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Results from Lab and Field Testing of Novel CO_2 Sorbents for Existing Coal-Fired Power Plants

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ABSTRACT

Technologies for carbon capture from existing coal-fired utilities are rapidly being developed. Solid sorbents have many potential benefits compared to other technologies for CO_2 capture, such as ease of handling, greater capacity, reduced energy for regeneration, etc. ADA-ES has completed lab-scale testing (simulated and actual flue gas) of solid sorbents designed to capture CO_2. The traits tested included the CO_2 capacity, regeneration potential, reactivity to other flue gas constituents, and energy necessary for regeneration. CO_2 capacities ranged from < 1 wt% to > 6 wt%. Most sorbents regenerated completely and were suited for multiple-cycle use. This paper will compare the sorption/regeneration characteristics for several different sorbents and discuss the potential of the technology.

INTRODUCTION

There is great public pressure to reduce emissions of greenhouse gases. Stationary point sources, such as coal-fired power plants, offer one of the most feasible options for significant emission reductions in the foreseeable future. Currently, half of the electricity in the United States is generated using coal, amounting to 320 GW.[1] New generation can be designed for carbon capture and increased efficiency, but the carbon emissions from the conventional coal-fired power plants must be addressed. Post-combustion capture technologies are being developed rapidly in order to meet the carbon management needs of the existing fleet of power plants. These technologies are widely varied in the mechanism of separation and it is expected that a portfolio of carbon capture options will be necessary to address the wide array of coal types, air pollution control systems, and operating conditions.

Solid sorbents are one of the many promising CO_2 capture technologies in the early stages of development. Although CO_2 capture by solid sorbents has yet to be demonstrated on the scale necessary to reduce emissions from power plants, this is not a new technology. For years, solid sorbents designed for CO_2 capture have been used to purify breathing air in confined spaces such as space shuttles and submarines.[2] Potential advantages of solid sorbents over other CO_2 capture options, such as aqueous amines, are as follows:

- Safe material for local environment and low disposal/treatment costs
- Higher CO_2 capacity
- Lower regeneration energy
- Multi-pollutant control

Potential technical hurdles for the use of solid sorbents for CO_2 capture are as follows:

- Feedstock supply
- Movement of material and related attrition
- Thermal energy management

Although solid sorbents are a promising CO_2 capture technology, most evaluations are currently being conducted on the lab-scale using compressed gases. To advance development to the next level, it is important to test sorbents on actual flue gas. ADA-ES has developed sorbents as well as a testing procedure and apparatus that can be used for both lab and field testing. The sorbents discussed in this work include both supported reactants, using amines or carbonates to enhance capture, and untreated adsorbents. All are designed for post-combustion capture using temperature swing for regeneration.

Sorbents can be classified into two general families: those that chemically react with the CO_2, called supported reactants, and those that adsorb or use their molecular structure to screen CO_2 from other gases, called non-reacting adsorbents. For both types of sorbents, the act of separating CO_2 from the flue gas will be exothermic; recovering the CO_2 from the sorbent is endothermic and will require heat input. Budgeting the thermal energy is a top priority when developing an economically feasible full-scale process. Although coal-fired power plants are experienced with solids handling, the design of the contactor must still be developed and optimized for this application.

Chemical sorbents that react with the CO_2 in the flue gas include a support, which usually has a high surface area, with an immobilized amine or other reactant on the surface. The surface area allows for numerous sites for the desired reaction to occur. Examples of commonly used supports are alumina or silica, while common reactants include amines such as polyethylenimine[3,4] or chemicals such as sodium carbonate[5] (Na_2CO_3) which react with CO_2 to form carbamates and bicarbonates. When heated, the reaction will reverse, releasing the CO_2, and often water, which can then be separated from each other during cooling and compression. After this step, the pure CO_2 can be geologically sequestered. While moisture may present a problem for many CO_2 capture options, the moisture in the flue gas stream is necessary for some chemisorption reactions.

Physical adsorbents can separate the CO_2 from the other flue gas constituents, but do not react with it. Instead, they use their cage-like structure to act as molecular sieves or adsorb it onto their surface. These sorbents can be regenerated using a pressure swing or a temperature swing, although the costs associated with pressure swing may be prohibitively high. Physisorbents such as activated carbon and zeolites are non-toxic, and could be relatively inexpensive to manufacture.

DOE laboratories and universities have spearheaded many solid-sorbent development projects geared towards CO_2 capture. This research encompasses a wide range of technical areas, including carbonate chemical sorbents, metal organic frameworks (MOFs), amine grafted zeolites, and supported amine sorbents.[6,7] However, a majority of these projects are currently being conducted on either lab- or bench-scale and will require further support and development before they are commercially viable.[6] Due the to the urgency of addressing CO_2 emissions, it is important that the development of these technologies is accelerated. Testing on actual flue gas is necessary to evaluate and compare different capture options. Therefore, ADA-ES built and operated a lab-scale sorbent screening device to quickly evaluate potential CO_2 sorbents on simulated and actual flue gas. The sorbent key characteristics evaluated during this program were:

1. Working CO_2 capacity (when reported as a percentage): $\frac{100 * mass_{CO_2-removedfromgas}}{mass_{sorbent}}$
2. Regeneration potential: ability of a sorbent to be used repeatedly without any reduction in capacity
3. Poisoning from other flue gas constituents: Decrease in capacity due to SO_2, NO_x, etc.
4. $\Delta T_{capture\text{-}regen}$: The difference between capture and regeneration temperatures

EXPERIMENTAL METHODS

Sorbent Development

The CO_2 sorbents tested during this program can be divided into the two following categories:

- Supported reactants
- Non-reacting adsorbents

Supported reactants included amines (e.g., MEA, MDEA, TEA) or carbonates (Na_2CO_3 and K_2CO_3) supported on an activated carbon. The percentage, by weight, of these chemicals ranged from 1% to 30%. For these sorbents, the activated carbon simply acts as a high surface area support and, ideally, a monolayer of the chemical was added to exterior surface of the carbon.

The non-reacting adsorbents included benchmark commercial activated carbons, as well as new activated carbons designed specifically for CO_2 capture. Initially, untreated commercial granular activated carbons were tested. Although commercial activated carbons are able capture CO_2, the capacity at flue gas temperature and pressure is prohibitively low to be used on the necessary scale. Several different modifications or treatments were used to increase the CO_2 capacity of activated carbon.

All sorbents discussed in this paper were produced either at a University of Denver laboratory or in-house by ADA-Environmental Solutions.

Lab-Scale Sorbent Screening

All testing of the sorbents developed during this program was carried out using the same test fixture. This unit was designed to be used in the laboratory on simulated flue gas as well as in the field on actual flue gas with minimal modifications. The flow rate of the simulated or actual flue gas was approximately 0.3 LPM, and the amount of sorbent tested varied from 1–5 g. The sorbent was held in a fixed bed. Although the team does not expect that a fixed bed represents the final contactor design for a large-scale system, this configuration allowed for fast, efficient lab-scale sorbent screening. Figure 1 is a schematic of the sorbent screening testing unit, while Figure 2 is a picture of the unit. Note that the CO_2 monitor 90% response time was 10 seconds.

Figure 1. Sorbent screening test unit.

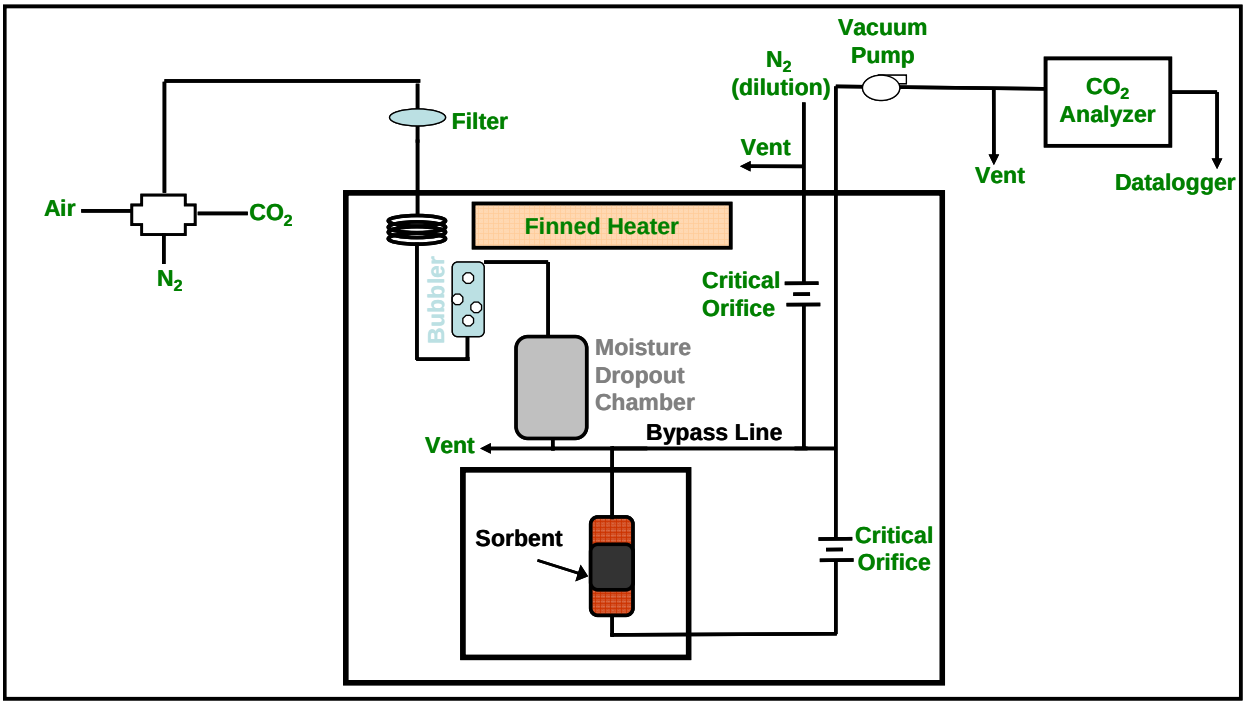


Figure 2. Picture of lab-scale sorbent screening unit.

The steps to carry out the capture/regeneration cycles were the same whether the gas was simulated or actual flue gas. First, the sorbent was placed in the fixed bed. Then, the sorbent was heated to the adsorption temperature. A probe was used to monitor the temperature. When the bed temperature matched the desired capture temperature, the sorbent was flushed with dry N_2 for 10 minutes. Then, the simulated flue gas, composed by mixing compressed air from tanks, was sent through the bypass line, so that it did not contact the sorbent. The composition of the laboratory sample gas, by volume, was approximately 10–14% CO_2, 4% O_2, balance of N_2 and saturated with moisture. When the CO_2 monitor reading was stable and represented the correct concentration of CO_2, the datalogger was enabled and the gas flow was directed through the sorbent. After the CO_2 levels returned to their original levels (i.e., the sorbent was saturated with CO_2) the gas was sent through the bypass, which was the end of the capture step.

In most cases, a temperature swing was used to regenerate the sorbents and desorb the CO_2. First, the bed was heated with no flow. When the probe in the fixed bed indicated the desired desorption temperature, dry N_2 was sent through the bed to flush out the CO_2. Clearly, this does not represent a final desorption process, but was necessary due to the fixed-bed size restrictions and the amount of gas required by the analyzer. In a few cases, the sorbent did not require a temperature swing to be regenerated; when flushed with pure N_2 the zero CO_2 partial pressure was enough to complete regeneration. This was a good indication that the CO_2 was weakly bound to the sorbent.

One key issue that will limit the use of commercial-scale fixed beds for this application is the heat management. Since all the reactions between the sorbents and CO_2 are exothermic, whether physical or chemical, the sorbent will heat up as it reacts with the CO_2. Unfortunately, in most cases the sorbent CO_2 capacity decreases with increasing temperature. Therefore, if the sorbent is allowed to heat during the capture step of the cycle, the test results will show a reduced amount of CO_2 capture. Similarly, if the sorbent is allowed to cool due to the endothermic desorption, all the CO_2 may not be released. To control the temperature of the sorbent during these lab-scale tests, the flow rate of the gas through the fixed bed was kept high proportional to the amount of sorbent in the bed. Therefore, the sample gas during capture maintained lower temperatures, while the hot purge gas maintained higher temperatures during regeneration. However, by using a high ratio of gas to sorbent, the breakthrough curves were affected. Since the gas flow rate is high, the residence time is low (~1 s) and some CO_2 may pass through the fixed bed unreacted, even when adsorption sites are available. Therefore, the percent removal obtained during laboratory tests does not necessarily represent the total removal that can be realized by the sorbents. In fact, it should be considered a minimum of achievable percent removal.

Simulated Flue Gas

Figure 1 is a schematic of the sorbent screening unit set up to use compressed gases to simulate flue gas. During in-house testing, N_2, O_2, CO_2, trace materials in air, and moisture were the included in the simulated flue gas. Other compounds, such as SO_2, NO_x, and Hg that are present in actual flue gas were not included for this portion of the testing. During capture, the gas temperature was approximately 55–60 ºC and saturated with moisture, based on conditions downstream of a wet scrubber. To determine the effect of temperature on the CO_2 capacity of the sorbents, some were also tested at room temperature. The regeneration temperature varied between sorbents, but was generally within the range of 55–150 º C.

Actual Flue Gas

In order to accelerate development, the effect of flue gas constituents on the sorbents' performance must be known. By completing up to 10 multiple capture/regeneration cycles with the same sorbent, serious poisoning issues can be identified and addressed. Table 1 lists the key characteristics of the flue gas used for sorbent screening.

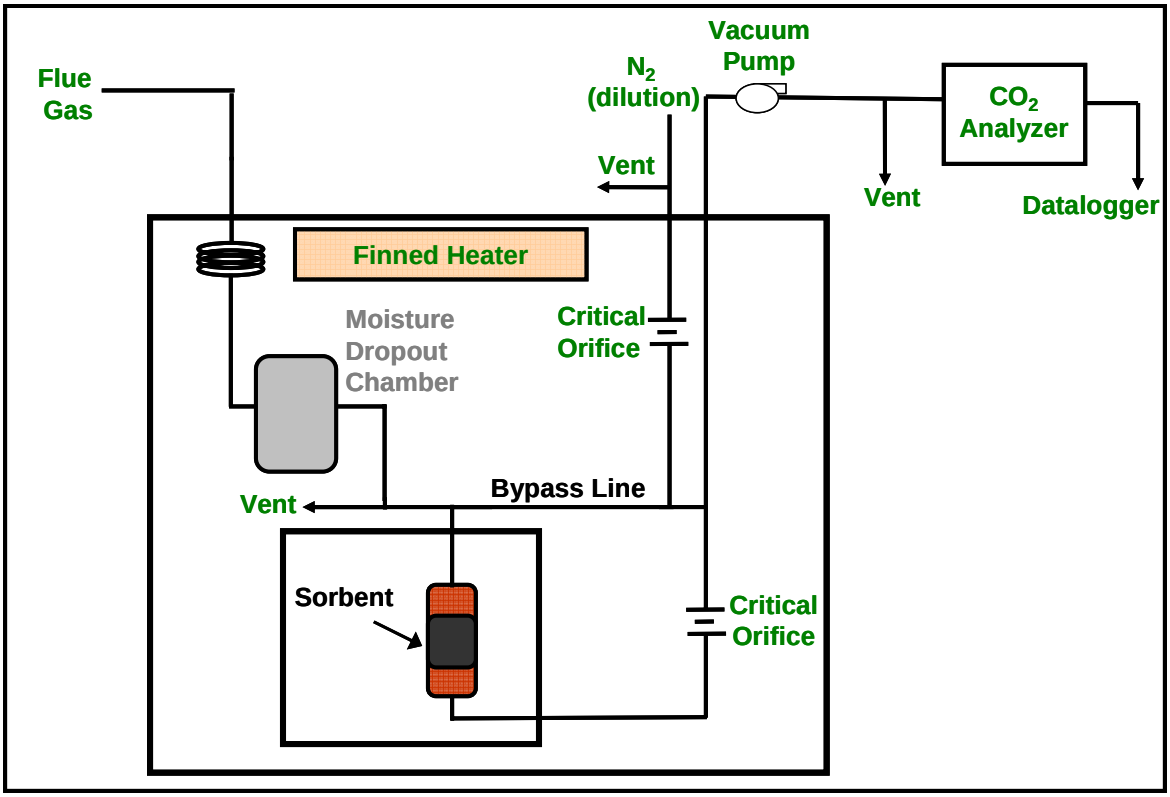
Table 1. Key flue gas characteristics for field tests.

Temperature (ºF)	140
CO_2 Concentration (%)	10–12
Moisture	Saturated

The field testing location was downstream of a wet scrubber for SO_2 removal at a plant firing lignite coal. Because the sample port was downstream of the scrubber, the SO_2 levels were low, the temperature was reduced, and the gas stream was saturated with moisture.

The same apparatus was used for lab and field sorbent screening. However, a few minor modifications were necessary. Figure 3 is a schematic of the sorbent screening unit adapted for field testing. First, only a single gas stream, which was pulled from a sample port, was needed versus the several gas streams used from the compressed bottles in the laboratory. Also, the bubbler was unnecessary. The experimental procedure was the same for both laboratory and field testing.

Figure 3. Schematic of sorbent screening testing unit modified for field tests.



RESULTS AND DISCUSSION

The four key sorbent characteristics evaluated during this project were:

1. Working CO_2 capacity
2. Regeneration potential
3. Resistance to poisoning from other flue gas constituents
4. $\Delta T_{capture\text{-}regen}$

During laboratory testing, the working capacity, regeneration potential (up to five cycles), and $\Delta T_{capture\text{-}regen}$ were evaluated for > 40 sorbents. During field tests, all four key properties were evaluated for eight of the most promising sorbents.

Laboratory Tests

Since it is not possible to discuss each of the sorbents produced and tested within the scope of this paper, they have been listed by categories in Table 2, and will be grouped as such in the following discussion. From Table 2, it is clear that a wide range of performance was observed.

Table 2. Summary of laboratory test results.

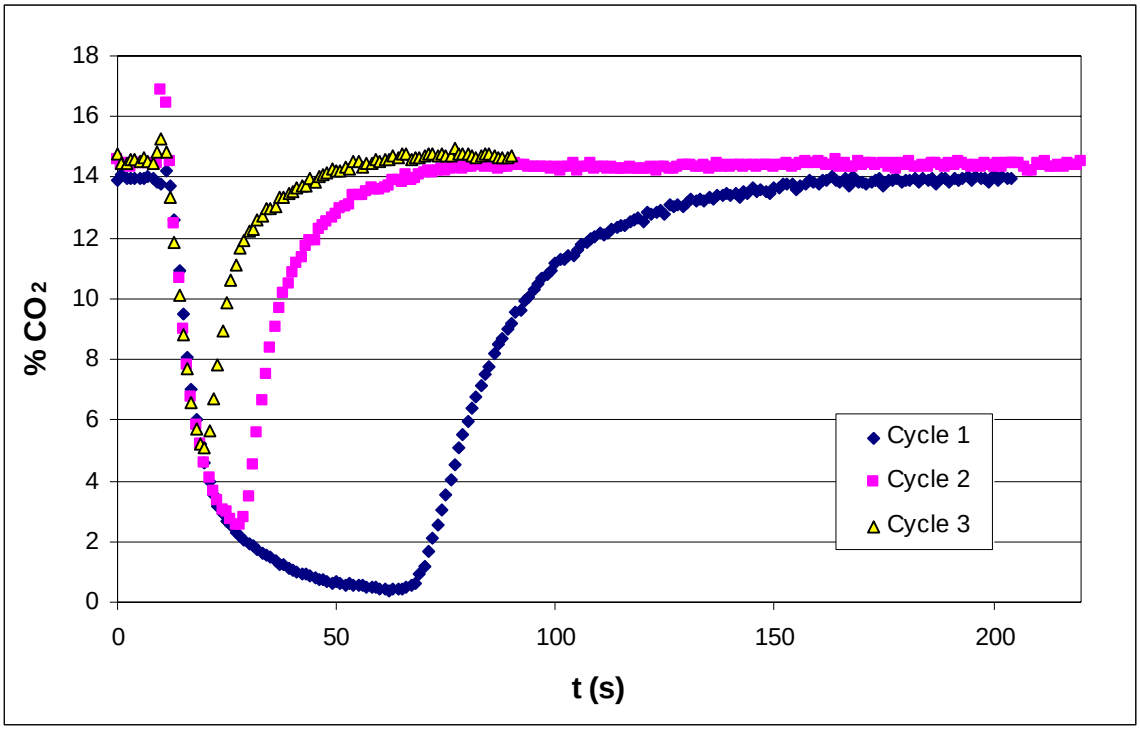
Sorbent Description	**$T_{capture}$ (ºC)**	**T_{regen} (ºC)**	**$\Delta T_{capt\text{-}regen}$ (ºC)**	**Complete Regen (Y or N)**	**Working Capacity (wt%)**
Commercial activated carbon	70	115	45	Y	0.7
Single amine on AC	22	100–120	78–98	N	0.2–3.2
Single amine on AC	75	100–120	45–25	N	0.4–2.0
Combination of Amines or Amine and Glycol on AC	22	100–120	78–98	N	1.2–6.1
Combination of Amines or Amine and Glycol on AC	75	100–120	25–45	N	0.5–2.0
Carbonates on AC	22	100	78	Y	1.2
Carbonates on AC	55	55–75	120–150	Y	0.7–3.2
Chemically-Activated Carbon	55	55–100	0–45	Y	0.2–1.2

Single or Combination of Amines and/or Glycols on Activated Carbon

Of any of the types of sorbents listed in Table 2, the amines supported on activated carbon demonstrated the highest capacity. At average flue gas temperatures downstream of a wet scrubber (55 ºC), the increase in temperature required for desorption, $\Delta T_{capture\text{-}regen}$, was between 45–65 ºC. Also, if the amount of amine on the sorbent is increased, it is believed that the working CO_2 capacity will increase as well, until the reaction becomes diffusion limited. However, the amines supported on activated carbon did not regenerate well. Figure 4 shows the adsorption profiles for the first three cycles of one such sorbent. The capacity of the sorbent decreased dramatically between each cycle. After this test was completed, the sorbent bed was weighed—the amine compound had evaporated. It is possible that decreasing the vacuum from

the pump feeding the CO_2 analyzer could reduce this problem. However, considering the final application, it is a high priority that the sorbent be completely stable. Therefore, improving these sorbents would require absorption of the amine into the solid or grafting the amine on the surface; several groups are working in this area[8–10], although in most cases the support is not activated carbon.

Figure 4. Adsorption profiles of an amine on activated carbon.



Carbonates on Activated Carbon

Both sodium carbonate and potassium carbonate are solids at ambient and flue gas temperatures and pressures. However, these substances have low surface area, which limits reaction rate. In addition, if used in a moving or fluidized bed, they could easily suffer from severe attrition problems. Supporting these materials on a substrate, such as activated carbon, addresses these problems.

The supported carbonate sorbents were observed to have CO_2 capacities in the range of 0.7–3.2 wt%. In addition, they were fully regenerable when the regeneration step was carried out at the appropriate temperature. Figure 5 shows the adsorption profiles from the first three cycles of a supported carbonate sorbent. Note that these profiles vary significantly. This can be attributed to the temperature at which the sorbent was regenerated. Table 3 lists the working CO_2 capacity for the three cycles and the regeneration temperature. To recover the entire capacity of this particular sorbent, it must be heated above 140 ºC. (Further evaluation of this sorbent is currently underway.)

Figure 5. Adsorption profiles of carbonate on activated carbon with different regeneration temperatures.

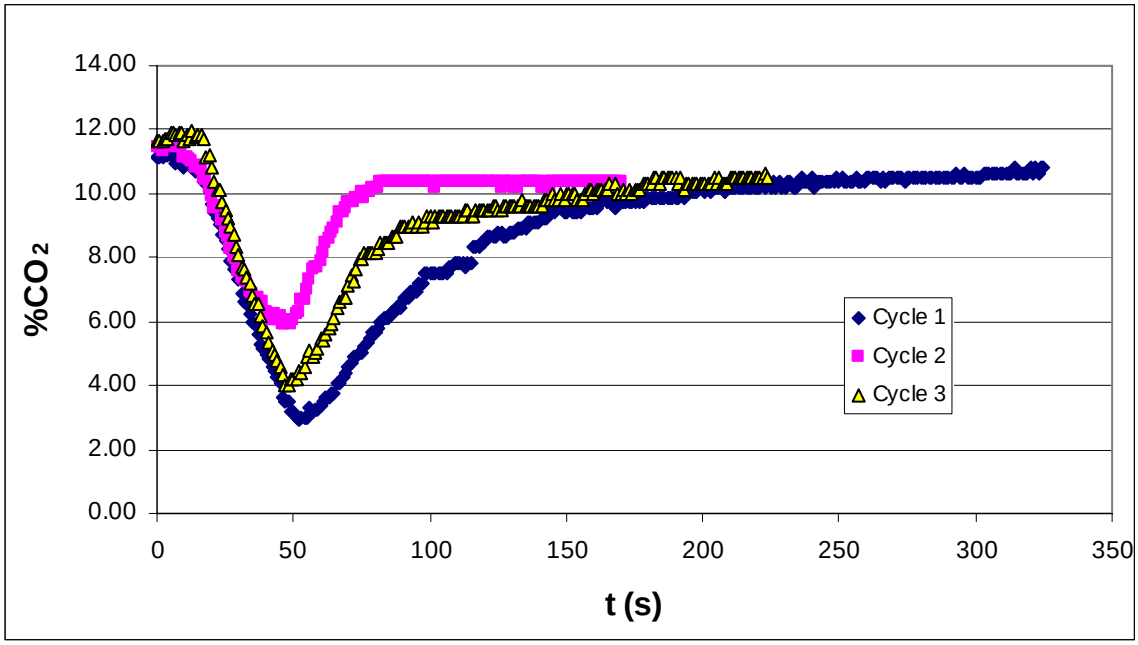


Table 3. Working CO_2 capacity and regeneration temperature of carbonate-based sorbent.

Cycle	T_{regen} (°C)	Working Capacity (wt%)
1	N/A	3.2
2	110	1.4
3	140	2.2

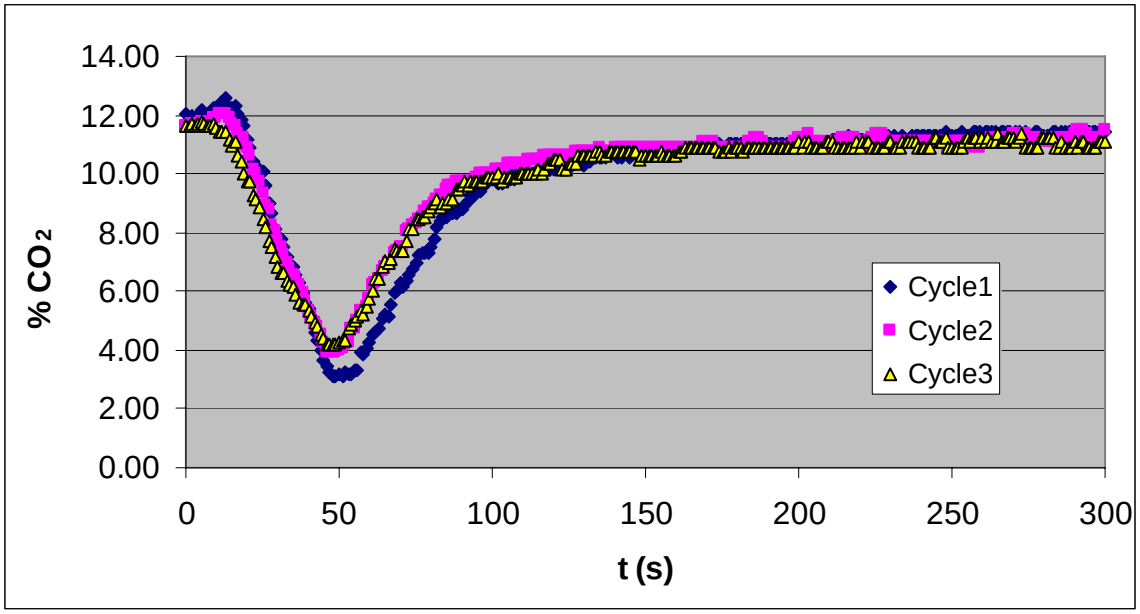
The carbonate-based sorbents show promise, but will require further improvement.

Chemically Activated Carbon

When considering the entire CO_2 capture process, heat management is a critical factor. The heat of reaction for amines is approximately -59 kJ/mol$_{CO2}$[11] and carbonates can be in the range of -125 kJ/mol$_{CO2}$.[12] Although activated carbon has a lower capacity than some supported chemisorbents, the heat of reaction is only ~ -3kJ/mol (at 25 ºC and 1 bar).[13,14] Therefore, removing CO_2 from activated carbon can require far less energy than other sorbents or solvents.

Figure 6 shows the adsorption profiles for the first three cycles of one chemically activated carbon. The difference between the curves is within the experimental error. No significant reduction in CO_2 working capacity was observed, although it is important to run many more cycles to fully assess the regeneration potential. Although chemical activation nearly doubled the capacity above that of a steam-activated carbon, the capacity will need to be increased further to improve the process economics and feasibility. However, early results are promising.

Figure 6. Adsorption profiles for first three cycles of a chemically activated carbon.



Field Tests

Based on the laboratory tests, the most promising sorbents were then tested on actual flue gas, downstream of a wet scrubber. Figure 7 shows the adsorption curves for a chemically modified sorbent on the flue gas slipstream. This figure shows up to 50% CO_2 removal. Similar to the laboratory tests, a vacuum pump was used to pull the flue gas through the sample line and through the fixed bed—the amount of sorbent that could be tested was limited by the pressure drop. Therefore, the percent removal obtained during field tests does not represent the actual total removal that can be reached by the particular sorbents. In fact, it should be considered a minimum of achievable percent removal.

Figure 7. Adsorption curves on a flue gas slipstream.

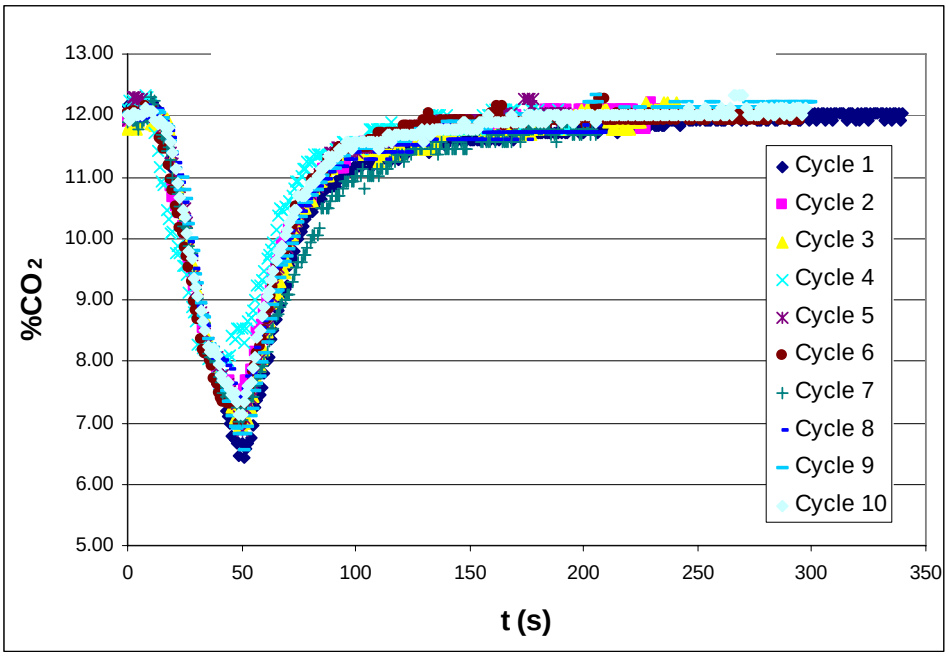


Figure 8 shows the multiple desorption curves for the same sorbent that was used to generate the data shown in Figure 7. The desorption of CO_2 was accomplished by flushing the sorbent with dry N_2 at the same temperature as the adsorption. No temperature change was required due to the weakness of the bonds between the sorbent and the CO_2. Although this is not considered a feasible method for desorption in a commercial CO_2 capture system, it was simple and informative during lab-scale analysis. In larger-scale testing, the desorption step will be carried out differently, since the system design will be one of the main focus points.

Figure 8. Desorption curves from slipstream testing.

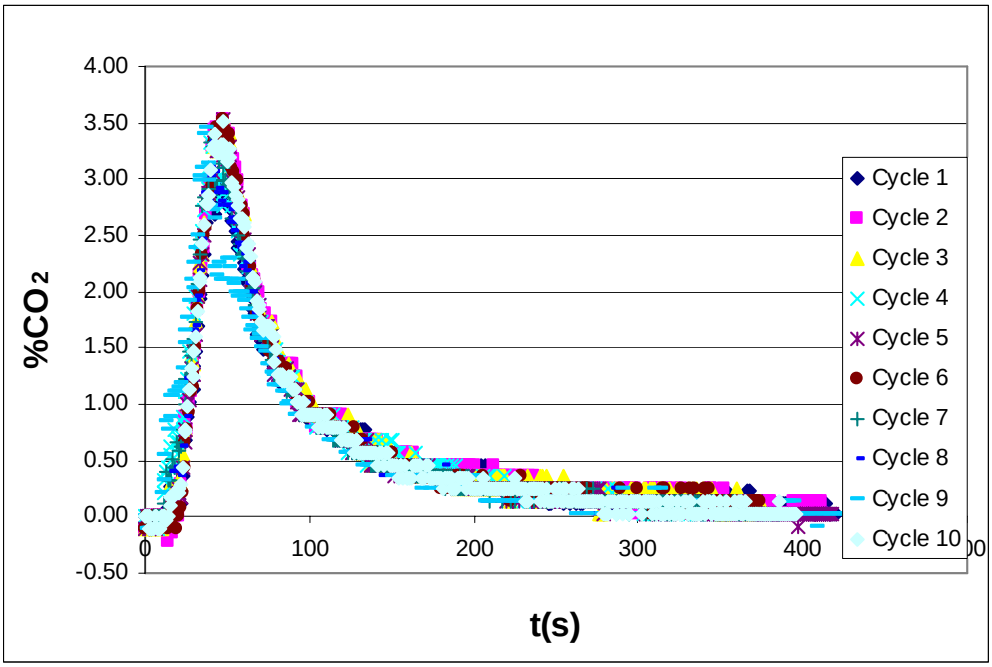
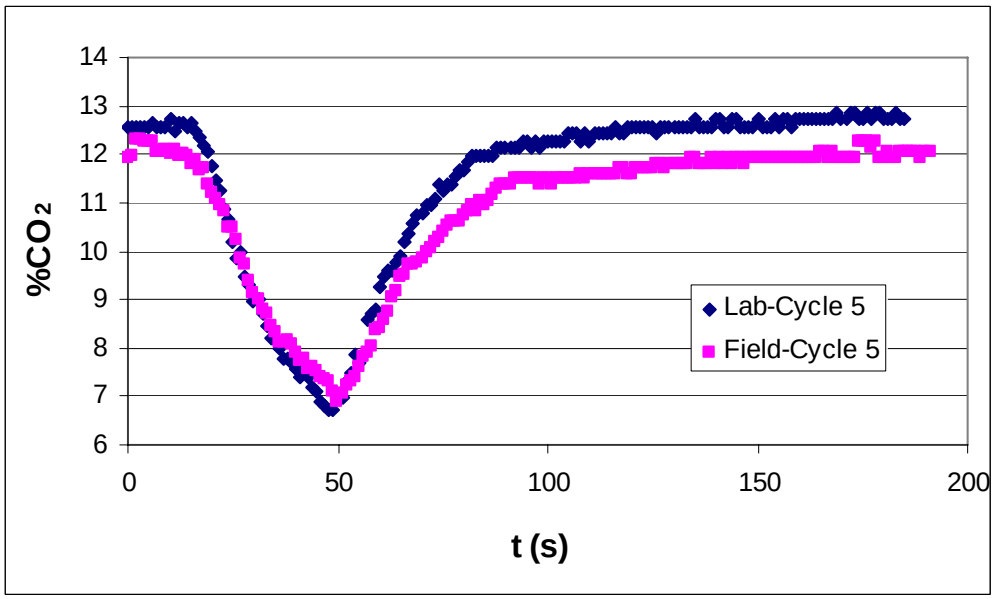


Figure 9 shows a comparison between laboratory testing and slipstream testing for the 5th cycle in the adsorption/regeneration process. Clearly, the ADA-ES laboratory test fixture produced results that closely predict the actual flue gas results. In these laboratory tests, SO_2 was not included in the simulated flue gas. In the flue gas slipstream, there was approximately 50 ppm SO_2. This data shows that the sorbent is essentially unaffected by SO_2 at these concentrations within the number of cycles tested during this program.

Figure 9. Comparison of laboratory and field testing of an activated carbon.



SUMMARY

Retrofitting the existing fleet of coal-fired power plants for carbon capture and sequestration is one of the most important opportunities for a significant reduction in CO_2 emissions in the U.S. Among the many different post-combustions technologies being studied and developed, solid sorbents have emerged as one promising options. This paper discussed results from lab-scale tests on activated carbon-based solid sorbents. Two general families of sorbents were evaluated. The supported reactants family included amines and carbonates on activated carbon, while the non-reacting adsorbents included several different activated carbons.

Supported amines showed good CO_2 capacity, but poor regeneration potential. Carbonates supported on activated carbon had good regeneration potential, but required a significant temperature swing to desorb the reacted CO_2. Finally, chemically activated carbons showed complete regeneration, and required a small temperature swing to desorb the CO_2. In addition, during field tests, these sorbents showed no poisoning from flue gas constituents. Little difference was observed between the CO_2 capture on laboratory simulated flue gas and actual flue gas. While many characteristics of these sorbents are promising, it will be important to further improve the capacity of the chemically activated carbons before they can be applied to a process at power-plant scales.

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Dr. Don Stedman and Nick Holubowitch at the University of Denver Chemistry Department developed and tested many of the sorbents discussed in this paper. Their hard work and dedication made it possible to quickly screen through a wide array of sorbents.

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KEY WORDS

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