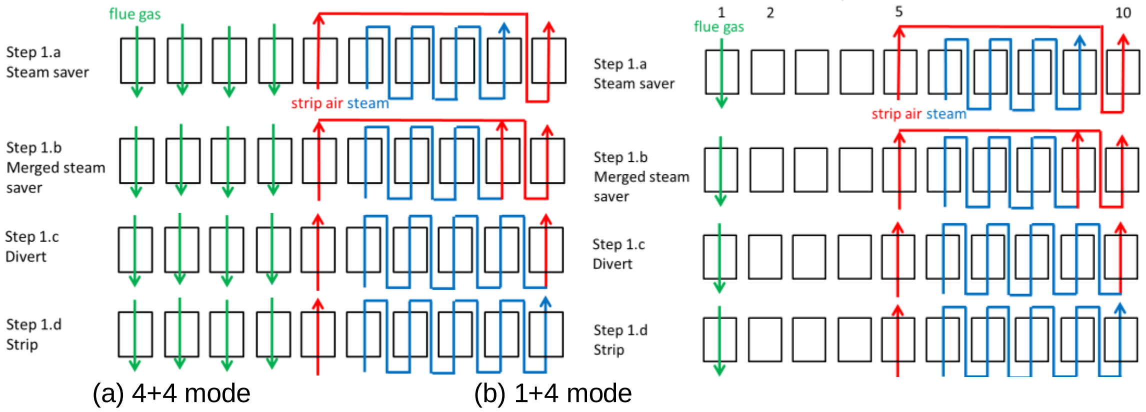


Figure 68. Performance results under 1+4 flow mode with the same conditions

4.13.2 Split Steam Saver Flow Mode

During the 2019 pilot testing, we showed that adding the merge SS step after the regular SS improved the performance. The merge SS utilizes the moisture in the regeneration outlet to hydrate the SS receiver bed in order to reduce steam usage. When we ran the test in 2019, the divert step (step 1.c) was not included. We added the divert step in 2021 testing to control the product purity as shown in Figure 69.



(a) 4+4 mode (b) 1+4 mode

Figure 69. Flow mode for split steam saver case

We reran the comparison case in 1+4 mode to confirm this improvement. The result, based on Bed 7, is shown in Table 28. On 7/27/2021, the humidity sensor on the strip outlet had issues, so only A capture is reported. The total SS time was 60 s. “20+40” is a condition meaning 20 seconds of normal SS followed by 40 seconds of merge SS. The capture rate for the split SS cases were higher than the regular SS case. When the ratio of regular SS/merge SS was 1:1, the capture rate was highest.

Table 28. Comparison between regular steam saver and split steam saver (1st data set)

Date	Total step time, s	SS setting, s	Divert time, s	Flue gas SV, 1hr	Ratio of steam/flue gas	Ratio of Strip air/flue gas	A Capture
7/27/2021	255	60	50	267	0.41	0.24	87.7%
		20+40					89.2%
		30+30					89.7%
		40+20					89.3%

After the humidity sensor on the strip outlet was fixed, a direct comparison was run for regular SS and split SS cases under 1+4 mode. The results based on the average of Beds 6-10 are shown in Table 29. The total SS time and divert time were 60 s and 45 s, respectively. Other conditions were controlled to be as close to previous tests as possible. The spilt SS case had slightly lower R capture than the regular SS case, which was caused by the slightly higher CO_2% in the flue gas. However, the product purity for the split SS case was higher. For this particular run, it was possible that the H_2O% at the end of the regeneration was not high enough to assist the regeneration of the SS receiver bed.

Table 29. Comparison between regular steam saver and split steam saver (2nd data set)

Date	Total step time	Steam saver time	Flue gas SV, 1hr	Ratio of steam /flue gas	Ratio of Strip air/flue gas	CO_2 % (wet) in flue gas	A capture	R capture	Strip CO_2 in total CO_2	Purity
8/3/2021	305	60	317	0.424	0.257	11.7 %	91.9%	90.4%	15.4%	91.6%
		30+30	317	0.426	0.254	12.0 %	91.1%	89.3%	16.4%	96.2%

In the 2021 pilot test, split SS was normally applied when searching for lowest steam/CO_2 captured ratio with 90% capture and 95% purity unless the data showed split SS was not better than the regular SS.

4.13.3 Experiments for Coal Flue Gas

The results from the tests run under the coal flue gas were reported in this section. The wet CO_2% from Unit 5 ranged from 11.1% to 12.3%. In DOE's baseline coal fired plant (the case used for process comparisons), the flue gas contains 13.5% CO_2. With strip air recycle included, the CO_2% at TDA capture unit inlet is designed to be 15.5%. We would expect our system to work better at the higher CO_2% condition (15.5%) than at the flue gas condition present at NCCC.

4.13.3.1 Effect of Total Step Time on Performance

Generally, when the steam flow rate is fixed, there should be an optimal step time setting that produces the highest capture rate. The typical influence of step time on capture rate was shown in Figure 70. To determine this, we ran the 1+4 flow mode shown in Figure 69. The flow rates for flue gas, steam and strip air were 275 scfm, 111 scfm and 66 scfm, respectively. The total step time was varied while the SS time was 60 s for all cases. The R capture (Refer to Nomenclature section), which is calculated as CO_2 in regen outlet/(CO_2 in green flue gas + CO_2 in regen outlet), was shown for Bed 7. If the total step time is too short, the sorbent doesn't have enough steam dosage in regeneration, resulting in less regeneration and reducing the CO_2 capture rate. On the other hand, if the total step time is too long, the sorbent has a higher extent of breakthrough and CO_2% in the flue gas outlet is higher. As a result, the capture rate is compromised. Thus, there is an optimal step time that maximize the capture rate. For the cases shown in Figure 70, the optimal total step time was ~305 s. In the pilot test, when the steam flow rate was changed, we normally ran a few cases with various step times to identify the optimum. We started from a low steam flow rate. If 90% R capture could not be achieved by adjusting the total step time, the steam flow rate was raised.

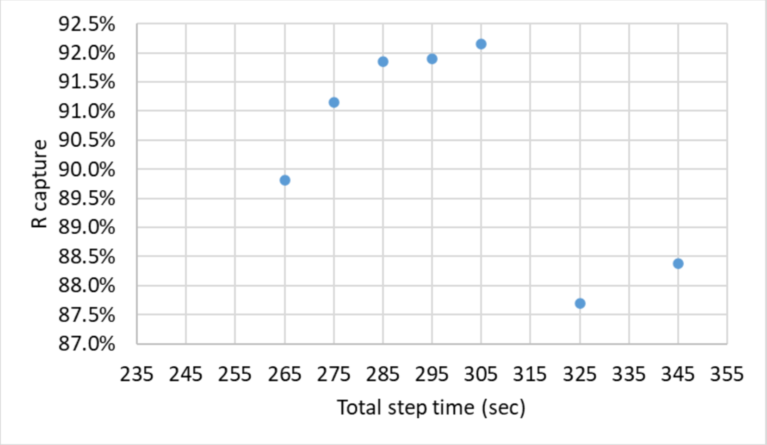


Figure 70. The effect of total step time on capture rate

4.13.3.2 Effect of Flue Gas Space Velocity on Performance

We studied the influence of flue gas space velocity (SV) on the performance. Running in the 1+4 mode allowed us to vary the flue gas SV on one reactor over a wide range. The flow rate of flue gas was gradually increased up to 151% of the designed value. The steam and strip air flow rates were increased proportionally; strip air flow rate was 25% of that of the flue gas. The step time was adjusted to achieve the highest R capture. The results based on the average of Beds 6-10 are shown in Table 30. The CO_2% in the feed varied from day to day, and was recorded. If possible, the direct comparison tests were run on the same afternoon in order to have the same flue gas input conditions. As the flue gas SV increases, the capture rate decreases. However, when the SV is 24% higher than the designed value, the capture rate was still over 90%. Thus, the reactor size could be reduced and we would still be able to process the same amount of flue gas, which would save capital costs.

Table 30. Effect of flue gas space velocity on the performance

Date	Flue gas SV, 1/hr	Total step time, s	SS setting, s	Divert, s	Compared to the design	CO_2% (wet) in flue gas	Strip CO_2 in total CO_2	R capture	Purity
7/28/2021	270	305	35+35	45	1.01	11.5	22.0%	92.0%	95.2%
8/3/2021	318	305	30+30	45	1.19	11.8	16.9%	90.8%	96.6%
8/7/2021	332	280	30+30	45	1.24	11.7	16.7%	90.6%	96.1%
8/3/2021	404	280	20+20	30	1.51	11.8	12.6%	87.3%	94.9%

4.13.3.3 Effect of Strip Air Space Velocity on Performance

Further, we explored whether the strip air flow rate can be reduced. In these tests, the flow rates of flue gas and steam were held the same, and the strip air flow rate was reduced. The total step time was kept at 305 s. The SV for the flue gas was set at 318 1/hr. As illustrated in Table 31, reducing the strip air/flue gas to 0.18 leads to a capture rate was still acceptable. Strip air is used to further regenerate the sorbent after steam regeneration. It is also the driving force to transfer the moisture in the SS step. When we reduce the strip air flow, the sorbent is less regenerated and its working adsorption capacity is reduced. However, the fraction of strip CO_2 out of the total CO_2 is reduced as well, which helps the steam/CO_2 captured ratio. Initially, we designed the ratio of strip air to flue gas as 0.25. With this ratio reduced, the blower power required to drive the strip air flow is lowered.

Table 31. Effect of strip air space velocity on the performance

Date	Flue gas SV, 1/hr	SS setting, s	Divert, s	Ratio of strip air/flue gas	CO_2% (wet) in flue gas	Steam/CO_2 captured	Strip CO_2 in total CO_2	R capture	Purity
8/6/2021	318	30+30	45	0.25 (design basis)	12.0	4.60	16.9%	90.7%	96.3%
		38+38	45	0.18	12.0	4.45	13.7%	89.6%	98.1%
		50+50	45	0.13	12.0	4.50	13.6%	88.6%	99.1%

4.13.4 Experiments for NGCC Flue Gas

In August 2021, TDA diluted the coal derived flue gas to simulate NGCC derived flue gas. Then, beginning 8/30/2021, we used the flue gas and steam provided by the NCCC NG boiler system. The H_2O% in the NG flue gas was in the range of 5.7-8.2%, which is lower than the actual NG derived flue gas.

The optimization of the operating parameters under the NGCC flue gas was run with the 4+4 flow mode shown in Figure 69 (a). The performance data is reported in Table 32. The flue gas SV was set at 268 1/hr due to the flow limit for 10-bed operation. For 8/12/2021 case, the steam flow rate was 274 scfm, and the strip air was only 12% of the flue gas flow. The R capture was almost 90% and the purity was over 95%.

Table 32. Performance data for the optimized NGCC case

Date	Flue gas SV, 1/hr	Total step time, s	SS setting, s	Divert, s	Ratio of strip air/flue gas	CO_2% (wet) in flue gas	Strip CO_2 in total CO_2	A capture	R capture	Purity
8/12/2021 (average of 10 beds)	268	168	20+20	30	0.12	5.8 (diluted from coal flue gas)	11.8%	90.7%	89.4%	97.1%

4.13.5 Long-term Test

Long-term testing began on August 18th, 2021, and Unit 5 supplied the coal derived flue gas until August 30th. After August 30th, Unit 5 was shut down and the NCCC NG boiler provided the flue gas. The CO_2% (wet basis) stayed at ~4%. On October 1st, the CO_2% in the flue gas was increased to ~9%. The operating parameters were routinely adjusted to keep the capture rate over 90% and CO_2 purity over 95%. Some representative data during the test is shown in Table 33. The long-term test was completed on October 20th.

Table 33. TDA skid performance in long-term test

Date	Flue gas SV, 1/hr	CO_2% (wet) in flue gas	Capture rate	Purity
8/25/2021	261	10.9	90.9%	99.2%
9/2/2021	268	4.0	90.4%	99.7%
9/9/2021	264	4.2	93.5%	95.0%
9/23/2021	268	4.2	90.6%	96.3%
9/29/2021	258	4.2	90.2%	99.2%
10/4/2021	260	9.0	90.8%	97.9%
10/12/2021	265	8.9	90.7%	97.2%

4.13.6 Pressure Drop in the Reactor

TDA installed a pressure drop (Dp) sensor to monitor the Dp across Bed 6. When the flow went downward, the Dp reading was positive. When the flow went upward through the bed, the Dp reading was negative. Figure 71 shows the Dp reading for a flow mode 4+4 case. When Bed 6 was in the adsorption mode, the Dp was not constant and decreased over time. This is likely due to displacing the water that remains on the bed after regeneration.

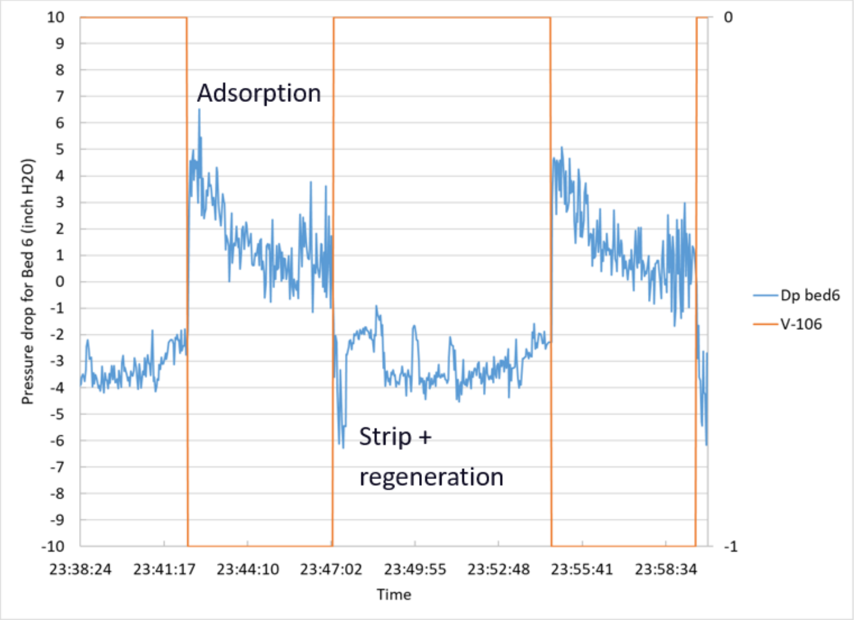


Figure 71. Bed 6 pressure drop data for flow mode of 4+4 on 10/13/2021

TDA measured Bed 6 Dp with both air (30 °C) and flue gas. The Dp for the flue gas case was higher. The flue gas was 140 °C in the test, and the actual flow rate of the flue gas was much higher than the flow rate expressed in form of standard conditions. Thus, the Dp was higher. The measured results for the air case were compared with data calculated by the Ergun equation (Figure 72). The measured results for 30 °C air were less than 1/3 of the calculated value. The lower pressure drop across the sorbent could allow us to save on both capital cost and running costs due to the reduction of the size and load of the blower.

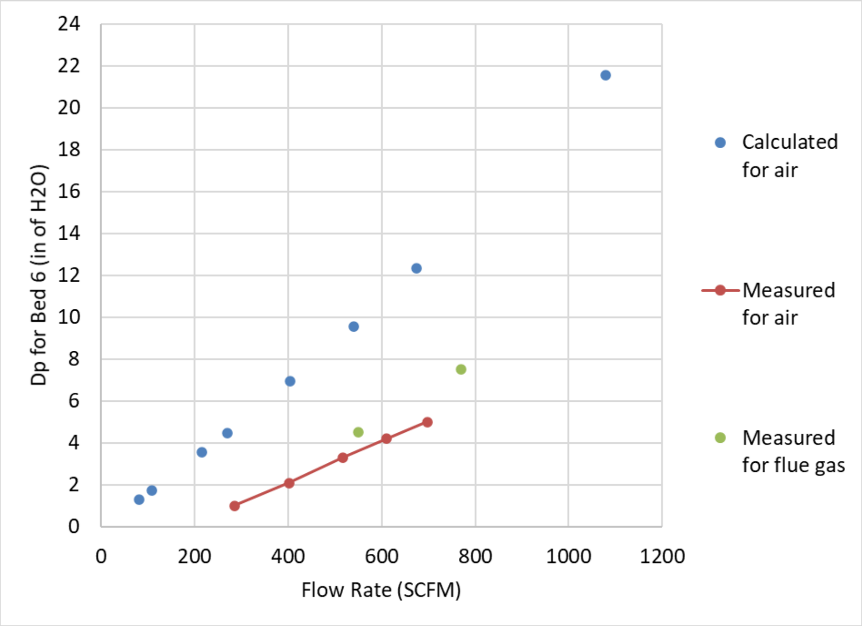


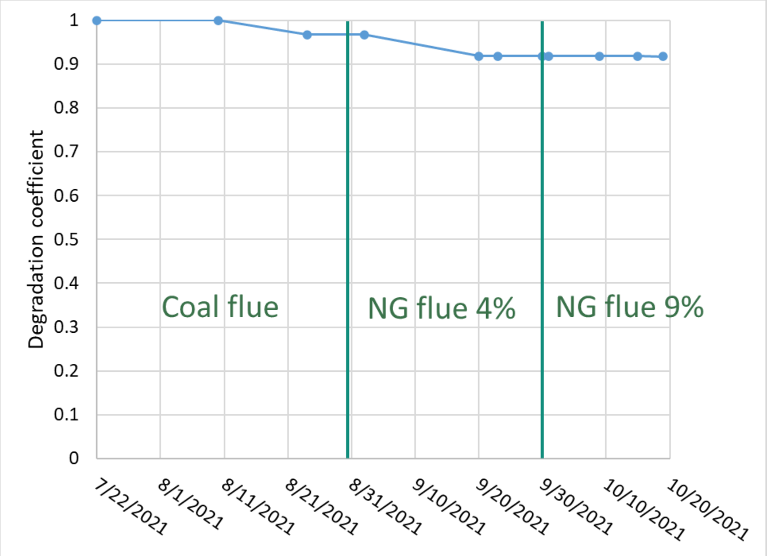
Figure 72. Bed 6 pressure drop for air and flue gas

4.13.7 Sorbent Degradation

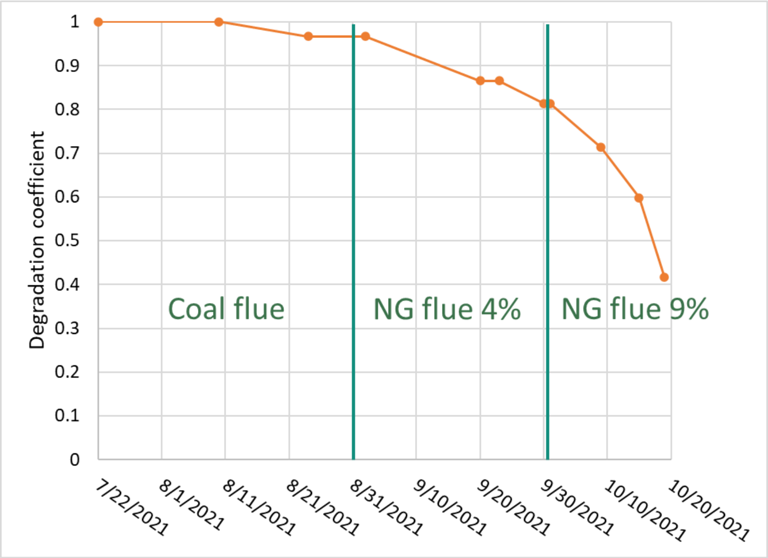
After 8/18/2021, we changed to the long-term test mode, in which a 4+4 case with 90% R capture. We maintained a 95% CO_2 purity (except that several new flow modes were tested for a short period). In this 2021 pilot test, we had two major shifts in the CO_2% in the flue gas. Before 8/30/2021, the flue gas was supplied by the coal boiler Unit 5. The remainder of the test used the flue gas was from the NCCC NG boiler. From 8/30/2021 to 10/1/2021, CO_2% (wet basis) in the flue gas was about 4%. From 10/1/2021 to 10/20/2021, then CO_2% (wet basis) in the flue gas was about 9%. Due to the change of the flue gas, it was hard to use a standard condition to track the degradation. What we did was to run a repeat case following the previous point. The R capture was used to track the performance. If the R capture was the same for the two points, there was no change on the degradation coefficient. If the R capture for the following point was lower than the previous one, the following degradation coefficient was calculated as below:

$$\text{The following coefficient} = \text{the previous coefficient} \times \frac{R\ capture\ for\ the\ following\ case}{R\ capture\ for\ the\ previous\ case}$$

When the flue gas concentration changed, we assumed no degradation occurred for the two points. The results are shown in Figure 73. After the 3-month steady state test, Dynocel still had 91.7% of its original capacity. The degradation for Chlorocel was much worse. In the last month, Dynocel's degradation curve became almost flat, while Chlorocel's curve decreased at a faster rate. The only difference between these two sorbents is that additional high temperature calcination is applied in Dynocel production. The TDA sorbent made in small batch had better performance than Dynocel, and the sorbent went through high temperature calcination in production. Therefore, we expect that the TDA sorbent can preserve the capacity in the long term as well or better than does Dynocel.



(a) Dynocel



(b) Chlorocel

Figure 73. Degradation curves for two sorbents

4.14 Characterization of Sorbent After the 2021 Pilot Test

The sorbent in the pilot unit was extracted in late November 2021. TDA ran XRD measurements and single bed tests, and the results are shown below.

4.14.1 XRD Data

The XRD results for the fresh sorbents used in 2021 pilot test were shown in Figure 74. Fresh Dynocel was very similar to fresh Chlorocel, even though Dynocel was a calcined (765 ^{o}C) version of Chlorocel. The XRD curve for Batch 1 was included for comparison. The Dynocel and Chlorocel had higher crystallinity than the Batch 1 sorbent.

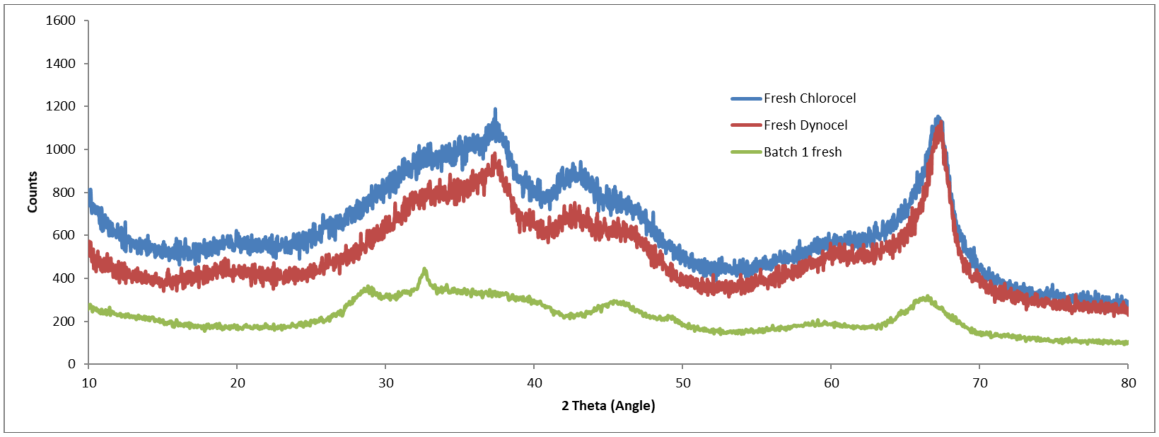


Figure 74. XRD result for fresh sorbents

The XRD result for cycled Dynocel sorbent in Bed 1 are shown in Figure 75. Dawsonite and Boehmite were both seen in the cycled Dynocel. What was not clear was whether Boehmite was formed during or after the pilot test. The sorbent stayed in the trailers for ~one month before extraction. When the pilot unit was shut down, TDA flowed NG flue gas over the sorbent to load CO_2 on it. We expected this step could reduce the conversion of gamma alumina to Boehmite.

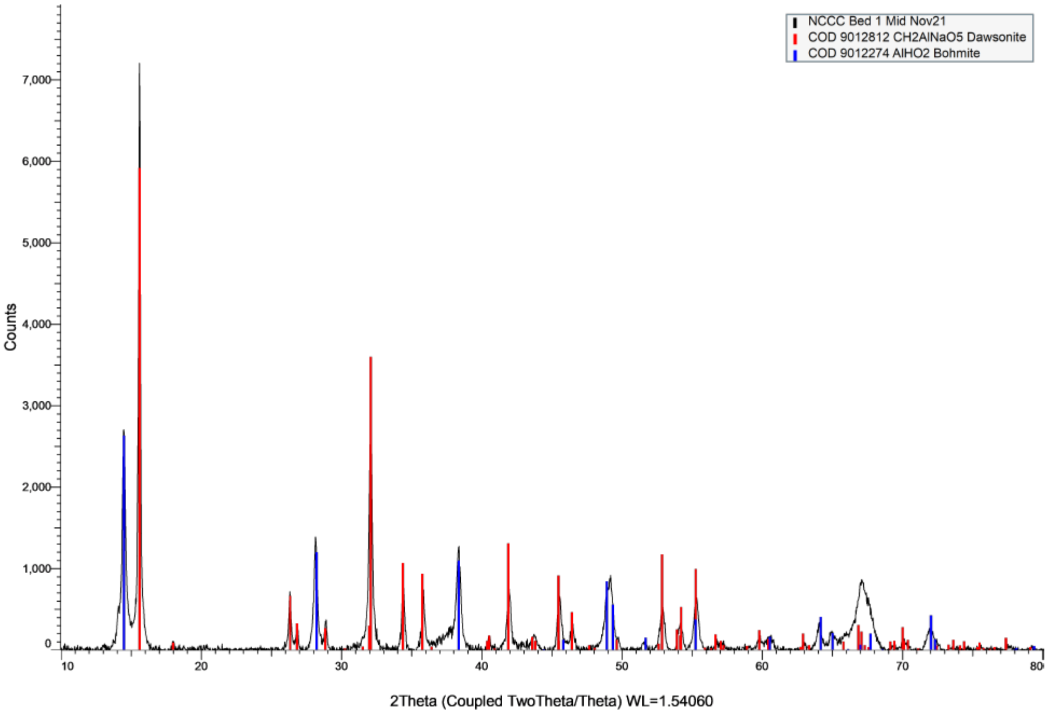


Figure 75. XRD result for used sorbent in Bed 1 (Dynocel)

As in the cycled Dynocel, both Dawsonite and Boehmite were present in cycled Chlorocel sorbent in Bed 10 (Figure 76).

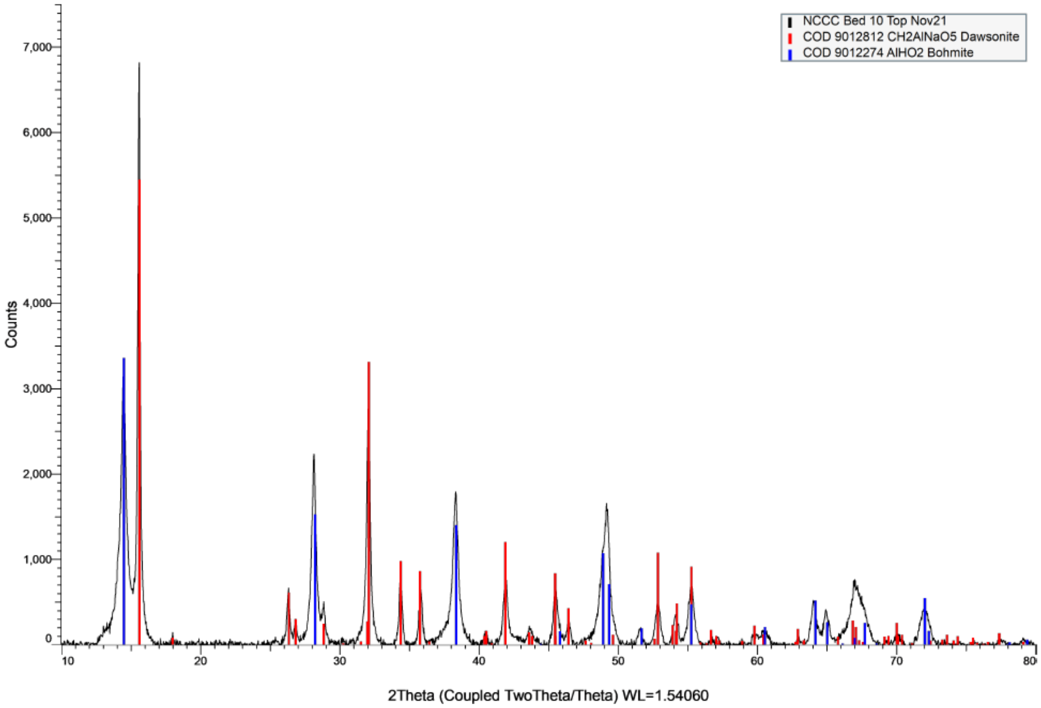


Figure 76. XRD result for used sorbent in Bed 10 (Chlorocel)

We recalcined the cycled Dynocel to see if the capture capacity could be restored. We ran the calcination at 538 °C and 765 °C. The sorbent was heated up at a rate of 15 °C/minute from room temperature, and held at the final target temperature for 2 hours. From the XRD results, the Dynocel recalcined at both temperatures was very similar to the fresh Dynocel. The boehmite was not seen in the recalcined sorbents.

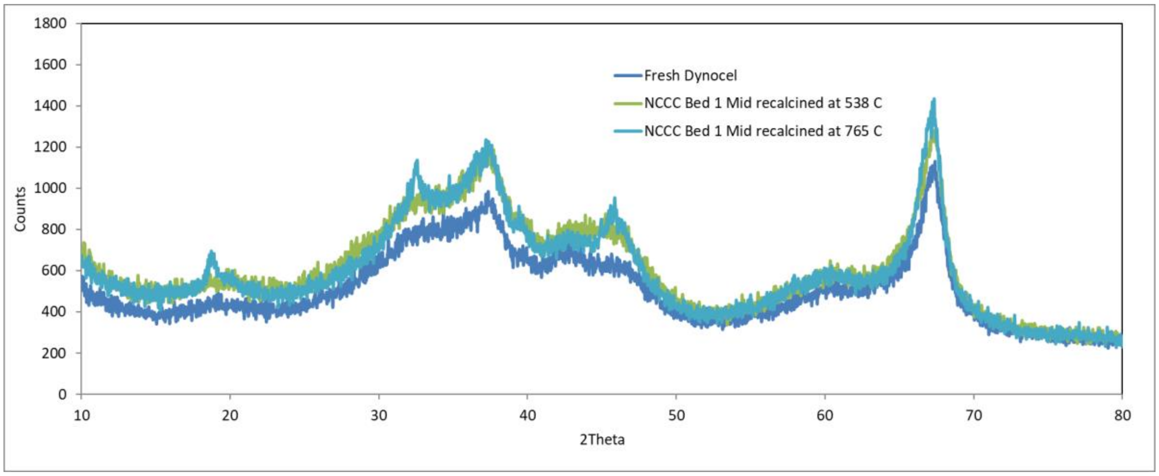


Figure 77. XRD results for Bed 1 sorbent after calcination

4.14.2 Single Bed Test Results

The sorbents were tested in single bed at TDA lab. The single bed alternates operation between adsorption and regeneration. A picture of the single bed apparatus is shown in Figure 20. This apparatus is computer controlled for automated 24-hour operation. In the single bed tests, the flow rates for flue gas and steam were kept at 2400 sccm and 1050 sccm, respectively, over a 300 cc sorbent bed. The adsorption and regeneration both lasted 9 minutes. The CO_2 loading results were shown in Table 34. After the pilot test, the CO_2 loading for both Dynocel and Chlorocel reduced, and the reduction for Chlorocel was much worse. This was consistent with the pilot test data. The recalcination of Dynocel at 538 °C slightly restored the capacity, but it didn't restore to the same level as the fresh Dynocel.

Table 34. The results for sorbent loading

Date	Sorbent	CO_2 loading, wt%
2/12/2021	Fresh Chlorocel	1.14
3/29/2021	Fresh Dynocel	1.01
12/14/2021	As-received Chlorocel (Bed 10)	0.26
12/16/2021	As-received Dynocel (Bed 1)	0.74
12/15/2021	Used Dynocel recalcined at 538 °C (Bed 1)	0.79
12/27/2021	Used Dynocel recalcined at 765 °C (Bed 1)	0.63

4.15 Environmental, Health and Safety Risk Assessment

The preliminary EH&S analyses for the sorbent production and pilot plant operation show that our technology poses no environmental risk for the local community. After the pilot test, the spent sorbent was tested to confirm the disposal method is appropriate. NCCC had conduct analyses to measure the concentration of sulfur, heavy metals (Ag, As, Ba, Cd, Cr, Pt, Se and

Hg) and some organic compounds in the cycled sorbent. The result showed none of them was detected, which confirms the pilot plant operation poses no environmental issue.

The detailed EH&S analyses can be viewed in our seperate EH&S report.

4.16 Techno-Economic Analysis

In Budget Period 1, three cases were studied. Based on the bench-scale test result for Batch #1 sorbent under DOE Case 12 condition for 90% CO_2 capture, four more cases (4, 5, 6 and 7) were analyzed. And 2021 pilot test data was applied in Case 8.

The modifications for the five cases are summarized below. In Case 4, the process was improved (from Case 3) by simplifying the process to remove the breakthrough recycle process. The breakthrough recycle process step directs the outlet of the last adsorption bed back to the inlet of adsorption. The goal is to achieve higher capture rate as CO_2 breaks through the saturated bed. However, experimental data collected in BP2 indicated that breakthrough recycle did not provide sufficient benefit to justify its added complexity. Case 4 is based on bench-scale experimental data with operation without the breakthrough recycle. In the next two cases (Case 5 and Case 6), new process optimizations were applied to the Case 4 process design (no breakthrough recycle process). These optimizations were made in order to further reduce the energy usage in the power plant. In Case 5, a CO_2 compressor was moved upstream on the CO_2/steam outlet stream so that more usable heat can be recovered by condensing this stream. For Case 6, additional heat was recovered from the stripping air return stream by adding a heat exchanger. Case 6 saved the most energy and thus the heat exchanger on the stripping air return was used in the subsequent cases. Case 7, which has the same process as Case 6, explored the CO_2 capture cost with 80% CO_2 capture. Finally, Case 8 used the same process design as Case 6 and steam usage data was from pilot test for 90% CO_2 capture, which is less than Case 6. Since Case 8 used data (SVs for flue gas, steam, strip air and pressure drop in the bed) directly from the pilot test, the result was the most relevant to the scale-up case.

The TEA results are summarized in Table 35. The analysis was performed in 2007$ to be

Table 35. The TEA results for the Cases 4-8

CASE NO.	DOE 12	4	5	6	7	8
Description		TDA – Air Stripping W/O BTR	Same as Case 4 except Raw CO2 Compressor as Heat Pump	Same as Case 4 except additional Stripped Air Heat Recovery	Same as Case 6 except Lower Carbon Capture & Steam Use	Same as Case 6 except Lower Steam Use
Carbon Captured, %	90	90	90	90	80	90
Steam Turbine Power, KWe	662,800	658,848	663,702	658,448	647,171	654,485
Total Auxiliary Consumption, KWe	112,830	108,848	113,702	108,448	97,171	104,485
Net Power Output, KWe	550,000	550,000	550,000	550,000	550,000	550,000
Net plant efficiency (HHV), %	28.4	29.85	29.94	29.96	31.66	30.25
As-received coal feed, kg/h	256,652	244,481	243,692	243,575	230,486	241,215
Natural Gas Feed, kg/h	0	0	0	0	0	0
Raw Water Withdrawal, m^3/min	38.1	33.1	32.9	32.9	29.6	32.4
1st year cost of electricity (COE) w/o CO_2 TS&M, $/MWh, 2007$	100.9	94.6	94.9	94.5	87.8	92.2
1st year CO2 capture cost w/o TS&M, $/tonne, 2007$	42.1	37.00	37.51	37.02	35.57	34.90
1st year CO2 avoided cost w/o TS&M, $/tonne, 2007$	61	51.28	51.79	51.09	47.96	47.65
1st year CO2 avoided cost with TS&M, $/tonne, 2007$	75.2	65.14	65.60	64.89	61.45	61.30

consistent with previous work performed on other cases at the start of BP1. For the two cases with system heat integrations (Cases 5 and 6), the net plant efficiencies were both higher than Case 4. Case 5 had higher capital cost, and resulted in higher capture cost than Case 4. The capital cost in Case 6 was also high, but it was offset by the gain in the plant efficiency. Thus, the capture cost of Case 6 was the same as Case 4. When pursuing high plant efficiency, the capital cost needs to be carefully considered.

Reducing the capture rate from 90% to 80% as Case 7, the plant efficiency increased by 1.7 percentage points from Case 6. However, the 1st year CO_2 capture cost without TS&M decreased by $1.45/ tonne CO_2 from 37.02 (Case 6) to 35.57$/tonne. Case 7 had much lower COE than Case 6, but it also had less CO_2 captured, so the capture cost per tonne did not drop significantly.

Case 8 used the pilot test data and applied the same process as Case 6 with 90% capture. The process flow diagram and stream table for Case 8 were shown in Figure 78 and Table 36, respectively. Pilot test showed multiple improvements from bench-scale tests, including higher SV for flue gas, lower pressure drop than calculation from the empirical equation, and lower strip air/flue gas ratio. These improvements resulted in lower capital and operating costs. Case 8 showed significant improvement over DOE baseline Case 12. Compared to DOE Case 12, the net plant efficiency of Case 8 increased by 1.45 percentage points. The 1st year CO_2 capture cost without TS&M was lower than Case 12 by $ 7.2/ tonne CO_2 (17.1% reduction). Case 8 also used 15% less raw water than DOE Case 12, which is very helpful for area short of water supply.

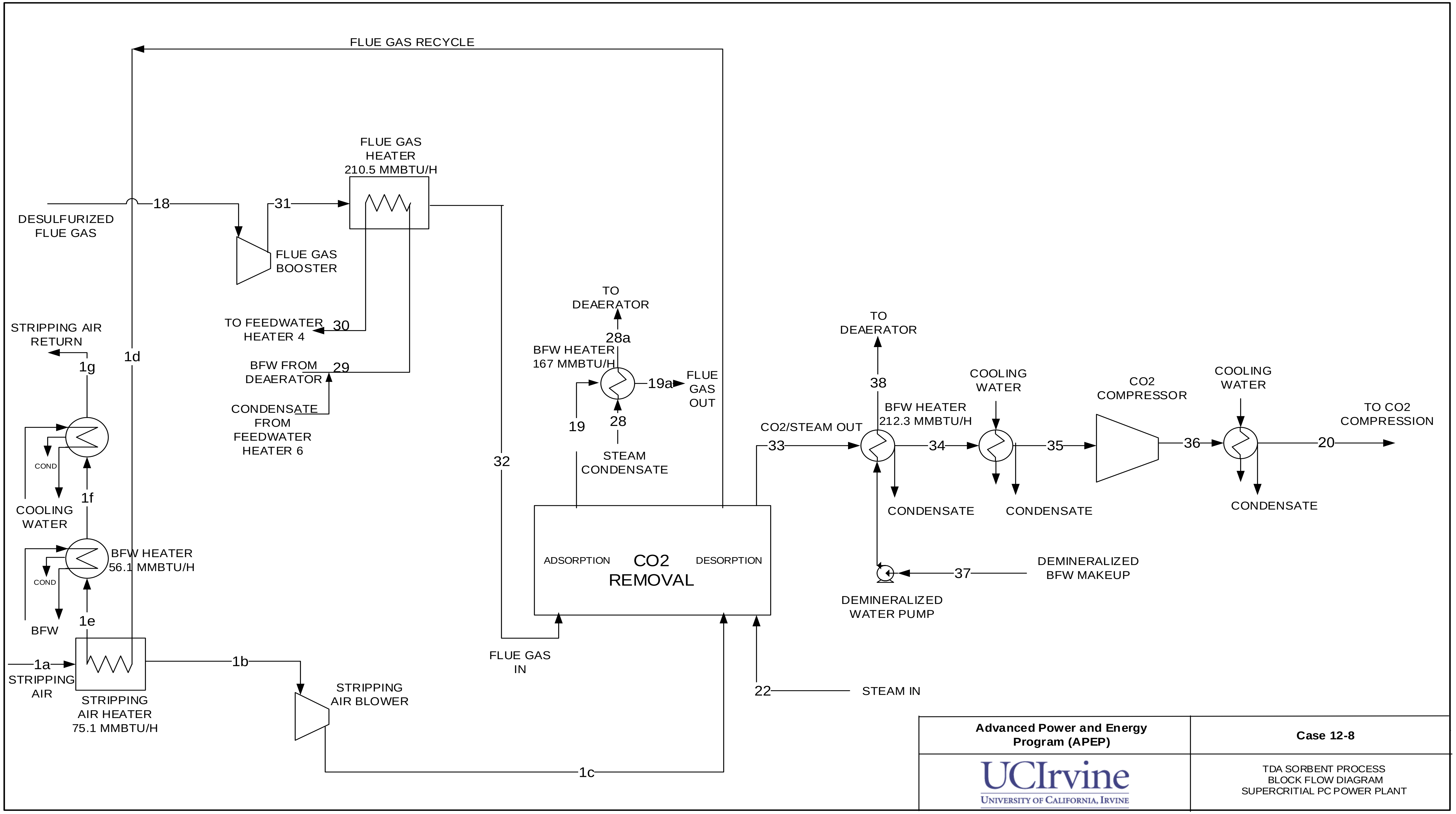


Figure 78. Process flow diagram of Case 8

Table 36. Stream table for case 8

Stream number	1+7	1a	1b	1c	1d	1e	1f	1g	2	3	4	5	6	8	9	10	11	12	13	14	15	16	17
Temperature C	15	15	123	140	140	101	84	38	26	26	15	26	26	0	15	169	0	169	182	15	15	181	58
Pressure bar	1.01	1.01	1.01	1.12	1.02	1.02	1.01	1.01	1.05	1.05	1.01	1.11	1.11	0.00	1.01	0.99	0.00	0.98	1.06	1.01	1.01	3.1	1.01
Mass Flow kg/hr (Solid)	-	-	-	-	-	-	-	-	-		-	-		241,214	5,386	18,712	18,712	-	-	24,404			37,724
Vapor Frac	1.00	1.00	1.00	1.00	1.00	1.00	0.98	1.00	1.00	1.00	1.00	1.00	1.00			1.00		1.00	1.00	0.00	0.00	1.00	0.00
Mole Flow kmol/hr (w/o Solids)	46,101	18,197	18,197	18,197	45,622	45,622	45,622	21,731	67,832	2,019	19,752	19,752	2,710			92,391		92,391	92,391	3,181	12,674	916	235
Mass Flow kg/hr (w/o Solids)	1,330,013	524,974	524,974	524,974	1,080,753	1,080,753	1,080,753	649,344	1,979,358	58,906	569,833	569,833	78,181			2,766,307		2,766,307	2,766,307	57,307	228,328	26,587	4,227
Density kg/m3 (w/o Solid)	1.22	1.22	0.88	0.94	0.70	0.78	0.82	1.17	1.24	1.24	1.22	1.29	1.29			0.81		0.80	0.84	-	1003.10	2.40	-
Molecular Weight (w/o Solid)	28.85	28.85	28.85	28.85	23.69	23.69	23.69	29.88	29.18	29.18	28.85	28.85	28.85			29.94		29.94	29.94	-	18.02	29.03	-
Mole Frac (w/o Solids)																							
O2	0.2076	0.2076	0.2076	0.2076	0.0828	0.0828	0.0828	0.1736	0.1967	0.1967	0.2076	0.2076	0.2076			0.0247		0.0247	0.0247	0.0000	0.0000	0.2300	0.0000
N2	0.7719	0.7719	0.7719	0.7719	0.3079	0.3079	0.3079	0.6457	0.7315	0.7315	0.7719	0.7719	0.7719			0.7032		0.7032	0.7032	0.0000	0.0000	0.7506	0.0000
AR	0.0094	0.0094	0.0094	0.0094	0.0037	0.0037	0.0037	0.0079	0.0089	0.0089	0.0094	0.0094	0.0094			0.0085		0.0085	0.0085	0.0000	0.0000	0.0128	0.0000
H2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000			0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000			0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2	0.0003	0.0003	0.0003	0.0003	0.0522	0.0522	0.0522	0.1081	0.0348	0.0348	0.0003	0.0003	0.0003			0.1642		0.1642	0.1642	0.0000	0.0000	0.0005	0.0004
H2O	0.0108	0.0108	0.0108	0.0108	0.5534	0.5534	0.5534	0.0647	0.0281	0.0281	0.0108	0.0108	0.0108			0.0973		0.0973	0.0973	1.0000	1.0000	0.0062	0.9996
CH4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000			0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000			0.0020		0.0020	0.0020	0.0000	0.0000	0.0000	0.0000
C2H6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000			0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
C3H8	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000			0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
C4H10-01	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000			0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOTAL	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000			1.0000		1.0000	1.0000	1.0000	1.0000	1.0001	1.0000

Stream number	18	19	19a	20	21	22	23	24	25	26	27	28	28a	28b	29	30	31	32	33	34	35	36	37	38
Temperature C	58	140	86	25	35	138	59	593	354	593	39	63	101	285	156	99	69	140	150	64	25	72	15	80
Pressure bar	1.03	1.01	0.98	1.62	152.68	1.19	0.96	242.33	49.01	45.22	0.07	16.62	14.89	288.55	6.34	5.65	1.12	1.12	1.01	1.00	0.96	1.65	1.01	16.62
Mass Flow kg/hr (Solid)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Vapor Frac	1.00	1.00	1.00	1.00	1.00	1.00	0.00	1.00	1.00	1.00	0.91	-	-	-	-	-	1.00	1.00	1.00	1.00	1.00	1.00	-	-
Mole Flow kmol/hr (w/o Solids)	101,093	100,017	100,017	12,371	12,147	46,076	31,470	118,390	96,609	96,609	24,024	81,725	81,725	118,390	52,258	52,258	101,093	101,093	19,726	15,948	12,543	12,543	46,076	46,076
Mass Flow kg/hr (w/o Solids)	2,914,343	2,527,612	2,527,612	528,504	524,461	830,065	567,965	2,132,831	1,740,441	1,740,441	432,801	1,472,294	1,472,294	2,132,831	941,437	941,437	2,914,343	2,914,343	661,017	592,935	531,598	531,598	830,065	830,065
Density kg/m3 (w/o Solid)	1.08	0.75	0.83	2.81	721.47	0.63	233.06	69.11	18.66	11.57	0.05	982.20	958.41	774.59	911.06	959.13	1.14	0.94	0.97	1.33	1.65	2.45	999.22	972.30
Molecular Weight (w/o Solid)	28.83	25.27	25.27	42.72	43.18	18.02	18.05	18.02	18.02	18.02	18.02	18.02	18.02	18.02	18.02	18.02	28.83	28.83	33.51	37.18	42.38	42.38	18.02	18.02
Mole Frac (w/o Solids)																								
O2	0.0226	0.0226	0.0226	0.0016	0.0017	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0226	0.0226	0.0010	0.0013	0.0016	0.0016	0.0000	0.0000
N2	0.6427	0.6438	0.6438	0.0467	0.0476	0.0000	0.0005	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.6427	0.6427	0.0293	0.0362	0.0461	0.0461	0.0000	0.0000
AR	0.0078	0.0078	0.0078	0.0006	0.0006	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0078	0.0078	0.0004	0.0004	0.0006	0.0006	0.0000	0.0000
H2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2	0.1500	0.0128	0.0128	0.9310	0.9482	0.0000	0.0010	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.1500	0.1500	0.5839	0.7223	0.9183	0.9183	0.0000	0.0000
H2O	0.1769	0.3130	0.3130	0.0201	0.0020	1.0000	0.9984	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.1769	0.1769	0.3854	0.2398	0.0335	0.0335	1.0000	1.0000
CH4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
C2H6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
C3H8	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
C4H10-01	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOTAL	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

The enthalpy reference state for a compound is that of the constituent elements in their standard states at 25 C and 1.01 bar.

4.17 Decommissioning

The TDA skid was removed from the test site by a crane in the week of May 9, 2022. The empty site is shown in Figure 79. The sorbent trailers were scrapped in Wilsonville, AL by A&R Metal Recycling. The service unit was stored at NCCC temporarily before picking up by an extended flatbed trailer hauler.

Figure 79. The test site after TDA skid was removed.

The service unit was delivered to Denver on May 26, 2022 by Stevens West Freight. A crane was rented to unload it from the truck. It was stored in a storage yard relatively close to TDA's facilities. The blowers, heat exchangers and power panel can be used future projects. All externally accessible sensors or equipment was removed and stored at TDA. All electronics cabinets were secured and locked with padlocks for long term storage.

Figure 80. TDA service unit in a storage yard in Denver

4.18 Sorbent Development

4.18.1 Recalcination of Cycled Batch 1 Sorbent

TDA sorbent degrades over a long period of time, and it is therefore very useful if the sorbent can be recalcined and restore to its original capacity and properties. In early 2022, we found that we could restore the Batch 1 sorbent's capture capacity by calcining it at 538 ^{o}C. We continued the cycles of Batch 1 sorbent in bench unit (Figure 6) to see if it could hold performance in long term testing.

The standard 5+5 flow mode was used to track the performance of the sorbent. To provide a good measurement of the sorbent performance, we periodically ran the same test. The results are shown in Figure 81. The sorbent recalcined at 538 ^{o}C was run for about 1260 hours, and the degradation rate was less than half that of the original sorbent (blue dots). We kept the sorbent over 120 ^{o}C when the bench unit is in idle mode during weekends, instead of cooling the sorbent to 20 ^{o}C like before. Keeping the sorbent warm slowed down the formation of the undesirable component, which is not effective in CO_2 capture. This new finding is important to us since we now know how to maintain the CO_2 capture capacity of the sorbent.

After the capture rate in the 5+5 mode dropped to 83.8%, we recalcined the sorbent at 380 ^{o}C regeneration for 4 hours. The calcination temperature was lower than that used in 2022/1 (538 ^{o}C). We chose the 380 ^{o}C temperature because we could run the calcination in situ without extracting the sorbent from the reactors. This would greatly simplify the reprocessing at commercial scale. The XRD results for the calcinations at two temperatures, shown in Figure 82, were very similar to each other, mainly showing amorphous phases.

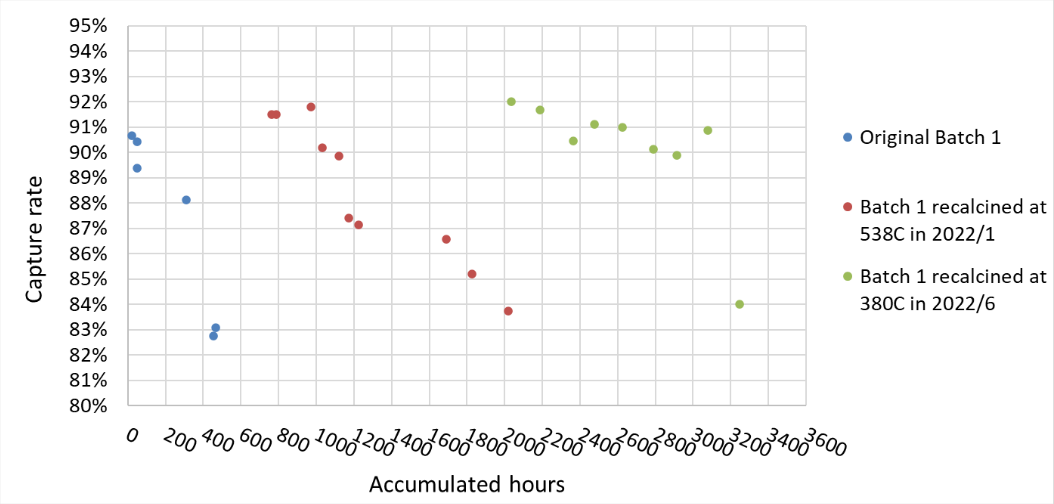


Figure 81. The capture rate under 5+5 mode for Batch 1 sorbent

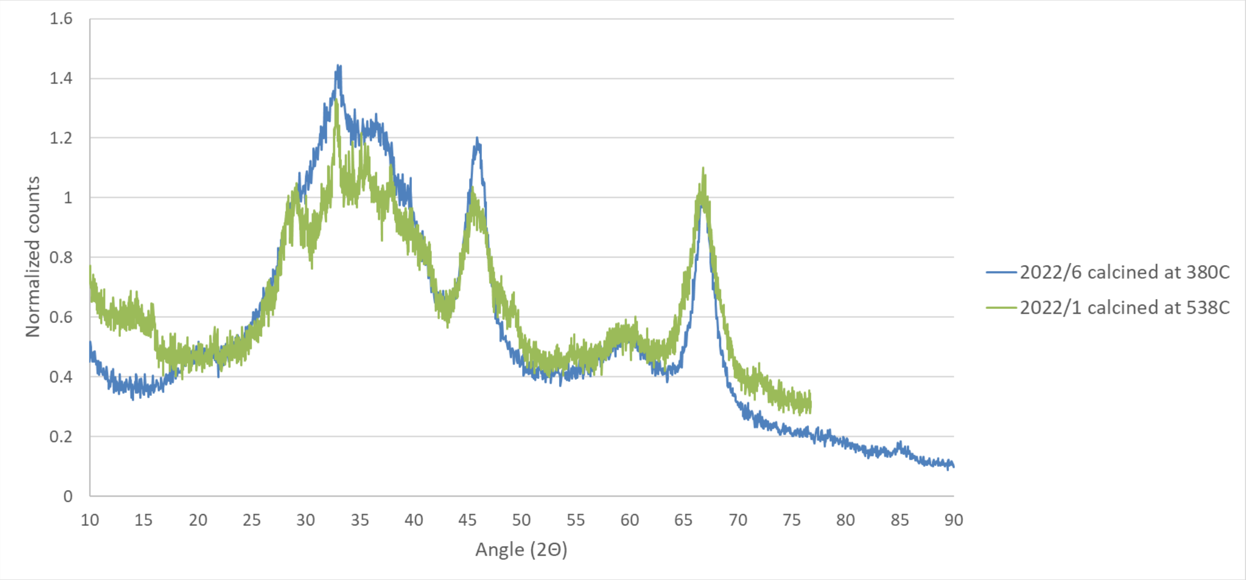


Figure 82. The XRD result for the recalcined Batch 1

The Batch 1 sorbent recalcined at 380 °C also restored the capture capacity and maintained the performance very well. In the first 1000 hours after calcination, it had even slower degradation rate than the Batch 1 recalcined at 538 °C. The sorbent performance after the two recalcinations demonstrated that this reprocessing approach was viable to recover the sorbent capture capacity and could be used repeatedly. With reprocessing, the longevity of the sorbent could be extended significantly.

4.18.2 Sorbent Production at TDA

Porocel did not produce a sorbent of good quality for the pilot test, and it is very likely the insufficient calcination step was the issue. It was done in a belt dryer, which is not the best equipment for calcination at the temperature we want. Our partner said a rotary calciner should be used. TDA has a rotary calciner (6.5” diameter), which could be used for intermediate scale production in a continuous mode. We tried to reproduce Batch 1 sorbent in TDA lab.

The sorbent production process was summarized in Figure 83. The raw alumina was mixed with DI water to make a paste. We extruded the paste into 1/16” pellets. After the extrudates was dried, alkali solution was impregnated on them. Then, the sorbents were dried again. Finally, the sorbents were calcined at 538 °C in our rotary calciner. XRD measurements were run for the collected sorbents to confirm no boehmite was present in the products.

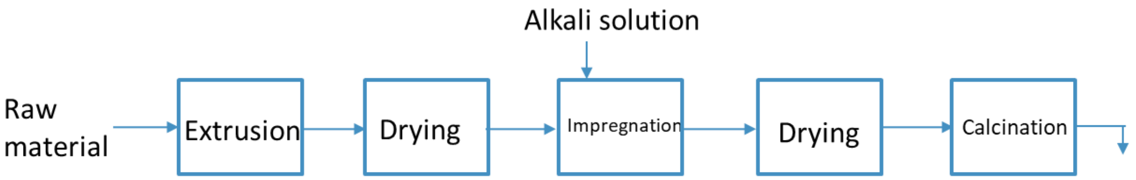


Figure 83. The process to make TDA’s sorbent

The material at the surface of the sorbents fell off and turned into dust due to attrition in the calcination. Typically, about 20 wt.% of the collected sorbents from the calcination was less than

1 mm. We loaded the fraction of sorbents larger than 1 mm in the single bed for the characterization tests.

One obvious difference between the sorbents TDA made and the Batch 1 sorbent Porocel made was the bulk density. Batch 1 had a density of 0.724 g/ml, while the density of TDA made sorbents ranged 0.50~0.61 g/ml. We tried to mill the raw alumina before making a paste, but the density increased slightly. However, our lighter sorbents had performance that was similar to or better than the Batch 1. The single bed tests under 8% CO_2 flue gas were summarized in Table 37. The flow rates for flue gas and steam were 2202 sccm and 968 sccm, respectively. The step time was 300 seconds.

Table 37. Capture rates for TDA made sorbents and Batch 1 for 8% CO_2 flue gas

	Capture rate%
Batch 1	88.47
030722B	89.45
030722C	87.53
030822C	87.64
090222B	89.28
090222C	92.13

The results in Table 37 showed that we can reproduce the performance of the Batch 1 sorbent. With the calcination step running the rotary calciner, the quality of the sorbents was consistent. If the low density sorbents TDA made can be scaled up, we can significantly save the material to produce the same volume of sorbents.

5. Conclusion

TDA Research, Inc. has developed a low-cost sorbent (alkalized alumina) based technology for post-combustion CO_2 capture. The sorbent runs in an isothermal process for adsorption and regeneration. Neither temperature swing nor pressure swing is needed. We designed a system which operated 10 fixed beds to simulate a moving bed process. The flow pattern was optimized to minimize the steam usage for regeneration. An excellent sorbent (Batch 1) was also developed with collaboration with our partner. The sorbent degraded after long term operation. We developed a reprocessing procedure, which can be conducted in situ, to restore the sorbent capture capacity as the fresh sorbent after running for about 1250 hours. The reprocessing extended the sorbent longevity significantly.

TDA designed a pilot unit (40’ x 32’ x 11.5’), processing flue gas equivalent to 0.5 MW of power generation. It had 10 beds and each bed could hold 1.75 m^3 of sorbent. We worked with Springs Fabrication, Inc. to complete the construction of the pilot unit. It was then shipped and installed at NCCC. The pilot unit was kept running in 24-hour mode when the flue gas and steam were available. It could run automatically without operator on site. Parametric and long-term (2 months) tests were carried out successfully. The results showed that TDA’s process can achieve 90% capture and 95% CO_2 purity for both coal and NG flue gases. For coal flue gas, the system reached performance target when processing up to 0.62 MW flue gas, 24% higher than the design capacity. Thus, capital cost could be saved on the reactors and sorbent. The strip air flow was designed to be 0.25 of that of the flue gas. The test data showed the strip/flue ratio can be reduced to as little as 0.18, which saves the power consumption for the strip air blower. The pressure drop was found to be lower than what the empirical equation calculated. The sorbent still had 91.7% of original capacity after 3-month test.

With the data from the pilot test, we updated the TEA. For a 550-MW_e supercritical coal fired power plant with CO_2 capture, the capture cost for TDA's process is \$34.9/tonne CO_2 captured, which meets DOE's goal of \$40/tonne and is 17.1% less than the DOE baseline Case 12. Therefore, TDA's process has a good potential for commercialization.

Nomenclature

Legend	Meaning
A Capture	Adsorption capture rate, which is calculated as 1 - CO_2 in green flue gas/CO_2 in feed
R-Capture	Capture rate including recycle, which is calculated as CO_2 in regen outlet/(CO_2 in green flue gas + CO_2 in regen outlet)

References

1. Cost and Performance Baseline for Fossil Energy Plants, Volume 1: Bituminous Coal and Natural Gas to Electricity. 2019.
2. Cost and Performance Baseline for Fossil Energy Plants, Volume 1: Bituminous Coal and Natural Gas to Electricity (Rev. 2). 2013.