Pilot Tests for Sorbent Based Post-Combustion CO_2 Capture

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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 has constructed a pilot-scale skid, which was installed and tested at National Carbon Capture Center (NCCC) using a slipstream of the flue gas. It was designed to process coal derived flue gas equivalent to 0.5 MW 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 NG flue gas was derived either from diluted coal flue gas or from the NG boiler that was installed in 2021 at NCCC.

In the 4th quarter of 2017, the skid was installed at NCCC and the pilot sorbent was loaded. TDA later found the sorbent was manufactured incorrectly at the factory of TDA's partner. The lab test showed the sorbent had good performance initially, but its long-term stability was bad. 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 a 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 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, 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 in TDA's process. 90% capture rate 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, it was 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. It was possible that the moisture in the gas phase caused the change of 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 Chlorocel (a commercial sorbent). 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. 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 flue gas was supplied by a coal boiler until August, 30^{th} 2021. Then, it 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, 24% higher than the 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, Dynocel still maintained 91% capture capacity and the degradation rate reached a plateau. The degradation for Chlorocel was much worse (as expected), since it is not designed for use as a long-term carbon capture sorbent, but the only available sorbent when we wanted to replace the previous sorbent.

1. TDA's Sorbent Based 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 low cost and can be regenerated without temperature-swing or pressure-swing via steam regeneration (low pressure, 140°C superheated steam). Due to this regeneration mechanism, 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.

The simplified flow diagram is shown in Figure 1. Multiple reactors are used in the system and each reactor alternates between the adsorption and desorption modes via the flow pattern. Simple fixed bed design is applied to the reactor and saves on cost. 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 1. 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.

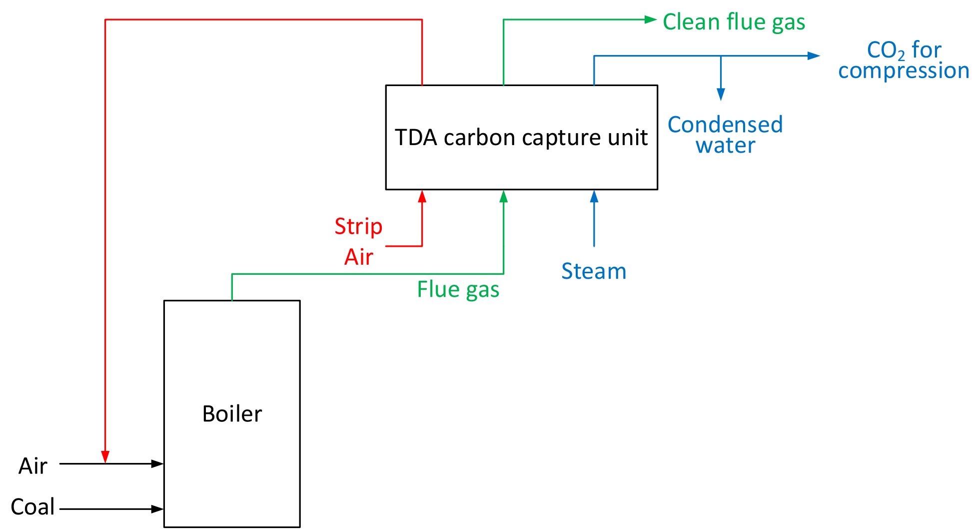


Figure 1. Simplified flow diagram of TDA's CO_2 capture process

2. Pilot Unit System

The TDA pilot unit is skid mounted with ten fixed beds. The fixed beds cycle between adsorption, regeneration and purge/recycle operations. TDA's slipstream system includes three units: adsorber/regeneration beds, the service unit (heat exchangers, blowers, flow metering, exhaust coolers) and the instrument/control unit (Figure 2). The sorbent beds operate near isothermally at 140°C. The pilot unit was sized for a 0.5 MW_e demonstration taking 5000 lb/hr of flue gas. It was installed at NCCC in the 4th quarter of 2017.

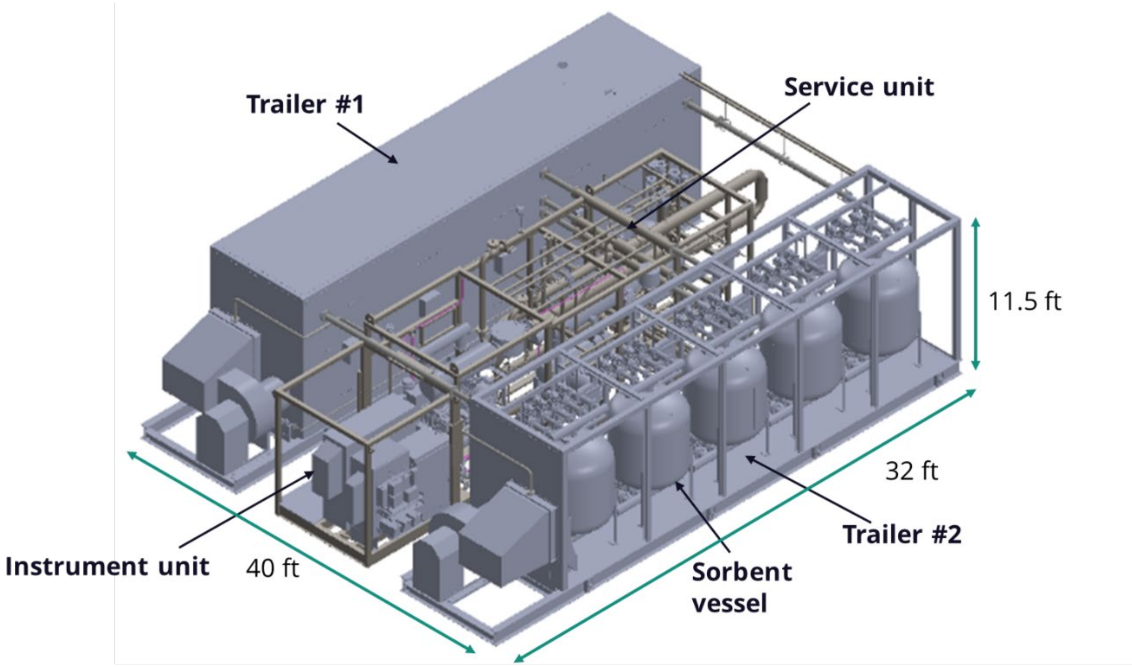


Figure 2. TDA's pilot unit installation at NCCC. TDA’s system includes two sorbent bed trailers (Trailer #1 and Trailer #2), the service unit (which contains heat exchangers, blowers, flow metering, exhaust coolers) and the instrument unit (which contains analyzers and the Programmable Logic Controller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

The ten fixed beds are housed in two trailers, each holding five beds (Figure 2). 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 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 contains process control and analysis components, and is maintained at ambient temperature through wall mounted A/C units. The service unit is not heated, but most of the major gas streams flowing through it are heat traced to maintain process operating conditions (~140°C). The service unit is the main structure for connecting streams from the NCCC to the reactor units containing TDA's sorbent. The service unit contains equipment such as blowers, electric resistive heaters, in-line heat exchangers, condensers, water knock-outs and valves (relief, flow/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.

3. Pilot Test in 2018-2020

In the 4th quarter of 2017, TDA's partner had produced 15 tons of sorbent for the pilot unit. Immediately following production, TDA performed QA/QC testing on the sorbent. These tests showed the sorbent had good CO_2 loading. This sorbent was therefore approved and loaded into the pilot unit at NCCC during the week of November 6-10, 2017. In the 1st quarter of 2018, while the Gaston U5 plant was shut down, TDA conducted an extended cycling test on the pilot unit sorbent in our labs in Colorado. The testing showed the large batch pilot unit sorbent precipitously lost capacity with extended cycling. Further characterization tests determined the sorbent contained unreacted raw materials, which led to the lack of stability. The significant degradation of the sorbent was unacceptable for tests that run for several months in the pilot unit, let alone operation in a commercial process. Therefore, TDA worked with our partner to reprocess it.

The sorbent was vacuumed out of the reactors at NCCC during the week of May 16, 2018. It was immediately shipped back to the TDA's partner. Reprocessing of the sorbent started on June 27, 2018 and was completed by July 2, 2018. TDA characterized samples of the reprocessed sorbent at our laboratory and confirmed its activity and improved stability (Figure 3). The sorbent was loaded back into the pilot unit the week of July 19, 2018. Due to unavoidable volume loss in the sorbent reprocessing, only 8 reactors were filled with reprocessed sorbent. Beds 1 and 2 were loaded with Dynocel, a modified commercial sorbent.

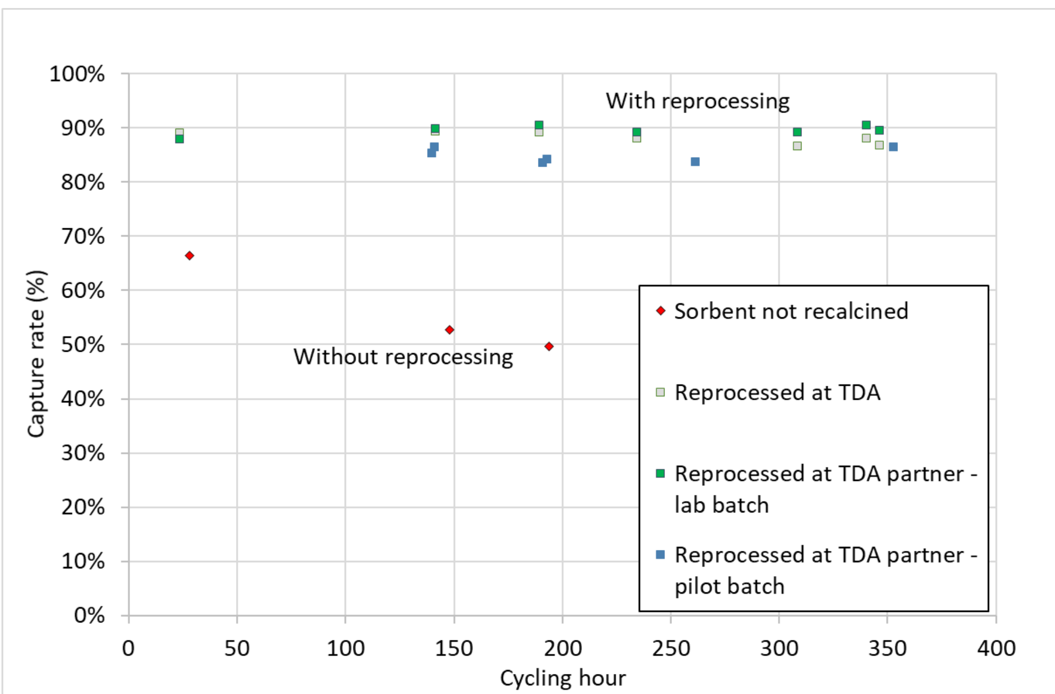


Figure 3. Improved performance of the reprocessed sorbent

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% 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 4 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.

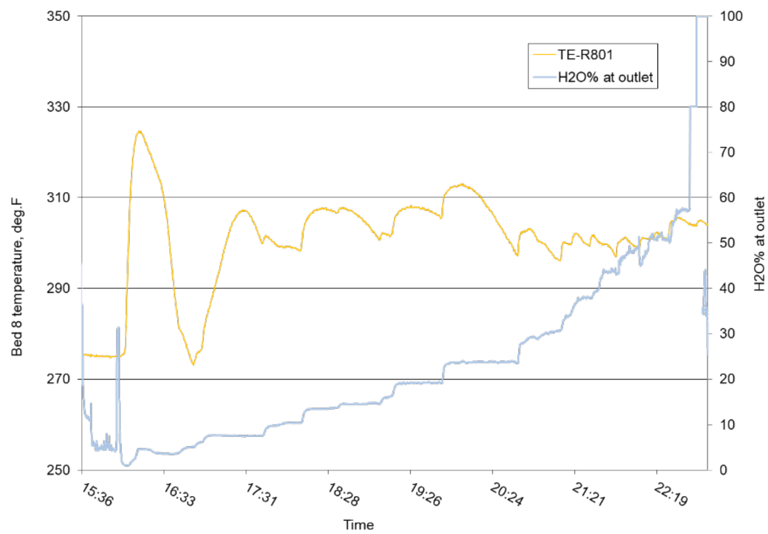


Figure 4. Temperature inside of bed 8 and H_2O% at outlet with controlled hydration (5/25/19)

In the 2019 test, 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. In 5+5 mode, the reactors simply alternated between adsorption and regeneration. 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 strip step further regenerated 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 increased. The SS step routed the wet 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 increased regeneration purity by purging the inert diluents.

The flue gas, steam and strip air (if involved) flow rates were kept the same for three cases. The total step time was 70 seconds. Adding a strip step, the capture rate increased about 30 percentage points. Applying the additional SS step gave another 10 percentage points increase in the capture rate. The results clearly showed the advantage of strip and SS steps.

Table 1. Results of the tests showing the advantage of strip and steam saver

Date	Running mode	Capture rate
8/17/19	5+5	53.8%
8/17/19	Strip only	82.4%
8/17/19	Strip + SS 20s	92.2%

In 2019, we tested both coal and NG flue gases (diluted from coal flue gas, ~7.9% CO_2 in flue gas (wet basis)). 90% capture rate and 95% CO_2 purity were achieved for both flue gases.

Table 2. Highlight of 2019 pilot test

Date	Flue gas type	Purity, %	Capture rate
8/26/19	Coal	96.7%	90.5%
9/28/19	NG (simulated)	94.8%	89.2%

The TDA team returned to NCCC in late January 2020 after the pilot unit was shut down on October 4, 2019. The performance was significantly lower than it was before the shut-down in October 2019, as shown in Table 3. Thus, TDA decided to replace the sorbent in the beds at NCCC due to the severe performance loss. The reactors were purged with air during the shut-down in 2019. Apparently, the moisture in the reactors was not fully removed and changed the form of the sorbent, which decreased its performance.

Table 3. 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%

4. Pilot Test in 2021

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.

4.1. Parametric Test

We studied the influence of flue gas space velocity (SV) on the performance. The flow rate of flue gas was gradually increased up to 151% of the designed flow rate. The steam and strip air flow rates were increased proportionally. The step time was shortened accordingly. The result is shown in Table 4. As the flue gas SV increases, the capture rate decreases. However, when the SV is 24% higher than the designed value, the capture rate is still over 90%. Thus, the reactor size can be reduced if processing the same amount of flue gas, which saves capital costs.

Table 4. Effect of flue gas space velocity on the performance

Date	Flue gas SV, 1/hr	Compared to the design	CO_2% (wet) in flue gas	Capture rate	Purity
7/28/2021	270	1.01	11.5	92.0%	95.2%
8/3/2021	318	1.19	11.8	90.8%	96.6%
8/7/2021	332	1.24	11.7	90.6%	96.1%
8/3/2021	404	1.51	11.8	87.3%	94.9%

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. As illustrated in Table 5, reducing the strip air/flue gas to 0.18, the capture rate is still acceptable. 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 saved.

Table 5. Effect of strip air space velocity on the performance

Date	Flue gas SV, 1/hr	Ratio of strip air/flue gas	CO_2% (wet) in flue gas	Capture rate	Purity
8/6/2021	318	0.25 (design basis)	12.0	90.7%	96.3%
8/6/2021	318	0.18	12.0	89.6%	98.1%
8/6/2021	318	0.13	12.0	88.6%	99.1%

For the coal derived flue gas, the skid met the performance goals as shown in Table 6. TDA diluted the coal derived flue gas to simulate the NGCC flue gas. Due to the strip air recycle, the CO_2% (wet basis) is 5.8%. We were able to achieve very close to 90% capture and over 95% CO_2 purity.

Table 6. TDA skid achieved performance target for different flue gases

Date	Flue gas SV, 1/hr	Ratio of strip air/flue gas	CO2% (wet) in flue gas	Capture Rate	Purity
8/6/2021	318	0.13	10.9	91.7%	98.5%
8/12/2021	268	0.12	5.8 (diluted from coal flue gas)	89.4%	97.1%

4.2. 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 7. The long-term test was completed on October 20th.

Table 7. TDA skid performance in long-term test

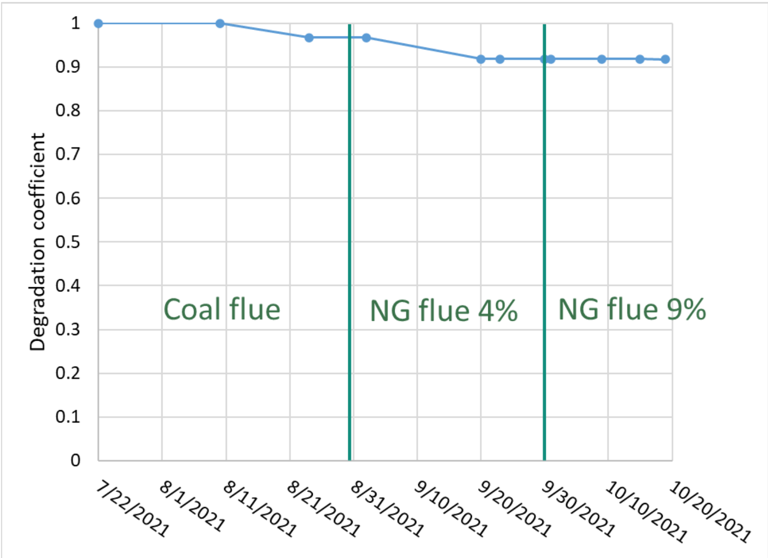
Date	Flue gas SV, 1/hr	CO_2% (wet) in flue gas	Capture rate	Purity
8/25/2021	261	10.9	90.9%	99.2%
9/2/2021	268	4.0	90.4%	99.7%
9/9/2021	264	4.2	93.5%	95.0%
9/23/2021	268	4.2	90.6%	96.3%
9/29/2021	258	4.2	90.2%	99.2%
10/4/2021	260	9.0	90.8%	97.9%
10/12/2021	265	8.9	90.7%	97.2%

4.3. Sorbent Degradation

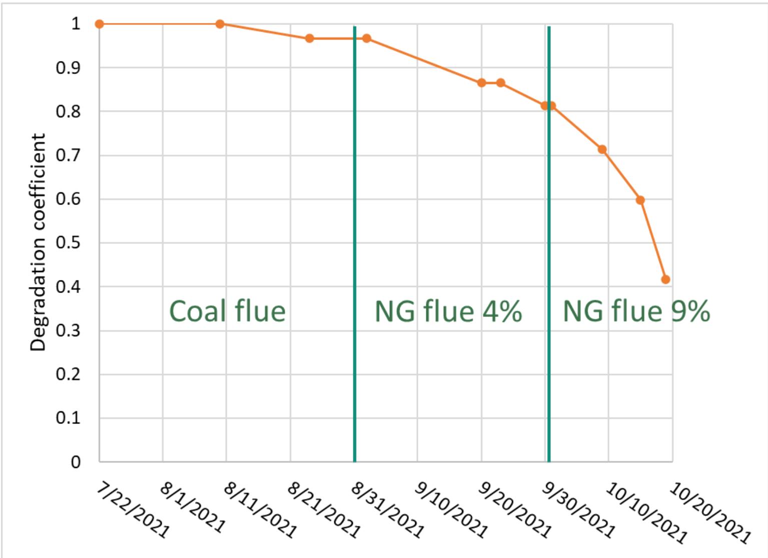
We experienced two major shifts in the CO_2% in the flue gas during 2021 pilot test, so it was hard to use a standard condition to track the degradation. What we did was to run a repeat case following the previous point. The capture rate was used to track the performance. If the capture rate was the same for the two points, there was no change on the degradation coefficient. If the capture rate for the following point was lower than the previous one, the following degradation coefficient was calculated as below:

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

When the flue gas concentration changed, we assumed no degradation occurred for the first point after the CO_2% change. The results are shown in Figure 5. After the 3-month pilot test, Dynocel retained 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 accelerated. For Dynocel, there was an initial period when the sorbent lost 8.3% of its capture capacity, but after that it lost very little. The TDA sorbent made in a small batch had better performance than Dynocel, where both went through a



(a) Dynocel



(b) Chlorocel

Figure 5. Degradation curves for two sorbents

similar production process. Therefore, we expect that the capacity of TDA's small batch sorbent would be at least equal to and likely better than that of Dynocel in the long term.

5. Techno-economic Analysis

With the pilot data, we designed the carbon capture unit for a power plant with net 550 MW output. The techno-economic analysis was conducted to evaluate TDA's technology. The results are summarized in Table 8. The reference case is the Case 12 in "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity, Rev. 2". TDA started this project in 2014, and we used Rev. 2 since then. TDA's process has almost 2 percentage points higher net plant efficiency than the Case 12. The capture cost is $34.90/tonne, which is 17% less than the Case 12.

Table 8. Techno-economic analysis of TDA technology

CO_2 Capture Technology	No Capture Case 11	Amine Capture Case 12	TDA
Carbon Captured, %	0	90	90
Steam Turbine Power, KWe	580,400	662,800	654,485
Total Auxiliary Consumption, KWe	30,410	112,830	104,485
Net Power Output, KWe	550	550	550
% Net Plant Efficiency, HHV	39.3	28.4	30.3
1st year cost of electricity (COE) w/o CO2 TS&M, $/MWh, 2007$	58.9	100.9	92.2
1st year CO_2 capture cost w/o TS&M, $/tonne, 2007$		42.10	34.90
1st year CO_2 avoided cost w/o TS&M, $/tonne, 2007$		60.75	47.65

6. Accomplishments and Future Work

The accomplishments from the pilot tests are summarized below:

- 90+% capture and 95+% purity CO_2 product were achieved for both coal fired (0.62 MW) and natural gas fired flue gases.
- The pilot unit can process up to 24% more flue gas that it was designed for, without compromising its performance.
- The strip air flow rate can be reduced to 72% and 50% of the design value for coal and NG flue gases, respectively.
- TDA's Dynocel sorbent has performed well throughout the 3-month test, and we have developed even more efficient and stable sorbent.

In the pilot test at NCCC, a simple version of the reactor was used. We will test a new reactor in the following studies. And we want to demonstrate our technology at a scale equivalent to process flue gas from a 25 MW power generation unit.