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ABSTRACT

ADA-ES has completed an extensive sorbent screening program funded primarily through DOE NETL cooperative agreement DE-NT0005649 with support from EPRI and industry cost-share participants. Tests were completed on simulated and actual flue gas. The overall project objective is to address the viability and accelerate development of a solid-based post-combustion CO_2 capture technology that can be retrofit to the existing fleet of coal-fired power plants. An important component of the viability assessment was to evaluate the state of development of sorbents and measure key performance characteristics under realistic operating conditions.

The first step of the sorbent screening program was to evaluate a large number of materials using simulated flue gas in an automated fixed bed system. The results were used to select the most promising materials for evaluation using the same laboratory-scale piece of equipment during field tests. All the laboratory results were used to select the most promising sorbents that were produced in over 500 lb quantities for testing on actual flue gas using a unique 1 kW pilot system.

Supported amine sorbents consist of various types of amines supported on inert substrates. In general these materials exhibited high CO_2 capacities under simulated flue gas conditions (up to 14 wt%). Many of these materials, but not all, demonstrated cyclic stability over many adsorption/regeneration cycles. For this reason, several supported amines were selected for laboratory-scale fixed bed testing on actual flue gas. The laboratory-scale fixed bed field tests in conjunction with specialized laboratory testing, revealed that SO_2 can permanently degrade the supported amine sorbents. In addition, NO_2 can also partially degrade the sorbents, while NO does not cause a concern for these materials.

Several different carbon-based sorbents were also evaluated. These materials also demonstrated the ability to remove CO_2 from simulated and actual flue gas at the laboratory scale. However, the CO_2 capacities of these materials were much lower than that of supported amine sorbents, usually <1.2 wt%. An advantage of carbon-based sorbents is that many of these sorbents demonstrated cyclic stability on simulated and actual flue gas.

Several zeolites were also evaluated on simulated flue gas using the fixed bed apparatus and a single zeolite was evaluated on actual flue gas using the same test equipment. On dry flue gas zeolites are able to separate CO_2 effectively. However, in the presence of moisture these materials preferentially adsorb H_2O over CO_2, making them ineffective for the purpose of post-combustion CO_2 capture.

Prior to the initiation of DE-NT0005649 several supported carbonates were produced and evaluated. The materials were not optimized, but allowed for some screening and evaluation to be completed in the laboratory (no field testing). The greatest CO_2 capacity measured for one of the ADA-ES supported carbonates was approximately 3.2 wt%. With such a low CO_2 capacity and such a high heat of reaction, the calculated regeneration energy for such materials was prohibitively high.

Several hydrotalcites were included in the sorbent screening program. These materials were only evaluated on simulated flue gas in the laboratory. The fixed bed tests were conducted without any study of the optimal adsorption and regeneration temperatures. Based on the hydrotalcites evaluated, there may be some applicability for post-combustion CO_2 capture, although these materials may be useful at temperatures greater than what was used for the simulated flue gas in this project.

Based on the laboratory screening four supported amine sorbents were selected for evaluation at the 1 kW scale at two different field sites. The first host site was Luminant's Martin Lake Steam Electric Station and the second host site was Xcel Energy's Sherburne County Generating Station (Sherco). The 1 kW pilot concept was provided by Southern Company.

At Martin Lake the 1 kW pilot was operated in continuous mode as well as batch mode. In batch mode sorbent R was able to remove up to 90% CO_2 for several cycles. Approximately 50% of the total removal occurred in the first three feet of the transport reactor used for adsorption. Several supported amine sorbents were selected for evaluation using the 1 kW pilot at Sherco. Sorbent AX was operated in batch mode and performed similarly to sorbent R at Martin Lake (i.e. could achieve up to 90% removal when given adequate regeneration time). For sorbent R used in continuous mode, the CO_2 removal was initially high, but decreased to lower removal levels at steady state. The lack of continuous removal was due primarily to the combination of a co-current adsorption system with a fluidized bed for regeneration, a combination which did not provide an adequate driving force for regeneration. In addition, because sorbent R consisted of a polymeric amine coated on a silica substrate, it was believed that the 50% amine loaded resulted in mass diffusion limitations related to the CO_2 uptake rate. Therefore, sorbent BN was also tested, which was not expected to be subject to the same mass diffusion limitations. When sorbent BN was used in continuous mode the steady state CO_2 removal was approximately double that of sorbent R, which highlighted the importance of sorbents without kinetic limitations.

The sorbent screening program conducted under DE-NT0005649 and other funding was more extensive and inclusive than most other sorbent evaluation programs in the world. Based on the program results, supported amine sorbents offer the potential to significantly reduce the energy penalty associated with post-combustion CO_2 capture if they can be used in a system/process that can take advantage of their beneficial properties. With further development it is possible that carbon-based sorbents may also be useful for this application. Future work in the area of CO_2 capture must focus on 1) identifying processes/reactors that are optimal for this application and 2) identifying the sorbent physical properties required to operate in such reactors. Based on this stage of testing, it is concluded that a temperature swing sorbent-based process for post-combustion CO_2 capture can offer viability and energy savings, but continued support for development will be required.

Table of Contents

1.0 EXECUTIVE SUMMARY 1

2.0 INTRODUCTION 4

3.0 APPROACH.....6

3.1 Laboratory-Scale Screening..... 6

3.1.1 Fixed Bed 6

3.1.2 Thermogravimetric Analyzer 14

3.1.3 Attrition Testing..... 14

3.1.4 Additional Physical Sorbent Properties..... 15

3.2 1 kW Pilot Testing..... 16

4.0 RESULTS AND DISCUSSION.....25

4.1 Laboratory-Scale Screening..... 25

4.1.1 Fixed Bed Testing..... 25

4.1.2 Thermogravimetric Analyzer 45

4.1.3 Attrition Testing..... 48

4.1.4 Additional Physical Sorbent Properties..... 51

4.2 1 kW Pilot Testing..... 53

4.2.1 Host Site 1: Martin Lake..... 53

4.2.2 Host Site 2: Sherco 59

5.0 CONCLUSIONS 65

6.0 DISCLAIMER 68

7.0 REFERENCES.....69

8.0 LIST OF ACRONYMS AND ABBREVIATIONS.....71

APPENDIX A: Sorbent Developer Report 1 72

APPENDIX B: Sorbent Developer Report 2.....73

APPENDIX C: Sorbent Developer Report 3 74

APPENDIX D: Sorbent Developer Report 4 75

APPENDIX E: Jenike & Johanson Sorbent Attrition Testing Report 76

APPENDIX F: Adsorption Research, Inc. Particle Density and Crush Strength Test Report 77

List of Figures

Figure 1: Generic Post-Combustion Temperature Swing Process 4
Figure 2: Schematic of the Sorbent Screening Test Unit 9
Figure 3: Example of an Adsorption Breakthrough Profile 10
Figure 4: Example of a Regeneration Breakthrough Profiles 11
Figure 5: Schematic of Sorbent Screening Test Unit Configured for Field Testing 13
Figure 6: Attrition Testing Equipment Operated by Jenike & Johanson 15
Figure 7: Diagram of 1 kW Pilot CO_2 System 16
Figure 8: 3D Model Sketch and Photo of 1 kW System 18
Figure 9: Sketch of Gas Sampling Locations 19
Figure 10: Sketch of Temperature Measurement Locations 19
Figure 11: Sketch of Pressure Measurement Locations 20
Figure 12: Picture of the 1 kW Pilot Installed at Martin Lake 21
Figure 13: Picture of 1 kW Pilot Installed at Sherco 22
Figure 14: 1 kW Pilot with Theoretical Isotherms 23
Figure 15: Select Supported Amine Adsorption Profiles 26
Figure 16a: Theoretical Regeneration Energy of Supported Amine Sorbents 27
Figure 16b: Theoretical Regeneration Energy of Supported Amine Sorbents 27
Figure 17: Sorbent CU Laboratory Adsorption Profiles 28
Figure 18: First and Second Generation Supported Amine Clay-Based Sorbent 29
Figure 19: Sorbent CQ Laboratory Adsorption Profiles 29
Figure 20: Sorbent CE Laboratory Total CO_2 Capacities 30
Figure 21: CO_2 Capacity versus Cycle Number for 100 ppm SO_2, 100 ppm NO_2, and 100 ppm NO 31
Figure 22: Theoretical Regeneration Energies for Carbon-Based Sorbents 32
Figure 23: Sorbent AM Laboratory Adsorption Profiles 33
Figure 24: Theoretical Regeneration Energies for Several Zeolites 34
Figure 25: Sorbent J Laboratory Adsorption Profiles 35
Figure 26: Theoretical Regeneration Energies for Several Hydrotalcites 36
Figure 27: Sorbent DM Laboratory Total CO_2 Capacities 37
Figure 28: Sorbent BR Field CO_2 Capacity 39
Figure 29: Sorbent BR Field Adsorption Profiles 40

Figure 30: Sorbent AY Field CO_2 Capacity 41
Figure 31: Sherco Sorbent R Breakthrough Adsorption Profiles 41
Figure 32: Sherco Sorbent AX Adsorption Breakthrough Profiles 42
Figure 33: Sherco Sorbent F Adsorption Breakthrough Profiles 43
Figure 34: Sherco Sorbent BN Adsorption Breakthrough Profiles 44
Figure 35: Crushed and Beaded Sorbent BN Breakthrough Profiles.....45
Figure 36: Sorbent CE Isotherms.....46
Figure 37: Sorbent BN Isotherms.....47
Figure 38: CARiACT® G10 granular 48
Figure 39: CARiACT® Q10.....49
Figure 40: Sorbent R Substrate Particle Size Distribution.....50
Figure 41: Sorbent X Particle Size Distribution 51
Figure 42: Sorbent BN Crush Strength Analysis.....53
Figure 43: CO_2 Concentration, CO_2 Removal, and Temperature Information Collected During Parametric Testing of Sorbent R.....54
Figure 44: Outlet CO_2 and CO_2 Removal after Batch Regeneration.....55
Figure 45: CO_2 Concentrations and Removal during Continuous 1kW Testing of Sorbent R 56
Figure 46: CO_2 Concentrations at different locations in the riser 57
Figure 47: CO_2 Concentrations and Removal during Batch 1kW Testing of Sorbent R 58
Figure 48: CO_2 Removal Levels during Batch Operation of Sorbent R.....58
Figure 49: Summary of Sorbent Screening Results.....59
Figure 50: Maximum CO_2 Removal for Sorbent R at Martin Lake and Sorbent AX at Sherco.....60
Figure 51: 1 kW Pilot Evaluation of Sorbent R at Sherco 61
Figure 52: 1 kW Pilot Evaluation of Sorbent BN at Sherco 63

List of Tables

Table 1: Key flue gas characteristics for field tests 13

Table 2: TGA Operating Conditions.....14

Table 3: CO_2 Capacity Measured During Field Tests.....38

1.0 EXECUTIVE SUMMARY

ADA-ES has completed an extensive sorbent screening program funded primarily through DOE NETL cooperative agreement DE-NT0005649 with support from EPRI and industry cost-share participants. Tests were completed on simulated and actual flue gas. The overall project objective is to address the viability and accelerate development of a solid-based post-combustion CO_2 capture technology that can be retrofit to the existing fleet of coal-fired power plants. An important component of the viability assessment was to evaluate the state of development of sorbents and measure key performance characteristics under realistic operating conditions.

The first step of the sorbent screening program was to evaluate a large number of materials using simulated flue gas in an automated fixed bed system. The results were used to select the most promising materials for evaluation using the same laboratory-scale piece of equipment during field tests. All the laboratory results were used to select the most promising sorbents that were produced in over 500 lb quantities for testing on actual flue gas using a unique 1 kW pilot system.

The laboratory-scale fixed bed apparatus and simulated flue gas were used to screen the following types and quantities of sorbents during initial evaluation:

- 87 supported amines
- 31 carbon based materials
- 6 zeolites
- 7 supported carbonates (evaluated under separate funding)
- 10 hydrotalcites

Supported amine sorbents consist of various types of amines supported on inert substrates. There is a great deal of ongoing research to invent and improve these materials. In general these materials exhibited high CO_2 capacities under simulated flue gas conditions (up to 14 wt%). Many of these materials, but not all, demonstrated cyclic stability over many adsorption/regeneration cycles. For this reason, several supported amines were selected for laboratory-scale fixed bed testing on actual flue gas. The laboratory-scale fixed bed field tests in conjunction with specialized laboratory testing, revealed that SO_2 can permanently degrade the supported amine sorbents. In addition, NO_2 can also partially degrade the sorbents, while NO does not cause a concern for these materials.

Several different carbon-based CO_2 sorbents were also evaluated. These materials also demonstrated the ability to remove CO_2 from simulated and actual flue gas at the laboratory scale. However, the CO_2 capacities of these materials were much lower than that of supported amine sorbents, usually <1.2 wt%. An advantage of carbon-based sorbents is that many of these sorbents demonstrated cyclic stability on simulated and actual flue gas. They were much more resistant to poisoning and degradation from flue gas constituents compared to supported amines. If the CO_2 capacity for carbon-based sorbents is improved and selectivity is quantified, it is possible that a process can be developed using carbon-based sorbents that will decrease the regeneration energy penalty versus aqueous MEA.

Several zeolites were also evaluated on simulated flue gas using the fixed bed apparatus and a single zeolite was evaluated on actual flue gas using the same test equipment. On dry flue gas zeolites are able to separate CO_2 effectively. However, in the presence of moisture these materials preferentially adsorb H_2O over CO_2, making them ineffective for the purpose of post-combustion CO_2 capture.

Prior to the initiation of DE-NT0005649 several supported carbonates were produced by ADA-ES and their breakthrough curves were measured. The materials produced and evaluated by ADA-ES were not optimized, but allowed for some screening and evaluation to be completed in the laboratory (no field testing). The greatest CO_2 capacity measured for one of the ADA-ES supported carbonates was approximately 3.2 wt%. The heat of reaction for carbonates is significantly higher than that of other materials (i.e. approximately -130 kJ/mol for regeneration of sodium carbonate versus -60 kJ/mol for supported amines). Using this CO_2 capacity to calculate the theoretical regeneration energy, and assuming a sorbent specific heat of 1.0 kJ/kg·K, the theoretical regeneration energy was approximately 5000 kJ/kg CO_2. Since this was significantly greater than the benchmark MEA system, and no other materials were supplied to the program by other sorbent developers, supported carbonates were not pursued further.

Several hydrotalcites were included in the sorbent screening program. These materials were only evaluated on simulated flue gas in the laboratory. The fixed bed tests were conducted without any study of the optimal adsorption and regeneration temperatures. Based on the hydrotalcites evaluated, there may be some applicability for post-combustion CO_2 capture, although these materials may be useful at temperatures greater than what was used for the simulated flue gas in this project.

Based on the laboratory screening four supported amine sorbents were selected for evaluation at the 1 kW scale at two different field sites. The first host site was Luminant's Martin Lake Steam Electric Station and the second host site was Xcel Energy's Sherburne County Generating Station (Sherco). The 1 kW pilot concept was provided by Southern Company. Although the system did not represent a viable option for a commercial CO_2 capture process for the sorbents evaluate under the program, it was useful to compare the CO_2 removal properties of several different supported amine sorbents on actual flue gas.

The equipment operation was first successfully demonstrated at Martin Lake using sand as a surrogate for sorbent. Then sorbent R was evaluated at Martin Lake. The 1 kW pilot was operated in continuous mode as well as batch mode. In batch mode sorbent R was able to remove up to 90% CO_2 for several cycles. Approximately 50% of the total removal occurred in the first three feet of the adsorption reactor, which was a transport reactor.

Several supported amine sorbents were selected for evaluation using the 1 kW pilot at Sherco. Sorbent AX was operated in batch mode and performed similarly to sorbent R at Martin Lake (i.e. could achieve up to 90% removal when given adequate regeneration time). For sorbent R used in continuous mode, the CO_2 removal was initially high, but decreased to lower removal levels at steady state. The lack of continuous removal was due primarily to the combination of a co-current adsorption system with a fluidized bed for regeneration, a combination which did not provide an adequate driving force for regeneration. In addition, because sorbent R consisted of a polymeric amine coated on a silica substrate, it was believed that the 50% amine loaded resulted

in mass diffusion limitations related to the CO_2 uptake rate. Therefore, sorbent BN was also tested, which was not expected to be subject to the same mass diffusion limitations. When sorbent BN was used in continuous mode the steady state CO_2 removal was approximately double that of sorbent R, which highlighted the importance of sorbents without kinetic limitations.

The sorbent screening program conducted under DE-NT0005649 and other funding was more extensive and inclusive than most other sorbent evaluation programs in the world. Based on the program results, supported amine sorbents offer the potential to significantly reduce the energy penalty associated with post-combustion CO_2 capture if they can be used in a system/process that can take advantage of their beneficial properties. With further development it is possible that carbon-based sorbents may also be useful for this application. Future work in the area of CO_2 capture must focus on 1) identifying processes/reactors that are optimal for this application and 2) identifying the sorbent physical properties required to operate in such reactors. Based on this stage of testing, it is concluded that a temperature swing sorbent-based process for post-combustion CO_2 capture can offer viability and energy savings, but continued support for development will be required.

2.0 INTRODUCTION

Before the industrial revolution, anthropogenic greenhouse gas emissions were negligible. However, it was projected that over 30 billion tons of carbon dioxide were released in 2007.[1] In addition, emissions are expected to grow with increased power consumption of highly populated developing countries. Stationary point sources, such as coal-fired power plants, offer the most promising option for a reduction in carbon dioxide emissions in the near future.

The most important difference between CO_2 and other emissions is the volume at which they are produced. SO_x, NO_x, and mercury concentrations are measured in parts per million (ppm) or parts per billion (ppb) while CO_2 is measured as a percentage of the flue gas. Without any modifications, 10 to 15% of the gas released by coal-fired power plants is CO_2. Each ton of carbon in the coal produces nearly 4 tons of gaseous CO_2. Carbon capture and sequestration (CCS) is the most promising option for reducing CO_2 emissions from coal-fired power plants. Obtaining a pure CO_2 stream is the first step of CCS. After the separation, CCS includes compression of the pure CO_2 and sequestration so that it does not enter the atmosphere.

The vast majority of coal-fired power plants burn pulverized coal in a boiler and are thus referred to as PC plants. Post-combustion capture is one of the few viable options to retrofit such plants. Currently, the most advanced post-combustion capture options are based upon contacting CO_2-laden flue gas with a solvent containing amines or ammonia and regenerating the solvent via a temperature-swing absorption process. A generic sketch of a post-combustion temperature swing system is shown in Figure 1.

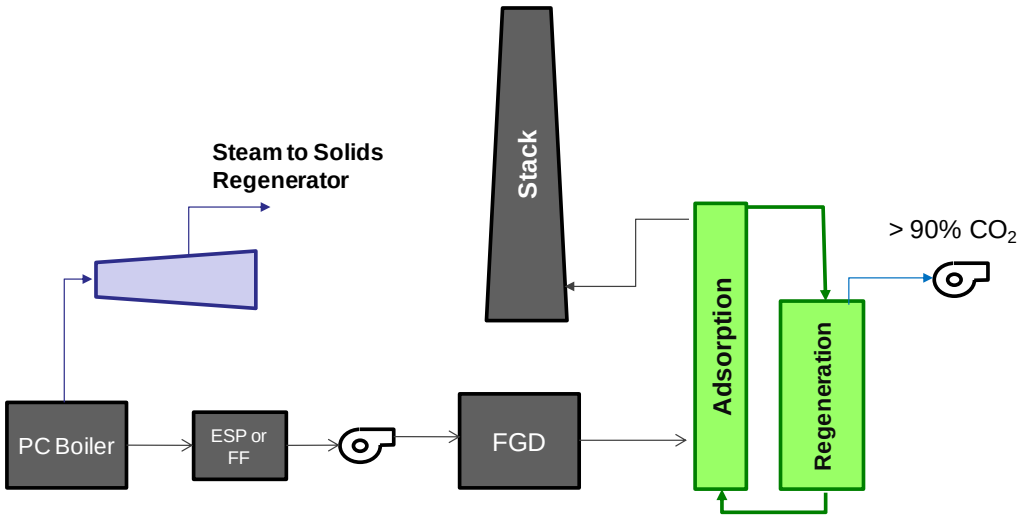

Figure 1: Generic Post-Combustion Temperature Swing Process

The energy penalty associated with solvent-based temperature swing processes is relatively high. For example, recent studies have shown that aqueous monoethanolamine (MEA) for 90% CO_2 capture from a retrofit coal-fired power plant can reduce the thermal efficiency from approximately 35% (HHV basis) to 24.4% and cost $80 per ton CO_2 removed.[3] Most of this cost is associated with the energy penalty incurred when releasing the purified CO_2 in the regeneration step shown in Figure 1. To reduce the costs associated with commercial-scale CCS,

emissions control options must continue to be evaluated and improved. One promising option to reduce the energy penalty and cost associated with the material regeneration is to use solid sorbents; these materials require less energy to heat due to a lower specific heat.

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 or Van der Waals forces to screen CO_2 from other gases, called non-reacting adsorbents. Chemically reacting sorbents usually include an inert, high surface area support, with an immobilized amine or other reactant on the surface. The surface area allows for numerous sites for the desired reaction to occur. Many different types of solid materials for CO_2 capture have been or are currently being investigated including: supported amines[4-10], carbon-based sorbents[11-14], supported carbonates[15,16], zeolites[17], metal organic frameworks (MOFs)[18-22], etc. These materials are being developed and tested at universities, government laboratories, and by private institutions worldwide.

Although, research institutions throughout the world have spearheaded many solid-sorbent development projects geared towards CO_2 capture a majority of these projects are currently being conducted on either lab- or bench-scale and will require further support and development before the materials are commercially viable.[2] In addition, the testing conditions often utilized in such development research are often highly varied, leading to difficulty in comparing material performance. Due to the urgency of addressing CO_2 emissions, it is important that the development of these technologies is accelerated.

Under cooperative agreement DE-NT0005649 supported by the U.S. Department of Energy (DOE), National Energy Technology Laboratory (NETL), the Electric Power Research Institute (EPRI), and several utility companies, ADA Environmental Solutions (ADA-ES) completed a multi-year study to assess the viability of solid sorbents for post-combustion CO_2 capture. This effort included a dual focus approach; both the sorbents and the related process/equipment were evaluated. This report is focused on the procedures, results, and conclusions from the sorbent screening phase of the viability assessment.

3.0 APPROACH

There are many different solid sorbents being developed and assessed for the application of post-combustion CO_2 capture. However, when many different laboratories complete these evaluations, the testing conditions (temperature, moisture level, CO_2 concentration, etc.) are highly varied and often are not representative of the conditions observed at coal-fired power plants. In addition, minimal resources have been dedicated to date to find a process and equipment to utilize these sorbents. During cooperative agreement DE-NT0005649, ADA-ES completed an extensive sorbent screening effort, which included a great deal of fundamental data collected on the laboratory scale. The laboratory-scale data was used to down select the most promising materials for testing at the 1 kW pilot scale. The 1 kW pilot and laboratory-scale field tests were conducted at the two host sites: Luminant's Martin Lake Steam Electric Station and Xcel Energy's Sherburne County Generating Station (Sherco). A description of the experimental apparatus and procedure for all sorbent screening is discussed in the following sections.

3.1 Laboratory-Scale Screening

Sorbent developers throughout the world were invited to contribute materials to be evaluated under the sorbent screening program. Using funding from several different sources, over 140 different sorbents from 23 different sorbent developers were evaluated. The vast majority of the sorbent screening was conducted at the laboratory scale to save time and money. Several different types of laboratory-scale tests were completed. The results were used to draw general conclusions about different types of solid sorbents as well as to down select the most promising materials for testing at increased scales and at power plants where experiments are considerably more expensive.

3.1.1 Fixed Bed

ADA-ES built and operated a lab-scale fixed bed sorbent screening device to quickly evaluate potential CO_2 sorbents on simulated and actual flue gas. Initially the screening device was operated by manually turning valves to change the gas flow. However, it quickly became apparent that to run an adequate number of adsorption/regeneration cycles the system should be automated. The description below was based on the final configuration of the fixed bed system. Included in Appendices A, B, C, and D are four sorbent developer reports that include detailed description of the fixed bed screening device at different stages of the project.

The specialized fixed bed reactor 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. A Programmable Logic Controller (PLC) was employed to completely automate the testing process. With an automated system, a series of adsorption/regeneration cycles were completed with little to no supervision. The flow rate of either simulated or actual flue gas was approximately 400 mL/min, and the amount of sorbent in the reactor was usually in the range of 0.4 to 2.5 g, depending on the material particle size and how much sorbent was provided for testing. The sorbent and flue gas were contacted in a fixed bed through a sequence of temperature controlled lines and electrically controlled valves.

The fixed bed was used to measure the adsorption and regeneration breakthrough curves. The adsorption breakthrough curve was measured using simulated or actual flue gas (field testing

with actual flue gas is described in section 3.1.1.2). The regeneration profile was measured while the sorbent was being heated under a nitrogen (N_2) purge. The sorbent key characteristics evaluated using the fixed bed included:

1. CO_2 capacity (when reported as a weight percentage): $\frac{100 * mass_{CO_2-removedfromgas}}{mass_{sorbent}}$
2. Cyclic stability (i.e. 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
5. Theoretical energy required for regeneration (calculated)

Equation 1 shows a simplified energy balance that can be used to calculate the heat duty during regeneration (i.e. theoretical regeneration energy).

$$\boxed{\frac{Q}{m_c} = \frac{m_e}{m_c} C_e \Delta T + \frac{B}{L} C_s \Delta T + \frac{Q_r}{m_c}} \qquad (1)^{22}$$

Where Q is the regeneration heat input, kJ
m_c is the mass of adsorbed CO_2, kg
m_e is the equipment mass, kg
ΔT is the temperature difference between adsorption and regeneration, °C or K
L is the CO_2 loading, g CO_2/g sorbent
C_e is the equipment specific heat, kJ/kg·K
B is a dimensional conversion term
Q_r is the heat of reaction (positive for endothermic regeneration), kJ/mol CO_2

Due to pressure drop, heat transfer, and mixing concerns, ADA-ES does not believe that a fixed bed reactor will be a viable option beyond the laboratory scale. Therefore, the first term on the right hand side of Equation 1 can be neglected because no equipment heating will be required during regeneration (i.e. the regeneration system will be kept at the regeneration temperature and the sorbent will be moved). The second term on the right hand side of Equation 1 is the energy required to heat the sorbent from the adsorption temperature to the regeneration temperature (i.e. sensible heat). To reduce the energy related to this term, sorbent loading can be increased or the difference between the adsorption and regeneration temperature can be decreased. The second term on the right hand side of Equation 1 is the energy required to overcome the endothermic reaction associated with desorbing the CO_2 from the sorbent (i.e. latent heat of reaction). For physical adsorbents, this term can be an order of magnitude lower than sorbents that chemically react with the CO_2. However, the CO_2 working capacity is also usually significantly lower.

For all the sorbents tested in this program, the theoretical energy required for regeneration was calculated using Equation 1. The purpose of this calculation was to compare different materials and assess their respective viability for use in a commercial-scale CO_2 capture system. The calculation of the theoretical regeneration energy involved the average CO_2 capacity and the median regeneration temperature from the adsorption/regeneration cycles completed with

moisture in the flue gas. Note that from previous reports a liquid MEA CO_2 capture system requires approximately 3600 kJ/kg CO_2 (1550 BTU/lb CO_2).[23] This is not a theoretical regeneration energy, but is an actual regeneration energy based on achievable working capacities and heat integration. Although the sorbents' theoretical regeneration energies are often compared with the actual regeneration energy for MEA, it is important to realize that this is only a high level assessment. If the theoretical regeneration energy for a sorbent is greater than the actual regeneration energy for MEA, it is unlikely that the sorbent can be utilized in a cost-saving process versus the benchmark technology.

The theoretical regeneration energy does not include important contributions to the overall process cost such as pressure drop, CO_2 compression costs, water usage, environmental concerns, etc. In addition, the total CO_2 capacity was used to determine the loading term, L. In reality, the loading should be based on the delta loading term (i.e. working capacity), which was not measured during the fixed bed tests. The calculation of the theoretical regeneration energy was used only to compare different sorbents and down select the most promising materials. Far more intensive studies are required to determine realistic values for the energy penalty of a sorbent used in a commercial-scale temperature swing adsorption (TSA) CO_2 capture process.

3.1.1.1 Simulated Flue Gas

Figure 2 is a schematic of the sorbent screening testing unit when configured for laboratory testing. The CO_2 analyzer was a continuous NDIR sensor with a 90% response time of 10 seconds. This response time should be taken into consideration when examining results. It is probable that the response time of the instrument affected results for materials tested in 0.4 g quantities more extensively than those tested in 2.5 g quantities.

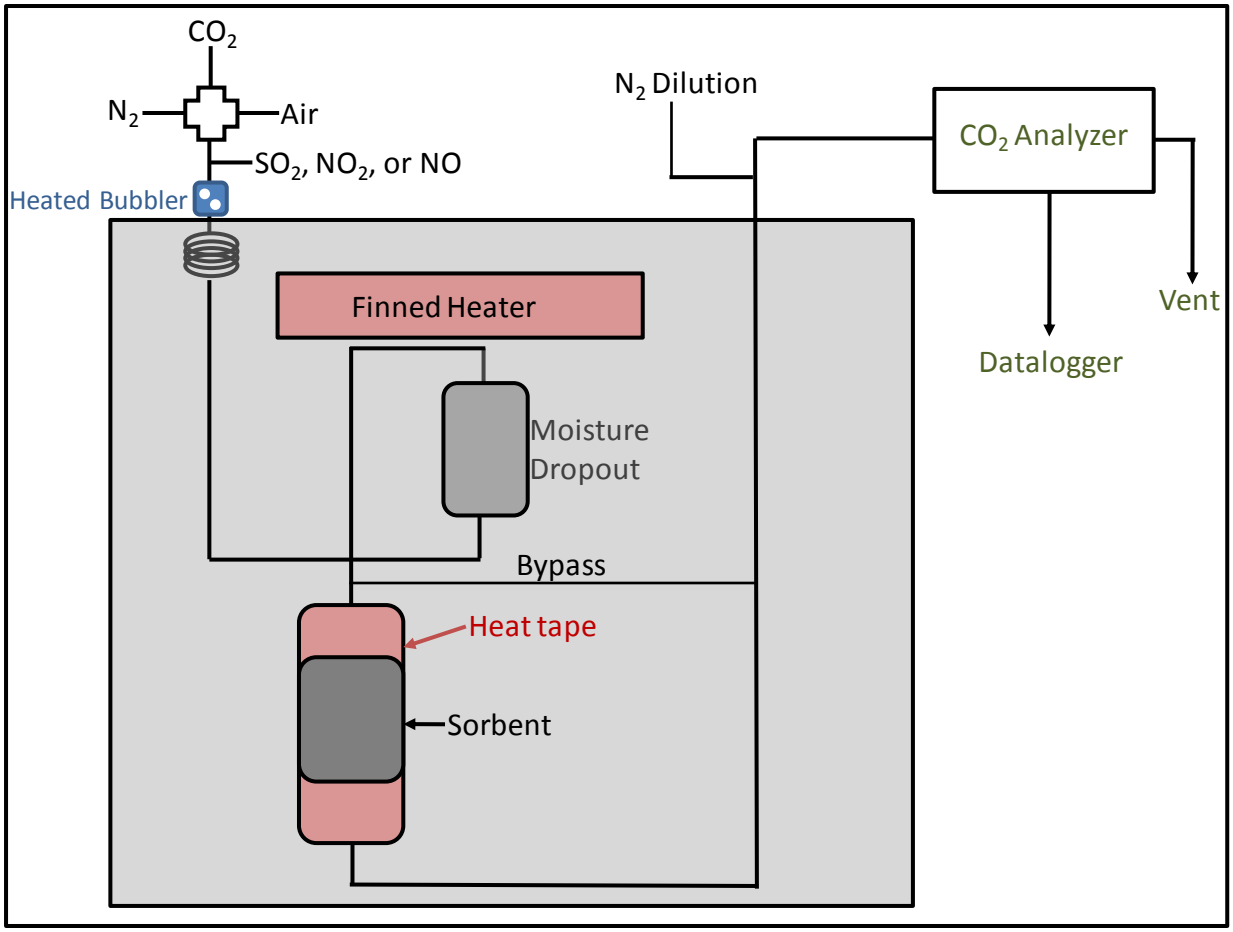

Figure 2: Schematic of the Sorbent Screening Test Unit

After the sorbent was placed into the fixed bed it was heated to an initial flushing temperature. The initial flushing temperature was based on the lowest regeneration temperature. A thermocouple on the outside of the glass fixed bed was used to determine when the bed had reached the desired temperature. When the bed temperature matched the desired adsorption temperature, the sorbent was flushed with dry N_2 for 10 minutes or until no CO_2 was measured in the purge gas stream, whichever was longer. Then the simulated flue gas, an admixture of compressed gases, was sent through the bypass line circumventing the sorbent. The composition of the laboratory sample gas, by volume, was approximately 12% CO_2, 4% O_2, with a balance of N_2. Approximately 9% moisture by volume was added directing the simulated flue gas through a bubbler at a temperature of 40°C. When the CO_2 reading was stabilized at the known CO_2 concentration (i.e. baseline reading), the gas flow was directed through the sorbent. The CO_2 concentration dropped as the sorbent removed the CO_2 and then as this removal decreased the CO_2 concentration would, thus, increase. After the CO_2 levels returned to their original levels (i.e., the sorbent was saturated with CO_2) it marked the end of the adsorption step. Figure 3 is an example of a breakthrough curve for sorbent R (a supported amine sorbent).

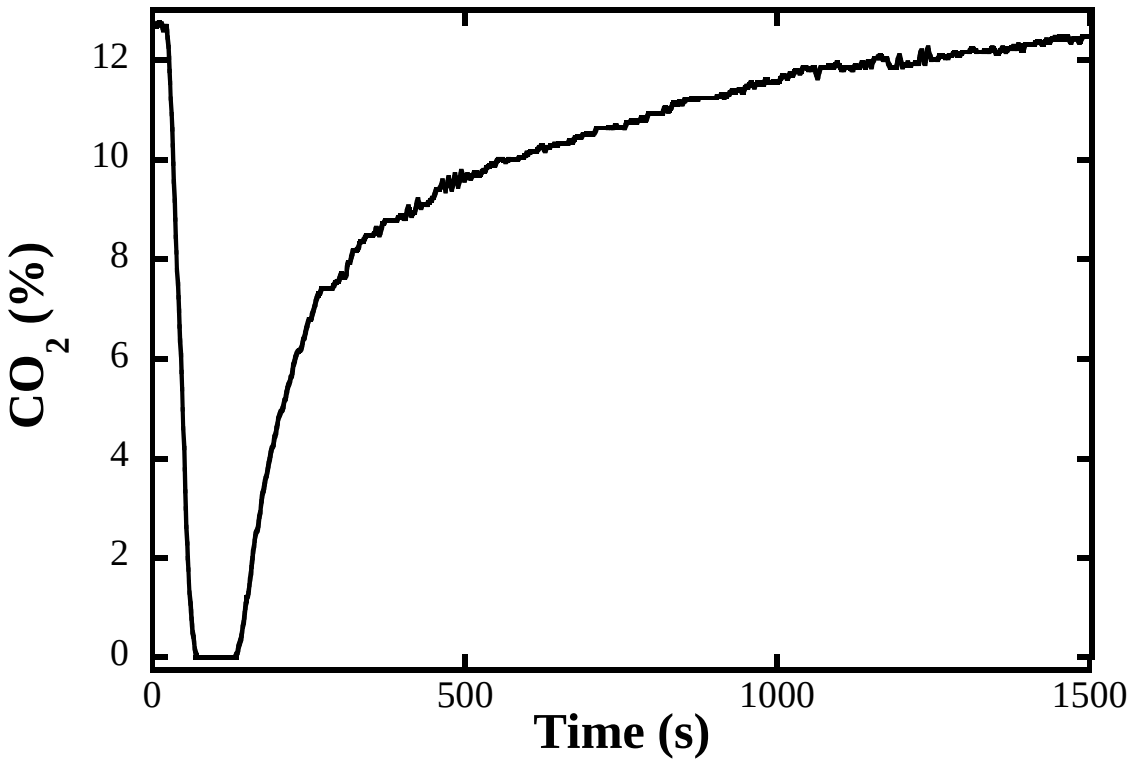

Figure 3: Example of an Adsorption Breakthrough Profile

A temperature swing with a N_2 purge gas was used to regenerate the sorbents and desorb the CO_2. The regeneration purge gas flow rate was the same as that of the flue gas, approximately 300 mL/min. The regeneration step began with the system stopping flue gas flow in order to switch to heated N_2 gas only. While the heated purge gas was flowing through the sorbent, heat tape on the outside of the fixed bed was used to ensure that the sorbent was fully heated to the selected regeneration temperature. Upstream of the reactor the N_2 purge gas was directed through a bubbler separate from the one used for adsorption. This bubbler was primarily used at room temperature to add less than 2% by volume moisture to the regeneration gas. Figure 4 is an example of a regeneration breakthrough curve measured for sorbent R.

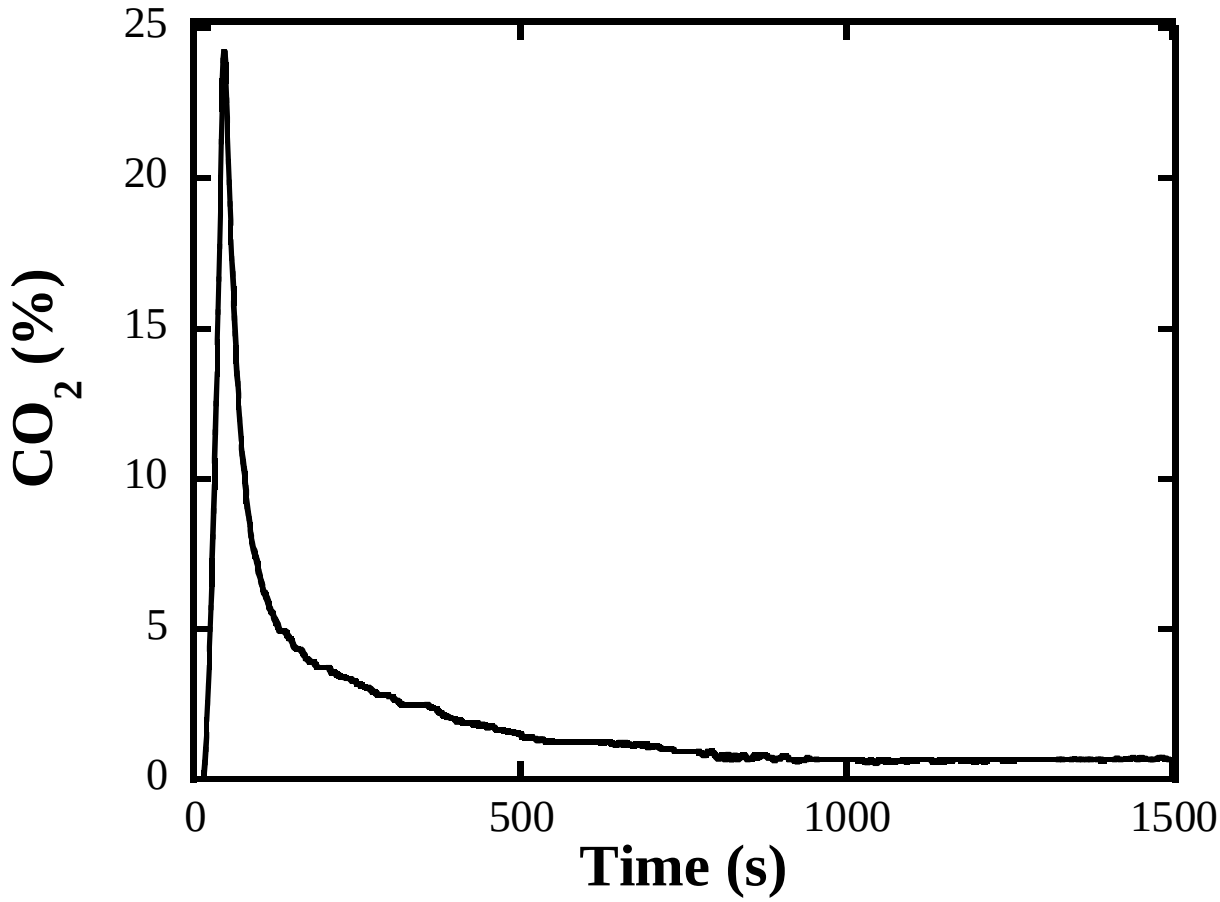

Figure 4: Example of a Regeneration Breakthrough Profiles

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 temperature increases as it reacts with the CO_2. Because the sorbent CO_2 capacity decreases with increasing temperature, the test results will show a reduced amount of CO_2 capture if the sorbent temperature is allowed to increase. 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 at high proportions to the amount of sorbent in the bed. Therefore, the sample gas during adsorption was maintained at a lower temperature, while the hot purge gas was maintained at a higher temperature during regeneration. However, by using a high ratio of gas to sorbent, the breakthrough curves are affected. Since the gas flow rate was high, the residence time was low (~1 s), and some CO_2 may pass through the fixed bed un-reacted, even when adsorption sites were available. Therefore, the percent removal obtained during laboratory tests does not necessarily represent the total removal that could be realized by the sorbents. In fact, it should be considered a minimum of achievable removal. Even with a high volumetric flow rate of gas through the system, the temperature of the fixed bed would still elevate up to 10°C above the temperature set point due to the exothermic reaction. In these cases the adsorption step was not considered complete until the bed temperature had returned to the set point temperature (usually 55°C).

Figure 2 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 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 except for a few specific tests.

There were two types of tests completed during laboratory testing: 1) parametric and 2) constant conditions or extended testing. Many materials were evaluated parametrically during which the regeneration temperature changed after a specified number of adsorption/regeneration cycles. In many cases ten adsorption/regeneration cycles were completed at each regeneration temperature and the step change in the regeneration temperature was 10°C. For example, cycles 1-10 for a particular sorbent were completed using a regeneration temperature of 90°C, cycles 11-20 were completed using a regeneration temperature of 100°C, cycles 21-30 were completed using a regeneration temperature of 110°C, etc., until the maximum temperature set by ADA-ES and the sorbent developer was achieved. When the maximum temperature was achieved the tests could continue, but the regeneration temperature would remain constant.

The other type of laboratory test completed was extended cycle. These types of tests were focused on measuring the CO_2 capacity and cyclic stability of the materials when the same adsorption and regeneration conditions were used repeatedly. Constant conditions or extended tests were often conducted when the sorbent developer had already completed extensive parametric testing and could provide the optimal operating conditions. In practice, very few sorbent developers have evaluated cyclic stability for more than 10 or 20 adsorption/regeneration cycles, so the results of this type of test provided valuable feedback to the developers.

3.1.1.2 Actual Flue Gas

The same laboratory-scale fixed bed apparatus that was used to initially evaluate over 140 sorbents in the laboratory was also used to collect data related to cyclic testing using a small slipstream of actual flue gas at Martin Lake and at Sherco. This lab-scale equipment was specifically designed to be used in the laboratory on simulated flue gas as well as in the field on actual flue gas with minimal modifications. Similar to the laboratory tests, the flow rate of the actual flue gas was approximately 400 mL/min, and the amount of sorbent in the reactor was usually in the range of 0.7 to 2.5 g, depending on the material particle size. Figure 5 is a schematic of the sorbent screening testing unit when setup for field testing.

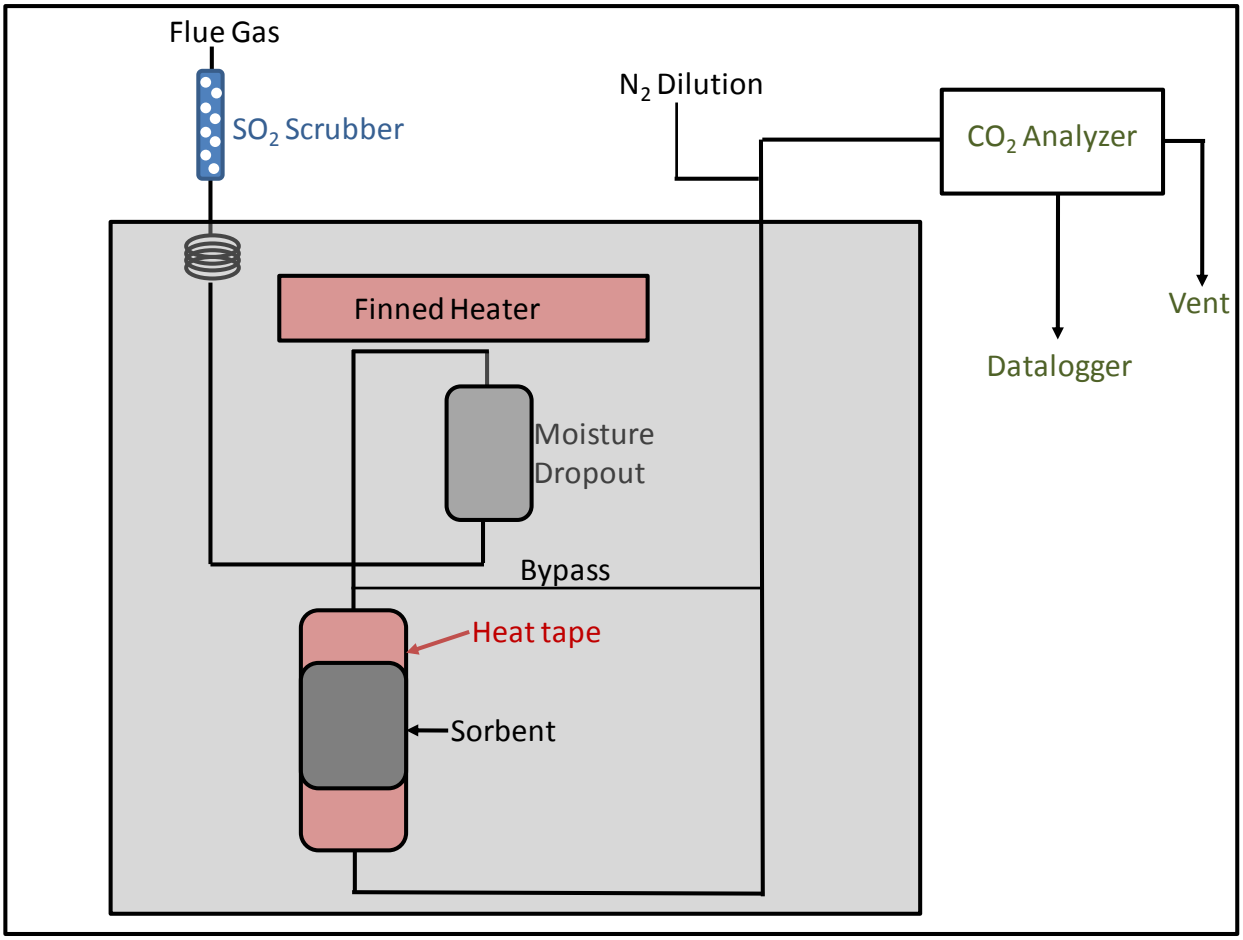

Figure 5: Schematic of Sorbent Screening Test Unit Configured for Field Testing

Note that in several cases the flue gas was treated in a laboratory-scale SO_2 scrubber (consisting of sodium bicarbonate and water) before entering the system. This laboratory-scale SO_2 scrubber reduced the flue gas SO_2 concentration to less than 10 ppm. Table 1 lists the key characteristics of the flue gas used for sorbent screening.

Table 1: Key flue gas characteristics for field tests

Temperature ºC (ºF)	55 (140)
CO_2 Concentration (%)	10 to 14
Moisture	Saturated
O_2 (%)	4 to 8
NO_x (ppm)	100 to 120
SO_2 (ppm)	0 to 250 (<10 ppm when a SO_2 scrubber was used)

3.1.2 Thermogravimetric Analyzer

A thermogravimetric analyzer (TGA) was used to measure the CO_2 loading for select sorbents under different temperatures and CO_2 partial pressures. The purpose of this testing was to determine the working capacity for the sorbents. The TGA was a Perkin Elmer Pyris 1. The TGA was operated at less than standard atmospheric pressure, because the tests were located at the company headquarters in Littleton, CO (elevation 1643 m); therefore, even when 100% CO_2 gas was used, the CO_2 partial pressure was only 0.81 bar. Note that a small amount of moisture was added to the gas during ADA-ES's TGA tests because others have shown that completely dry conditions lead to loss of amine reactivity.[24,25] The moisture levels were approximately less than 1% by volume, so the effect on the weight change of the sorbent would be minimal. The test details are provided in Table 2.

Table 2: TGA Operating Conditions

TGA	Sample Size (mg)	Gas Flow Rate (mL/min)	Temperatures Evaluated (°C)	CO_2 Partial Pressure (bar)	Dew Point (°C)
Perkin Elmer Pyris 1	1-5	100	40-120 (increments of 10°C)	0.04, 0.081, 0.5, 0.81	<22

3.1.3 Attrition Testing

Depending on the contactor configuration and sorbent properties, sorbent losses due to attrition could be a more costly operating expense than the energy penalty associated with sorbent regeneration. For this reason, the CARiACT® Q10 and CARiACT® G10 substrates, the supports for two promising supported amine sorbents (R and X, respectively) were evaluated by attrition experts at Jenike & Johanson. The substrate particle size distribution was measured prior to any testing. Then, the material was added to a bench-scale circulating fluidized bed, heated to approximately 55ºC. A vacuum system was used to induce an air velocity of 4.6 m/s. The solids were entrained by the gas with an average air-to-solids ratio of 4.41. A picture of the test setup is provided in Figure 6. A particle distribution size was recorded before and after 6 hours, of testing in the circulating fluidized bed, approximately 3600 cycles.

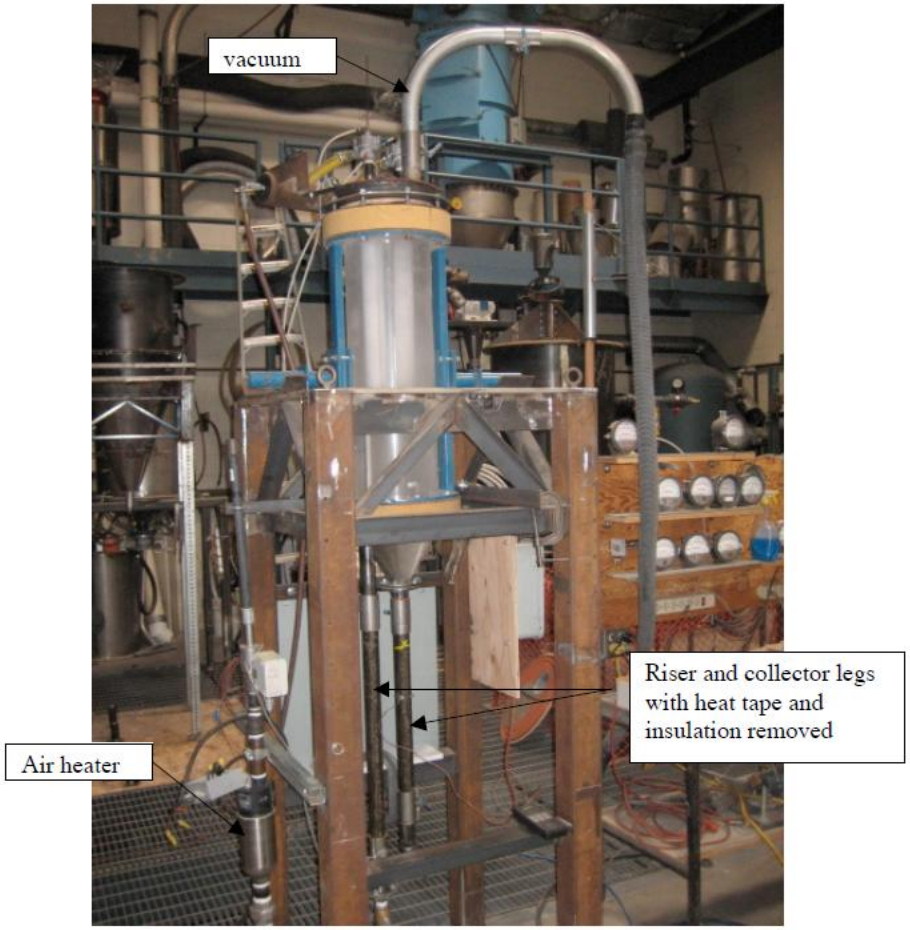

Figure 6: Attrition Testing Equipment Operated by Jenike & Johanson

3.1.4 Additional Physical Sorbent Properties

3.1.4.1 Particle Density

Under a separate project particle (DE-FE0004343) densities were measured for two promising sorbents. The testing was conducted by Adsorption Research, Inc. using a proprietary experimental method. The particle density is defined as the mass per unit particle. This quantity is useful for determining fluidization and entrainment related properties.

3.1.4.2 Crush Strength

Crush strength provides a quantitative measurement of particle hardness. However, it does not provide a means to directly predict attrition because this is a highly process dependent quantity. For the most promising beaded material provided to the sorbent screening program the crush strength was measured, note that the crush strength measurement was conducted by Adsorption Research, Inc. and was funded through a different project (DE-FE0004343).

3.2 1 kW Pilot Testing

The 1 kW pilot was operated only on actual flue gas at the two host sites: Luminant's Martin Lake Steam Electric Station and Xcel Energy's Sherburne County Generating Station (Sherco). The 1 kW pilot system was a state of the art, one of a kind CO_2 capture system designed and constructed to characterize the CO_2 capture effectiveness of solid sorbents. It was used to evaluate CO_2 sorbents with highly varied physical and chemical properties. The equipment included a flue gas pretreatment section and a capture system. The capture system included both CO_2 adsorption and sorbent regeneration. A diagram of the system is shown in Figure 7 for reference.

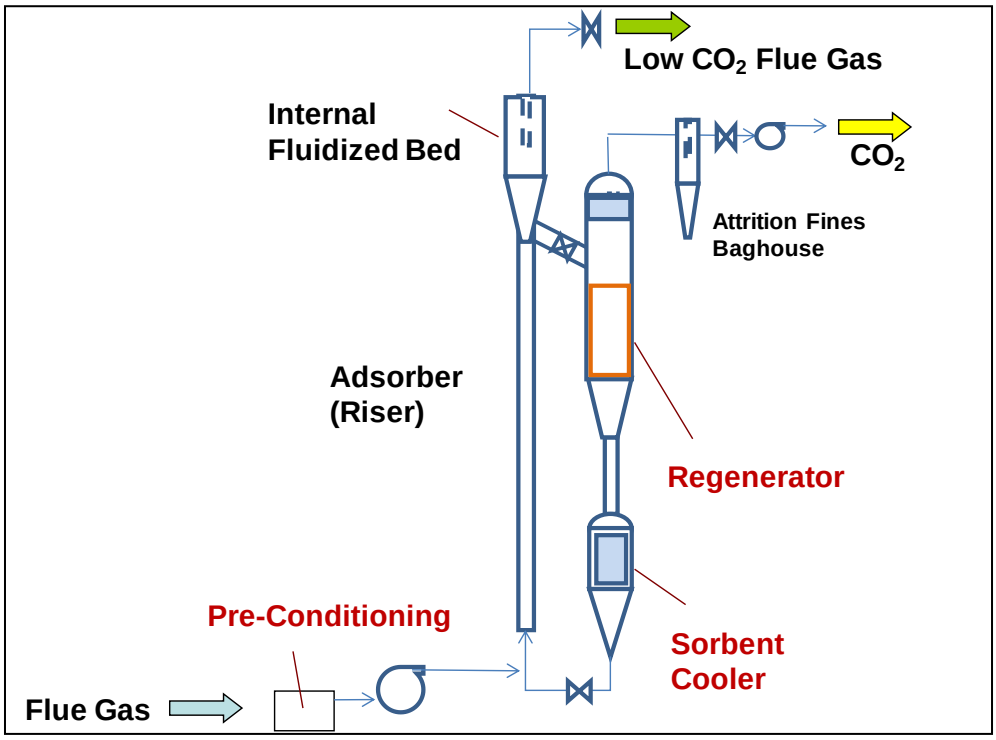

Figure 7: Diagram of 1 kW Pilot CO_2 System

Preliminary laboratory results indicated that flue gas constituents affected sorbents differently. For example, chemisorbents that capture CO_2 via a chemical reaction also react with SO_2 to form a heat stable salt, which leads to a slow deactivation of the sorbent, which is also the case for aqueous amine or carbonate based processes. However, the CO_2 uptake by other physical adsorbents, such as activated carbon, was not necessarily impacted by typical moisture or SO_2 concentrations in flue gas. The flue gas conditioning system was designed to control the following parameters:

- Pressure (expected operating conditions ~15 to 40 in H_2O)
- Temperature (heating and cooling)
- Moisture level
- SO_2 concentration

A blower was included in the flue gas conditioning system. This blower drew the sample of flue gas from the duct. It also slightly pressurized this gas so that it had enough pressure to entrain

the sorbent and carry it up a 50 foot contactor (i.e. riser). The flue gas pressure at the inlet to the CO_2 capture system was ~15 to 40 in H_2O.

Lowering the flue gas temperature could potentially improve the CO_2 capture performance of some sorbents since the adsorption (whether through a chemical or physical reaction) is exothermic. Therefore, a flue gas cooler was incorporated into the conditioning system. A heater was also included to characterize the impact of higher adsorption temperatures on capture effectiveness. A demister was incorporated to remove droplets before they entered the adsorption section. The flue gas moisture concentration was decreased by cooling the gas to promote condensation, passing the gas through a demister to remove the condensed moisture, and subsequently heating up the gas to the original temperature.

The conditioning system included sodium bicarbonate scrubbers to decrease the flue gas SO_2 concentration. Two scrubber towers were installed so that one could be in-service while the chemical was replaced in the second tower. Each scrubber was designed to remove enough SO_2 from the flue gas to maintain concentrations below 10 ppm. All four sorbents evaluated at Martin Lake and Sherco were supported amine chemisorbents, and thus susceptible to contamination from SO_2. Therefore, one of the SO_2 scrubbers was employed upstream of the 1 kW pilot for all testing. Note that due to the moisture dropout that occurred in the SO_2 scrubber, the CO_2 concentration at the 1 kW pilot inlet was 13-14% CO_2 (by volume), rather than the 11.5% measured at the Sherco stack.

A 3D model sketch and photo of the 1 kW CO_2 capture system is shown in Figure 8. Nominally 5 cfm of treated flue gas was sent through the adsorption riser, where it entrained and reacted with the sorbents. Unless otherwise specified, the sorbent circulation rate was 40 lb/hr. This sorbent circulation rate would provide 90% CO_2 removal if the sorbent working CO_2 capacity was approximately 10 wt%, depending on the CO_2 concentration in the flue gas. The riser temperature was maintained at approximately 130°F, although the exothermic reaction often made isothermal operation impossible. The riser was only 1 inch in diameter and it was 40 feet tall. In a commercial system of this type, the riser diameter would increase, but riser height would remain approximately the same. This height provided a contact time of approximately 3 seconds. There was also an added option for sorbent recirculation in the Internal Circulating Fluidized Bed (ICFB) if additional contact time was required.

The CO_2 capture occurred as the solids were entrained by the flue gas in the 1-inch riser, but at the top of the riser the diameter expanded, which resulted in significant solids dropout and permitted the CO_2-lean flue gas to pass through a filter bag, which separated the remainder of the solids. Due to the small size of this pilot, the CO_2-lean gas was vented to the atmosphere rather than routing it back to the host duct.

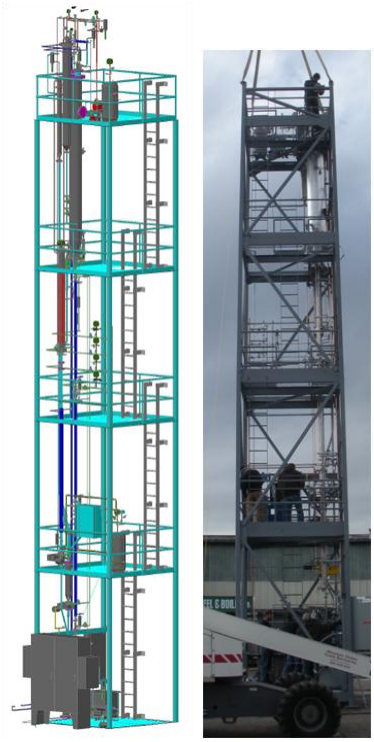

Figure 8: 3D Model Sketch and Photo of 1 kW System

Expected regeneration temperatures for post-combustion CO_2 capture using sorbents were generally in the range of 210°F to 250°F. For the 1 kW system, electric heaters were used for the heat input, although in a commercial system indirect steam or some other source of heat would likely be more advantageous. The regenerator consisted of a fluidized bed. The fluidizing media was N_2, although in a commercial-system CO_2 or a mixture of CO_2 and steam would be a superior selection for fluidization gas. The maximum sorbent residence time in the regenerator was approximately 60 minutes. After the sorbent was heated and the CO_2 was removed in the regenerator, the sorbent was sent through a cooler. This cooler utilized jacketed cooling to reduce the temperature of the sorbents to approximately the riser temperature or lower.

The pilot was instrumented to provide monitoring and control of pressures and temperatures throughout the system. Key gas measurement, pressure, and temperature measurement locations are indicated in the sketches in Figure 9, Figure 10, and Figure 11.

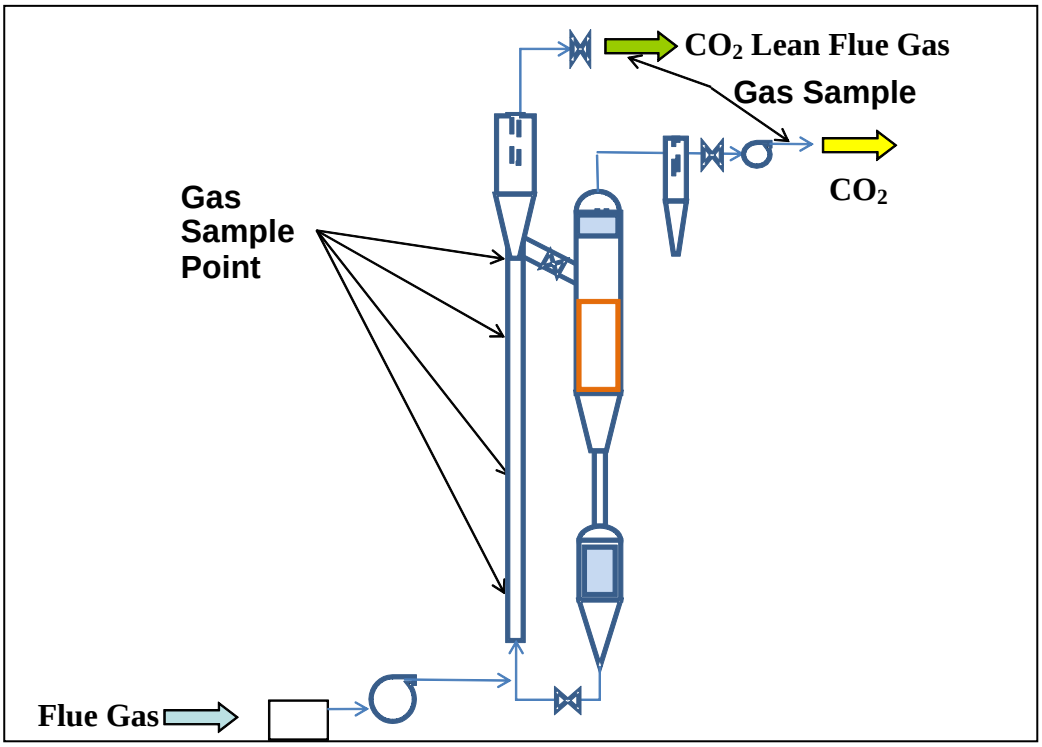

Figure 9: Sketch of Gas Sampling Locations

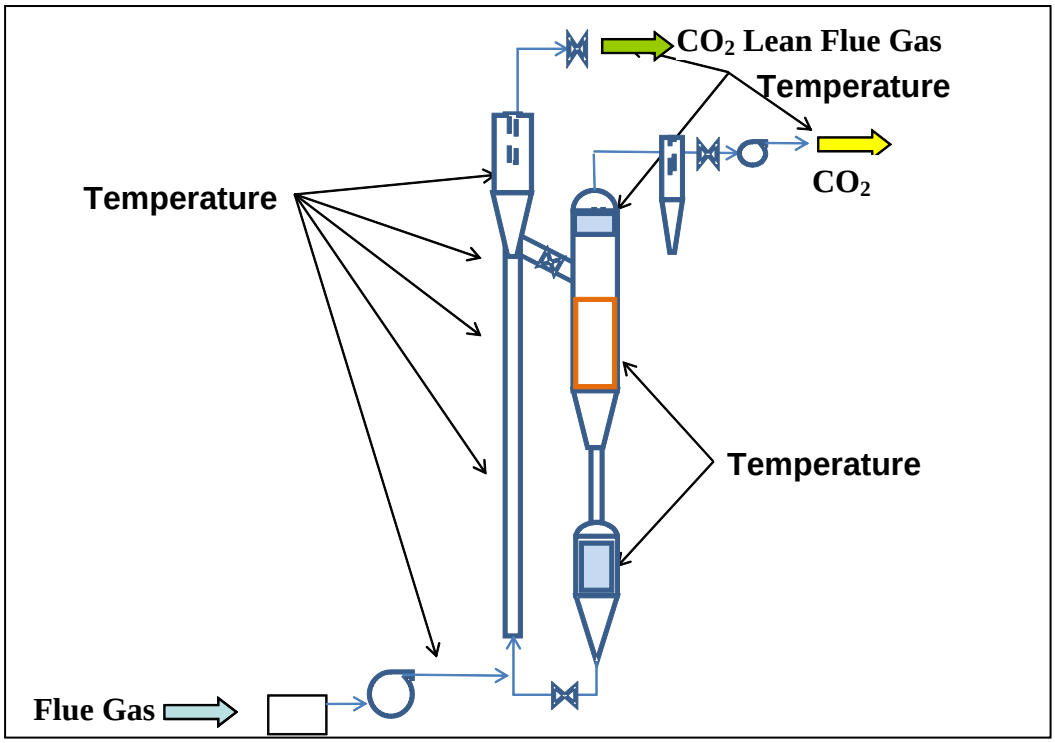

Figure 10: Sketch of Temperature Measurement Locations

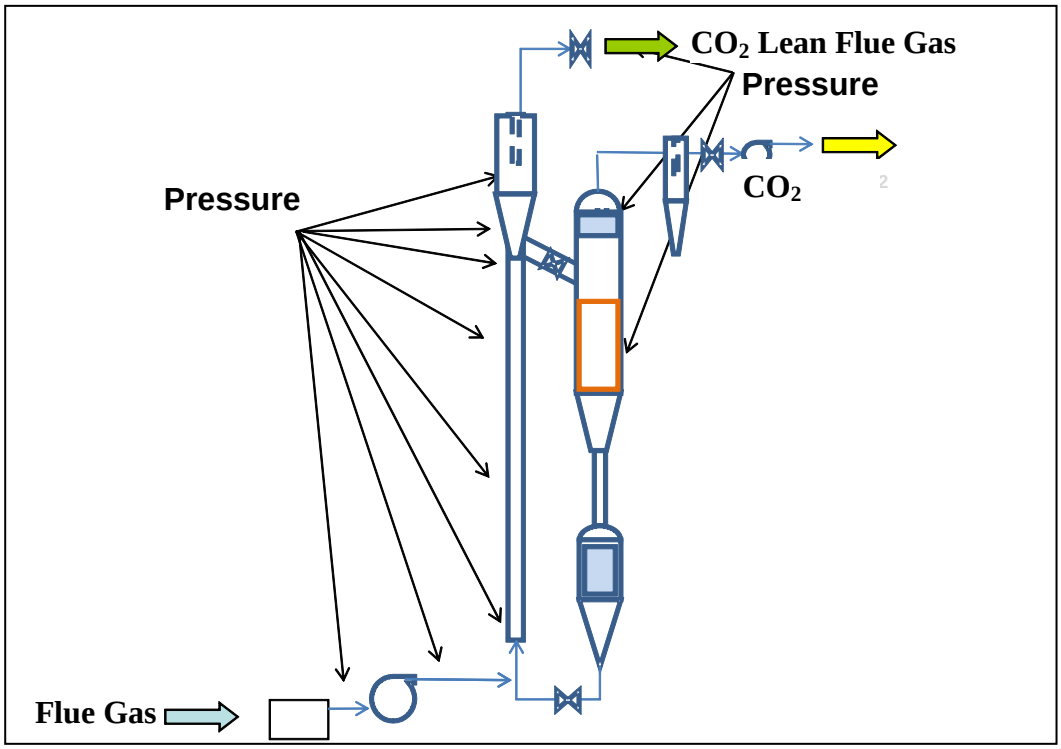

Figure 11: Sketch of Pressure Measurement Locations

A picture of the 1 kW pilot installed at Martin Lake and Sherco plant are provided in Figure 12 and Figure 13, respectively.

Figure 12: Picture of the 1 kW Pilot Installed at Martin Lake

Figure 13: Picture of 1 kW Pilot Installed at Sherco

Due to the cold ambient temperatures of the Minnesota winter at Sherco, the lower section of the tower was tarped. This tarping and heaters added to the lower levels prevented freezing of the moisture laden flue gas and SO_2 scrubbers.

The concept for the 1 kW pilot was provided by engineers at Southern Company. It was designed by ADA-ES and fabricated at Western Steel and Boiler in Denver, CO. The purpose of the 1 kW pilot was to test several different sorbents with highly varied physical characteristics. Equipment options that would allow for sorbents with different densities and particle sizes are limited. The 1 kW pilot design was selected because the project team thought that it would offer the greatest potential to evaluate several different sorbents and would offer the greatest ease of use with respect to sorbent circulation. The 1 kW pilot was not intended to be a proposed commercial-design, but was intended to be used to compare different sorbents while using actual flue gas.

The 1 kW pilot was used to effectively compare different sorbents under the same operating conditions. However, it is difficult to achieve 90% continuous CO_2 capture with any of the sorbents tested to date using such a configuration. Two theoretical isotherms and the 1 kW pilot configuration are provided together in Figure 14 to facilitate explanation of why it was difficult to achieve high removal levels in the 1 kW pilot with the sorbents evaluated in the screening program.

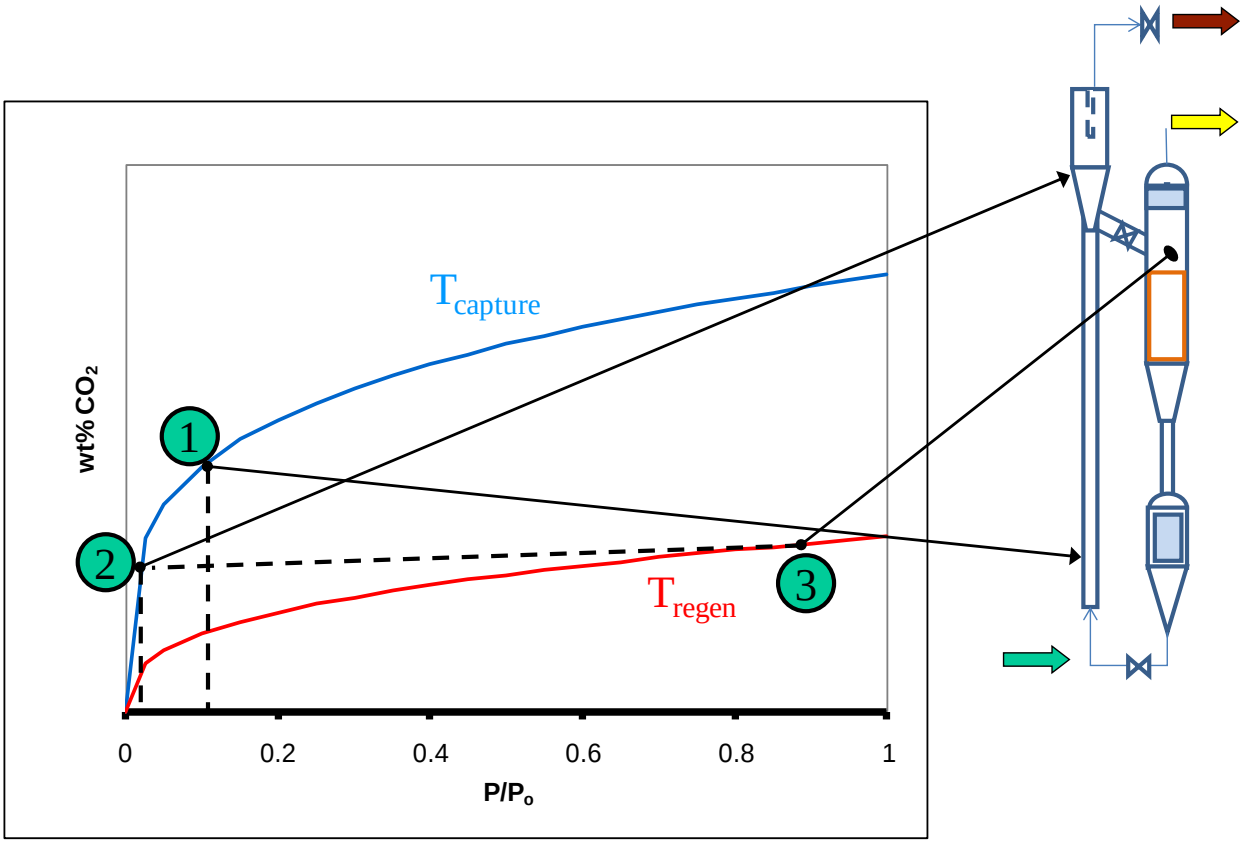

Figure 14: 1 kW Pilot with Theoretical Isotherms

The two isotherms provided in Figure 14 are theoretical, but are similar in shape to what has been measured previously for supported amine sorbents. The y-axis corresponds to the equilibrium CO_2 capacity (in wt%) of a sorbent and the x-axis corresponds to the partial pressure of CO_2 in the gas. The blue isotherm signifies the relationship between sorbent CO_2 loading and CO_2 partial pressure in the gas at the adsorption/capture temperature, while the red isotherm

represents the same relationship at the regeneration temperature. The 1 kW pilot consists of a riser (i.e. transport reactor) for adsorption. Therefore, the maximum driving force for CO_2 uptake to the sorbent is at the bottom of the riser where the flue gas CO_2 concentration is the greatest (point 1). As the sorbent begins to remove the CO_2 from the gas, the driving force for the sorbent to continue removing CO_2 decreases because the partial pressure of CO_2 in the gas is decreasing. At the top of the riser the partial pressure of CO_2 in the gas is lower than that at the bottom, thus, the equilibrium CO_2 loading of the sorbent is lower (point 2). A fluidized bed with a downcomer tube was used for the regenerator. Ideally when the sorbent moved from the riser to the regenerator it would release CO_2 due to only a temperature swing with only CO_2 as the fluidization gas. Because the regenerator was a slow bubbling fluidized bed the sorbent was not always in contact with N_2. To regenerate quickly in this type of fluidized bed the sorbent would have to regenerate in the presence of pure CO_2. Although different sorbent isotherms (shown in section 3.1.2) demonstrate that some sorbents can regenerate in the presence of CO_2, this will only occur if the CO_2 loading during adsorption is high enough to create a driving force for high partial pressure regeneration. When comparing the CO_2 loading on the sorbent at the top of the riser (point 2) to the CO_2 loading in the regenerator (point 3) there is no driving force for regeneration. Therefore, the regeneration is slow as the sorbent only regenerates when in the presence of the fluidization N_2. The sorbents evaluated in the screening program cannot be used to maintain 90% CO_2 removal in this type of adsorption/regeneration system. However, the removal level for different materials was effectively compared using this system.

4.0 RESULTS AND DISCUSSION

4.1 Laboratory-Scale Screening

The vast majority of the laboratory-scale screening was conducted using the fixed bed system described in the Approach section of this report. This unit was used to quickly measure CO_2 adsorption and regeneration breakthrough curves. Although this was only one measure of a potential sorbent's performance, it was an effective means of comparing different materials in an efficient, inexpensive manner.

4.1.1 Fixed Bed Testing

The objectives of the fixed bed testing were to 1) collect enough information to draw general conclusions about sorbent types; 2) down select the most promising materials for testing with actual flue gas during field tests; and 3) work in an iterative process with sorbent developers to accelerate the technology development through improvements in the sorbents. The original statement of project objectives for DE-NT0005649 stated that at least twenty materials would be evaluated in the laboratory. Under this cooperative agreement over 100 materials were evaluated; when testing completed under different funding mechanisms is included the total number of sorbents evaluated at the laboratory-scale was over 140. Many were evaluated during cyclic stability studies that spanned over a week. All the results from the fixed bed tests using simulated flue gas in the laboratory are available in the attached sorbent developers reports, which are included in Appendices A-D. The key observations and main conclusions that were drawn from the test results are provided in the text of this report.

4.1.1.1 Simulated Flue Gas

Using simulated flue gas in the ADA-ES laboratory, the following types and quantities of sorbents were evaluated:

- 87 supported amines
- 31 carbon based materials
- 6 zeolites
- 7 supported carbonates (evaluated under separate funding)
- 10 hydrotalcites

Clearly the sorbent screening program was extensive. However, the results cannot and should not be extrapolated to materials that were not included in the program. There is still a great deal of ongoing sorbent development, with the potential to lead to continued improvement. The discussion for different sorbents is divided by the sorbent families in the following sub sections.

<u>4.1.1.1.1 Supported Amines</u>

Supported amine sorbents consist of some type of amine supported on an inert substrate. There is a great deal of ongoing research to invent and improve these materials. The adsorption and regeneration breakthrough profiles were measured for approximately 87 supported amine sorbents under several funding mechanisms.

An adsorption profile for sorbents R, EM, and EN are provided in Figure 15 to serve as examples of the shape of the breakthrough curve characteristic for supported amines. These materials were similar and consisted of an amine on a silica substrate. Sorbent R contained 50% amine loading, while sorbent EM contained 40% amine loading and sorbent EN contained 30% amine loading. The amine was similar for all three materials, but EN and EM contained an additive not included for sorbent R. All three of these sorbents were able to remove over 90% of the CO_2 from the simulated flue gas stream used for fixed bed testing. Sorbent R exhibited first an initial breakthrough that resulted in a fast increase in CO_2 concentration, followed by a much slower increase in the CO_2 concentration to achieve complete saturation. The second generation sorbents EM and EN, which were submitted to the program from the same sorbent developer, exhibited initial breakthrough and then a fast increase in the CO_2 concentration to achieve complete saturation. Although the total CO_2 capacity of sorbent R is greater than that of sorbents EM and EN, the slow tail in the adsorption profile reveals a reaction with CO_2 that is limited by mass diffusion. In an actual CO_2 capture process, it is likely that the working capacity of sorbents EM and EN would be greater than that of R because they do not exhibit the same mass diffusion limitations. These materials are just one of many examples of supported amine sorbents that have been improved throughout the duration of the sorbent screening phase of this project.

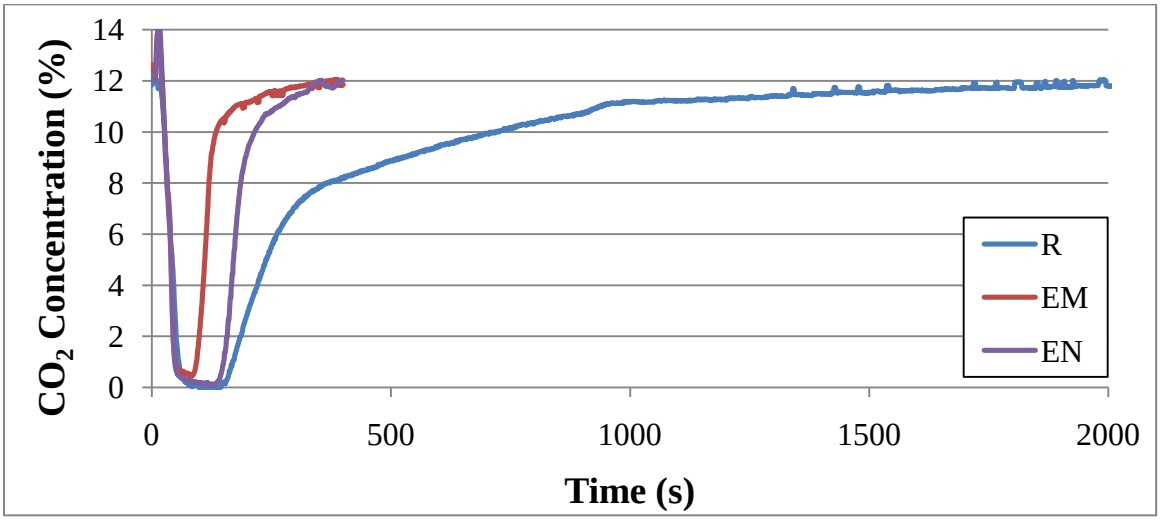

Figure 15: Select Supported Amine Adsorption Profiles

Based on the extensive laboratory results collected, supported amines exhibit the greatest CO_2 capacities under simulated flue gas conditions. The theoretical regeneration energies, calculated using the method described in section 2.1.1, are provided in Figure 16a and Figure 16b. The red dashed line represents the regeneration energy for the benchmark aqueous MEA[3]. Due to their high CO_2 capacities and low specific heat, many supported amines have the potential to significantly reduce the energy penalty associated with CO_2 capture.

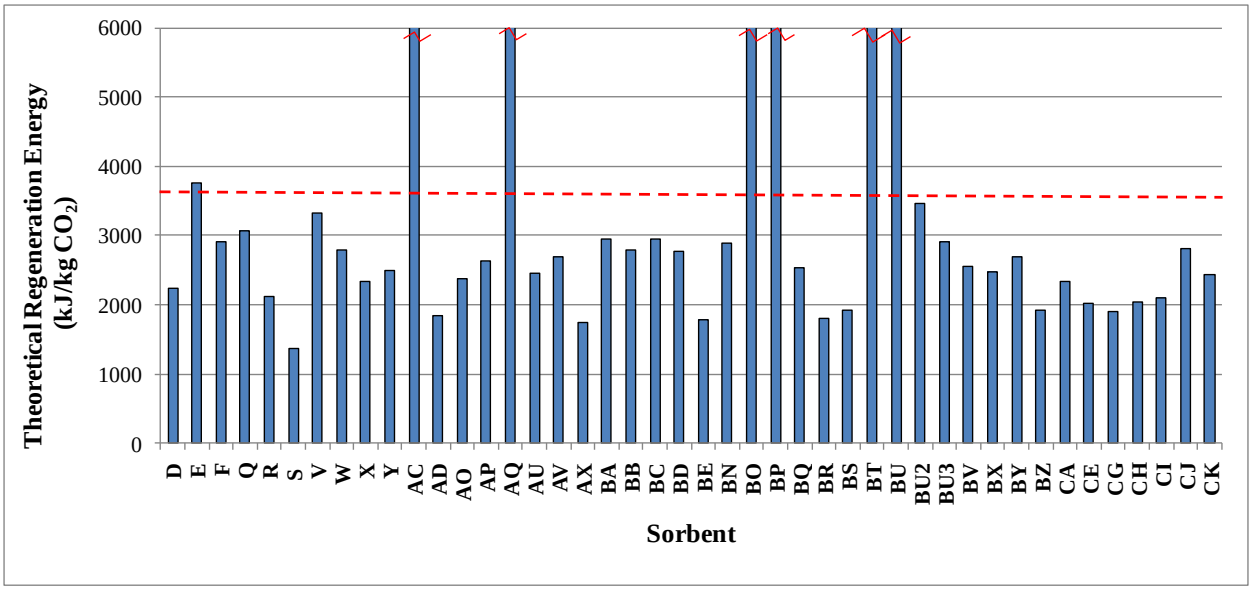

Figure 16a: Theoretical Regeneration Energy of Supported Amine Sorbents

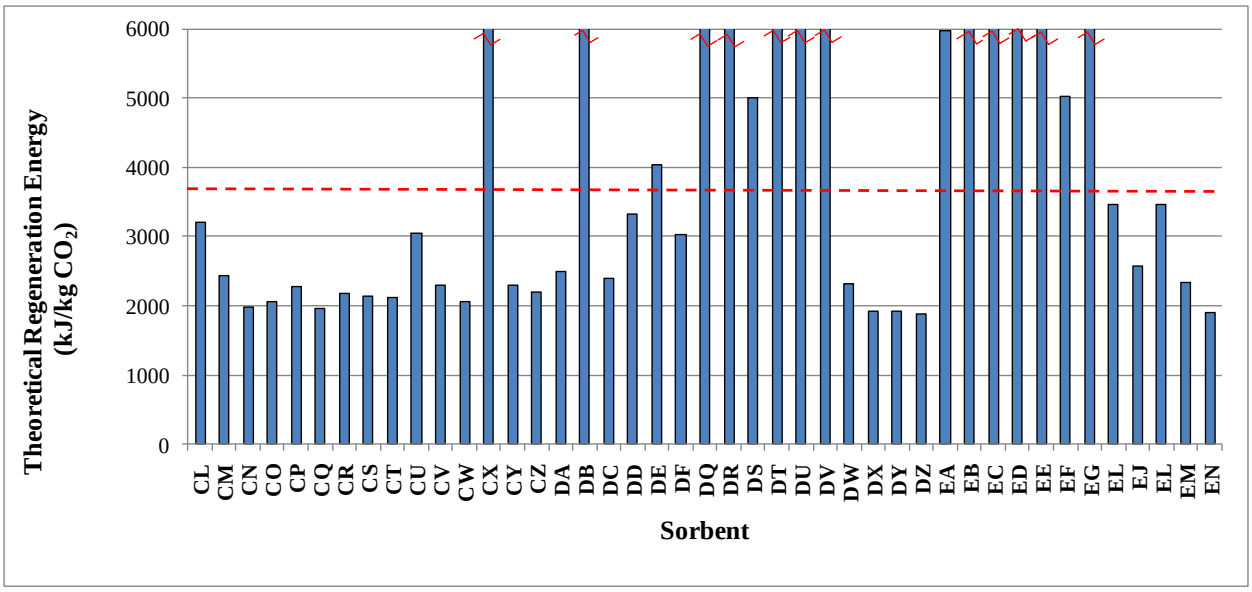

Figure 16b: Theoretical Regeneration Energy of Supported Amine Sorbents

The most important challenges for supported amine sorbents are related to long-term cyclic stability, poisoning by flue gas constituents, cost, and finding a process that can take advantage of their high CO_2 capacities. Several, but not all, of the supported amine sorbents demonstrated a loss in CO_2 capacity when using simulated flue gas in the laboratory. As an example, select adsorption profiles from laboratory tests for sorbent CU are provided in Figure 17. Although the testing conditions were the same for all cycles, the adsorption profiles revealed a slow, progressive decrease in the CO_2 capacity of the material.

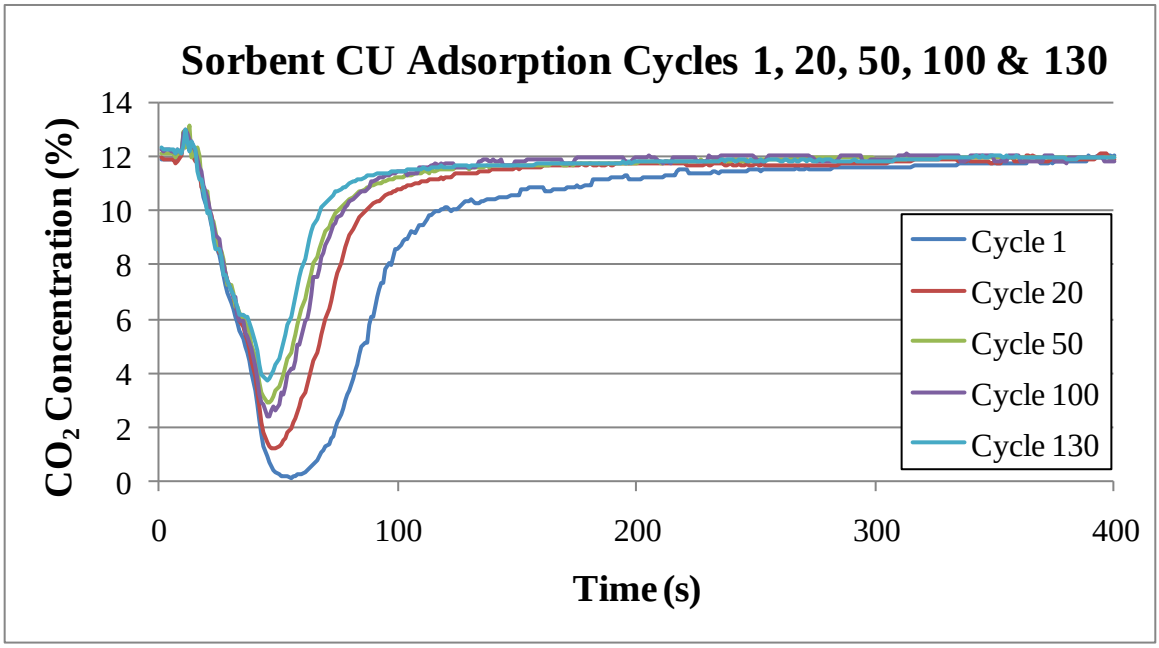

Figure 17: Sorbent CU Laboratory Adsorption Profiles

One important goal of this program was to work closely with sorbent developers; ADA-ES's testing results were provided to the developers in the hopes of leading to improvements in sorbent performance. In several cases, collaboration between ADA-ES and sorbent developers has led to second or third generation sorbents exhibiting significantly improved performance properties compared to their first generation counterparts. The CO_2 capacity versus cycle number for two sorbents is shown in Figure 18. Both sorbents are variations of an amine supported by a clay substrate. The generation 1 sorbent was tested by ADA-ES and was found to degrade with cycle number, even when using simulated flue gas in the laboratory. Several months later the developer provided a similar sorbent that was also tested for multiple cycles. During the 56 cycle test, there was no sign of a decrease in capacity. The improvement of this material is an example of how collaboration can lead to better sorbent options and thus an increase in the chance of success.

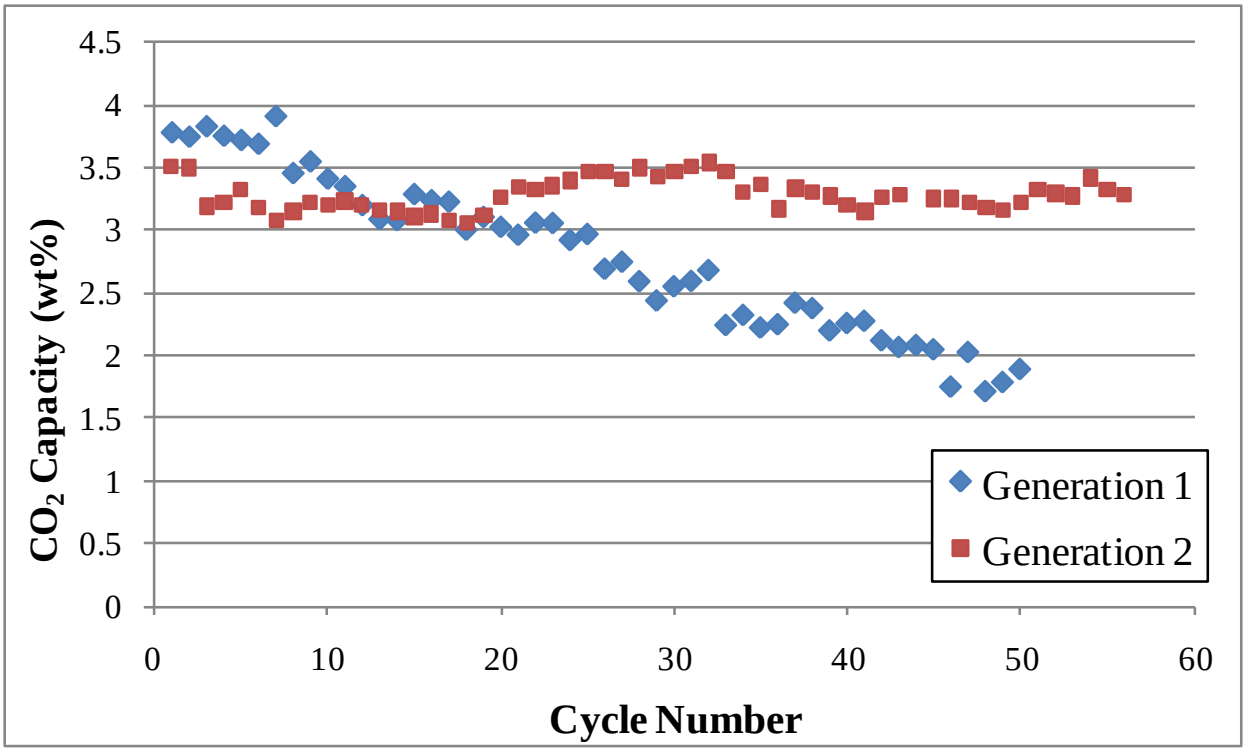

Figure 18: First and Second Generation Supported Amine Clay-Based Sorbent

Cyclic stability is a key parameter when comparing potential sorbents. In general there were many supported amines that demonstrated cyclic stability. As an example, select adsorption profiles for sorbent CQ, an amine grafted to an aerogel substrate, are provided in Figure 19. The repeatability in the adsorption profiles for this material was exceptional.

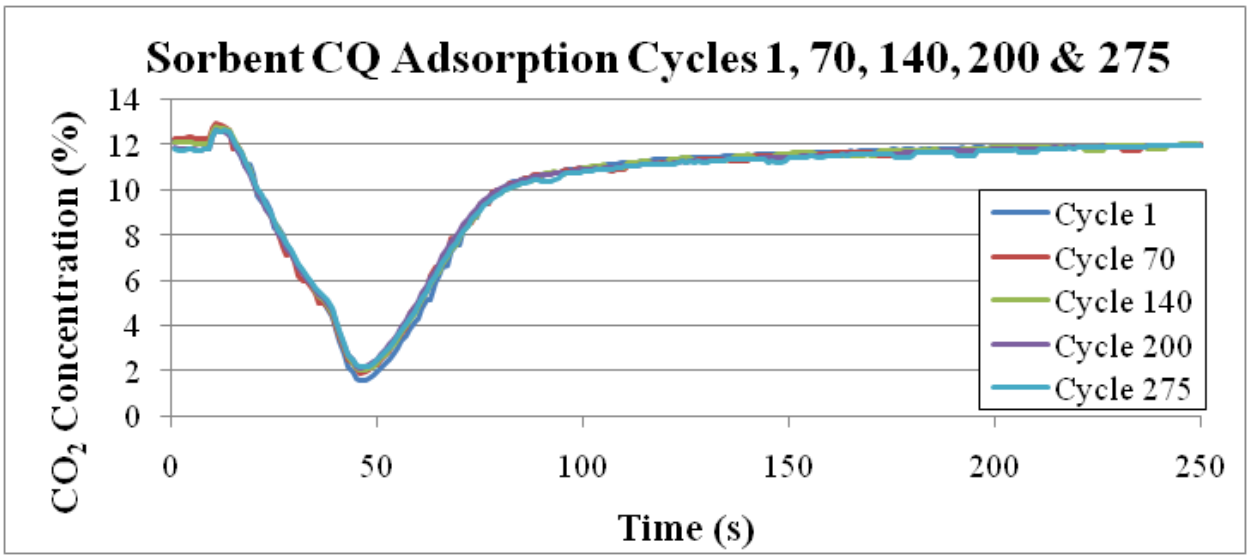

Figure 19: Sorbent CQ Laboratory Adsorption Profiles

To provide another example of a supported amine sorbent that demonstrated cyclic stability, the CO_2 capacity for sorbent CE is provided in Figure 20. This sorbent exhibited a large CO_2

capacity (>8 wt%). Sorbent CE was stable using a regeneration temperature of 100°C for the 261 cycles. Note that there was an initial decrease in the CO_2 capacity, but that the overall stability of the material was superior.

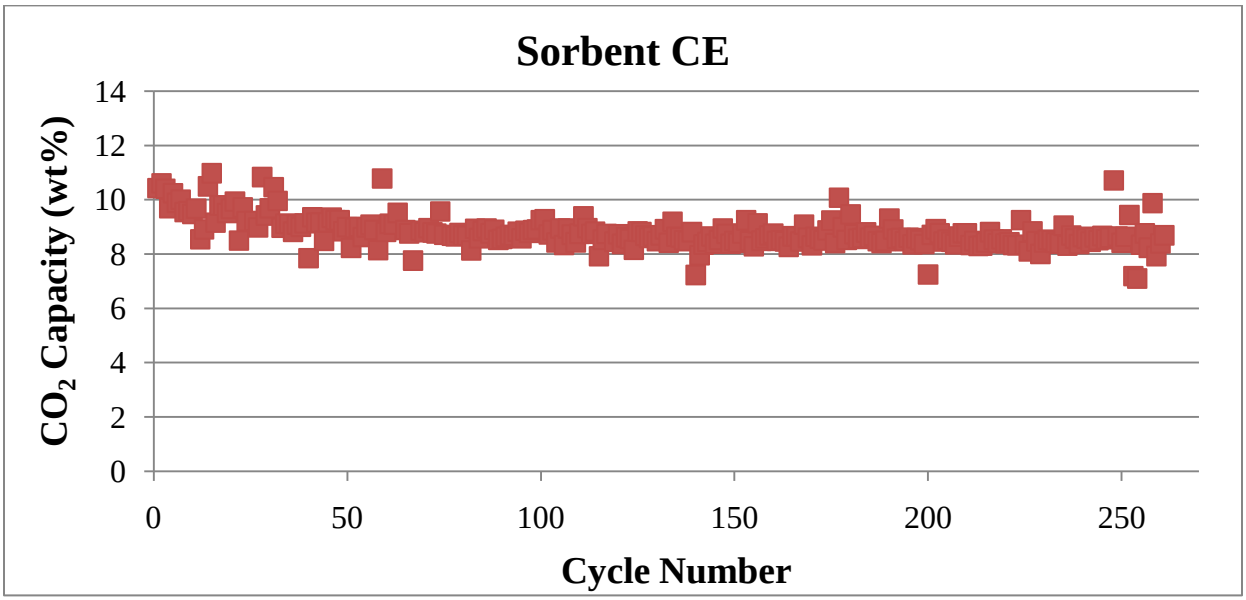

Figure 20: Sorbent CE Laboratory Total CO_2 Capacities

While the breakthrough curves measured on simulated flue gas demonstrated that supported amine sorbents could be a promising option for post-combustion CO_2 capture, a major concern was the effect of flue gas constituents. The field tests revealed that flue gas caused degradation for supported amine sorbents (see section 3.1.1.2.1), such tests cannot be used to determine which flue gas constituent(s) is/are of concern. Therefore, several laboratory tests were conducted to measure the effect of specific gases of concern (SO_2, NO_2, and NO). Sorbent R was exposed to either 100 ppm SO_2, 100 ppm NO_2, or 100 ppm NO during the CO_2 adsorption step. To single out the effect of each gas, three separate tests were run and only one of these flue gas constituents was included at a time. The CO_2 capacity versus cycle number for these tests is provided in Figure 21. The loss in active CO_2 adsorption sites due to irreversible reaction is most important for $SO_2 > NO_2 >> NO$. In fact, NO does not appear to have a permanently degenerative affect on the sorbent. For this reason, it is most important that SO_2 concentrations upstream are reduced of any amine-based CO_2 capture system.

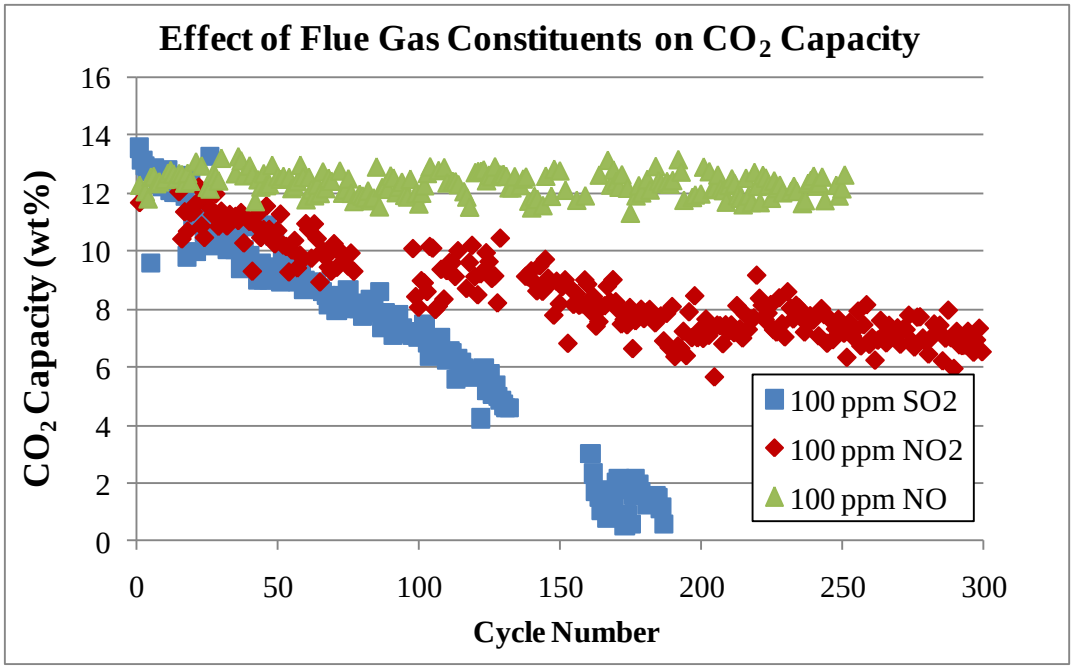

Figure 21: CO_2 Capacity versus Cycle Number for 100 ppm SO_2, 100 ppm NO_2, and 100 ppm NO

Many different supported amine sorbents were evaluated using the fixed bed contactor. These materials generally exhibited high CO_2 capacities. Many, but not all, of these materials were cyclically stable within the number of cycles completed. Flue gas constituents, especially SO_2, are of concern for supported amine sorbents similar to aqueous amine systems. Based on the results collected, supported amine sorbents were the most promising sorbent types for post-combustion CO_2 capture.

4.1.1.1.2 Carbon Based Sorbents

The carbon-based sorbents evaluated by ADA-ES on simulated flue gas in the fixed bed screening device consisted of carbon nanotubes, carbon fibers, monoliths, and many different activated carbons. The breakthrough profiles for 31 different carbon-based sorbents were measured in the laboratory-scale fixed bed system using simulated flue gas. The theoretical regeneration energies for most of these materials are provided in Figure 22. The red dashed line represents the regeneration energy for the benchmark MEA process.[3]

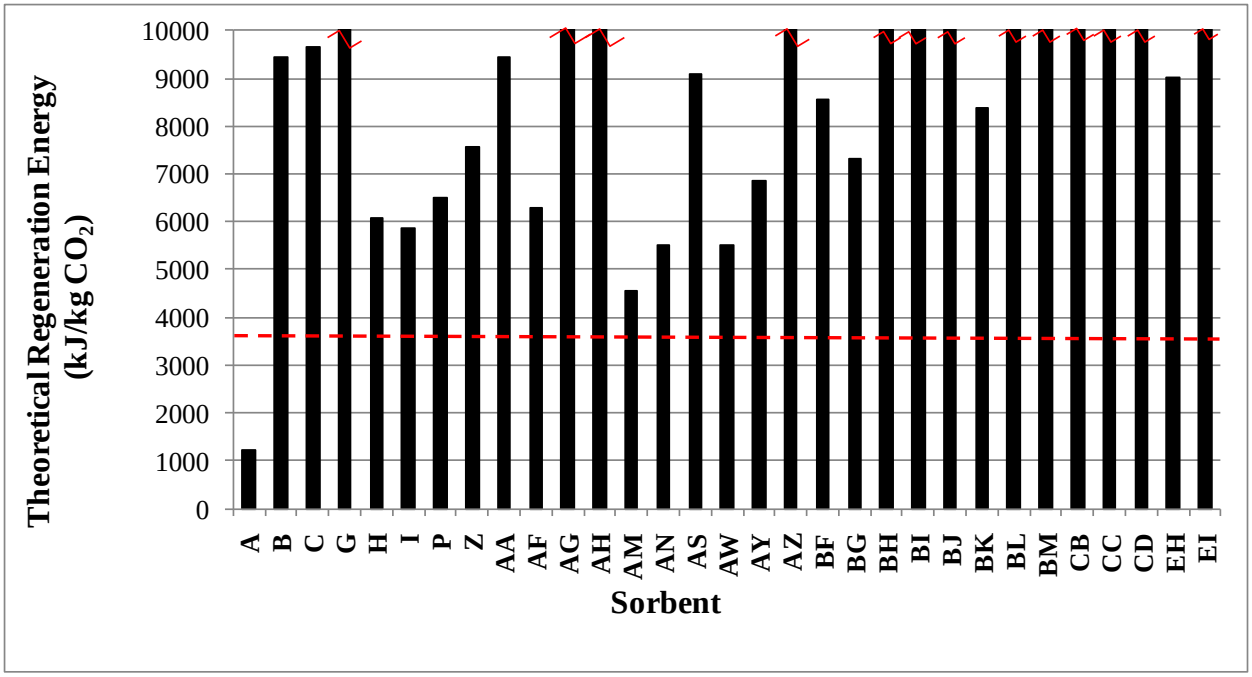

Figure 22: Theoretical Regeneration Energies for Carbon-Based Sorbents

With the exception of sorbent A (produced using carbon nanotubes) all the CO_2 capacities at simulated flue gas conditions were significantly lower than those of the supported amines. In general the CO_2 capacities were lower than 1.1 wt%. In terms of a materials handling issue, to achieve 90% CO_2 capture using low-capacity carbons would require a prohibitively large amount of energy to move the materials. However, there are also advantages to using carbon-based materials. Specifically, they are commercially produced today, they can be burned after they are spent (i.e. less waste generated by the CO_2 capture process), and they are less easily poisoned by flue gas constituents compared to both amines (negatively affected by SO_2) and zeolites (prohibitively affected by moisture). Some carbons have exhibited a decrease in CO_2 performance in moist versus dry flue gas, but this only decreases the capacity to some equilibrium value, it does not remove all the CO_2 capacity.

To serve as an example select adsorption profiles for sorbent AM, one of the better activated carbons evaluated during sorbent screening, are provided in Figure 23. Cycles 1-5 were run using dry simulated flue gas, while cycles 31 to 35 were run using simulated flue gas with 90% relative humidity. Although there is a noticeable difference in the profiles, the majority of the adsorption capacity is maintained regardless of moisture levels.

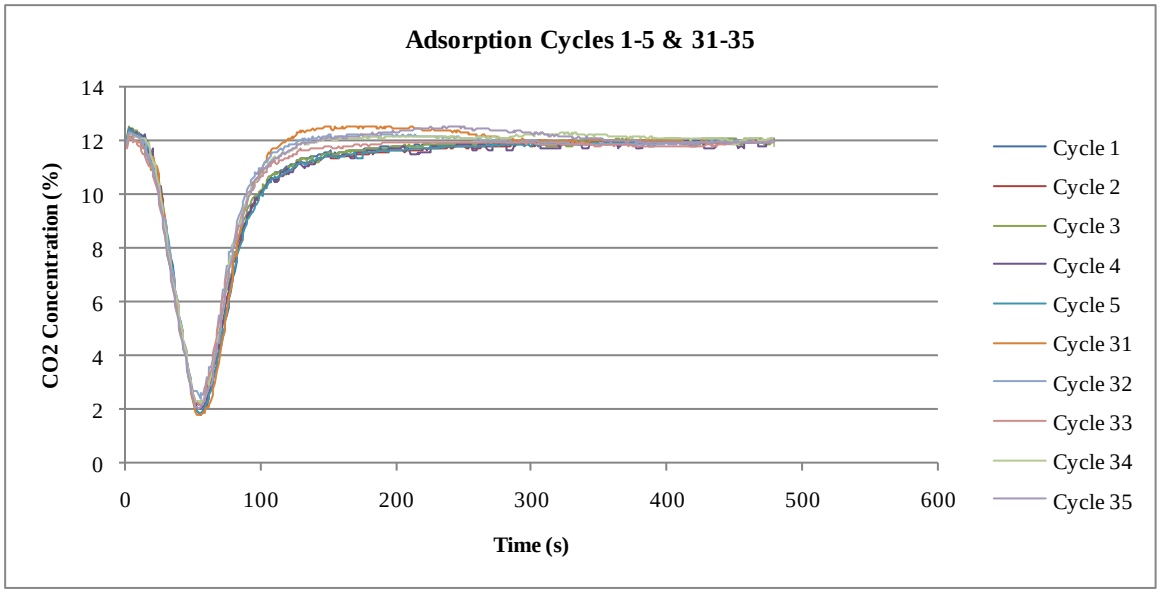

Figure 23: Sorbent AM Laboratory Adsorption Profiles

In general, the simulated flue gas screening of different carbon-based sorbents revealed that they are able to remove CO_2 from simulated flue gas. However, the CO_2 capacities are currently prohibitively low and selectivity is also a concern. If these materials are to be considered a viable option for post-combustion CO_2 capture, further advances are required to increase the CO_2 capacity (under flue gas conditions) and selectivity towards CO_2.

4.1.1.1.3 Zeolites

At first glance zeolites are an attractive option for CO_2 capture because several of these materials are commercially available, and may be durable for many adsorption / regeneration cycles even in the presence of other flue gas constituents. During initial fixed bed testing a few zeolites exhibited the ability to remove CO_2 from dry simulated flue gas. However, as moisture was added to the simulated flue gas the capacity of the materials dropped dramatically. Even at high regeneration temperatures (up to 200°C), they perform poorly in the presence of moisture. The theoretical regeneration energies for several different zeolite sorbents when evaluated using humid simulated flue gas are provided in Figure 24.

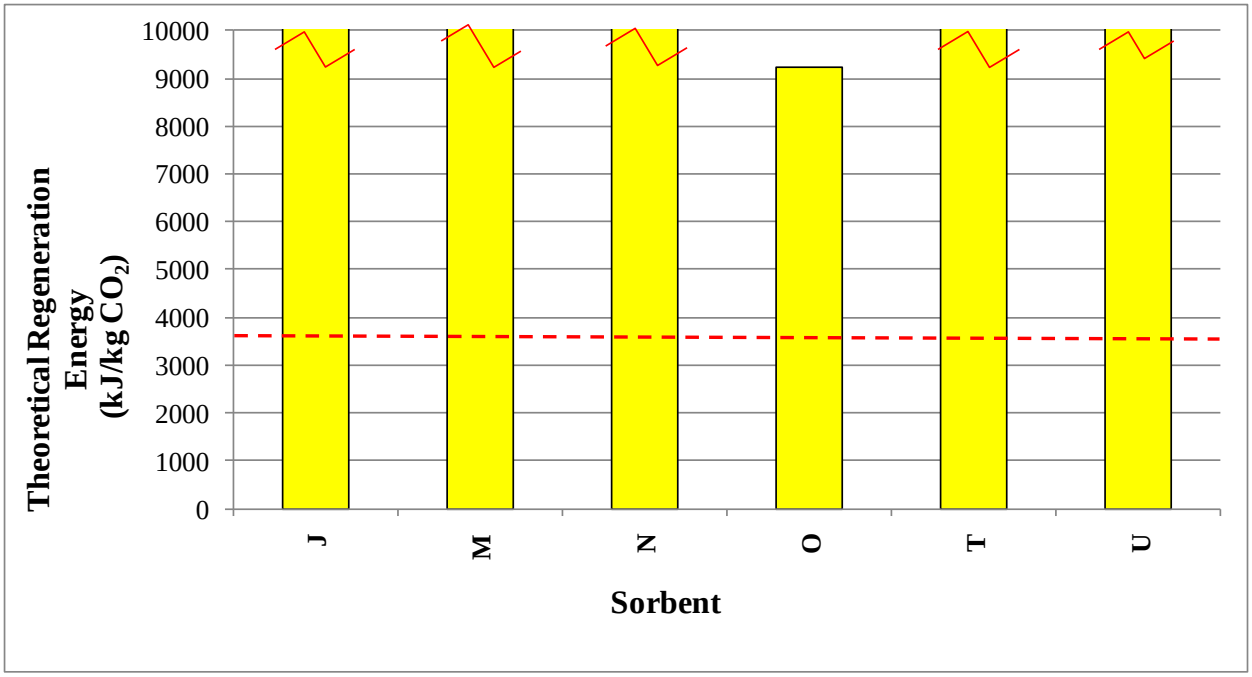

Figure 24: Theoretical Regeneration Energies for Several Zeolites

Select adsorption profiles from laboratory screening of sorbent J are provided in Figure 25. The first four adsorption/regeneration cycles were conducted using dry simulated flue gas while cycles 5-8 were conducted using humid flue gas. The decrease in CO_2 capture performance is clear. When humid simulated flue gas was used, the final CO_2 concentration was actually greater than the starting CO_2 concentration. Initially, this was a source of confusion; however, additional testing with longer adsorption times revealed that the CO_2 concentration would eventually return to the baseline gas CO_2 concentration. This can be attributed to the displacement of adsorbed CO_2 by H_2O; the adsorption of CO_2 is more rapid initially, but given enough time exposure to moist simulated flue gas the H_2O molecules will actually displace the adsorbed CO_2 due to the hydrophilic nature of the zeolites.

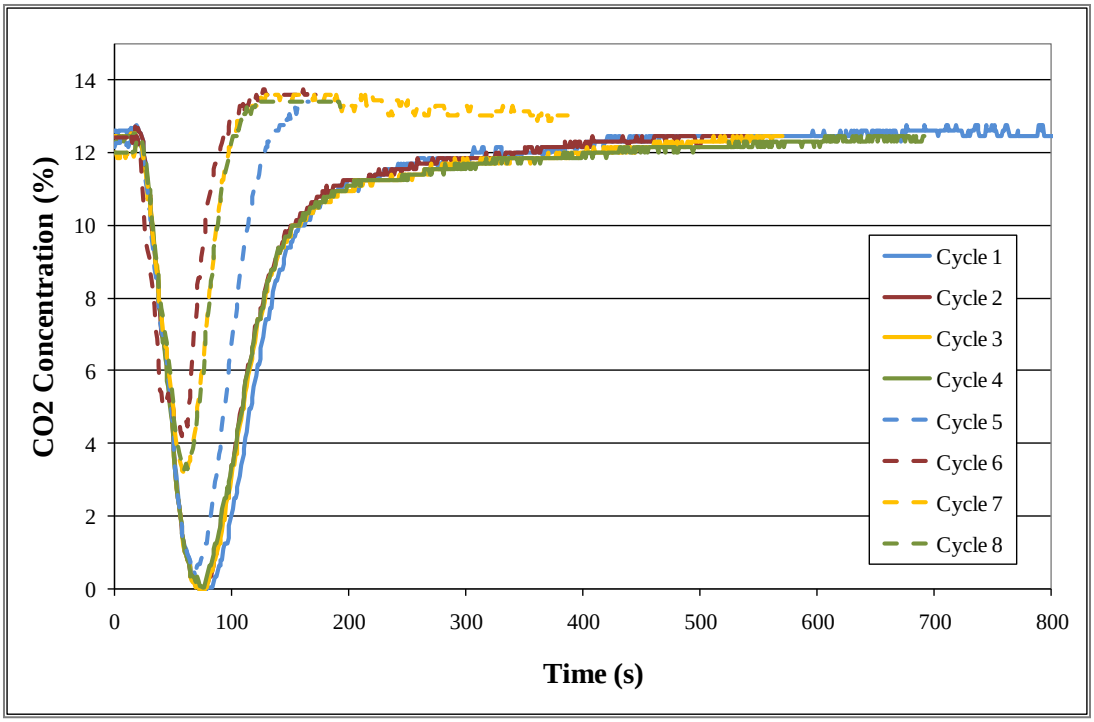

Figure 25: Sorbent J Laboratory Adsorption Profiles

When a low CO_2 capacity and a high regeneration temperature are exhibited, the theoretical regeneration energy is exceedingly high, as is shown in Figure 24. Unless flue gas dehumidification is considered a viable pretreatment option (this was not considered the case under this project) zeolites cannot be utilized for effective post-combustion CO_2 capture.

4.1.1.1.4 Supported Carbonates

No supported carbonates were submitted during DE-NT0005649 for inclusion in the sorbent screening program, although sorbent developers working on such materials were contacted repeatedly. Prior to initiation of DE-NT0005649, ADA-ES produced several supported carbonate sorbents that consisted of either sodium carbonate or potassium carbonate distributed on an inert support. The heat of reaction between such carbonates and CO_2 is significantly larger than that of other materials (i.e. approximately -130 kJ/mol for regeneration of sodium carbonate versus -60 kJ/mol for supported amines). The materials produced and evaluated by ADA-ES were not optimized, but allowed for some screening and evaluation to be completed. The best CO_2 capacity measured for one of the ADA-ES supported carbonates was approximately 3.2 wt%. Using this CO_2 capacity to calculate the theoretical regeneration energy, and assuming a sorbent specific heat of 1.0 kJ/kg·K, the theoretical regeneration energy was approximately 5000 kJ/kg CO_2. Since this was significantly greater than the benchmark MEA system, supported carbonates were not pursued further.

4.1.1.1.5 Hydrotalcites

Hydrotalcites are anionic clays that can occur naturally or can be produced synthetically. For the application of CO_2 capture all the hydrotalcites evaluated were produced synthetically by a single sorbent developer. This family of sorbents exhibited stability at greater temperatures than most other sorbents evaluated by ADA-ES. Often these materials are referenced in the public literature when discussing pre-combustion CO_2 capture. However, one sorbent developer

believed that the materials could be effectively utilized at post-combustion conditions and provided several materials to ADA-ES for evaluation. The fixed bed tests were conducted without any study of the optimal adsorption and regeneration temperatures. Therefore, the theoretical regeneration energies provided in Figure 26 can only be considered order of magnitude estimates with the possibility for significant improvement.

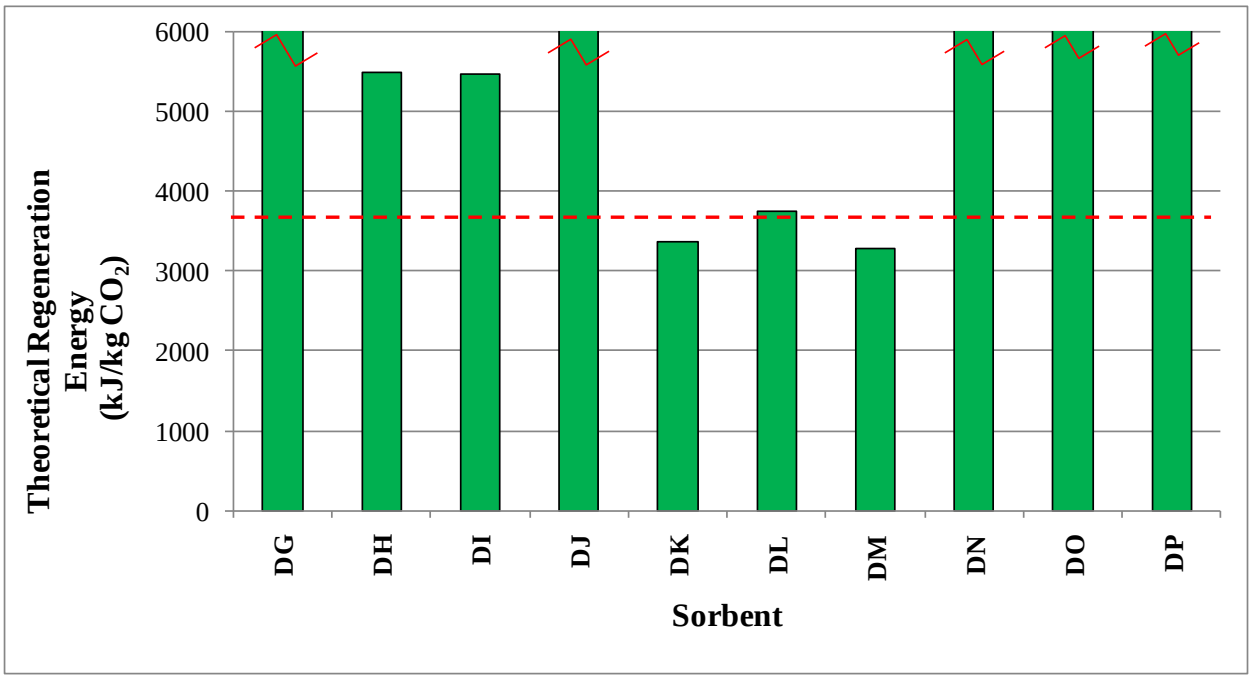

Figure 26: Theoretical Regeneration Energies for Several Hydrotalcites

As an example, Sorbent DM exhibited cyclic stability at all regeneration temperatures tested below 190°C, as is shown in Figure 27. This sorbent didn't show any signs of degradation until the regeneration temperature was increased to 190°C. This temperature stability could be useful for creating high driving forces for heat transfer or a reduced concern of damaging sorbent if it was unexpectedly exposed to elevated temperatures.

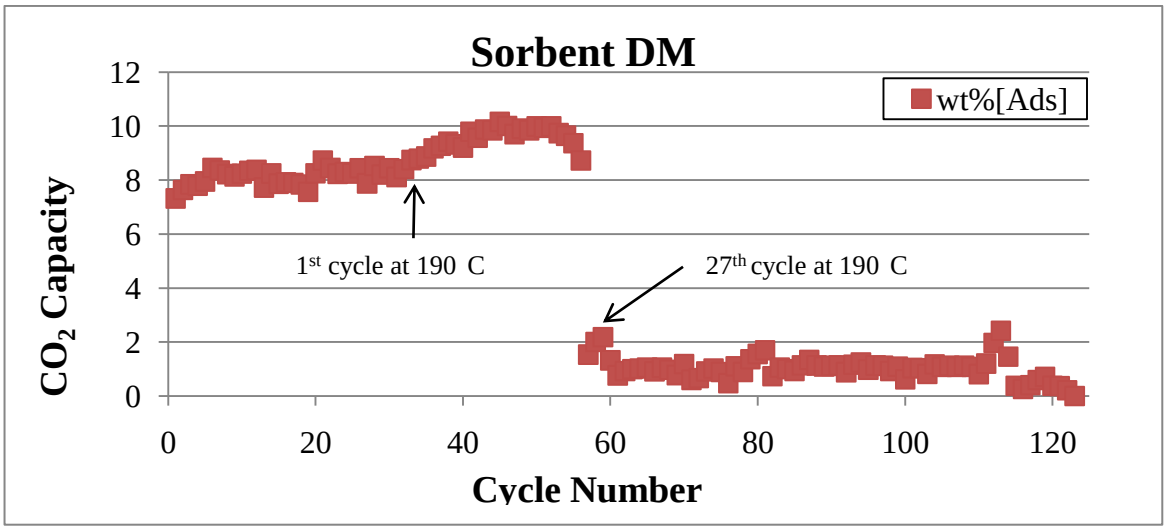

Figure 27: Sorbent DM Laboratory Total CO_2 Capacities

Based on the hydrotalcites evaluated, there may be some applicability for post-combustion CO_2 capture. Although it will not be completed under this project, ADA-ES may complete more testing to evaluate the optimal operating conditions (i.e. adsorption and regeneration temperature) for these materials.

4.1.1.2 Actual Flue Gas

Several field tests were completed using the laboratory-scale fixed bed sorbent screening device. The first field test site was Martin Lake and the second field test site was Sherco (similar to the 1 kW pilot testing). The first test was completed before the unit was fully automated and the sorbents were tested for thirty five or less adsorption/regeneration cycles. However, later after the system was automated up to 250 adsorption/regeneration cycles were completed on actual flue gas. The summary of all the laboratory-scale field tests is provided in Table 3.

Table 3: CO_2 Capacity Measured During Field Tests

Sorbent	Type	Site Tested	Number of Cycles	CO_2 Capacity (wt%)			SO_2 Scrubbing
				Max	Min	Average	
D*	Supported Amine	Martin Lake	11	8.2	4.8	6.2	No
F*	Supported Amine	Martin Lake	35	7.2	0.9	3.9	No
H*	Carbon	Martin Lake	18	1.1	0.7	0.9	No
O*	Zeolite	Martin Lake	18	0.8	0.3	0.5	No
Q*	Supported Amine	Martin Lake	17	3.5	1.2	2.4	No
R	Supported Amine	Martin Lake	43	16.9	4.8	9.7	No
V	Supported Amine	Martin Lake	11	6.1	3	4.1	No
BR**	Supported Amine	Martin Lake	250	14.1	6.1	8.2	Yes
AY**	Carbon	Martin Lake	250	1.3	0.1	0.5	Yes
F	Supported Amine	Sherco	79	9.5	1	5.8	Yes
R	Supported Amine	Sherco	51	8.8	5.6	6.5	Yes
AX	Supported Amine	Sherco	82	7.1	2.8	5.5	Yes
BN	Supported Amine	Sherco	53	9.2	4.8	6.5	Yes
*Funding provided by Luminant							
**Funding provided by TVA and EPRI							

4.1.1.2.1 Martin Lake

Five sorbents were evaluated during the first laboratory-scale field test. During the first field test sorbents D, F, H, O, and Q were evaluated. In the second field test sorbents R and V were evaluated. During these first two tests it was determined that flue gas constituents that were not typically included in the simulated flue gas (likely SO_2 or NO_2) were degrading the supported amine sorbents. Laboratory tests were used to determine the main flue gas constituent that was causing a problem for the supported amine sorbents was SO_2 (see discussion in section 4.1.1.1.1). Therefore, a sodium bicarbonate scrubber was added to the fixed bed system for subsequent field tests. The sorbent H breakthrough curves measured on actual flue gas were very similar to those measured in the laboratory on simulated flue gas. This indicated that the carbon-based sorbent was affected to a much lesser degree (if at all) by trace flue gas constituents. The zeolite sorbent performed similarly in the field as in the laboratory; it exhibited an extremely low CO_2 capacity due to preferential adsorption of moisture. After the first two field tests the test equipment was automated, which allowed for a greater number of adsorption/regeneration cycles to be completed.

Additional funds from TVA and EPRI were secured to complete extended field testing (up to 250 adsorption/regeneration cycles for sorbents BR and AY). The results from the extended testing of sorbent BR (supported amine sorbent) and sorbent AY (carbon-based sorbent) helped to provide enough information to draw general conclusions about the state of development for these two types of materials.

Sorbent BR was selected for extended field tests because of its superior theoretical regeneration energy and because it was produced from commercially available materials. The flue gas was pre-treated with a laboratory-scale SO_2 scrubber (discussed in the experimental apparatus and procedure section). The CO_2 capacities as a function of the cycle number are shown in Figure 28. Although there was an overall decrease in the CO_2 capacity with cycle number, the CO_2 capacity was still approximately 8 wt% after the 250 cycles. In addition, the capacity appeared to be relatively stable between cycles 150 to 250. However, the only means of ensuring stability is to complete a greater number of cyclic tests.

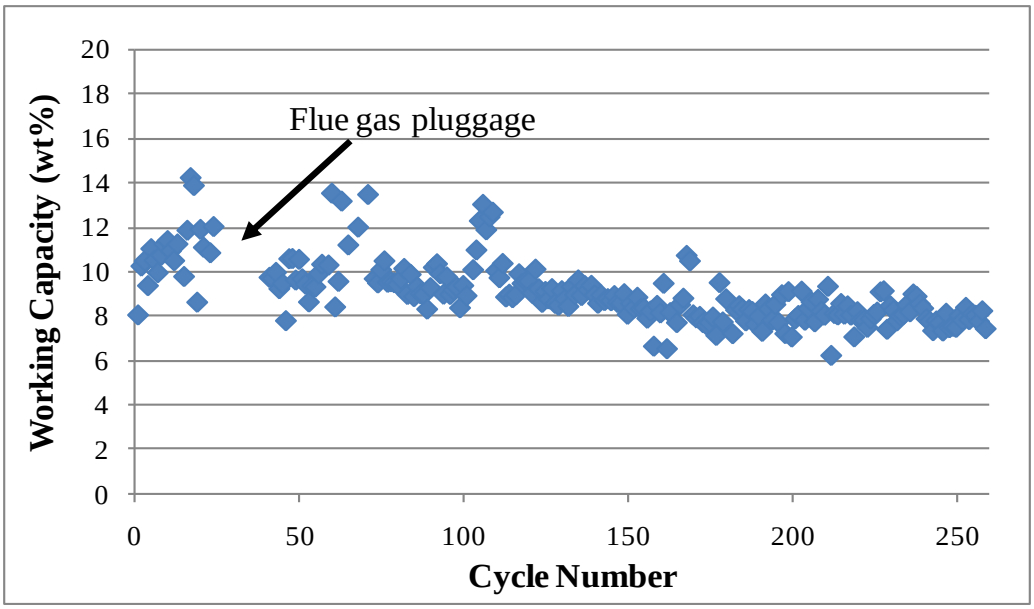

Figure 28: Sorbent BR Field CO_2 Capacity

Note that early in the testing, a sample gas line became plugged and flue gas could not flow into the testing system. Also, for the initial series of adsorption/regeneration cycles (up to approximately cycle 100) the sample line that was being used by ADA-ES was shared by a host site SO_2 emissions monitor. Therefore, if the host site sample pump happened to be operating simultaneously with the ADA-ES sample pump, too little flue gas was drawn into the ADA-ES system. If too little flue gas was provided to the sorbent screening unit, then integration of the adsorption profile would result in the calculation of an inaccurately high CO_2 capacity, which explains the outliers during the earlier cycles Figure 28.

Based on the data provided in Figure 28, the CO_2 capture performance of sorbent BR decreased notably. However, the breakthrough profiles generated by fixed bed tests are not representative of what will be observed during more realistic evaluations in a larger-scale moving bed or fluidized bed. In such systems the sorbent/flue gas contact time may not be adequate to achieve complete CO_2 saturation. However, the better mixing and the ability to remove the heat due to the reaction may have a positive effect on the CO_2 capacity.

A breakthrough curve from early in the extended tests (cycle 10) as well as one from late in the extended tests (cycle 240) are provided together in Figure 29. When comparing these two curves, the loss in CO_2 capacity is noticeable only after longer time periods (i.e. late in the breakthrough curve); this change may not be observable in more realistic systems. Therefore, after over 250 cycles, if the only CO_2 capacity that has been lost is the slower reaction leading up

to saturation, this loss may not be important or noticeable in larger systems, depending on the result of using a different type of system.

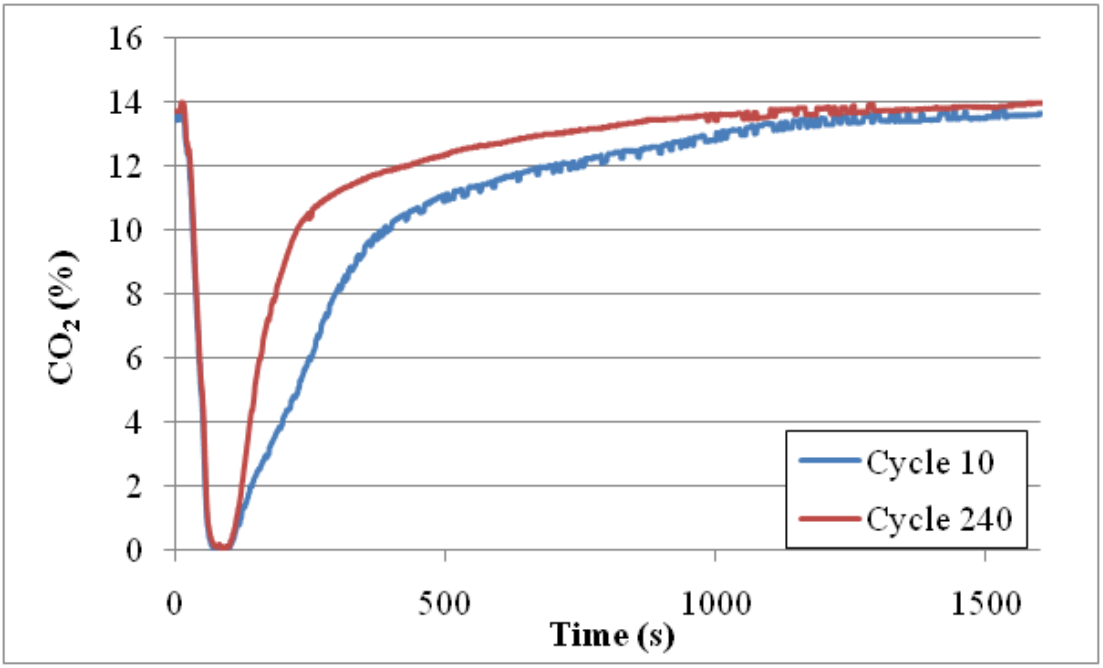

Figure 29: Sorbent BR Field Adsorption Profiles

Sorbent AY was selected for extended cyclic field testing as a representative for activated carbons. Since flue gas constituents quickly degraded the performance of other types of CO_2 sorbents, it was important to determine the effect of these constituents on activated carbons as well. For the field tests of sorbent AY, ADA-ES's laboratory-scale SO_2 scrubber was not employed. Raw flue gas was utilized for this field test with the exception of a moisture dropout chamber designed to keep droplets from causing operation issues.

It should be noted that only 0.7 g of sorbent was used for the field testing. Originally the same sample size that was used in the laboratory tests was to be used in the field test. However, once onsite this sample size resulted in an unacceptably high pressure drop across the fixed bed. Therefore a smaller sample size of 0.7 g was used. As discussed in the experimental and apparatus section, a smaller sample size can lead to greater error due, in part, to the analyzer response time. However, the central purpose of this test was to evaluate the cyclic stability and general trends can still be identified.

The CO_2 capacities versus cycle number for the field test of sorbent AY are provided in Figure 30. Over 250 adsorption/regeneration cycles were completed using actual flue gas without any sign of a decrease in CO_2 capacity. The activated carbon is clearly more stable than the supported amine sorbent. This can be attributed to 1) the activated carbon is not susceptible to reaction with flue gas constituents (physical adsorption) and 2) there is no loss of active material (in some cases the amine evaporated from the substrate). Therefore, the main goal of researchers developing and demonstrating activated carbon CO_2 sorbents should be to increase the capacity and CO_2 selectivity; the cyclic stability is superior to other types of CO_2 sorbents.

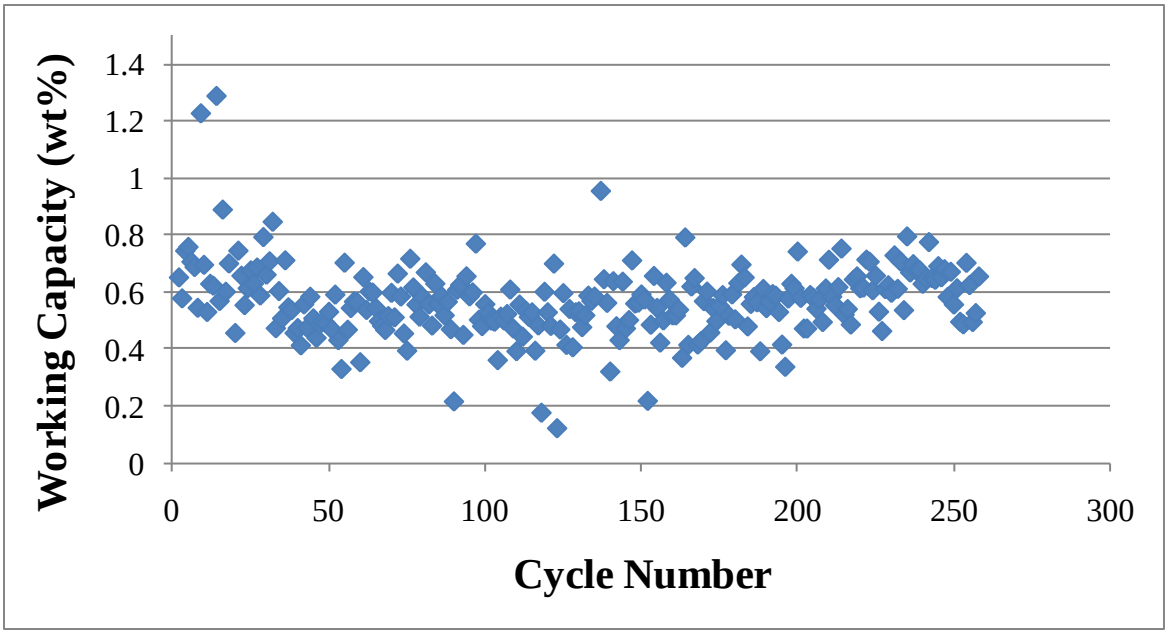

Figure 30: Sorbent AY Field CO_2 Capacity

4.1.1.2.2 Sherco

Sorbent R was a supported amine sorbent that was evaluated in the laboratory-scale fixed bed system at both Martin Lake and Sherco. The regeneration temperature was 100°C. At Sherco, the sorbent that was used for the laboratory-scale tests was collected from the 1 kW pilot after that testing was completed. Select adsorption breakthrough curves are provided in Figure 31.

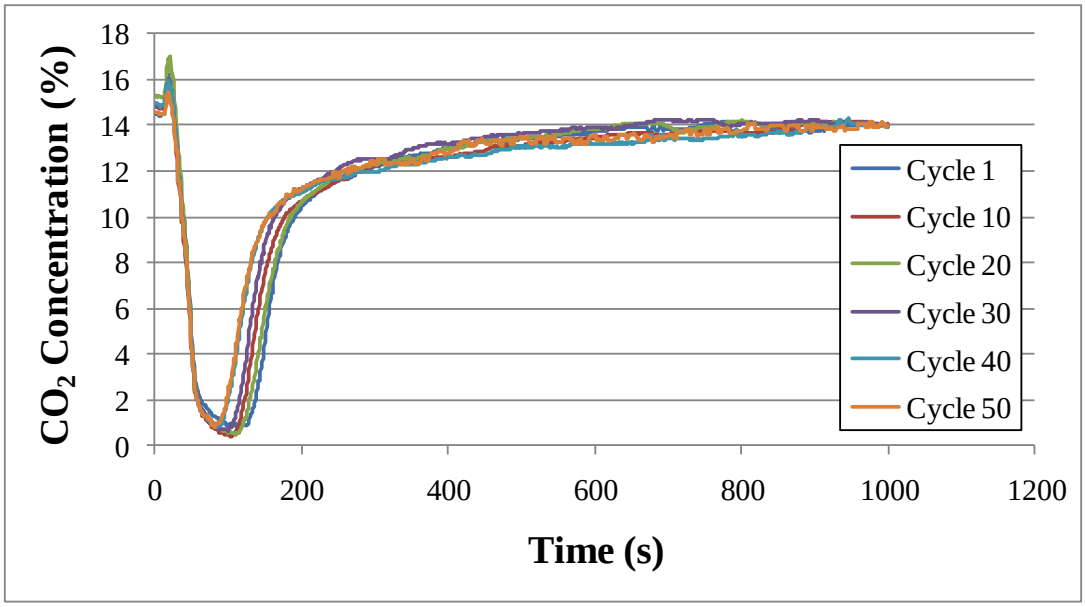

Figure 31: Sherco Sorbent R Breakthrough Adsorption Profiles

The changing shape of the breakthrough curves indicates that the performance of sorbent R was not completely stable during the 50+ adsorption/regeneration cycles. In addition, the average CO_2 capacity for sorbent R was approximately 6.5 wt%, which is nearly 50% lower than what

was measured in the laboratory using simulated flue gas. It is believed that this degradation in CO_2 capture performance was actually caused by SO_2 in the flue gas because the scrubber solution had not been changed adequately. This is supported by the fact that sorbent AX, which consisted of the same amine and a similar support, was completely stable during cyclic evaluations (see discussion in subsequent sections).

Sorbent AX was evaluated for over eighty adsorption/regeneration cycles in the laboratory-scale fixed bed system at Sherco. The regeneration temperature was 100°C. However, during cycles eight through twenty eight the flue gas sample line became completely plugged. During the cycles where flue gas was not available the sorbent was still exposed to the temperature swing, but not the flue gas. Several adsorption profiles for sorbent AX are provided in Figure 32.

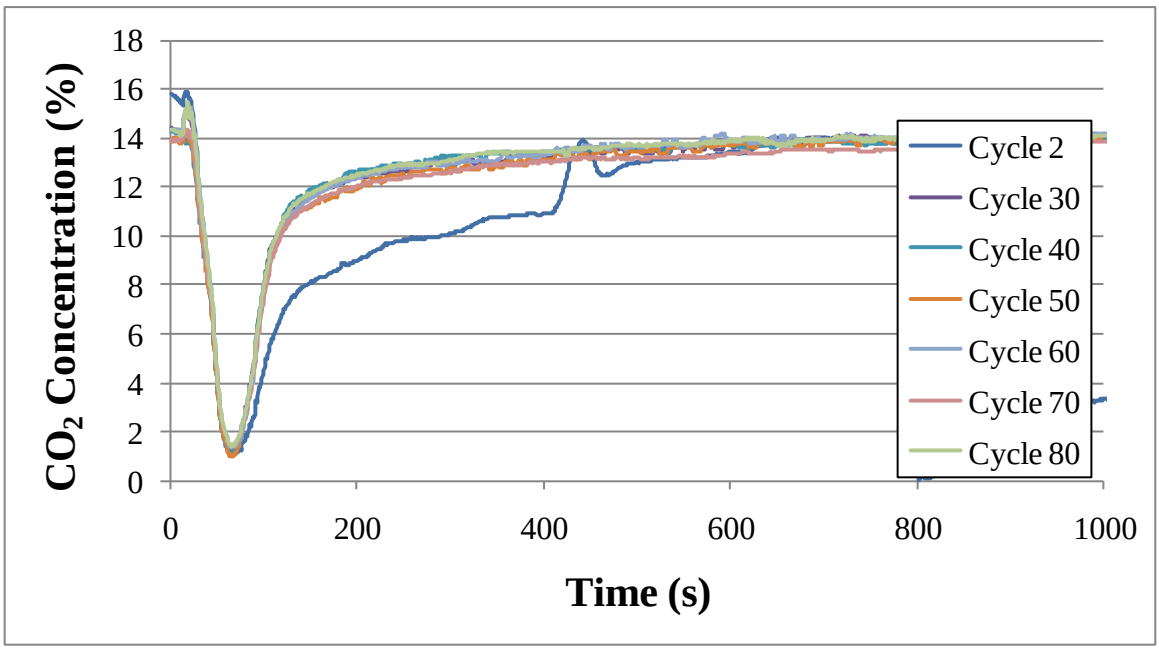

Figure 32: Sherco Sorbent AX Adsorption Breakthrough Profiles

With the exception of cycle 2, where the flue gas line was already partially plugged, the breakthrough curves for sorbent AX are consistent. This material did not exhibit any loss in CO_2 capacity due to the exposure to the scrubbed Sherco flue gas or the repeated temperature swing. Because the same amine was used to produce sorbents R and AX, this further supports the conclusion that the SO_2 levels were elevated during the fixed bed evaluation of sorbent R. The average CO_2 capacity of sorbent AX was 5.5 wt%, which is significantly lower than what was measured previously in the laboratory. It is possible that some damage occurred to the sorbent in the 1 kW pilot before it was transferred to the fixed bed system.

Sorbent F was evaluated in the laboratory-scale fixed bed system for 79 adsorption/regeneration cycles using a slipstream of Sherco flue gas. The regeneration temperature was 120°C. Because the fine particles resulted in a greater pressure drop across the fixed bed compared to the other sorbents, only 0.7 grams of sorbent F was used during the laboratory-scale tests. Select adsorption profiles for sorbent F are provided in Figure 33.

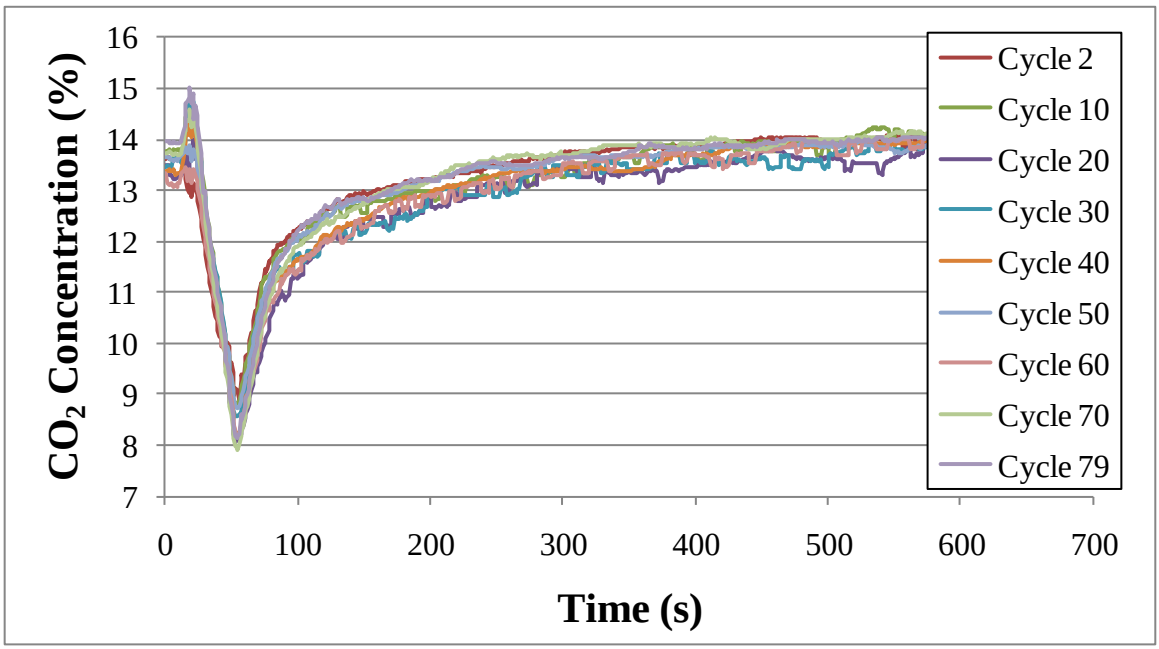

Figure 33: Sherco Sorbent F Adsorption Breakthrough Profiles

The shape of the adsorption profiles for sorbent F is different from the other sorbents, in part, because the sample size was smaller. The average CO_2 capacity measured during the fixed bed tests was 5.8 wt%, which was similar to what was measured during previous laboratory tests using simulated flue gas. Over the 80+ adsorption/regeneration cycles completed in the fixed bed the CO_2 capacity of sorbent F was constant.

Using crushed BN, over 50 adsorption/regeneration cycles were completed. The regeneration temperature was 120°C. Select adsorption profiles are provided in Figure 34. During the extent of cyclic testing completed at Sherco, no change in the CO_2 capacity was observed.

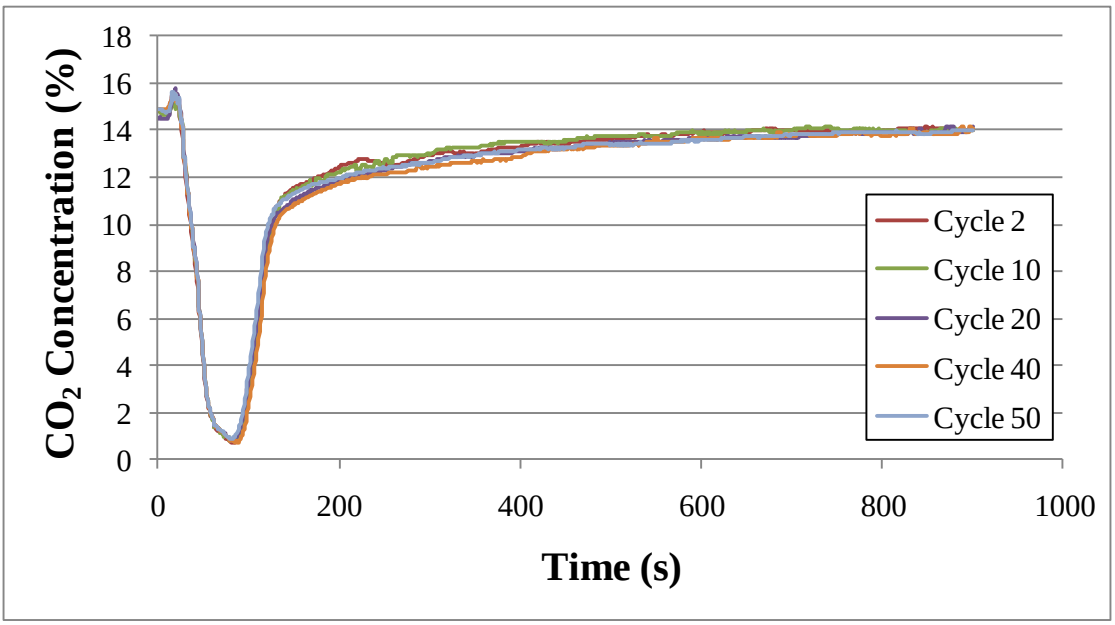

Figure 34: Sherco Sorbent BN Adsorption Breakthrough Profiles

The average CO_2 capacity of the crushed sorbent BN was 6.5 wt%, which was similar to what was measured using simulated flue gas in the laboratory. When the beaded form of sorbent BN was used to generate breakthrough curves, the CO_2 capacity dropped from 6.5 wt% to approximately 3.1 wt%. A comparison of a breakthrough curve for both forms of sorbent is provided in Figure 35. Per unit mass, both types of sorbent include the same amount of amine content. Therefore, the difference in the breakthrough profiles can be attributed to the diffusion limitations caused by the larger particles. When considering how different reaction times will affect the larger CO_2 capture process the reactor type must be taken into consideration. If the gas/solids contact time is short, such as is the case in a fixed bed, faster reactions will be required to achieve the desired CO_2 loading levels.

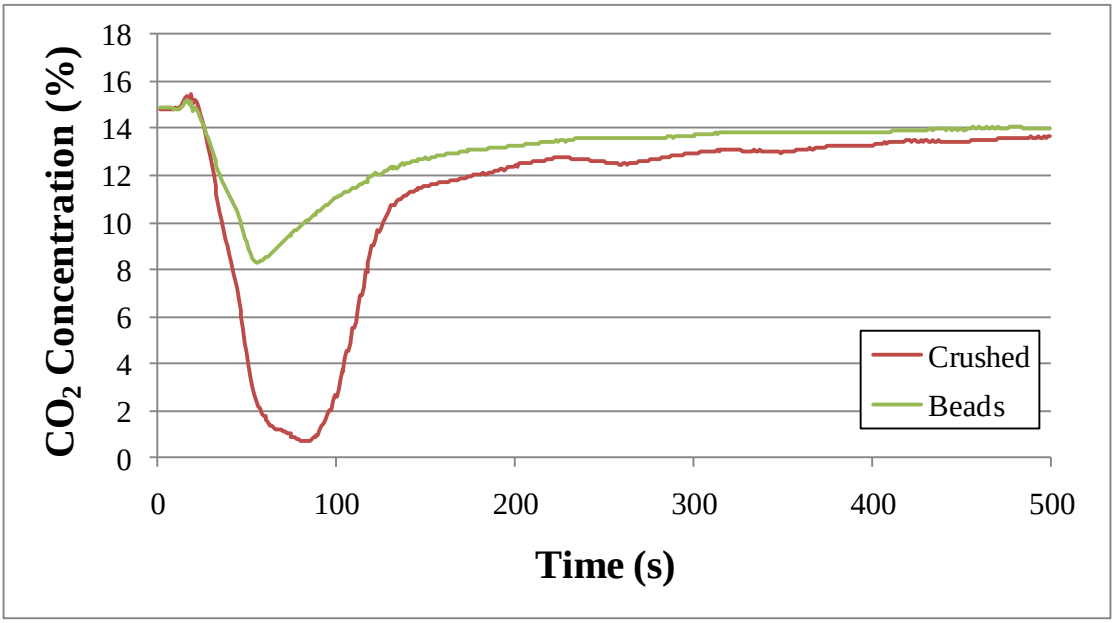

Figure 35: Crushed and Beaded Sorbent BN Breakthrough Profiles

4.1.2 Thermogravimetric Analyzer

In addition to the long-term tests, ADA-ES also completed TGA evaluations to determine the CO_2 capacity at multiple CO_2 partial pressures and temperatures. In the public literature discussing potential CO_2 sorbents, there has been a great deal of focus on the total CO_2 capacity, which is measured when regenerating the sorbent under a purge gas with minimal CO_2 partial pressure, similar to the fixed-bed tests discussed in this work. However, to minimize compression costs in an actual CO_2 capture and compression system, the CO_2 partial pressure during regeneration must be as high as possible. The data collected by ADA-ES is important because it can be used to calculate working capacity under different adsorption and regeneration conditions.

Ideally, CO_2 capture will occur rapidly and effectively at lower temperature (40-60°C) shown with unfilled symbols in Figure 36 and lower CO_2 partial pressure (0.08-0.15 bar). Regeneration will then occur at increased temperature (90-120 °C) shown with filled symbols in Figure 36 as well as increased partial pressure (>0.15 bar). ADA-ES measured the CO_2 capacity at temperatures between 40°C and 120°C in 10°C increments at four different partial pressures, 0.04, 0.081, 0.5, and 0.81 bar. The results of these tests are provided in Figure 36.

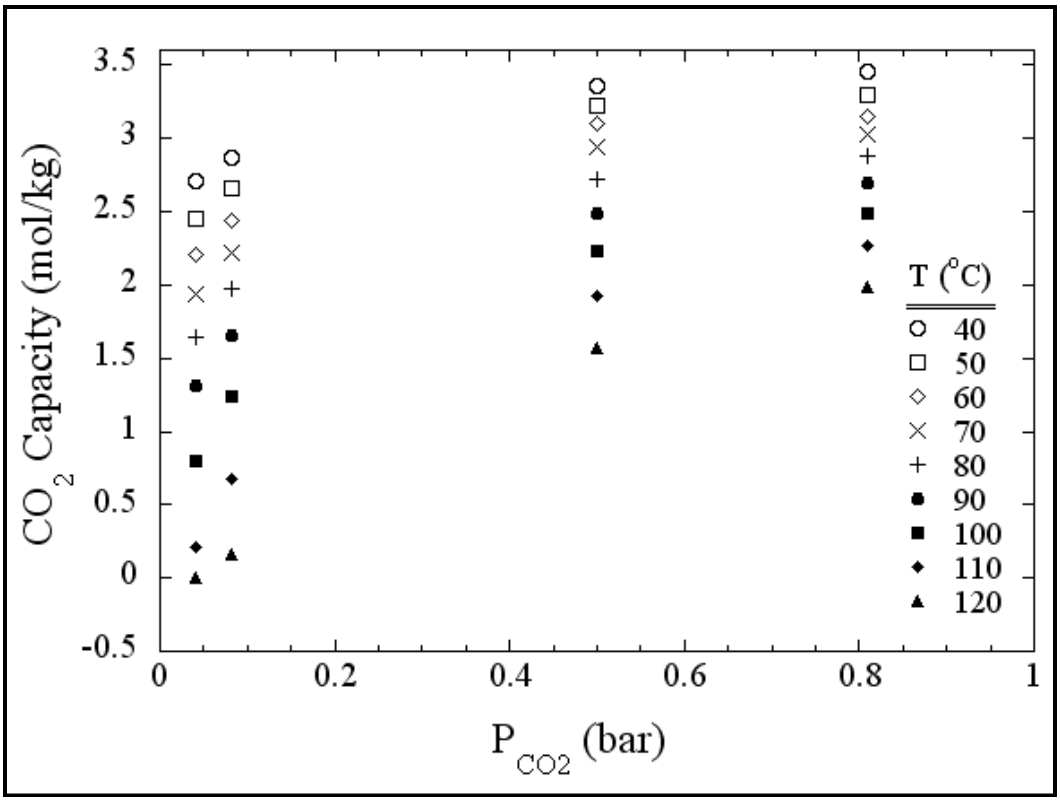

Figure 36: Sorbent CE Isotherms

To keep compression costs as low as possible in a commercial CO_2 capture system, it is desired to regenerate the sorbent under the highest possible CO_2 partial pressure. However, the data provided in Figure 36 clearly illustrate how regeneration at higher CO_2 partial pressure will lead to a decrease in the overall CO_2 working capacity. For example, if CO_2 capture occurred at 50°C and 0.081 bar partial pressure and regeneration occurred at 120°C and 0.81 bar partial pressure, the working capacity would be the difference between the total CO_2 capacities at the respective adsorption and regeneration conditions (i.e. 2.7 mol/kg – 2.0 mol/kg = 0.7 mol/kg = 3.1 wt%). This calculation is provided only as an illustration. At most coal-fired power plants the partial pressure will be greater than 0.081 bar, which would lead to an increase in the working CO_2 capacity.

The isotherms were also measured for a different supported amine sorbent, sorbent BN, which are provided in Figure 37. This material exhibited lower total CO_2 capacities during fixed bed tests, but can be produced relatively inexpensively. Using the same procedure described above to determine the working capacity for sorbent CE, the working capacity for sorbent BN is in the range of 1.3 mol/kg (5.7 wt%). Different supported amine sorbents clearly react differently depending on the temperature and CO_2 partial pressure.

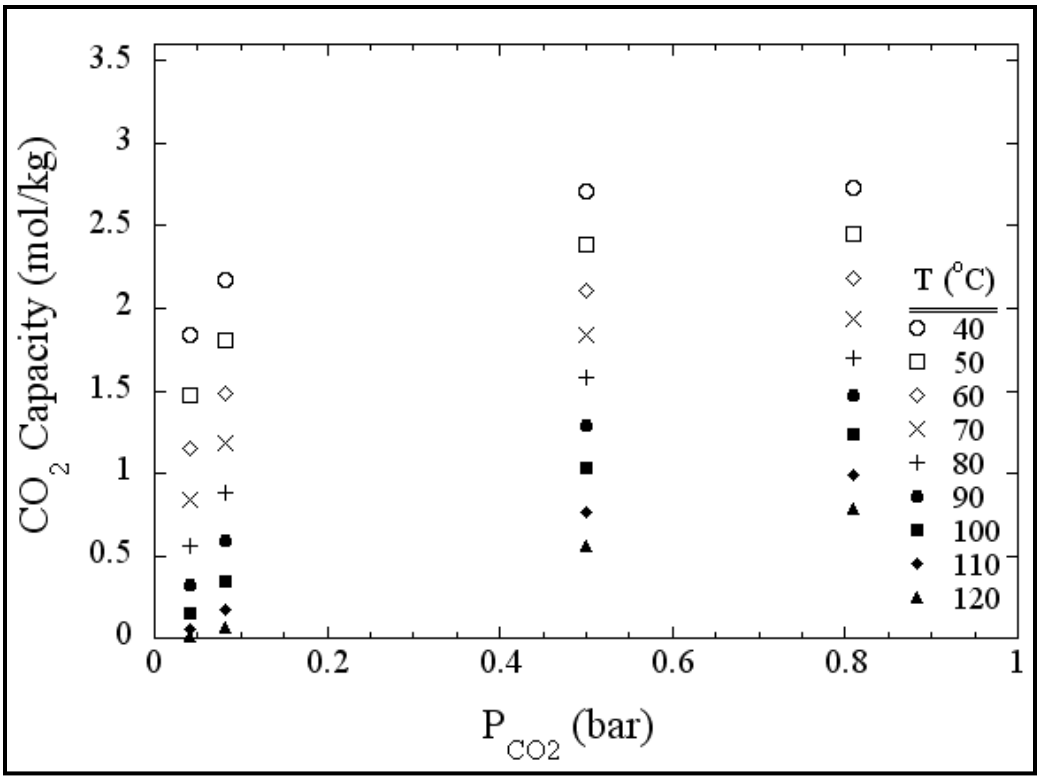

Figure 37: Sorbent BN Isotherms

Although the working capacity for sorbent BN is greater than that of CE, it is still desirable to increase this working CO_2 capacity as much as possible, which will reduce the process energy penalty and potentially will also decrease the equipment size. There are several different means to increase working capacity:

- Decrease the capture temperature;
- Increase the regeneration temperature (within the limits of the amine stability);
- Decrease the partial pressure of the CO_2 during regeneration by using a vacuum or diluting with steam.

Each option for increasing the working capacity will have associated costs. It is outside the scope of this work to determine optimal CO_2 capture/regeneration options. However, as sorbents are evaluated at increasing scales and complexity and the equipment/process options are taken into greater consideration, such evaluations will become imperative. Process optimization will be considered in depth in future projects.

The results shown in Figure 36 and Figure 37 were collected during TGA tests with minimal (~1.1 vol%) moisture. It is not only possible, but expected, that an increase in moisture content during the adsorption step will increase CO_2 capacities. If less moisture is present in the regenerator, the overall CO_2 working capacity could be greater than what was measured in previous tests. Although this type of detailed analysis is outside the scope of this project, future projects where one or two sorbents are studied in depth, in contrast to the broad screening program completed during this project, the effect of moisture will be quantified.

4.1.3 Attrition Testing

In a commercial sorbent-based CO_2 capture system, costs will dictate that sorbents must be used for thousands of cycles. Therefore, if the process involves equipment that can lead to significant levels of attrition, such as has been observed during operation of a circulating fluidized bed, it is important to understand the strength properties of the sorbent. The substrates for sorbent R (shown in Figure 38) and X (shown in Figure 39) were circulated in a fluidized bed for 6 hours and the particle size distribution before and after were measured. The full report provided by Jenike & Johanson is included in Appendix E. Due to the short duration and the equipment used, the results from the attrition tests carried out during this study can only be discussed qualitatively for comparing two different shapes of similar substrates.

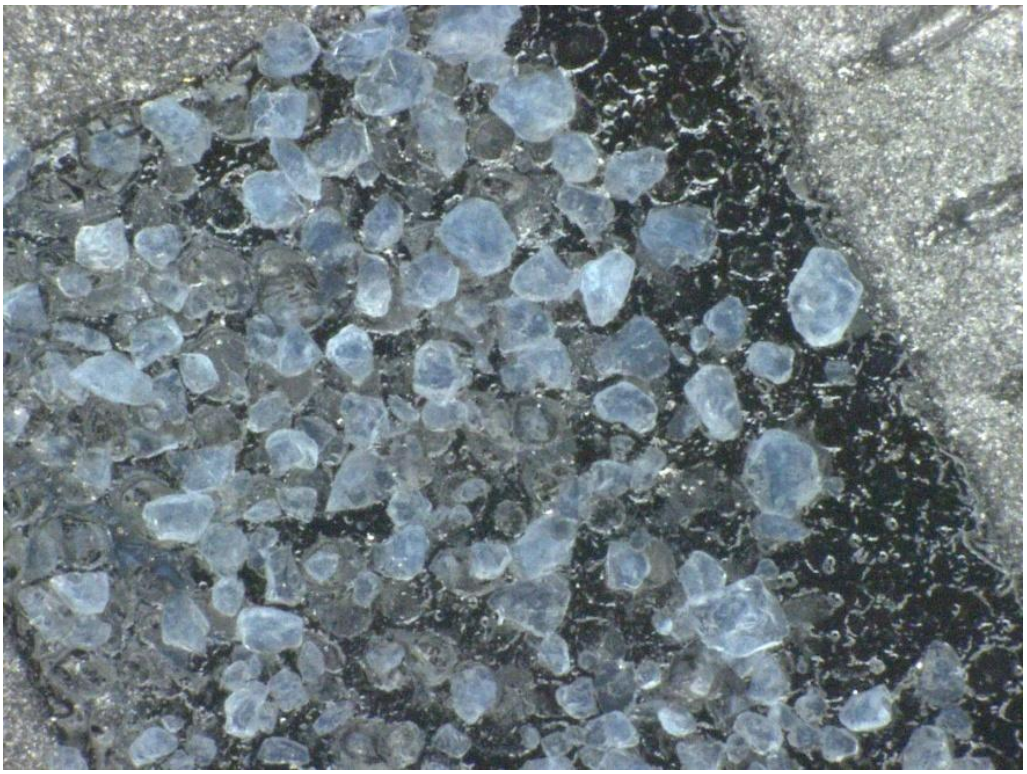

Figure 38: CARiACT® G10 granular

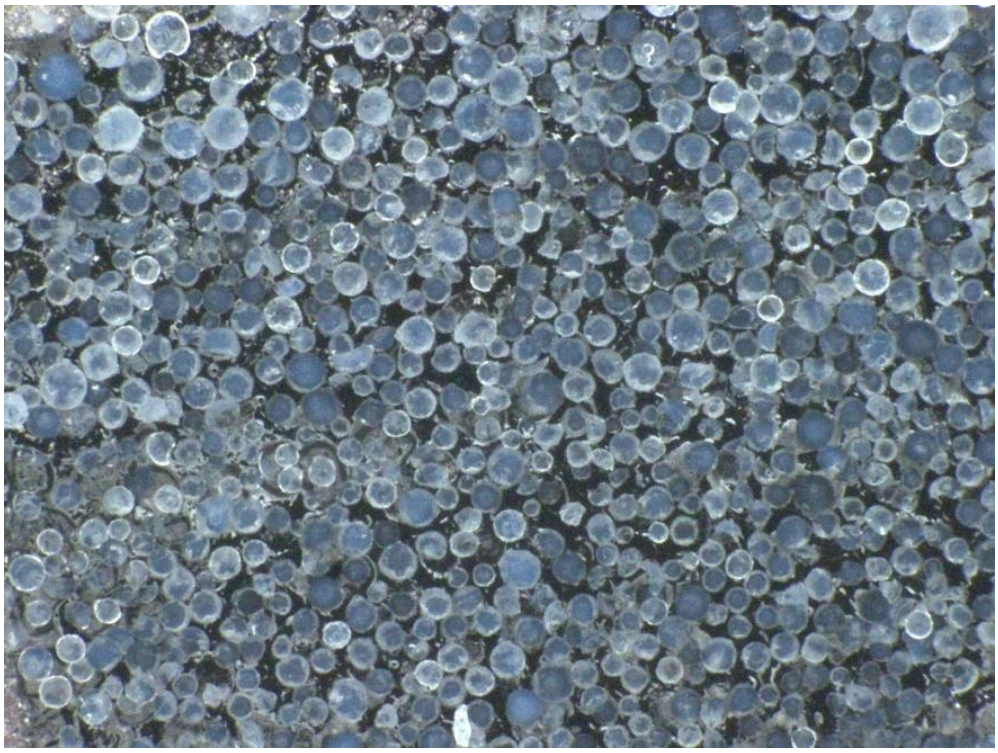

Figure 39: CARiACT® Q10

The particle distribution for the substrate CARiACT® G10 (sorbent R substrate) before and after it was circulated in a fluidized bed system is provided in Figure 40. The median particle size before circulation was approximately 185 μm; after circulation the median particle size was approximately 155 μm. This represents a decrease of approximately 16% in the median. However, when the two curves in Figure 40 are compared, the distribution curves are relatively similar with a small shift to the left (i.e. smaller particles) after circulation.

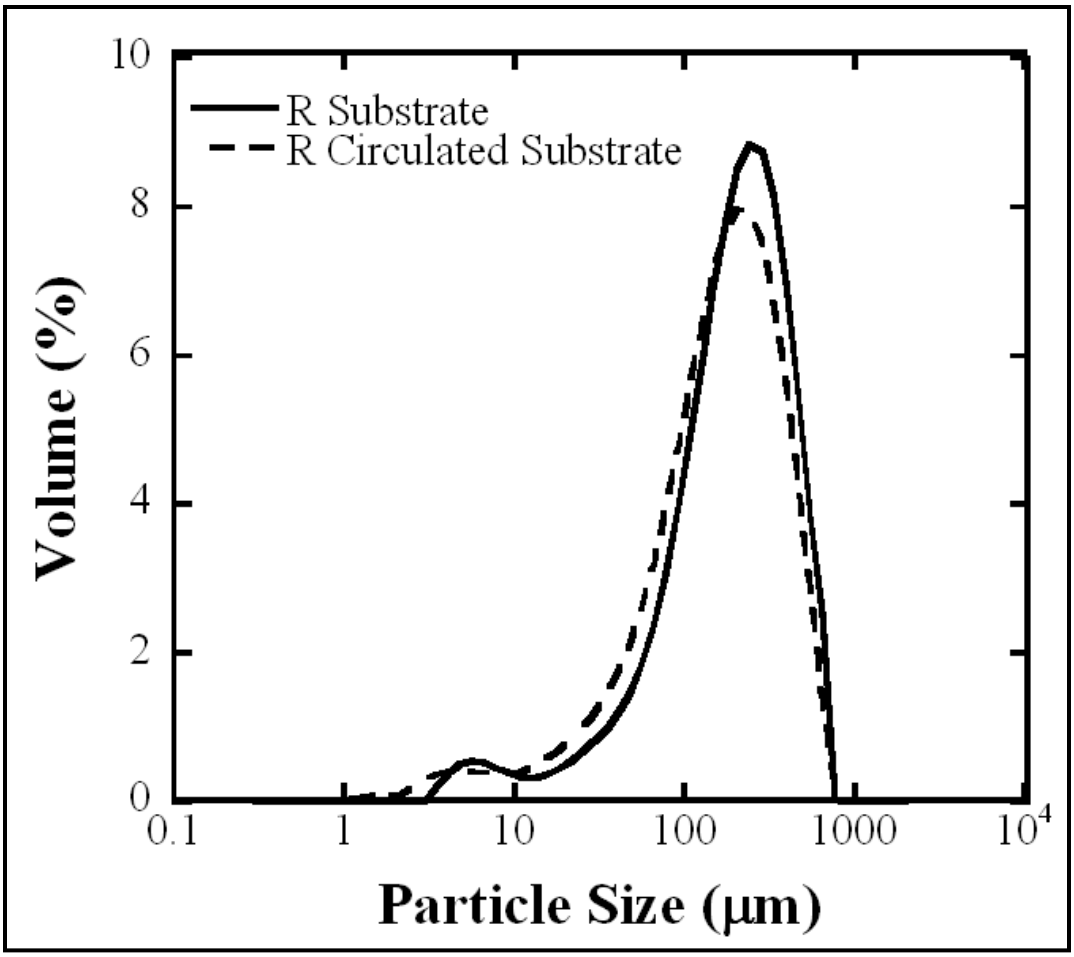

Figure 40: Sorbent R Substrate Particle Size Distribution

The particle size distribution of the CARiACT® Q10 (sorbent X substrate) before and after circulation are provided in Figure 41. In this case, the median particle size decreased from approximately 212 μm to 191 μm, representing a decrease of 10%. This decrease is less than that observed for the sorbent R substrate, but the particle distribution curve between the before and after samples are clearly distinguishable.

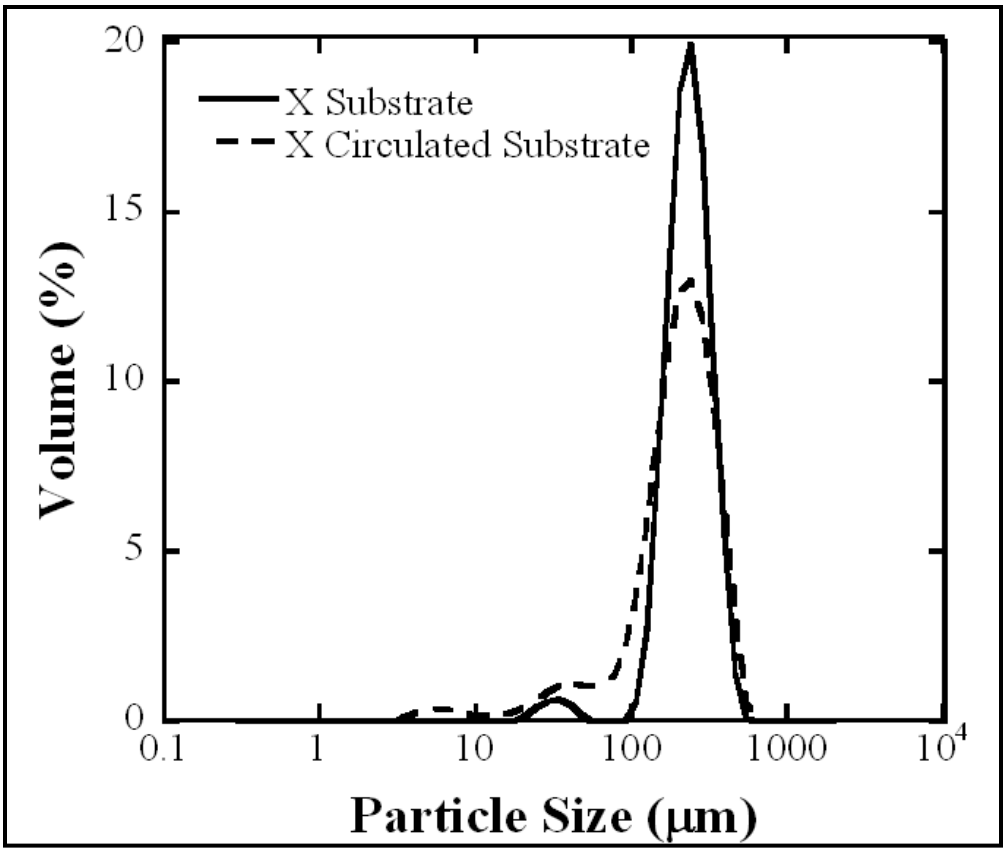

Figure 41: Sorbent X Particle Size Distribution

The CARiACT® G10 substrate is non-uniform and non-spherical as is shown in Figure 38. The CARiACT® Q10 is spherical and more uniform as is shown in Figure 39. The uniformity of the materials is confirmed by the particle size distribution curves. It was expected that the non-spherical material would exhibit higher attrition levels. However, it was somewhat unexpected that the change in median particle size would be similar for the two materials. Longer tests could be conducted in the future to obtain more quantitative results. However, to get a truly quantitative measurement, attrition analysis must be completed after circulating the sorbent in the type of system that will be used for CO_2 capture; although outside the scope of this work this will be the focus of future projects.

4.1.4 Additional Physical Sorbent Properties

4.1.4.1 Particle Density

The particle density is an important property that must be known to design different reactors. Although it was prohibitively expensive to test the particle density for all the sorbents screened under DE-NT0005649, the particle density was measured by Adsorption Research, Inc. for two promising supported amine sorbents under DE-FE0004343. The sorbents evaluated were sorbent AX, which was produced using the same porous silica substrate as sorbent CE and sorbent X, as well the beaded sorbent BN, which was manufactured using a polystyrene resin substrate.

The particle density for AX, as delivered, was found to be 0.821± 0.016 g/cm^3. The particle density for BN was 0.646 ± 0.012 g/cm^3. Because the moisture in the sorbent was more of a concern for sorbent BN, the particle density for this material was measured after the sorbent was treated with H_2O saturated N_2 at 55°C. The particle density for sorbent BN after pre-treating at 55°C was 0.586 ± 0.009 g/cm^3. There was a 38.9% mass loss during pretreatment. The change in particle density, however, was only 9.3%, indicating that the particle size also changed somewhat with the moisture pre-treatment. The difference in the particle density for the silica substrate supported amine and the polystyrene supported amine was approximately 29%. These two sorbents would behave very differently regarding fluidization and entrainment. Therefore, it would be difficult, if not impossible, to design a single reactor where such different materials could simply be interchanged.

4.1.4.2 Crush Strength

For beaded or granular materials crush strength can provide a quantitative measurement for comparison. Although the crush strength alone will not provide exact attrition rates for different types of reactors, it can be valuable for designing systems/processes. For example, silo specifications or sorbent distribution devices could require stacking or piling of sorbent. The height of the sorbent could be limited by the crush strength. The only promising beaded material that was evaluated under the program was sorbent BN. Crush strength values were measured by Adsorption Research, Inc. under DE-FE0004343. The full report is included in Appendix F for reference.

Crush strength values were measured for BN. They ranged from 232 to 1019 g. The average mass required was 412.5 ± 175.8 g. The median of the masses was 363.3 g. The distribution of measured values is shown in Figure 42. The lowest masses required were for the smallest particles and the particle was determined to be “crushed” when the particle audibly cracked.

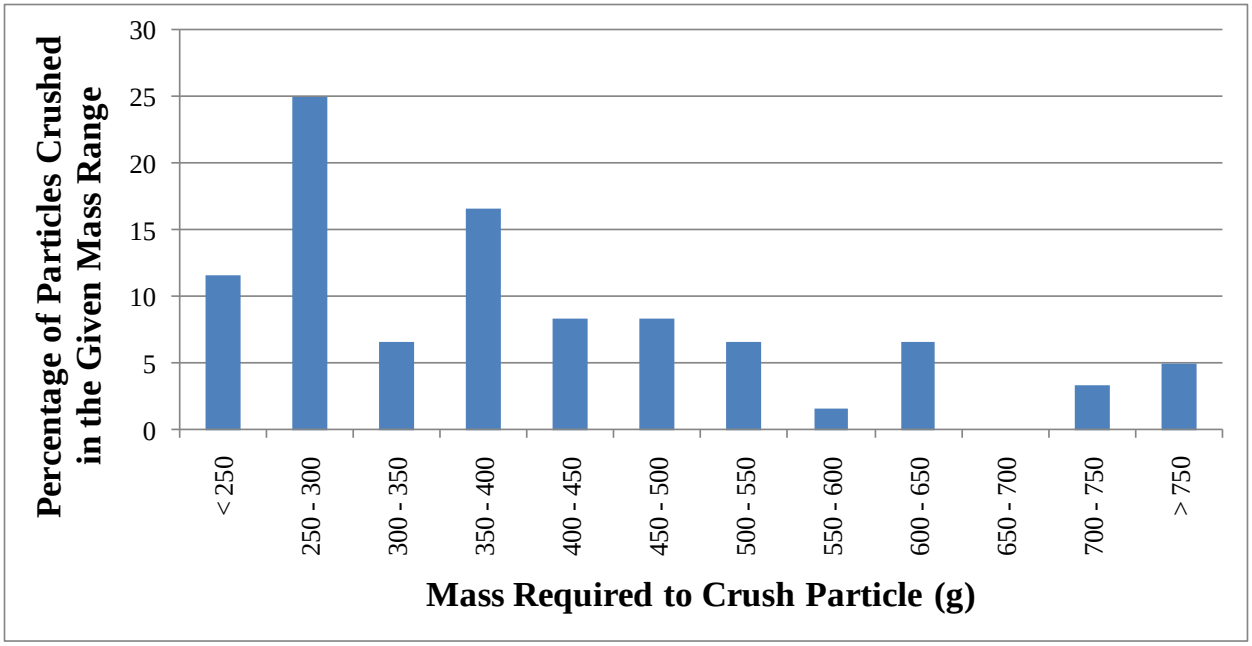

Figure 42: Sorbent BN Crush Strength Analysis

4.2 1 kW Pilot Testing

4.2.1 Host Site 1: Martin Lake

The first host site for 1 kW pilot testing was Luminant's Martin Lake Steam Electric Station. The test equipment was first operated with sand as a surrogate for sorbent to ensure proper operation of the system. Then, sorbent R, which was a supported amine sorbent developed by researchers at NETL was evaluated. This was the only sorbent tested in the 1 kW pilot at Martin Lake. Sorbent R was selected for because it exhibited the greatest total CO_2 capacity under simulated flue gas conditions and superior cyclic stability compared to many other supported amine sorbents evaluated to date. During laboratory testing the theoretical regeneration energy for sorbent R was calculated to be approximately 2200 kJ/kg CO_2, compared to the MEA benchmark of 3600 kJ/kg CO_2. The first 1 kW pilot scale parametric test of sorbent R occurred on 3/10/2010. During this first test, the temperature in the regenerator was maintained low enough to prevent regeneration. This approach was used to confirm the cycle time of the sorbent through the system by monitoring when spent sorbent re-entered the bottom of the riser. If the CO_2 removal levels decreased significantly in less than two hours, the sorbent was not moving through the system as expected.

Two graphs including data collected during the first test are presented in Figure 43, the inlet CO_2 concentration, outlet CO_2 concentration, and CO_2 removal are shown in the top graph while several temperatures in the riser and ICFB are provided in the second graph. Flue gas was introduced into the system at approximately 17:00 with sorbent already circulating. The CO_2 removal in the riser stabilized at approximately 60%. Then, at approximately 17:50 fluidization gas was added to the ICFB, which caused the sorbent in the ICFB to begin circulating. Over 90% removal was achieved before the CO_2 capture decreased.

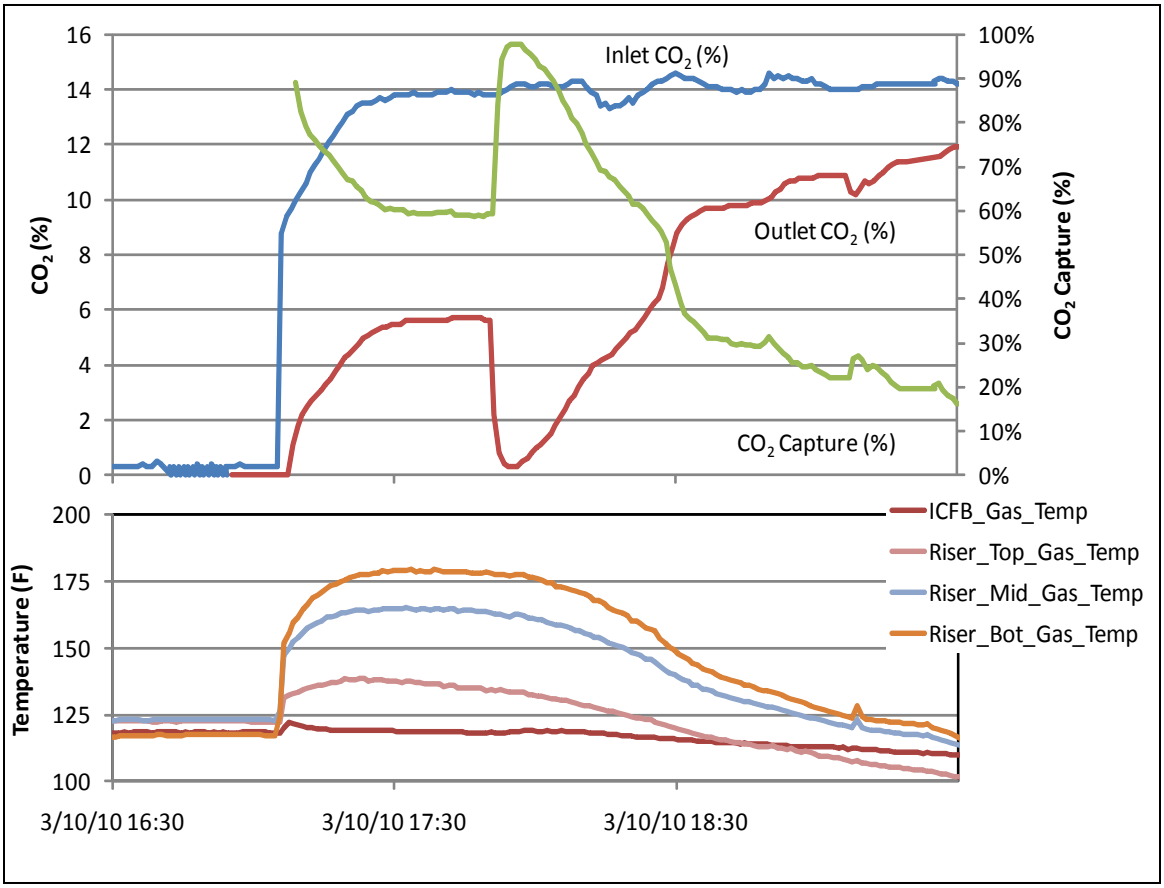

Figure 43: CO_2 Concentration, CO_2 Removal, and Temperature Information Collected During Parametric Testing of Sorbent R

The temperature increases observed in the second graph in Figure 43 were caused by the exothermic reaction between the sorbent and CO_2. Since the temperature increase at the bottom of the riser was significantly larger than that at the top of the riser, the residence time in the riser is likely sufficient for most of the reaction to occur. In the laboratory testing the reaction between sorbent R and the CO_2 was characterized by a fast reaction rate followed by a much slower reaction rate before equilibrium was achieved. In a system where the gas/solid contact times are characterized be seconds, rather than minutes or hours, only fast reactions can be utilized as part of the working capacity. A fast reaction will reduce the overall size and capital cost of the equipment, but it also increases the challenge related to controlling the temperature. If most of the reaction occurs at one location, the heat of reaction must be removed at that location.

Although the 1 kW pilot was designed to operate continuously, it was flexible enough to be operated in batch mode. There were two different ways to operate in batch mode. The first method was to halt sorbent circulation, which led to only the sorbent in the regenerator being regenerated, approximately one half of the sorbent inventory. Similarly, the system could be operated in batch mode by circulating sorbent using air instead of flue gas in the riser. The second method of batch regeneration results in regeneration of the entire sorbent inventory. During the initial operation of the system the first method of batch regeneration was utilized to

determine whether the sorbent had been permanently degraded (i.e. it will not regenerate). In addition, if the heat input into the system was sufficient and fairly uniform, the time required for sorbent regeneration should reflect the lab-scale results (i.e. less than 30 minutes). After heating and fluidizing the sorbent in batch mode for over four hours, CO_2 release was still measurable, suggesting that the temperature was not the only important condition to instigate regeneration. Even though the sorbent was not fully regenerated, it was clear that improved regeneration had been achieved during batch regeneration compared to continuous operation. The outlet concentration and CO_2 removal levels after the batch regeneration are provided in Figure 44.

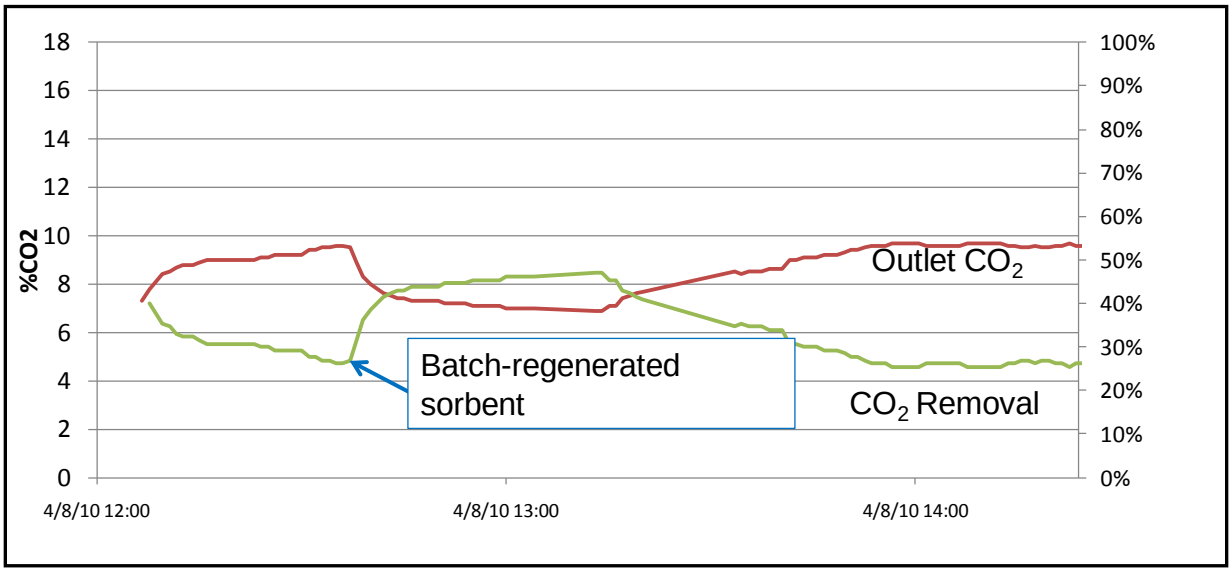

Figure 44: Outlet CO_2 and CO_2 Removal after Batch Regeneration

In Figure 44, testing began at approximately 12:10 when sorbent was introduced into the riser from the cooler section; material in the cooler had not been included in the batch regenerated material. Initially, the CO_2 removal level began decreasing, which could be expected from partially spent material. At approximately 12:40 a significant increase in the CO_2 capture level was observed. This was attributed to the introduction of the sorbent that had been regenerated in batch mode. Since the regenerator contained approximately 50% of the sorbent inventory (40 lbs out of 80 lbs), at a sorbent circulation rate of 40 lb/hr, the higher CO_2 removal levels were expected to continue for one hour, the estimated time required to feed all material included in batch regeneration into the riser. However, after 30 to 40 minutes a significant decrease in the CO_2 removal was observed, suggesting that some regenerated material was being retained in the regenerator and some spent material was short circuiting through the regenerator.

To resolve the presumed sorbent flow issue through the regenerator, the team decided to fabricate and operate a cold-flow model of the regenerator at the ADA offices in Littleton, Colorado. New fluidization nozzles were added to the regenerator to promote better fluidization gas distribution and then the team resumed 1 kW pilot testing of sorbent R. Based on the amount of time required for the CO_2 removal level to decrease, it was concluded that the modifications to the regenerator had been successful and the sorbent was moving through the regenerator in a much more uniform manner. However, as is shown in Figure 45, the CO_2 removal could still not

be maintained at the desired level of ≥90%. The lower removal levels can be attributed to the design of the 1 kW pilot (see discussion surrounding Figure 14).

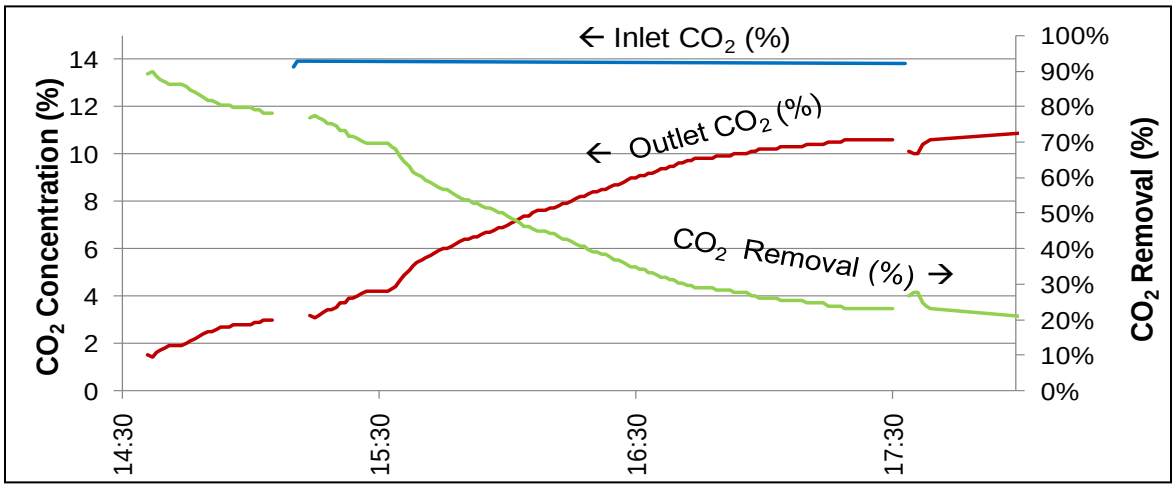

Figure 45: CO_2 Concentrations and Removal during Continuous 1kW Testing of Sorbent R

In addition to measuring the overall CO_2 removal the riser was fabricated with several ports that allowed sample gas to be collected from a number of different locations. The CO_2 concentration at the system inlet, ICFB outlet, and three locations along the riser are provided in Figure 46. Note that for sorbent R 50% of the total CO_2 removal occurs in the first three feet of the riser.

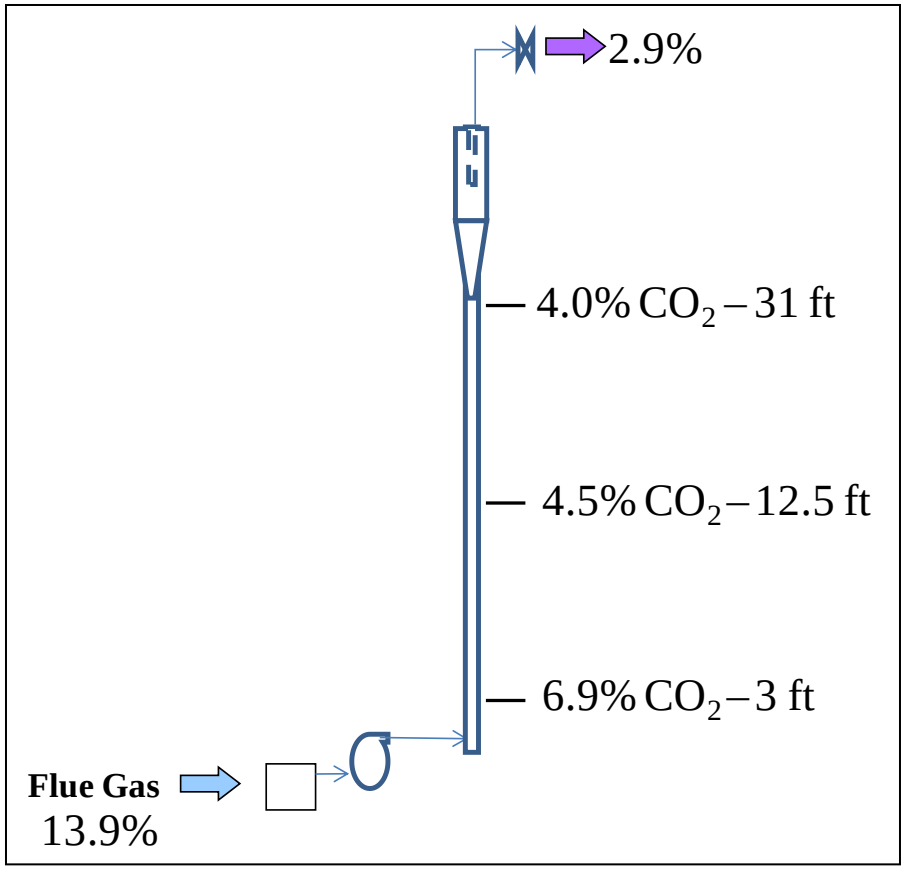

Figure 46: CO_2 Concentrations at different locations in the riser

To ensure that the failure to maintain 90% CO_2 removal in continuous mode testing was not caused by sorbent degradation, the system was operated in batch mode. To operate in batch mode, the flue gas in the riser (adsorption section) was replaced with air, while all other operating parameters, except occasionally the sorbent circulation rate, remained unchanged from the continuous operating conditions. An example of the CO_2 concentration and removal during one batch adsorption step is shown in Figure 47.

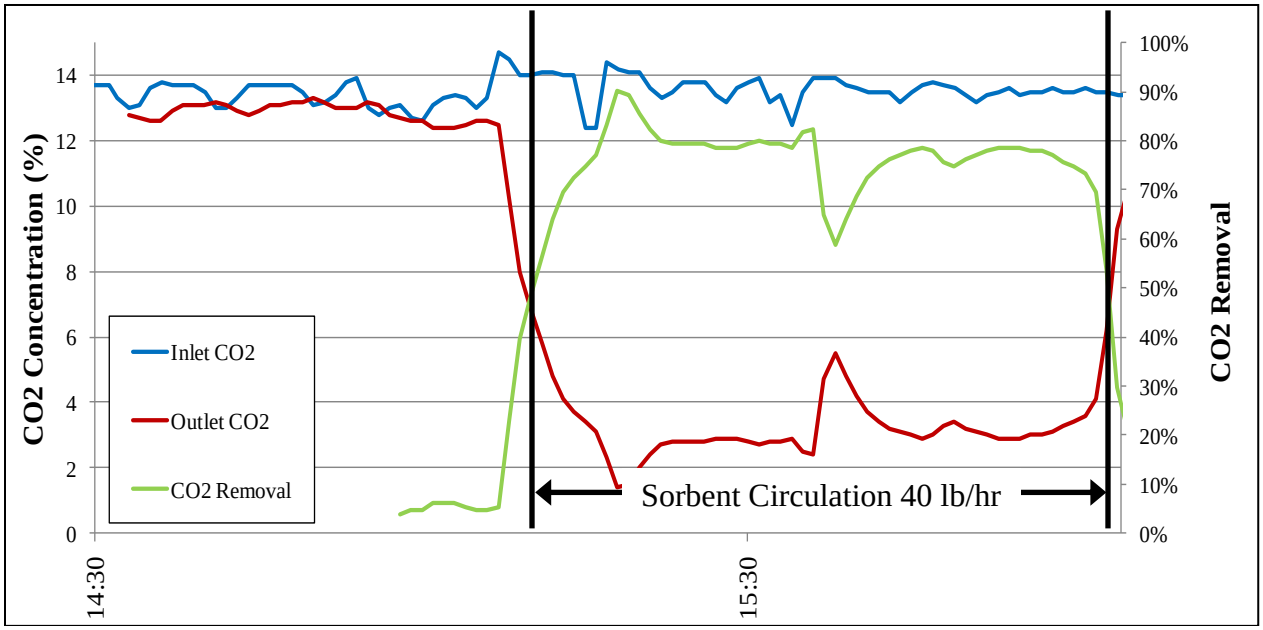

Figure 47: CO_2 Concentrations and Removal during Batch 1kW Testing of Sorbent R

Ten adsorption/regeneration cycles were completed in batch mode using sorbent R. The CO_2 removal levels during these ten cycles are shown in Figure 48. Note that several conditions were varied during the different cycles, such as the time allowed for regeneration and the sorbent circulation rate during regeneration, so the difference in the CO_2 removal levels can mostly be attributed to such factors.

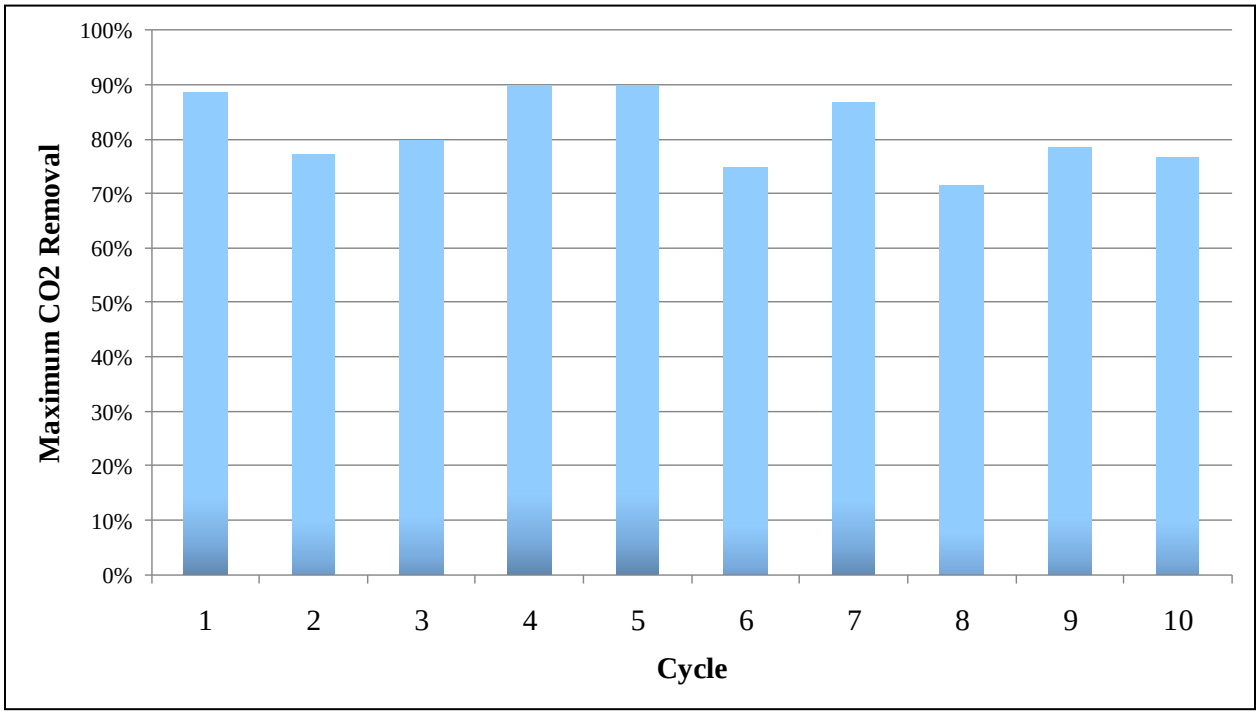

Figure 48: CO_2 Removal Levels during Batch Operation of Sorbent R

It was determined that the sorbent could be fully regenerated in batch mode; hence the 1 kW pilot system was operating as designed, but this system due to the means of gas/solids contacting was unable to achieve high CO_2 removal levels (see discussion surrounding Figure 14 for additional details).

4.2.2 Host Site 2: Sherco

Xcel Energy's Sherburne Generating Station (Sherco) was the second field site at which the 1 kW pilot was operated. Sorbents for 1 kW testing at Sherco were down-selected from more than 140 screened by ADA on simulated flue gas in the laboratory. The theoretical regeneration energy (described in section 2.1.1) was used to compare different sorbents to each other as well as the aqueous MEA benchmark. If the theoretical regeneration energy calculated for a sorbent was greater than the benchmark MEA then the sorbent was immediately ruled out for testing at the 1 kW pilot scale. A summary of the laboratory screening results, showing the theoretical regeneration energy for several materials compared to aqueous MEA (represented by the red dashed line)[3], is presented in Figure 49.

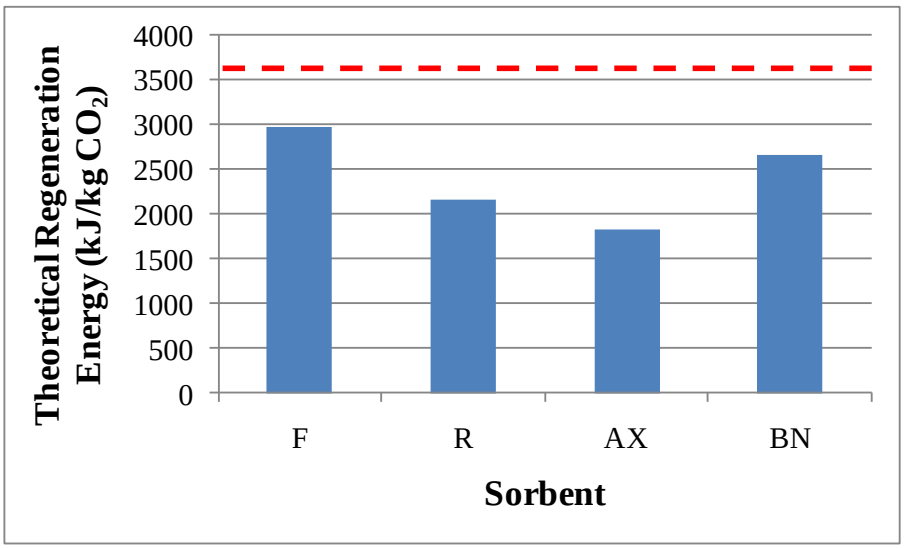

Figure 49: Summary of Sorbent Screening Results

In addition to the theoretical regeneration energy the cyclic stability of the sorbent was also considered as a key sorbent selection criteria. Sorbents F, R, AX, and BN all exhibited superior cyclic stability when evaluated for up to 260 adsorption/regeneration cycles in the laboratory. The final selection criterion was that the materials could be produced in greater than 225 kg (500 lb) quantities. Several potentially promising sorbents were not tested at the 1 kW scale because they could not be produced in the appropriate quantities due to toxic or exotic raw materials. The four supported amine sorbents selected for evaluation at Sherco are discussed in the following subsections.

Sorbent R was a supported amine sorbent, originally invented by researchers at NETL. During the ten batch mode adsorption cycles measured during tests at Martin Lake 90% CO_2 removal could not be maintained when operating the 1 kW pilot continuously with sorbent R; however, over 90% CO_2 removal was possible when the system was operated in batch mode. Sorbent AX, which was similar to sorbent R except the substrate was a different porous silica, was operated in

batch mode at Sherco. The maximum CO_2 removal demonstrated by the two sorbents is provided in Figure 50. Although the removal observed in cycle 5 for sorbent AX was significantly lower than the other cycles, it is believed that this was caused by equipment issues due to extremely low temperatures, rather than a decrease in sorbent performance.

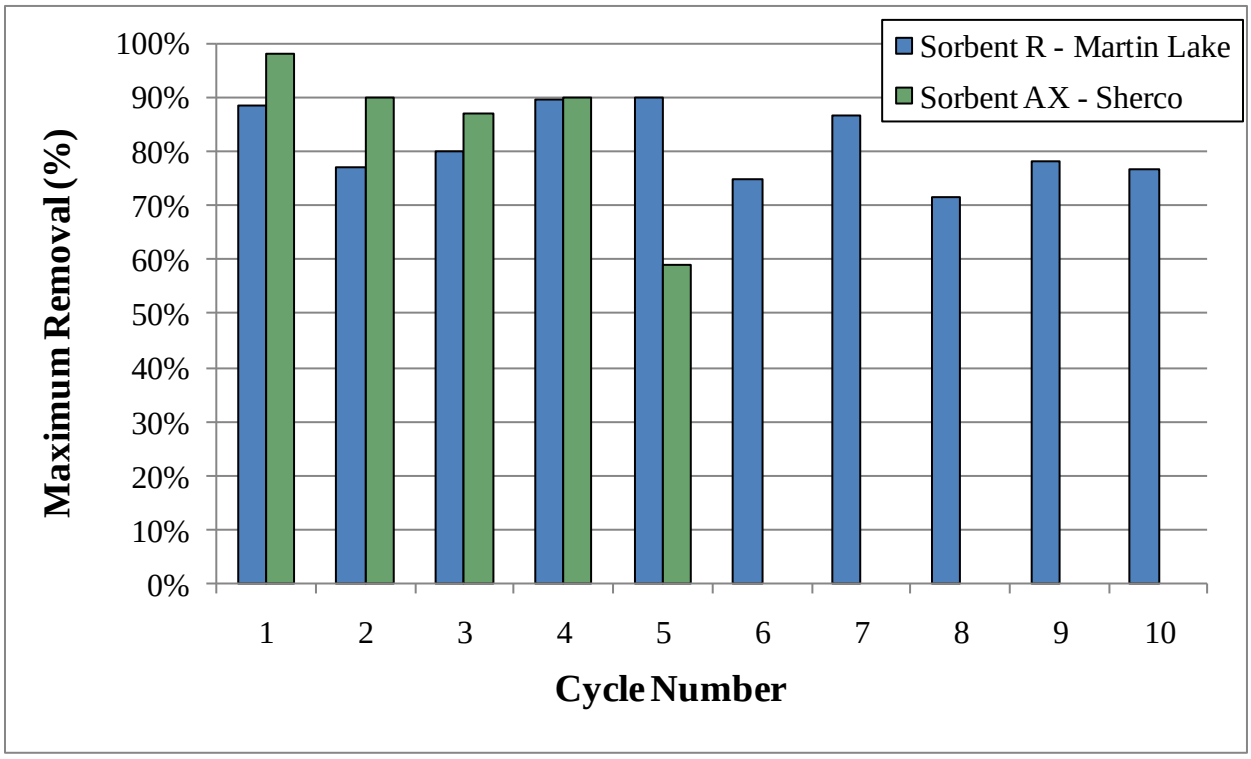

Figure 50: Maximum CO_2 Removal for Sorbent R at Martin Lake and Sorbent AX at Sherco

When operated in batch mode using sorbent R or AX at Martin Lake or Sherco, respectively, there was little difference in the performance of the system or the sorbents. Note that the different removal levels shown in Figure 50 can be attributed to changing conditions, such as the time allowed for regeneration. Because the test conditions were not consistent for the different batch cycles, changes in CO_2 removal are not necessarily related to changes in the sorbent performance. Although demonstrating that the sorbents were able to remove 90% of CO_2 was an important project goal, it was also important to compare the level of CO_2 removal for different sorbents in steady state operation.

It was the goal of the test team to evaluate the four supported amine sorbents on a slipstream of Sherco flue gas using both laboratory-scale fixed bed system and the 1 kW pilot. The 1 kW pilot was used to actually carry out steady state separation of CO_2 from the flue gas and compare the different CO_2 removal levels for different sorbents. In some instances the 1 kW pilot was also operated in batch mode (for sorbent AX) to demonstrate that 90% CO_2 capture could be achieved.

At Sherco Sorbent R was evaluated using both the 1kW system during March 2011. In the 1 kW pilot, Sorbent R was evaluated for several cycles during a continuous test (i.e. not operated in batch mode). The CO_2 concentration at the 1 kW pilot inlet, outlet, and regenerator as well as the CO_2 removal measured at Sherco are provided in Figure 51.

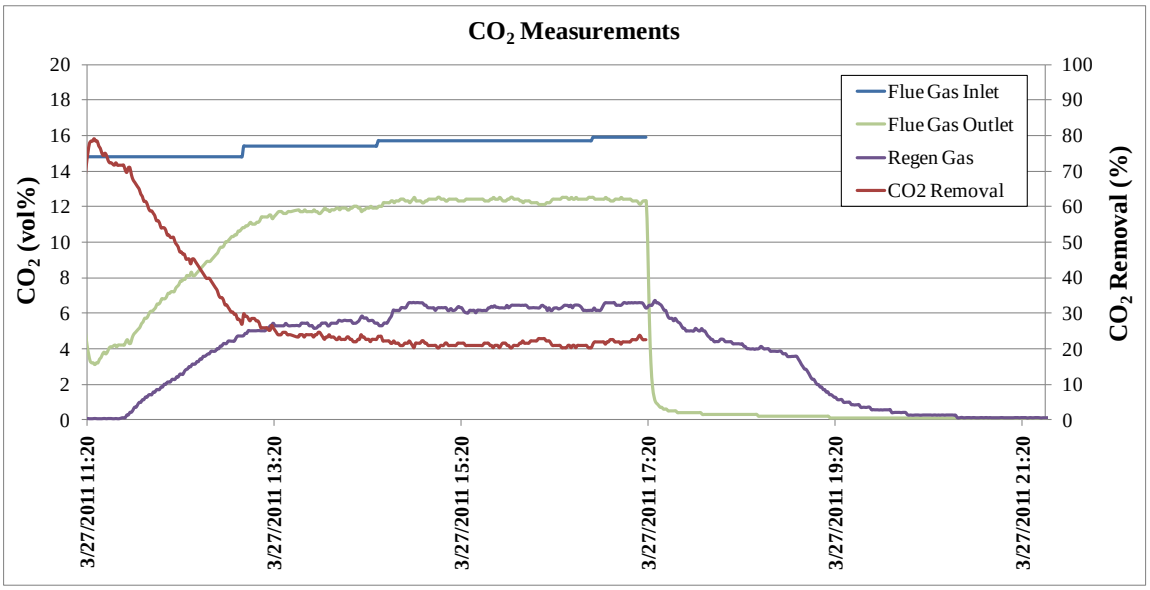

Figure 51: 1 kW Pilot Evaluation of Sorbent R at Sherco

As was observed consistently at Martin Lake, the CO_2 removal was initially high (~80% as sorbent circulation was begun), but decreased to approximately 20% removal at steady state. The lack of continuous removal was due primarily to the combination of a co-current adsorption system with a fluidized bed for regeneration, a combination which did not provide an adequate driving force for regeneration (see text surrounding Figure 14 for additional details). Sorbent R consisted of a polymeric amine coated on a silica substrate. It is believed that the 50% amine loaded resulted in mass diffusion limitations related to the CO_2 uptake rate and further reduce the CO_2 loading achieved during the adsorption step.

Sorbent F was also a supported amine, but differed significantly from sorbents R and AX. Rather than silica coated by an amine, an aminosilane compound was actually grafted to the surface of a mesoporous silica during a series of pore expansion steps. In theory, this sorbent was particularly promising because the amine groups were covalently bonded to the surface of the substrate, which was expected to lead to 1) increased stability and 2) faster kinetics because the pores were more easily accessible by the gaseous CO_2. Although the total CO_2 capacity of sorbent AX measured in the laboratory was greater than that for sorbent F, it was believed that the working capacity of sorbent F could be superior in the 1 kW pilot because the time required for the reaction to occur was significantly lower. One major concern with sorbent F was that the smaller particle size (mean particle diameter of ~10μm). Although the transport reactor and fluidized bed used in the 1 kW pilot were designed to operate with different materials, this particle size was outside the system specifications. Still, the project team decided to attempt to test this sorbent in the hopes that positive results would outweigh any testing difficulties. The maximum regeneration temperature for sorbent F was 120°C (250°F). ADA-ES worked with Gelest, Inc., a specialty chemical production company, to produce sorbent F in the bench-scale

quantity of 250 kg. Similar to the material that has been produced at the laboratory scale previously, the average particle diameter for sorbent F was approximately 10 μm, which can be considered a fine powder.

Although the particle size was non-ideal for operation in the fluidized bed, ADA attempted to circulate sorbent F through the 1 kW pilot by reducing the fluidization gas. However, the sorbent was immediately entrained in the fluidization gas and carried out the top of the regenerator, often plugging the line downstream of the regenerator. After conferring with the research team at Southern Company who helped develop the 1 kW pilot, it was decided to mix sorbent F with inert sand with the same particle size as sorbents R, AX, and BN. The basis of this decision was that the circulation of the sand could be easily accomplished. If the sand mixed well with the sorbent then it was hoped that it would entrain the sorbent and both the sorbent and the inert material would move through the 1 kW pilot together. Unfortunately, the sand and the sorbent particle size and density differences were too large for a homogenous mixture to be maintained. Even with the addition of sand sorbent F could not be circulated through the system.

Prior to testing at Sherco, some of the potential issues with sorbent F were recognized. ADA-ES operated a physical model of the regenerator at the ADA-ES corporate office in Littleton, CO to evaluate whether sorbent F could be circulated. During this short cold flow model test, it was demonstrated that sorbent F could move as designed through the mock up regenerator. The only significant obstacle was that particle carry-over (i.e. entrainment in the fluidization gas) was visually higher for the smaller particle size than previously witnessed for sorbent R or AX. However, there were two primary differences in the physical model from the field full scale system. The first difference in the configuration of the system is the transfer line set up between the ICFB and the regenerator. The physical model allowed a higher sorbent head pressure to be developed, allowing greater sorbent height in the regenerator. The second difference between the model and field configuration was the regenerator fluidizing exhaust layout. The field system is a single exhaust through the top of the regenerator. The sorbent downcomer has a rotary valve and manual valve to provide a seal. The model has a PVC valve that does not create a seal. The actual system operates with a greater gas velocity through the regenerator exhaust. This greater velocity likely resulted in increased sorbent entrainment in the actual system. Due to the high level of sorbent carryover from the regenerator to the attrition fines baghouse during operation at Sherco, the baghouse became plugged rapidly. The pluggage could be overcome by a bag cleaning cycle, but the due to the small size of the system, the attrition fines bag cleaning pulse resulted in a large impact on flow patterns and system pressures. For example, the backpressure caused by frequent bag cleaning reversed the regenerator fluidizing flows up through the transfer leg, preventing sorbent flow down the transfer leg from the ICFB to the regenerator.

Although the 1 kW pilot could not be used to collect data related to the CO_2 uptake, the experience of attempting to operate the system with this material highlighted the importance of including the physical properties in the sorbent selection criteria. Much of the sorbent development occurring at the laboratory scale is being completed without respect to physical properties; these more realistic field tests highlight the true importance of such characteristics. Sorbent BN consisted of a primary amine covalently bonded to a cross linked polystyrene support. Sorbent BN was originally produced in a beaded form. For it to be tested in the 1 kW

pilot, it was ground to a particle size of approximately 80-120 μm, similar to sorbents R and AX. The maximum regeneration temperature for sorbent BN was 120°C (250°F). Sorbent BN was selected for inclusion in the Sherco field tests based on previous laboratory results when after exhibiting 1) a greater than average (>4 wt%) working CO_2 capacity when regenerated in pure CO_2 at 120°C, 2) superior cyclic stability, and 3) demonstrated faster kinetics compared to many other. Sorbent BN was evaluated at Sherco using the 1 kW pilot on 03/14/11. The CO_2 inlet, outlet, concentration downstream of the regenerator, and the removal level are provided in Figure 52.

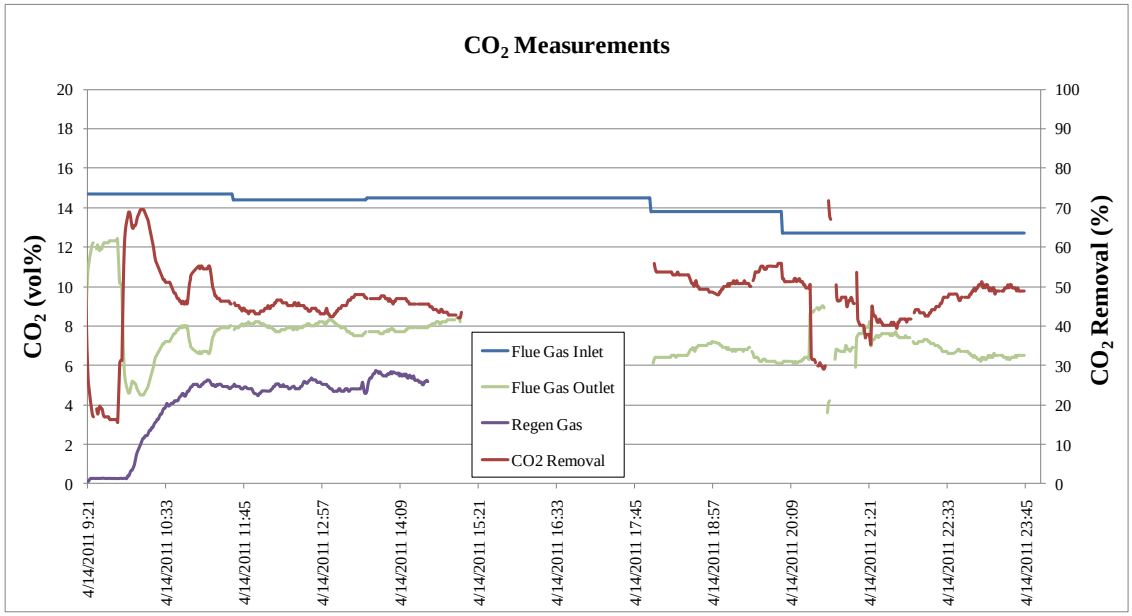

Figure 52: 1 kW Pilot Evaluation of Sorbent BN at Sherco

The 1 kW pilot testing of sorbent BN can be divided into two separate phases. Prior to 15:00 the system was operating under the same conditions as had been used previously for sorbent R and sorbent AX (sorbent circulation rate of 40 lb/hr and gas flow rate of ~4.5-5.3 acfm). These conditions were maintained and CO_2 removal was consistently above 40% and often as high as 45%. Under these conditions maintaining 90%+ CO_2 capture would require the sorbent to maintain a working CO_2 capacity of approximately 11 wt%, which is more than double the working capacity of aqueous MEA systems.

At approximately 15:00 the flue gas sample was lost and the pump had to be repaired. After 18:00 the sorbent circulation was resumed. However, the flue gas flow rate was decreased in the hopes of increasing the CO_2 removal level. At 19:30 the flue gas circulation rate was reduced to 4.1 acfm. Then at 22:25 the sorbent circulation rate was increased to 45 lb/hr. By changing the gas and sorbent flow rates the CO_2 removal was increased to over 50%. With a sorbent circulation rate of 45 lb/hr and a flue gas flow rate of 4.1 acfm the sorbent working capacity would have to be approximately 8 wt% to achieve 90% CO_2 capture, which was not achieved. Although working capacities of 8 wt% were demonstrated in the laboratory for sorbent BN when regenerating in an atmosphere of pure N_2, this working capacity could not be achieved when operating with a co-current flue gas/sorbent contactor. However, the 1 kW pilot was used to

demonstrate that using a different sorbent (i.e. BN compared to AX and R) can significantly increase the CO_2 capture levels.

5.0 CONCLUSIONS

ADA-ES has completed an extensive sorbent screening program funded primarily through DOE NETL cooperative agreement DE-NT0005649 with support from EPRI and industry cost-share participants. This report includes the highlights and key conclusions from sorbent evaluation at the laboratory-scale to the 1 kW scale. Tests were completed on simulated and actual flue gas. The project objective is to address the viability and accelerate development of a solid-based post-combustion CO_2 capture technology that can be retrofit to the existing fleet of coal-fired power plants.

Using simulated flue gas and an automated fixed bed system, the following types and quantities of sorbents were evaluated:

- 87 supported amines
- 31 carbon based materials
- 6 zeolites
- 7 supported carbonates (evaluated under separate funding)
- 10 hydrotalcites

Supported amine sorbents consist of various types of amines supported on inert substrates. There is a great deal of ongoing research to invent and improve these materials. In general these materials exhibited high CO_2 capacities under simulated flue gas conditions (up to 14 wt%). Many of these materials, but not all, demonstrated cyclic stability over many adsorption/regeneration cycles. For this reason, several supported amines were selected for laboratory-scale fixed bed testing on actual flue gas. The laboratory-scale fixed bed field tests in conjunction with specialized laboratory testing revealed that SO_2 can permanently degrade the supported amine sorbents. In addition, NO_2 can also partially degrade the sorbents, while NO does not cause a concern for these materials. Working CO_2 capacities, qualitative attrition characteristics for two substrates, and crush strength for a beaded sorbent were also measured.

Several different carbon-based CO_2 sorbents were also evaluated under this program. These materials also demonstrated the ability to remove CO_2 from simulated and actual flue gas at the laboratory scale. However, the CO_2 capacities of these materials were much lower than that of supported amine sorbents, usually <1.2 wt%. An advantage of carbon-based sorbents is that many of these sorbents demonstrated cyclic stability on simulated and actual flue gas. They were much more resistant to poisoning and degradation from flue gas constituents compared to supported amines. If the CO_2 capacity for carbon-based sorbents is improved and selectivity is quantified, it is possible that a process can be developed using carbon-based sorbents that will decrease the regeneration energy penalty versus aqueous MEA.

Several zeolites were also evaluated on simulated flue gas using the fixed bed apparatus and a single zeolite was evaluated on actual flue gas using the same test equipment. On dry flue gas zeolites are able to separate CO_2 effectively. However, in the presence of moisture these materials preferentially adsorb H_2O over CO_2, making them ineffective for the purpose of post-combustion CO_2 capture.

Prior to the initiation of DE-NT0005649 several supported carbonates were produced by ADA-ES and their breakthrough curves were measured. The materials produced and evaluated by

ADA-ES were not optimized, but allowed for some screening and evaluation to be completed in the laboratory (no field testing of these materials). The best CO_2 capacity measured for one of the ADA-ES supported carbonates was approximately 3.2 wt%. The heat of reaction for carbonates is significantly higher than that of other materials (i.e. approximately -130 kJ/mol for regeneration of sodium carbonate versus -60 kJ/mol for supported amines). Using this CO_2 capacity to calculate the theoretical regeneration energy, and assuming a sorbent specific heat of 1.0 kJ/kg·K, the theoretical regeneration energy was approximately 5000 kJ/kg CO_2. Since this was significantly greater than the benchmark MEA system, supported carbonates were not pursued further.

Several hydrotalcites were included in the sorbent screening program. These materials were only evaluated on simulated flue gas in the laboratory. The fixed bed tests were conducted without any study of the optimal adsorption and regeneration temperatures. Based on the hydrotalcites evaluated, there may be some applicability for post-combustion CO_2 capture, although these materials may be useful at temperatures greater than what was used for the simulated flue gas in this project.

Based on the laboratory screening four supported amine sorbents were selected for evaluation at the 1 kW scale at two different field sites. The first host site was Luminant's Martin Lake Steam Electric Station and the second host site was Xcel Energy's Sherburne County Generating Station (Sherco). The 1 kW pilot concept was provided by Southern Company. Although the system could not maintain continuous 90% CO_2 removal with the sorbents evaluated under this program, it was useful to compare the CO_2 removal properties of several different sorbents on actual flue gas.

The equipment operation was first demonstrated successfully at Martin Lake using sand as a surrogate for sorbent. Then sorbent R was evaluated at Martin Lake. The 1 kW pilot was operated in continuous mode as well as batch mode. In batch mode sorbent R was able to remove up to 90% CO_2 for several cycles. Approximately 50% of the total removal occurred in the first three feet of the adsorption reactor, which was a transport reactor.

Sorbents R, AX, F, and BN were selected for evaluation using the 1 kW pilot at the second host site, Sherco. Sorbent AX was operated in batch mode and performed similarly to sorbent R at Martin Lake (i.e. could achieve up to 90% removal when given adequate regeneration time). For sorbent R used in continuous mode, the CO_2 removal was initially high (~80% as sorbent circulation was begun), but decreased to approximately 20% removal at steady state. The lack of continuous removal was due primarily to the combination of a co-current adsorption system with a fluidized bed for regeneration, a combination which did not provide an adequate driving force for regeneration. In addition, because sorbent R consisted of a polymeric amine coated on a silica substrate, it was believed that the 50% amine loaded resulted in mass diffusion limitations related to the CO_2 uptake rate. Therefore, sorbent BN was also tested, which was not expected to be subject to the same mass diffusion limitations. When sorbent BN was used in continuous mode the steady state CO_2 removal was approximately double that of sorbent R, which highlighted the importance of sorbents without kinetic limitations. Sorbent F was not tested in the 1 kW pilot because the particle size made operation impossible. Although the 1 kW pilot could not be used to collect data related to the CO_2 uptake, the experience of attempting to operate the system with this material highlighted the importance of including the physical properties in the sorbent selection criteria. Much of the sorbent development occurring at the

laboratory scale is being completed without respect to physical properties; these more realistic field tests highlight the true importance of such characteristics.

The sorbent screening program conducted under DE-NT0005649 and other funding is more extensive and inclusive than most other sorbent evaluation programs in the world. Based on the program results, supported amine sorbents offer the potential to significantly reduce the energy penalty associated with post-combustion CO_2 capture if they can be used in a system/process that can take advantage of their beneficial properties. With further development it is possible that carbon-based sorbents may also be useful for this application. Future work in the area of CO_2 capture must focus on 1) identifying processes/reactors that are optimal for this application and 2) identifying the sorbent physical properties required to operate in such reactors. Based on this stage of testing, it is concluded that a temperature swing sorbent-based process for post-combustion CO_2 capture can offer viability and energy savings, but development support will be required.

6.0 DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

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8.0 LIST OF ACRONYMS AND ABBREVIATIONS

CO_2	Carbon Dioxide
CCS	Carbon Capture and Sequestration
DOE	Department of Energy
EPRI	Electric Power Research Institute
ICFB	Internal Circulating Fluidized Bed
Hg	Mercury
HHV	Higher Heating Value
H_2O	Water
kW	Kilowatt
MEA	Monoethanolamine
min	Minute
mL	Milliliter
MOF	Metal Organic Frameworks
NDIR	Nondispersive Infrared Sensor
NETL	National Energy Technology Laboratory
NO_2	Nitrogen Dioxide
NO	Nitrogen Monoxide
NO_x	Nitrogen Oxides
PC	Post-Combustion
PC	Pulverized Coal
PLC	Programmable Logic Controller
ppb	Parts Per Billion
ppm	Parts Per Million
sccm	Standard Cubic Centimeters per Minute
SO_2	Sulfur Dioxide
SO_x	Sulfur Oxides
TGA	Thermogravimetric Analyzer
TSA	Temperature Swing Adsorption

APPENDIX A: SORBENT DEVELOPER REPORT 1

The report included in this appendix was generated based on data collected with funding other than that of DE-NT0005649.

Phase I Development and Demonstration of CO_2 Sorbents Report

Introduction and Research Objectives

Technologies for carbon capture from coal-fired utilities are rapidly being developed. The magnitude of the volume of CO_2 to be removed and stored has forced technology developers to redefine the traditional models that were used to evaluate whether a new technology would meet the market performance and cost points. The new model, in parallel with the speed with which new legislation is being proposed, is unleashing an eruption of new ideas and technologies that are being developed to not only compete with, but replace the current costly options.

Luminant Power is evaluating options to reduce CO_2 output from its coal fired power generating stations. Under a contract with Luminant Power, ADA-ES conducted Phase I research during the 4th Quarter of 2007. The goal of this research was the development of solid sorbents for use in a retrofit process designed to separate CO_2 from coal-fired power plant flue gas. Solid sorbents offer potential advantages over other means of capturing CO_2, such as increased capacity, lower regeneration energy, decreased local environmental impact, durability and lower system pressure drop compared to other technologies.

Phase I of this project focused on the following tasks:

1. Assess the ability of sorbents to capture CO_2 in a laboratory test fixture
2. Evaluate the ability of sorbents to desorb CO_2
3. Screen the performance of select sorbents on a slipstream of flue gas at Martin Lake
4. Demonstrate favorable initial economics (including base cost, regeneration potential, transportation costs, etc.)

Solid sorbents capture CO_2 by two possible mechanisms, chemisorption or physisorption. Chemisorbents react with the CO_2 to form chemical bonds; they are characterized by high capacity and strong bonds. Physisorbents utilize much weaker forces to hold CO_2; they are characterized by lower capacity and less energy requirements for regeneration. Phase I work included an analysis of both types of sorbents.

The results from lab-scale testing of sorbents during Phase I were very encouraging, showing effective adsorption and desorption of CO_2. The sorbents also appear to have favorable properties for a much lower cost of regeneration than other sorbents currently being developed.

Experimental Apparatus and Procedure

Phase I research included lab scale (>1 LPM) experiments conducted in the University of Denver and ADA-ES laboratories. Hundreds of hours of testing resulted in important information that allowed for comparison between the potential sorbents. The points of interest include the CO_2 capacity and ability of the sorbent to be repeatedly regenerated. The same experimental apparatus was used for all laboratory and all field tests during Phase I work. Figure 1 is a simplified diagram of the testing unit. Figure 2 is a picture of the actual apparatus.

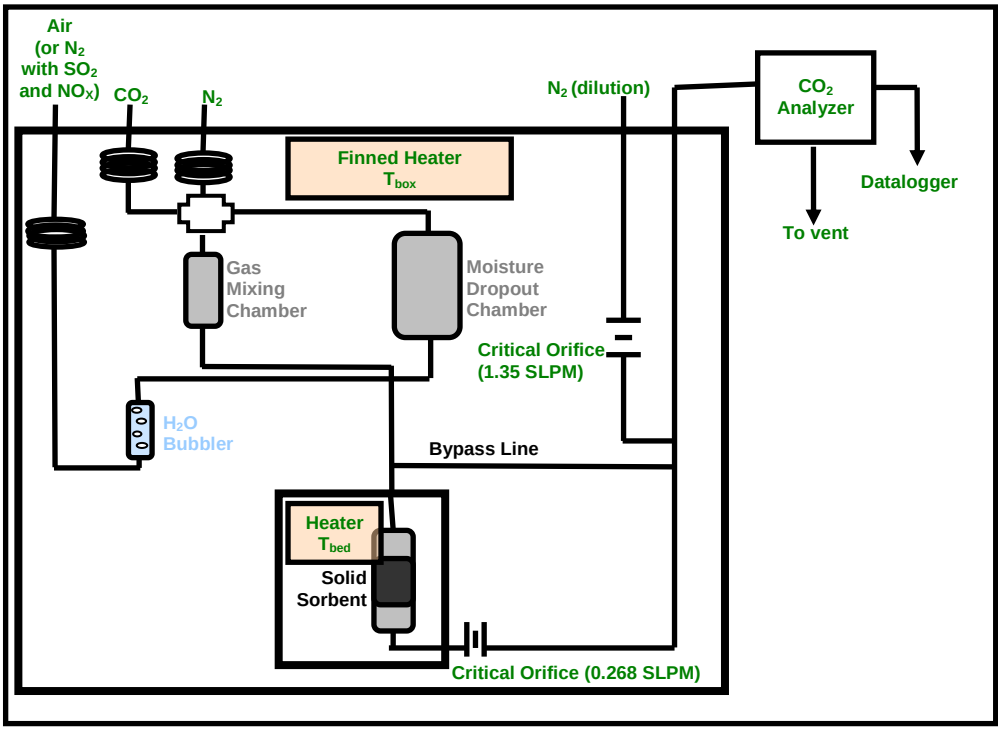

Figure 1. Simplified Schematic of the Experimental Setup.

Figure 2. Laboratory Sorption/Desorption Apparatus

The experimental procedure was effectively the same for all laboratory and field tests. First, the sorbent was placed in the reactor and given adequate time to reach the adsorption temperature. Then the sorbent was flushed with dry N_2 to remove any excess moisture. Next, the simulated flue gas was sent through the bypass until the reading on the CO_2 analyzer reflected the correct concentration. Since the NDIR sensor in the analyzer is sensitive to high temperatures and condensation, the sample gas (during both adsorption and desorption) was diluted with pure N_2 before being passed through the analyzer. For the adsorption step the sample gas was diverted from the bypass line to the reactor, where the gas passed through a fixed bed of solid sorbent. As the solid sorbent captured CO_2 from the sample stream, the $\%CO_2$ reading from the gas analyzer decreased. When the sorbent was saturated with CO_2 the sample gas passed through the sorbent without additional adsorption. Therefore, the $\%CO_2$ reading returned to the original level, and the sample gas was sent back through the bypass. A data logger recorded the $\%CO_2$ in the gas as a function of time during the adsorption step.

The temperature during desorption was dependent upon the type of sorbent being tested. Physisorbents, characterized by weaker bonds, did not require an elevation in temperature; chemisorbents were observed to have higher CO_2 capacity, but required a temperature swing to provide the energy to break the chemical bonds. When the sorbent was at the appropriate desorption temperature, dry N_2 was sent through the sorbent to carry off the CO_2. Although this is not a feasible method for large-scale desorption, this approach was simple and informative during lab-scale experiments. The dry N_2 carried the CO_2 to the analyzer and the data logger was used to record this data. Multiple adsorption/desorption cycles were carried out with the most promising sorbents in order to test the regeneration potential.

Experiments at the University of Denver were conducted using a simulated flue gas. The temperature and moisture of the simulated gas was modeled after a flue stream that had not been sent through a wet scrubber, although the SO_2 and NO_x were not included for these tests. The specifications for the DU simulated flue gas are as follows:

- 75^oC during adsorption
- 12.5-14% CO_2
- ≥10% moisture
- 3–5% O_2
- Balance N_2

In order to prepare the experimental apparatus for field tests, the unit was moved to the ADA-ES lab. When the field testing location was set as Martin Lake, with flue downstream of a wet scrubber, the specifications of the simulated flue gas were altered. Simulated flue gas conditions for the sorbents tested at the ADA-ES lab were as follows:

- 55^oC during adsorption
- 11% CO_2
- >10% moisture (saturated)
- ~4% O_2
- Balance N_2

Results and Discussion

Over 35 sorbent formulations were tested at the DU Lab. To determine the effect of temperature on CO_2 capacity, adsorption cycles were completed at two different temperatures. In addition, the most promising sorbents were sent through multiple adsorption/regeneration cycles to test whether the sorbents were well-suited for reuse. Figure 3 shows the first cycle adsorption curves for selected sorbents at 22°C while Figure 4 shows similar curves at 75°C.

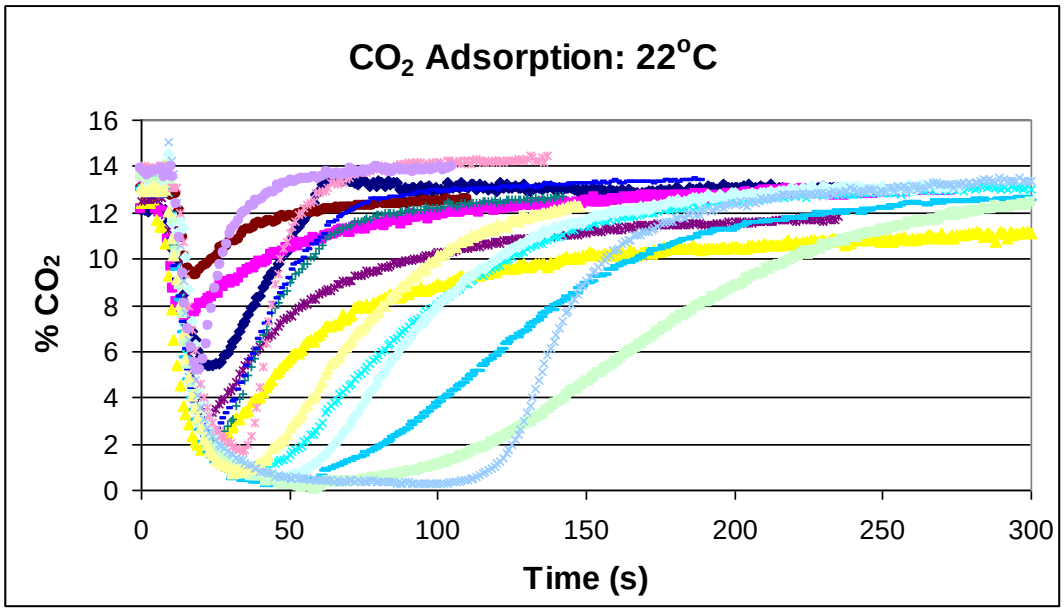

Figure 3. First Cycle Adsorption Curves for Select Sorbents during DU Experiments

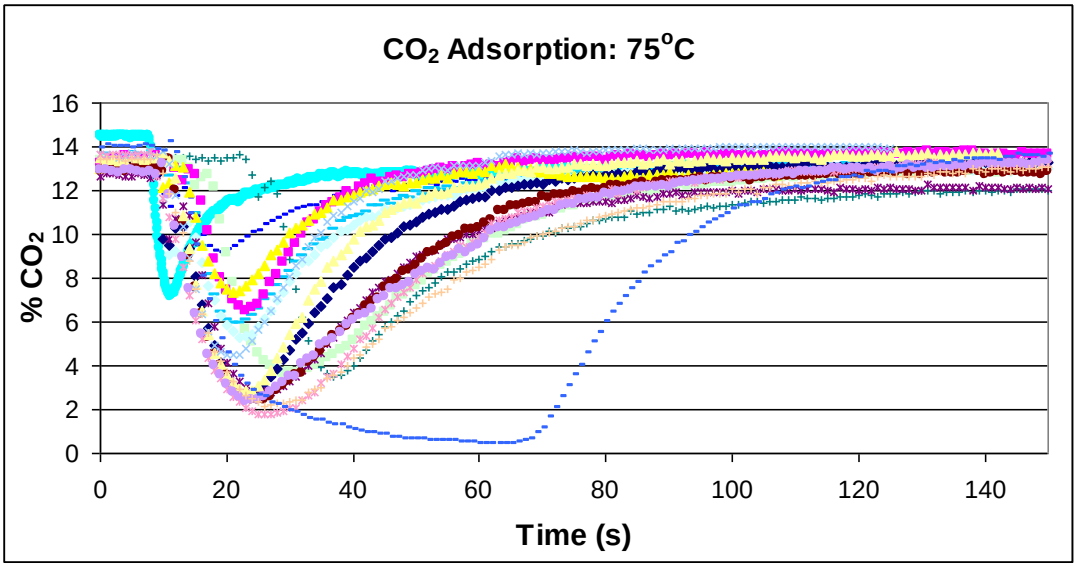

Figure 4. First Cycle Adsorption Curves for Select Sorbents during DU Experiments

Laboratory screening was continued at the ADA-ES lab. Sorbents were developed with the goal in mind of creating a physisorbent, requiring very low regeneration energy, with optimized capacity. Over a dozen sorbents were tested at the ADA-ES lab. These sorbents showed complete regeneration using a partial pressure swing (no temperature swing). In addition, different treatments and modifications were identified that increased the capacity.

ADA-ES recognizes the importance of testing potential sorbents in actual flue gas early in the development process. Therefore, following review of initial laboratory results and consensus that the sorbents show sufficient promise, ADA-ES tested the materials in the field (Martin Lake Steam Electric Station) on a slipstream of actual flue gas. The tests were run using flue gas downstream of a wet scrubber. The test apparatus was the same as that used in the laboratory for consistency and comparison of results.

In the interest of time, sorbents were only tested over 3-5 adsorption/regeneration cycles in the laboratory testing. The field tests provided the opportunity to run 10 or more cycles on each sorbent, as well as to consider the effect from flue gas constituents not included in the laboratory experiments. Figure 5 shows the adsorption curves for a chemically modified sorbent on the Martin Lake flue gas slipstream. This figure shows up to 50% removal of the CO_2. Since 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.

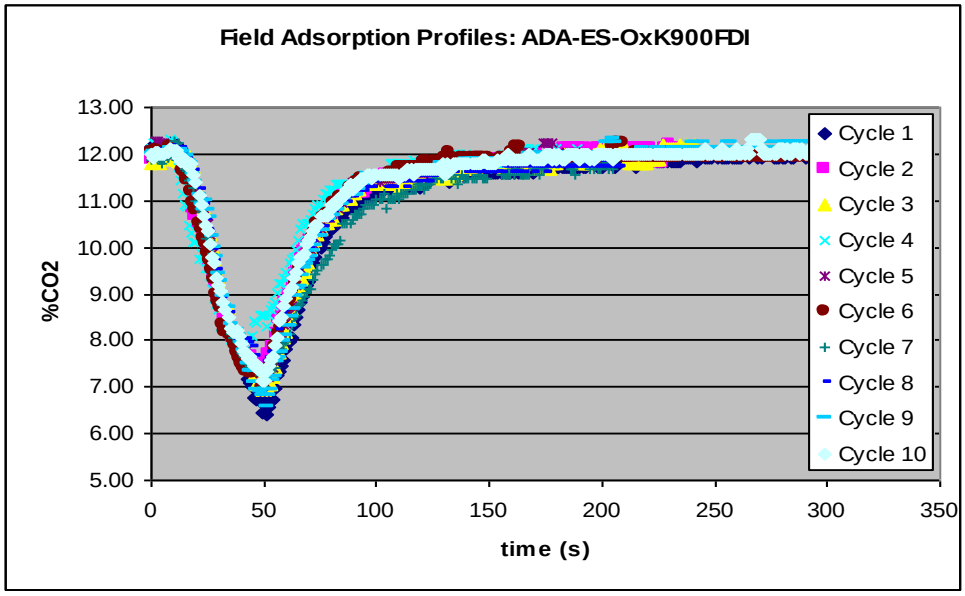

Figure 5. Adsorption Curves on a Flue Gas Slipstream

Figure 6 shows the multiple desorption curves for the same sorbent that was used to generate the data shown in Figure 5. 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.

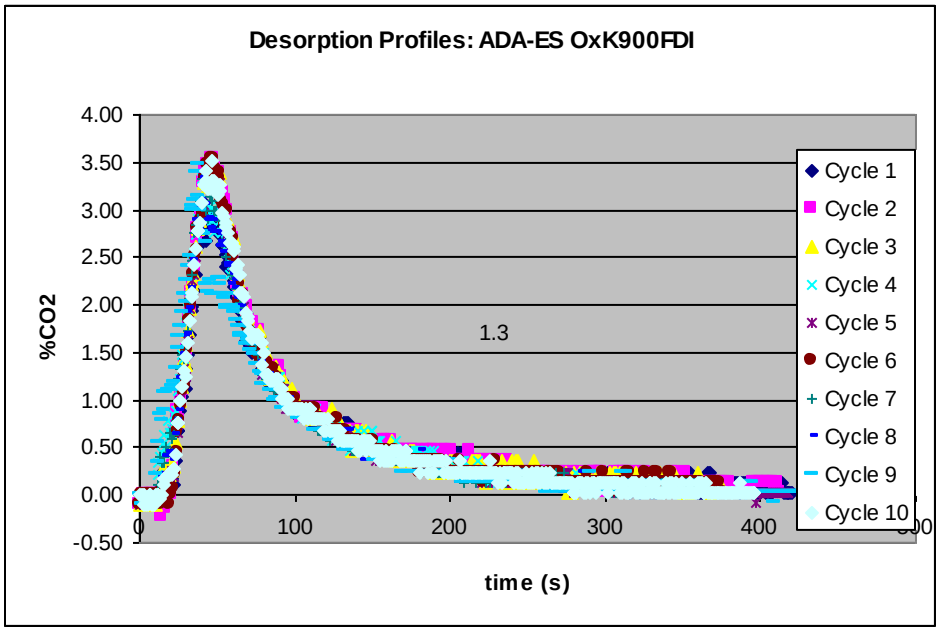

Figure 6. Desorption Curves from Slipstream Testing

A key element of the ADA-ES sorbent development model is to field test using actual flue gas early in the development process. This will lead to an accelerated development path as well as reveal any interactions between the sorbent and flue gas constituents that can not be simulated in the laboratory. However, as a first step, laboratory screening can be an important, economical testing method. Figure 7 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 produces 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.

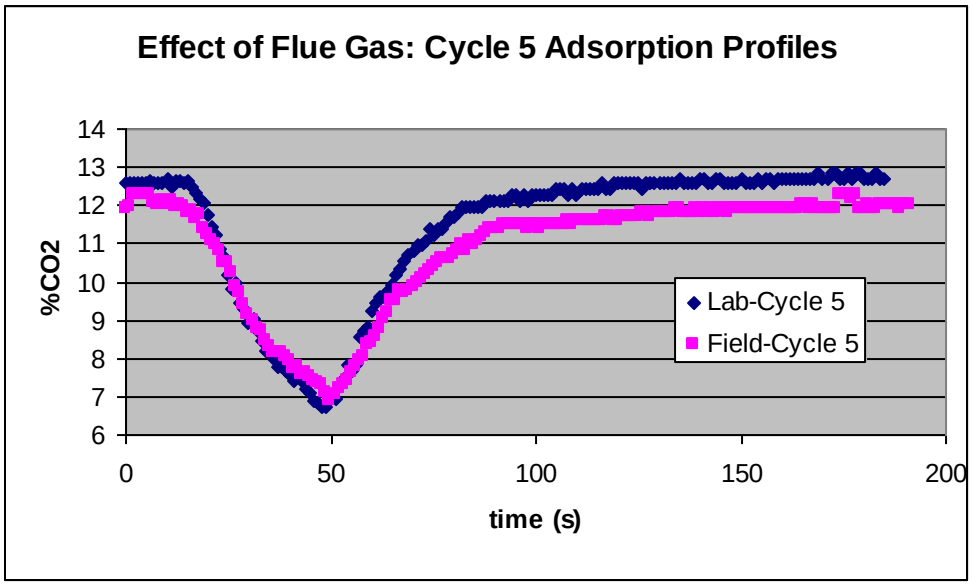

Figure 7. Comparison of Laboratory and Field Testing of the ADA-ES Sorbent.

The sorbents developed during Phase I research met the following criteria:

- Effective sorption at temperatures between 100 – 180°F
- Negligible interference from typical flue gas constituents, including moisture and SO_2
- Capable of rapid regeneration
- Capable of desorbing adsorbed CO_2 using a temperature-swing adsorption mode at temperatures less than 180°F for the modified sorbents
- Complete desorption of captured CO_2 using a partial pressure swing
- Safe sorbent for local environment

Preliminary Economics

Although it is difficult to predict full-scale economics from lab-scale tests, there are several potential benefits of ADA-ES developed solid sorbents over competing CO_2 capture technologies. The advantages identified during Phase I work are as follows:

- Inexpensive starting material
- No costs associated with disposal of hazardous waste
- Pressure or temperature swing (or a combination) can be used
- Ease of handling
- No local environmental hazard and reduced clean-up costs
- Negligible effect from flue gas constituents (i.e. SO_2)
- Complete regeneration

Future Work

The Phase I work yielded a great deal of information about potential solid sorbents for CO_2 capture. However, additional work is suggested to provide information in areas that would help further improve the sorbents and help scale up the process. A major focus of the next phase of work is to investigate the process of contacting and regenerating this sorbent in a safe and economical manner. The Phase II proposal, already delivered to Luminant, describes the logical progression of this work. The proposed tasks for Phase II are as follows:

1. Sorbent Optimization and Laboratory Screening
2. Develop Conceptual System Designs
3. Design and Fabricate Bench-Scale Equipment
4. Bench-Scale Field Testing (5-100 acfm)
5. Data Analysis, Economics and Reporting

Phase I work has given promising results and proof-of-concept information. Phase II is an important next step that will lead to process development, bench-scale tests and optimization of sorbents. All of these factors will lead to informative economical analysis that will direct the future of this work.

APPENDIX B: SORBENT DEVELOPER REPORT 2

The report included in this appendix was generated based on data collected with funding other than that of DE-NT0005649.

CO_2 Sorbent Screening Program:

Second Round Screening Results

Prepared by:

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January 1, 2009

EXECUTIVE SUMMARY

Carbon capture and sequestration (CCS) is the most important option to reduce CO_2 emissions from stationary point sources such as coal-fired power plants. However, for CCS to be widely implemented, the cost for CO_2 capture must be reduced. Solid sorbents used in a temperature swing adsorption process have a significant potential to reduce the energy required to operate a commercial-scale CCS system over current state of the art technologies. However, such sorbents are commonly produced in small quantities and studied under highly varied conditions. ADA-ES has collected and screened potential materials from developers throughout the world. This report discusses the results from these tests.

The first step of the sorbent screening included running several CO_2 adsorption/regeneration cycles on simulated flue gas composed by blending compressed gas from tanks. Between 0.5 to 2.5 g of the materials were tested in a fixed bed with different levels of moisture and regeneration temperatures. The key sorbent performance properties under investigation in this research included:

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

Three different types of sorbents were tested: carbon-based, supported amines, and zeolites. After testing the materials on simulated flue gas the five best performing materials were taken to the field and tested for multiple adsorption/regeneration cycles using actual flue gas.

The CO_2 capacities of carbon-based materials included in this round of tests were in the range of 0.3 to 1.1 wt% both in the laboratory and in the field (excluding the carbon nanotube materials). These materials also exhibited superior repeatability between cycles, both in the laboratory and field tests, leading to the conclusion that they are not significantly altered by actual flue gas constituents and conditions. One carbon nanotube material exhibited a repeatable working CO_2 capacity of up to 5 wt%, which will be examined more closely in future tests. Because carbon-based materials rely on physical adsorption, the $\Delta T_{capture\text{-}regeneration}$ can be determined based on optimization, but the regeneration temperature will likely fall in the range of 35-65°C.

The supported amine materials exhibited high CO_2 capacities, all within the range of 1.3 to greater than 13 wt%. However, the adsorption profiles were less repeatable; in the field tests these materials exhibited signs of degradation and decreasing capacity whereas in the laboratory most were more stable. The ideal $\Delta T_{capture\text{-}regeneration}$ can also be determined based on process optimization, but will likely be in the range of 35-65°C.

The zeolites exhibited capacities up to 1.6 wt% on dry flue gas, but performance was degraded quickly by the presence of moisture. On actual flue gas the working capacity of a zeolite was ~0.4 wt%, even with a $\Delta T_{capture\text{-}regeneration}$ of 145°C.

Several materials have been tested thus far in the program that have exhibited a lower theoretical regeneration energy than aqueous MEA. Specifically, the carbon nanotube material and several of the supported amines were calculated to use less energy for regeneration than the benchmark based on laboratory results. Results from initial field testing indicate that ten sorbents tested have a lower theoretical regeneration energy than the reported value for aqueous MEA. However, several others are close and may surpass this goal with a slight change in sorbent or operating conditions (i.e. regeneration temperature). One carbon-based material is close to this benchmark, and may achieve it with small process modifications. Although more testing will be conducted, early results were promising.

TABLE OF CONTENTS

EXECUTIVE SUMMARY 2
TABLE OF CONTENTS 4
INTRODUCTION 5
EXPERIMENTAL APPARATUS AND PROCEDURE 6
Laboratory Testing 9
Field Testing 10
Theoretical Regeneration Energy 11
RESULTS 12
Sorbent Specific Results 12
Sorbent A 12
Sorbent F 14
Sorbent J 18
Sorbent M 19
Sorbent P 20
Sorbent R 21
Sorbent S 24
Sorbent T 25
Sorbent U 26
Sorbent V 28
Sorbent W 30
Sorbent X 31
Sorbent Y 32
Sorbent Z 34
Sorbent AA 34
Sorbent AB 35
Comparison of All Materials Tested 35
CONCLUSIONS 40
REFERENCES 41

INTRODUCTION

Before the industrial revolution, anthropogenic greenhouse gas emissions were negligible. However, it was projected that over 30 billion tons of carbon dioxide were released in 2007;[1] in addition, emissions are expected to grow with increased power consumption of highly populated developing countries. Stationary point sources, such as coal-fired power plants, offer the most promising option for a reduction in carbon dioxide emissions in the near future.

The most important difference between CO_2 and other emissions is the volume at which they are produced. SO_x, NO_x and Hg concentrations are measured in parts per million (ppm) or parts per billion (ppb) while CO_2 is measured as a percentage of the flue gas. Without any modifications, 10 to 15% of the gas released by coal-fired power plants is CO_2. Each ton of carbon in the coal produces nearly 4 tons of gaseous CO_2. Carbon capture and sequestration (CCS) is the most promising option for reducing CO_2 emissions from coal-fired power plants. Obtaining a pure CO_2 stream is the first step of CCS. After the separation, CCS includes compression of the pure CO_2 and sequestration so that it does not enter the atmosphere.

The vast majority of coal-fired power plants burn pulverized coal in a boiler, and are thus referred to as PC plants. Post-combustion capture is one of the few viable options to retrofit such plants. The most developed separation technologies utilize liquid solvents. Unfortunately, estimates project that the energy penalty associated with such technologies may be devastating. A great deal of this energy penalty can be attributed to heating up the aqueous solution.[2] One option to reduce the regeneration energy required for CO_2 capture is to use a material with a lower heat capacity, such as many solid sorbents. These sorbents can either react with the CO_2 or adsorb it onto the surface.

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; releasing 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.

Chemically reacting sorbents usually include an inert, high surface area support, such as 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, polymers, and silica, while common reactants include amines such as polyethylenimine or chemicals such as sodium carbonate (Na_2CO_3), which react with CO_2 to form carbamates and bicarbonates. When heated, the reaction will reverse, releasing the CO_2, and potentially H_2O, 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.

Research institutions throughout the world have spearheaded many solid-sorbent development projects geared towards CO_2 capture. This research encompasses a wide range of technical areas, including activated carbons, carbonate chemical sorbents, metal organic frameworks (MOFs), amine grafted zeolites, and supported amine sorbents. However, a majority of these projects are currently being conducted on either lab- or bench-scale and will require further support and development before the materials are commercially viable.[3] Due the to the urgency of addressing CO_2 emissions, it is important that the development of these technologies is accelerated.

Under a project supported by the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL), the Electric Power Research Institute (EPRI), and several utility companies, ADA Environmental Solutions is conducting a program to characterize CO_2 sorbents and options for process equipment. The objective of this program is to assess the viability and accelerate development of solid sorbents as a CO_2 capture technology that can be retrofit to the existing fleet of coal-fired power plants. The first step in this process is to determine whether appropriate materials are available.

Testing on actual flue gas is necessary to evaluate and compare different capture options. Therefore, ADA has built and is operating a lab-scale sorbent screening device to quickly evaluate potential CO_2 sorbents on simulated and actual flue gas. Under the ADA sorbent screening program, sorbents have been collected from developers all over the world. These materials are being tested under the same conditions for multiple temperature swing adsorption (TSA) cycles. Sorbents have been targeted that are designed to operate at temperatures and pressure consistent with post-combustion CO_2 capture from PC plants. All sorbents discussed in this report have been given a non-descriptive identifier to protect the identity of the developers.

The sorbent key characteristics evaluated during this program were:

1. Working CO_2 capacity (when reported as a weight percentage): $\frac{100 * mass_{CO_2-removed from gas}}{mass_{sorbent}}$
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. $\Delta T_{capture-regen}$: The difference between capture and regeneration temperatures
5. Theoretical energy required for regeneration

EXPERIMENTAL APPARATUS AND PROCEDURE

All testing of the sorbents screened 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 0.5 to 2.5 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 when setup for laboratory testing (only minor modifications are necessary for field testing). Figure 2 is a picture of

the unit. Note that the CO_2 monitor 90% response time was 10 seconds. This response time should be taken into consideration when examining results. It is probable that the response time of the instrument affected results for materials tested in 0.5 g quantities more extensively than those tested in 2.5 g quantities.

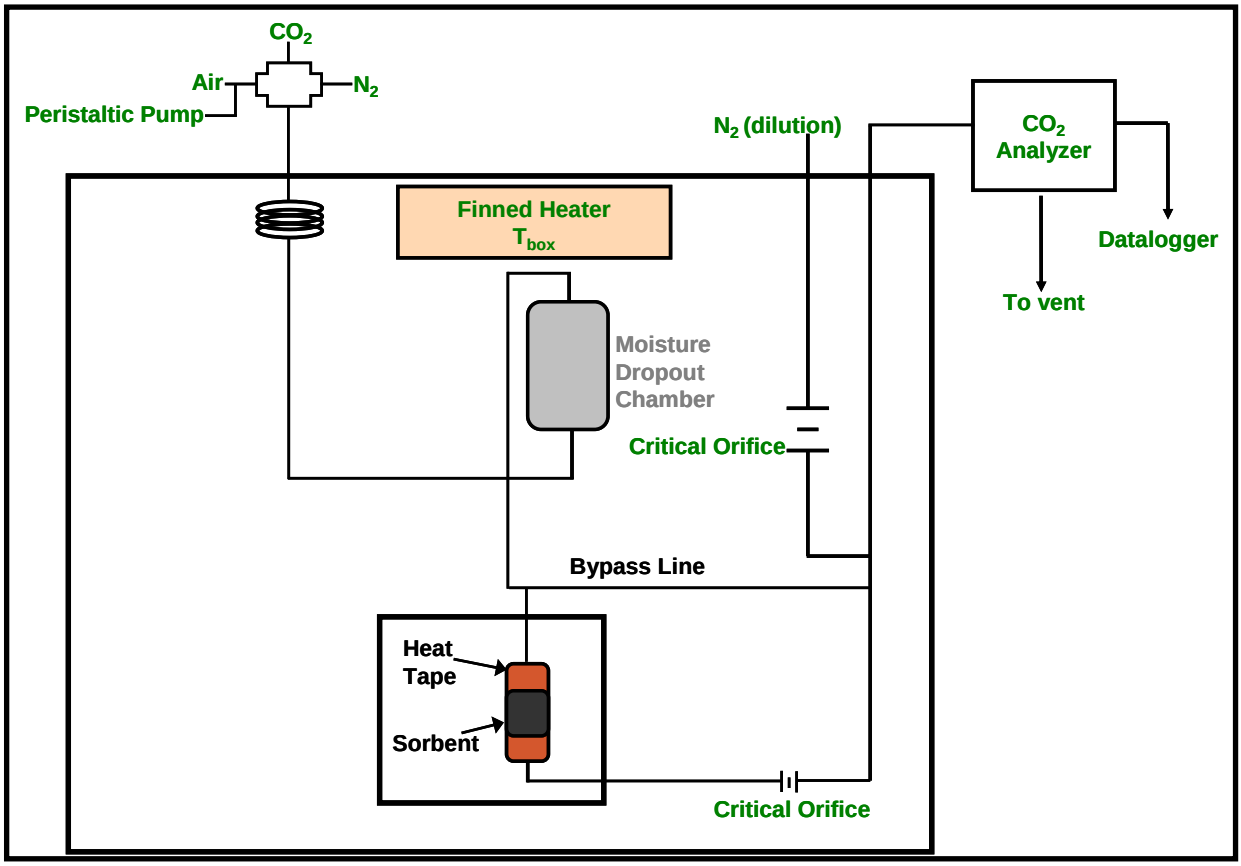

Figure 1: Schematic of Sorbent Screening Test Unit

Figure 2: Picture of Lab-Scale Screening Unit

The steps to carry out the capture/regeneration cycles were the same whether tests were conducted on simulated or actual flue gas. First, the sorbent was placed in the fixed bed. Then, the sorbent was heated to an initial flushing temperature. The initial flushing temperature was set based on the expected regeneration temperature, unless a different temperature was recommended by the sorbent developer. A thermocouple on the outside of the glass fixed bed was used to determine when the bed had reached the desired 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 gas 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 to 14% CO_2, 4% O_2, balance of N_2. The relative humidity, controlled by adding water using a peristaltic pump and then evaporating, was 0%, 45%, or 90%. 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.

A temperature swing with N_2 flushing was used to regenerate the sorbents and desorb the CO_2. First, the bed was heated with no gas flow. When the thermocouple on 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. The working capacity, also referred to as the delta loading or wt %, can be calculated by integration of the adsorption and regeneration profiles. In addition, the minimum level of CO_2 achieved in the gas stream is often noted as a means of determining whether the CO_2 removal performance of the materials is stable over multiple cycles.

After completion of the first round of field testing, which was completed under a separate EPRI-sponsored program, an initial report was sent to sorbent developers. All of the amine-based sorbents exhibited a reduction in working CO_2 capacity with an increasing number of cycles using actual flue gas. Based on this feedback, the regeneration procedure was slightly modified for the second round of field testing. Instead of heating the sorbents in the presence of flue gas (in the interparticle void space), dry N_2 was sent through the sorbent bed during heating. However, this did not improve the sorbents' performance with an increasing number of cycles and will not be continued for future tests.

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. Although the minimum percentage of CO_2 in the flue gas is presented in tables throughout this report, it is only used to determine the effect of change the adsorption/regeneration conditions (i.e. moisture levels and regeneration temperature) or to identify a decrease in CO_2 removal performance over many repeated cycles. **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.**

Laboratory Testing

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. The laboratory tests were carried out parametrically; the moisture level, regeneration temperature and adsorption temperature (in a few cases only thus far, were varied to identify fatal flaws and the optimal operating conditions. During capture, the gas temperature was approximately 55 ºC and either dry, 45%, or 90% relative humidity, to simulate conditions downstream of a dry or wet scrubber. The regeneration temperature varied between sorbents, but was generally within the range of 65 to 250 º C.

Field Testing

In order to accelerate sorbent development, the effect of actual flue gas constituents on sorbent performance must be known. First, the optimal regeneration temperature was identified during the laboratory screening. Then, the best materials were selected for field tests and were tested for many adsorption/regeneration cycles using the same regeneration temperature. By completing over 10 capture/regeneration cycles with the same sorbent, serious poisoning issues were identified. Table 1 lists the key characteristics of the flue gas used for sorbent screening.

Table 1: Key flue gas characteristics for field tests.

Temperature (°F)	140
CO_2 Concentration (%)	10 to 12
Moisture	Saturated
O_2 (%)	5 to 6
NO_x (ppm)	100 to 120
SO_2 (ppm)	50 to 250

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 (typically less than 200 ppm), 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 for the field tests. 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 inlet gas streams used from the compressed bottles in the laboratory. Also, the peristaltic pump to introduce moisture to the gas was unnecessary. The experimental procedure was the same for both laboratory and the first round of field testing. For the second round of field testing, the system was automated so that the sorbents could be tested continuously. Another important modification, based on feedback from sorbent developers, was to heat the sorbents while flushing with dry N_2 instead of using the N_2 only to flush the CO_2 from the sorbent bed after the material had reached the regeneration temperature.

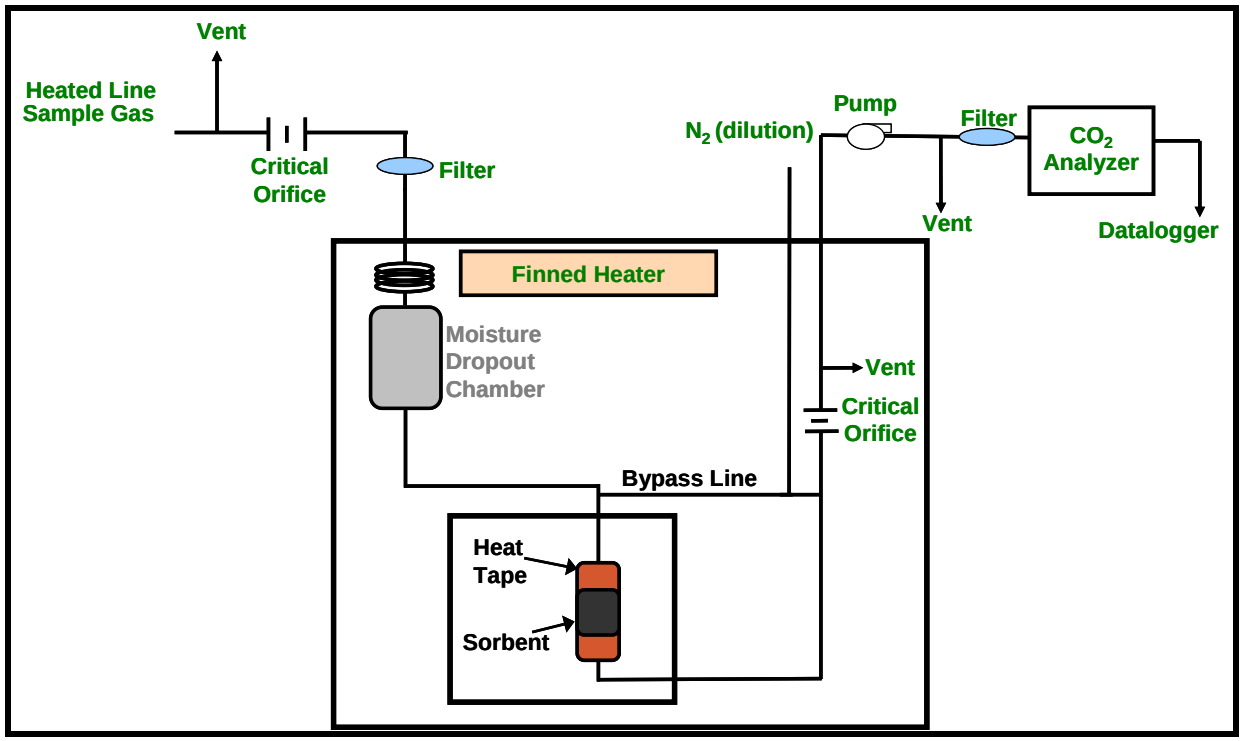

Figure 3: Schematic of sorbent screening testing unit modified for field tests.

For the first two rounds of field testing, there was one significant issue with sample flue gas. The sample was drawn using a probe common to the plants continuous emissions monitoring systems (CEMS). Since this probe could become clogged over time, the plant periodically would flush the probe. During this blowback, the sample gas was unavailable. This led to increased error in the adsorption profiles during field testing. When using these adsorption profiles to calculate the working CO_2 capacity, this could lead to either an overly high or low value. To overcome the issues caused by this additional error involved in the field tests, many adsorption/regeneration cycles were completed and the working capacities were averaged.

Theoretical Regeneration Energy

When evaluating and comparing sorbents for use in a commercial-scale CO_2 capture and sequestration system, one of the most important evaluation criteria is the energy required for regeneration. Equation 1 shows the energy balance for regeneration.

$$\frac{Q}{m_c} = \frac{m_e}{m_c} C_e \Delta T + \frac{B}{L} C_s \Delta T + C_{p.c} T_2 - C_s T_1 + \frac{Q_r}{m_c} \qquad (1)^4$$

Where Q is the regeneration heat input, kJ
m_c is the mass of adsorbed CO_2, kg
m_e is the equipment mass, kg
ΔT is the temperature difference between adsorption and regeneration, °C or K
T_1 is the adsorption temperature, °C or K
T_2 is the regeneration temperature, °C or K

L is the CO_2 loading, g CO_2/g sorbent
C_s is the sorbent specific heat, kJ/kg·K
$C_{p.c}$ is the constant pressure specific heat for CO_2, kJ/kg·K
C_e is the equipment specific heat, kJ/kg·K
B is a dimensional conversion term
Q_r is the heat of reaction (positive for endothermic regeneration), kJ/mol CO_2

Due to pressure drop, heat transfer, and mixing concerns, ADA will not be using a fixed bed for testing beyond the laboratory scale. Therefore, the first term on the right hand side of Equation 1 can be neglected because no equipment heating will be required during regeneration (i.e. the regeneration system will be kept at the regeneration temperature and the sorbent will be moved). The second term on the right hand side of Equation 1 is the energy required to heat the sorbent from the adsorption temperature to the regeneration temperature. To reduce the energy due to this term, sorbent loading can be increased or the difference between the adsorption and regeneration temperature can be decreased. The third and fourth term on the right hand side of Equation 1 can be combined to determine the energy required for the phase change of CO_2 from a free gas to one adsorbed on a solid. The final term on the right hand side of Equation 1 is the energy required to overcome the endothermic reaction associated with desorbing the CO_2 from the sorbent. For physical adsorbents, this term is usually an order of magnitude lower than sorbents that chemically react with the CO_2. However, the loading is also lower.

For all the sorbents testing in this program, the theoretical energy required for regeneration was calculated using Equation 1. The result of this calculation is used to compare different materials, and assess their respective viability for use in a commercial-scale CO_2 capture system. Note that from previous reports a liquid MEA CO_2 capture system requires approximately 4530 kJ/kg CO_2 (1934 BTU/lb CO_2).[5]

RESULTS

Sorbent Specific Results

Sorbent A

Sorbent A is a treated carbon nanotube material that was evaluated initially during an EPRI sponsored project, and again under the current DOE/NETL project. All results concerning this material are included in this report for comparison. A 0.5 g of sorbent A was tested for 5 adsorption/regeneration cycles in the laboratory using simulated flue gas from compressed gas tanks. No moisture was included in the initial cycles, although it was included for a second round of laboratory testing. Table 2 lists the dry testing conditions for sorbent A as well as the working CO_2 capacity. Note that the wt % is the working CO_2 capacity and the min % CO_2 is the lowest level of CO_2 observed in the gas stream during the adsorption step. The capacity observed during cycle 1 is significantly lower than the others observed. This can be attributed to the low flushing temperature, D0 = 55°C. Note that in cycle 3 when sorbent A is regenerated at 120°C, it has a working capacity >5 wt%. Based upon discussions and publications by the sorbent developer, the capture of CO_2 by this material is mostly attributable to physical adsorption. Therefore, this is a remarkably high working capacity for such a material under realistic testing conditions. The results for the adsorption profiles run with moisture are slower than the dry runs, although the same bed of sorbent

was used for both tests. The capacity is still over 4 wt% for several of the cycles that included moisture.

Table 2. Laboratory Testing Conditions and Results for Sorbent A

Cycle	T_{adsorb} (°C)	% Sat.	CO_2 (vol%)$_{-wet}$	Cycle	T_{desorb} (°C)	$t_{adsorption}$ (s)	$m_{CO2-adsorbed}$ (g)	wt %	min % CO_2
				D0	55				
A1	55	0	12	D1	90	165	0.016	2.82	4.70
A2	55	0	12	D2	100	290	0.028	4.75	2.72
A3	55	0	12	D3	110	264	0.029	5.05	2.41
A4	55	0	12	D4	120	264	0.029	5.05	1.79
A5	55	0	12	D5	130	209	0.029	4.96	2.33
				D0	120				
A6	55	90	12	D6	80	191	0.024	4.85	3.03
A7	55	90	12.3	D7	90	83	0.010	2.05	7.22
A8	55	90	12	D8	100	202	0.017	3.43	4.59
A9	55	90	12	D9	110	141	0.019	3.72	3.91
A10	55	90	12	D10	120	140	0.022	4.30	3.24
A11	55	90	12	D10	120	140	0.021	4.11	3.33

Figure 4 shows the adsorption profiles for sorbent A. With the exception of the first cycle, these curves are repeatable and do not show any signs of degradation of material or decrease in sorbent performance.

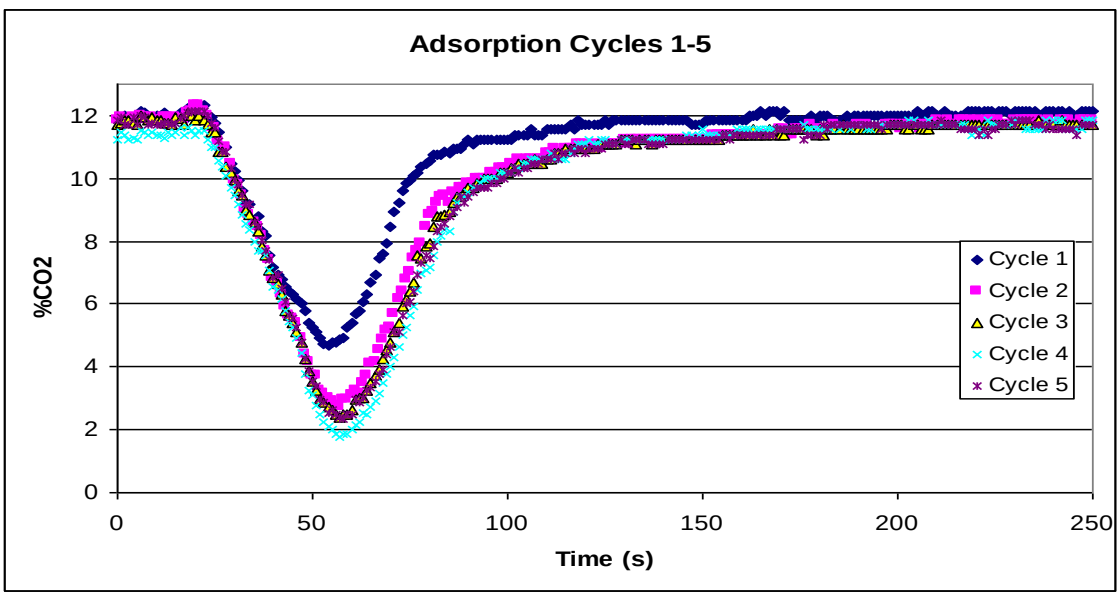

Figure 4: Sorbent A Laboratory Adsorption Profiles 1-5

Figure 5 shows the regeneration profiles for sorbent A. Note in Table 2 that the temperature of regeneration was increased between cycles. Although this increase in temperature did not have a significant effect on the working capacity of material, it was important for the time required for regeneration. For example, at a regeneration temperature of 90°C, complete regeneration of the sorbent required flushing with N_2 for over 400s. However, by increasing the regeneration temperature to 130°C, the regeneration time is reduced by nearly a factor of 5 to approximately 50 seconds. If this sorbent was considered for a full-scale commercial process, the regeneration temperature would be based on process optimization.

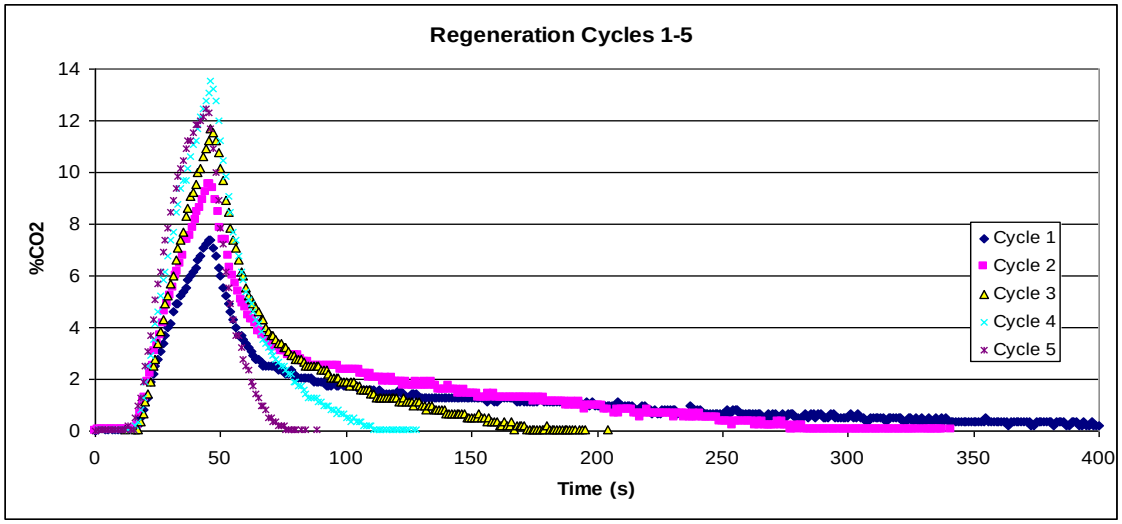

Figure 5: Sorbent A Laboratory Regeneration Cycles 1-5

Further testing was completed to analyze the effect of moisture on sorbent A's CO_2 removal performance. The CO_2 capacities observed were similar, when regenerated at temperatures greater than 80°C. Based on Equation 1 and the preliminary test results with moisture, the theoretical regeneration energy for sorbent A adsorbing at 55°C and regenerating at 110°C is 1700 kJ/kg CO_2 (720 BTU/lb CO_2). Sorbent A is a very promising option for post-combustion CO_2 capture, based on the low regeneration energy. It is currently under investigation whether sorbent A could be economically produced in the necessary quantities to supply a 500 MW power plant with a commercial CO_2 capture system.

Sorbent F

Sorbent F is a powdered supported amine. Due to the small particle size of this material, only 0.5 g of material was tested during both laboratory and field testing. During the laboratory tests, seven adsorption/regeneration cycles were completed, the conditions and results of which are shown in Table 3. Since previous supported amines had shown sensitivity to high regeneration temperatures, the initial flushing for Sorbent F was carried out at only 70°C. However, based on the results this precaution was unnecessary; sorbent F was safely regenerated for several cycles at 120°C. The increasing CO_2 capacity listed in Table 3 can be attributed to this low initial flushing temperature. In addition, since only 0.5 g of material was tested, the error caused by CO_2 monitor response time of 10 s is more significant than those samples that were tested in 2.5 g quantities. Therefore, it can be assumed that the CO_2 capacities reported are lower than the actual values.

Table 3. Sorbent F Laboratory Testing Conditions and Results

Cycle	T_{adsorb} (°C)	% Sat.	CO_2 (vol%)$_{-wet}$	T_{desorb} (°C)	$t_{adsorption}$ (s)	wt %	min % CO_2
A1	55	45	12	100	70	1.7	7.2
A2	55	45	12	100	144	3.7	4.6
A3							
A4	55	45	12	100	166	4.0	4.8
A5	40	45	12	100	160	4.1	4.6
A6	40	45	12	110	207	4.6	4.0
A7	40	45	12	120	209	4.7	4.1

Figure 6 shows the seven laboratory CO_2 adsorption profiles for sorbent F. The cycle 1 profile is not indicative of sorbent F performance, for the previously discussed reasons.

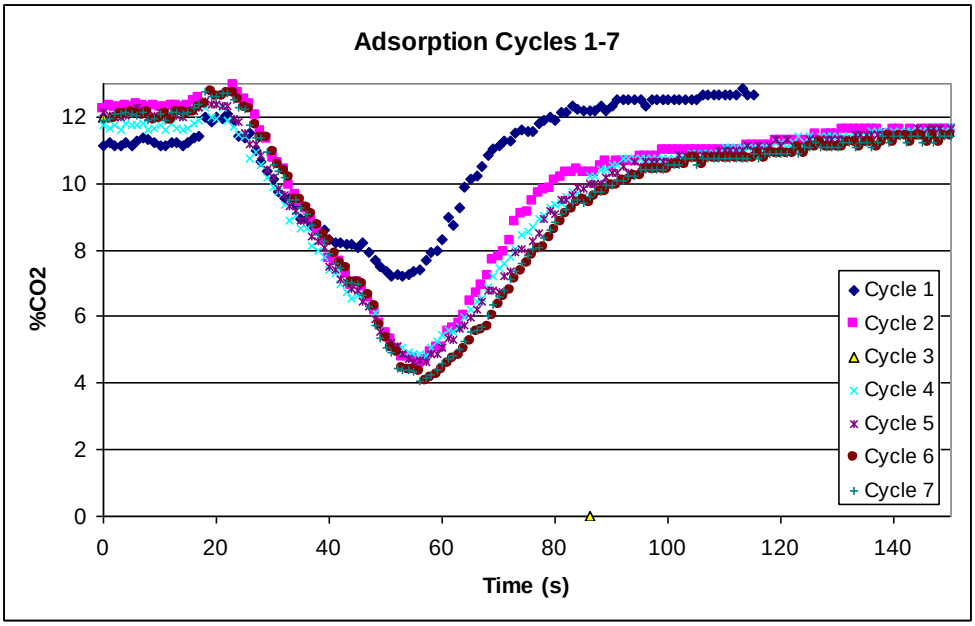

Figure 6. Sorbent F Laboratory Adsorption Cycles 1-7

Based on the good performance and lack of sensitivity to temperature, sorbent F was selected as one of the materials to be tested on actual flue gas during field tests. Thirty-four adsorption/regeneration cycles were completed over two consecutive days using actual flue gas. For these cycles, the initial flushing temperature was increased to 140°C based on discussions with the sorbent developer, and all regenerations were carried out at 120°C. Table 4 lists the field testing conditions and results.

Table 4. Sorbent F Field Testing Conditions and Results

Cycle	T_{adsorb} (^oC)	Cycle	T_{desorb} (^oC)	$t_{adsorption}$ (s)	wt %	min % CO_2
		D0				
A1	55	D1	140	226	4.5	6.9
A2	55	D2	120	231	5.4	5.7
A3	55	D3	120	214	4.1	6.6
A4	55	D4	120	145	4.3	6.2
A5	55	D5	120	113	4.2	6.3
A6	55	D6	120	141	4.7	6.0
A7	55	D7	120	179	4.3	6.9
A8	55	D8	120	141	4.6	6.2
A9	55	D9	120	143	4.4	6.6
A10	55	D10	120	117	4.0	6.0
A11	55	D11	120	132	4.2	6.3
A12	55	D12	120	154	4.8	6.0
A13	55	D13	120	131	4.2	6.0
A14	55	D14	120	134	3.8	7.2
A15	55	D15	120	128	4.0	6.6
A16	55	D16	120	215	4.5	6.6
A17	55	D17	120	131	4.0	6.4
A18	55	D18	120	76	3.5	6.6
A19	55	D19	120	229	4.3	6.1
A20	55	D20	120	213	4.3	6.4
A21	55	D21	120			
A22	55	D22	120	171	3.9	6.5
A23	55	D23	120	144	3.4	6.4
A24	55	D24	120	162	3.9	6.5
A25	55	D25	120			
A26	55	D26	120	158	3.5	6.8
A27	55	D27	120	204	3.6	6.6
A28	55	D28	120	185	3.9	6.4
A29	55	D29	120	199	3.8	6.6
A30	55	D30	120	171	3.8	5.7
A31	55	D31	120	114	3.0	7.1
A32	55	D32	120			
A33	55	D33	120	174	3.4	6.8
A34	55	D34	120	215	4.0	6.8

Figure 7 shows the adsorption profiles for cycles 1 through 10 of the field tests. The repeatability of the adsorption step can be observed from inspection of these data. A slight decrease in the CO_2 capacity with an increasing number of cycles was observed. Further tests will be required to determine the cause of this decrease in capacity. Specifically, the same material that was used during field tests will be used again in an abbreviated round of laboratory tests to identify whether or not this material regains CO_2 capacity that was lost during field tests. Using the average CO_2 capacity during field tests, the theoretical regeneration energy for sorbent F is 3530 kJ/kg CO_2 (1520 BTU/lb CO_2). Note that this value is lower than that of an aqueous amine even with the underestimation of working capacity caused by the CO_2 analyzer response time.

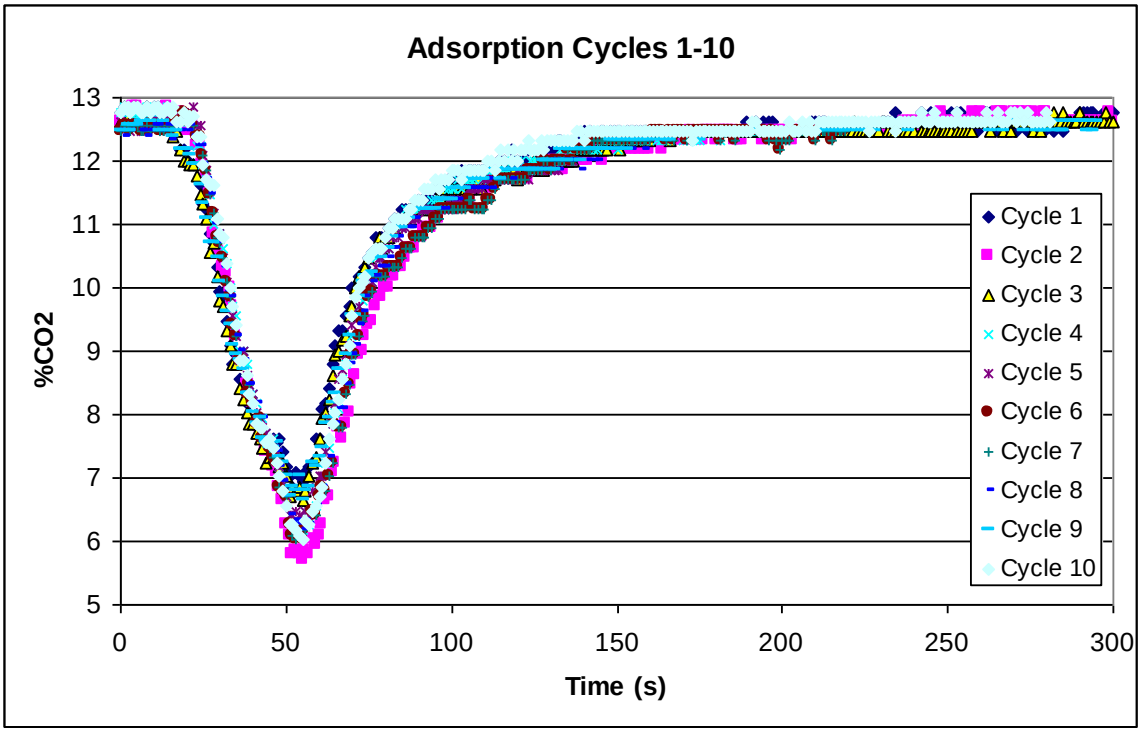

Figure 7. Sorbent F Field Adsorption Profiles for Cycles 1-10

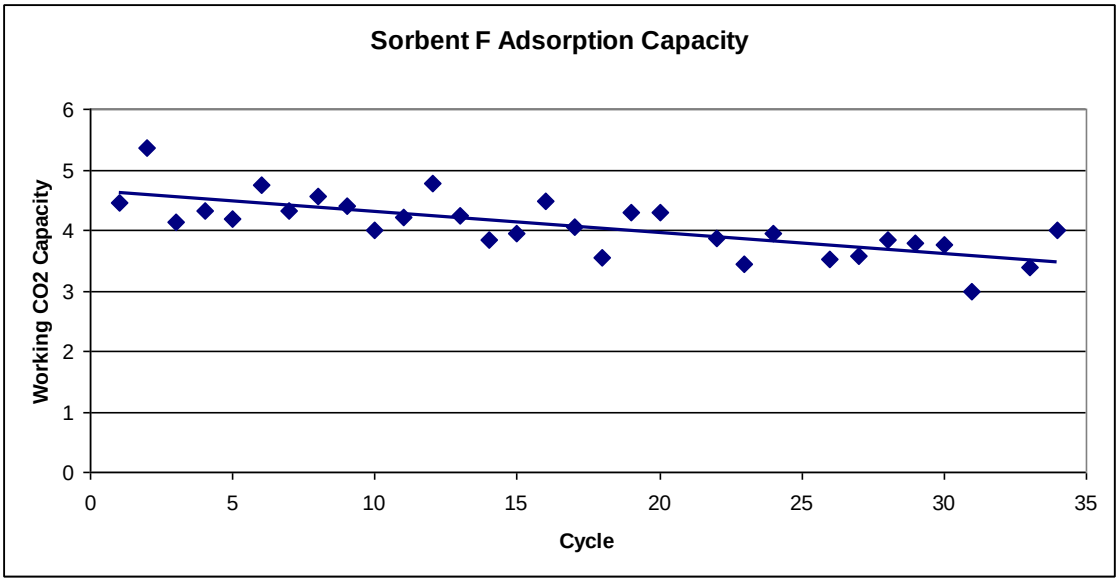

Figure 8. Sorbent F Field Working CO_2 Capacity with Increasing Cycles

Based on discussion with the sorbent developer, sorbent F was included in the second round of field testing. It was proposed that the decrease in working CO_2 capacity observed in Figure 8 may be due to heating of the sorbent with flue gas. Therefore, for the second round of field testing, the regeneration step was modified so that the sorbents were heated in the presence of N_2. This did not change the decrease in working capacity observed. Therefore, the loss in CO_2 capacity for sorbent F and the other supported amines is likely due to reaction with SO_2 to form heat stable salts. This is also an issue for aqueous amines,

and must be considered when designing and developing cost estimates for a commercial-scale system.

Sorbent J

Sorbent J is a zeolite, 2.5 of which were tested on simulated flue gas in the ADA laboratory. Table 5 lists the laboratory testing conditions and results for sorbent J. Although the regeneration temperature was high relative to the other materials tested, sorbent J did exhibit a good ability to remove CO_2 from dry flue gas. When the moisture was added, the working capacity was quickly diminished, regardless of the high regeneration temperature.

Table 5. Sorbent J Laboratory Testing Conditions and Results

Cycle	T_{adsorb} (^oC)	% Sat.	CO_2 (vol%)$_{-wet}$	Cycle	T_{desorb} (^oC)	$t_{adsorption}$ (s)	$m_{CO2-adsorbed}$ (g)	wt %	min % CO_2
				D0	250				
A1	55	0	12.6	D1	200	614	0.084	3.37	-0.12
A2	55	0	12.5	D2	200	440	0.075	3.01	-0.07
A3	55	0	12.5	D3	200	517	0.081	3.23	-0.12
A4	55	0	12.5	D4	200	477	0.080	3.20	0.03
A5	55	90	12.8	D5	200	124	0.047	1.87	3.20
A6	55	90	12	D6	200	75	0.019	0.77	3.20
A7	55	90	12	D7	200	77	0.022	0.89	3.20
A8	55	90	12	D8	200	75	0.022	0.88	3.20
A9	55	90	12	D9	200	72	0.020	0.80	3.20
A10	55	90	12	D10	200	71	0.017	0.69	3.20

Figure 9 shows the laboratory adsorption profiles for sorbent J. Cycle 5 is the first adsorption profile where the moisture was included in the simulated flue gas. The moisture clearly leads to a decrease in the CO_2 removal. In addition, for all cycles run with moisture, the final CO_2 concentration is higher than the baseline level. This can be attributed to the CO_2 that had been adsorbed actually being released in favor of water. Clearly sorbent J is highly selective towards moisture and can not be used in a commercial process to remove CO_2 from flue gas with high moisture content.

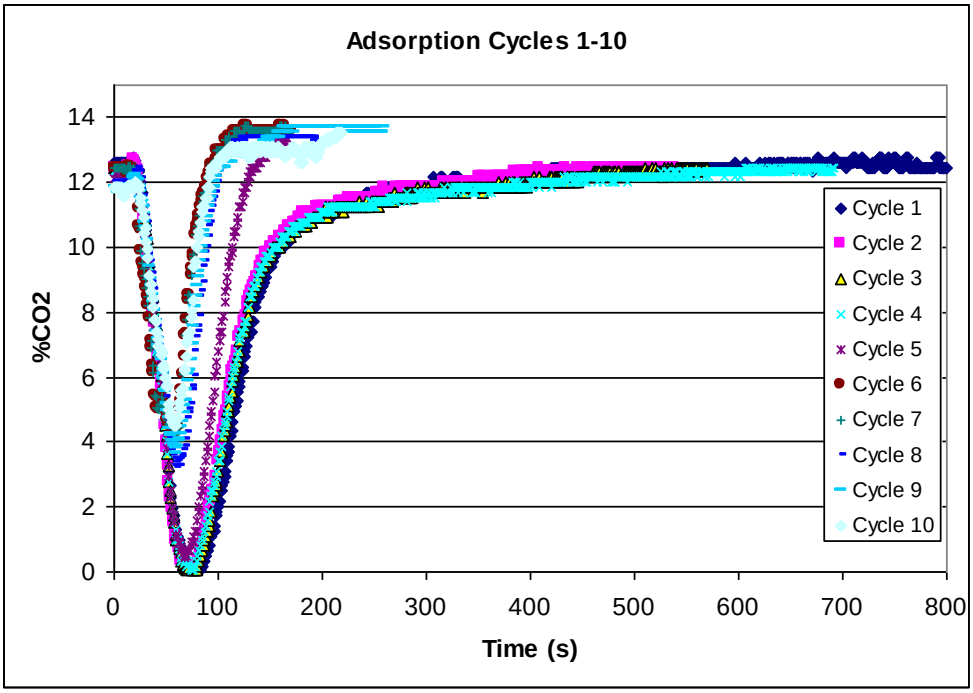

Figure 9. Sorbent J Laboratory Adsorption Profiles 1-10

Based on the laboratory experiment observations, even using dry simulated flue gas the theoretical regeneration energy was 5200 kJ/kg CO_2 (2250 BTU/lb CO_2), which is greater than the benchmark aqueous MEA. When the moisture was included in the gas stream, the theoretical regeneration energy is much higher, approximately 19,000 kJ/kg CO_2 (8200 BTU/lb CO_2).

Sorbent M

Sorbent M is a zeolite, 2.5 of which were tested during nine adsorption/regeneration cycles in the ADA laboratory. Table 6 lists the testing conditions and results for sorbent M. At a regeneration temperature of 200°C, this zeolite was observed to have a working CO_2 capacity of nearly 5 wt%. However, similar to other zeolites, when moisture was introduced into the gas stream, the ability of the material to remove CO_2 was quickly diminished.

Table 6. Sorbent M Laboratory Testing Conditions and Results

Cycle	T_{adsorb} (°C)	% Sat.	CO_2 (vol%)$_{wet}$	Cycle	T_{desorb} (°C)	$t_{adsorption}$ (s)	$m_{CO2\text{-}adsorbed}$ (g)	wt %	min % CO_2
				D0	250				
A1	55	0	12	D1	200	564	0.123	4.91	-0.28
A2	55	0	12	D2	200	632	0.117	4.67	-0.43
A3	55	0	12	D3	200	666	0.120	4.79	-0.43
A4	55	0	12	D4	200	617	0.129	5.14	-0.58
A5	55	90	12	D5	200	190	0.073	2.93	-0.58
A6	55	90	12	D6	200	89	0.035	1.42	0.34
A7	55	90	12	D7	200	86	0.033	1.33	0.54
A8	55	90	12	D8	200	61	0.013	0.51	5.66
A9	55	90	12	D9	200	66	0.006	0.22	9.24

Figure 10 is a plot of the adsorption profiles for sorbent M. The distinction between adsorption steps run with and without moisture is quite clear. In fact, the CO_2 capacity is decreased from over 5 wt% to nearly zero in only a few cycles.

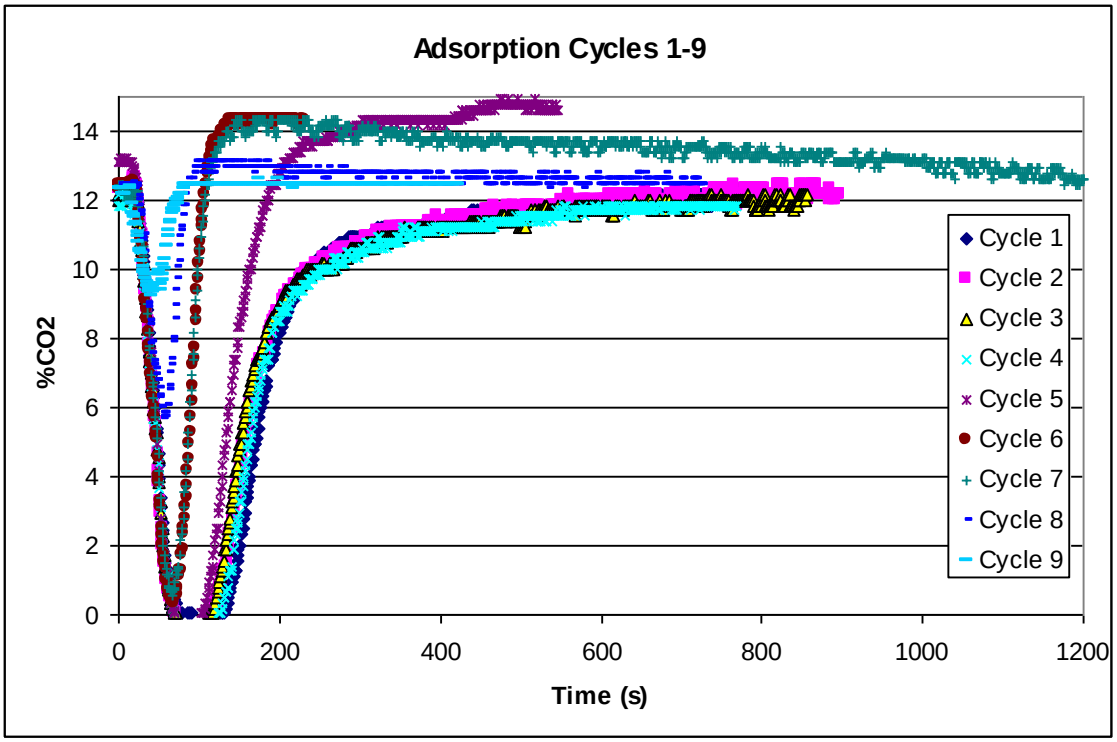

Figure 10. Sorbent M Laboratory Adsorption Profiles

The theoretical regeneration energy for sorbent M in a dry gas stream is approximately 3600 kJ/kg CO_2 (1560 BTU/lb CO_2). Although this is below the benchmark aqueous MEA, when the moisture is added to the gas stream, this value increases by an order of magnitude to approximately 73,000 kJ/kg CO_2 (31,600 BTU/lb CO_2). Further investigation into the added energy penalty of cooling and drying the flue gas stream may be warranted based on the results from sorbent M and the other zeolites examined.

Sorbent P

Sorbent P is a carbon-based material; 2.5 g of this material was tested on simulated flue gas in the laboratory for ten cycles. Table 7 lists the testing conditions and results for sorbent O. This material exhibited an ability to capture CO_2, but the results were not good enough to warrant including sorbent P in the field tests. Based on results from the laboratory testing, the theoretical regeneration energy for sorbent P is approximately 6500 kJ/kg CO_2 (2800 BTU/lb CO_2).

Table 7. Sorbent P Laboratory Testing Conditions and Results

Cycle	T_{adsorb} (°C)	% Sat.	CO_2 (vol%)$_{wet}$	Cycle	T_{desorb} (°C)	$t_{adsorption}$ (s)	$m_{CO2\text{-}adsorbed}$ (g)	wt %	min % CO_2
				D0	120				
A1	55	0	12	D1	80	90	0.020	0.81	3.56
A2	55	0	12	D2	90	106	0.020	0.81	4.18
A3	55	0	12	D3	100	109	0.017	0.70	4.59
A4	55	0	12	D4	110	112	0.019	0.76	4.28
A5	55	0	12	D5	120	98	0.018	0.74	4.59
A6	55	90	12	D6	80	67	0.016	0.63	4.72
A7	55	90	12	D7	90	66	0.016	0.62	4.76
A8	55	90	12	D8	100	71	0.017	0.68	4.43
A9	55	90	12	D9	110	66	0.015	0.61	4.89
A10	55	90	12	D10	120	69	0.016	0.62	4.78

Figure 11 shows the first ten adsorption cycles for sorbent P. For most carbon-based materials, no significant decrease in capacity is observed. However, sorbent P did show a fairly consistent decrease in working capacity as the cycle number increased. This may be attributable to the parametric testing, but was not further investigated due to the low initial capacity.

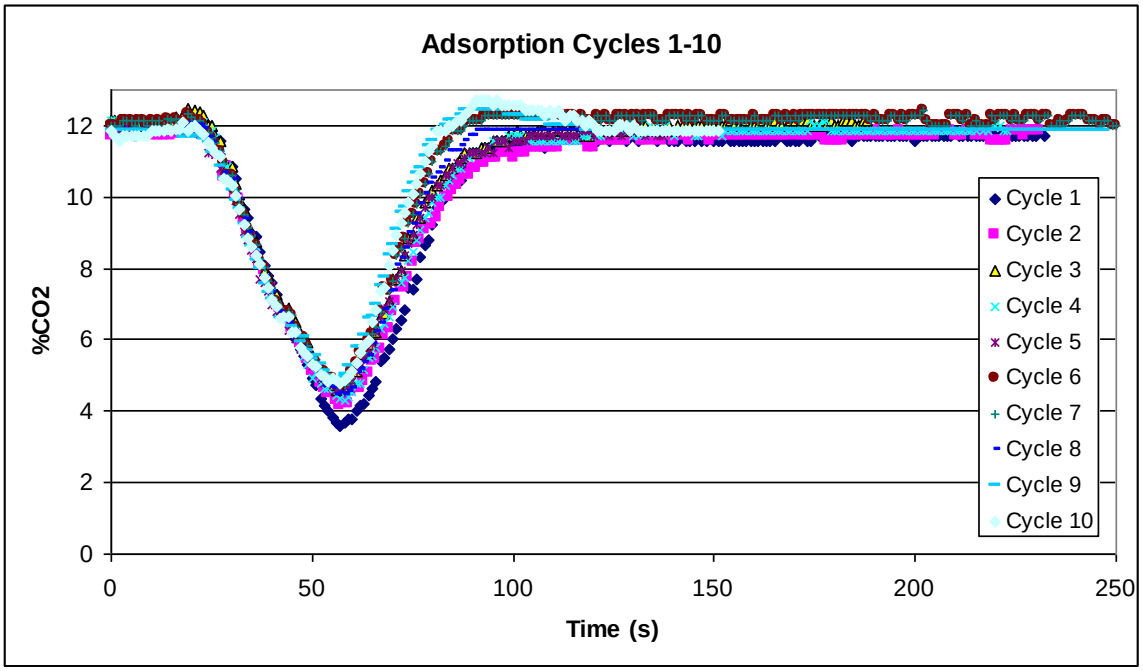

Figure 11. Sorbent P Laboratory Adsorption Cycles 1-10

The theoretical regeneration energy for sorbent P, based on the laboratory test with 90% relative humidity and a regeneration temperature of 100°C, is 6500 kJ/kg CO_2 (2800 BTU/lb CO_2).

Sorbent R

Sorbent R is a supported amine, 2.5 of which were tested in the laboratory as well as in the field. The sorbent developer expressed concern about the sensitivity of this material to temperature. Based on this concern, the highest regeneration temperature for this material was 100°C. Table 8 lists the laboratory testing conditions and results for sorbent R. Two different beds of this material were used, one for the dry tests and a new bed for the tests at 90% relative humidity. During the dry tests, the critical orifice downstream of the sorbent bed was plugged, so the results were not accurate. Sorbent R had the highest CO_2 working capacity measured in the laboratory, and was therefore included in the second round of field testing.

Table 8. Sorbent R Laboratory Testing Conditions and Results

Cycle	T_{adsorb} (°C)	% Sat.	CO_2 (vol%)$_{-wet}$	Cycle	T_{desorb} (°C)	$t_{adsorption}$ (s)	mCO2-adsorbed (g)	wt %	min % CO_2
				D0	100				
A1	55	0	12	D1	80	1435	0.336	13.43	-0.43
A2	55	0	12	D2	90	1440	0.311	12.45	-0.58
A3	55	0	12	D3	100				
A4	55	0	12	D4	100				
				D0	100				
A1	55	90	12.6	D1	80	2264	0.272	10.89	-0.58
A2	55	90	12.5	D2	90	1736	0.259	10.35	-0.43
A3	55	90	12.5	D3	100	1828	0.266	10.65	-0.58
A4	55	90	12.3	D4	100	1166	0.220	8.79	-0.82
A5	55	90	12.5	D5	100	1164	0.243	9.70	-0.82
A6	55	90	12.5	D6	100	1317	0.211	8.44	-0.58

Figure 12 shows the 90% relative humidity laboratory adsorption profiles for sorbent R. Initially, this material is able to remove all the CO_2 from the gas stream. Then the CO_2 concentration increases quickly at first, and then more slowly. Note that the adsorption step was often carried out for 1800 s (30 min), which is unlikely to be feasible in a commercial-scale system. In a commercial-scale system it is likely that only the fast reaction-sites can be utilized, although fixed bed tests make it difficult to predict a working capacity for a different system. In any case, sorbent R had the highest working CO_2 capacity of any material tested thus far in the program. This high CO_2 capacity led to a lower theoretical regeneration energy, approximately 1700 kJ/kg CO_2 (740 BTU/lb CO_2) when using the highest laboratory working capacity and a regeneration temperature of 100°C, because less sorbent will need to be heated to release the CO_2.

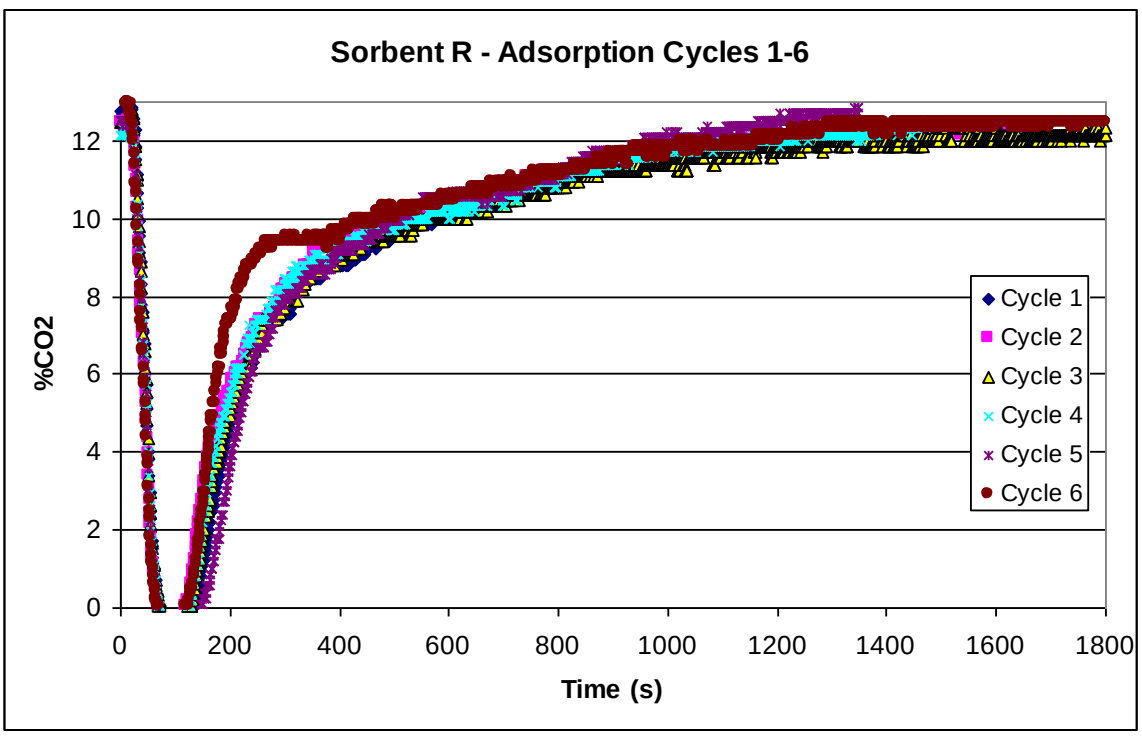

Figure 12. Sorbent R Laboratory Adsorption Profiles

Based on the promising laboratory results, sorbent R was included in the second round of field testing. The power plant flue gas characteristics are given in the Experimental Apparatus and Procedures section. The average working CO_2 capacity measured during the

field tests was >9 wt%, which is significantly higher than most other materials tested thus far in the program. Figure 13 shows the adsorption profiles for the first 10 cycles completed in the field tests. A multi-gas analyzer was used for these field tests, rather than the CO_2 analyzer used in the laboratory. The flue gas used during these tests was unavailable periodically due to sample probe blowback. Figure 13 contains an example (circled in red) of one such period. When the flue gas was unavailable for the tests, it was difficult to accurately calculate the working capacity. However, by automating the testing unit, many more cycles were completed during the field tests.

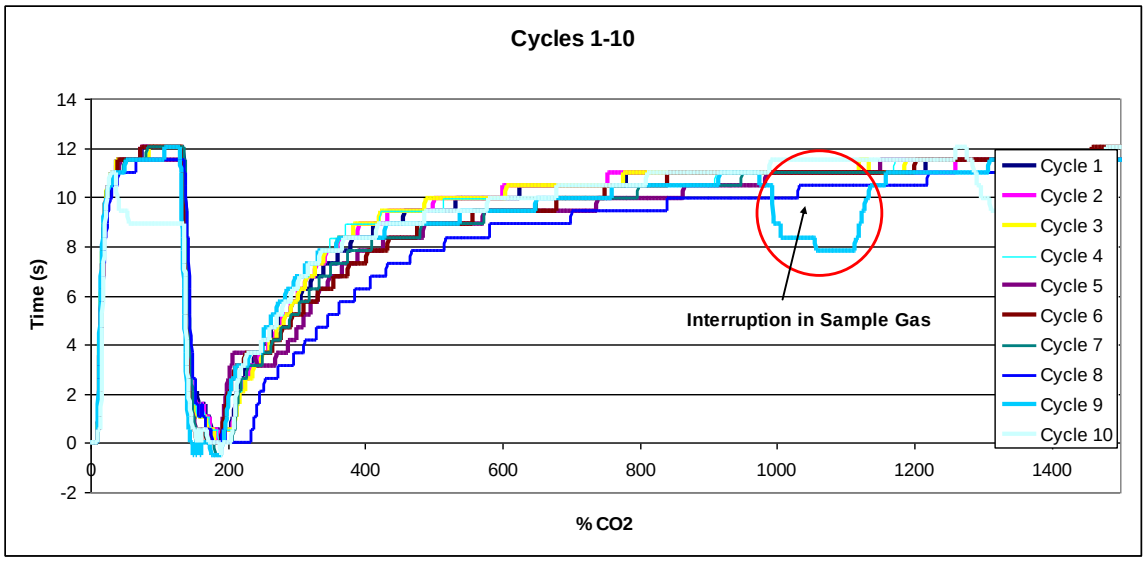

Figure 13. Sorbent R Field Adsorption Profiles 1-10

During the field test, 43 adsorption/regeneration cycles were completed using sorbent R. Although the field tests presented issues that were not present in the laboratory, clear trends concerning the CO_2 removal performance of sorbent R can be drawn. Figure 14 shows the CO_2 working capacity of sorbent R with an increasing number of cycles using actual flue gas. The decrease in capacity is clear. However, it is theorized that most, if not all, of this loss in capacity can be attributed to reaction with SO_2 to form heat-stable salts, which is also a concern for aqueous amines. Therefore, in a commercial-scale system, it may be necessary to lower the SO_2 levels below 50 ppm to 250 ppm (the levels in the field testing flue gas).

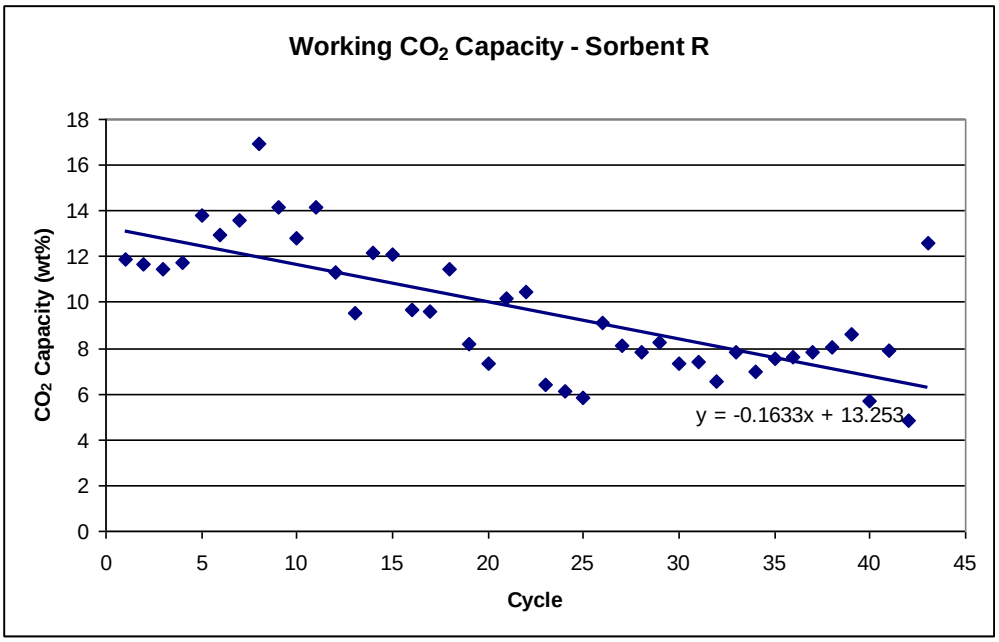

Figure 14. Sorbent R Field Working Capacity with Cycle Number

The theoretical regeneration energy based on the average working capacity during the field tests was similar to that observed during the laboratory tests, 1900 kJ/kg CO_2 (800 BTU/lb CO_2). Based on this calculation, sorbent R is one of the most promising materials included in this screening program to date.

Sorbent S

Sorbent S is a supported amine, 2.5 g of which were tested in the laboratory on simulated flue gas for nine adsorption/regeneration cycles. Based on concerns about thermal sensitivity, this material was not heated above 100°C. Table 9 lists the laboratory testing conditions and results for sorbent R. This material was able to remove over 90% of the CO_2 from the flue gas for a short period during every adsorption step.

Table 9. Sorbent S Laboratory Testing Conditions and Results

Cycle	T_{adsorb} (°C)	% Sat.	CO_2 (vol%)$_{-wet}$	Cycle	T_{desorb} (°C)	$t_{adsorption}$ (s)	$m_{CO2-adsorbed}$ (g)	wt %	min % CO_2
				D0	100				
A1	55	0	12	D1	80	603	0.065	2.60	0.66
A2	55	0	12.3	D2	90	744	0.072	2.89	0.50
A3	55	0	12.3	D3	100	584	0.067	2.68	0.65
A4	55	0	12.3	D4	100	711	0.071	2.82	0.85
A5	55	90	12	D5	80	545	0.045	1.82	0.51
A6	55	90	12	D6	90	628	0.057	2.26	0.45
A7	55	90	12.5	D7	100	935	0.082	3.29	0.15
A8	55	90	12	D8	100	747	0.064	2.55	0.04
A9	55	90	12	D9	100	986	0.077	3.08	0.23

Figure 15 shows the adsorption profiles for the nine cycles completed using simulated flue gas. Although the adsorption step was carried out for over 100s, the majority of the CO_2 was adsorbed relatively rapidly during the first 100s.

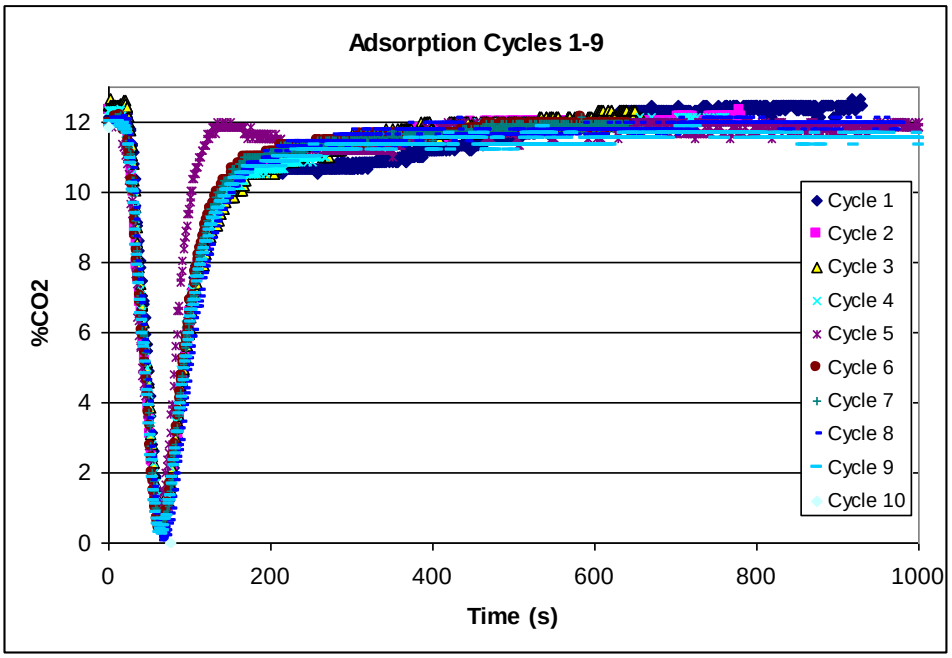

Figure 15. Sorbent S Laboratory Adsorption Profiles

Several of the supported amine sorbents left a yellow residue in or downstream of the sorbent bed. This observation was more pronounced for sorbent S. Figure 16 is a picture of the liquid downstream of the sorbent bed after testing sorbent S. Based on discussions with the sorbent developer, the loss of this liquid was not unexpected. Additional testing of sorbent S will be completed to determine if the loss of this liquid will lead to a decrease in CO_2 capacity.

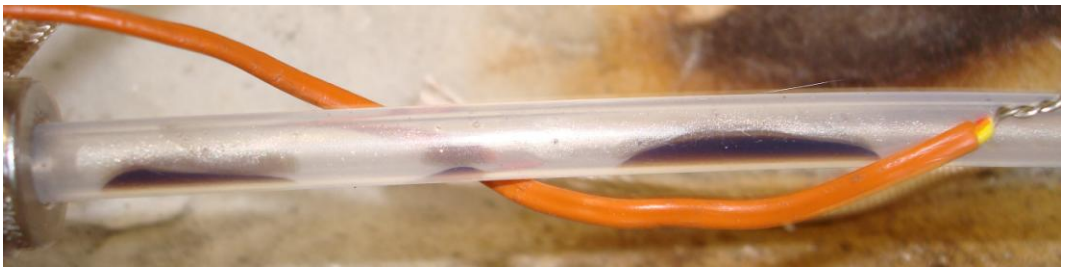

Figure 16. Picture of Tubing Downstream of Sorbent Bed After Testing Sorbent S

The theoretical regeneration energy for sorbent S, based on the highest working capacity observed in the laboratory and a regeneration temperature of 100°C, is 2500 kJ/kg CO_2 (1070 BTU/lb CO_2). This is lower than that of the benchmark, so further screening of sorbent S is warranted. Discussions are underway with the developer to determine if a pre-treatment step is necessary to stop the liquid from coming off of the sorbent.

Sorbent T

Sorbent T is a zeolite that was treated to increase its hydrophobicity. This material was tested for nine adsorption/regeneration cycles using simulated flue gas. Table 10 lists the testing conditions and results for sorbent T. The working CO_2 capacity was low both under dry and moist conditions.

Table 10. Sorbent T Laboratory Testing Conditions and Results

Cycle	T_{adsorb} (°C)	% Sat.	CO_2 (vol%)$_{-wet}$	Cycle	T_{desorb} (°C)	$t_{adsorption}$ (s)	$m_{CO2-adsorbed}$ (g)	wt %	min % CO_2
				D0	150				
A1	55	0	12	D1	100	259	0.021	0.83	6.43
A2	55	0	12	D2	125	104	0.012	0.47	7.20
A3	55	0	12	D3	150	319	0.017	0.68	6.79
A4	55	90	12	D4	100	62	0.010	0.42	8.94
A5	55	90	12	D5	125	50	0.006	0.23	6.48
A6	55	90	12	D6	150	59	0.011	0.44	8.32
A7	55	90	12	D7	200	56	0.007	0.28	4.59
A8	55	90	12	D8	200	88	0.020	0.80	6.02
A9	55	90	12			76	0.014	0.57	0.00

Figure 17 shows the adsorption profiles measured for sorbent T. The same issues with moisture that were observed for other zeolites were also observed when testing sorbent T. Beginning with cycle 4, the moisture actually begins to displace CO_2 that had previously been captured by the material.

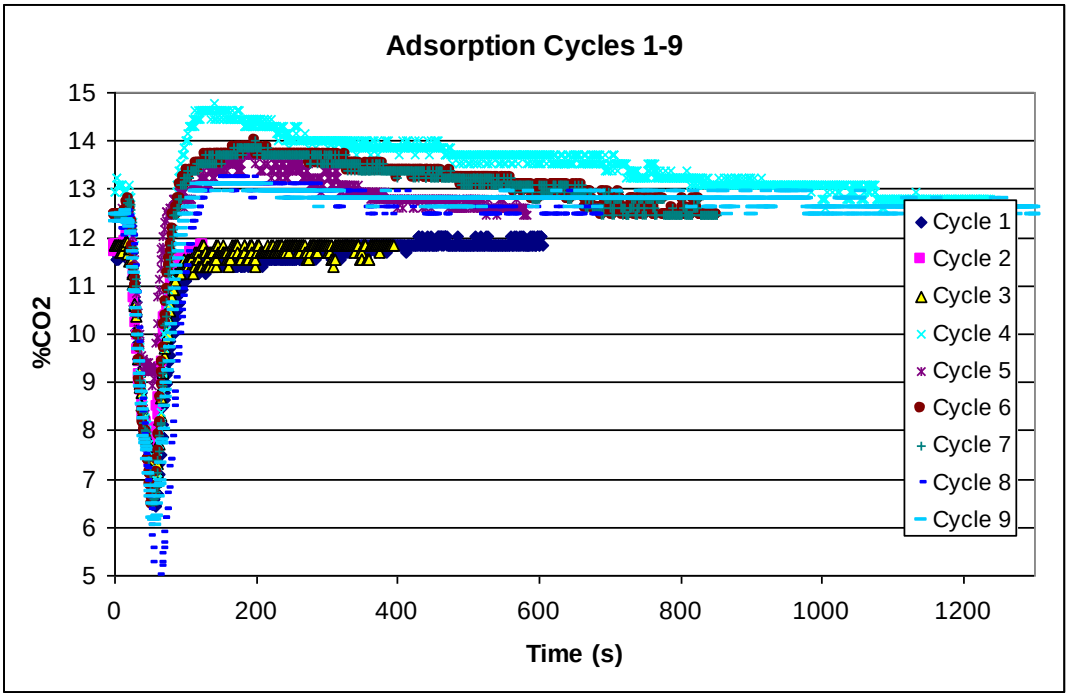

Figure 17. Sorbent T Laboratory Adsorption Profiles

Based on the highest working capacity observed for sorbent T, the theoretical regeneration energy for this material is 19,000 kJ/kg CO_2 (8200 BTU/lb CO_2). Since this regeneration energy is prohibitively high, no further testing of sorbent T is planned.

Sorbent U

Sorbent U is a zeolite, similar to sorbent T, which was modified to decrease the hydrophilicity of the material. Table 11 shows the testing conditions and results for sorbent U. In all gases the material exhibited a low working capacity, with or without moisture.

Table 11. Sorbent U Laboratory Testing Conditions and Results

Cycle	T_{adsorb} (°C)	% Sat.	CO_2 (vol%)$_{-wet}$	Cycle	T_{desorb} (°C)	$t_{adsorption}$ (s)	$m_{CO2-adsorbed}$ (g)	wt %	min % CO_2
				D0	150				
A1	55	0	12	D1	100	81	0.005	0.20	9.19
A2	55	0	12	D2	125	105	0.008	0.30	8.32
A3	55	0	12	D3	150	167	0.013	0.51	6.94
A4	55	90	12	D4	100	62	0.009	0.35	9.71
A5	55	90	12	D5	125	42	0.004	0.15	9.86
A6	55	90	12	D6	150	53	0.003	0.13	8.94
A7	55	90	12	D7	200	61	0.005	0.22	5.20
A8	55	90	12	D8	200	82	0.017	0.67	4.07
A9	55	90	12			98	0.023	0.93	0.00

Figure 18 shows the laboratory adsorption profiles for sorbent U. Although the CO_2 removal is poor in all cases, the steps run with moisture have profiles that show a final CO_2 concentration higher than the starting baseline level. This has been observed with other zeolites, and is attributed to the displacement of adsorbent CO_2 by H_2O. This is not reflected by the calculated working capacity in Table 11 because the data under consideration was only that before the CO_2 rebounded. In theory, a commercial scale system could be operated with an appropriate cycle time so that the flue gas was not in contact with the sorbent long enough to displace the adsorbent CO_2. Based on the experimental results it is believed that the treatment did not make the zeolite less selective towards moisture.

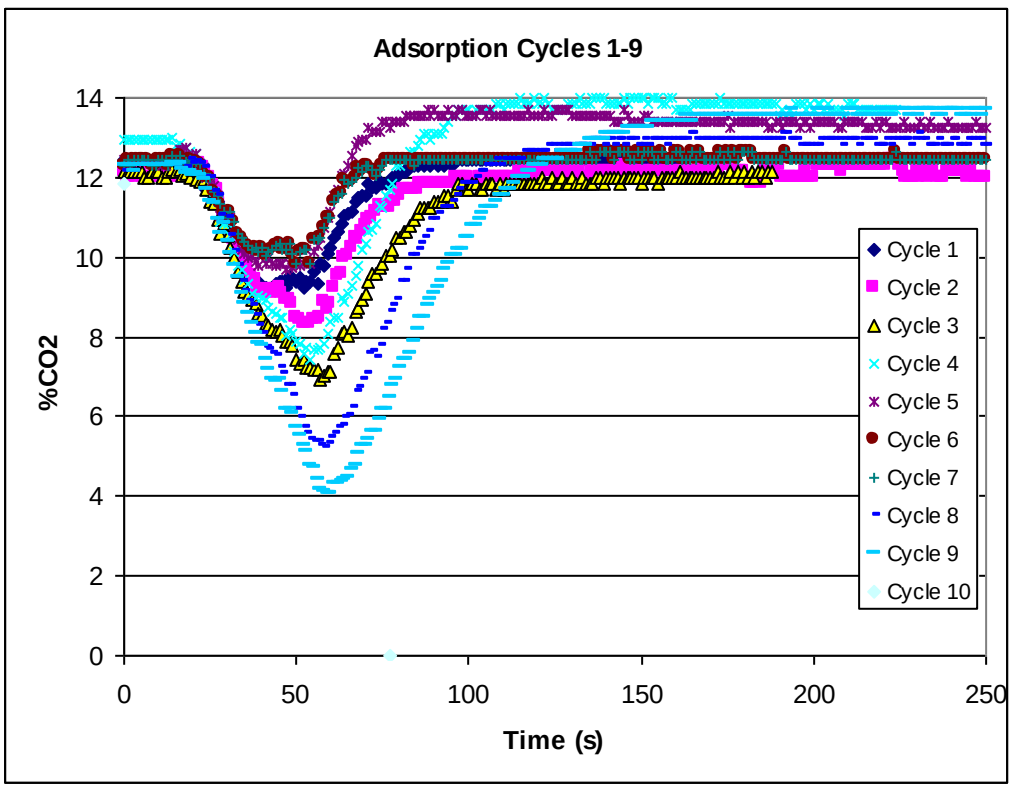

Figure 18. Sorbent U Laboratory Adsorption Profiles

Using the highest CO_2 capacity measured during for sorbent U, the theoretical regeneration energy is 17,000 kJ/kg CO_2 (7300 BTU/lb CO_2). This regeneration energy is an order of magnitude off those observed for other materials. Therefore, no further testing of sorbent U is planned.

Sorbent V

Sorbent V is a powdered supported amine. The particle size of this material is relatively small (estimated at 10 to 20 micrometers by the sorbent developer), so only 0.5 g of the material could be tested in the fixed bed with an acceptable pressure drop. Sorbent V was tested for eleven adsorption/regeneration cycles on simulated flue. Because the sorbent developer reported that this material was stable up to 150°C, based on his own thermogravimetric analysis (TGA), the regeneration temperature was varied between 80°C to 120°C. Table 12 lists the laboratory testing conditions for sorbent V. Although the data is scatter, due in part to the smaller sample size, there is no sign of performance issues from moisture. The average CO_2 working capacity is 2.5 wt% (which may also be underestimated due to the reduced sample size).

Table 12. Sorbent V Laboratory Testing Conditions and Results

Cycle	T_{adsorb} (°C)	% Sat.	CO_2 (vol%)$_{-wet}$	Cycle	T_{desorb} (°C)	$t_{adsorption}$ (s)	$m_{CO2-adsorbed}$ (g)	wt %	min % CO_2
				D0	120				
A1	55	0	12	D1	80	335	0.021	4.21	6.28
A2	55	0	12	D2	90	191	0.012	2.41	7.71
A3	55	0	12	D3	100	188	0.015	2.97	7.09
A4	55	0	12	D4	110	214	0.015	3.06	7.25
A5	55	0	12	D5	120	146	0.015	3.10	7.25
A6	55	90	12.6	D6	80				
A7	55	90	12.5	D7	90	173	0.015	2.95	7.71
A8	55	90	12.5	D8	100	332	0.021	4.11	7.09
A9	55	90	12.3	D9	110	142	0.006	1.11	7.25
A10	55	90	12.5	D10	120	193	0.010	2.08	7.25
A11	55	90	12.5	D11	120	191	0.011	2.27	6.17

Figure 19 is a plot of the first ten laboratory adsorption profiles. No decrease in the CO_2 removal performance of sorbent V was observed during these tests. In addition, the CO_2 adsorption step was relatively fast, with the majority of the removal occurring within the first 80 seconds of being in contact with the flue gas. Due to the thermal stability and short reaction time, sorbent V was included in the second round of field tests. Based on the laboratory tests, the theoretical regeneration energy for sorbent V at a working CO_2 capacity of 2.2 wt% and a regeneration temperature of 120°C is 5200 kJ/kg CO_2 (2200 BTU/lb CO_2).

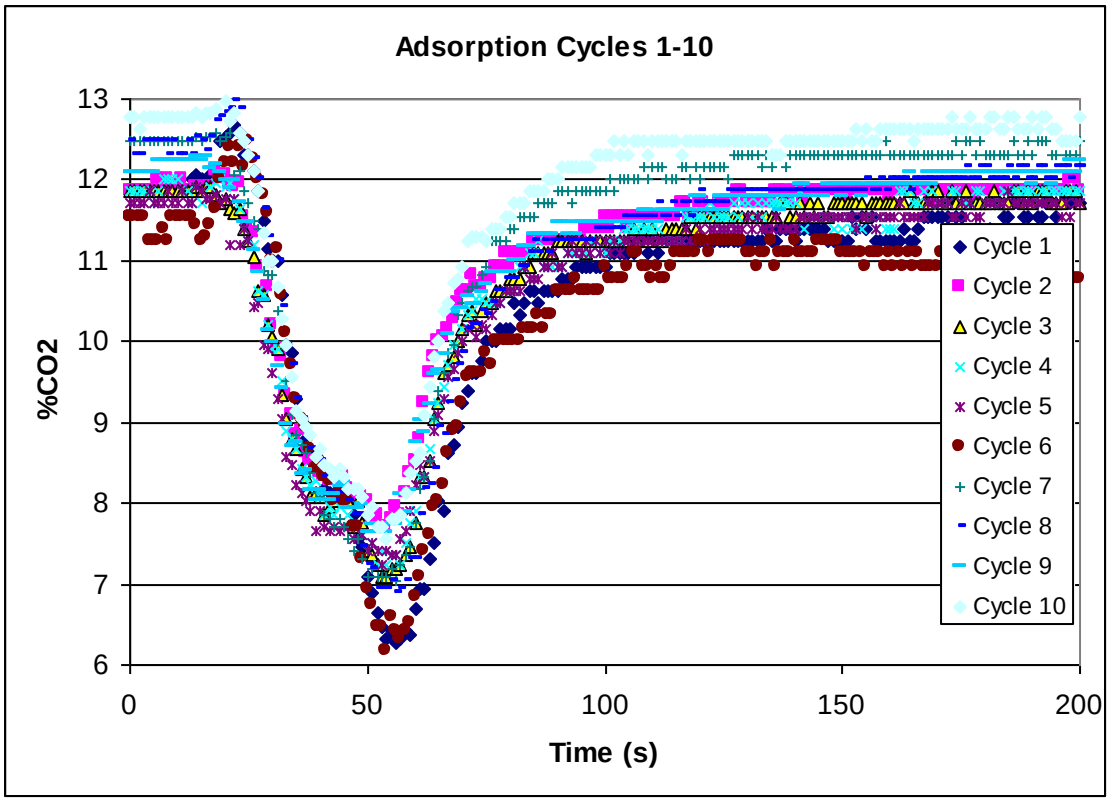

Figure 19. Sorbent V Laboratory Adsorption Profiles

Sorbent V was tested for 60 adsorption/regeneration cycles in the second round of field testing. The average working CO_2 capacity measured over these 60 cycles was approximately 2.7 wt%. Unfortunately, issues with equipment and periodic loss of flue gas sample resulted in increased error in the data. Figure 20 shows the field working capacity versus the number of adsorption/regeneration cycles. Although the data is scattered, the decrease in working capacity that has been observed with other supported amine sorbents is also an issue for sorbent V. Therefore, additional SO_2 control may be required upstream of a commercial-scale CO_2 capture system to reduce sorbent degradation.

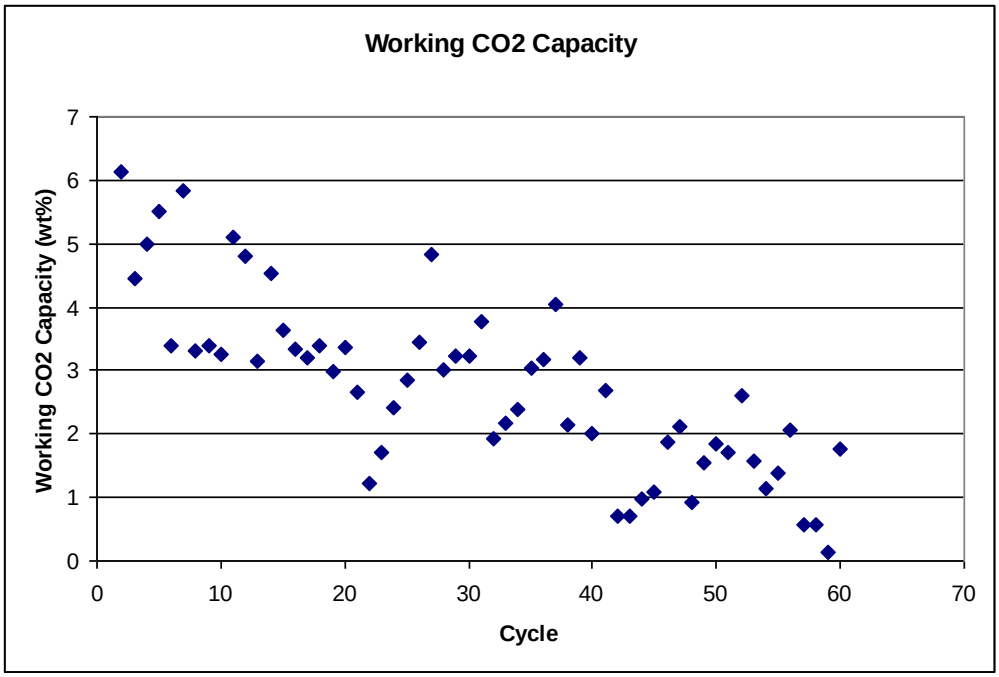

Figure 20. Sorbent V Field Working Capacity

The promising properties for sorbent V are that it reacts quickly, and it thermally stable up to 150°C, which is significantly higher than other supported amines included in this screening program. Based on an average field working capacity of 2.7 wt%, the theoretical regeneration energy of sorbent V is comparable to that of aqueous MEA, at a calculated value of 4400 kJ/kg CO_2 (1900 BTU/lb CO_2). This theoretical regeneration energy can be further lowered by decreasing the regeneration temperature, which may lead to longer regeneration times, or increasing the working CO_2 capacity. However, it should be pointed out that due to the gas analyzer response time and the fact that only 0.5 g of material were tested, the measured weight capacity likely underestimates the actual value for sorbent V. Based on the promising results obtained thus far, further testing of sorbent V is warranted.

Sorbent W

Similar to sorbent V, sorbent W was a powdered material (~10 to 20 micrometers). Therefore, to limit the pressure drop across the sorbent bed, only 0.4 g of material was tested. Sorbent W was used for eleven adsorption/regeneration cycles using simulated flue gas. Table 13 lists the testing conditions and results for sorbent W. Sorbent W is less sensitive to increases in temperature than other supported amine sorbents. Therefore, this material was regenerated at temperatures as high as 120°C. The average working CO_2 capacity for sorbent W was approximately 3 wt%, with no sign of a decrease in capacity due to moisture in the flue gas.

Table 13. Sorbent W Laboratory Testing Conditions and Results

Cycle	T_{adsorb} (°C)	% Sat.	CO_2 (vol%)$_{-wet}$	Cycle	T_{desorb} (°C)	$t_{adsorption}$ (s)	$m_{CO2-adsorbed}$ (g)	wt %	min % CO_2
				D0	120				
A1	55	0	12	D1	80	133	0.006	1.44	9.55
A2	55	0	12	D2	90	113	0.006	1.62	9.71
A3	55	0	12	D3	100	143	0.009	2.31	8.63
A4	55	0	12	D4	110	159	0.010	2.43	9.24
A5	55	0	12	D5	120	161	0.010	2.46	9.24
A6	55	90	12.6	D6	80	367	0.014	3.42	9.55
A7	55	90	12.5	D7	90	196	0.013	3.34	9.71
A8	55	90	12.5	D8	100	322	0.021	5.22	8.63
A9	55	90	12.3	D9	110	159	0.014	3.41	9.24
A10	55	90	12.5	D10	120	174	0.015	3.82	9.24
A11	55	90	12.5	D11	120	160	0.016	3.92	10.01

Figure 21 is a plot of the first ten adsorption profiles for sorbent W. The smaller sorbent sample size resulted in a smaller percentage of the CO_2 being removed from the simulated flue gas. Based on the laboratory parametric tests, the average working capacity for sorbent W was 3 wt%.

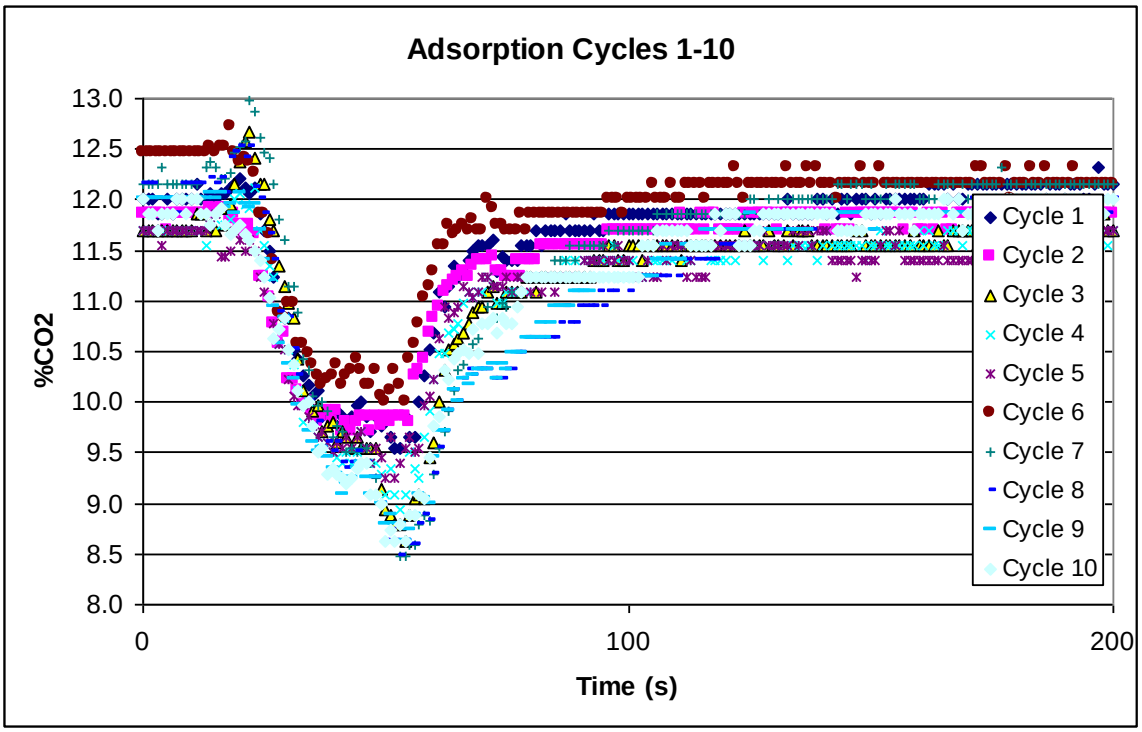

Figure 21. Sorbent W Laboratory Adsorption Profiles

Based on a working CO_2 capacity of 4 wt% and regenerating at 120°C, the theoretical regeneration energy of sorbent W is 3400 kJ/kg CO_2 (1500 BTU/lb CO_2), which is lower than that of the benchmark. Therefore, further examination of sorbent W may be warranted.

Sorbent X

Sorbent X is a supported amine, 2.5 g of which were tested for seven adsorption/regeneration cycles on simulated flue gas. Since this material may be sensitive to high temperature, the highest regeneration temperature for sorbent X was 100°C. This

material exhibited good working capacity, measured at over 9 wt% in two runs. Table 14 lists the laboratory testing conditions and results for sorbent X.

Table 14. Sorbent X Laboratory Testing Conditions and Results

Cycle	T_{adsorb} (°C)	% Sat.	CO_2 (vol%)$_{-wet}$	Cycle	T_{desorb} (°C)	$t_{adsorption}$ (s)	$m_{CO2-adsorbed}$ (g)	wt %	min % CO_2
				D0	100				
A1	55	0	12	D1	80	796	0.193	7.72	-0.79
A2	55	0	12	D2	90	1120	0.227	9.09	-0.79
A3	55	0	11.7	D3	100	1303	0.227	9.09	-0.79
A4	55	0	11.6	D4	100	1346	0.224	8.95	-0.63
A5	55	90	12	D5	80	713	0.179	7.17	-0.76
A6	55	90	12	D6	90	824	0.148	5.92	-0.60
A7	55	90	12.3	D7	100	1252	0.172	6.90	-0.60

Figure 22 is a plot of the laboratory adsorption profiles for sorbent X. This material was able to remove all of the CO_2 from the simulated flue gas stream, whether the gas was dry of at 90% relative humidity.

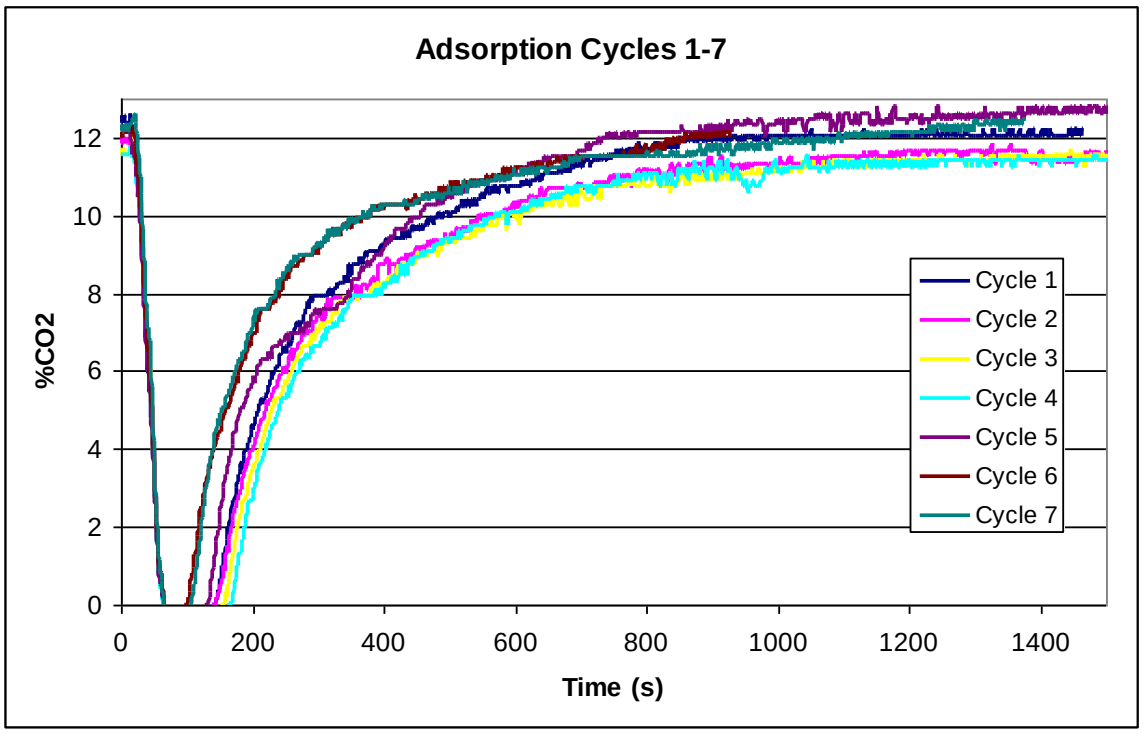

Figure 22. Sorbent X Laboratory Adsorption Profiles

Sorbent X exhibited a working CO_2 capacity of approximately 7 wt% when regenerated at 100°C. Based on this test, the theoretical regeneration energy for sorbent X is 2100 kJ/kg CO_2 (1100 BTU/lb CO_2). Since this value is approximately half that of the benchmark aqueous MEA, further testing of sorbent X is warranted, including possible inclusion in future field testing.

Sorbent Y

Sorbent Y is a supported amine 2.5 g of which was tested for eight adsorption/regeneration cycles using simulated flue gas. Table 15 lists the laboratory testing conditions and results

for sorbent Y. Initially, sorbent Y exhibited a high (>9 wt%) working capacity. However, this level clearly decreased during subsequent tests.

Table 15. Sorbent Y Laboratory Testing Conditions and Results

Cycle	T_{adsorb} (°C)	% Sat.	CO_2 (vol%)$_{-wet}$	Cycle	T_{desorb} (°C)	$t_{adsorption}$ (s)	$m_{CO2-adsorbed}$ (g)	wt %	min % CO_2
				D0	100				
A1	55	0	12	D1	80	1569	0.235	9.39	-0.44
A2	55	0	12	D2	90	341	0.091	3.63	-0.44
A3	55	0	11.7	D3	100	406	0.098	3.91	-0.60
A4	55	0	11.6	D4	100	996	0.180	7.21	-0.60
A5	55	90	12	D5	80	348	0.115	4.59	-0.38
A6	55	90	12	D6	90	790	0.092	3.68	0.08
A7	55	90	12	D7	100	660	0.100	3.99	0.03
A8	55	90	12	D8	100	492	0.109	4.38	0.56

Figure 23 is a plot of the laboratory adsorption profiles for sorbent Y. In some cases, the adsorption profile does not quickly return to the original baseline levels. This is actually due to a plug in the critical orifice downstream of the sorbent bed, and not due to additional CO_2 removal by the sorbent. The critical orifice was plugged several times during sorbent Y testing. This may be attributed to loss of amine from the support surface, although further testing is required to support or invalidate this theory.

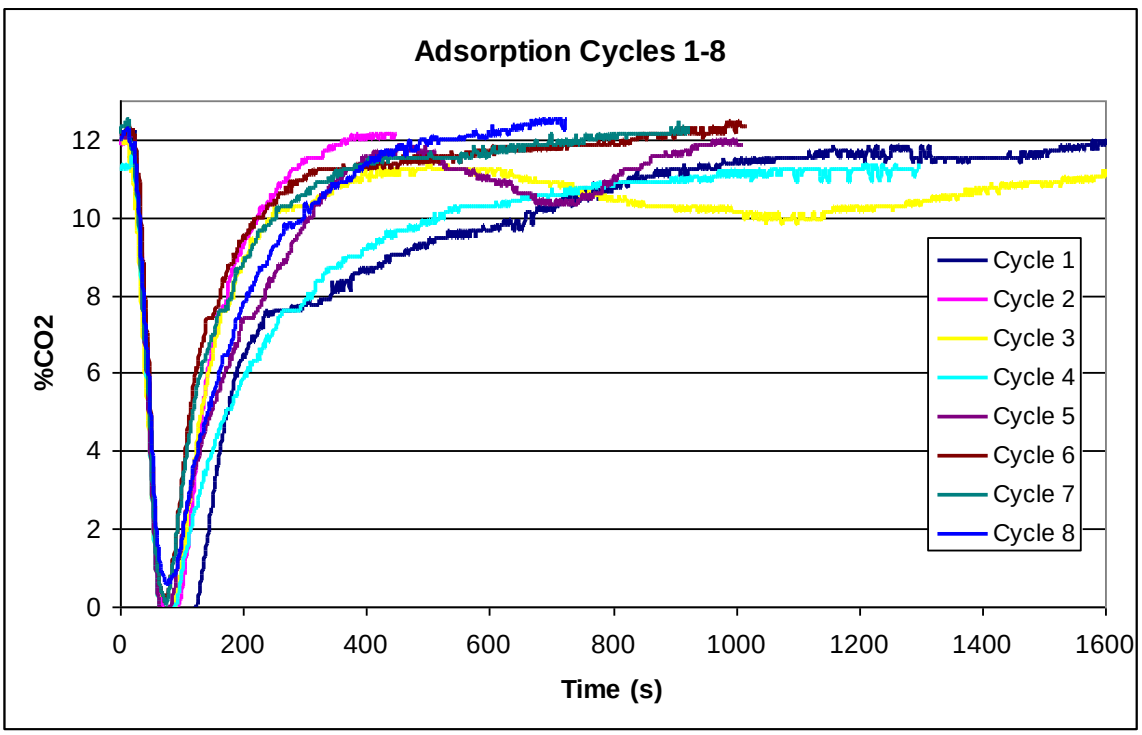

Figure 23. Sorbent Y Laboratory Adsorption Profiles

Since the working CO_2 capacity for sorbent Y was measured at several different values during the lab-scale tests, the value and corresponding testing conditions for cycle 8 was used to calculate the working CO_2 capacity. Therefore, using a working CO_2 capacity of 4.4 wt% and a regeneration temperature of 100°C, the theoretical regeneration energy is 2600 kJ/kg CO_2 (1100 BTU/lb CO_2). Since this is significantly below the benchmark value, further testing of sorbent Y will be performed.

Sorbent Z

Sorbent Z is a treated carbon-based material that was tested for two cycles using simulated flue gas. This material was only tested for two cycles because it did not show any signs of significant CO_2 adsorption.

Sorbent AA

Sorbent AA is a treated carbon-based material, 2.5 g of which was tested for eleven adsorption/regeneration cycles using simulated flue gas. This material was produced by treating a previously tested activated carbon sample. The treatment did not improve the CO_2 removal performance. Table 16 is a list of the laboratory testing conditions and results for sorbent AA.

Table 16. Sorbent AA Laboratory Testing Conditions and Results

Cycle	T_{adsorb} (°C)	% Sat.	CO_2 (vol%)$_{-wet}$	Cycle	T_{desorb} (°C)	$t_{adsorption}$ (s)	$m_{CO2\text{-}adsorbed}$ (g)	wt %	min % CO_2
				D0	120				
A1	55	0	12	D1	80	134	0.015	0.61	5.71
A2	55	0	12	D2	90	110	0.012	0.49	6.48
A3	55	0	12	D3	100	109	0.013	0.52	6.48
A4	55	0	12	D4	110	102	0.013	0.50	6.48
A5	55	0	12	D5	120	127	0.013	0.54	6.48
A6	55	90	12	D6	80	131	0.009	0.38	5.71
A7	55	90	12	D7	90	75	0.011	0.45	6.48
A8	55	90	12	D8	100	97	0.010	0.42	6.48
A9	55	90	12	D9	110	155	0.015	0.61	6.48
A10	55	90	12	D10	120	138	0.013	0.53	6.48
A11	55	90	12	D11	120	86	0.011	0.42	7.17

Although the working CO_2 capacity for sorbent AA was low the adsorption profile was relatively repeatable, considering the parametric testing conditions. Figure 24 is a plot of the first ten adsorption profiles for sorbent AA.

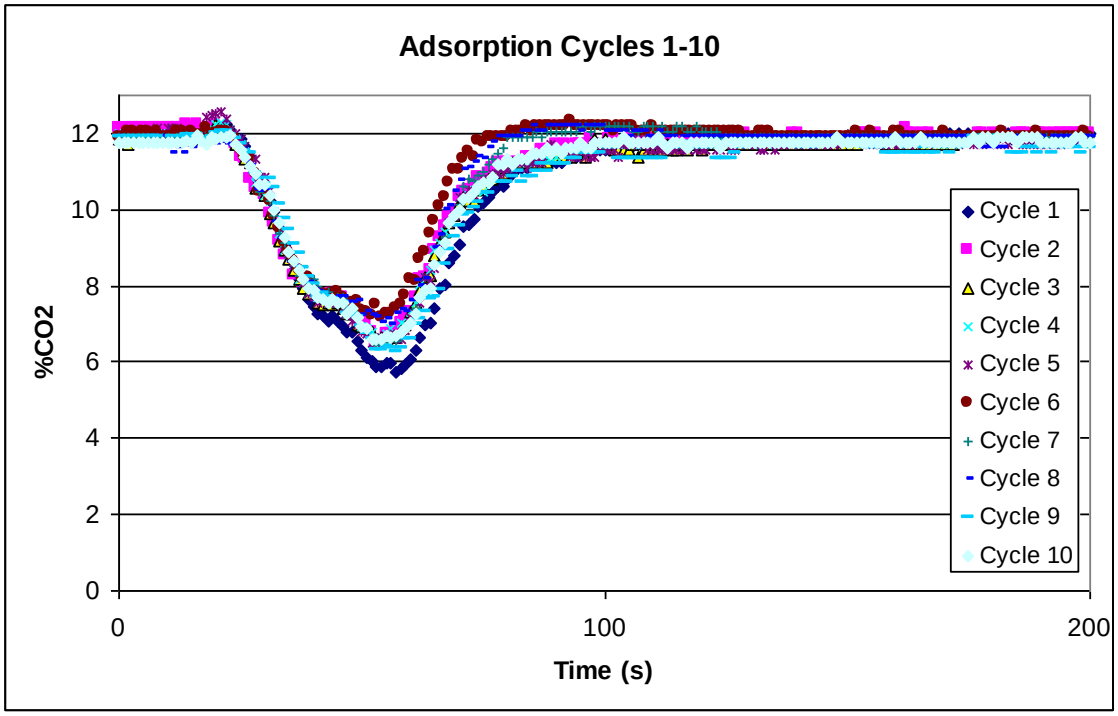

Figure 24. Sorbent AA Laboratory Adsorption Profiles

Based on the cycle 10 results and conditions, the theoretical regeneration energy is approximately 18,000 kJ/kg CO_2 (7800 BTU/lb CO_2).

Sorbent AB

Sorbent AB was a treated carbon-based material that was tested for eight cycles using simulated flue gas. This material did not show any signs of significant CO_2 adsorption.

Comparison of All Materials Tested

Table 17 lists the 24 sorbents that exhibited CO_2 removal properties during laboratory screening using simulated flue gas. Note that these materials have been sorted according to the theoretical regeneration energy (right column). The maximum, minimum, and average CO_2 working capacities for each material are presented in this table. In addition, the theoretical regeneration energy for each of the materials is also given. Note that the details discussing how the theoretical regeneration energy was calculated can be found in the individual sorbent section. For those sorbents that were tested on actual flue gas, the theoretical required regeneration energies, based on field results, are presented in Table 18.

Table 17. CO_2 Working Capacities During Laboratory Tests

Laboratory					
Sorbent ID	Sorbent Type	Working CO_2 Capacity			Q_{regen} (kJ/kg CO_2)
		Max.	Min.	Average	
A	Carbon Nanotubes[a]	5.05	2.05	4.10	1700
R	Supported Amine	13.43	8.44	10.59	1700
X	Supported Amine	9.09	5.92	7.83	2100
D	Supported Amine	7.48	3.92	6.10	2200
S	Supported Amine	3.29	1.82	2.67	2500
F	Supported Amine[a,b]	4.71	3.70	3.81	2550
Y	Supported Amine	9.39	3.63	5.38	2600
Q	Supported Amine	4.22	1.13	2.79	2990
W	Supported Amine	5.22	1.44	2.95	3400
E	Supported Amine	1.34	0.72	1.04	4100
Benchmark Aq MEA					4500
V	Supported Amine	4.21	1.11	2.83	5200
H	Carbon-based	1.07	0.66	0.86	6500
P	Carbon-based	0.81	0.61	0.70	6500
I	Carbon-based	1.09	0.57	0.78	7580
C	Carbon-based	0.54	0.43	0.49	8020
B	Carbon-based[b]	0.58	0.38	0.48	8820
G	Carbon-based	0.97	0.28	0.62	11330
O	Zeolite	1.61	0.83	1.26	11560
U	Zeolite	0.93	0.13	0.39	17000
AA	Carbon-based	0.61	0.38	0.50	18000
J	Zeolite	3.37	0.69	1.87	19000
T	Zeolite	0.83	0.23	0.52	19000
N	Zeolite	0.40	0.33	0.37	24500
M	Zeolite	5.14	0.22	2.88	73000

[a]Low first cycle neglected (when due to low flushing temp.)

[b]Test did not include 90% relative humidity

Sorbents A, B, C, G, H, I and AA rely primarily on physical adsorption. Therefore, with the exception of sorbent A, the CO_2 capacities of these materials are lower than the supported amine materials. For physical adsorbents, the energy required during regeneration to counteract the endothermic reaction is low. However, if the CO_2 capacity is low, more sorbent will have to be heated during regeneration. In addition, more material will have to be moved, which is outside the scope of this report, but is certainly an important consideration. Based on the laboratory results, sorbent A is the only physical adsorbent that is currently competitive with the theoretical regeneration energy of aqueous MEA (~4530 kJ/kg CO_2). However, sorbent H is also close to the benchmark theoretical regeneration energy. Since the physical adsorbents are expected to have longer lives, and may not require additional SO_2 scrubbing, this option may be attractive as well, especially if further improvements in working CO_2 capacity can be achieved.

Zeolites rely on their structure to act as a molecular sieve for gases. Thus far sorbents J, M, N, O, T, and U tested during this program showed signs of CO_2 removal from simulated flue gas. Sorbent O was included in the field tests and did remove CO_2 during all adsorption cycles.

Sorbents D, E, F, Q, R, S, V, W, X, and Y were variations of supported amine materials. Several of these materials were powders, and could only be tested in quantities of 0.5 g or less. These materials exhibited high CO_2 capacities. It should be noted that the CO_2 capacities of all these materials varied significantly from cycle to cycle. Based on the theoretical energy for regeneration under the laboratory testing conditions, all the supported amines were competitive with aqueous MEA, although sorbent E did show sensitivity to high temperature and possibly amine loss. The other three supported amines were included in the first round of field testing. Figure 25 shows the maximum, minimum, and average laboratory working CO_2 capacities of all the sorbents. For testing conditions and other details, refer to the individual material sections.

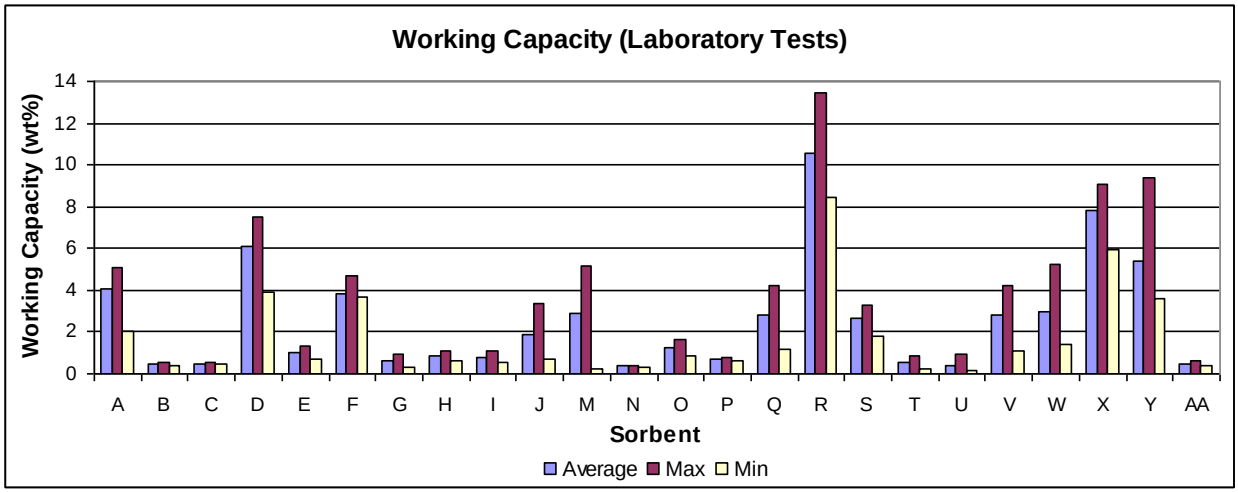

Figure 25. CO_2 Working Capacity During Laboratory Tests

Based on the laboratory testing results, the theoretical regeneration energy was calculated for all sorbents that were able to remove CO_2 from the simulated flue gas. Figure 26 shows the theoretical regeneration energy for all the materials, and also includes a red dotted line for the benchmark aqueous MEA value. Based on the laboratory tests, ten materials included in the screening program exhibited significantly lower theoretical regeneration energies compared to the benchmark. In addition, several more show promise, and may reach the benchmark with slight improvements.

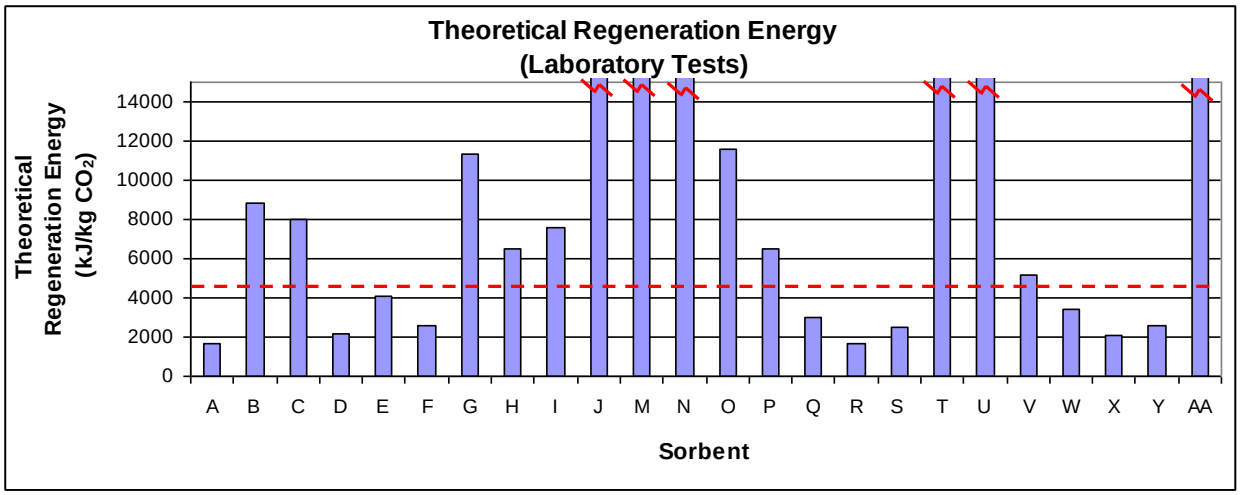

Figure 26. Theoretical Regeneration Energy Based on Laboratory Test Results

Out of all of the sorbents tested in the laboratory, five were selected for the first round of lab-scale field-testing. One carbon-based material, three supported amines, and one zeolite were tested for multiple CO_2 adsorption/regeneration cycles using actual flue gas. Table 18 lists the sorbents that were included, the mass tested, regeneration temperatures, the number of field cycles run and key results from these experiments.

Table 18. Field Testing Round 1 Results

Field 1				
Sorbent ID	Working CO_2 Capacity			Q_{regen} (kJ/kg CO_2)
	Max.	Min.	Average	
D	8.2	4.8	6.2	2900
F	5.4	3.0	4.1	3500
H	1.1	0.7	0.9	6600
O	0.8	0.3	0.5	37000
Q	3.5	1.2	2.4	6900

The minimum, maximum, and average working capacities recorded during the field test are also shown in Figure 27. The three supported amines, D, F, and Q exhibited the highest working capacities, with averages ranging from >6 to ~2.5 wt%. The carbon-based material had an average working CO_2 capacity of nearly 1 wt%, while the zeolite, sorbent O, had an average capacity of approximately 0.5 wt%.

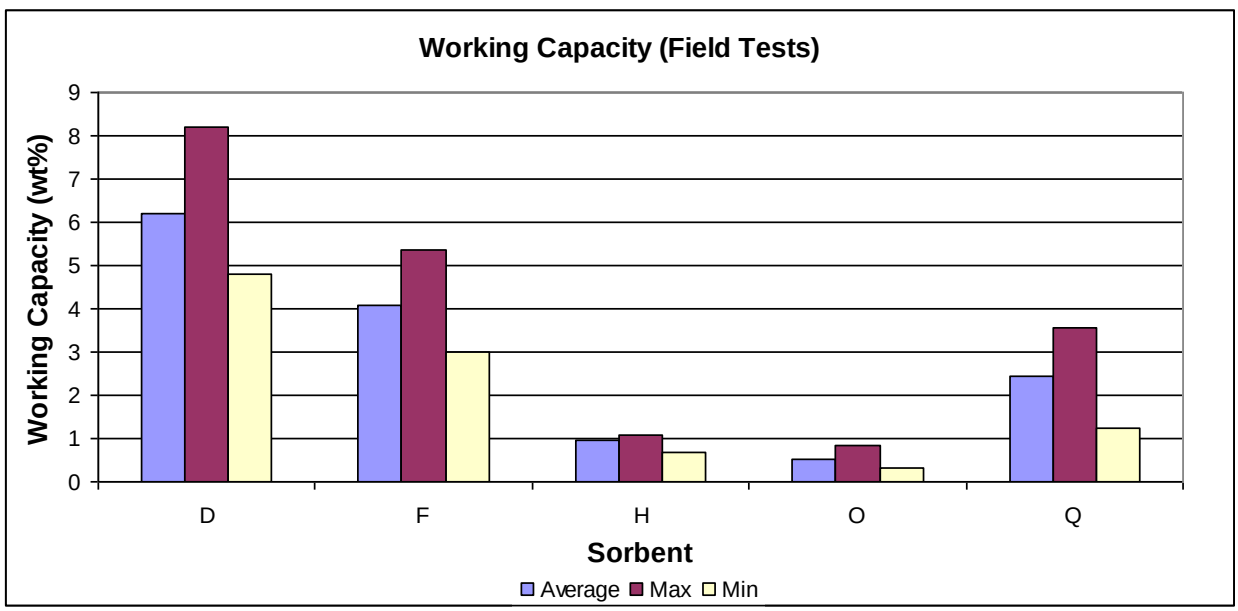

Figure 27. CO_2 Working Capacity During First Round Field Tests

Although the CO_2 capacities are an important component of sorbent performance, the ability of these materials to retain this capacity for a high number of cycles is also a key consideration. In commercial-scale CO_2 capture system, sorbents must retain their capacity for long periods of time,

likely thousands of cycles and up to multiple years of operation. Therefore, the field tests included testing the sorbents for many repeated cycles to identify any consistent loss in capacity.

A fresh bed of Sorbent D was used for eleven cycles during field tests. Although this material continued to exhibit high CO_2 capacity, the field tests showed significantly reduced CO_2 removal when compared to the laboratory results. In addition, a slow decrease in the CO_2 capacity of this material was observed, with the last three adsorption cycles resulting in an average of ~5 wt%. Out of the supported amines used during field testing, sorbent D performance decreased the most during field testing. Future laboratory tests will be aimed at determining whether this can be attributed to loss of amine over time, or sensitivity to flue gas constituents and/or conditions.

Sorbent F was also included in field tests due to its high CO_2 capacity and complete regeneration during laboratory testing. This material was tested in 34 adsorption/regeneration cycles on actual flue gas. Between the first cycles and the last cycles, the CO_2 capacity had decreased by approximately 20%. Similar to sorbent D, further testing and discussions with the sorbent developer will be conducted to determine the cause of this loss.

Sorbent Q was the third supported amine material included in the field testing. The first adsorption cycle yielded a CO_2 capacity greater than 6 wt%, but all others were less than 4 wt%. Between cycles 2 and 17, the working capacity of sorbent Q decreased by over 50%, which is certainly unsustainable for any commercial-scale system.

Sorbent H is a carbon-based material that was included in field tests. With the exception of a few outlier data points towards the end of testing, this material did not exhibit any loss in capacity over the eighteen cycles that were completed in the field.

Sorbent O is a zeolite that was included in the field testing. For the ten cycles following the initial flushing, the working capacity of decreased dramatically. In fact, between the first cycle and cycle 10, sorbent O lost nearly half its CO_2 working capacity. This is attributed to the preferential selectivity of sorbent O towards H_2O versus CO_2. Towards the end of the tests, the working capacity began to plateau, which likely signaled that equilibrium was achieved under the field operating conditions.

Finally, the theoretical regeneration energy was calculated based on the working CO_2 capacity and field operating conditions. Of those listed in Table 18, only sorbents D and F have a lower theoretical regeneration energy than the reported value for aqueous MEA. However, two others are close and may surpass this goal with a slight change in sorbent or operating conditions (i.e. regeneration temperature).

In the second round of laboratory screening several additional materials were selected for the second round of field testing. The materials included in the second round of field testing were sorbents A, F, R, and V. This was the second round of field testing for sorbent F. However, based on discussions with several of the sorbent developers and the project team, two important changes were made to the experimental apparatus and procedures. First, the system was automated so that an increased number of tests could be completed. Second, the regeneration step was slightly altered so that the N_2 flush gas began to flow as the materials were heating. There were concerns that the decrease in CO_2 capacity may be due to heating the sorbent with flue gas in the interparticle void spaces. However, changing the regeneration procedure did not change the decrease in capacity

observed for sorbent F, which was tested using both regeneration methods. Table 19 is a list of the maximum, minimum, and average working capacities during field testing. Although the system was automated, a different analyzer was used to measure the CO_2 concentration, and the regeneration procedure was changed the sorbent F average working capacity was nearly identical to that measured during the first round of field testing. The results for sorbent A are not included due to a suspected equipment malfunction. This material will be screened again during the third round of lab-scale field testing.

Table 19. Field Testing Round 2 Results

Field 2				
Sorbent ID	Working CO_2 Capacity			Q_{regen} (kJ/kg CO_2)
	Max.	Min.	Average	
F	7.2	0.9	3.9	3500
R	16.9	4.8	9.7	1900
V	6.1	3.0	4.1	4400

The average, maximum, and minimum working capacities measured during the second round of lab-scale field testing are shown in Figure 28. For all three of these supported amines, there is significant difference between the maximum and minimum values measured, although some of this difference can be attributed to loss of sample flue gas (see experimental equipment and apparatus section for details).

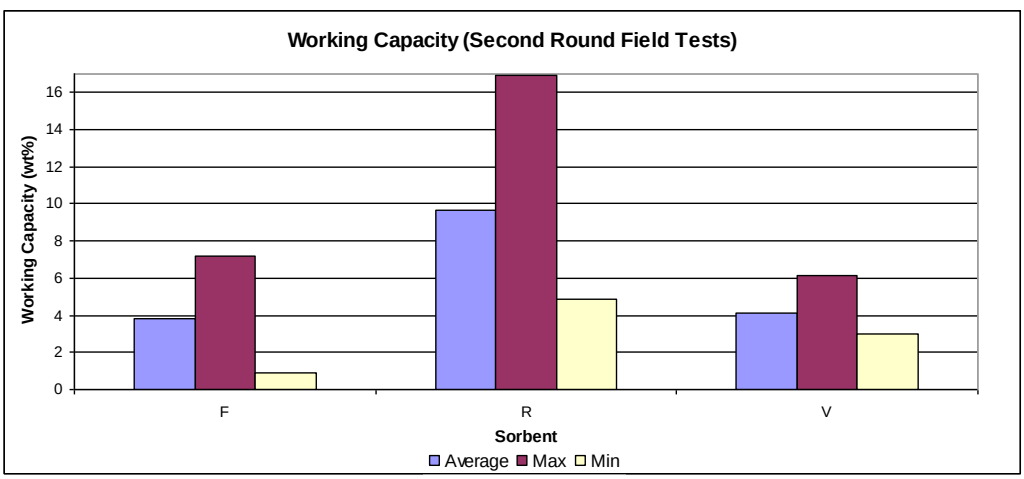

Figure 28. Working Capacity During Second Round Field Tests

Sorbent F performed similarly to the first round of field tests. Sorbent R had an average working capacity of 9.7 wt% over the 43 adsorption/regeneration cycles that were completed. Sorbent V performed well, also, with a working CO_2 capacity of nearly 4 wt%. One important characteristic that was shared between all the materials was a slow loss in capacity, which can likely be attributed to reaction with SO_2 to form heat-stable salts.

CONCLUSIONS

Many different materials have been tested thus far in the ADA CO_2 sorbent screening program. All materials that have been contributed to the program either have been, or will be tested in multiple CO_2 adsorption/regeneration cycles. This report discusses in detail the 24 materials that showed any

signs of CO_2 removal from either simulated or actual flue gas. Based on the theoretical regeneration energy, several sorbents are superior to the current state of the art CO_2 capture technologies. Further testing will be performed to determine whether these materials are stable enough to be used in a commercial-scale CO_2 capture system. In addition, follow up reports will contain test results for several more sorbents that have been submitted to the program, but have yet to be tested.

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APPENDIX C: SORBENT DEVELOPER REPORT 3

CO_2 Sorbent Screening Program:

Third Round Screening Results

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EXECUTIVE SUMMARY

Carbon capture and sequestration (CCS) is the most important option to reduce CO_2 emissions from stationary point sources such as coal-fired power plants. However, for CCS to be widely implemented, the cost for CO_2 capture must be reduced. Solid sorbents used in a temperature swing adsorption process have a significant potential to reduce the energy required to operate a commercial-scale CCS system over current state of the art technologies. However, such sorbents are commonly produced in small quantities and studied under highly varied conditions. ADA-ES has collected and screened potential materials from developers throughout the world. This report discusses the results from the third round of these tests.

The first step of the sorbent screening included running several CO_2 adsorption/regeneration cycles on simulated flue gas composed by blending compressed gas from tanks. Between 0.4 to 2.5 g of the materials were tested in a fixed bed with different levels of moisture and regeneration temperatures. The key sorbent performance properties under investigation in this research included:

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

Three different types of sorbents were tested: carbon-based, supported amines, and zeolites. After testing the materials on simulated flue gas, the five best performing materials were taken to the field and tested for multiple adsorption/regeneration cycles using actual flue gas.

The CO_2 capacities of carbon-based materials were in the range of 0.3 to 1.2 wt% both in the laboratory and in the field. These materials also exhibited superior repeatability between cycles in both the laboratory and field tests, leading to the conclusion that they are not significantly altered by actual flue gas constituents and conditions. The supported amine materials exhibited high CO_2 capacities, up to over 14 wt%. However, in many cases, the adsorption profiles were less repeatable due to a lack of cyclic stability. ADA is working with sorbent developers to provide the feedback necessary to improve long-term sorbent performance. No additional zeolites were evaluated in the third round of laboratory screening based on poor results in previous tests.

Several materials have been tested thus far in the program that have exhibited a significantly lower theoretical regeneration energy than aqueous monoethanol amine (MEA). Although additional modifications may be necessary before commercial viability can be assured, significant improvements have already been observed since the beginning of testing.

TABLE OF CONTENTS

EXECUTIVE SUMMARY 2
TABLE OF CONTENTS 3
INTRODUCTION 4
EXPERIMENTAL APPARATUS AND PROCEDURE 5
Laboratory Testing 8
Field Testing 8
Theoretical Regeneration Energy 9
RESULTS 10
Comparison of All Materials Tested 10
Carbon-Based Sorbents 13
Supported Amines 14
Zeolites 18
CONCLUSIONS 18
REFERENCES 18

INTRODUCTION

Before the industrial revolution, anthropogenic greenhouse gas emissions were negligible. However, it was projected that over 30 billion tons of carbon dioxide were released in 2007.[1] In addition, emissions are expected to grow with increased power consumption of highly populated developing countries. Stationary point sources, such as coal-fired power plants, offer the most promising option for a reduction in carbon dioxide emissions in the near future.

The most important difference between CO_2 and other emissions is the volume at which they are produced. SO_x, NO_x and Hg concentrations are measured in parts per million (ppm) or parts per billion (ppb) while CO_2 is measured as a percentage of the flue gas. Without any modifications, 10 to 15% of the gas released by coal-fired power plants is CO_2. Each ton of carbon in the coal produces nearly 4 tons of gaseous CO_2. Carbon capture and sequestration (CCS) is the most promising option for reducing CO_2 emissions from coal-fired power plants. Obtaining a pure CO_2 stream is the first step of CCS. After the separation, CCS includes compression of the pure CO_2 and sequestration so that it does not enter the atmosphere.

The vast majority of coal-fired power plants burn pulverized coal in a boiler and are thus referred to as PC plants. Post-combustion capture is one of the few viable options to retrofit such plants. The most developed separation technologies utilize liquid solvents. Unfortunately, estimates project that the energy penalty associated with such technologies may be devastating. A great deal of this energy penalty can be attributed to heating up the aqueous solution.[2] One option to reduce the regeneration energy required for CO_2 capture is to use a material with a lower heat capacity, such as many solid sorbents. These sorbents can either react with the CO_2 or adsorb it onto the surface. If the solids can hold more CO_2 per unit mass, this also has the potential to help reduce the energy penalty associated with 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; releasing 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.

Chemically reacting sorbents usually include an inert, high surface area support, such as 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, polymers, and silica, while common reactants include amines such as polyethylenimine or chemicals such as sodium carbonate (Na_2CO_3), which react with CO_2 to form carbamates and bicarbonates. When heated, the reaction will reverse, releasing the CO_2 and potentially H_2O, 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.

Research institutions throughout the world have spearheaded many solid-sorbent development projects geared towards CO_2 capture. This research encompasses a wide range of technical areas, including activated carbons, carbonate chemical sorbents, metal organic frameworks (MOFs), amine grafted zeolites, and supported amine sorbents. However, a majority of these projects are currently being conducted on either lab- or bench-scale and will require further support and development before the materials are commercially viable.[3] Due to the urgency of addressing CO_2 emissions, it is important that the development of these technologies is accelerated.

Under a project supported by the U.S. Department of Energy (DOE), National Energy Technology Laboratory (NETL), the Electric Power Research Institute (EPRI), and several utility companies, ADA Environmental Solutions is conducting a program to characterize CO_2 sorbents and options for process equipment. The objective of this program is to assess the viability and accelerate development of solid sorbents as a CO_2 capture technology that can be retrofit to the existing fleet of coal-fired power plants. The first step in this process is to determine whether appropriate materials are available.

Testing on actual flue gas is necessary to evaluate and compare different capture options. Therefore, ADA built and operated a lab-scale sorbent screening device to quickly evaluate potential CO_2 sorbents on simulated and actual flue gas. Under the ADA sorbent screening program, sorbents have been collected from developers all over the world. These materials have been tested under the same conditions for multiple temperature swing adsorption (TSA) cycles. Sorbents have been targeted that are designed to operate at temperatures and pressures consistent with post-combustion CO_2 capture from PC plants. All sorbents discussed in this report have been given a non-descriptive identifier to protect the identity of the developers.

The sorbent key characteristics evaluated during this program were:

1. Working CO_2 capacity (when reported as a weight 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
5. Theoretical energy required for regeneration

EXPERIMENTAL APPARATUS AND PROCEDURE

All testing of the sorbents screened 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. A PLC controlling solenoid valves is employed so that the system is completely automated. For most sorbents discussed in this report, the automated system was used; however, for a few materials the system with manually operated valves was used. If the manual system was utilized, it will be noted in the section describing the specific sorbent

results. With the automated system, a series of adsorption/regeneration cycles can be completed with little to no supervision after they are initiated. The flow rate of the simulated or actual flue gas was approximately 255 sccm, and the amount of sorbent tested varied from 0.5 to 2.5 g. The sorbent and flue gas (either simulated or actual) were contacted 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 when setup for laboratory testing (only minor modifications are necessary for field testing). The CO_2 analyzer was a continuous NDIR sensor with a 90% response time of 10 seconds. This response time should be taken into consideration when examining results. It is probable that the response time of the instrument affected results for materials tested in 0.5 g quantities more extensively than those tested in 2.5 g quantities.

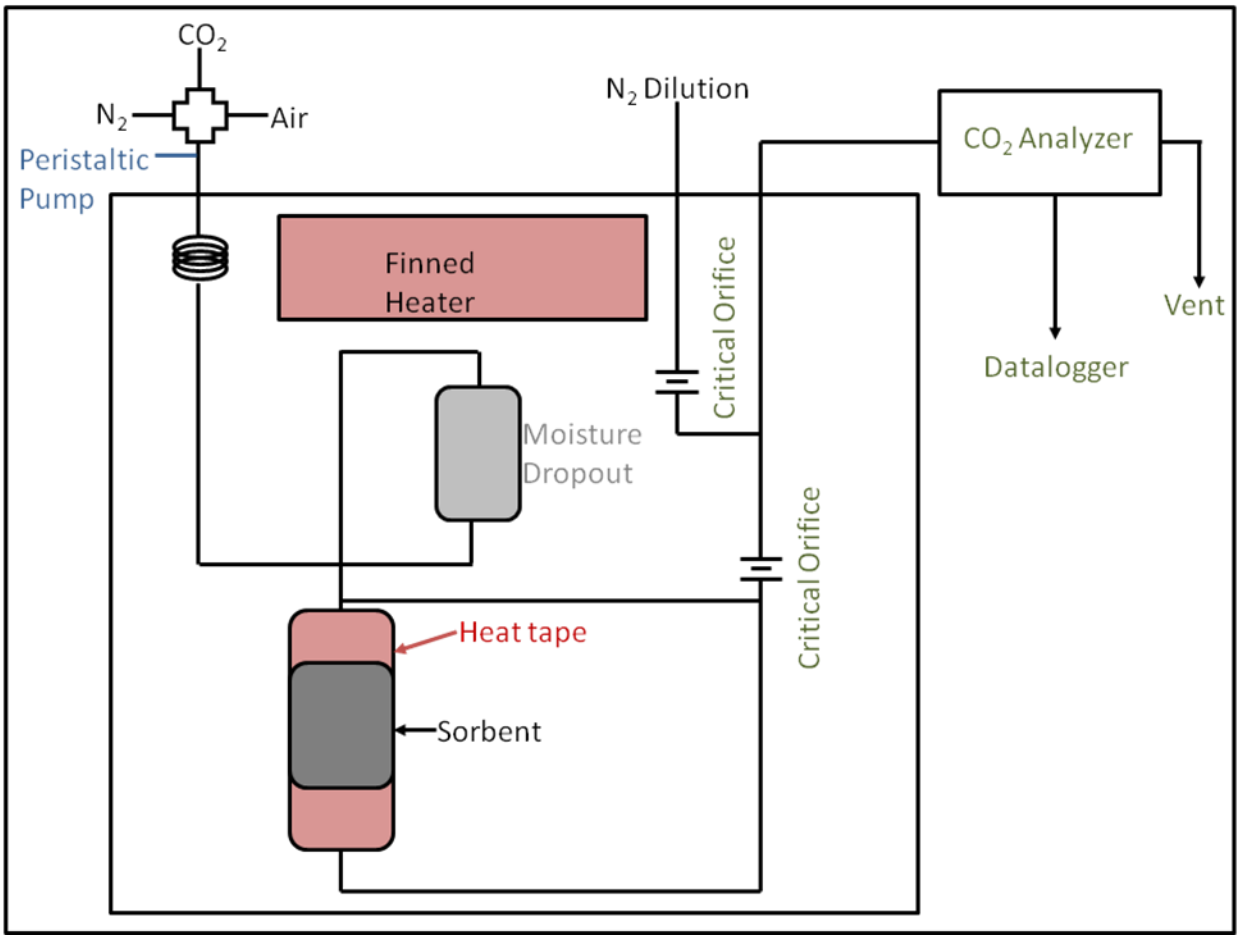

Figure 1: Schematic of Sorbent Screening Test Unit

The steps to carry out the adsorption/regeneration cycles were the same whether tests were conducted on simulated or actual flue gas. First, 2.5g sorbent was placed in the fixed bed, unless the sorbent developer provided less than 2.5g of material in which case the full sample was used. The pressure drop across the fixed bed was measured. If this pressure drop was less than 12 in H_2O, then 2.5g of sorbent was the sample size. However, if the pressure drop was greater than 12 in H_2O, then sorbent was removed until the pressure drop was less than or equal to this maximum limit. The pressure drop was measured because the pressure in the sorbent bed has a direct effect on the

working CO_2 capacity. Because ADA is testing many different materials with highly varied physical properties, a limit was set on pressure drop.

After the appropriate sorbent sample size was determined, it was heated to an initial flushing temperature. The initial flushing temperature was set based on the expected regeneration temperature, unless a different temperature was recommended by the sorbent developer. A thermocouple on the outside of the glass fixed bed was used to determine when the bed had reached the desired temperature. When the bed temperature matched the desired adsorption temperature, the sorbent was flushed with dry N_2 for 10 minutes. Then, the simulated flue gas, composed by mixing compressed gas 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 12% CO_2, 4% O_2, with a balance of N_2. The relative humidity, controlled by adding water using a peristaltic pump and then evaporating, was 0% or 90% (0 or ~15% by volume, respectively). When the CO_2 monitor reading was stable and represented the correct concentration of CO_2 (i.e. baseline reading), 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 adsorption step.

A temperature swing with N_2 purge gas was used to regenerate the sorbents and desorb the CO_2. First, the bed was heated with no gas flow. When the thermocouple on 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.

After completion of the first round of field testing, which was completed under a separate EPRI-sponsored program, an initial report was sent to sorbent developers. All of the amine-based sorbents exhibited a reduction in working CO_2 capacity with an increasing number of cycles using actual flue gas. Based on this feedback, the regeneration procedure was slightly modified for the second and third rounds of field testing. Instead of heating the sorbents in the presence of flue gas (in the interparticle void space), dry N_2 was sent through the sorbent bed during heating. However, it should be noted that this did not notably improve the sorbents' performance.

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 temperature increases as it reacts with the CO_2. Because the sorbent CO_2 capacity decreases with increasing temperature, the test results will show a reduced amount of CO_2 capture if the sorbent temperature is allowed to increase. 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.**

Laboratory Testing

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. The laboratory tests were carried out parametrically; the moisture level, regeneration temperature and adsorption temperature (in a few cases only thus far, were varied to identify fatal flaws and the optimal operating conditions. During capture, the gas temperature was approximately 55 ºC and was either dry or contained 45%, or 90% relative humidity, to simulate conditions downstream of a dry or wet scrubber. The regeneration temperature varied between sorbents but was generally within the range of 65 to 250 º C.

There are two types of tests that are completed during laboratory testing. Many materials are evaluated parametrically. Usually, the two variables for parametric testing are moisture and regeneration temperature. The moisture is usually 90% relative humidity (~15 vol% of the gas stream), but in some cases a dry simulated flue gas is used to determine the effect of moisture on sorbent performance. Usually, the sorbent is tested first with the dry gas and then with the moisture included. When the regeneration temperature is varied four adsorption/regeneration cycles are completed at each regeneration temperature and the step change in the regeneration temperature is 10°C. For example, cycles 1-4 would have a regeneration temperature of 90°C, cycles 5-8 would have a regeneration temperature of 100°C, cycles 9-12 would have a regeneration temperature of 110°C until the maximum temperature set by ADA and the sorbent developer is achieved. When the maximum temperature is achieved the tests can continue for a high number of cycles, but the regeneration temperature will remain constant.

The other type of laboratory test that is often completed is extended cycle. These types of tests are not parametric and are usually focused on determining the working CO_2 capacity and cyclic stability of the materials. Extended tests are often conducted when the sorbent developer has already completed extensive parametric testing and can provide the optimal operating conditions. Very few sorbent developers have evaluated cyclic stability, so this type of test can provide valuable feedback to the developer.

Field Testing

In order to accelerate sorbent development, the effect of actual flue gas constituents on sorbent performance must be known. First, the optimal regeneration temperature was identified during the laboratory screening. Then, the best materials were selected for field tests and were tested for many adsorption/regeneration cycles using the same regeneration temperature. By completing over 10 capture/regeneration cycles with the same sorbent, serious poisoning issues were identified. Table 1 lists the key characteristics of the flue gas used for sorbent screening.

Table 1: Key flue gas characteristics for field tests.

Temperature (°F)	130 to 140
CO_2 Concentration (%)	10 to 12
Moisture	Saturated
O_2 (%)	5 to 6
NO_x (ppm)	100 to 120
SO_2 (ppm)	50 to 250

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 (typically less than 200 ppm), 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 for the field tests. First, only a single gas stream, which was pulled from a sample port, was needed versus the several inlet gas streams used from the compressed bottles in the laboratory. Also, the peristaltic pump to introduce moisture to the gas was unnecessary. The experimental procedure was the same for both laboratory and the first round of field testing. For the second and third rounds of field testing, the system was automated so that the sorbents could be tested continuously. Another important modification, based on feedback from sorbent developers, was to heat the sorbents while flushing with dry N_2 instead of using the N_2 to flush the CO_2 from the sorbent bed only after the material had reached the regeneration temperature.

Theoretical Regeneration Energy

When evaluating and comparing sorbents for use in a commercial-scale CO_2 capture and sequestration system, one of the most important evaluation criteria is the energy required for regeneration. Equation 1 shows the energy balance for regeneration.

$$\boxed{\frac{Q}{m_c} = \frac{m_e}{m_c} C_e \Delta T + \frac{B}{L} C_s \Delta T + C_{p.c} T_2 - C_s T_1 + \frac{Q_r}{m_c}} \qquad (1)^4$$

Where Q is the regeneration heat input, kJ
m_c is the mass of adsorbed CO_2, kg
m_e is the equipment mass, kg
ΔT is the temperature difference between adsorption and regeneration, °C or K
T_1 is the adsorption temperature, °C or K
T_2 is the regeneration temperature, °C or K
L is the CO_2 loading, g CO_2/g sorbent
C_s is the sorbent specific heat, kJ/kg·K
$C_{p.c}$ is the constant pressure specific heat for CO_2, kJ/kg·K
C_e is the equipment specific heat, kJ/kg·K

B is a dimensional conversion term
Q_r is the heat of reaction (positive for endothermic regeneration), kJ/mol CO_2

Due to pressure drop, heat transfer, and mixing concerns, ADA will not be using a fixed bed for testing beyond the laboratory scale. Therefore, the first term on the right hand side of Equation 1 can be neglected because no equipment heating will be required during regeneration (i.e. the regeneration system will be kept at the regeneration temperature and the sorbent will be moved). The second term on the right hand side of Equation 1 is the energy required to heat the sorbent from the adsorption temperature to the regeneration temperature. To reduce the energy due to this term, sorbent loading can be increased or the difference between the adsorption and regeneration temperature can be decreased. The third and fourth term on the right hand side of Equation 1 can be combined to determine the energy required for the phase change of CO_2 from a free gas to one adsorbed on a solid. The final term on the right hand side of Equation 1 is the energy required to overcome the endothermic reaction associated with desorbing the CO_2 from the sorbent. For physical adsorbents, this term is usually an order of magnitude lower than sorbents that chemically react with the CO_2. However, the CO_2 working capacity is also usually significantly lower.

For all the sorbents tested in this program, the theoretical energy required for regeneration was calculated using Equation 1. The result of this calculation is used to compare different materials and assess their respective viability for use in a commercial-scale CO_2 capture system. To calculate the theoretical regeneration energy the average working capacity and the median regeneration temperature from the adsorption/regeneration cycles completed with moisture in the flue gas were used. Note that from previous reports a liquid MEA CO_2 capture system requires approximately 3600 kJ/kg CO_2 (1550 BTU/lb CO_2).[5]

RESULTS

Comparison of All Materials Tested

Under several different projects, ADA has evaluated well over 100 different potential CO_2 sorbents. These materials were highly varied in their chemical and physical properties. Since they are all being tested with the same final application in mind, the best means of comparing these different materials is their theoretical regeneration energy. If less energy penalty placed upon a power plant by the CO_2 capture system overall costs for the process will be reduced and the likelihood of widespread implementation will be increased.

When comparing materials ADA often divides them into different families so that general conclusions can be drawn regarding each sorbent type. The four types of materials tested by ADA (under all programs) to date include supported amines, carbon-based, carbonates, and zeolites. Only supported amines, carbon-based, and zeolite materials have been evaluated under the current project. The theoretical regeneration energy for most of the materials evaluated under the DOE NETL cooperative agreement as well as a supporting EPRI-funded project are provided together in Figure 2. These results are based on laboratory evaluations with 90% relative humidity in the flue gas. For many sorbents parametric evaluations were completed with multiple regeneration temperatures. The theoretical regeneration energy provided in Figure 2 is based on the average working capacity measured under 90% relative humidity and the median regeneration temperature.

In some cases the values may be different from those previously reported because a single test (i.e. one working capacity at a specific regeneration temperature rather than an average and a median) was used previously.

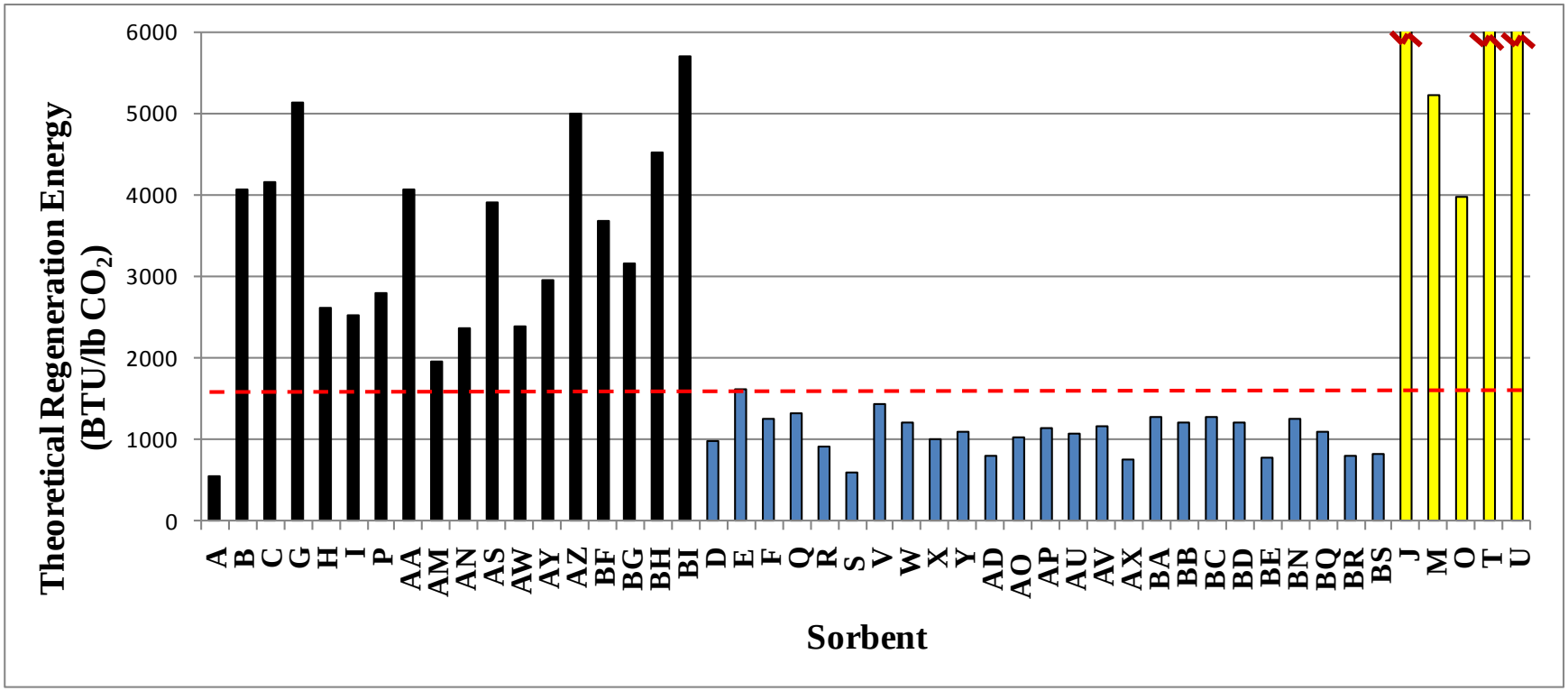

Figure 2: Comparison of Working Capacities Measured in the Laboratory Humid Simulated Flue Gas*

*The sorbents have been grouped according to the material type. Black bars represent carbon-based sorbents, blue bars represent supported amines, and yellow bars represent zeolites.

Although Figure 2 allows for different sorbents to be compared relatively quickly, it does not tell the entire story. For example, many sorbents were evaluated for multiple cycles and cyclic stability was evaluated; the cyclic stability is not adequately captured in this calculation. In addition, some sorbents are more susceptible to reaction with flue gas constituents. The following sections discuss specific performance criteria for each sorbent family.

Carbon-Based Sorbents

The carbon-based materials in this program have included everything from highly novel carbon nano-tubes to commercially available activated carbons. With the exception of the carbon nano-tubes, all the working capacities were significantly lower than those of the supported amines. In general the working capacities were lower than 1.1 wt%. In terms of a materials handling issue, to achieve 90% CO_2 capture using low-capacity carbons would require significant energy to move the materials. However, there are also advantages to using carbon-based materials. Specifically, they are commercially produced today, they can be burned after they are spent (i.e. less waste generated by the CO_2 capture process), and they are less easily poisoned by flue gas constituents compared to both amines (negatively affected by SO_2) and zeolites (prohibitively affected by moisture). Some carbons have shown a decrease in CO_2 performance in moist versus dry flue gas, but this only decreases the capacity to some equilibrium value, it does not remove all the CO_2 capacity.

To serve as an example select adsorption profiles for sorbent AM are provided in Figure 3. Cycles 1-5 were run using dry simulated flue gas, while cycles 31 to 35 were run using simulated flue gas with 90% relative humidity. Although there is a noticeable difference in the profiles, the majority of the adsorption capacity is maintained regardless of moisture levels.

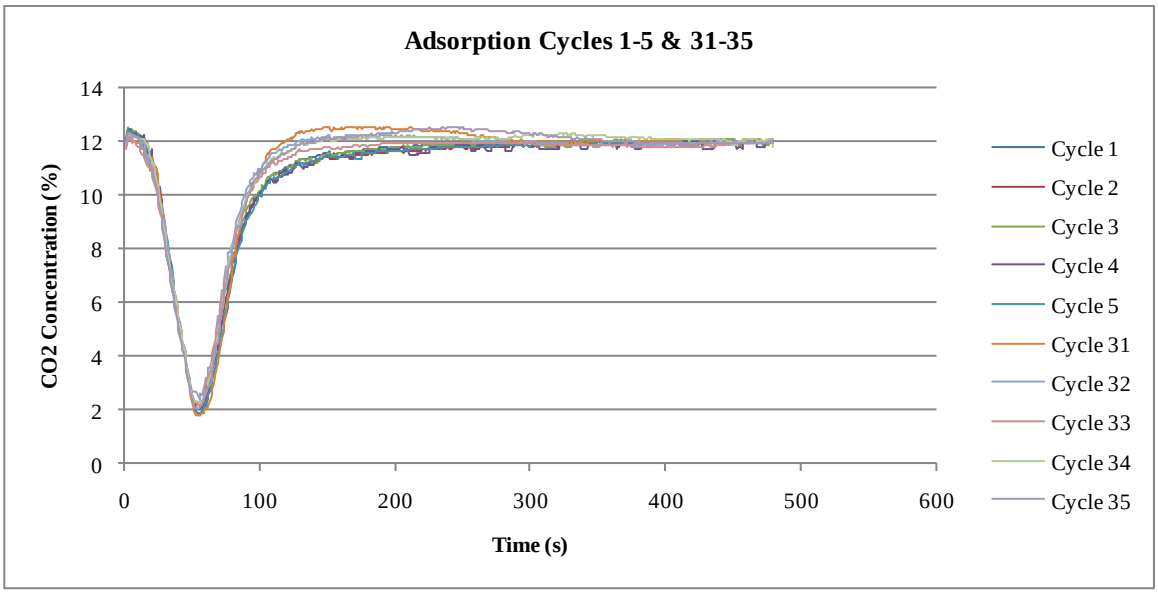

Figure 3: Sorbent AM Laboratory Adsorption Profiles

Moisture is not the only concern related to flue gas constituents. Chemicals that react with CO_2 usually react with SO_2 to form a heat stable salt. Over time this will result in a complete loss of CO_2 adsorption capacity. One potential advantage of carbon-based sorbents is that they do not chemically react with CO_2. Therefore, it is theoretized that they will not be permanently damaged by flue gas constituents. ADA tested this theory by completing over 250 adsorption/regeneration cycles on actual flue gas with a commercial activated carbon. Note that this material was not produced specifically for CO_2 capture. The flue gas used for the cyclic testing was drawn from the duct of a lignite fired power plant. The SO_2 concentration was in the range of 50 to 250 ppm and the flue gas was saturated with moisture. The working capacities from this test are provided in Figure 4. No permanent decrease in capacity is observed for the 250+ cycles, confirming that carbon-based materials are more resitant to poisoning compared to other materials. The challenge for carbon-based materials is to improve the CO_2 capacity and selectivity. ADA continues to work with sorbent developers to provide feedback in the hopes of improving these promsing materials.

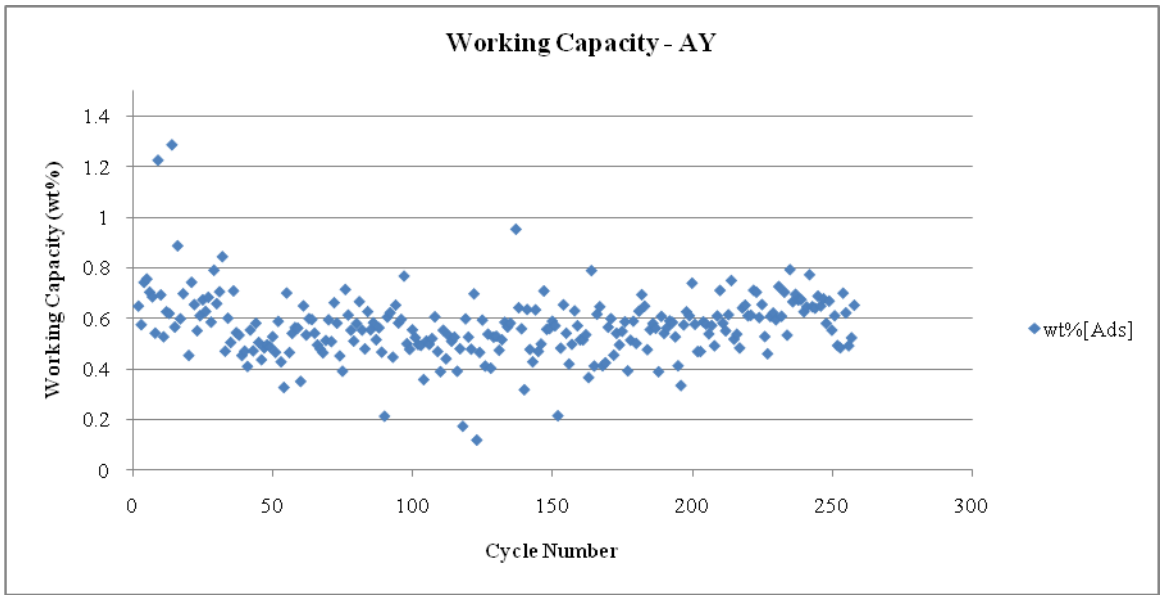

Figure 4: Sorbent AY Field Working Capacities

Supported Amines

Based on results to date, supported amines are the most promising sorbent family for CO_2 capture. As is shown in Figure 2, these materials have the potential to significantly reduce the energy penalty associated with CO_2 capture versus state of the art aqueous MEA systems. This can be attributed to high working CO_2 capacities (over 14 wt% has been measured) as well as low heat capacities.

An adsorption profile for sorbent R is provided in Figure 5 to serve as an example of the shape of the breakthrough curve characteristic for supported amines. Clearly this sorbent was able to remove all the CO_2 from the simulated flue gas stream. The initial breakthrough resulted in a fast increase in the CO_2 concentration, followed by a much slower increase in the CO_2 concentration to achieve complete saturation. One theory to explain the slow increase in CO_2 concentration after the initial breakthrough is related to the temperature in

the system. First, in a fixed bed system it is difficult to remove the heat from the exothermic reaction. ADA measured a significant increase in the bed temperature. Since the CO_2 capacity is directly related to temperature, this is likely to have some effect on the adsorption profile. However, others who used lower gas flow rates and may have had lesser increases in bed temperature have also measured similar breakthrough curves. The most important underlying conclusion is that the full adsorption capacity measured may not be utilized in a commercial system due to time constraints.

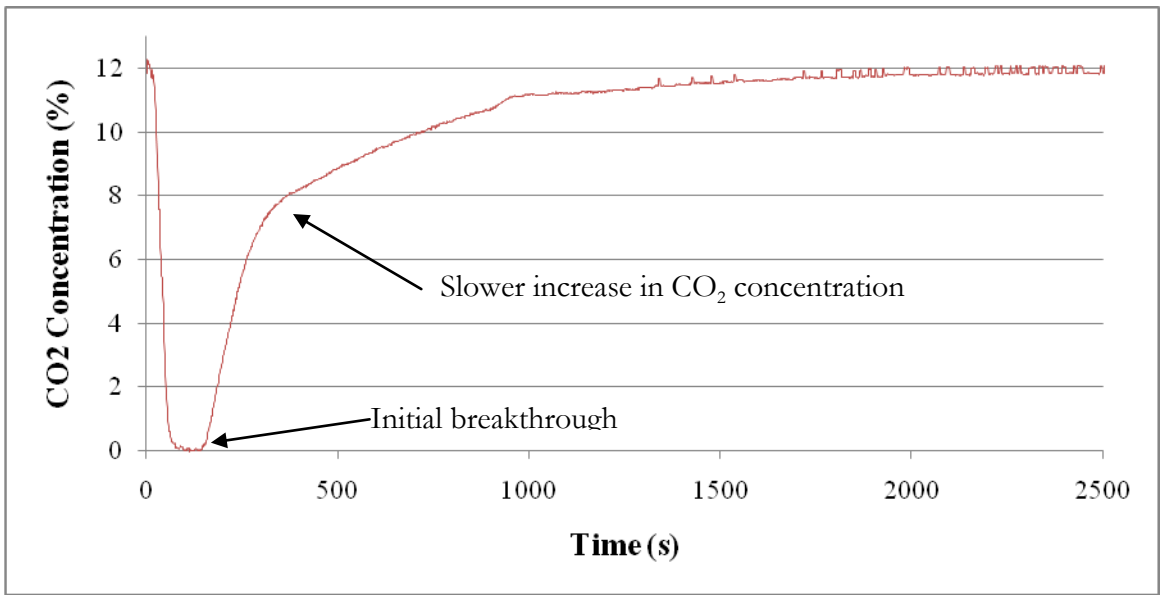

Figure 5: Sorbent R Adsorption Profile

Supported amines have already demonstrated working capacities high enough to dramatically reduce the energy penalty associated with CO_2 capture. The most important challenges for supported amine sorbents are related to long-term cyclic stability, poisoning by flue gas constituents, and cost. Many, but not all, of the supported amine sorbents demonstrated a loss in CO_2 capacity when using simulated flue gas in the laboratory. As an example, select adsorption profiles from laboratory tests for sorbent AX are provided in Figure 6. Although the testing conditions were the same for all cycles, the adsorption profiles reveal a slow, progressive decrease in the CO_2 capacity of the material.

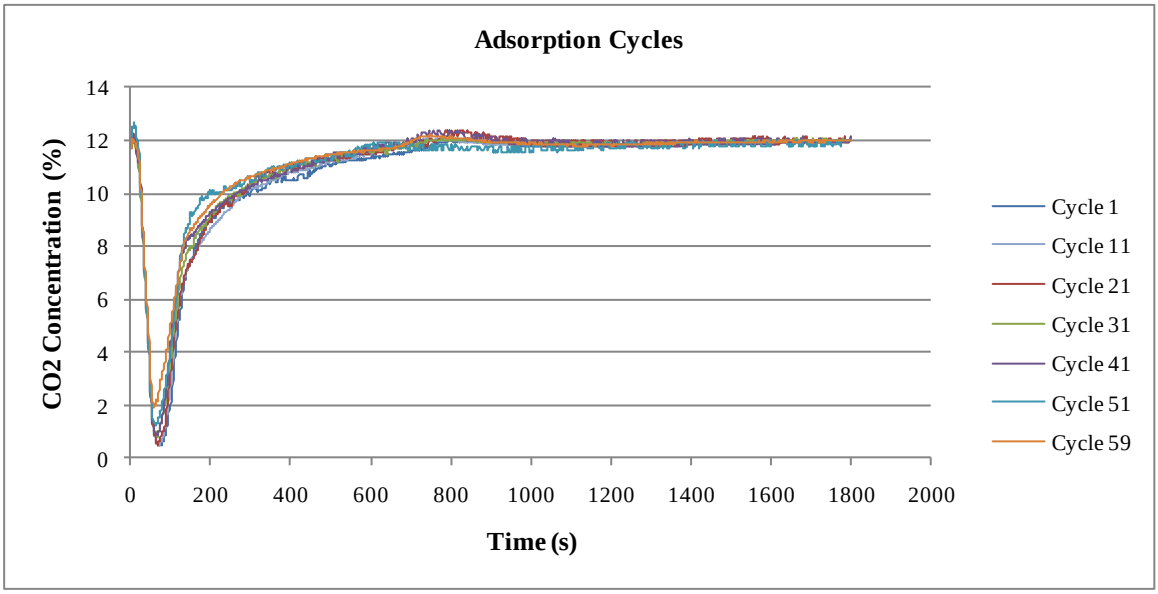

Figure 6: Sorbent AX Laboratory Adsorption Profiles

One important goal of this program is to work closely with sorbent developers; ADA's testing results are provided to the developers in the hopes of leading to improvements in sorbent performance. In several cases, collaboration between ADA and sorbent developers has led to second or third generation sorbents exhibiting significantly improved performance properties compared to their first generation counterparts. The working capacity versus cycle number for two different sorbents is shown in Figure 7. Both sorbents are variations of an amine supported by a clay substrate. The generation 1 sorbent was tested by ADA and was found to degrade with cycle number, even when using simulated flue gas in the laboratory. Several months later the developer provided a similar sorbent that was also tested for multiple cycles. During the 56 cycle test, there was no sign of a decrease in capacity. Based on these results, ADA will test the generation 2 material during long-term screening for over 250 cycles. Notably, the developer has measured a significantly higher CO_2 working capacity, which may be attributed to a very low gas residence time in the ADA fixed bed system (~1 s). In the 1 kW pilot field test the gas residence time will be closer to 5 s and may lead to greater working CO_2 capacities. The improvement of this material is an example of how collaboration can lead to better sorbent options and thus an increase in the chance of success.

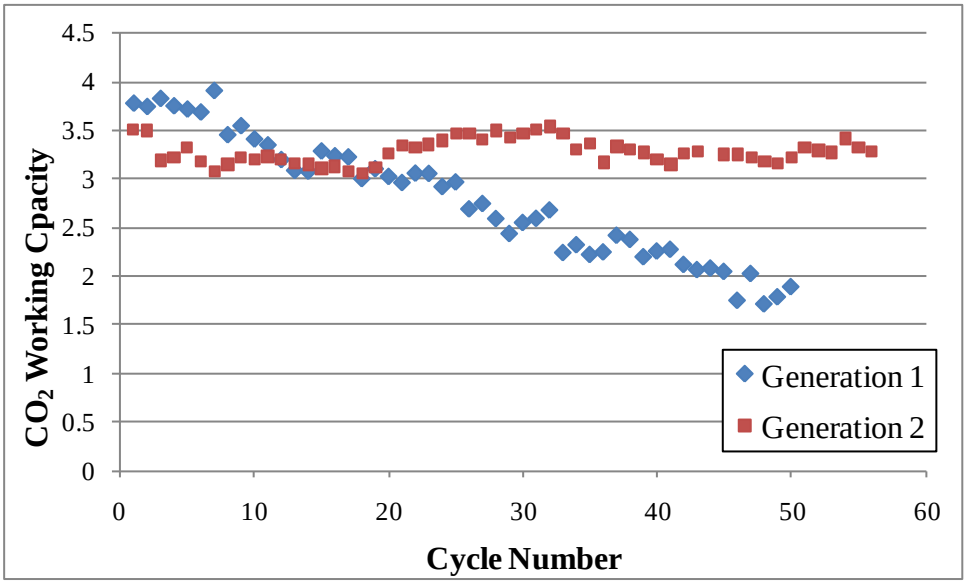

Figure 7: First and Second Generation Supported Amine Clay-Based Sorbent

Once acceptable cyclic stability is achieved in the laboratory, the next challenge is to determine if additional flue gas cleanup steps are required to achieve similar stability at a power plant. Sorbent BE was selected for extended field testing. Over 250 cycles were completed using actual flue gas. Because the reaction between SO_2 and amines to form heat stable compounds is well-documented, ADA fabricated a lab-scale SO_2 scrubber that was used to reduce the SO_2 concentration in the flue gas to less than 10 ppm. The working capacities measured during this field test are provided as a function of cycle number in Figure 8. Although there was some decrease in the working capacity over the 250 cycles, the stability is significantly improved when compared to other sorbents evaluated in actual flue gas. Additional modifications will be necessary to even further reduce the loss in capacity, but the improvement over the sorbents discussed in the previous sorbent screening report are noteworthy.

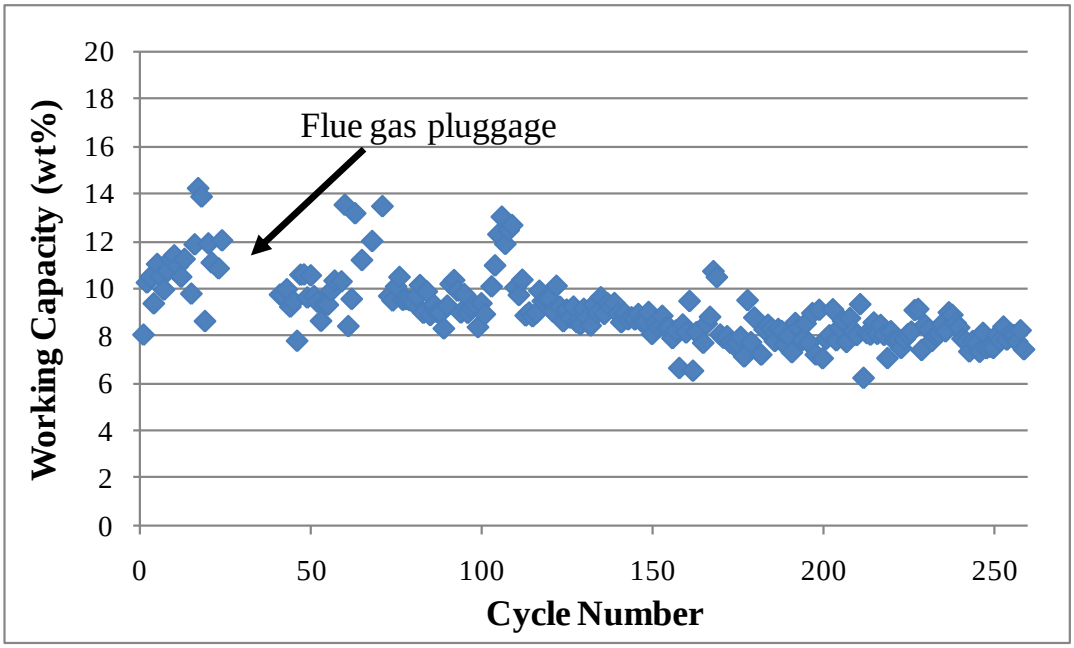

Figure 8: Sorbent BR Field Working Capacities

Zeolites

No additional zeolites have been evaluated since the first sorbent screening report. Even at high regeneration temperatures, they perform poorly in the presence of moisture. When a low CO_2 capacity and a high regeneration temperature are exhibited, the theoretical regeneration energy is exceedingly high, as is shown in Figure 2.

CONCLUSIONS

Many different materials have been tested thus far in the ADA CO_2 sorbent screening program. All materials that have been contributed to the program either have been or will be tested in multiple CO_2 adsorption/regeneration cycles. Based on the theoretical regeneration energy, many sorbents are superior to the current state of the art CO_2 capture technologies. Each sorbent family has its own advantages and disadvantages. Carbon-based sorbent have a low CO_2 capacity, but exhibit superior cyclic stability and a resistance to poisoning by flue gas constituents. Supported amines have exhibited high CO_2 capacities and low theoretical regeneration energies, but many are not cyclically stable and can be negatively affected by flue gas constituents. Zeolites have exhibited an extreme affiliation to moisture that makes their use for CO_2 capture unlikely. First and second generation materials will continue to be evaluated through continued testing. Follow up reports will contain test results for several more sorbents that have been submitted to the program, but have yet to be tested.

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APPENDIX D: SORBENT DEVELOPER REPORT 4

CO_2 Sorbent Screening Program: Fourth Round Screening Results

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EXECUTIVE SUMMARY

Carbon capture and sequestration (CCS) is the most important option to reduce CO_2 emissions from stationary point sources such as coal-fired power plants. However, for CCS to be widely implemented, the cost for CO_2 capture must be reduced. Solid sorbents used in a temperature swing adsorption process have a significant potential to reduce the energy required to operate a commercial-scale CCS system over current state of the art technologies. However, such sorbents are commonly produced in small quantities and studied under highly varied conditions. ADA-ES collected and screened potential materials from developers throughout the world. This report discusses the results from the fourth round of these tests.

The first step of the sorbent screening included running several CO_2 adsorption/regeneration cycles on simulated flue gas composed by blending compressed gas from tanks. Between 0.4 to 2.5 g of the materials were tested in a fixed bed with different levels of moisture and regeneration temperatures. The key sorbent performance properties under investigation in this research included:

- CO_2 capacity (when reported as a weight percentage): $\frac{100 * mass_{CO_2-removed from gas}}{mass_{sorbent}}$
- Regeneration potential: ability of a sorbent to be used repeatedly without any reduction in capacity
- Poisoning from other flue gas constituents: Decrease in capacity due to SO_2, NO_x, etc.
- $\Delta T_{capture-regeneration}$: The difference between capture and regeneration temperatures
- Theoretical energy required for regeneration

Three different types of sorbents were tested: carbon-based, supported amines, and hydrotalcites. The CO_2 capacities of carbon-based materials were in the range of 0.44 to 0.66 wt% in the laboratory. These materials exhibited superior repeatability between cycles in the laboratory tests, leading to the conclusion that they are not significantly altered by actual flue gas constituents and conditions. The supported amine materials exhibited high CO_2 capacities, up to 11.10 wt%. Many cases, the adsorption profiles were repeatable because of cyclic stability. Hydrotalcites had CO_2 capacities in the range of 0.70 to 8.10 wt%. These materials exhibited excellent stability at high temperatures. No additional zeolites were evaluated in the fourth round of laboratory screening based on poor results in previous tests. ADA-ES is working with sorbent developers to provide the feedback necessary to improve long-term sorbent performance.

A lot of materials evaluated during this testing period exhibited significantly lower theoretical regeneration energy than aqueous monoethanol amine (MEA). Additional modifications may be necessary before commercial viability can be assured; significant improvements have already been observed since the beginning of testing.

TABLE OF CONTENTS

EXECUTIVE SUMMARY 2
TABLE OF CONTENTS 3
INTRODUCTION 5
EXPERIMENTAL APPARATUS AND PROCEDURE 6
Laboratory Testing 8
Theoretical Regeneration Energy 10
RESULTS 11
Sorbent BT 11
Sorbent BU 11
Sorbent BU2 11
Sorbent BU3 12
Sorbent BV 14
Sorbent BX 15
Sorbent BY 16
Sorbent BZ 18
Sorbent CA 19
Sorbent CB 20
Sorbent CC 22
Sorbent CD 23
Sorbent CE 24
Sorbent CF 26
Sorbent CG 26
Sorbent CH 27
Sorbent CI 28
Sorbent CJ 30
Sorbent CK 31
Sorbent CL 32
Sorbent CM 34
Sorbent CN 35
Sorbent CO 36
Sorbent CP 38
Sorbent CQ 39
Sorbent CR 40
Sorbent CS 42
Sorbent CT 43
Sorbent CU 44
Sorbent CV 46
Sorbent CW 47
Sorbent CX 48
Sorbent CY 49
Sorbent CZ 50
Sorbent DA 51
Sorbent DB 53
Sorbent DC 53
Sorbent DD 54
Sorbent DE 55

Sorbent DF 56
Sorbent DG 57
Sorbent DH 57
Sorbent DI 58
Sorbent DJ 60
Sorbent DK 61
Sorbent DL 62
Sorbent DM 64
Sorbent DN 65
Sorbent DO 65
Sorbent DP 65
Sorbent DQ 65
Sorbent DR 66
Sorbent DS 66
Sorbent DT 67
Sorbent DU 67
Sorbent DV 67
Sorbent DW 67
Sorbent DX 69
Sorbent DY 70
Sorbent DZ 71
Sorbent EA 72
Sorbent EB 73
Sorbent EC 73
Sorbent ED 73
Sorbent EE 73
Sorbent EF 73
Sorbent EG 73
Sorbent EH 73
Sorbent EI 74
Sorbent EJ 74
Sorbent EK 75
Sorbent EL 75
Sorbent EM 76
Sorbent EN 78
Comparison of All Materials Tested 79
Carbon-Based Sorbents 81
Hydrolalcites 81
Supported Amines 82
CONCLUSIONS 86
REFERENCES 86

INTRODUCTION

Before the industrial revolution, anthropogenic greenhouse gas emissions were negligible. However, it was projected that over 30 billion tons of carbon dioxide were released in 2007.[1] In addition, emissions are expected to grow with increased power consumption of highly populated developing countries. Stationary point sources, such as coal-fired power plants, offer the most promising option for a reduction in carbon dioxide emissions in the near future.

The most important difference between CO_2 and other emissions is the volume at which they are produced. SO_x, NO_x and Hg concentrations are measured in parts per million (ppm) or parts per billion (ppb) while CO_2 is measured as a percentage of the flue gas. Without any modifications, 10 to 15% of the gas released by coal-fired power plants is CO_2. Each ton of carbon in the coal produces nearly 4 tons of gaseous CO_2. Carbon capture and sequestration (CCS) is the most promising option for reducing CO_2 emissions from coal-fired power plants. Obtaining a pure CO_2 stream is the first step of CCS. After the separation, CCS includes compression of the pure CO_2 and sequestration so that it does not enter the atmosphere.

The vast majority of coal-fired power plants burn pulverized coal in a boiler and are thus referred to as PC plants. Post-combustion capture is one of the few viable options to retrofit such plants. The most developed separation technologies utilize liquid solvents. Unfortunately, estimates project that the energy penalty associated with such technologies may be devastating. A great deal of this energy penalty can be attributed to heating up the aqueous solution.[2] One option to reduce the regeneration energy required for CO_2 capture is to use a material with a lower heat capacity, such as many solid sorbents. These sorbents can either react with the CO_2 or adsorb it onto the surface. If the solids can hold more CO_2 per unit mass, this also has the potential to help reduce the energy penalty associated with 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 or Van der Waals forces 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; releasing 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.

Chemically reacting sorbents usually include an inert, high surface area support, such as 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, polymers, and silica, while common reactants include amines such as polyethylenimine or chemicals such as sodium carbonate (Na_2CO_3), which react with CO_2 to form carbamates and bicarbonates, respectively. When heated, the reaction will reverse, releasing the CO_2 and potentially H_2O, 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.

Research institutions throughout the world have spearheaded many solid-sorbent development projects geared towards CO_2 capture. This research encompasses a wide range of technical areas, including activated carbons, carbonate chemical sorbents, metal organic frameworks (MOFs), amine grafted zeolites, and supported amine sorbents. However, a majority of these projects are currently being conducted on either lab- or bench-scale and will require further support and development before the materials are commercially viable.[3] Due to the urgency of addressing CO_2 emissions, it is important that the development of these technologies is accelerated.

Under a project supported by the U.S. Department of Energy (DOE), National Energy Technology Laboratory (NETL), the Electric Power Research Institute (EPRI), and several utility companies, ADA Environmental Solutions (ADA-ES) is conducting a program to characterize CO_2 sorbents and options for process equipment. The objective of this program is to assess the viability and accelerate development of solid sorbents as a CO_2 capture technology that can be retrofit to the existing fleet of coal-fired power plants. The first step in this process is to determine whether appropriate materials are available.

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. Under the ADA-ES sorbent screening program, sorbents have been collected from developers all over the world. These materials have been tested under the same conditions for multiple temperature swing adsorption (TSA) cycles. Sorbents have been targeted that are designed to operate at temperatures and pressures consistent with post-combustion CO_2 capture from PC plants. All sorbents discussed in this report have been given a non-descriptive identifier to protect the identity of the developers.

The sorbent key characteristics evaluated during this program were:

1. CO_2 capacity (when reported as a weight 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
5. Theoretical energy required for regeneration

EXPERIMENTAL APPARATUS AND PROCEDURE

All testing of the sorbents screened during this program was carried out using a specialized fixed bed reactor. 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. A Programmable Logic Controller (PLC) was employed to completely automate the testing process. With an automated system, a series of adsorption/regeneration cycles were completed with little to no supervision. The flow rate of either simulated or actual flue gas was approximately 400 mL/min, and the amount of sorbent in the

reactor was usually in the range of 0.4 to 2.5 g, depending on the material particle size. The sorbent and flue gas were contacted in a fixed bed through a sequence of temperature controlled lines and electrically controlled valves. Figure 1 is a schematic of the sorbent screening testing unit when setup for laboratory testing. The CO_2 analyzer is a continuous NDIR sensor with a 90% response time of 10 seconds. This response time should be taken into consideration when examining results. It is probable that the response time of the instrument affected results for materials tested in 0.4 g quantities more extensively than those tested in 2.5 g quantities.

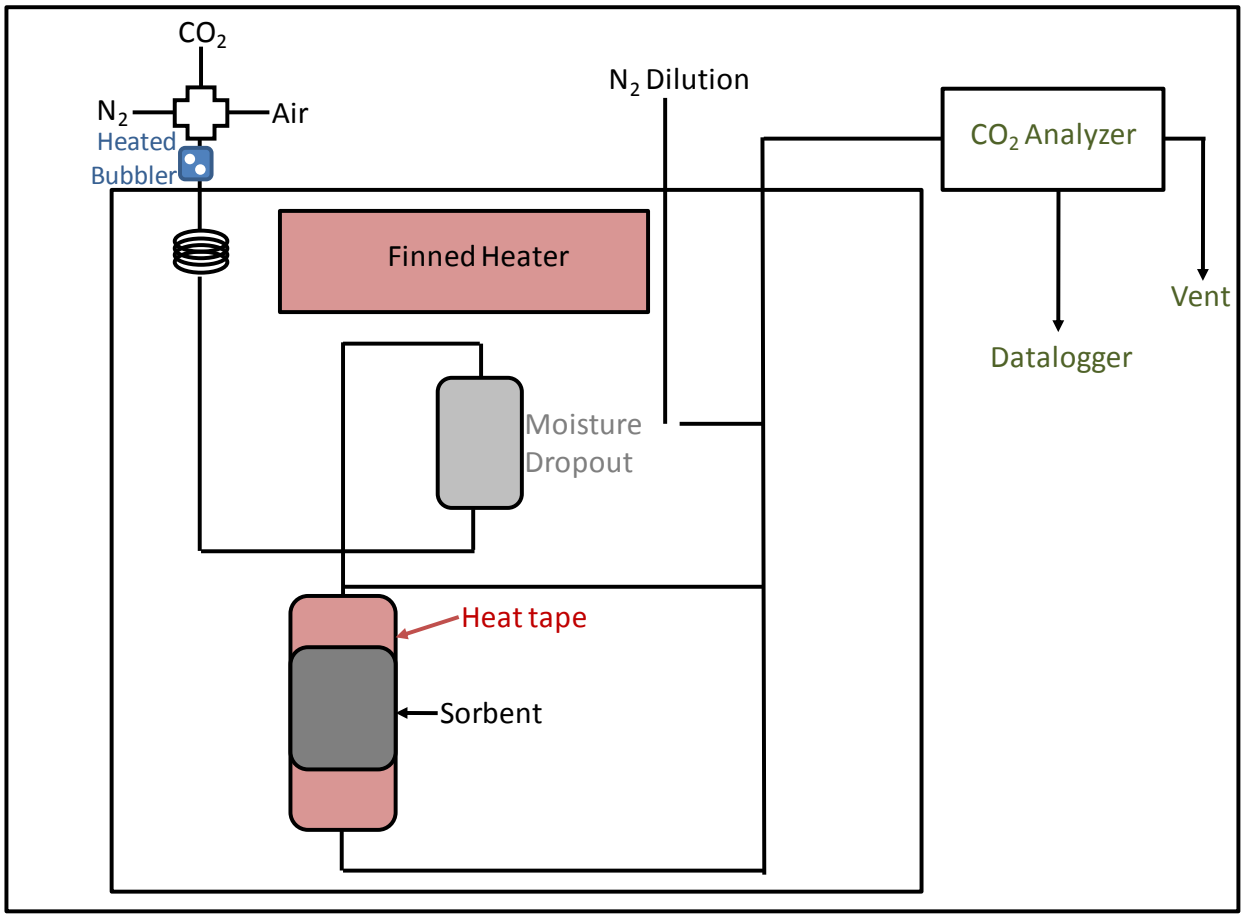

Figure 1: **Schematic of Sorbent Screening Test Unit**

After the sorbent was placed into the fixed bed it was heated to an initial flushing temperature. The initial flushing temperature was based on the lowest regeneration temperature. A thermocouple on the outside of the glass fixed bed was used to determine when the bed had reached the desired temperature. When the bed temperature matched the desired adsorption temperature, the sorbent was flushed with dry N_2 for 10 minutes or until no CO_2 was measured in the purge gas stream, whichever was longer. Then the simulated flue gas, an admixture of compressed gases, was sent through the bypass line circumventing the sorbent. The composition of the laboratory sample gas, by volume, was approximately 12% CO_2, 4% O_2, with a balance of N_2. Approximately 9% moisture by volume was added directing the simulated flue gas through a bubbler at a temperature of 40°C. When the CO_2 reading was stabilized at the known CO_2 concentration (i.e. baseline reading), the gas flow was directed through the sorbent. The CO_2 concentration dropped as the sorbent removed the CO_2 and then as this removal decreased the CO_2 concentration would, thus, increase. After the CO_2

levels returned to their original levels (i.e., the sorbent was saturated with CO_2) it marked the end of the adsorption step.

A temperature swing with a N_2 purge gas was used to regenerate the sorbents and desorb the CO_2. The regeneration purge gas flow rate was the same as that of the flue gas, approximately 300 mL/min. The regeneration step began with the system stopping flue gas flow in order to switch to heated N_2 gas only. While the heated purge gas was flowing through the sorbent, heat tape on the outside of the fixed bed was used to ensure that the sorbent was fully heated to the selected regeneration temperature. Upstream of the reactor the N_2 purge gas was directed through a bubbler separate from the one used for adsorption. This bubbler was primarily used at room temperature to add less than 2% by volume moisture to the regeneration gas.

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 temperature increases as it reacts with the CO_2. Because the sorbent CO_2 capacity decreases with increasing temperature, the test results will show a reduced amount of CO_2 capture if the sorbent temperature is allowed to increase. 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 adsorption was maintained at a lower temperature, while the hot purge gas was maintained at a higher temperature during regeneration. However, by using a high ratio of gas to sorbent, the breakthrough curves are affected. Since the gas flow rate was high, the residence time was low (~1 s), and some CO_2 may pass through the fixed bed un-reacted, even when adsorption sites were available. **Therefore, the percent removal obtained during laboratory tests does not necessarily represent the total removal that could be realized by the sorbents. In fact, it should be considered a minimum of achievable percent removal.** Even with a high volumetric flow rate of gas through the system, the temperature of the fixed bed would still elevate up to 10°C above the temperature set point due to the exothermic reaction. In these cases the adsorption step was not considered complete until the bed temperature had returned to the set point temperature (usually 55°C).

Laboratory Testing

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 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 except for a few specific tests.

There were two types of tests completed during laboratory testing: 1) parametric and 2) constant conditions or extended testing. Many materials were evaluated parametrically. Often the regeneration temperature was varied during the parametric tests. In many cases ten adsorption/regeneration cycles were completed at each regeneration temperature and the step change in the regeneration temperature was 10°C. For example, cycles 1-10 had a regeneration temperature of 90°C, cycles 11-20 had a regeneration temperature of 100°C, cycles 21-30 had a regeneration temperature of 110°C until the maximum temperature set by ADA-ES and the sorbent developer was achieved. When the maximum temperature was achieved the tests can continue, but the regeneration temperature will remain constant.

The other type of laboratory test completed was extended cycle. These types of tests are not parametric and usually were focused on determining the working CO_2 capacity and cyclic stability of the materials. Constant conditions or extended tests were often conducted when the sorbent developer had already completed extensive parametric testing and could provide the optimal operating conditions. Very few sorbent developers evaluated cyclic stability, so this type of test could provide valuable feedback to the developer.

Theoretical Regeneration Energy

When evaluating and comparing sorbents for use in a commercial-scale CO_2 capture and sequestration system, one of the most important evaluation criteria is the energy required for regeneration. Equation 1 shows a simplified energy balance that can be used to calculate the heat duty during regeneration.

$$\boxed{\frac{Q}{m_c} = \frac{m_e}{m_c} C_e \Delta T + \frac{B}{L} C_s \Delta T + \frac{Q_r}{m_c}} \qquad (1)^4$$

Where Q is the regeneration heat input, kJ
m_c is the mass of adsorbed CO_2, kg
m_e is the equipment mass, kg
ΔT is the temperature difference between adsorption and regeneration, °C or K
L is the CO_2 loading, g CO_2/g sorbent
C_e is the equipment specific heat, kJ/kg·K
B is a dimensional conversion term
Q_r is the heat of reaction (positive for endothermic regeneration), kJ/mol CO_2

Due to pressure drop, heat transfer, and mixing concerns, ADA-ES will not be using a fixed bed for testing beyond the laboratory scale. Therefore, the first term on the right hand side of Equation 1 can be neglected because no equipment heating will be required during regeneration (i.e. the regeneration system will be kept at the regeneration temperature and the sorbent will be moved). The second term on the right hand side of Equation 1 is the energy required to heat the sorbent from the adsorption temperature to the regeneration temperature. To reduce the energy related to this term, sorbent loading can be increased or the difference between the adsorption and regeneration temperature can be decreased. The second term on the right hand side of Equation 1 is the energy required to overcome the endothermic reaction associated with desorbing the CO_2 from the sorbent. For physical adsorbents, this term is usually an order of magnitude lower than sorbents that chemically react with the CO_2. However, the CO_2 working capacity is also usually significantly lower.

For all the sorbents tested in this program, the theoretical energy required for regeneration was calculated using Equation 1. The result of this calculation was used to compare different materials and assess their respective viability for use in a commercial-scale CO_2 capture system. The calculation of the theoretical regeneration energy involved the average working capacity and the median regeneration temperature from the adsorption/regeneration cycles completed with moisture in the flue gas. Note that from previous reports a liquid MEA CO_2 capture system requires approximately 3600 kJ/kg CO_2 (1550 BTU/lb CO_2).[3] It is important to note that this is only a high level assessment. This term does not include important contributions to the overall process cost such as pressure drop, CO_2 compression costs, water usage, environmental concerns, etc. In addition, the total CO_2 capacity was used during as m_c in this calculation. In reality, the m_c term should be based on the delta loading term, which was not measured during the fixed bed tests.

RESULTS

The results are provided for only those sorbents that have been evaluated since the release of the previous sorbent developers report. Detailed discussion is only included for those materials that demonstrated competitiveness with other similar materials evaluated to date.

Sorbent BT

Sorbent BT was classified as an amine based sorbent, and for the purposes of this test 2.50 g was the selected sample size. This sorbent achieved a total CO_2 capacity of 1.01 wt% under simulated flue gas conditions, which was lower than many amine-based materials evaluated under this program. Therefore, further testing of this material was not warranted.

Sorbent BU

Note that sorbents BU, BU2, and BU3 are different generations of the same sorbent. Sorbent BU was classified as an amine based sorbent, and for the purposes of this test 2.50 g was the selected sample size. This sorbent achieved a CO_2 capacity of 0.60 wt%, which was lower than many amine-based materials evaluated under this program. Therefore, further testing of this material was not warranted.

Sorbent BU2

Sorbent BU2 was classified as an amine based sorbent, and for the purpose of this test 1.00 g was the sample size. This sorbent was tested for 115 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 1. The regeneration temperatures during the parametric tests were varied from 90°C to 150°C. The adsorption profiles in Figure 2 and the CO_2 capacity in Figure 3 were measured during parametric testing.

Table 1: Sorbent BU2 Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
BU2	Parametric	115	1.00	4	12	90	55	400	90 (Cycles 1-10) 110 (Cycles 11-19) 130 (Cycles 20-29) 150 (Cycles 30-116)	1000

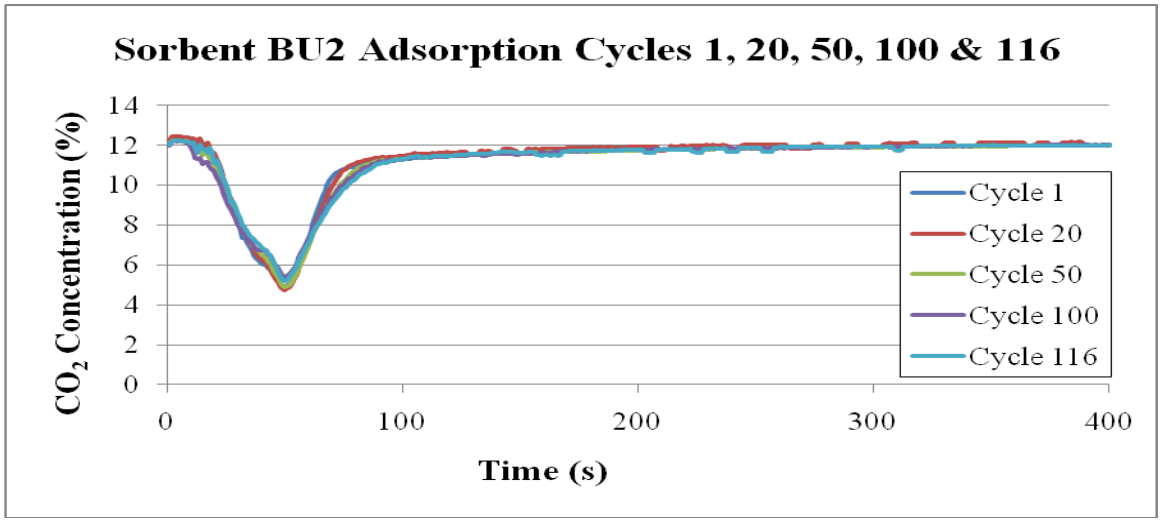

Figure 2: Sorbent BU2 Laboratory Adsorption Profiles

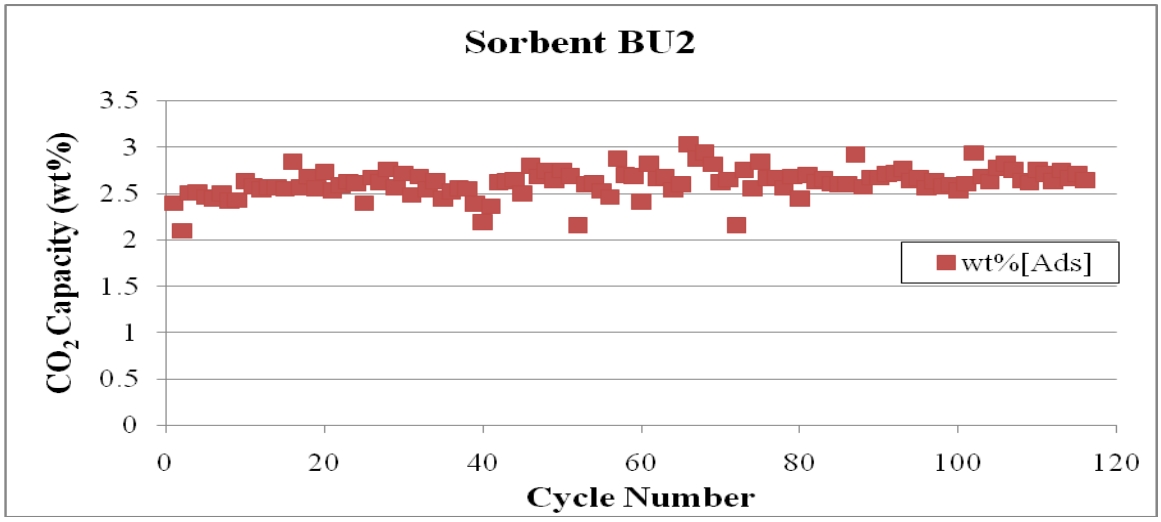

Figure 3: Sorbent BU2 Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 2.62 wt%, a specific heat of 1.0 kJ/kg·K, and a regeneration temperature of 110°C, the theoretical regeneration energy for sorbent BU2 was approximately 3460 kJ/kg CO_2.

Sorbent BU3

Sorbent BU3 was classified as an amine based sorbent, and for the purpose of this test 0.98 g was the sample size. This sorbent was tested for 34 full extended cycles under automated operation in the laboratory at 150°C. The testing conditions are listed in Table 2. The adsorption profiles in Figure 4 and the CO_2 capacity in Figure 5 were measured during extended testing.

Table 2: Sorbent BU3 Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
BU3	Extended	34	0.98	4	12	90	55	1000	150 (Cycles 1-35)	2000

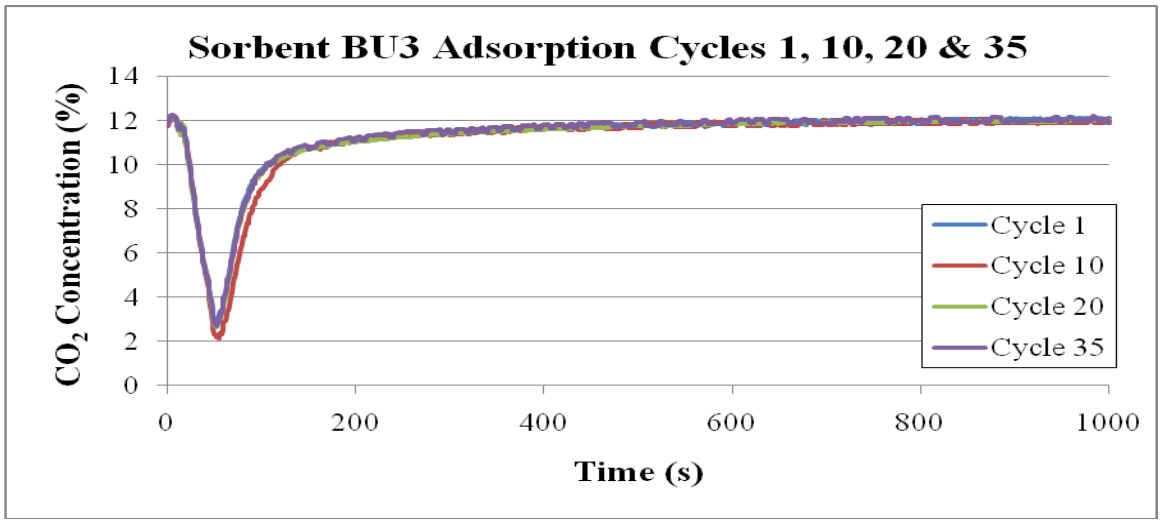

Figure 4: Sorbent BU3 Laboratory Adsorption Profiles

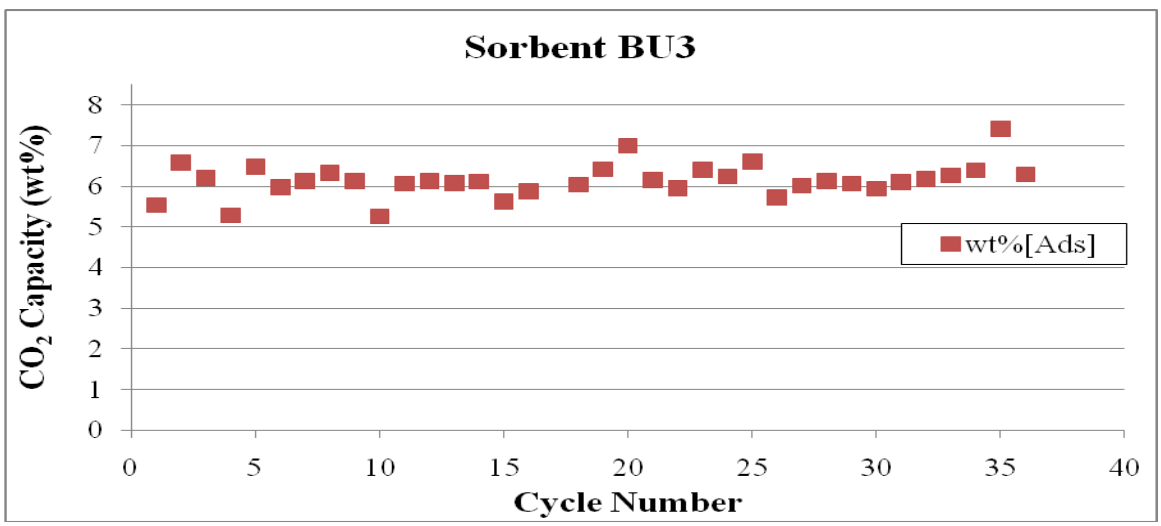

Figure 5: Sorbent BU3 Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 6.14 wt%, a specific heat of 1.0 kJ/kg·K, and a regeneration temperature of 150°C, the theoretical regeneration energy for sorbent BU3 was approximately 2910 kJ/kg CO_2. This material exhibited the most promising properties out of the three generations of materials and was identified as a potentially useful material for future evaluation.

Sorbent BV

Sorbent BV was classified as an amine based sorbent, and for the purpose of this test 2.50 g was the sample size. This sorbent was tested for 75 full extended cycles under automated operation in the laboratory at 98°C. The testing conditions are listed in Table 3. The adsorption profiles in Figure 6 and the CO_2 capacity in Figure 7 were measured during extended testing.

Table 3: Sorbent BV Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
BV	Extended	75	2.50	4	12	90	55	900	98 (Cycles 1-76)	1400

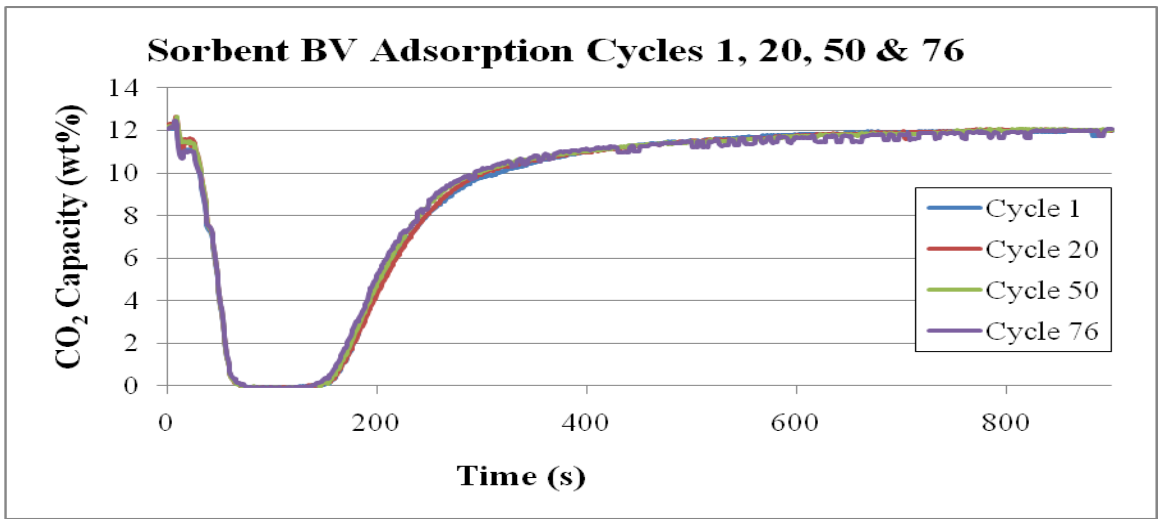

Figure 6: Sorbent BV Laboratory Adsorption Profiles

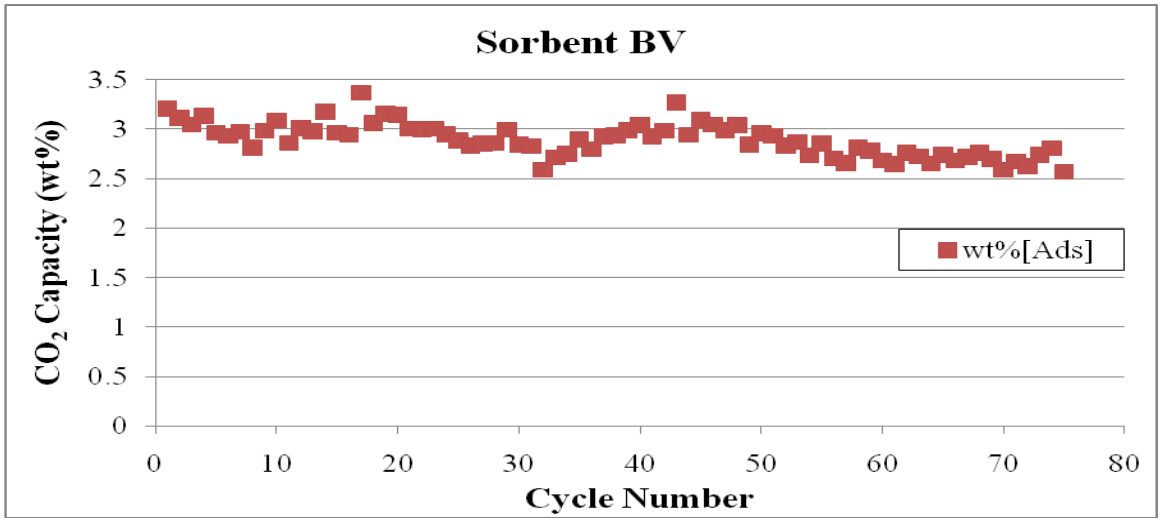

Figure 7: Sorbent BV Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 2.90 wt%, a specific heat of 0.8 kJ/kg·K, and a regeneration temperature of 98°C, the theoretical regeneration energy for sorbent BV was approximately 2550 kJ/kg CO_2, which was lower than the benchmark MEA.

Sorbent BX

Sorbent BX was classified as an amine based sorbent, and for the purpose of this test 2.50 g was the sample size. This sorbent was tested for 24 full extended cycles under automated operation in the laboratory at 100°C. The testing conditions are listed in Table 4. The adsorption profiles in Figure 8 and the CO_2 capacity in Figure 9 were measured during extended testing.

Table 4: Sorbent BX Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
BX	Extended	24	2.50	4	12	90	55	1100	100 (Cycles 1-25)	1500

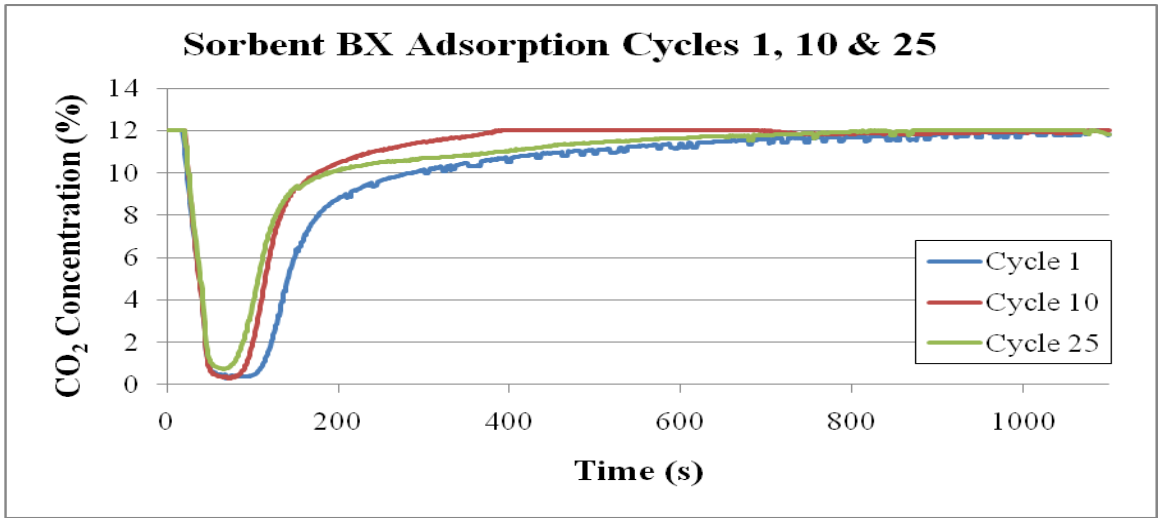

Figure 8: Sorbent BX Laboratory Adsorption Profiles

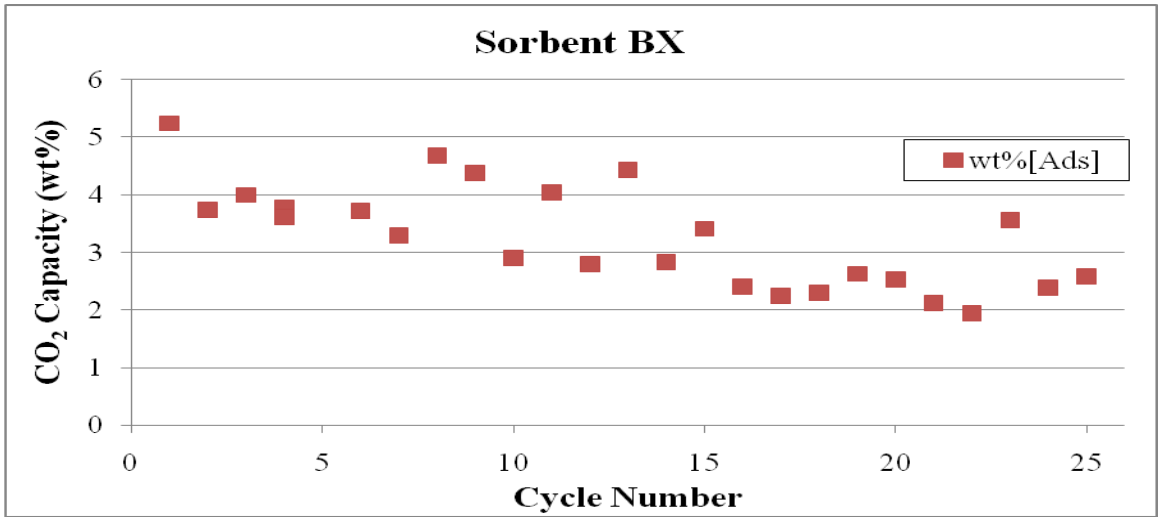

Figure 9: Sorbent BX Laboratory Total Capacities

Based on the laboratory results, using a CO_2 capacity of 3.26 wt%, a specific heat of 0.8 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent BX was approximately 2467 kJ/kg CO_2. Amines leached from this material during testing, which is not considered an acceptable characteristic for any sorbent. Therefore, no further testing of this material was warranted.

Sorbent BY

Sorbent BY was classified as an amine based sorbent, and for the purpose of this test 2.50 g was the sample size. This sorbent was tested for 62 full extended cycles under automated operation in the laboratory at 100°C. The testing conditions are listed in Table 5. The adsorption profiles in Figure 10 and the CO_2 capacity in Figure 11 were measured during extended testing.

Table 5: Sorbent BY Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
BY	Extended	62	2.50	4	12	90	55	2300	100 (Cycles 1-63)	1800

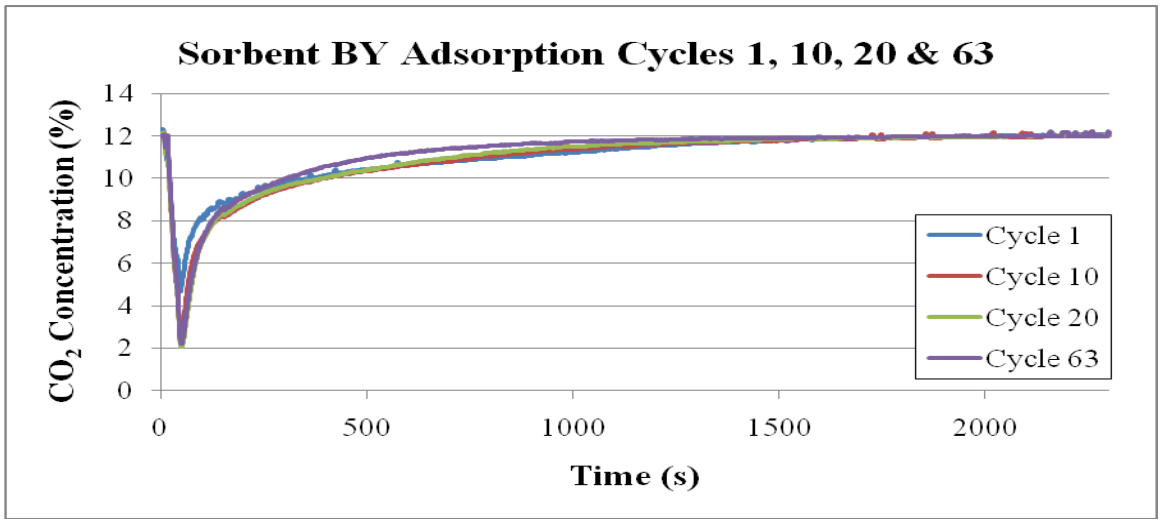

Figure 10: Sorbent BY Laboratory Adsorption Profiles

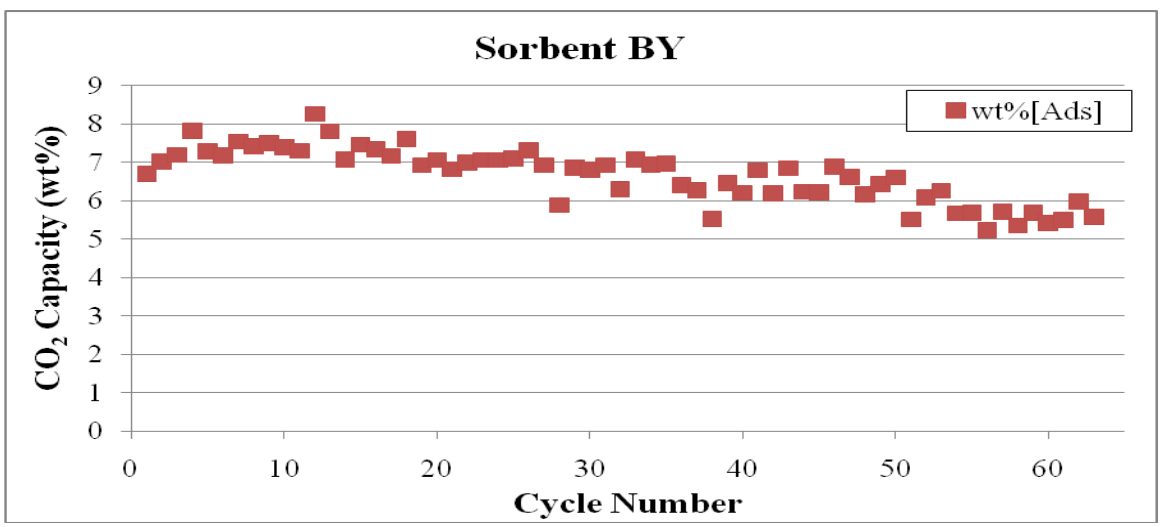

Figure 11: Sorbent BY Laboratory Working Capacities

Based on the laboratory results, using a CO_2 capacity of 6.66 wt%, a specific heat of 1.3 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent BY was approximately 2700 kJ/kg CO_2, which was lower than the benchmark MEA.

Note that the cyclic tests indicated an overall lack of cyclic stability. The sorbent developer is working to improve this material with a specific focus on cyclic stability.

Sorbent BZ

Sorbent BZ was classified as an amine based sorbent, and for the purpose of this test 2.50 g was the sample size. This sorbent was tested for 148 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 6. The regeneration temperatures during the parametric tests were varied from 100°C to 120°C. The adsorption profiles in Figure 12 and the CO_2 capacity in Figure 13 were measured during parametric testing.

Table 6: Sorbent BZ Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
BZ	Parametric	148	2.50	4	12	90	55	1800	100 (Cycles 1-131) 110 (Cycles 132-147) 120 (Cycles 148-149)	2600

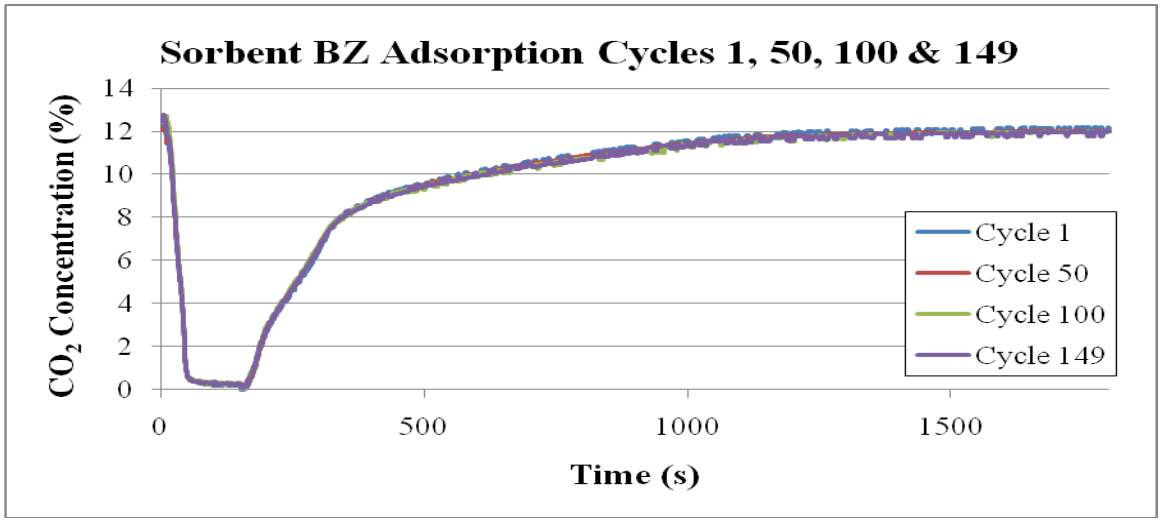

Figure 12: Sorbent BZ Laboratory Adsorption Profiles

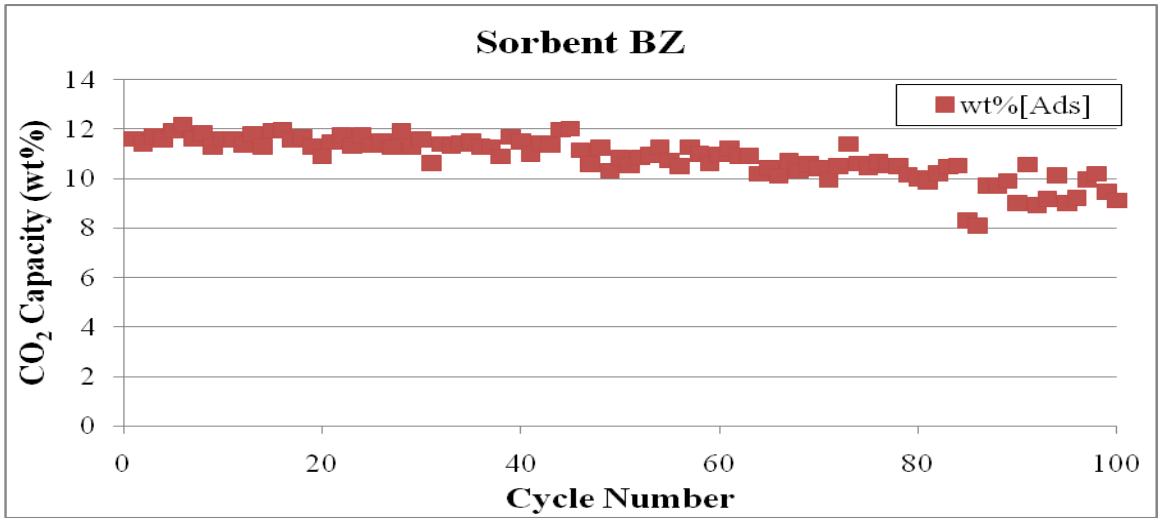

Figure 13: Sorbent BZ Laboratory Working Capacities

Based on the laboratory results, using a CO_2 capacity of 10.49 wt%, a specific heat of 1.3 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent BZ was approximately 1920 kJ/kg CO_2, which was lower than most sorbents tested and considerably lower than that of the MEA benchmark.

Sorbent CA

Sorbent CA was classified as an amine based sorbent, and for the purpose of this test 2.50 g was the sample size. This sorbent was tested for 28 full extended cycles under automated operation in the laboratory at 100°C. The testing conditions are listed in Table 7. The adsorption profiles in Figure 14 and the CO_2 capacity in Figure 15 were measured during extended testing.

Table 7: Sorbent CA Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CA	Extended	28	2.50	4	12	90	55	1000	100 (Cycles 1-29)	1900

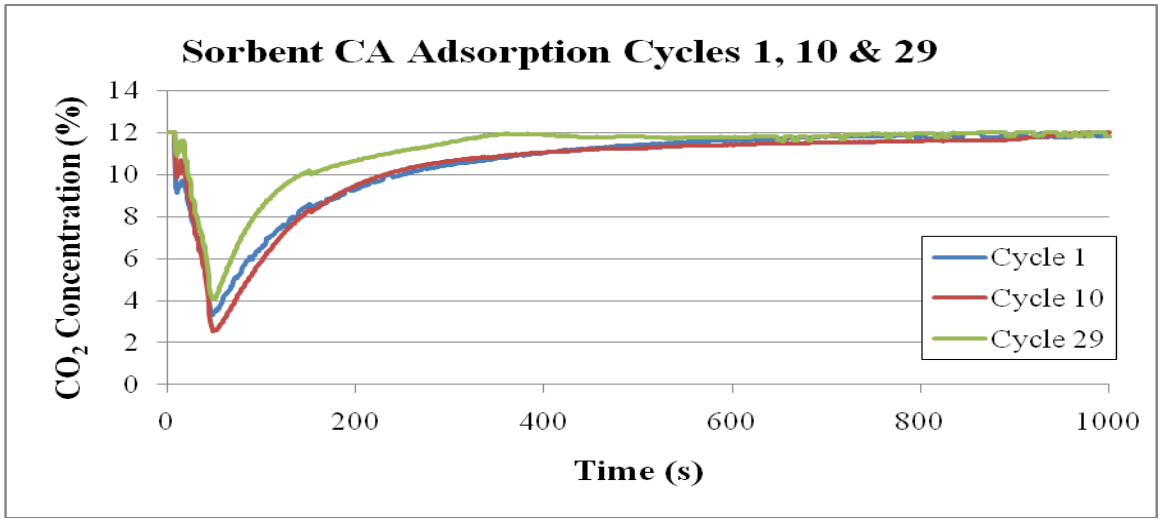

Figure 14: Sorbent CA Laboratory Adsorption Profiles

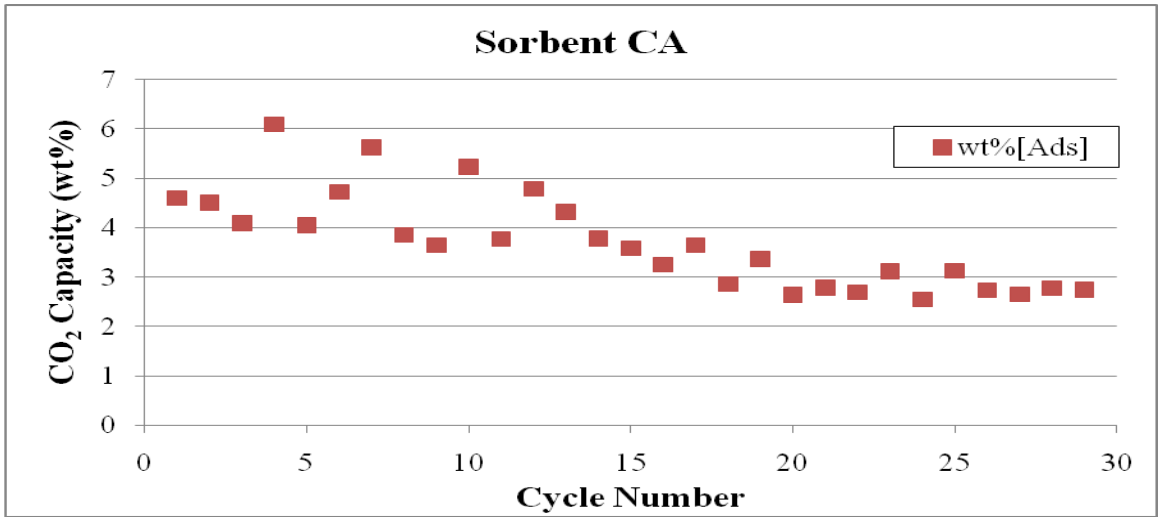

Figure 15: Sorbent CA Laboratory Working Capacities

Based on the laboratory results, using a CO_2 capacity of 3.71 wt%, a specific heat of 0.8 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CA was approximately 2330 kJ/kg CO_2, which was lower than the MEA benchmark.

Sorbent CB

Sorbent CB was classified a carbon based sorbent, and for the purposes of this test 2.50 g was the selected sample size. This sorbent was tested for 61 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 8. The regeneration temperatures during the parametric tests were varied from 100°C to 120°C. The adsorption profiles in Figure 16 and the CO_2 capacity in Figure 17 were measured during parametric testing.

Table 8: Sorbent CB Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CB	Parametric	61	2.50	4	12	90	55	450	100 (Cycles 1-23) 120 (Cycles 24-62)	1100

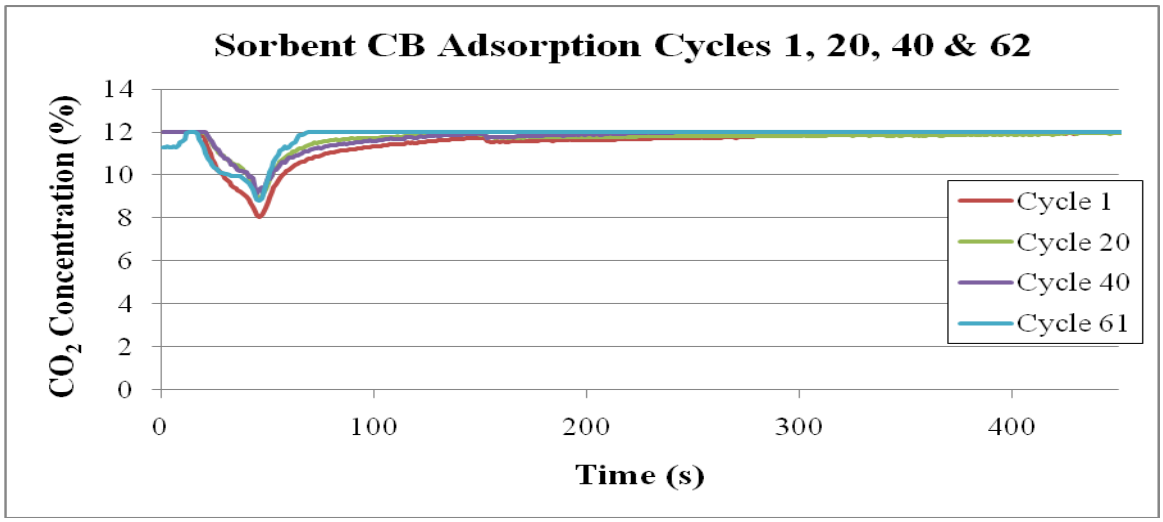

Figure 16: Sorbent CB Laboratory Adsorption Profiles

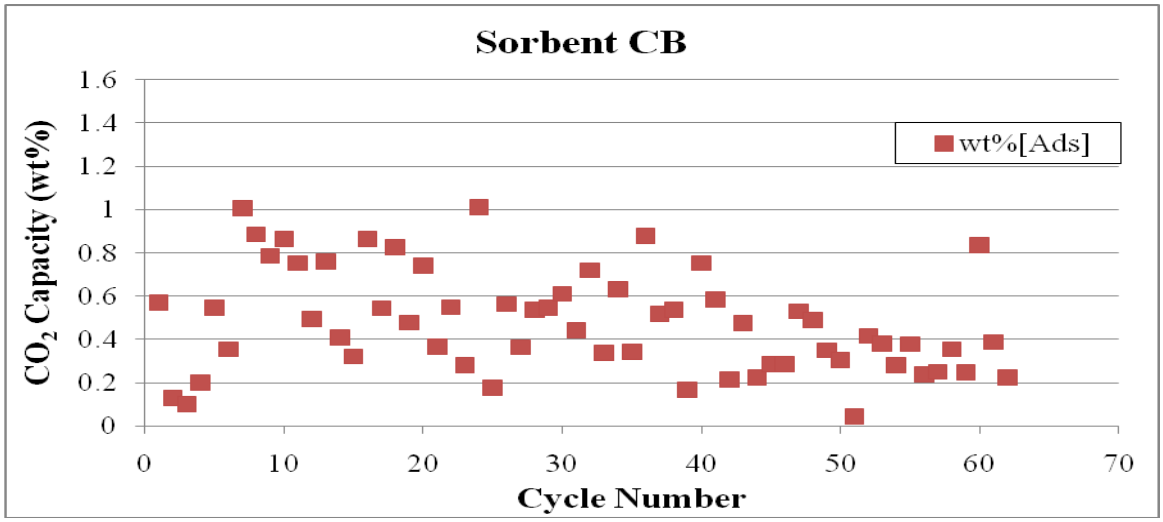

Figure 17: Sorbent CB Laboratory Working Capacities

Based on the laboratory results, using a CO_2 capacity of 0.50 wt%, a specific heat of 1.3 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CB was approximately 11770 kJ/kg CO_2. This achieved a CO_2 capacity of 0.50 wt%, which was lower than many materials evaluated under this program. Therefore, further testing of this material was not warranted.

Sorbent CC

Sorbent CC was classified a carbon based sorbent, and for the purposes of this test 2.50 g was the selected sample size. This sorbent was tested for 91 full extended cycles under automated operation in the laboratory at 120°C. The testing conditions are listed in Table 9. Select adsorption profiles are provided in Figure 18 and the CO_2 capacity is provided in Figure 19 as was measured during extended testing.

Table 9: Sorbent CC Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CC	Extended	91	2.50	4	12	90	55	400	120 (Cycles 1-92)	600

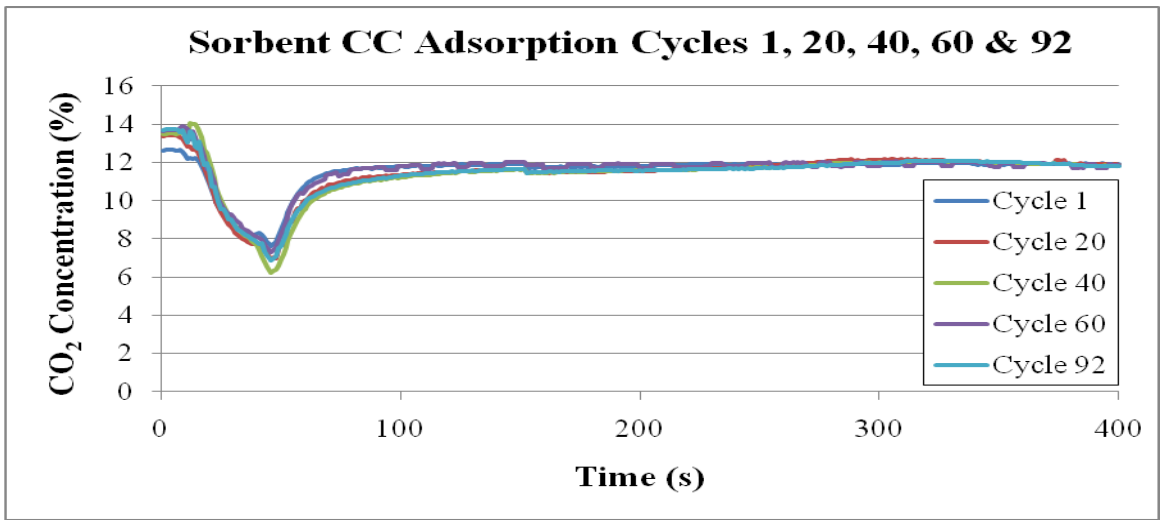

Figure 18: Sorbent CC Laboratory Adsorption Profiles

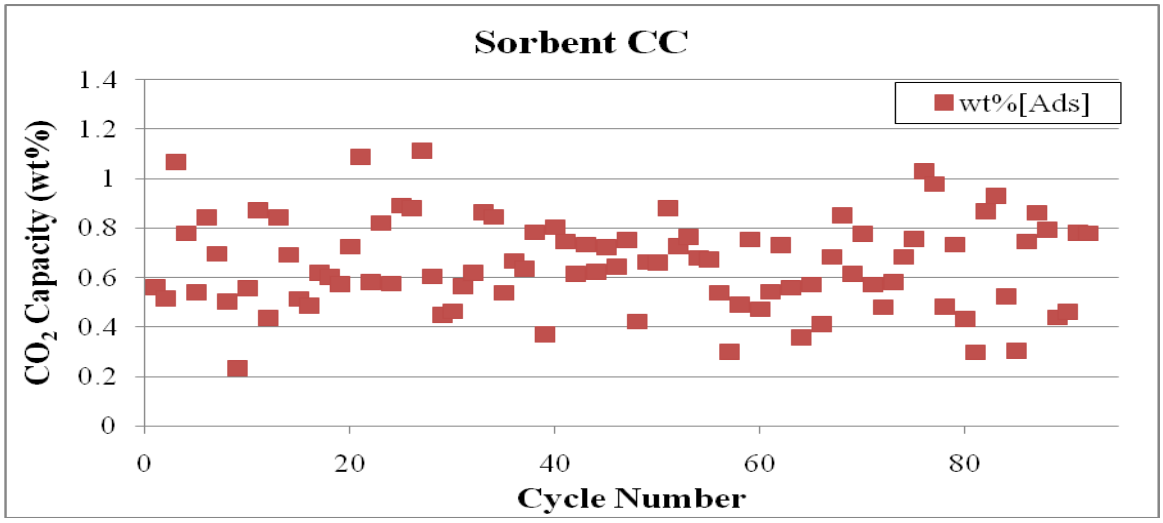

Figure 19: Sorbent CC Laboratory Working Capacities

Based on the laboratory results, using a CO_2 capacity of 0.66 wt%, a specific heat of 1.3 kJ/kg·K, and a regeneration temperature of 120°C, the theoretical regeneration energy for sorbent CC was approximately 12871 kJ/kg CO_2. This achieved a CO_2 capacity of 0.66 wt%, which was lower than many materials evaluated under this program. Therefore, further testing of this material was not warranted.

Sorbent CD

Sorbent CD was classified a carbon based sorbent, and for the purposes of this test 2.50 g was the selected sample size. This sorbent was tested for 54 full extended cycles under automated operation in the laboratory at 100°C. The testing conditions are listed in Table 10. The adsorption profiles in Figure 20 and the CO_2 capacity in Figure 21 were measured during extended testing.

Table 10: Sorbent CD Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CD	Extended	54	2.50	4	12	90	55	200	100 (Cycles 1-55)	300

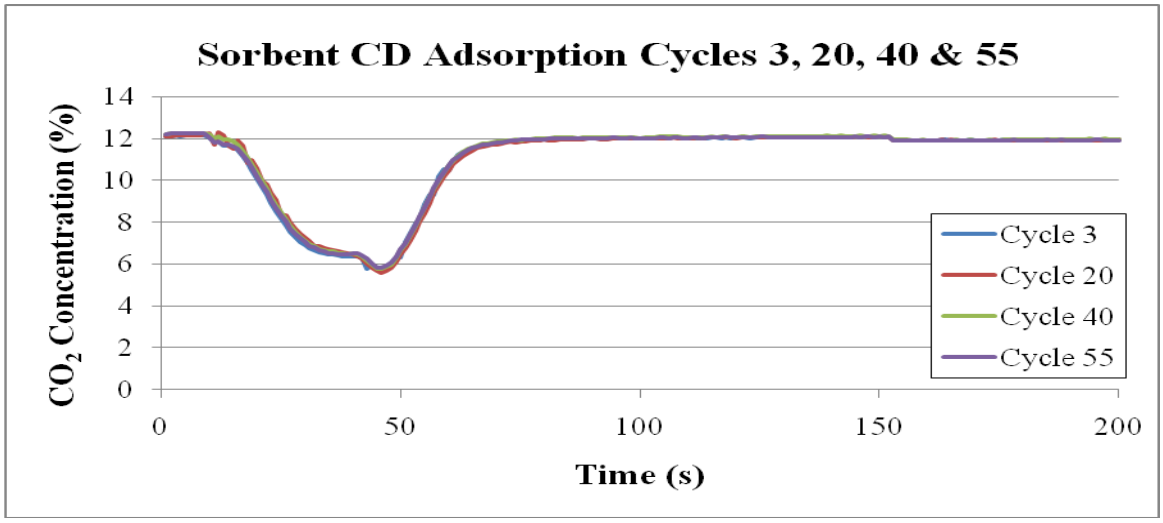

Figure 20: Sorbent CD Laboratory Adsorption Profiles

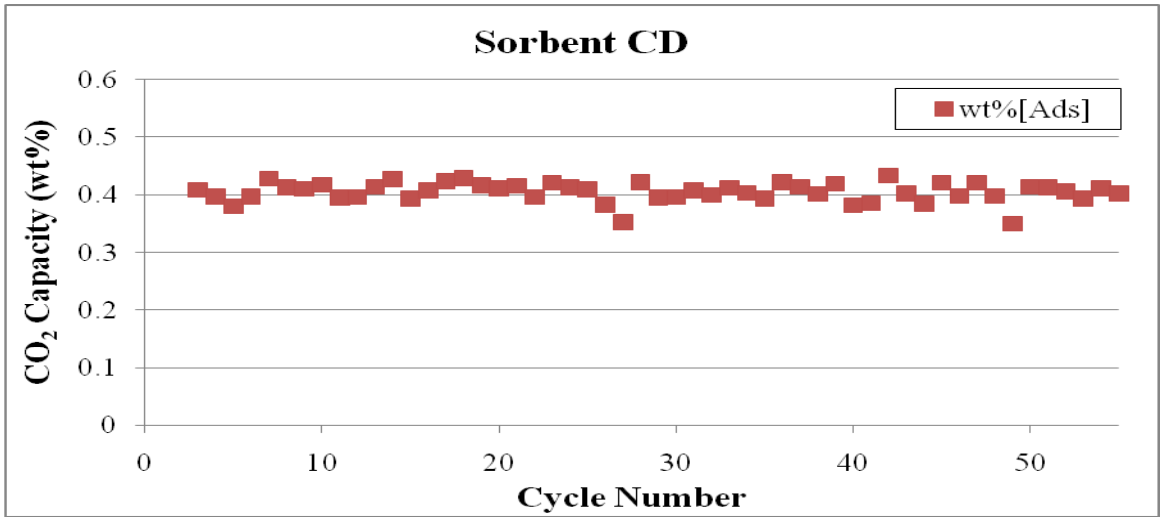

Figure 21: Sorbent CD Laboratory Working Capacities

Based on the laboratory results, using a CO_2 capacity of 0.40 wt%, a specific heat of 1.3 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CD was approximately 14520 kJ/kg CO_2. This achieved a CO_2 capacity of 0.40 wt%, which was lower than many materials evaluated under this program. Therefore, further testing of this material was not warranted.

Sorbent CE

Sorbent CE was classified as an amine based sorbent, and for the purpose of this test 2.51 g was the sample size. This sorbent was tested for 261 full extended cycles under automated operation in the laboratory at a regeneration temperature of 100°C. The testing conditions are listed in Table 11. The adsorption profiles in Figure 22 and the CO_2 capacity in Figure 23 were measured during extended testing.

Table 11: Sorbent CE Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CE	Extended	261	2.51	4	12	90	55	1300	100 (Cycles 1-262)	2100

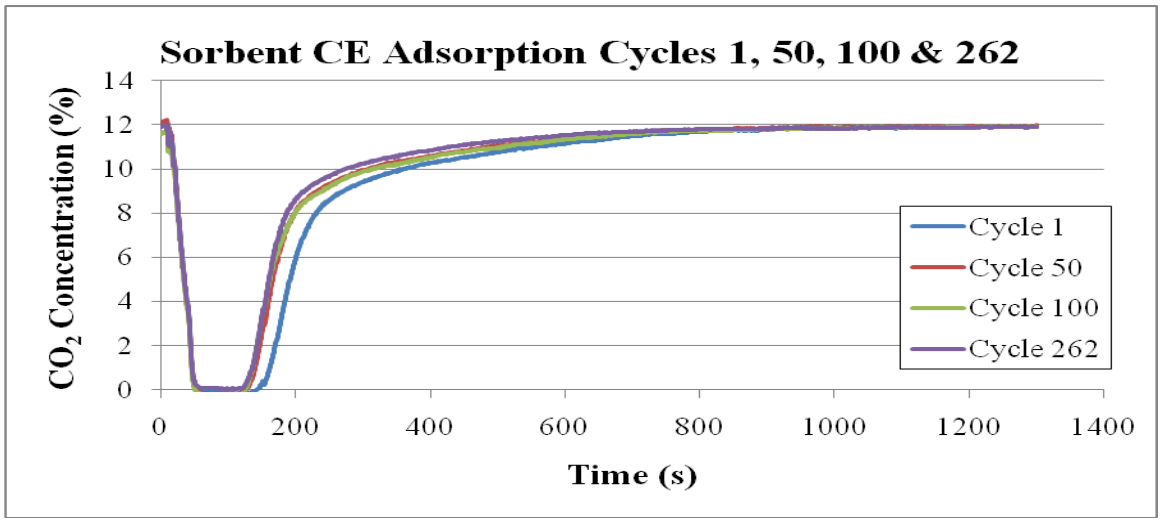

Figure 22: Sorbent CE Laboratory Adsorption Profiles

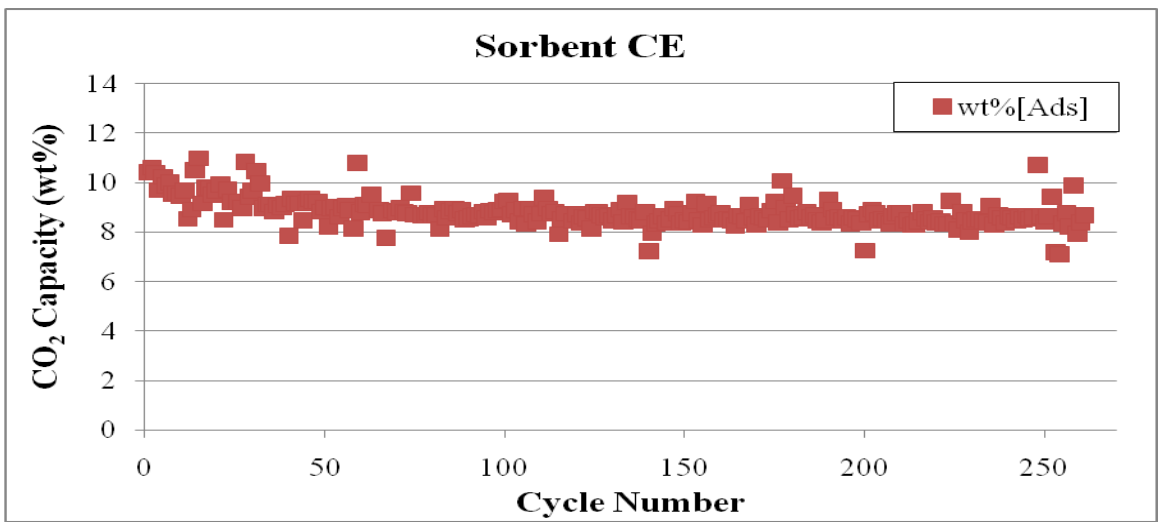

Figure 23: Sorbent CE Laboratory Working Capacities

Based on the laboratory results, using a CO_2 capacity of 8.81 wt%, a specific heat of 1.3 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CE was approximately 2028 kJ/kg CO_2. This material exhibited superior cyclic stability after approximately the first 50 cycles. In addition the total CO_2 capacity was greater than most sorbents evaluated under this program.

Sorbent CF

Sorbent CF was classified an amine based sorbent, and for the purposes of this test 2.51 g was the selected sample size. This sorbent achieved a CO_2 capacity of 0.22 wt%, which was lower than many amine-based materials evaluated under this program. Therefore, further testing of this material was not warranted.

Sorbent CG

Sorbent CG was classified as an amine based sorbent, and for the purpose of this test 2.50 g was the sample size. This sorbent was tested for 63 full extended cycles under automated operation in the laboratory at 100°C. The testing conditions are listed in Table 12. The adsorption profiles in Figure 24 and the CO_2 capacity in Figure 25 were measured during extended testing.

Table 12: Sorbent CG Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CG	Extended	63	2.50	4	12	90	55	1000	100 (Cycles 1-64)	1900

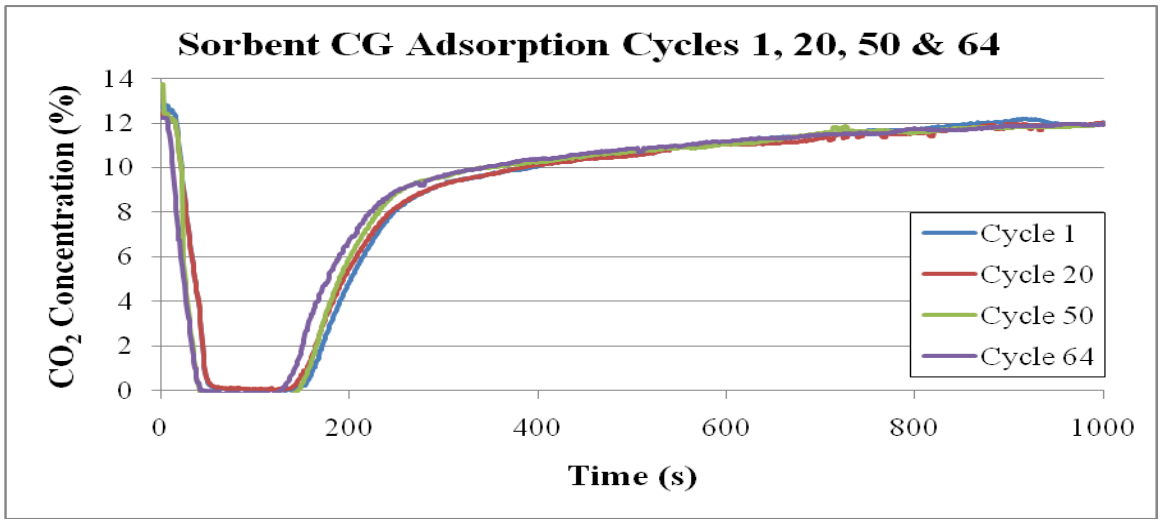

Figure 24: Sorbent CG Laboratory Adsorption Profiles

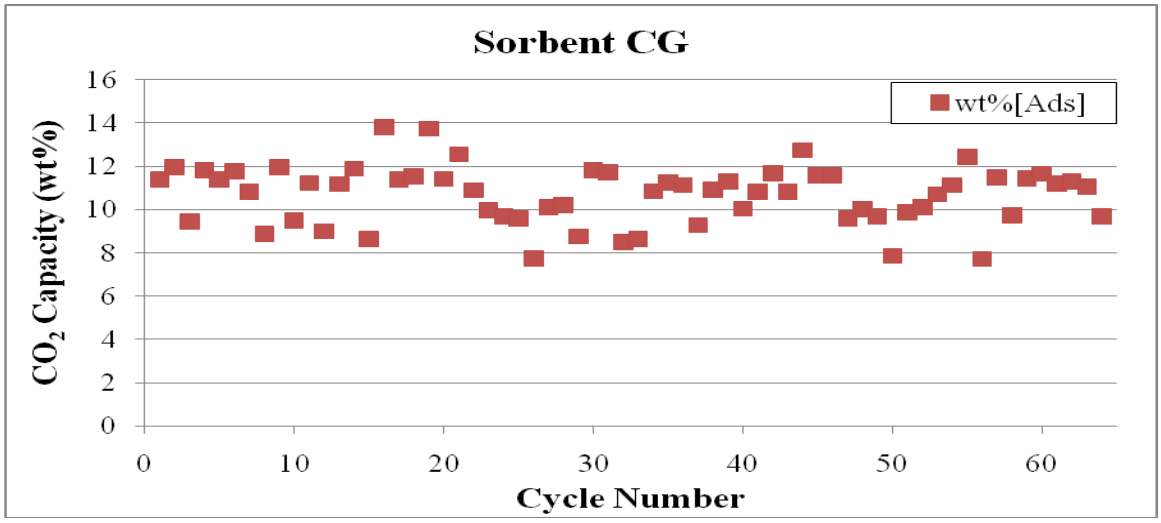

Figure 25: Sorbent CG Laboratory Working Capacities

Based on the laboratory results, using a CO_2 capacity of 10.68 wt%, a specific heat of 1.3 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CG was approximately 1910 kJ/kg CO_2, this was lower than the benchmark MEA. This material was considered promising compared to similar sorbents.

Sorbent CH

Sorbent CH was classified as an amine based sorbent, and for the purpose of this test 2.50 g was the sample size. This sorbent was tested for 140 full extended cycles under automated operation in the laboratory at 100°C. The testing conditions are listed in Table 13. The adsorption profiles in Figure 26 and the CO_2 capacity in Figure 27 were measured during extended testing.

Table 13: Sorbent CH Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CH	Extended	140	2.50	4	12	90	55	600	100 (Cycles 1-141)	1610

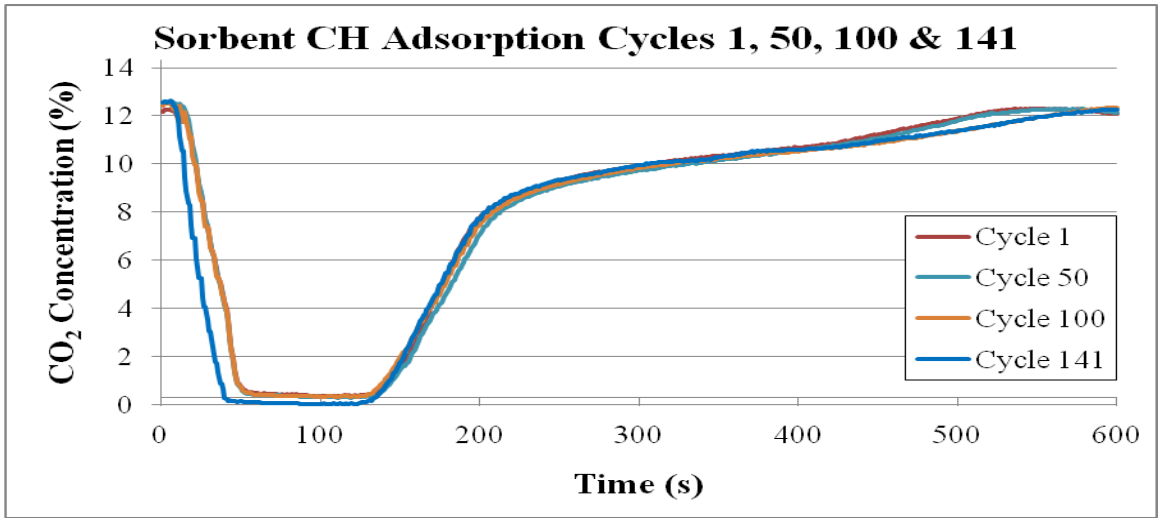

Figure 26: Sorbent CH Laboratory Adsorption Profiles

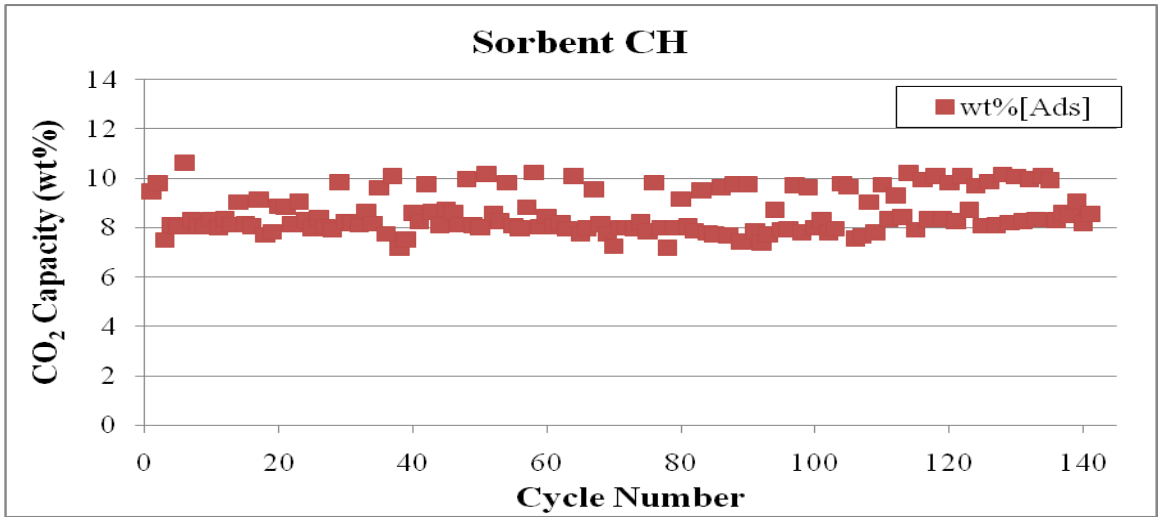

Figure 27: Sorbent CH Laboratory Working Capacities

Based on the laboratory results, using a CO_2 capacity of 8.59 wt%, a specific heat of 1.3 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CH was approximately 2045 kJ/kg CO_2. This material exhibited superior cyclic stability and low theoretical regeneration energy, making it a particularly promising material.

Sorbent CI

Sorbent CI was classified as an amine based sorbent, and for the purpose of this test 2.50 g was the sample size. This sorbent was tested for 55 full extended cycles under automated operation in the laboratory at 100°C. The testing conditions are listed in Table 14. The adsorption profiles in Figure 28 and the CO_2 capacity in Figure 29 were measured during extended testing.

Table 14: Sorbent CI Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CI	Extended	55	2.50	4	12	90	55	600	100 (Cycles 1-56)	1610

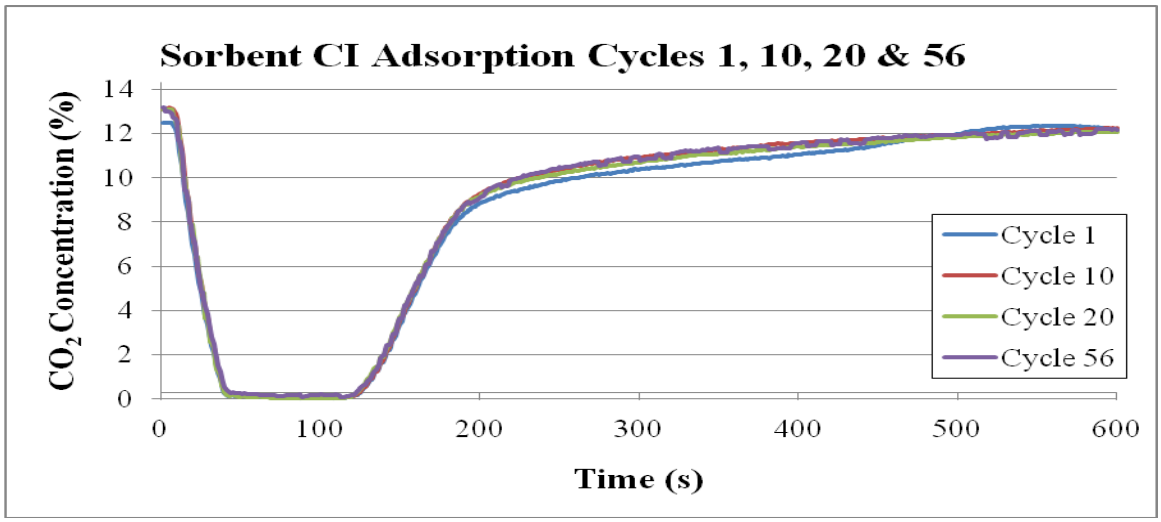

Figure 28: Sorbent CI Laboratory Adsorption Profiles

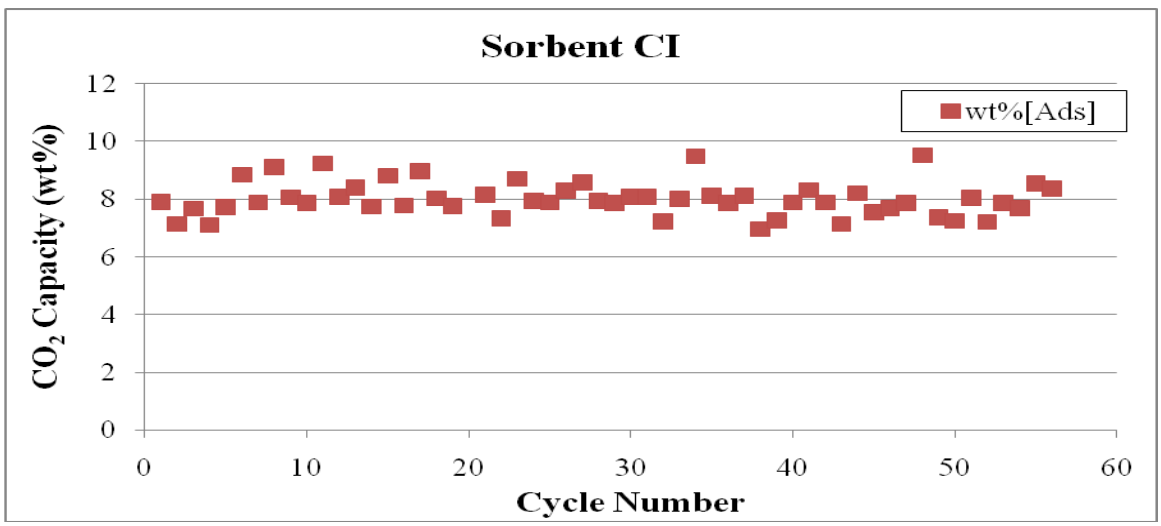

Figure 29: Sorbent CI Laboratory Working Capacities

Based on the laboratory results, using a CO_2 capacity of 8.01 wt%, a specific heat of 1.3 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CI was approximately 2090 kJ/kg CO_2. This material exhibited superior cyclic stability and low theoretical regeneration energy, making it a particularly promising material.

Sorbent CJ

Sorbent CJ was classified as an amine based sorbent, and for the purpose of this test 2.50 g was the sample size. This sorbent was tested for 46 full extended cycles under automated operation in the laboratory at 100°C. The testing conditions are listed in Table 15. The adsorption profiles in Figure 30 and the CO_2 capacity in Figure 31 were measured during extended testing.

Table 15: Sorbent CJ Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CJ	Extended	46	2.50	4	12	90	55	900	100 (Cycles 1-47)	2130

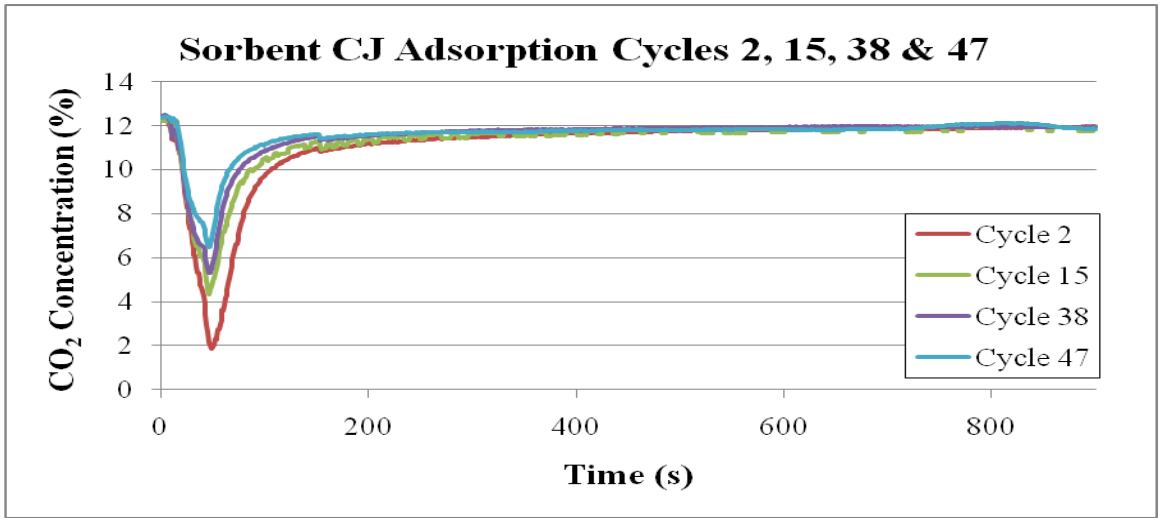

Figure 30: Sorbent CJ Laboratory Adsorption Profiles

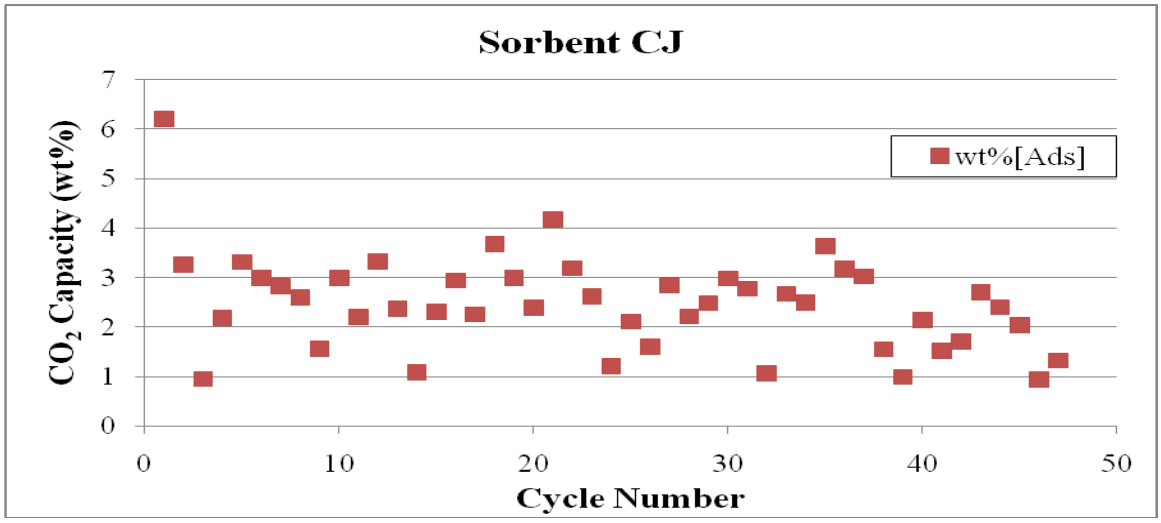

Figure 31: Sorbent CJ Laboratory Working Capacities

Based on the laboratory results, using a CO_2 capacity of 2.47 wt%, a specific heat of 0.8 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CJ was approximately 2820 kJ/kg CO_2. Although this was lower than the benchmark MEA, several other similar materials exhibited lower theoretical regeneration energies. In addition, based on the adsorption profiles this material clearly lost CO_2 capacity during the tests and cannot be considered cyclically stable.

Sorbent CK

Sorbent CK was classified as an amine based sorbent, and for the purpose of this test 2.45 g was the sample size. This sorbent was tested for 26 full extended cycles under automated operation in the laboratory at 100°C. The testing conditions are listed in Table 16. The adsorption profiles in Figure 32 and the CO_2 capacity in Figure 33 were collected during extended testing.

Table 16: Sorbent CK Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CK	Extended	26	2.45	4	12	90	55	800	100 (Cycles 1-27)	1100

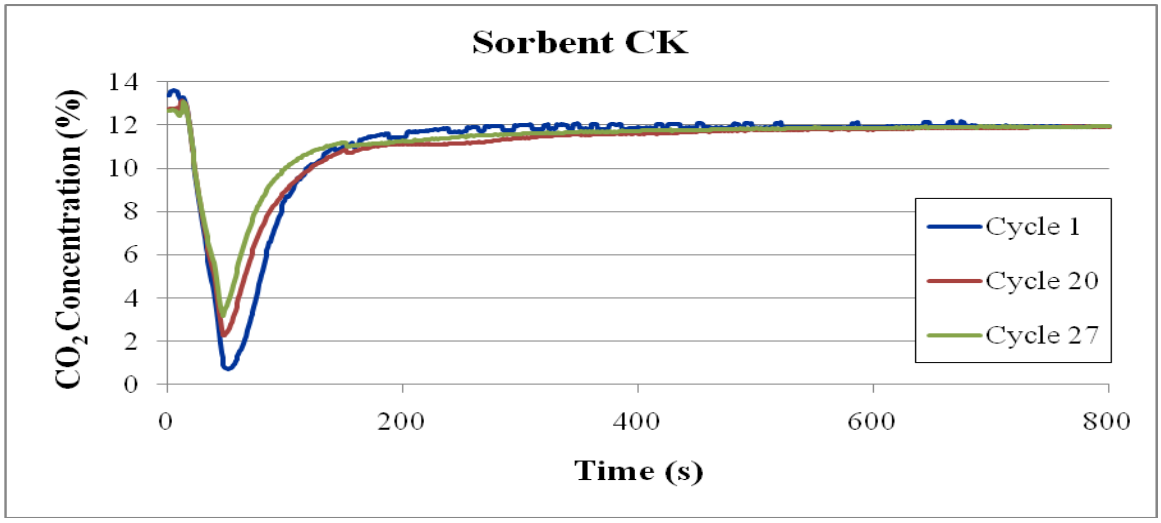

Figure 32: Sorbent CK Laboratory Adsorption Profiles

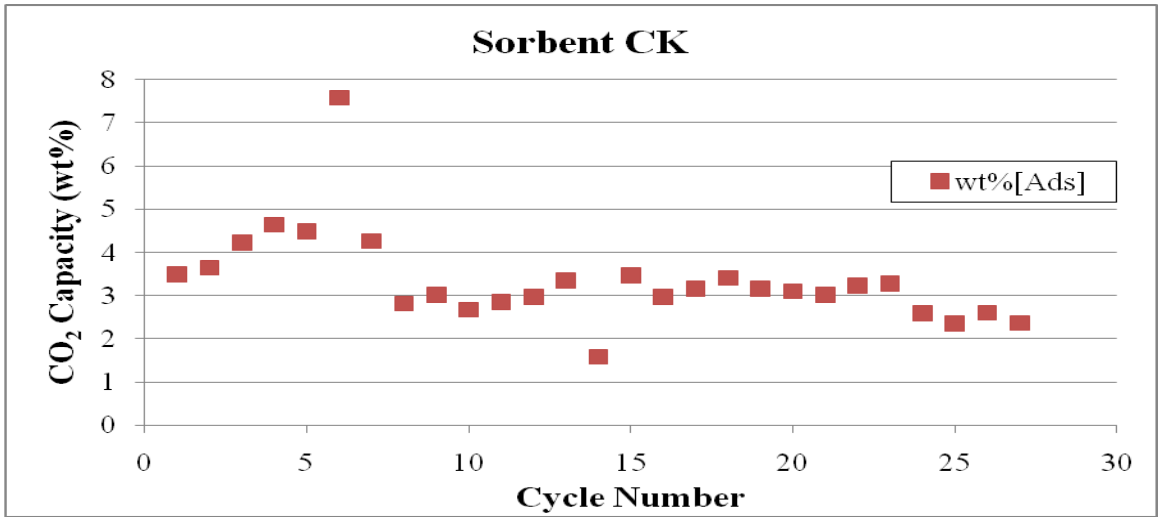

Figure 33: Sorbent CK Laboratory Working Capacities

Based on the laboratory results, using a CO_2 capacity of 3.35 wt%, a specific heat of 0.8 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CK was approximately 2440 kJ/kg CO_2. With such a low specific heat, the regeneration energy was still lower than the benchmark MEA, even with the relatively low CO_2 capacity.

Sorbent CL

Sorbent CL was classified an amine based sorbent, and for the purpose of this test 2.02 g was the sample size. This sorbent was tested for 136 full extended cycles at 100°C under automated operation in the laboratory. The testing conditions are listed in Table 17. The adsorption profiles in Figure 34 and the CO_2 capacity in Figure 35 were measured during extended testing.

Table 17: Sorbent CL Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Sample Final Size (g)	Weight Loss (%)	Adsorption Conditions					Regeneration Conditions	
						CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CL	Extended	136	2.02	1.76	12.99	12	4	50	55	300	100 (Cycles 1-137)	550

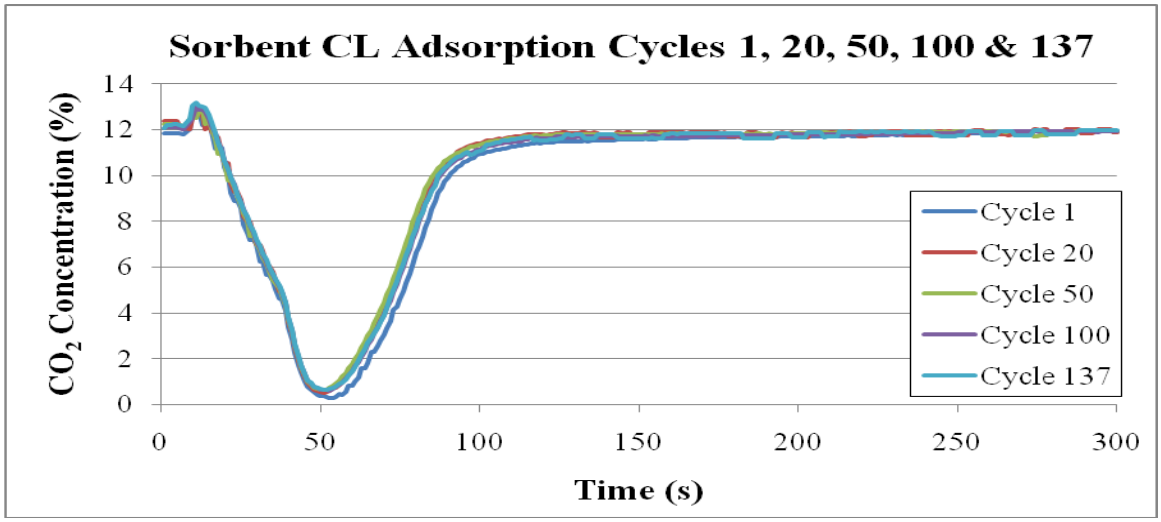

Figure 34: Sorbent CL Laboratory Adsorption Profiles

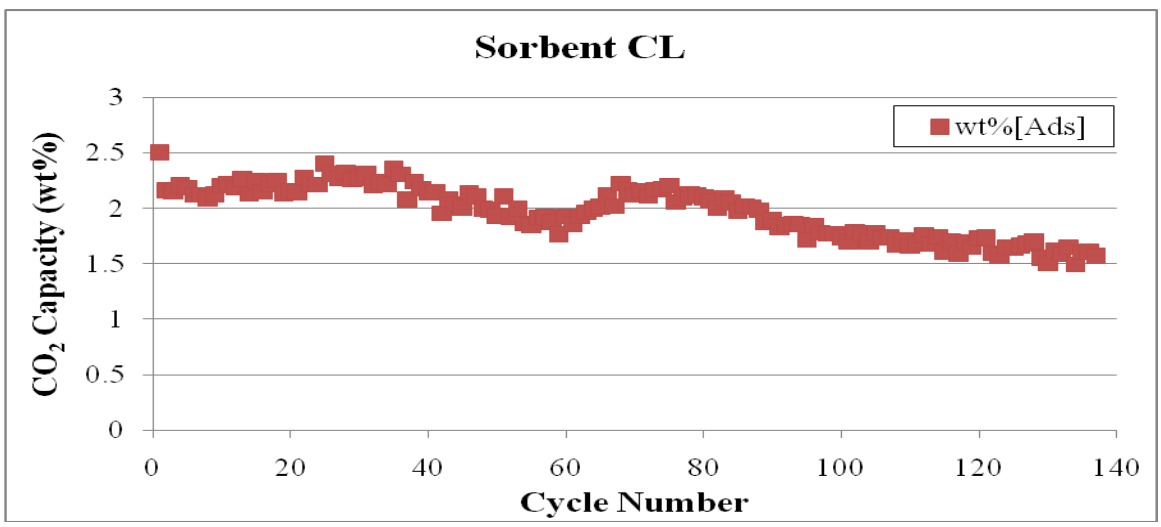

Figure 35: Sorbent CL Laboratory Total CO_2 Capacities

Based on the laboratory results, using a working CO_2 capacity of 1.97 wt%, a specific heat of 0.8 kJ/kg·K and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CL was approximately 3190 kJ/kg CO_2. Although this was lower than the benchmark MEA, it was too high to warrant further evaluation considering the 1) clear decrease in the CO_2 capacity indicating a lack of cyclic stability and 2) lower CO_2 capacity compared to similar materials.

Sorbent CM

Sorbent CM was classified as an amine based sorbent, and for the purpose of this test 0.51 g was the sample size. This sorbent was tested for 41 full extended cycles at 100°C under automated operation in the laboratory. The testing conditions are listed in Table 18. The adsorption profiles in Figure 36 and the CO_2 capacity in Figure 37 were measured during the extended testing.

Table 18: Sorbent CM Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CM	Extended	41	0.51	4	12	50	55	400	100 (Cycles 1-42)	550

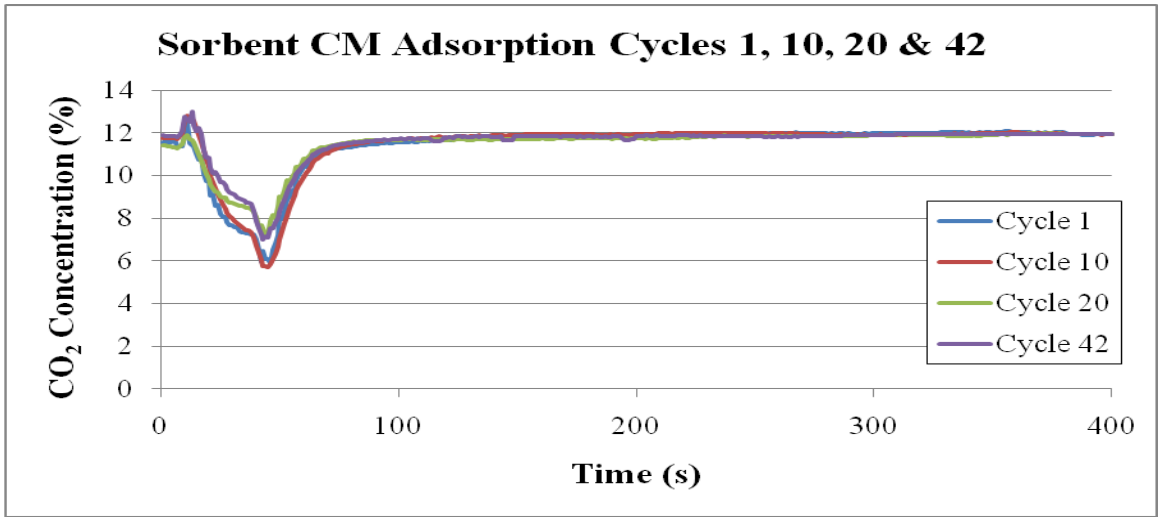

Figure 36: Sorbent CM Laboratory Adsorption Profiles

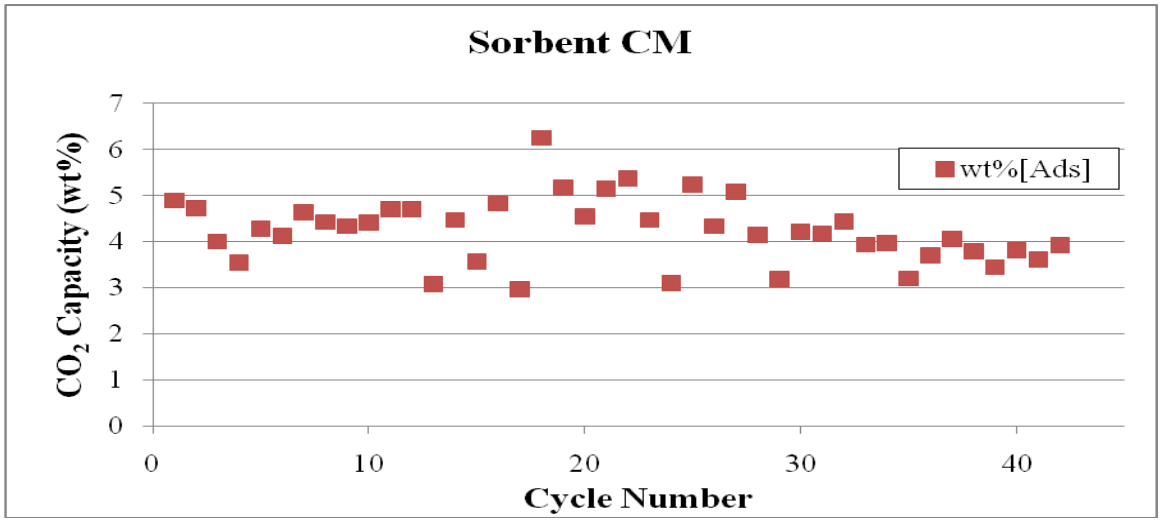

Figure 37: Sorbent CM Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 4.24 wt%, a specific heat of 1.0 kJ/kg·K and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CM was approximately 2430 kJ/kg CO_2. This material exhibited good cyclic stability, but the CO_2 capacity was not high enough to warrant further investigation.

Sorbent CN

Sorbent CN was classified as an amine based sorbent, and for the purpose of this test 0.48 g was the sample size. This sorbent was tested for 42 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 19. The regeneration temperatures during the parametric tests were varied from 80°C to 120°C. The adsorption profiles in Figure 38 and the CO_2 capacity in Figure 39 were measured during parametric testing.

Table 19: Sorbent CN Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CN	Parametric	42	0.48	4	12	50	55	300	80 (Cycles 1-9) 100 (Cycles 10-19) 120 (Cycles 20-43)	600

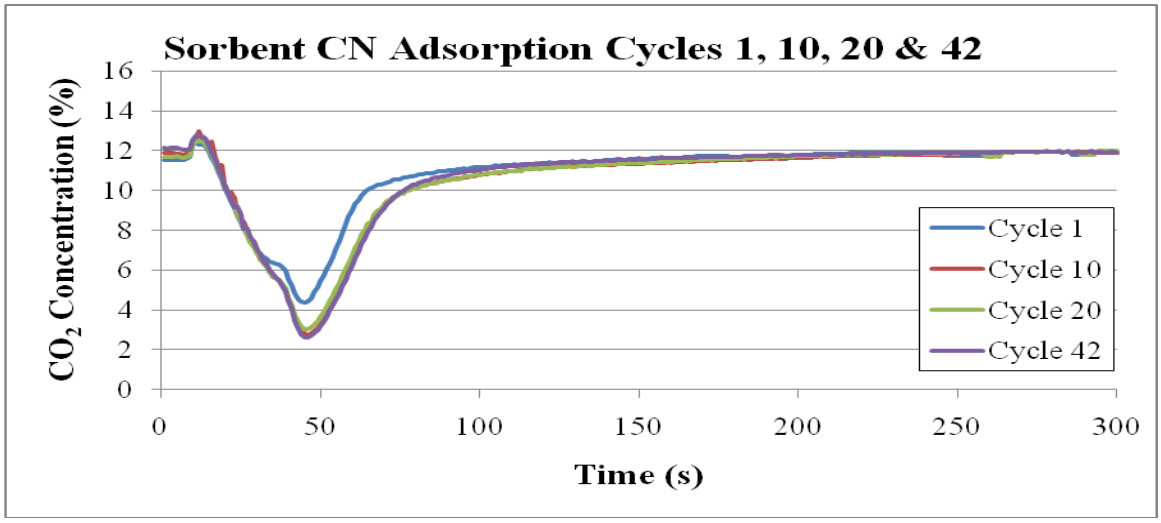

Figure 38: Sorbent CN Laboratory Adsorption Profiles

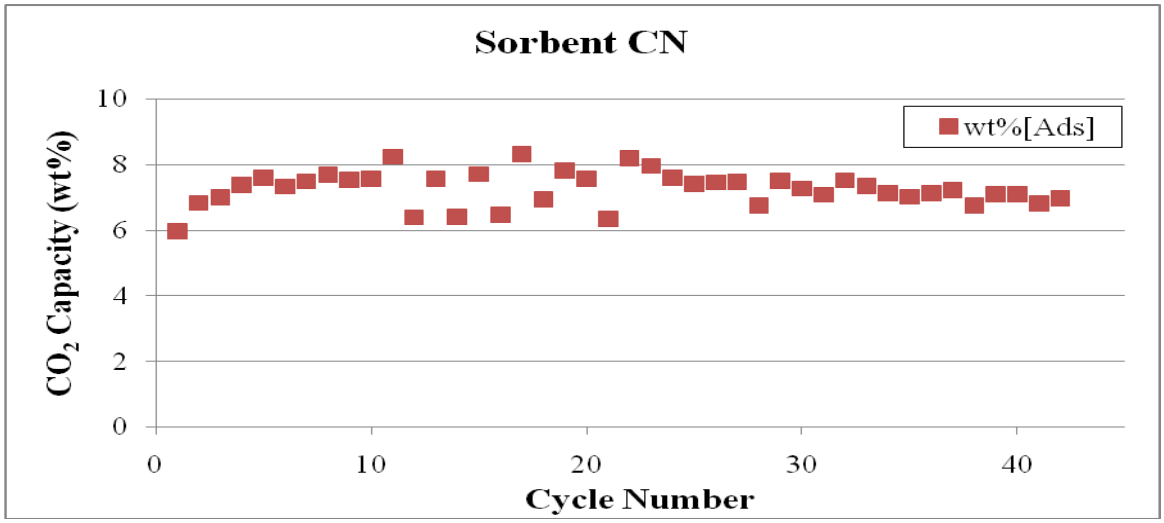

Figure 39: Sorbent CN Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 7.26 wt%, a specific heat of 1.0 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CN was approximately 1980 kJ/kg CO_2. There were no indications that this material lost any CO_2 capacity during the tests (at any temperature), indicating good cyclic stability. In addition, the CO_2 capacity was greater than many of the materials tested by ADA-ES to date, which resulted in a low theoretical regeneration energy. This material was considered a promising candidate.

Sorbent CO

Sorbent CO was classified as an amine based sorbent, and for the purpose of this test 0.50 g was the sample size. This sorbent was tested for 34 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 20. The regeneration temperatures during the parametric tests were varied from 80°C to 120°C. The adsorption profiles in Figure 40 and the CO_2 capacity in Figure 41 were measured during parametric testing.

Table 20: Sorbent CO Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CO	Parametric	34	0.50	4	12	50	55	300	80 (Cycles 1-9) 100 (Cycles 10-19) 120 (Cycles 20-35)	850

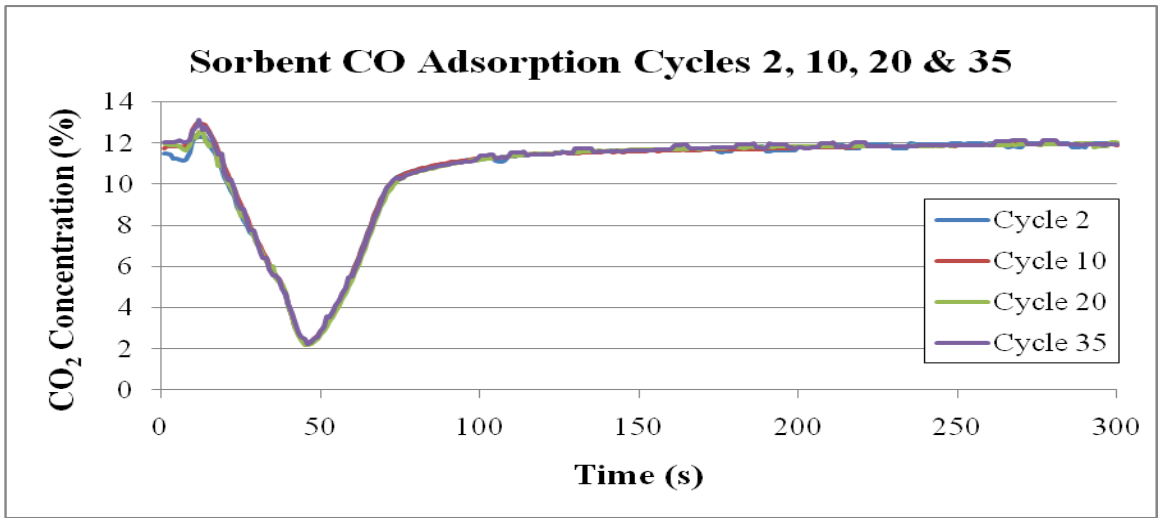

Figure 40: Sorbent CO Laboratory Adsorption Profiles

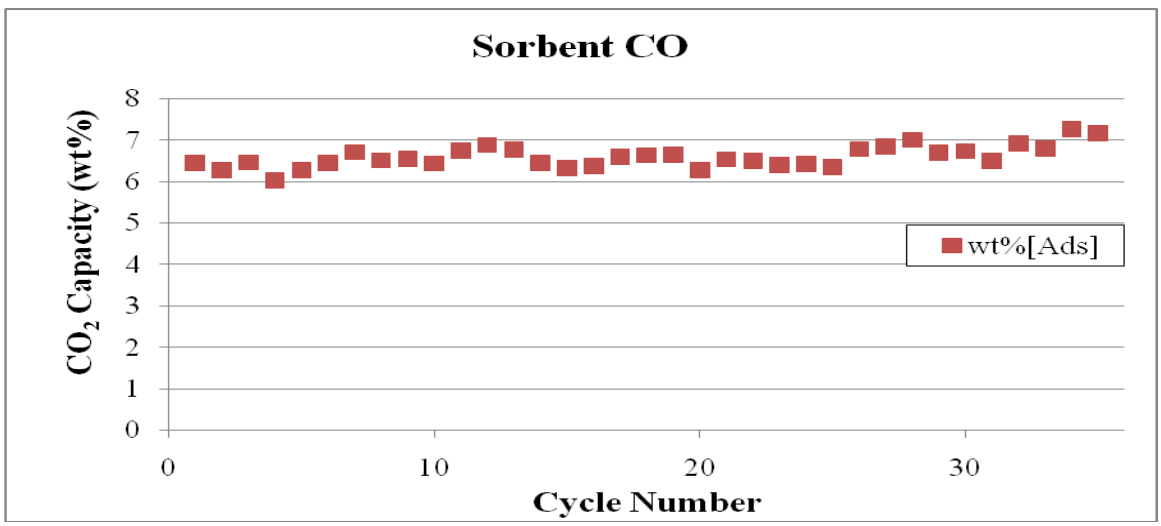

Figure 41: Sorbent CO Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 6.59 wt%, assuming a specific heat of 1.0 kJ/kg·K and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CO was approximately 2050 kJ/kg CO_2, which was lower than the MEA benchmark.

Sorbent CP

Sorbent CP was classified as an amine based sorbent, and for the purpose of this test 0.54 g was the sample size. This sorbent was tested for 110 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 21. The regeneration temperatures during the parametric tests were varied from 80°C to 120°C. The adsorption profiles in Figure 42 and the CO_2 capacity in Figure 43 were measured during parametric testing.

Table 21: Sorbent CP Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CP	Parametric	110	0.54	4	12	50	55	300	80 (Cycles 1-19) 100 (Cycles 20-25) 120 (Cycles 26-111)	650

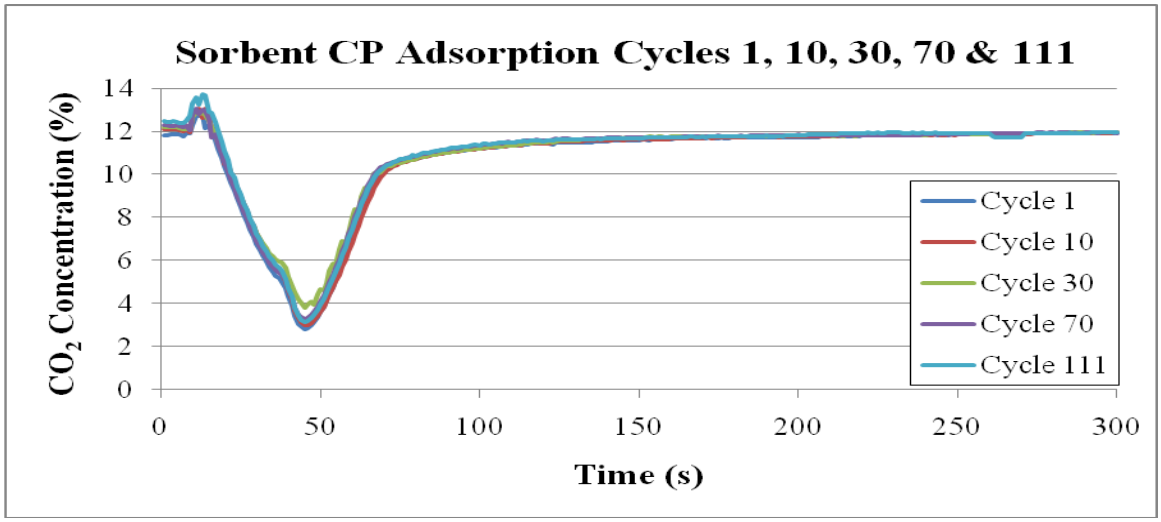

Figure 42: Sorbent CP Laboratory Adsorption Profiles

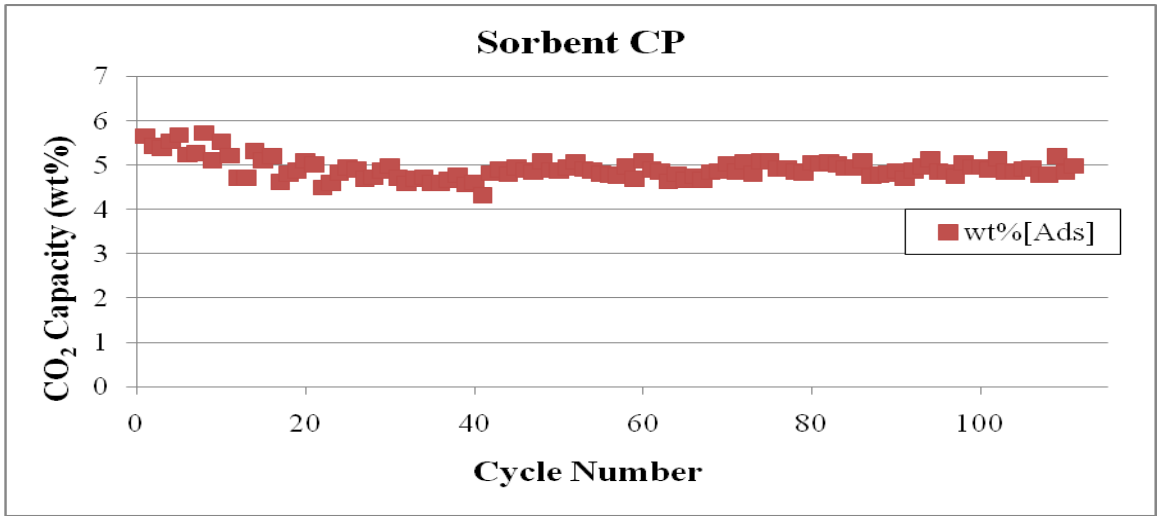

Figure 43: Sorbent CP Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 4.92 wt%, assuming a specific heat 1.0 kJ/kg·K and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CP was approximately 2280 kJ/kg CO_2. After an initial decrease in the CO_2 capacity, this material exhibited superior cyclic stability. However, the CO_2 capacity was not high enough to warrant further evaluation.

Sorbent CQ

Sorbent CQ was classified as an amine based sorbent, and for the purpose of this test 0.51 g was the sample size. This sorbent was tested for 274 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 22. The regeneration temperatures during the parametric tests were varied from 80°C to 120°C. The adsorption profiles in Figure 44 and the CO_2 capacity in Figure 45 were measured during parametric testing.

Table 22: Sorbent CQ Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Sample Final Size (g)	Weight Loss (%)	Adsorption Conditions					Regeneration Conditions	
						CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CQ	Parametric	274	0.51	0.46	9.67	12	4	50	55	250	80 (Cycles 1-9) 100 (Cycles 10-19) 120 (Cycles 20-35) 100 (Cycles 36-275)	600

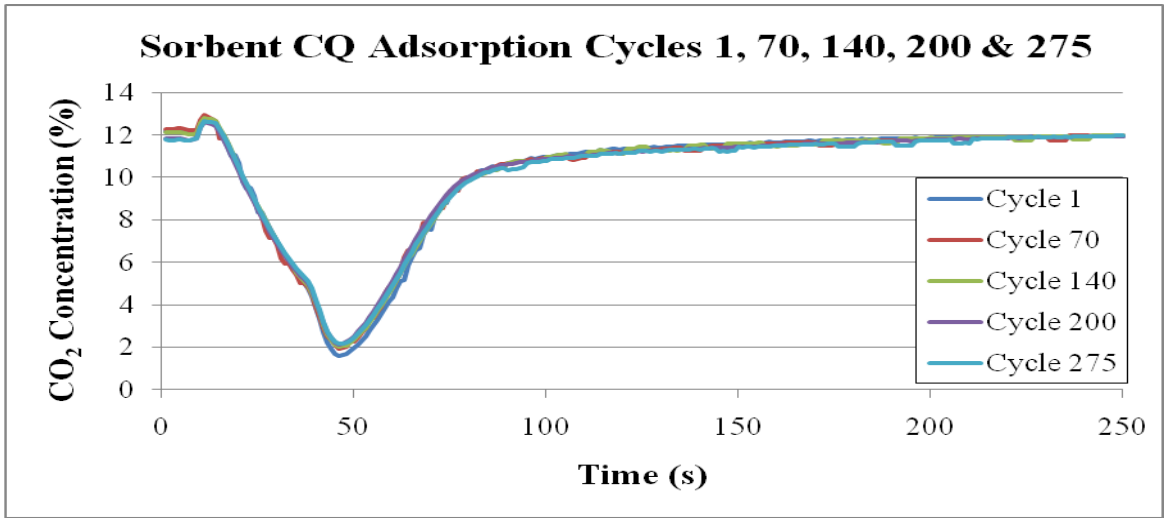

Figure 44: Sorbent CQ Laboratory Adsorption Profiles

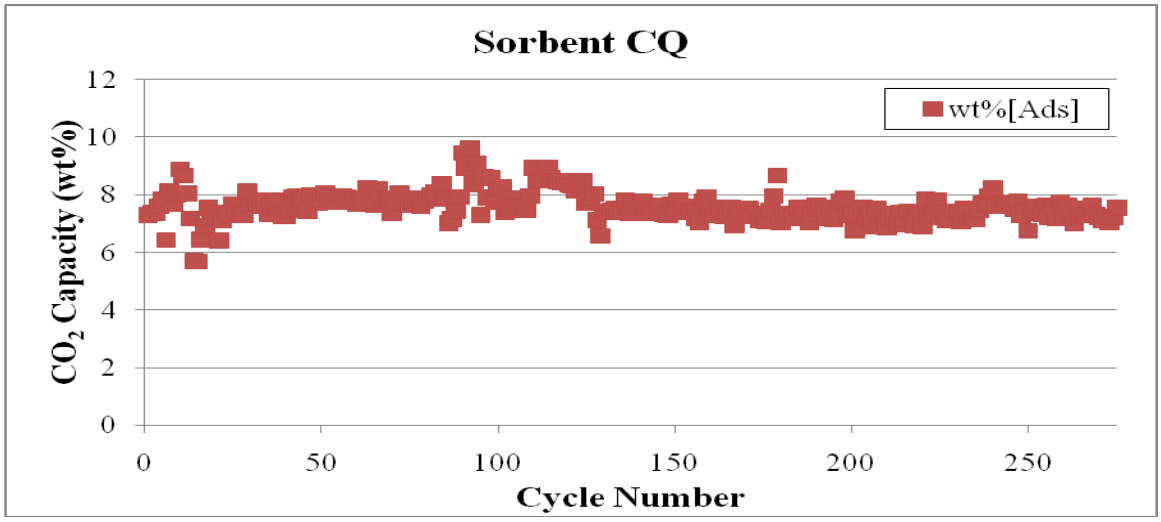

Figure 45: Sorbent CQ Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 7.59 wt%, a specific heat of 1.0 kJ/kg·K and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CQ was approximately 1960 kJ/kg CO_2. The CO_2 capacities were high enough to consider this sorbent above average and worth further evaluation.

Sorbent CR

Sorbent CR was classified as an amine based sorbent, and for the purpose of this test 0.53 g was the sample size. This sorbent was tested for 34 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 23. The regeneration temperatures during the parametric tests were varied from 80°C to 120°C. The adsorption profiles in Figure 46 and the CO_2 capacity in Figure 47 were measured during parametric testing.

Table 23: Sorbent CR Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CR	Parametric	34	0.53	4	12	50	55	300	80 (Cycles 1-9) 100 (Cycles 10-19) 120 (Cycles 20-35)	800

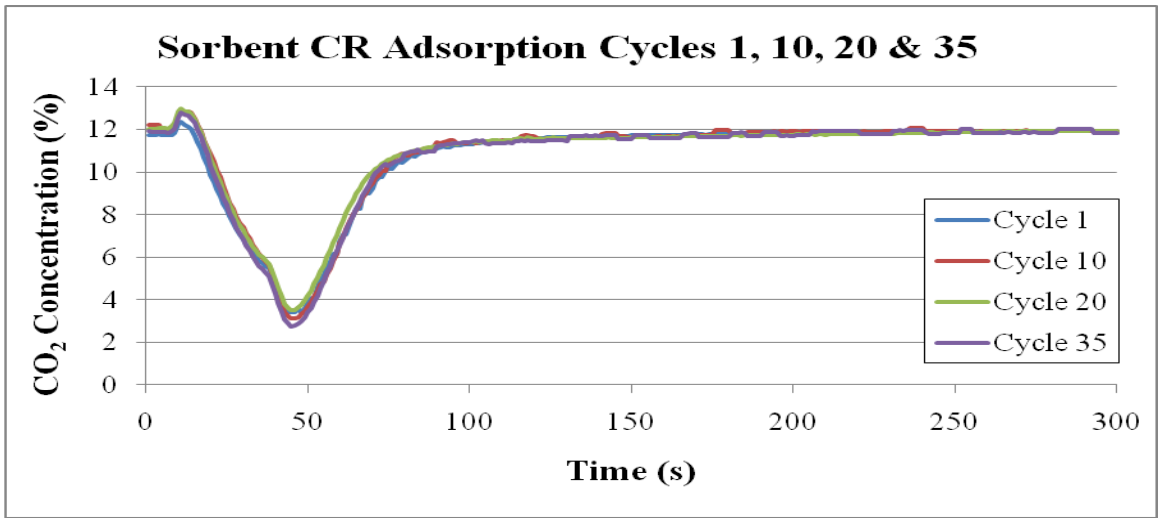

Figure 46: Sorbent CR Laboratory Adsorption Profiles

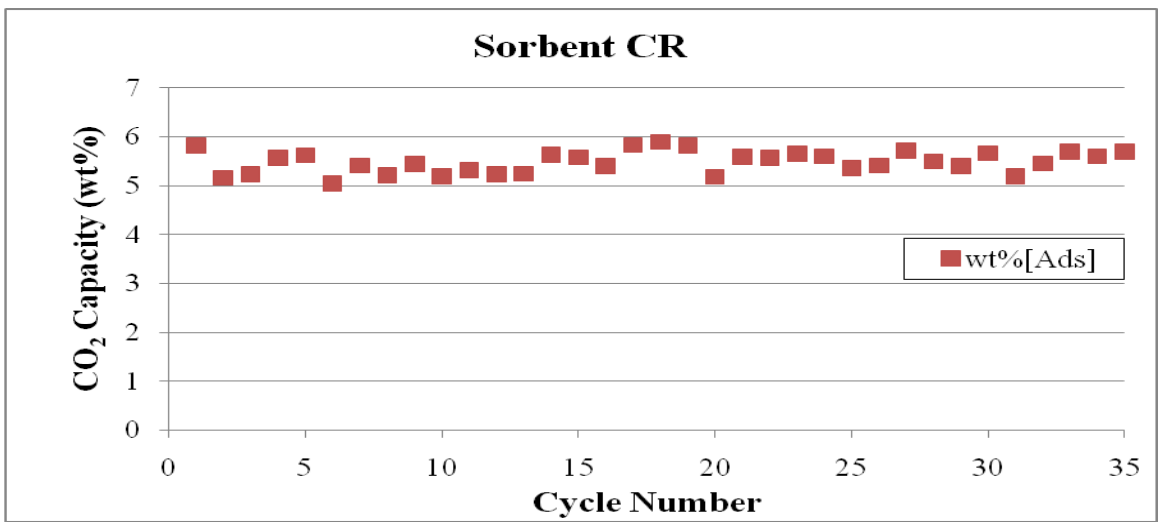

Figure 47: Sorbent CR Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 5.49 wt%, a specific heat of 1.0 kJ/kg·K and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CR was approximately 2180 kJ/kg CO_2. Although this material did not exhibit the largest working capacity, it exhibited superior cyclic stability. To be considered for further evaluation, however, the CO_2 capacity should be improved.

Sorbent CS

Sorbent CS was classified as an amine based sorbent, and for the purpose of this test 1.01 g was the sample size. This sorbent was tested for 31 full extended cycles at 100°C under automated operation in the laboratory. After an initial decrease in the CO_2 capacity, the sorbent was stable over the number of cycles tested. The testing conditions are listed in Table 24. The adsorption profiles in Figure 48 and the CO_2 capacity in Figure 49 were measured during extended testing.

Table 24: Sorbent CS Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CS	Extended	31	1.01	12	4	50	55	600	100 (Cycles 1-32)	1000

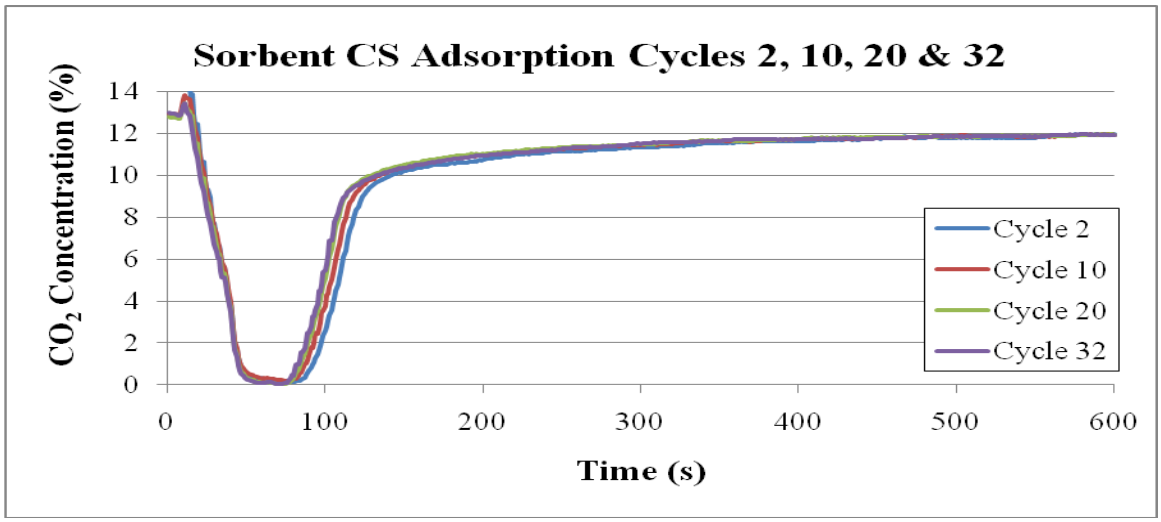

Figure 48: Sorbent CS Laboratory Adsorption Profiles

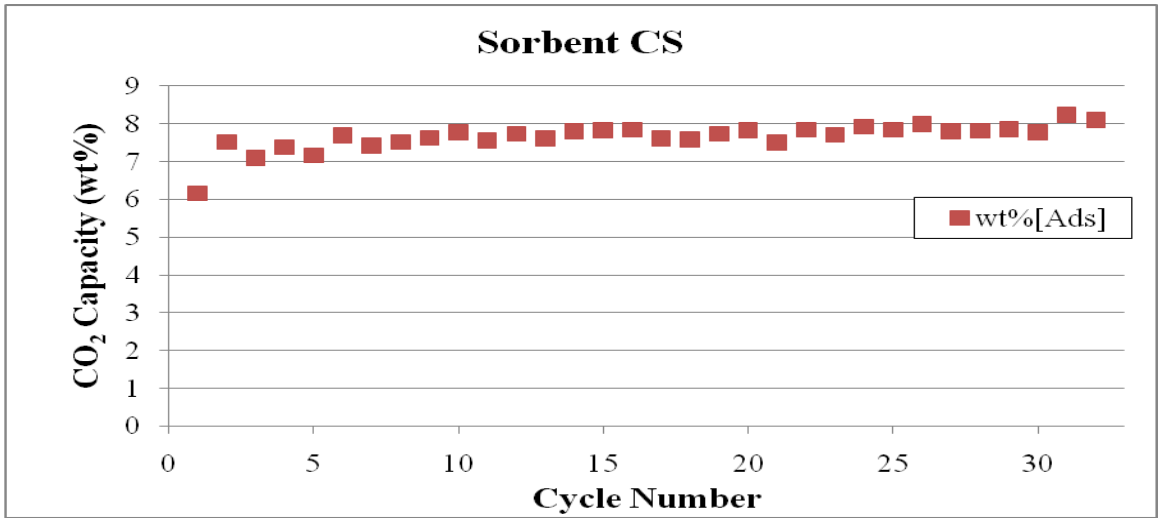

Figure 49: Sorbent CS Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 7.65 wt%, assuming a specific heat of 1.3 kJ/kg·K and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CS was approximately 2130 kJ/kg CO_2, which was lower than the MEA benchmark. Sorbent CS exhibited good CO_2 capacity relatively to other supported amines and good cyclic stability.

Sorbent CT

Sorbent CT was classified an amine based sorbent, and for the purpose of this test 1.00 g was the sample size. This sorbent was tested for 35 full extended cycles at 100°C under automated operation in the laboratory. The testing conditions are listed in Table 25. The adsorption profiles in Figure 50 and the CO_2 capacity in Figure 51 were measured during extended testing.

Table 25: Sorbent CT Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CT	Extended	35	1.00	12	4	50	55	400	100 (Cycles 1-36)	1100

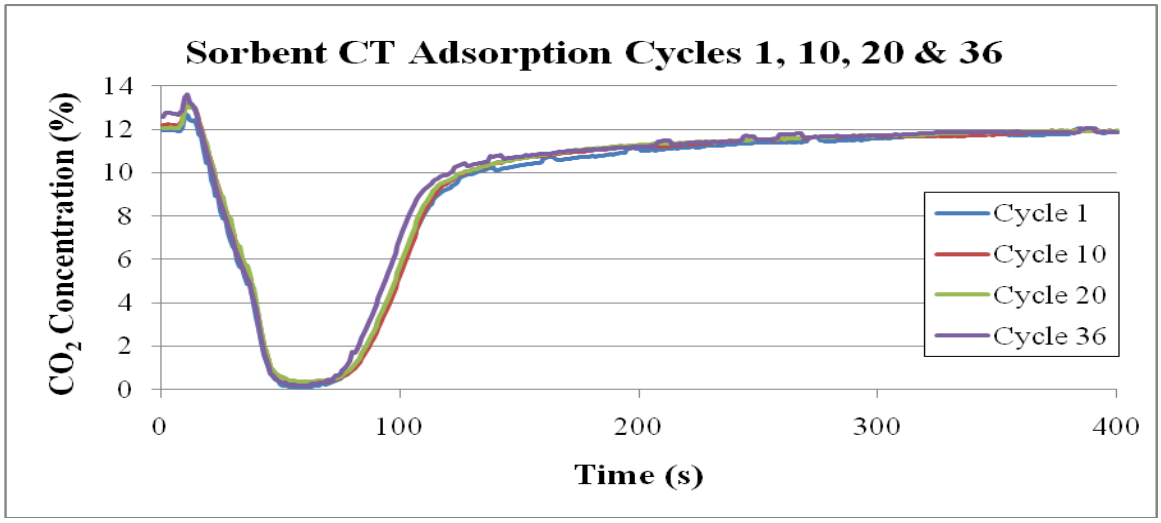

Figure 50: Sorbent CT Laboratory Adsorption Profiles

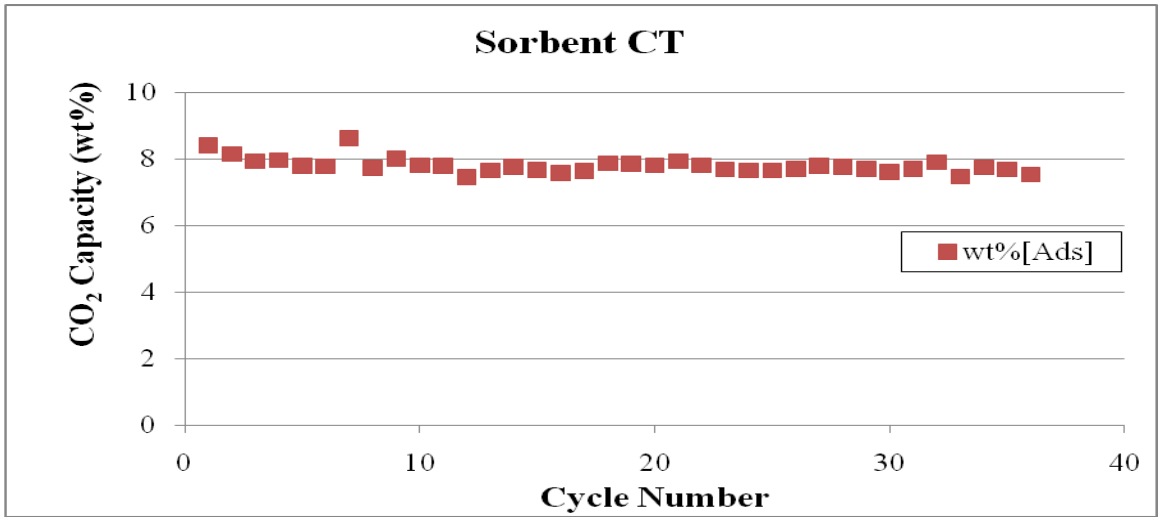

Figure 51: Sorbent CT Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 7.79 wt%, a specific heat of 1.3 kJ/kg·K and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CT is approximately 2110 kJ/kg CO_2, which was lower than the MEA benchmark. In addition, this material exhibited stability over the cyclic tests.

Sorbent CU

Sorbent CU was classified an amine based sorbent, and for the purpose of this test 1.02 g was the sample size. This sorbent was tested for 129 full extended cycles at 100°C under automated operation in the laboratory. The testing conditions are listed in Table 26. The adsorption profiles in Figure 52 and the CO_2 capacity in Figure 53 were measured during extended testing.

Table 26: Sorbent CU Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CU	Extended	129	1.02	12	4	50	55	400	100 (Cycles 1-130)	750

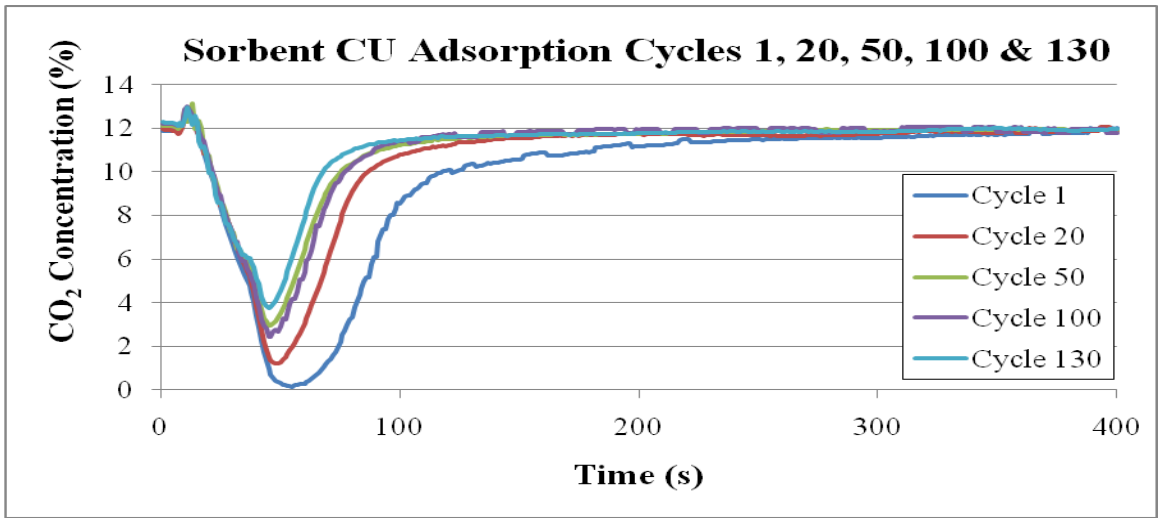

Figure 52: Sorbent CU Laboratory Adsorption Profiles

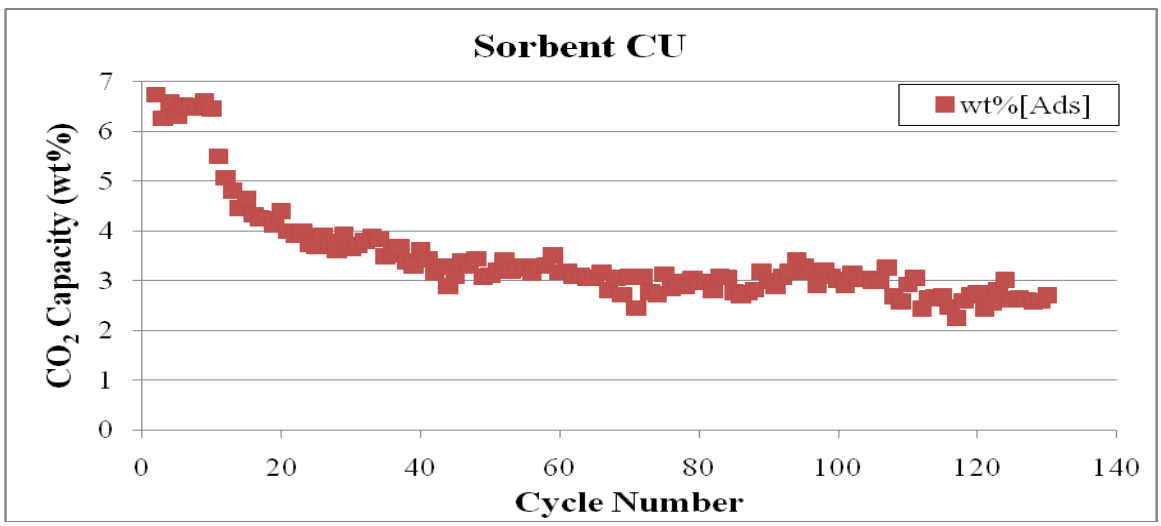

Figure 53: Sorbent CU Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 3.48 wt%, a specific heat of 1.3 kJ/kg·K and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CU was approximately 3040 kJ/kg CO_2. The CO_2 capacity of this material clearly decreased during the tests and, therefore, this material was not considered a viable.

Sorbent CV

Sorbent CV was classified an amine based sorbent, and for the purpose of this test 1.01 g was the sample size. This sorbent was tested for 38 full extended cycles at 100°C under automated operation in the laboratory. The testing conditions are listed in Table 27. The adsorption profiles in Figure 54 and the CO_2 capacity in Figure 55 were measured during extended testing.

Table 27: Sorbent CV Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CV	Extended	38	1.01	12	4	50	55	350	100 (Cycles 1-39)	900

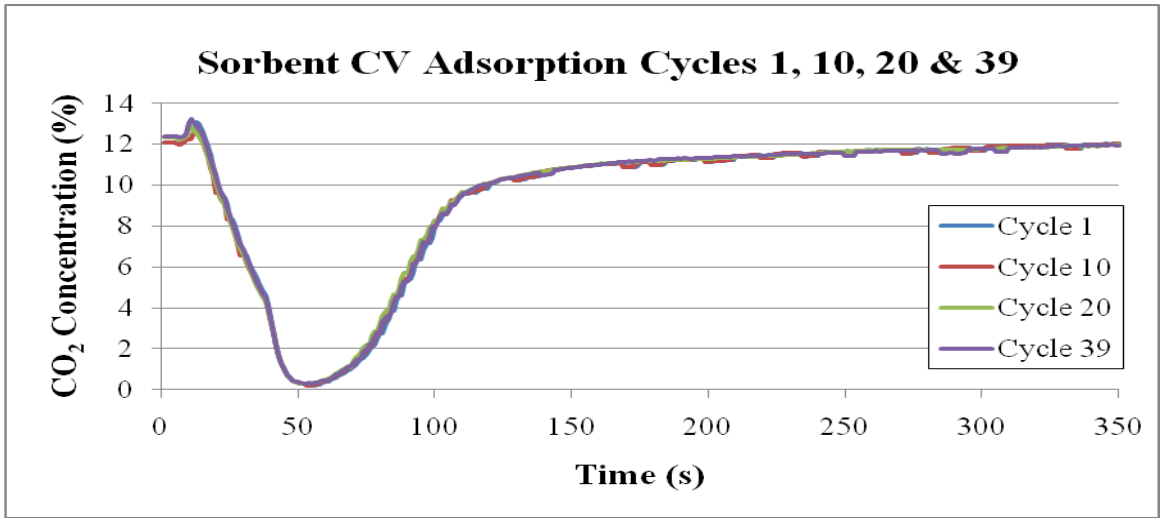

Figure 54: Sorbent CV Laboratory Adsorption Profiles

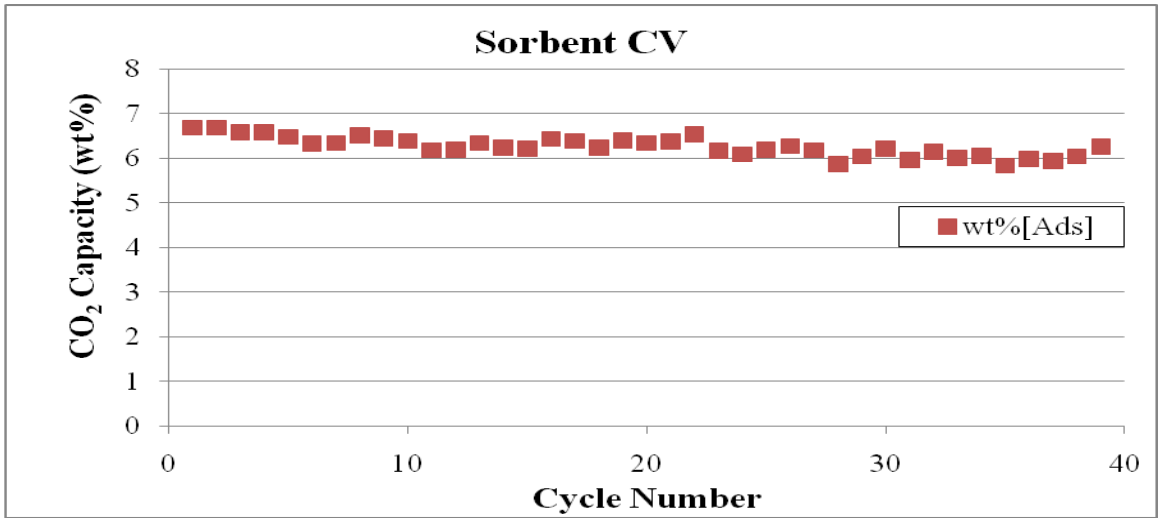

Figure 55: Sorbent CV Laboratory Total CO_2 Capacities

Based on the laboratory results, using a working CO_2 capacity of 6.26 wt%, a specific heat of 1.3 kJ/kg·K and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CV was approximately 2300 kJ/kg CO_2. Based on the adsorption profiles, this material exhibited good cyclic stability and the theoretical regeneration energy was lower than that of the MEA benchmark.

Sorbent CW

Sorbent CW was classified as an amine based sorbent, and for the purpose of this test 0.53 g was the sample size. This sorbent was tested for 39 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 28. The regeneration temperatures during the parametric tests were varied from 80°C to 120°C. The adsorption profiles in Figure 56 and the CO_2 capacity in Figure 57 were measured during parametric testing.

Table 28: Sorbent CW Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CW	Parametric	39	0.53	4	12	50	55	300	80 (Cycles 1-9) 100 (Cycles 10-19) 120 (Cycles 20-40)	700

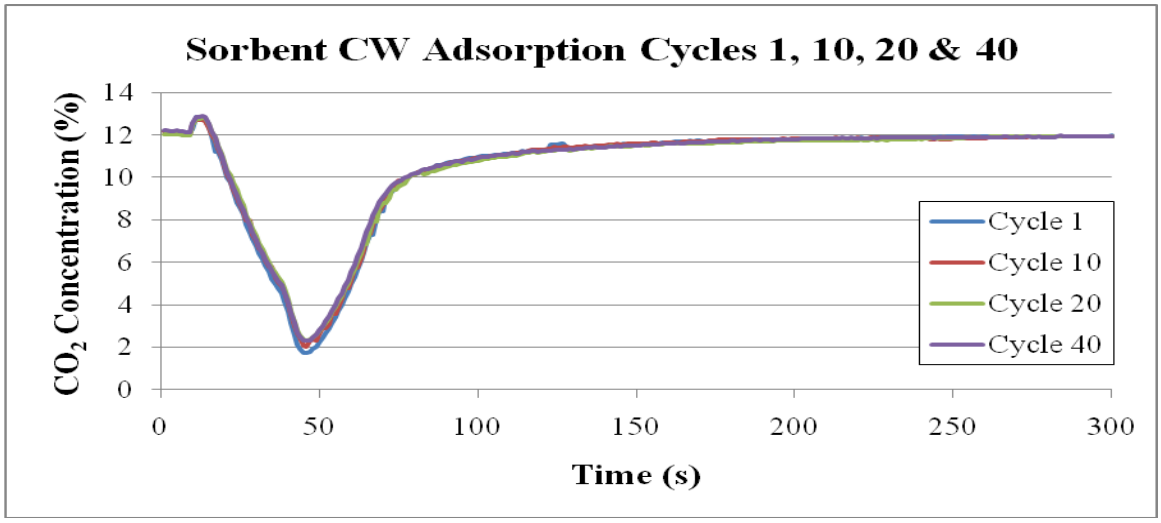

Figure 56: Sorbent CW Laboratory Adsorption Profiles

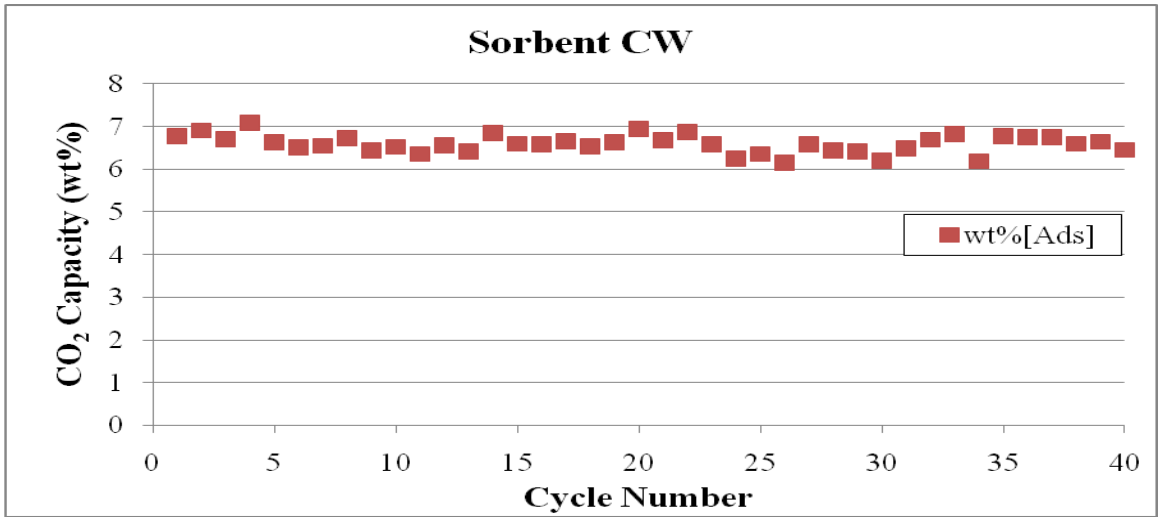

Figure 57: Sorbent CW Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 6.59 wt%, assuming a specific heat 1.0 kJ/kg·K and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CW was approximately 2050 kJ/kg CO_2, which was lower than the MEA benchmark. The behavior of this material was particularly promising because it exhibited a superior CO_2 cyclic stability.

Sorbent CX

Sorbent CX was classified as an amine based sorbent, and for the purposes of this test 1.16 g was the selected sample size. This sorbent achieved a CO_2 capacity of 0.76 wt%, which was lower than many amine-based materials evaluated under this program. Therefore, further testing of this material was not warranted.

Sorbent CY

Sorbent CY was classified as an amine based sorbent, and for the purpose of this test 1.07 g was the sample size. This sorbent was tested for 33 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 29. The regeneration temperatures during the parametric tests were varied from 80°C to 120°C. The adsorption profiles in Figure 58 and the CO_2 capacity in Figure 59 were measured during parametric testing.

Table 29: Sorbent CY Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CY	Parametric	33	1.07	4	12	50	55	300	80 (Cycles 1-9) 100 (Cycles 10-19) 120 (Cycles 20-34)	1250

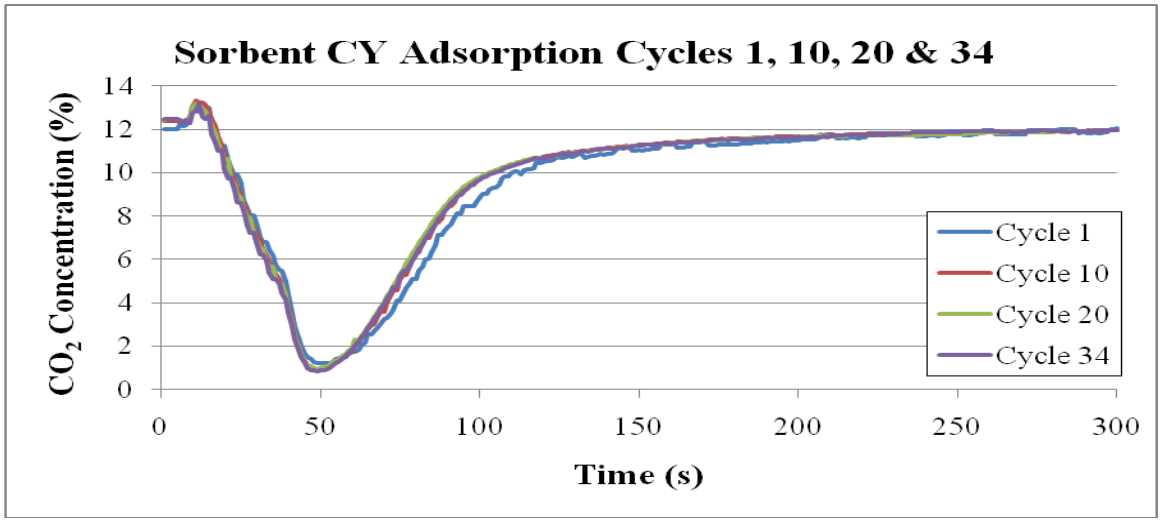

Figure 58: Sorbent CY Laboratory Adsorption Profiles

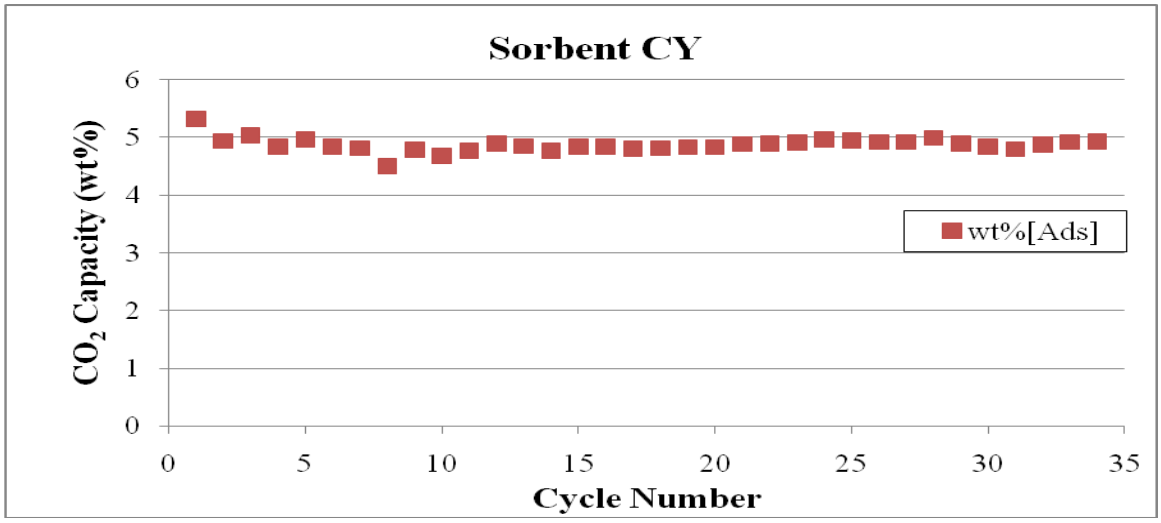

Figure 59: Sorbent CY Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 4.87 wt%, assuming a specific heat 1.0 kJ/kg·K and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CY was approximately 2290 kJ/kg CO_2. Although this material was stable, it did not exhibit a CO_2 capacity large enough, relative to other supported amines, to warrant further investigation.

Sorbent CZ

Sorbent CZ was classified as an amine based sorbent, and for the purpose of this test 1.10 g was the sample size. This sorbent was tested for 60 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 30. The regeneration temperatures during the parametric tests were varied from 80°C to 120°C. The adsorption profiles in Figure 60 and the CO_2 capacity in Figure 61 were measured during parametric testing.

Table 30: Sorbent CZ Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
CZ	Parametric	60	1.10	4	12	50	55	400	80 (Cycles 1-9) 100 (Cycles 10-19) 120 (Cycles 20-61)	1800

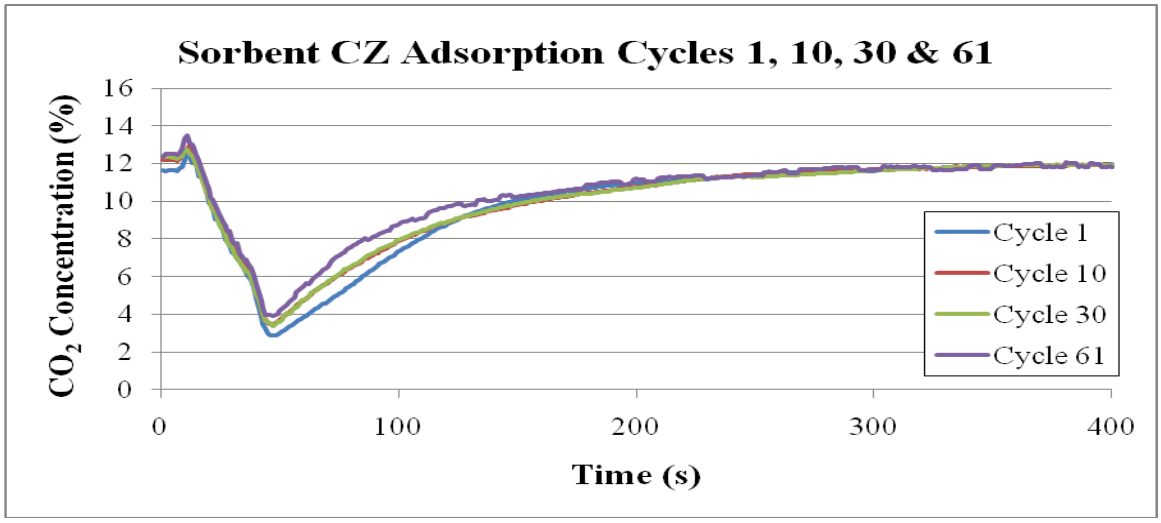

Figure 60: Sorbent CZ Laboratory Adsorption Profiles

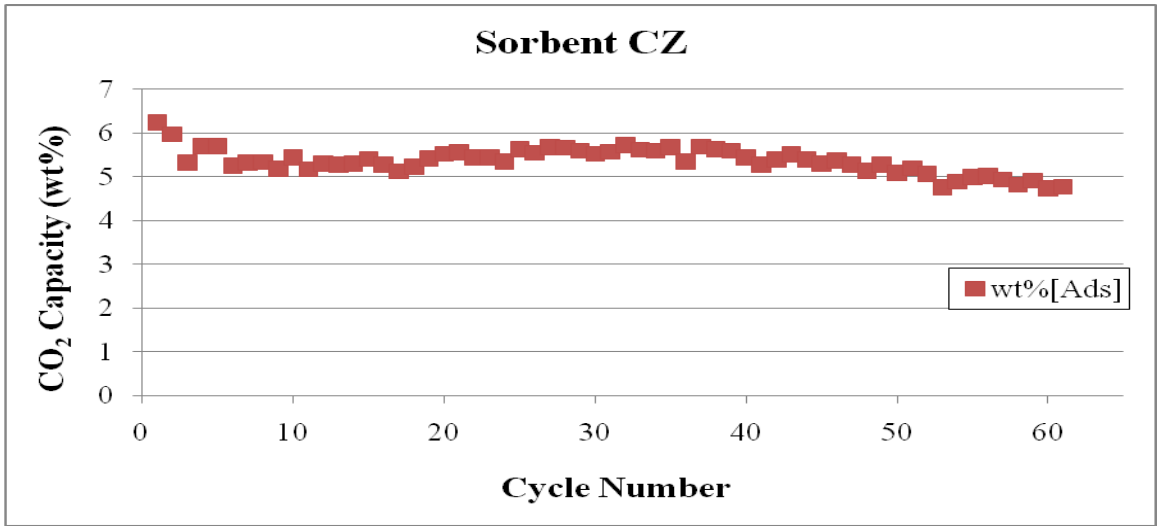

Figure 61: Sorbent CZ Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 5.36 wt%, a specific heat of 1.0 kJ/kg·K and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent CZ was approximately 2200 kJ/kg CO_2. Although this material did exhibit acceptable cyclic stability (except at 120°C), the shape of the adsorption profile shown in Figure 60 was not favorable. This type of adsorption profile indicates slow kinetics, possibly caused by mass diffusion limitations, which will become very important (and costly) as equipment/process options are considered for scale-up.

Sorbent DA

Sorbent DA was classified as an amine based sorbent, and for the purpose of this test 1.02 g was the sample size. This sorbent was tested for 30 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 31. The regeneration temperatures during the parametric tests were varied from 80°C to 120°C. The adsorption profiles in Figure 62 and the CO_2 capacity in Figure 63 were measured during parametric testing.

Table 31: Sorbent DA Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
DA	Parametric	30	1.02	4	12	50	55	400	80 (Cycles 1-9) 100 (Cycles 10-19) 120 (Cycles 20-31)	900

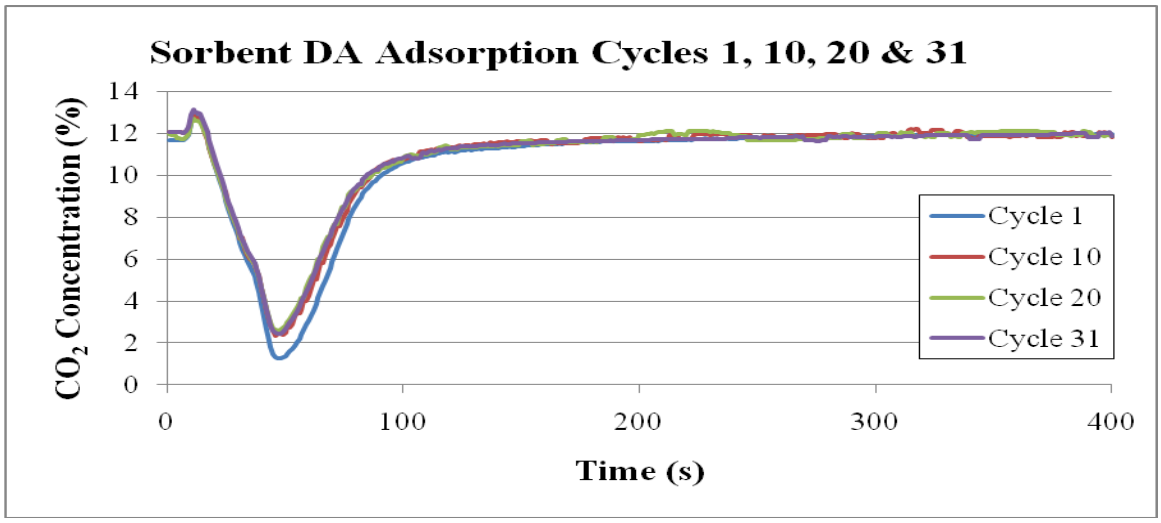

Figure 62: Sorbent DA Laboratory Adsorption Profiles

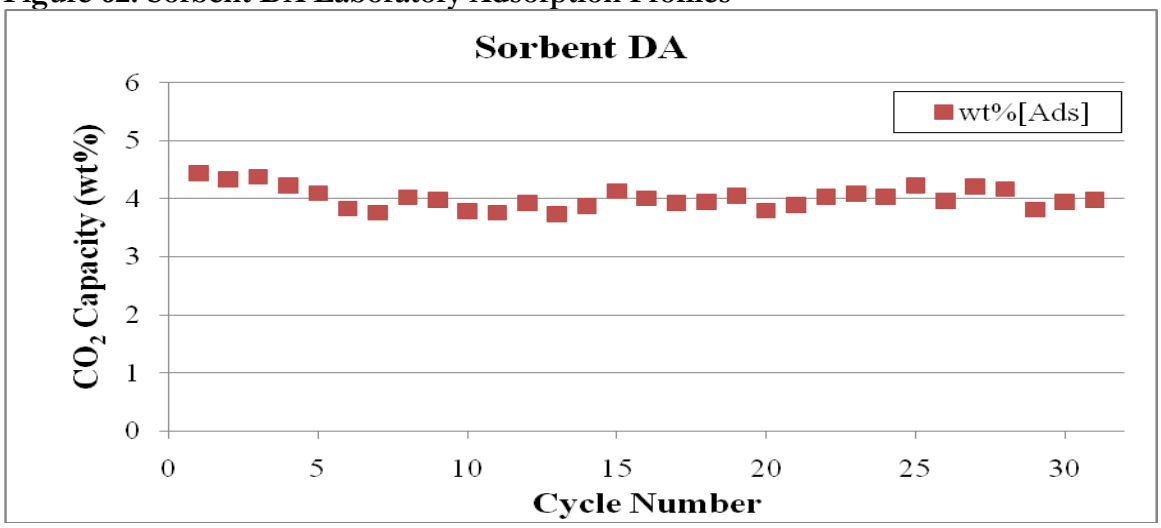

Figure 63: Sorbent DA Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 4.01 wt%, assuming a specific heat 1.0 kJ/kg·K and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent DA was approximately 2490 kJ/kg CO_2. This material exhibited good stability, but the CO_2 capacity was too low to warrant further evaluation.

Sorbent DB

Sorbent DB was classified as an amine based sorbent, and for the purposes of this test 1.09 g was the selected sample size. This achieved a CO_2 capacity of 0.73 wt%, which was lower than many amine-based materials evaluated under this program. Therefore, further testing of this material was not warranted.

Sorbent DC

Sorbent DC was classified as an amine based sorbent, and for the purpose of this test 1.02 g was the sample size. This sorbent was tested for 31 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 32. The regeneration temperatures during the parametric tests were varied from 80°C to 120°C. The adsorption profiles in Figure 64 and the CO_2 capacity in Figure 65 were measured during parametric testing.

Table 32: Sorbent DC Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
DC	Parametric	31	1.02	4	12	50	55	250	80 (Cycles 1-9) 100 (Cycles 10-19) 120 (Cycles 20-32)	750

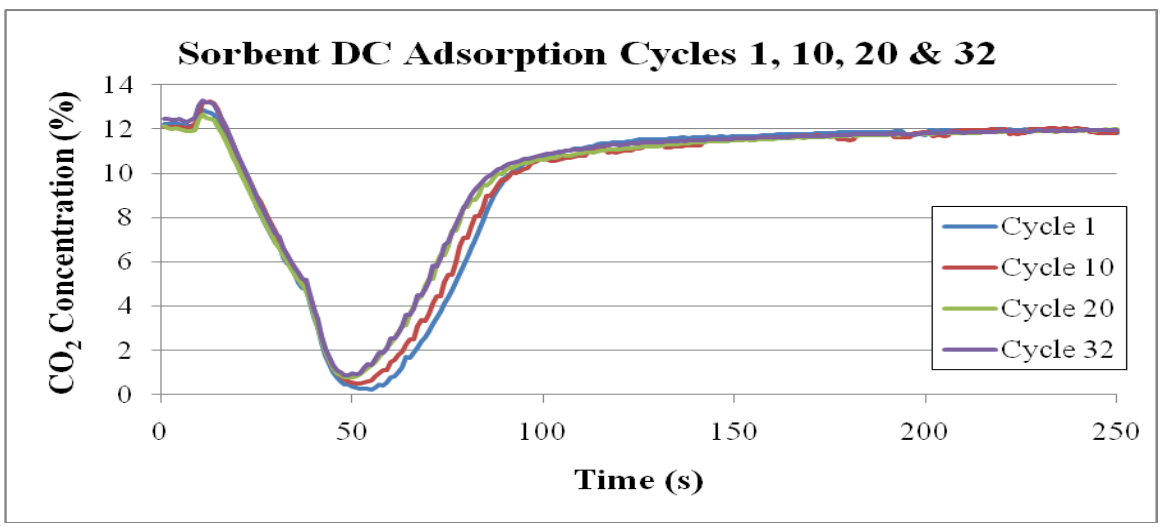

Figure 64: Sorbent DC Laboratory Adsorption Profiles

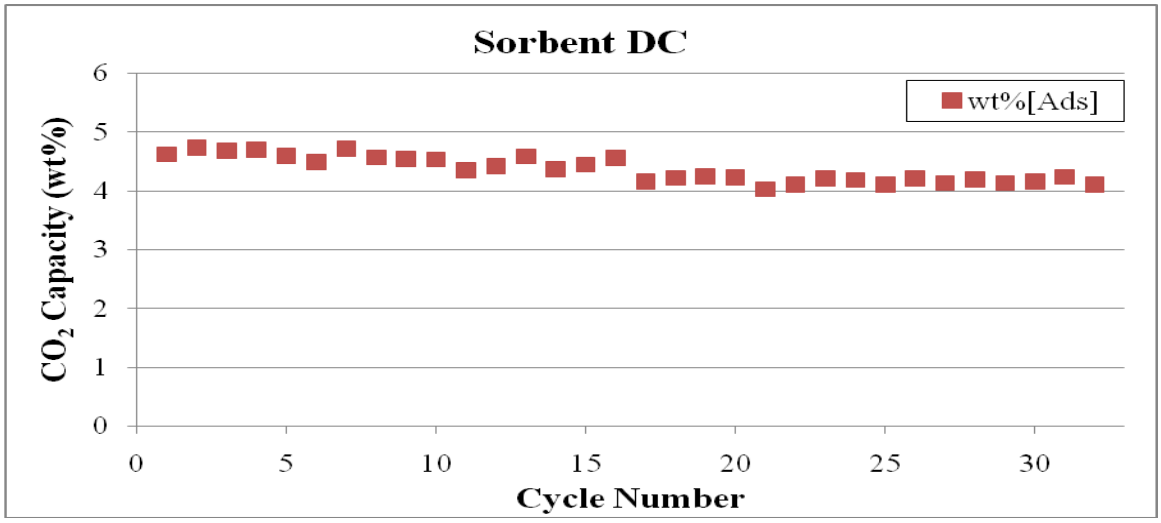

Figure 65: Sorbent DC Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 4.36 wt%, assuming a specific heat 1.0 kJ/kg·K and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent DC was approximately 2400 kJ/kg CO_2. The breakthrough curves indicate that there may have been a slight loss in CO_2 capacity, especially at regeneration temperatures greater than 80°C, although any degradation did not appear to be significant. Unfortunately, this material did not exhibit a CO_2 capacity high enough to warrant further evaluation.

Sorbent DD

Sorbent DD was classified as an amine based sorbent, and for the purpose of this test 1.00 g was the sample size. This sorbent was tested for 32 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 33. The regeneration temperatures during the parametric tests were varied from 80°C to 120°C. The adsorption profiles in Figure 66 and the CO_2 capacity in Figure 67 were measured during parametric testing.

Table 33: Sorbent DD Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
DD	Parametric	32	1.00	4	12	50	55	300	80 (Cycles 1-9) 100 (Cycles 10-19) 120 (Cycles 20-33)	800

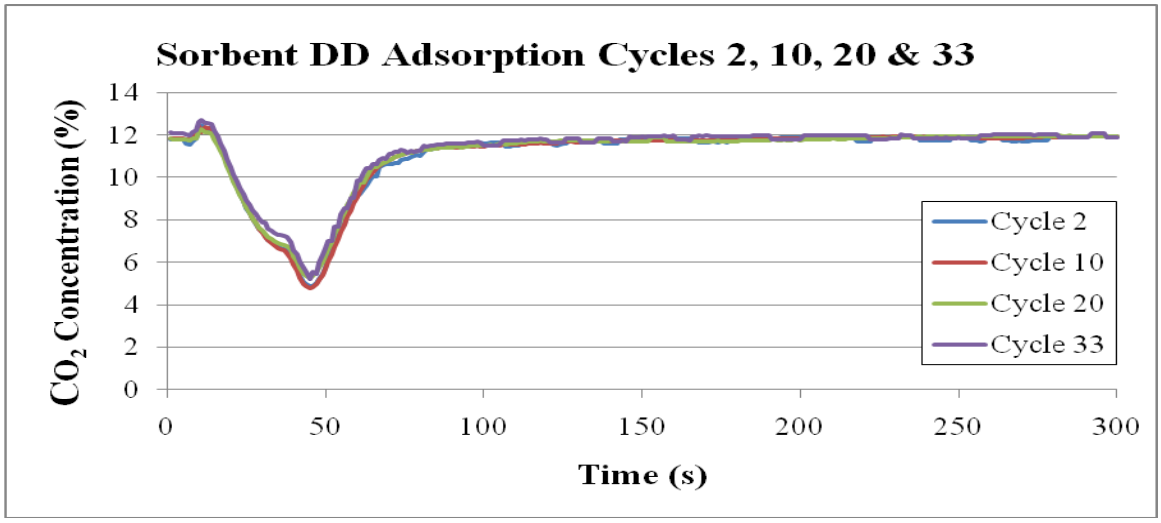

Figure 66: Sorbent DD Laboratory Adsorption Profiles

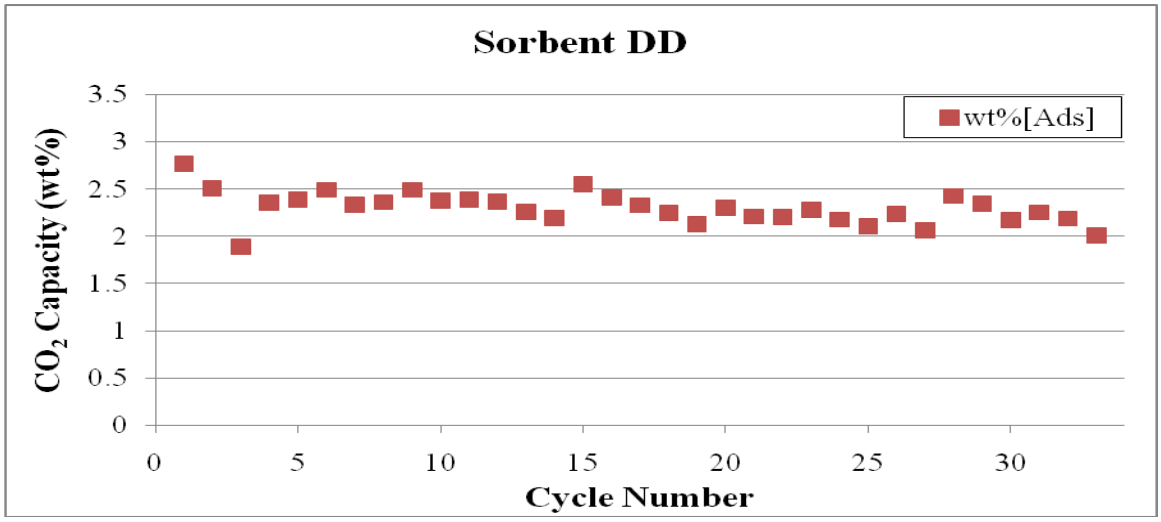

Figure 67: Sorbent DD Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 2.30 wt%, assuming a specific heat 1.0 kJ/kg·K and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent DD was approximately 3320 kJ/kg CO_2, which was higher than the MEA benchmark. Although this material exhibited good cyclic stability, the CO_2 capacity was not high enough to warrant further evaluation.

Sorbent DE

Sorbent DE was classified as an amine based sorbent, and for the purposes of this test 1.00 g was the selected sample size. This achieved a CO_2 capacity of 1.67 wt%, which was lower than many amine-based materials evaluated under this program. Therefore, further testing of this material was not warranted.

Sorbent DF

Sorbent DF was classified as an amine based sorbent, and for the purpose of this test 1.00 g was the sample size. This sorbent was tested for 22 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 34. The regeneration temperatures during the parametric tests were varied from 80°C to 120°C. The adsorption profiles in Figure 68 and the CO_2 capacity in Figure 69 were measured during parametric testing.

Table 34: Sorbent DF Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Adsorption Conditions					Regeneration Conditions	
				CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
DF	Parametric	22	1.00	4	12	50	55	300	80 (Cycles 1-9) 100 (Cycles 10-19) 120 (Cycles 20-23)	1500

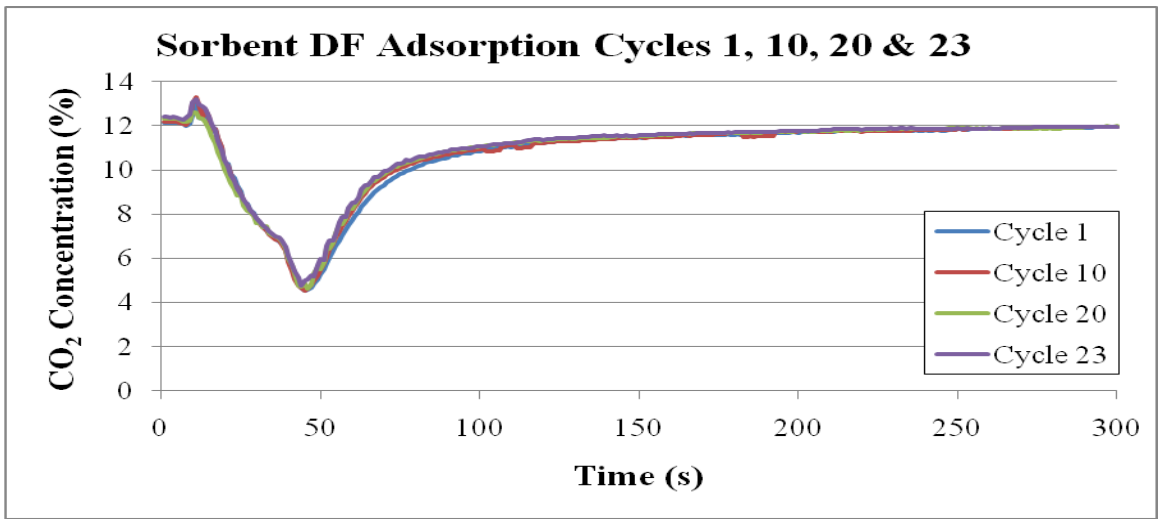

Figure 68: Sorbent DF Laboratory Adsorption Profiles

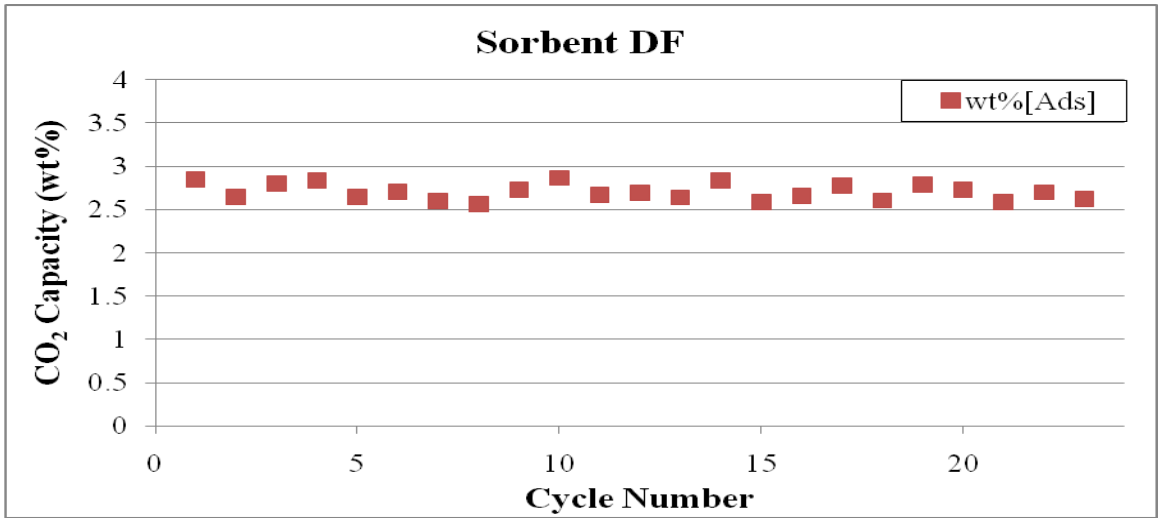

Figure 69: Sorbent DF Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 2.70 wt%, a specific heat of 1.0 kJ/kg·K and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent DF was approximately 3030 kJ/kg CO_2, which was approximately the same as the benchmark MEA. Although this sorbent exhibited good cyclic stability, the poor CO_2 capacity compared to the other materials leads to the conclusion that further testing was not necessary.

Sorbent DG

Sorbent DG was classified as a hydrotalcite, and for the purposes of this test 1.01 g was the selected sample size. This sorbent demonstrated a CO_2 capacity of 0.70 wt%, which was lower than many materials evaluated under this program. This CO_2 capacity was too low to warrant further investigation.

Sorbent DH

Sorbent DH was classified as a hydrotalcite, and for the purpose of this test 1.00 g was the sample size. This sorbent was tested for 31 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 35. The regeneration temperatures during the parametric tests were varied from 100°C to 190°C. The adsorption profiles in Figure 70 and the CO_2 capacity in Figure 71 were measured during parametric testing.

Table 35: Sorbent DH Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Sample Final Size (g)	Weight Loss (%)	Adsorption Conditions					Regeneration Conditions	
						CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
DH	Parametric	31	1.00	0.97	2.6	12	4	50	80	250	100 (Cycles 1-9) 130 (Cycles 8-15) 160 (Cycles 16-25) 190 (Cycles 26-32)	700

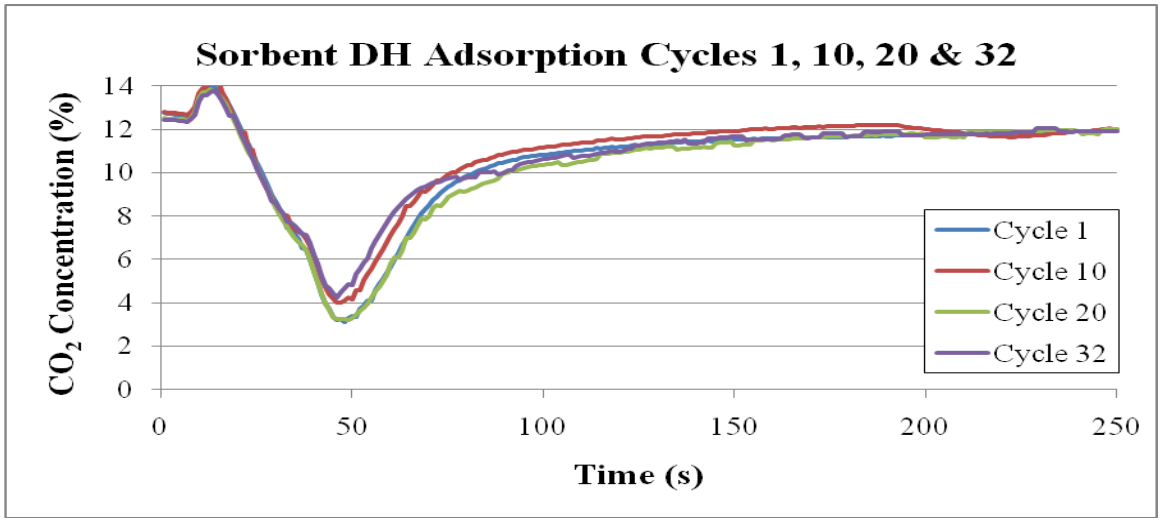

Figure 70: Sorbent DH Laboratory Adsorption Profiles

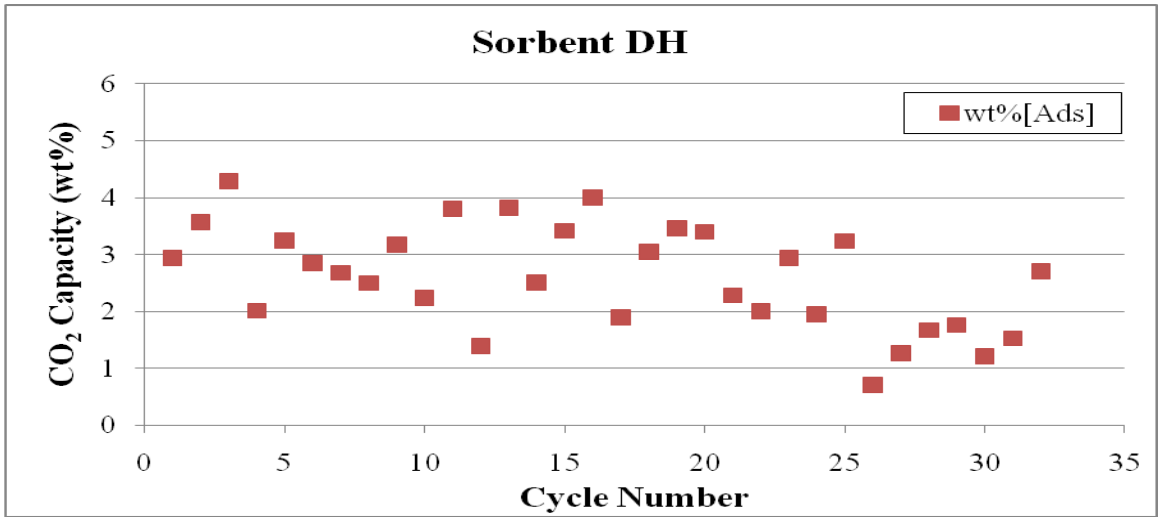

Figure 71: Sorbent DH Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 2.91 wt%, assuming a specific heat 2.0 kJ/kg·K and a regeneration temperature of 130°C, the theoretical regeneration energy for sorbent DH was approximately 5490 kJ/kg CO_2, which was significantly higher than the benchmark MEA. This CO_2 capacity was too low to warrant further investigation.

Sorbent DI

Sorbent DI was classified as a hydrotalcite, and for the purpose of this test 0.51 g was the sample size. This sorbent was tested for 159 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 36. The regeneration temperatures during the parametric tests were varied from 100°C to 190°C. The adsorption profiles in Figure 72 and the CO_2 capacity in Figure 73 were measured during parametric testing.

Table 36: Sorbent DI Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Sample Final Size (g)	Weight Loss (%)	Adsorption Conditions					Regeneration Conditions	
						CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
DI	Parametric	159	0.51	0.49	3.03	12	4	50	80	300	100 (Cycles 1-19) 130 (Cycles 20-39) 160 (Cycles 40-59) 190 (Cycles 60-160)	700

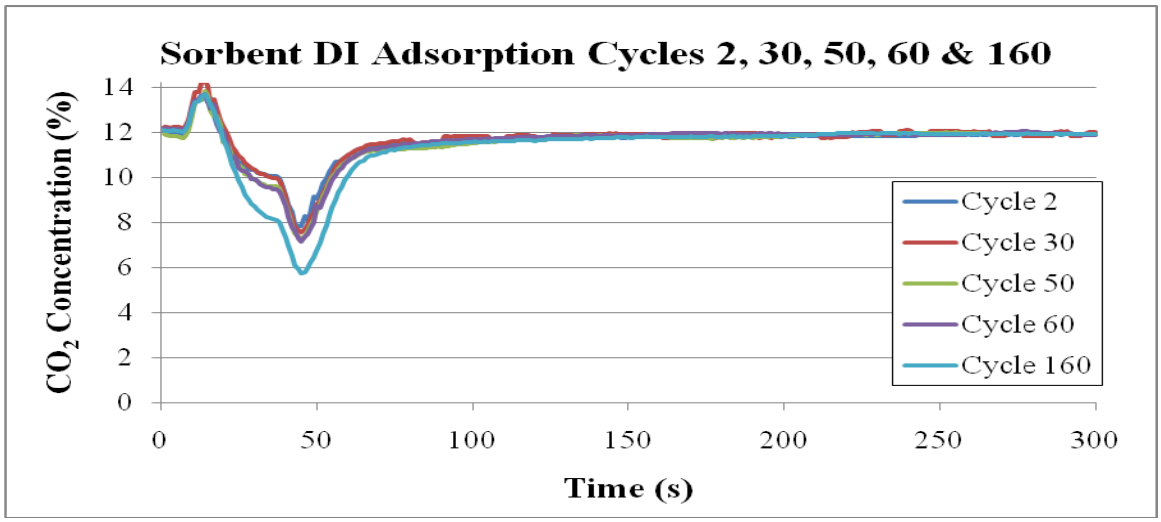

Figure 72: Sorbent DI Laboratory Adsorption Profiles

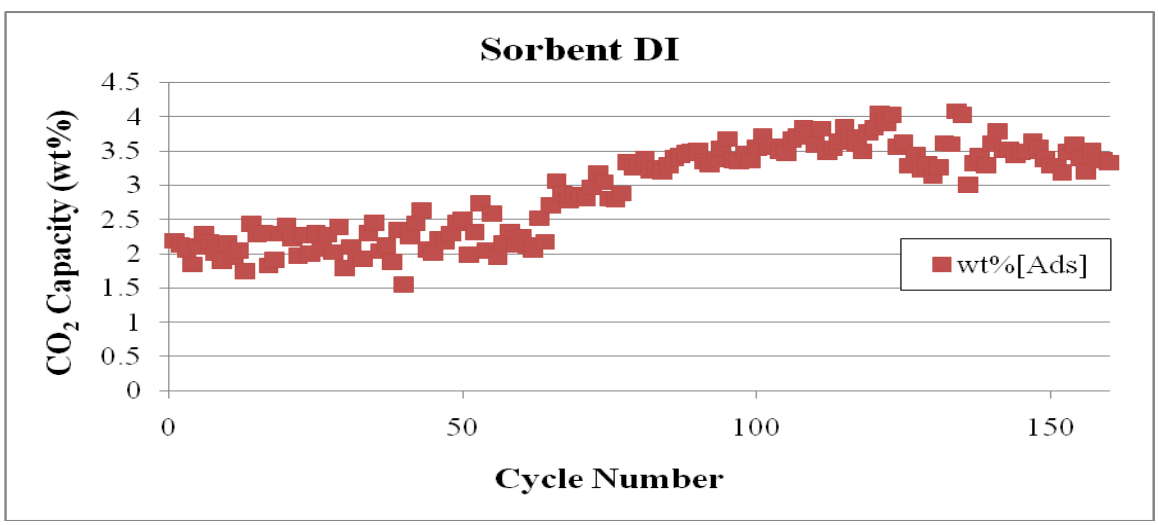

Figure 73: Sorbent DI Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 2.92 wt%, assuming a specific heat 2.0 kJ/kg·K and a regeneration temperature of 130°C, the theoretical regeneration energy for sorbent DI was approximately 5470 kJ/kg CO_2. This energy penalty was greater than that of aqueous amines, so this material was not a good candidate for CO_2 capture. However, it is important to note that this material exhibited superior stability, even at high regeneration temperatures.

Sorbent DJ

Sorbent DJ was classified as a hydrotalcite, and for the purpose of this test 0.24 g was the sample size. This sorbent was tested for 42 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 37. The regeneration temperatures during the parametric tests were varied from 100°C to 190°C. The adsorption profiles in Figure 74 and the CO_2 capacity in Figure 75 were measured during parametric testing. A significant decrease the in CO_2 uptake occurred once the regeneration temperature was increased to 190°C, this can be observed in Figure 74 because the CO_2 removal is reduced for cycle 43. Therefore, this material exhibited some sensitivity to high temperature, although 190°C is not within the expected range of operating temperatures.

Table 37: Sorbent DJ Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Sample Final Size (g)	Weight Loss (%)	Adsorption Conditions					Regeneration Conditions	
						CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
DJ	Parametric	42	0.24	0.24	1.62	12	4	50	80	300	100 (Cycles 1-9) 130 (Cycles 10-19) 160 (Cycles 20-29) 190 (Cycles 30-43)	700

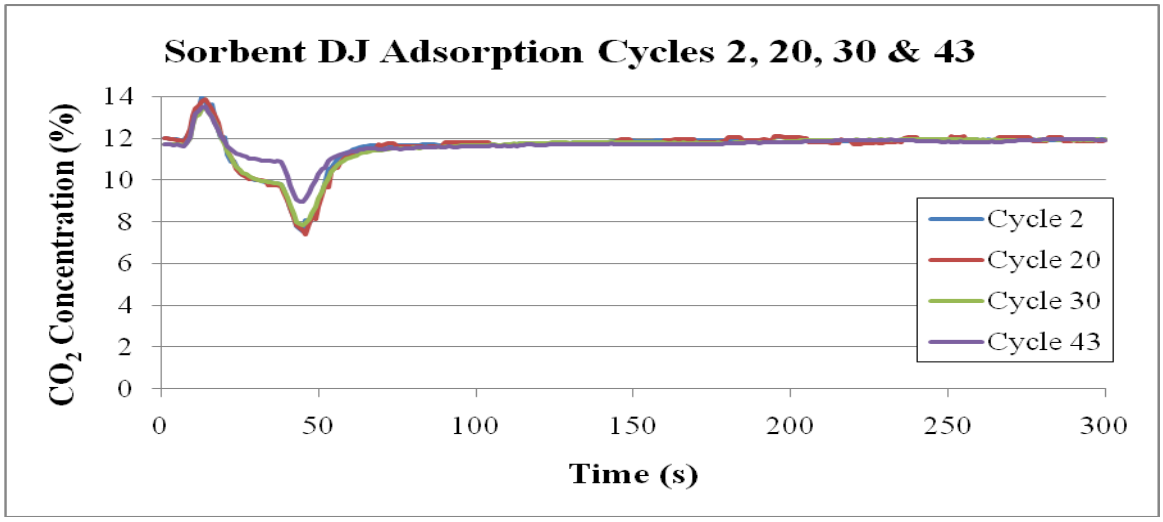

Figure 74: Sorbent DJ Laboratory Adsorption Profiles

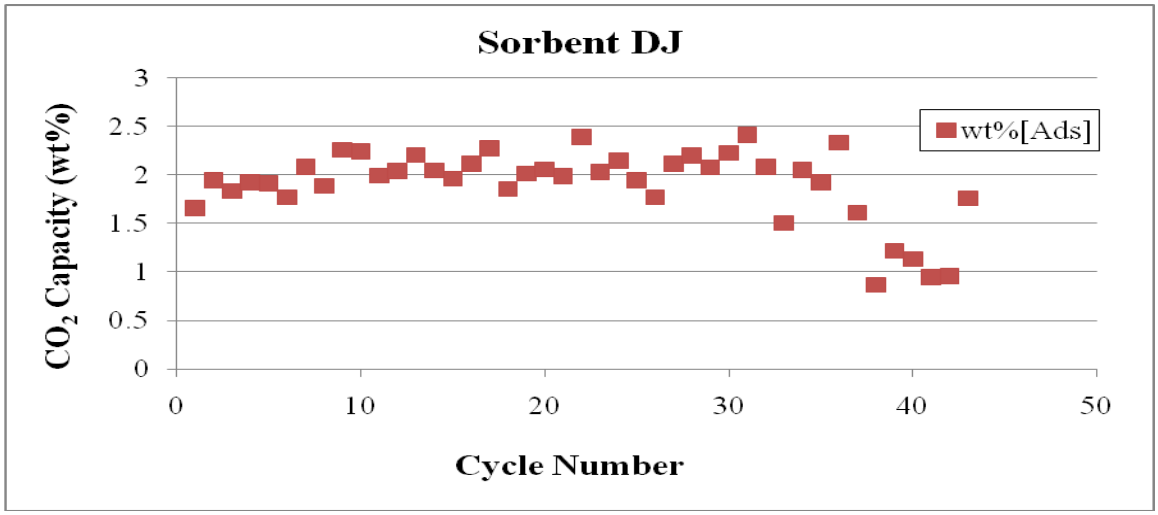

Figure 75: Sorbent DJ Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 2.02 wt%, assuming a specific heat 2.0 kJ/kg·K and a regeneration temperature of 130°C, the theoretical regeneration energy for sorbent DJ was approximately 6990 kJ/kg CO_2. This material exhibited good cyclic stability at temperatures below 190°C. This sorbent has low CO_2 capacity therefore was not considered a viable candidate for CO_2 capture.

Sorbent DK

Sorbent DK was classified as a hydrotalcite, and for the purpose of this test 0.25 g was the sample size. This sorbent was tested for 154 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 38. The regeneration temperatures during the parametric tests were varied from 100°C to 190°C. The adsorption profiles in Figure 76 and the CO_2 capacity in Figure 77 were measured during parametric testing.

Table 38: Sorbent DK Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Sample Final Size (g)	Weight Loss (%)	Adsorption Conditions					Regeneration Conditions	
						CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
DK	Parametric	154	0.25	0.25	0.20	12	4	50	80	300	100 (Cycles 1-19) 130 (Cycles 20-39) 160 (Cycles 40-59) 190 (Cycles 60-155)	600

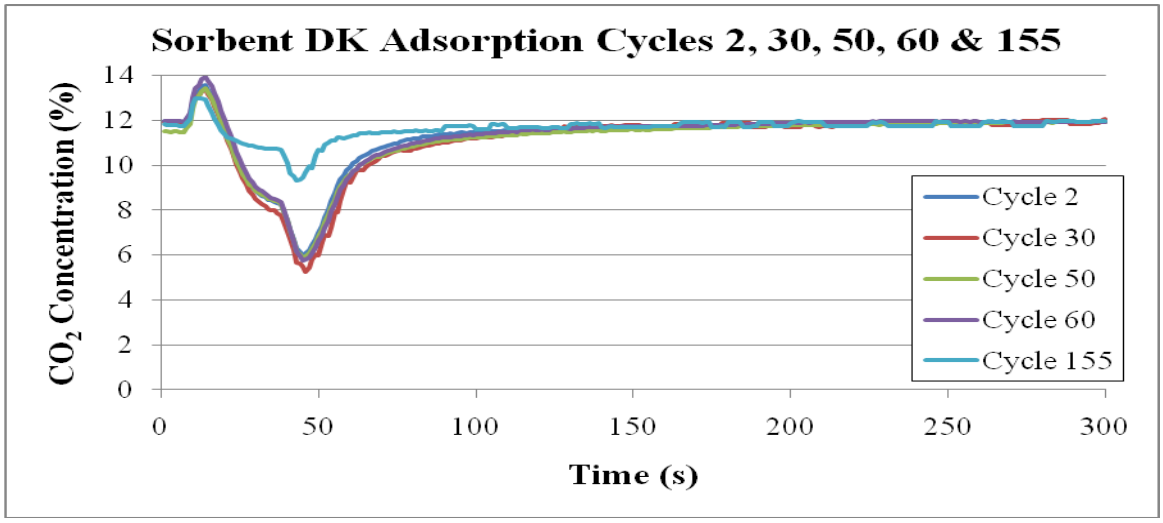

Figure 76: Sorbent DK Laboratory Adsorption Profiles

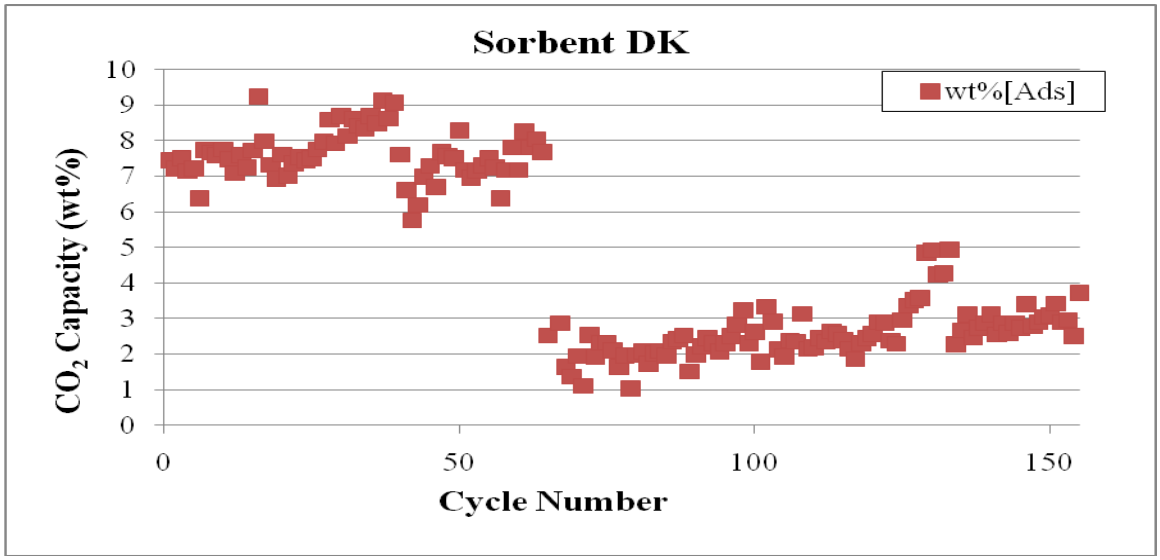

Figure 77: Sorbent DK Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 7.55 wt%, assuming a specific heat 2.0 kJ/kg·K and a regeneration temperature of 130°C, the theoretical regeneration energy for sorbent DK was approximately 3370 kJ/kg CO_2. The energy penalty is competitive with that of the benchmark MEA. This material exhibited good CO_2 capacity (i.e. >7.5 wt%) as well as good cyclic stability when regenerated at temperatures below 190°C. For these reasons, this sorbent could be considered a promising CO_2 sorbent and may be worth further testing.

Sorbent DL

Sorbent DL was classified as a hydrotalcite, and for the purpose of this test 1.01 g was the sample size. This sorbent was tested for 27 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 39. The regeneration temperatures during the parametric tests were varied from 100°C to 160°C. The adsorption

profiles in Figure 78 and the CO_2 capacity in Figure 79 were measured during parametric testing.

Table 39: Sorbent DL Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Sample Final Size (g)	Weight Loss (%)	Adsorption Conditions					Regeneration Conditions	
						CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
DL	Parametric	27	1.01	0.99	2.16	12	4	50	80	500	100 (Cycles 1-17) 130 (Cycles 18-25) 160 (Cycles 26-28)	900

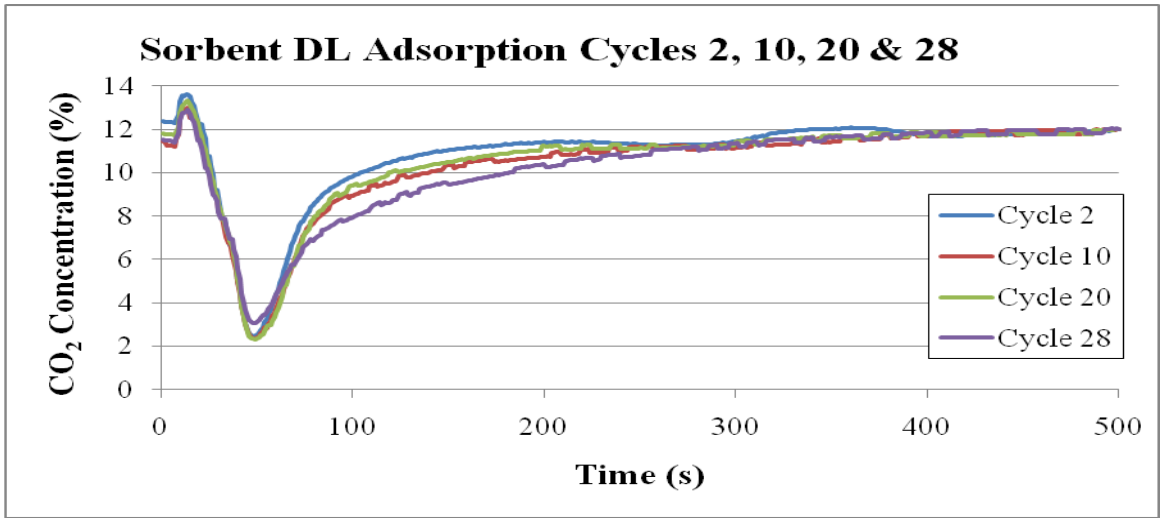

Figure 78: Sorbent DL Laboratory Adsorption Profiles

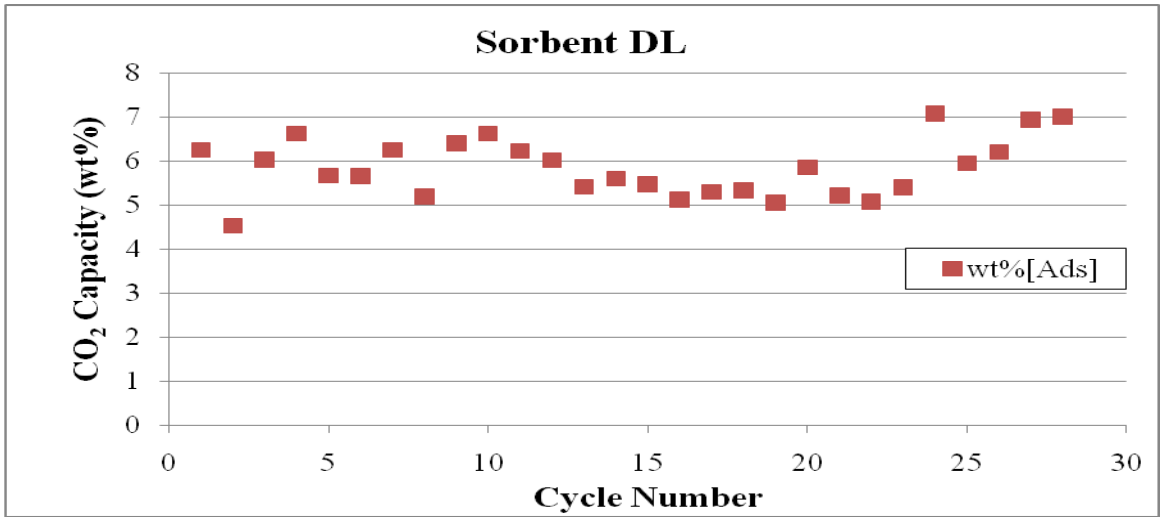

Figure 79: Sorbent DL Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 5.84 wt%, assuming a specific heat 2.0 kJ/kg·K and a regeneration temperature of 130°C, the theoretical regeneration energy for sorbent DL was approximately 3760 kJ/kg CO_2. This CO_2 capacity was too low to warrant further investigation.

Sorbent DM

Sorbent DM was classified as a hydrotalcite, and for the purpose of this test 0.50 g was the sample size. This sorbent was tested for 122 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 40. The regeneration temperatures during the parametric tests were varied from 100°C to 190°C. The adsorption profiles in Figure 80 and the CO_2 capacity in Figure 81 were measured during parametric testing. The adsorption profiles revealed that 190°C was too high for this sorbent. The sorbent was damaged after 27 cycles completed at 190°C during regeneration.

Table 40: Sorbent DM Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Sample Final Size (g)	Weight Loss (%)	Adsorption Conditions					Regeneration Conditions	
						CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
DM	Parametric	122	0.50	0.50	0.06	12	4	50	80	300	100 (Cycles 1-9) 130 (Cycles 10-19) 160 (Cycles 20-29) 190 (Cycles 30-123)	700

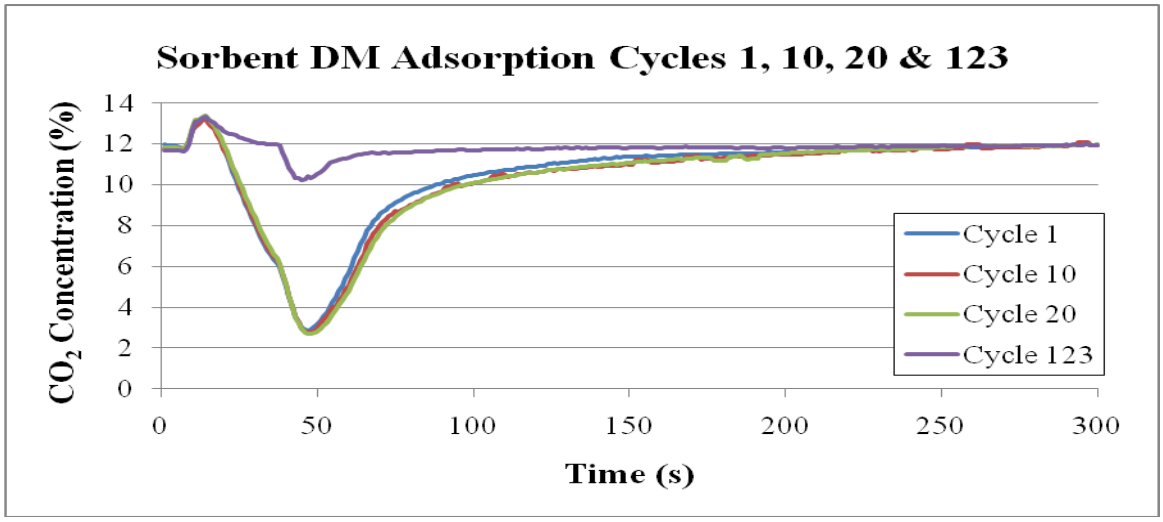

Figure 80: Sorbent DM Laboratory Adsorption Profiles

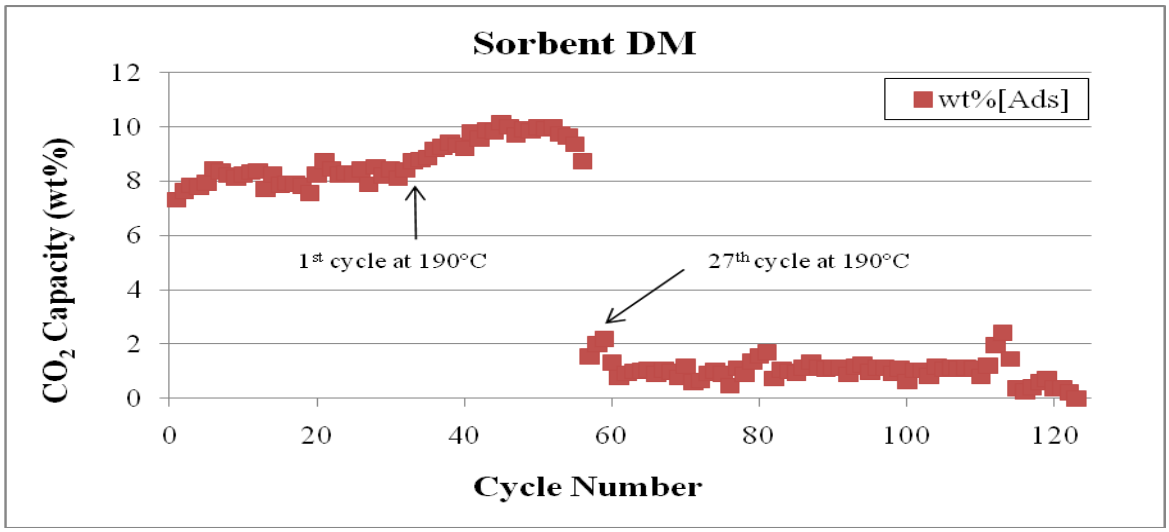

Figure 81: Sorbent DM Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 8.10 wt%, assuming a specific heat 2.0 kJ/kg·K and a regeneration temperature of 130°C, the theoretical regeneration energy for sorbent DM was approximately 3280 kJ/kg CO_2. The energy penalty was lower than that of the benchmark MEA. This material exhibited good CO_2 capacity (i.e. >8 wt%) as well as good cyclic stability at temperatures below 190°C. For these reasons, this material could be considered a promising CO_2 sorbent.

Sorbent DN

Sorbent DN was classified as a hydrotalcite, and for the purpose of this test 0.98 g was the sample size. This exhibited a CO_2 capacity of 1.10 wt%, which was lower than many materials evaluated under this program. This CO_2 capacity was too low to warrant further investigation.

Sorbent DO

Sorbent DO was classified as a hydrotalcite, and for the purpose of this test 0.625 g was the sample size. This exhibited a CO_2 capacity of 1.73 wt%, which was lower than many materials evaluated under this program. This CO_2 capacity was too low to warrant further investigation.

Sorbent DP

Sorbent DP was classified as a hydrotalcite, and for the purpose of this test 2.01 g was the sample size. This exhibited a CO_2 capacity of 1.34 wt%, which was lower than many materials evaluated under this program. This CO_2 capacity was too low to warrant further investigation.

Sorbent DQ

Sorbent DQ was classified as an amine based sorbent, and for the purpose of this test 0.50 g was the sample size. This exhibited a CO_2 capacity of 0.31 wt%, which was lower than many

amine-based materials evaluated under this program. This CO_2 capacity was too low to warrant further investigation.

Sorbent DR

Sorbent DR was classified as an amine based sorbent, and for the purpose of this test 0.50 g was the sample size. This exhibited a CO_2 capacity of 0.29 wt%, which was lower than many amine-based materials evaluated under this program. This CO_2 capacity was too low to warrant further investigation.

Sorbent DS

Sorbent DS was classified as an amine based sorbent, and for the purpose of this test 2.02 g was the sample size. This sorbent was tested for 24 full parametric cycles under automated operation in the laboratory. The testing conditions are listed in Table 41. The regeneration temperatures during the parametric tests were varied from 100°C to 130°C. The adsorption profiles in Figure 82 and the CO_2 capacity in Figure 83 were measured during parametric testing.

Table 41: Sorbent DS Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Sample Final Size (g)	Weight Loss (%)	Adsorption Conditions					Regeneration Conditions	
						CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
DS	Parametric	24	2.02	1.87	7.06	12	4	50	55	300	100 (Cycles 1-9) 115 (Cycles 10-19) 130 (Cycles 20-25)	1500

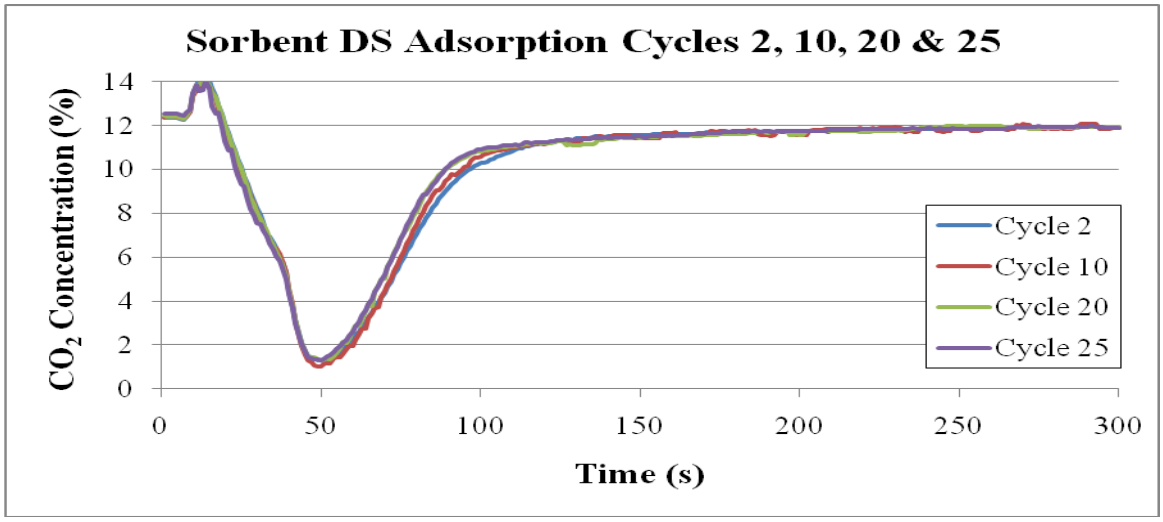

Figure 82: Sorbent DS Laboratory Adsorption Profiles

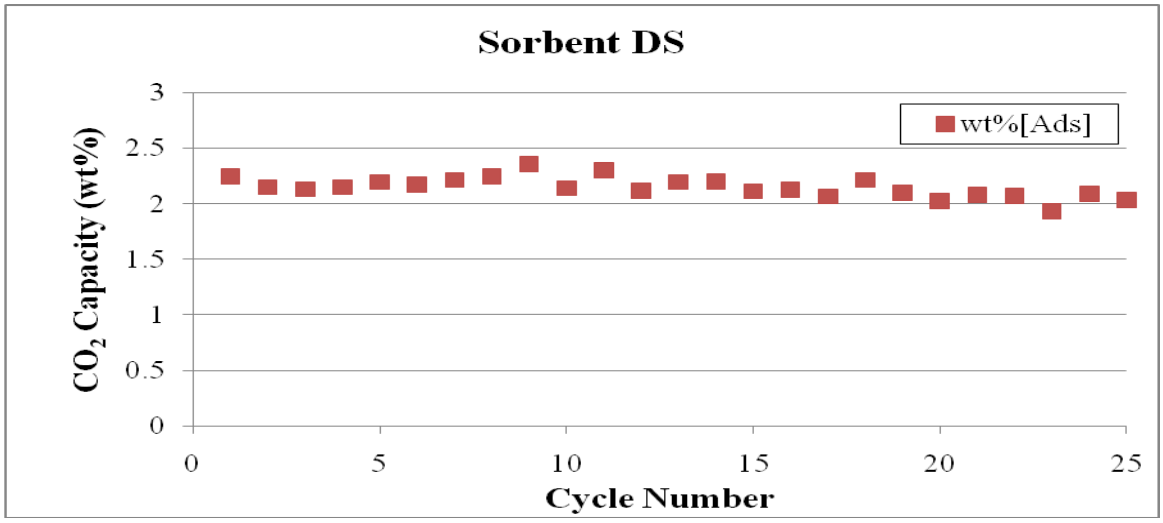

Figure 83: Sorbent DS Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 2.15 wt%, assuming a specific heat 1.3 kJ/kg·K and a regeneration temperature of 115°C, the theoretical regeneration energy for sorbent DS was approximately 5000 kJ/kg CO_2, which was greater than the MEA benchmark.

Sorbent DT

Sorbent DT was classified as an amine based sorbent, and for the purpose of this test 0.88 g was the sample size. This exhibited a CO_2 capacity of 0.48 wt%, which was lower than many amine-based materials evaluated under this program. This CO_2 capacity was too low to warrant further investigation.

Sorbent DU

Sorbent DU was classified as an amine based sorbent, and for the purpose of this test 2.02 g was the sample size. This exhibited a CO_2 capacity of 0.49 wt%, which was lower than many amine-based materials evaluated under this program. This CO_2 capacity was too low to warrant further investigation.

Sorbent DV

Sorbent DV was classified as an amine based sorbent, and for the purpose of this test 0.51 g was the sample size. This exhibited a CO_2 capacity of 0.50 wt%, which was lower than many amine-based materials evaluated under this program. This CO_2 capacity was too low to warrant further investigation.

Sorbent DW

Sorbent DW was classified as an amine based sorbent, and for the purpose of this test 2.00 g was the sample size. This sorbent was tested for 22 full extended cycles under automated operation in the laboratory. The testing conditions are listed in Table 42. The regeneration temperatures during the extended tests were 100°C. The adsorption profiles in Figure 84 and the CO_2 capacity in Figure 85 were measured during extended testing.

Table 42: Sorbent DW Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Sample Final Size (g)	Weight Loss (%)	Adsorption Conditions					Regeneration Conditions	
						CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
DW	Extended	22	2.00	1.83	8.43	12	4	50	55	400	100 (Cycles 1-23)	1700

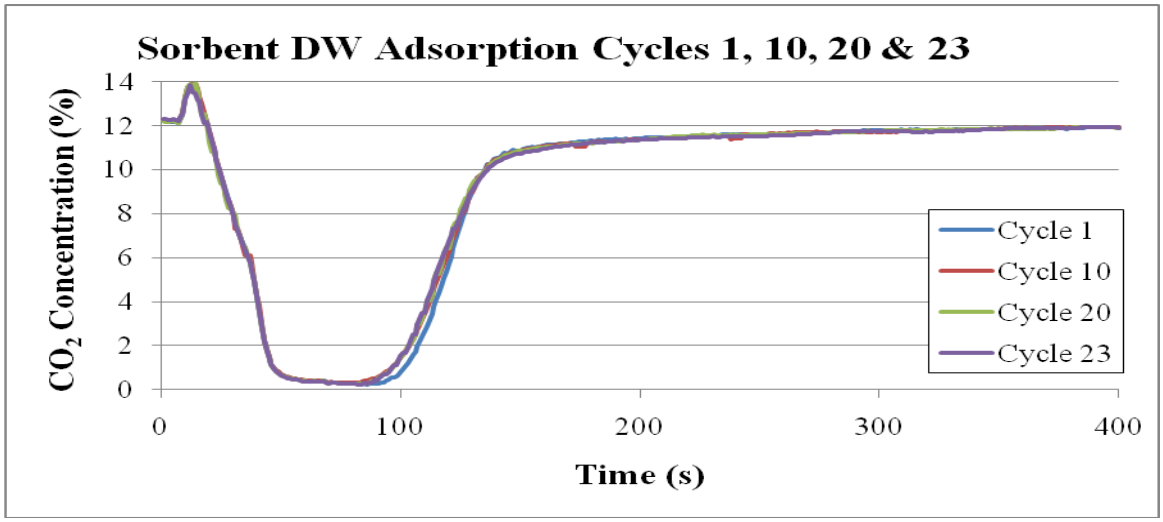

Figure 84: Sorbent DW Laboratory Adsorption Profiles

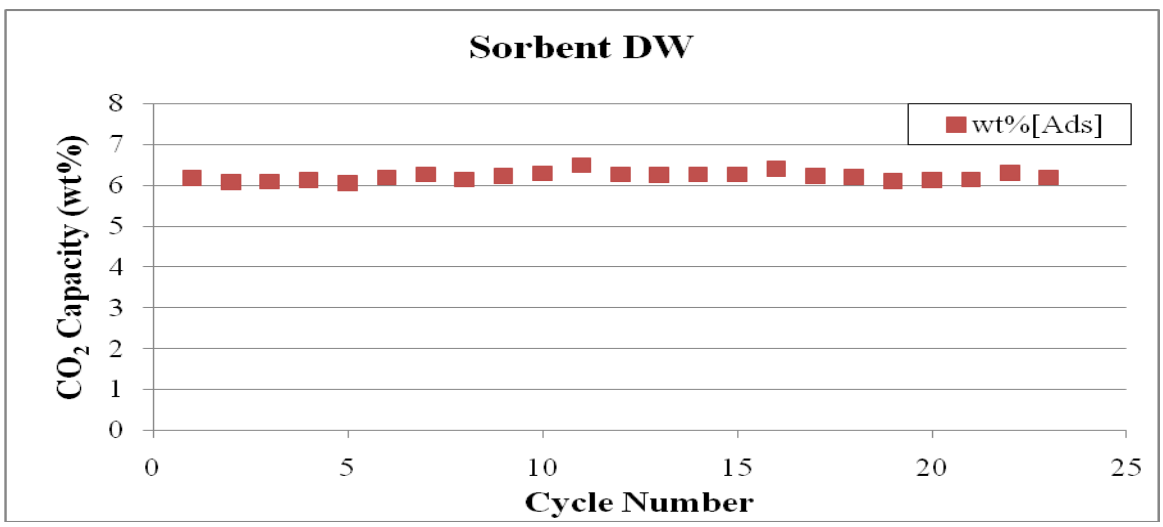

Figure 85: Sorbent DW Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 6.22 wt%, a specific heat of 1.3 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent DW was approximately 2310 kJ/kg CO_2, which was lower than the MEA benchmark. This material exhibited good CO_2 capacity (i.e. >6 wt%) as well as good cyclic stability at temperatures at 100°C. The 8.43% weight loss was suspected to be due to moisture in the sorbent. For these reasons, this sorbent could be considered a promising CO_2 sorbent.

Sorbent DX

Sorbent DX was classified as an amine based sorbent, and for the purpose of this test 2.00 g was the sample size. This sorbent was tested for 20 full extended cycles under automated operation in the laboratory. The testing conditions are listed in Table 43. The regeneration temperatures during the extended tests were 100°C. The adsorption profiles in Figure 86 and the CO_2 capacity in Figure 87 were measured during extended testing.

Table 43: Sorbent DX Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Sample Final Size (g)	Weight Loss (%)	Adsorption Conditions					Regeneration Conditions	
						CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
DX	Extended	20	2.00	1.91	4.71	12	4	50	55	600	100 (Cycles 1-21)	2000

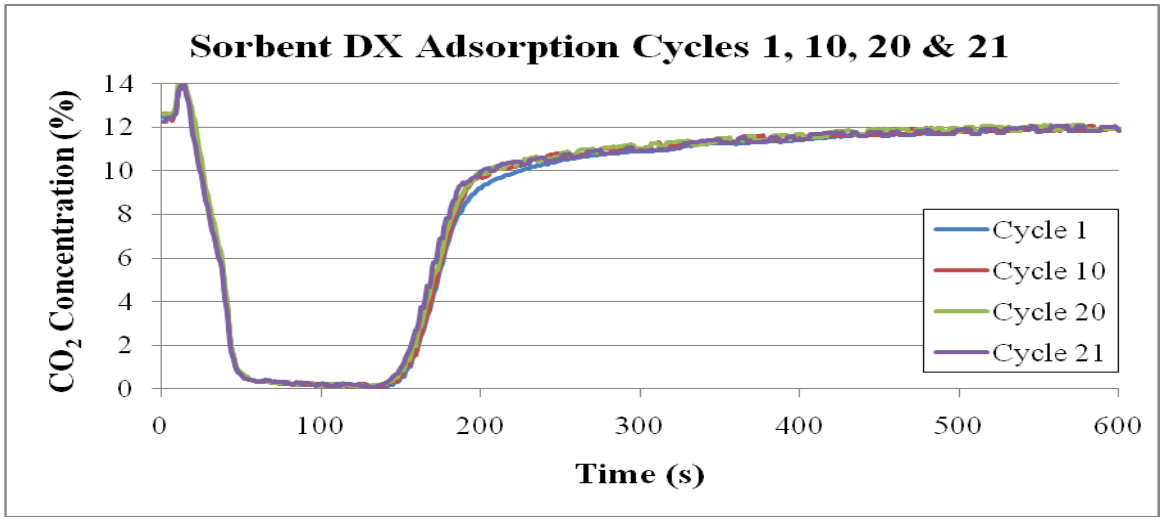

Figure 86: Sorbent DX Laboratory Adsorption Profiles

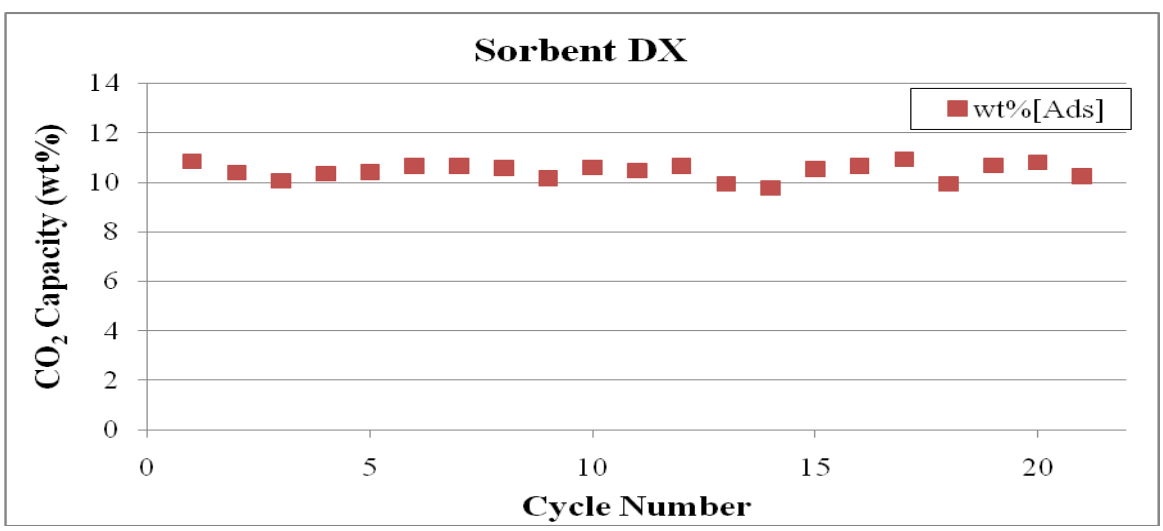

Figure 87: Sorbent DX Laboratory Total CO_2 Capacities

After the test was completed, the lab technician documented no noticeable color change in sorbent, but there was a small amount of light yellow amine in the tubing downstream of the fixed bed. Based on the laboratory results, using a CO_2 capacity of 10.45 wt%, a specific heat of 1.3 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent DX was approximately 1920 kJ/kg CO_2. This material exhibited good CO_2 capacity (i.e. >10 wt%) as well as good cyclic stability at temperatures at 100°C. The 4.71% weight loss was suspected to be due to moisture and amine loss in the sorbent.

Sorbent DY

Sorbent DY was classified as an amine based sorbent, and for the purpose of this test 2.01 g was the sample size. This sorbent was tested for 14 full extended cycles under automated operation in the laboratory. The testing conditions are listed in Table 44. The regeneration temperatures during the extended tests were 100°C. The adsorption profiles in Figure 88 and the CO_2 capacity in Figure 89 were measured during extended testing.

Table 44: Sorbent DY Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Sample Final Size (g)	Weight Loss (%)	Adsorption Conditions					Regeneration Conditions	
						CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
DY	Extended	14	2.01	1.92	4.04	12	4	50	55	600	100 (Cycles 1-15)	2300

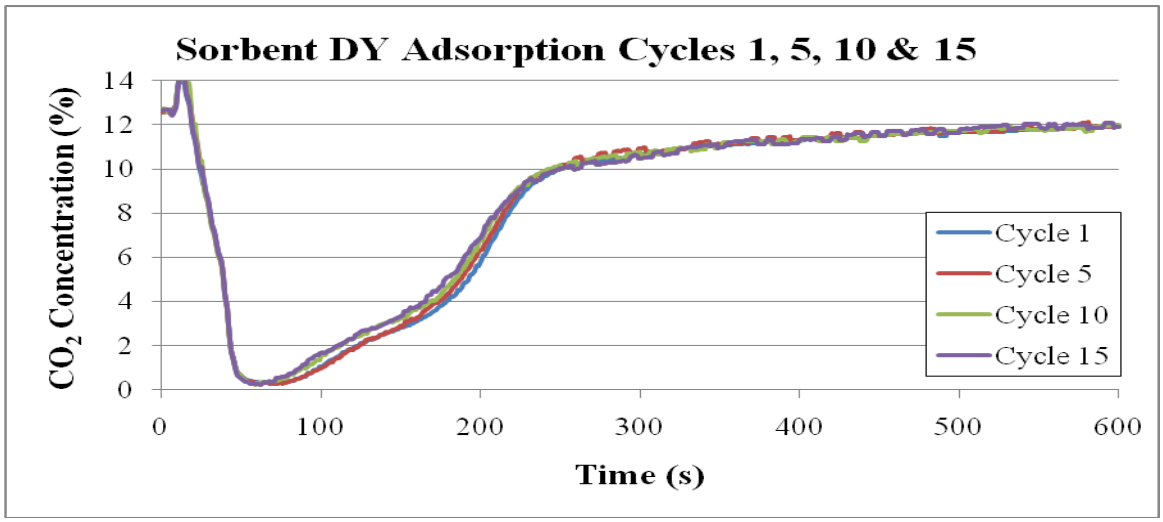

Figure 88: Sorbent DY Laboratory Adsorption Profiles

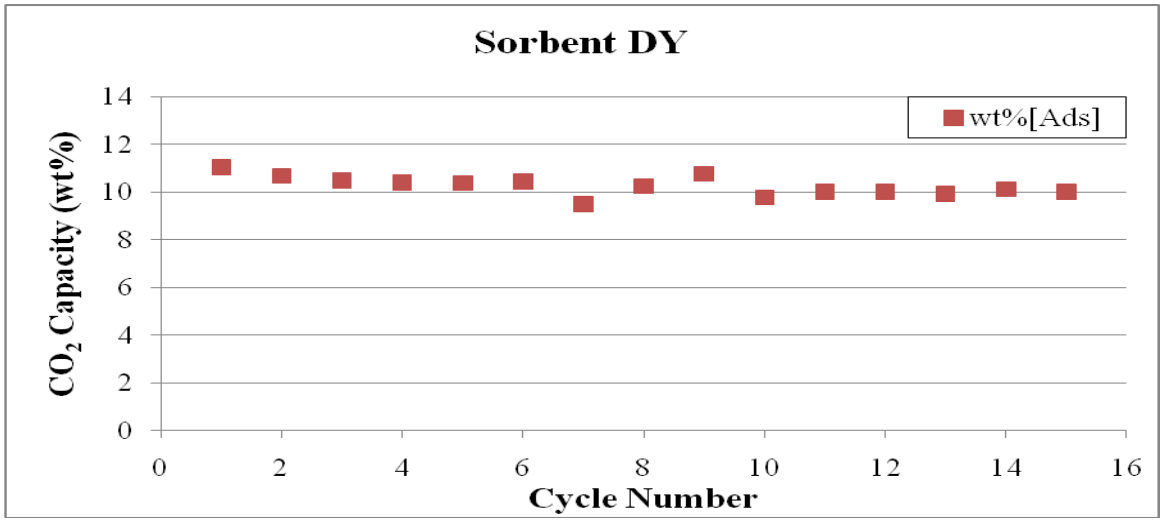

Figure 89: Sorbent DY Laboratory Total CO_2 Capacities

After the test was completed, the lab technician noticed light yellow amine in the tubing downstream of the fixed bed and no noticeable color change in sorbent. Based on the laboratory results, using a CO_2 capacity of 10.26 wt%, a specific heat of 1.3 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent DY was approximately 1930 kJ/kg CO_2, which was lower than the MEA benchmark. This material exhibited good CO_2 capacity (i.e. >10 wt%) as well as good cyclic stability at temperatures at 100°C. The 4.04% weight loss was suspected to be due to moisture and amine loss in the sorbent.

Sorbent DZ

Sorbent DZ was classified as an amine based sorbent, and for the purpose of this test 2.00 g was the sample size. This sorbent was tested for 54 full extended cycles under automated operation in the laboratory. The testing conditions are listed in Table 45. The regeneration temperatures during the extended tests were 100°C. The adsorption profiles in Figure 90 and the CO_2 capacity in Figure 91 were measured during extended testing.

Table 45: Sorbent DZ Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Sample Final Size (g)	Weight Loss (%)	Adsorption Conditions					Regeneration Conditions	
						CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
DZ	Extended	54	2.00	1.98	1.13	12	4	50	55	600	100 (Cycles 1-55)	2500

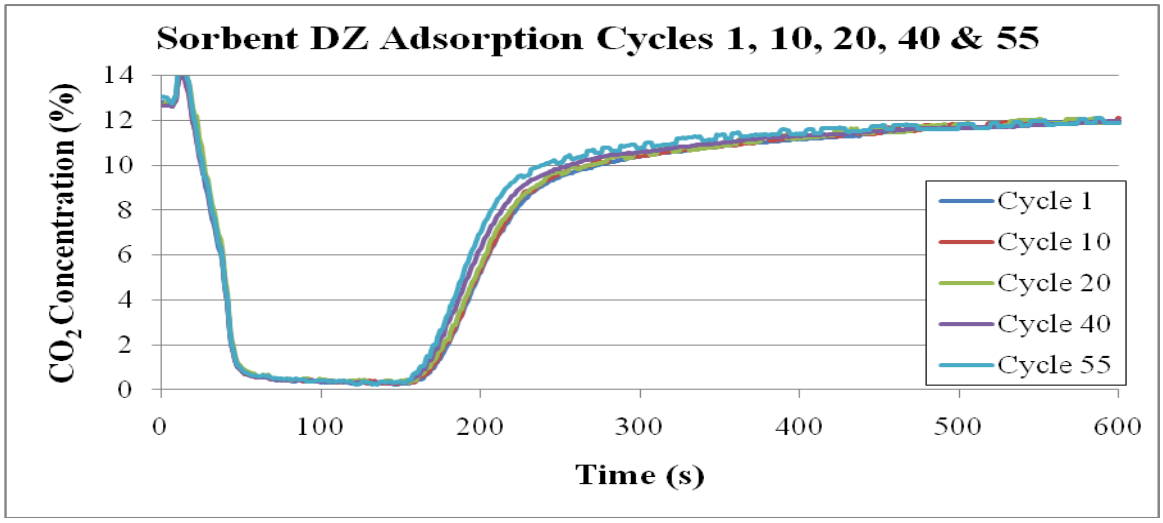

Figure 90: Sorbent DZ Laboratory Adsorption Profiles

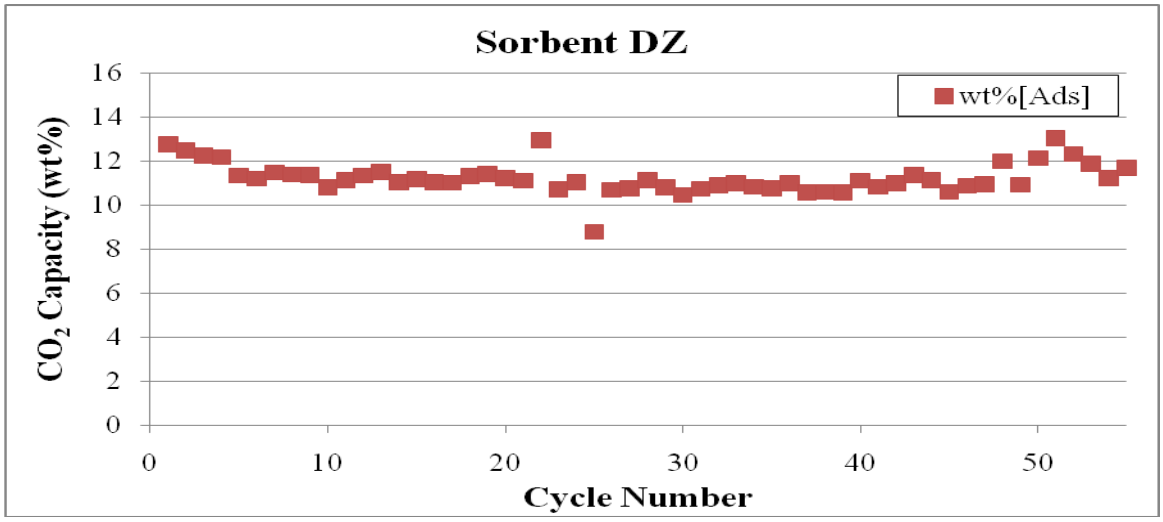

Figure 91: Sorbent DZ Laboratory Total CO_2 Capacities

After the test was completed, the lab technician documented no noticeable color change in sorbent, but there was a small amount of yellow amine in the tubing downstream of the fixed bed. Based on the laboratory results, using a CO_2 capacity of 11.14 wt%, a specific heat of 1.3 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent DZ was approximately 1890 kJ/kg CO_2. This material exhibited good CO_2 capacity (i.e. >11 wt%) as well as good cyclic stability at temperatures at 100°C. The 1.13% weight loss was suspected to be due to moisture and amine loss in the sorbent.

Sorbent EA

Sorbent EA was classified as an amine based sorbent, and for the purpose of this test 1.01 g was the sample size. This exhibited a CO_2 capacity of 1.30 wt%, which was lower than many amine-based materials evaluated under this program. This CO_2 capacity was too low to warrant further investigation.

Sorbent EB

Sorbent EB was classified as an amine based sorbent, and for the purpose of this test 1.03 g was the sample size. This exhibited a CO_2 capacity of 0.62 wt%, which was lower than many amine-based materials evaluated under this program. This CO_2 capacity was too low to warrant further investigation.

Sorbent EC

Sorbent EC was classified as an amine based sorbent, and for the purpose of this test 0.99 g was the sample size. This exhibited a CO_2 capacity of 0.70 wt%, which was lower than many amine-based materials evaluated under this program. This CO_2 capacity was too low to warrant further investigation.

Sorbent ED

Sorbent ED was classified as an amine based sorbent, and for the purpose of this test 1.08 g was the sample size. This exhibited a CO_2 capacity of 0.55 wt%, which was lower than many amine-based materials evaluated under this program. This CO_2 capacity was too low to warrant further investigation.

Sorbent EE

Sorbent EE was classified as an amine based sorbent, and for the purpose of this test 1.01 g was the sample size. This exhibited a CO_2 capacity of 0.93 wt%, which was lower than many amine-based materials evaluated under this program. This CO_2 capacity is too low to warrant further investigation.

Sorbent EF

Sorbent EF was classified as an amine based sorbent, and for the purpose of this test 0.49 g was the sample size. This exhibited a CO_2 capacity of 1.59 wt%, which was lower than many amine-based materials evaluated under this program. This CO_2 capacity was too low to warrant further investigation.

Sorbent EG

Sorbent EG was classified as an amine based sorbent, and for the purpose of this test 1.03 g was the sample size. This exhibited a CO_2 capacity of 1.27 wt%, which was lower than many amine-based materials evaluated under this program. This CO_2 capacity was too low to warrant further investigation.

Sorbent EH

Sorbent EH was classified as a carbon based sorbent, and for the purpose of this test 0.58 g was the sample size. This exhibited a CO_2 capacity of 0.45 wt%, which was lower than many amine-based materials evaluated under this program. This CO_2 capacity was too low to warrant further investigation.

Sorbent EI

Sorbent EI was classified as a carbon based sorbent, and for the purpose of this test 3.00 g was the sample size. This exhibited a CO_2 capacity of 0.24 wt%, which was lower than many amine-based materials evaluated under this program. This CO_2 capacity was too low to warrant further investigation.

Sorbent EJ

Sorbent EJ was classified as an amine based sorbent, and for the purpose of this test 2.02 g was the sample size. This sorbent was tested for 23 full extended cycles at 100°C under automated operation in the laboratory. The testing conditions are listed in Table 46. The adsorption profiles in Figure 92 and the CO_2 capacity in Figure 93 were measured during extended testing.

Table 46: Sorbent EJ Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Sample Final Size (g)	Weight Loss (%)	Adsorption Conditions					Regeneration Conditions	
						CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
EJ	Extended	23	2.02	2.01	0.61	12	4	50	55	500	100 (Cycles 1-24)	1800

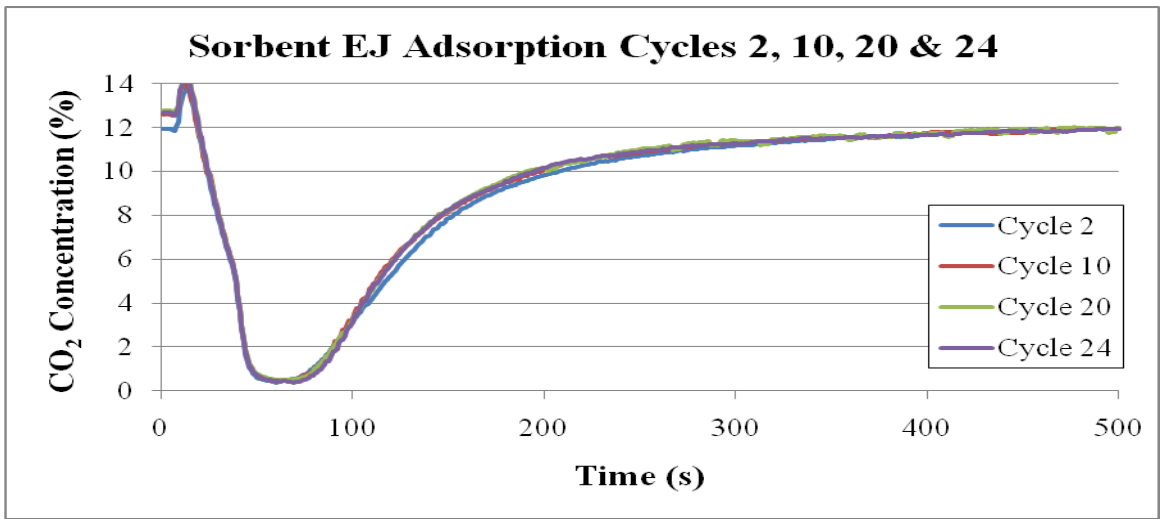

Figure 92: Sorbent EJ Laboratory Adsorption Profiles

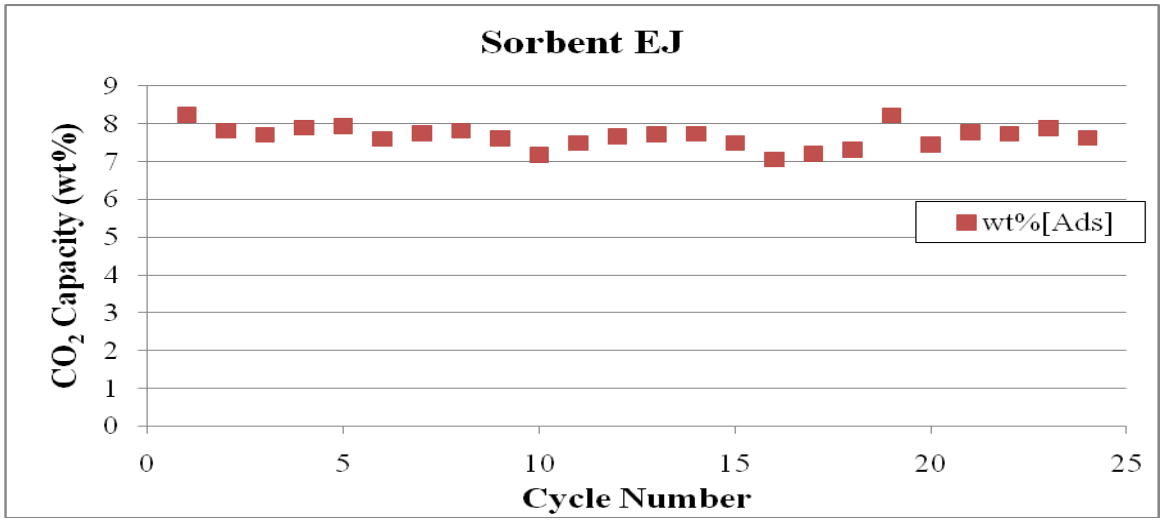

Figure 93: Sorbent EJ Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 7.67 wt%, a specific heat of 1.3 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent EJ was approximately 2580 kJ/kg CO_2. Sorbent EJ had an energy penalty lower than that of aqueous amines. This material exhibited good CO_2 capacity (i.e. >7 wt%) as well as good cyclic stability at 100°C for regeneration. For these reasons, this sorbent could be considered a promising CO_2 sorbent.

Sorbent EK

Sorbent EK was classified as an amine based sorbent, and for the purpose of this test 2.02 g was the sample size. This exhibited a CO_2 capacity of 1.28 wt%, which was lower than many amine-based materials evaluated under this program. This CO_2 capacity was too low to warrant further investigation.

Sorbent EL

Sorbent EL was classified as an amine based sorbent, and for the purpose of this test 2.01 g was the sample size. This sorbent was tested for 130 full extended cycles at 100°C under automated operation in the laboratory. The testing conditions are listed in Table 47. The adsorption profiles in Figure 94 and the CO_2 capacity in Figure 95 were measured during extended testing.

Table 47: Sorbent EL Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Sample Final Size (g)	Weight Loss (%)	Adsorption Conditions					Regeneration Conditions	
						CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
EL	Extended	130	2.01	1.94	3.04	12	4	50	55	250	100 (Cycles 1-131)	850

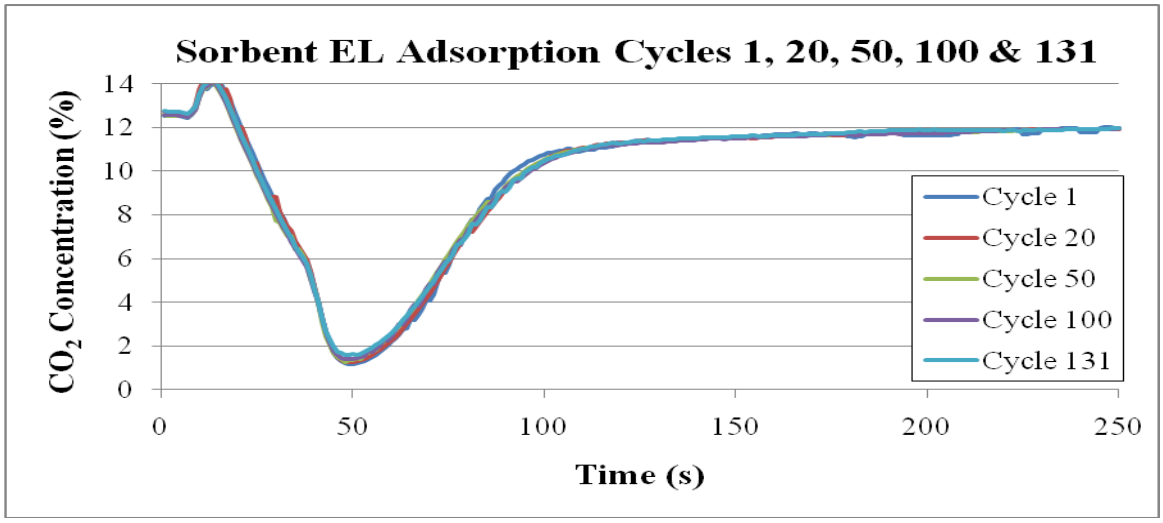

Figure 94: Sorbent EL Laboratory Adsorption Profiles

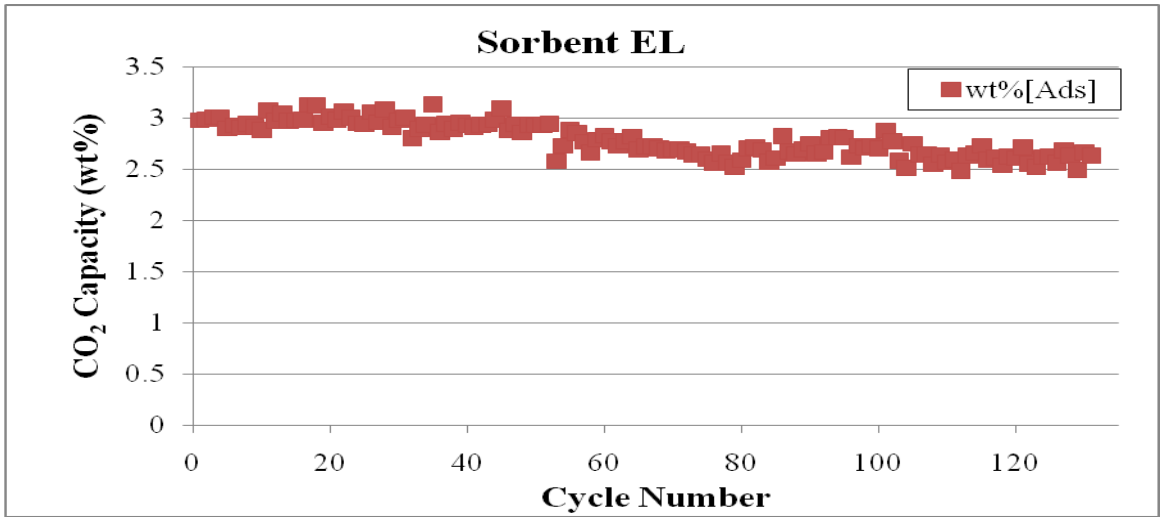

Figure 95: Sorbent EL Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 2.79 wt%, a specific heat of 1.3 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent EL was approximately 3460 kJ/kg CO_2, which was competitive with the benchmark MEA. However, the CO_2 capacity was significantly lower than that of other supported amine sorbents.

Sorbent EM

Sorbent EM was classified as an amine based sorbent, and for the purpose of this test 2.00 g was the sample size. This sorbent was tested for 25 full extended cycles at 100°C under automated operation in the laboratory. The testing conditions are listed in Table 48. The adsorption profiles in Figure 96 and the CO_2 capacity in Figure 97 were measured during extended testing.

Table 48: Sorbent EM Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Sample Final Size (g)	Weight Loss (%)	Adsorption Conditions					Regeneration Conditions	
						CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
EM	Extended	25	2.00	1.95	2.43	12	4	50	55	400	100 (Cycles 1-26)	1250

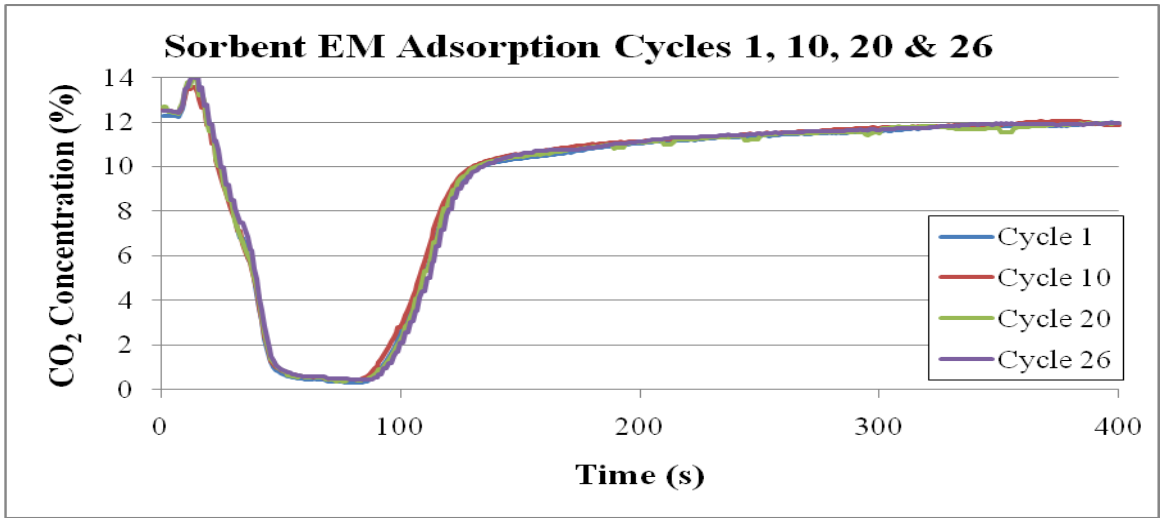

Figure 96: Sorbent EM Laboratory Adsorption Profiles

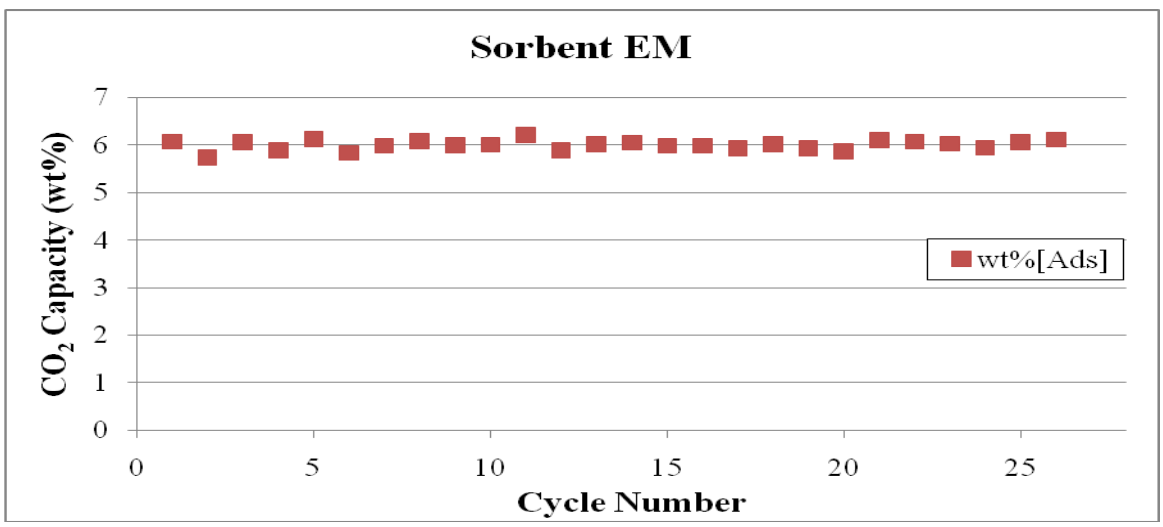

Figure 97: Sorbent EM Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 6.00 wt%, a specific heat of 1.3 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent EM was approximately 2340 kJ/kg CO_2, which was lower than that of the benchmark MEA. In addition, this material exhibited superior cyclic stability.

Sorbent EN

Sorbent EN was classified as an amine based sorbent, and for the purpose of this test 2.01 g was the sample size. This sorbent was tested for 93 full extended cycles at 100°C under automated operation in the laboratory. The testing conditions are listed in Table 49. The adsorption profiles in Figure 98 and the CO_2 capacity in Figure 99 were measured during extended testing.

Table 49: Sorbent EN Laboratory Testing Conditions

Sorbent	Test Type	Cycles Completed	Sample Initial Size (g)	Sample Final Size (g)	Weight Loss (%)	Adsorption Conditions					Regeneration Conditions	
						CO_2 Concentration (vol%)	O_2 Concentration (vol%)	Moisture Level (Relative Humidity, %)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
EN	Extended	93	2.01	1.90	5.15	12	4	50	55	400	100 (Cycles 1-94)	1600

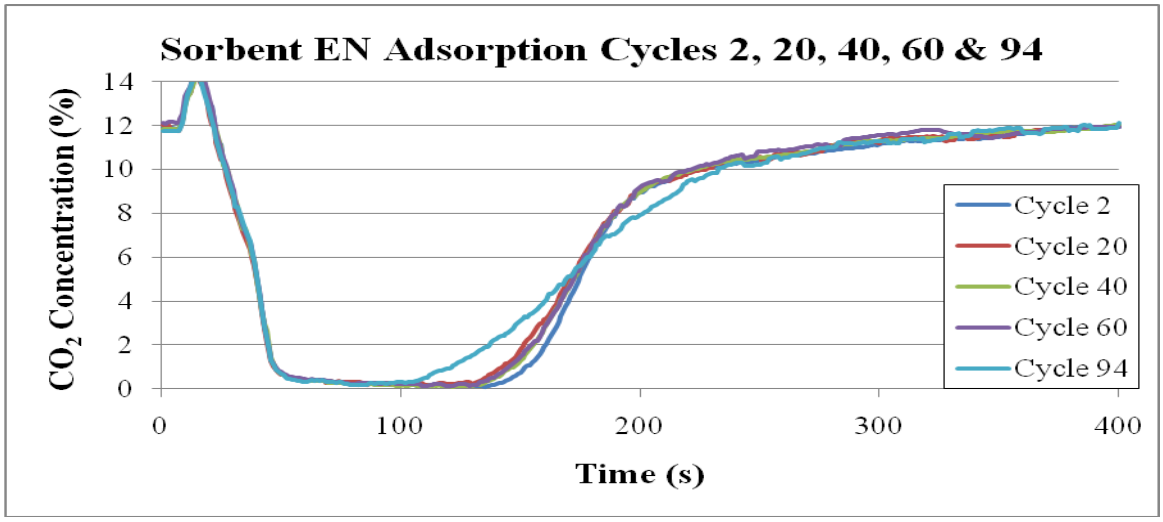

Figure 98: Sorbent EN Laboratory Adsorption Profiles

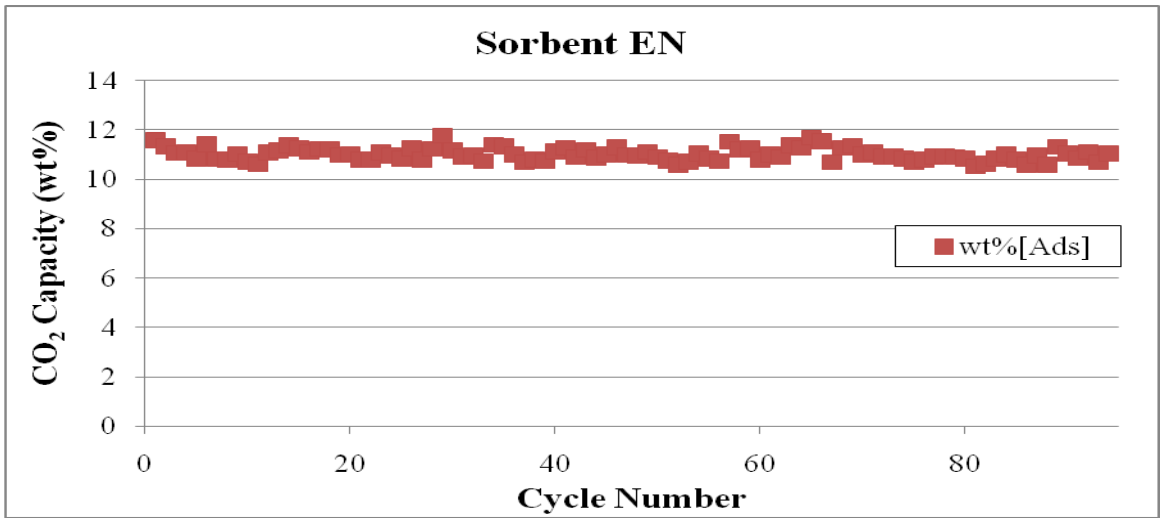

Figure 99: Sorbent EN Laboratory Total CO_2 Capacities

Based on the laboratory results, using a CO_2 capacity of 11.01 wt%, a specific heat of 1.3 kJ/kg·K, and a regeneration temperature of 100°C, the theoretical regeneration energy for sorbent EN was approximately 1900 kJ/kg CO_2, which was significantly lower than the benchmark MEA. In addition this material exhibited superior cyclic stability.

Comparison of All Materials Tested

Under several different projects, ADA-ES has tested over 140 different potential CO_2 sorbents; the results from the last batch of materials received are discussed in this report. These materials were highly varied in their chemical and physical properties. Since they were all evaluated with the final application of post-combustion CO_2 capture in mind, the key operating parameters identified and assessed during laboratory-scale fixed bed testing included:

1) Theoretical regeneration energy
2) Cyclic stability

By testing several different materials in each sorbent type (i.e. supported amines, carbon based, etc.), the fixed bed results provided the information necessary to draw general conclusions about advantages and disadvantages of different types of sorbents. The five types of materials tested by ADA-ES (under all programs) to date included supported amines, carbon-based, supported carbonates, hydrotalcites, and zeolites. A total of seventy four sorbents were evaluated during the current reporting period. Only supported amines, carbon-based, and hydrotalcites materials were evaluated under the current project. The theoretical regeneration energy for select materials discussed in this report are provided in Figure 100. For many sorbents parametric evaluations were completed with multiple regeneration temperatures. The theoretical regeneration energy provided in Figure 100 was calculated using the average total CO_2 capacity and the median regeneration temperature.

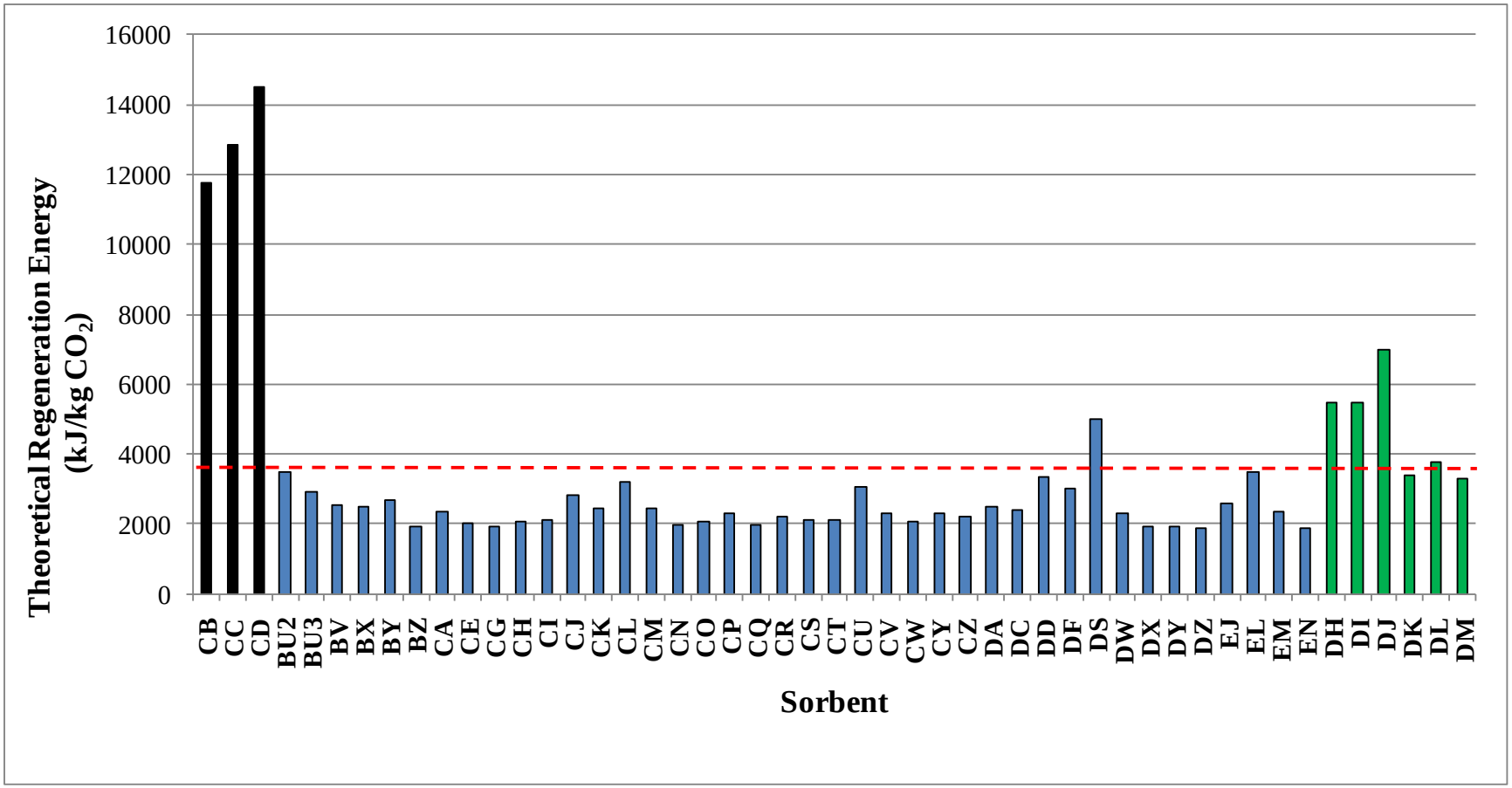

Figure 100: Comparison of Working Capacities Measured in the Laboratory Humid Simulated Flue Gas*

*The sorbents have been grouped according to the material type. Black bars represent carbon-based, blue bars represent supported amines, and green bars represent hydrotalcites. The red dashed line represents the regeneration energy for aqueous MEA as reported by the DOE.[3]

Clearly solid sorbents have the potential to reduce the energy penalty associated with post-combustion CO_2 capture. Of course a process and the related equipment must be designed that can effectively utilize the advantageous sorbent properties. Although Figure 100 allows for the theoretical regeneration energies of many different sorbents to be compared relatively quickly, it does not tell the entire story. Even at the laboratory-scale the cyclic stability can be assessed. In addition, some sorbents are more susceptible to reaction with flue gas constituents. The following sections discuss specific performance criteria for the sorbents evaluated during this testing period.

Carbon-Based Sorbents

The carbon-based materials in this program have included everything from highly novel carbon nanotubes to commercially available activated carbons. With the exception of the carbon nanotubes, the CO_2 capacities of the carbon-based materials were significantly lower than those of other types of sorbents such as supported amines. Breakthrough curves for five carbon-based sorbents were measured during the current testing period. The CO_2 capacities of the carbon-based sorbents evaluated during this testing period were lower than 0.66 wt%. In terms of a materials handling, to achieve 90% CO_2 capture using low-capacity carbons would require significant energy to move the materials. However, there are also advantages to using carbon-based materials. Specifically, they are commercially produced today, they can be burned after they are spent (i.e. less waste generated by the CO_2 capture process), and they are less easily poisoned by flue gas constituents compared to both amines (negatively affected by SO_2) and zeolites (prohibitively affected by moisture). Some carbons have shown a decrease in CO_2 performance in moist versus dry flue gas, but this only decreases the capacity to some equilibrium value, it does not remove all the CO_2 capacity. The challenge for carbon-based materials is to improve the CO_2 capacity and selectivity. Due to the low CO_2 capacities measured at the simulated flue gas conditions, none of the carbon-based sorbents evaluated during this period of testing (and discussed in this report) are considered viable options for post-combustion CO_2 capture.

Hydrolalcites

Hydrolalcites are a new family of sorbents discussed in this report that have exhibited stability at greater temperatures than most other sorbents evaluated by ADA-ES to date. Breakthrough curves for ten hydrotalcites were measured during the current testing period. These fixed bed tests discussed in this report were conducted without any study of the optimal adsorption and regeneration temperatures. As an example, Sorbent DM exhibited cyclic stability at all regeneration temperatures tested below 190°C, as is shown in Figure 101. This sorbent didn't get damaged until after 27 cycles at 190°C. This temperature stability could be useful for creating high driving forces for heat transfer or a reduced concern of damaging sorbent if it was unexpectedly exposed to elevated temperatures.

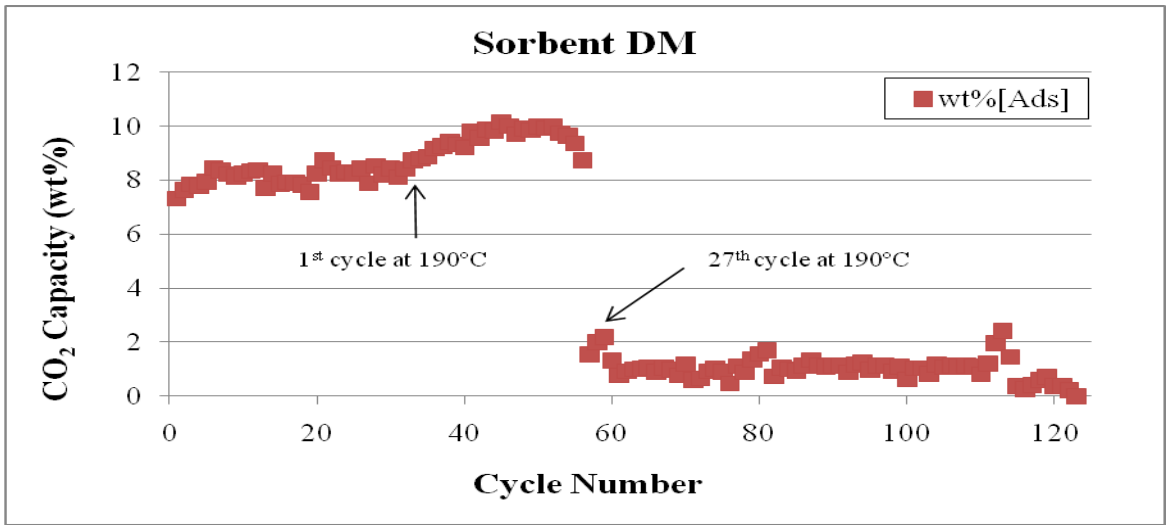

Figure 101: Sorbent DM Laboratory Total CO_2 Capacities

Based on the hydrotalcites evaluated to date, there may be some applicability for post-combustion CO_2 capture. Although it will not be completed under this project, ADA-ES may complete more testing to evaluate the optimal operating conditions (i.e. adsorption and regeneration temperature) for these materials.

Supported Amines

Based on results to date, supported amines are the most promising sorbent family for CO_2 capture. Breakthrough curves for fifty nine supported amines were measured during the current testing period. As is shown in Figure 100, these materials have the potential to significantly reduce the energy penalty associated with CO_2 capture versus state of the art aqueous MEA systems. This can be attributed to high CO_2 capacities (over 11 wt% was measured for this group) as well as low heat capacities and low regeneration temperatures.

An adsorption profile for sorbents R, EM, and EN are provided in Figure 102 to serve as an example of the shape of the breakthrough curve characteristic for supported amines. All three of these sorbents were able to remove over 90% of the CO_2 from the simulated flue gas stream. Sorbent R, which was discussed in detail in previous sorbent screening reports, exhibited first an initial breakthrough that resulted in a fast increase in CO_2 concentration, followed by a much slower increase in the CO_2 concentration to achieve complete saturation. The newer sorbents EM and EN, which were submitted to the program from the same sorbent developer, exhibited initial breakthrough and then a fast increase in the CO_2 concentration to achieve complete saturation. Although the total CO_2 capacity of sorbent R is greater than that of sorbents EM and EN, the slow tail in the adsorption profile reveals a reaction with CO_2 that is limited by mass diffusion. In an actual system, it is likely that the working capacity of sorbents EM and EN would be greater than that of R because they do not exhibit the same level of mass diffusion limitations. These materials are just one of many examples of supported amine sorbents that have been improved throughout the duration of the sorbent screening phase of this project.

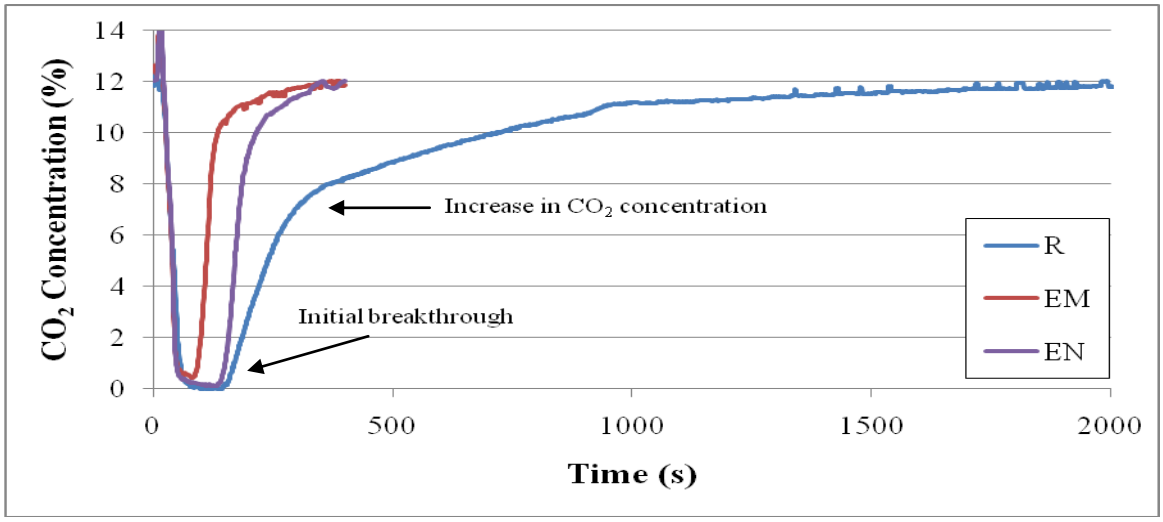

Figure 102: Select Supported Amine Adsorption Profiles

The most important challenges for supported amine sorbents are related to long-term cyclic stability, poisoning by flue gas constituents, and cost. Several, but not all, of the supported amine sorbents demonstrated a loss in CO_2 capacity when using simulated flue gas in the laboratory. As an example, select adsorption profiles from laboratory tests for sorbent CU are provided in Figure 103. Although the testing conditions were the same for all cycles, the adsorption profiles revealed a slow, progressive decrease in the CO_2 capacity of the material.

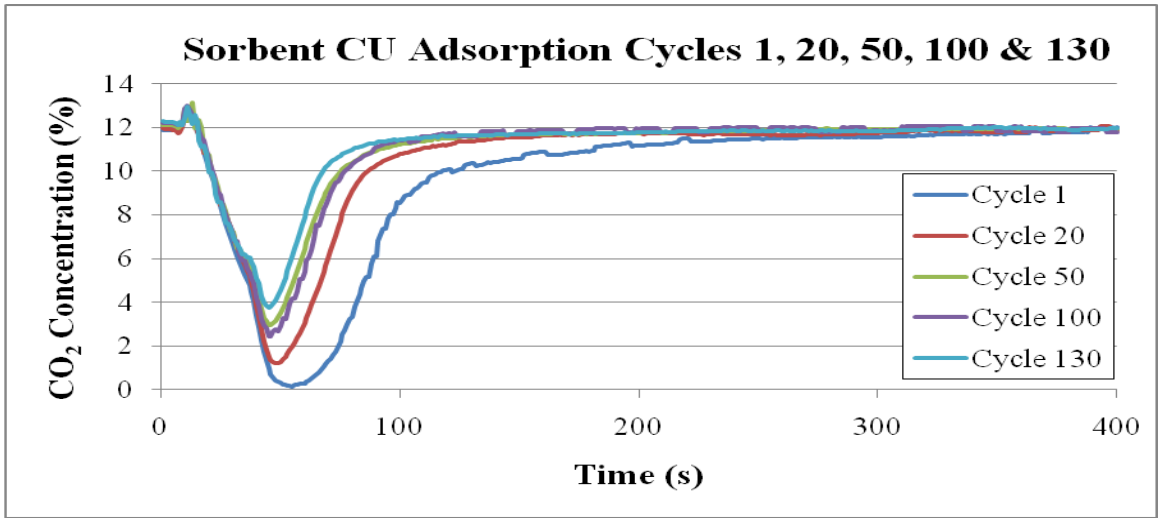

Figure 103: Sorbent CU Laboratory Adsorption Profiles

However, there were also many supported amines that demonstrated cyclic stability. As an example, select adsorption profiles for sorbent CQ are provided in Figure 104. The repeatability in the adsorption profiles for this material was exceptional.

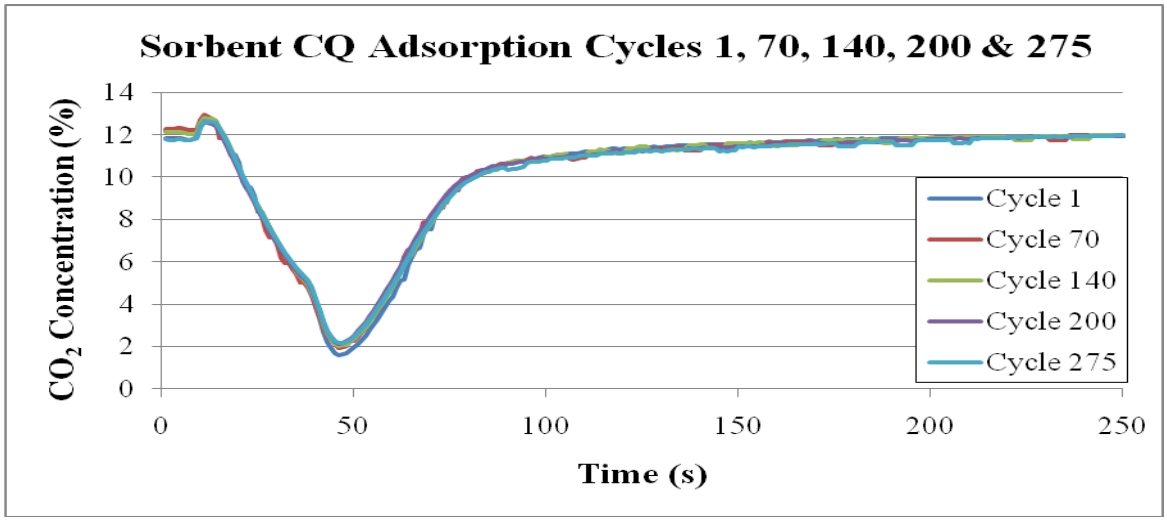

Figure 104: Sorbent CQ Laboratory Adsorption Profiles

To provide another example of a supported amine sorbent that demonstrated cyclic stability, the CO_2 capacity for sorbent CE is provided in Figure 105. This sorbent exhibited a large CO_2 capacity (>8 wt%). Sorbent CE was stable using a regeneration temperature of 100°C for the 261 cycles. Note that there was an initial decrease in the CO_2 capacity, but that the overall stability of the material was superior.

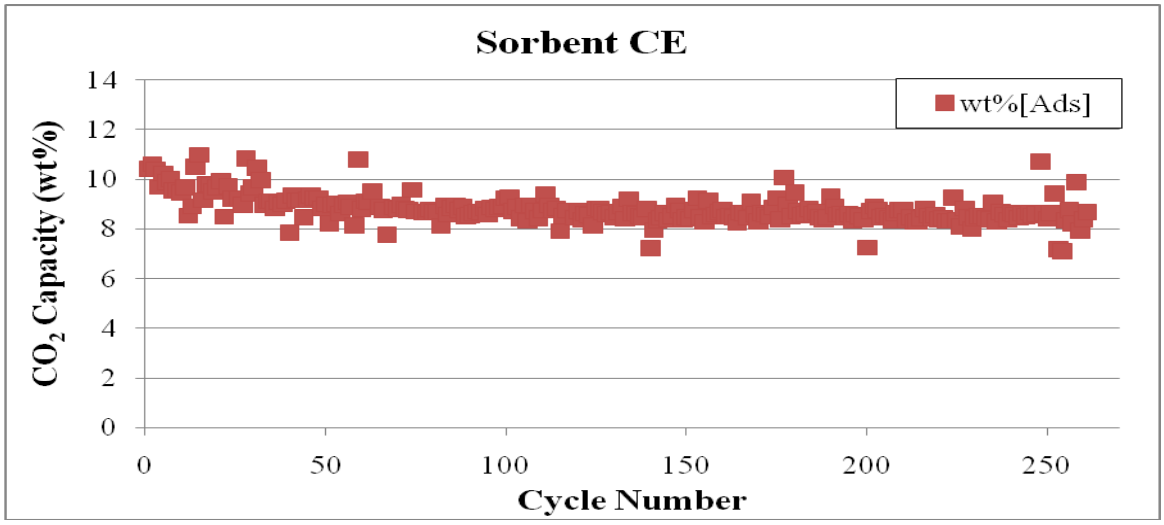

Figure 105: Sorbent CE Laboratory Total CO_2 Capacities

CONCLUSIONS

Many different materials have been tested in the ADA-ES CO_2 sorbent screening program. All materials that have been contributed to the program have been tested in multiple CO_2 adsorption/regeneration cycles. Based on the theoretical regeneration energy, many sorbents were superior the benchmark MEA process. Each sorbent family has its own advantages and disadvantages. Carbon-based sorbent have a low CO_2 capacity, but exhibit superior cyclic stability and a resistance to poisoning by flue gas constituents. Hydrolalcites exhibited superior working capacities under non-optimal conditions and cyclic stability at higher temperatures, but must be further evaluated to identify the optimal operation conditions. The supported amines tested in this round of sorbent screening exhibited high CO_2 capacities and low theoretical regeneration energies, but many were not cyclically stable. In addition, it is well documented that supported amines can be negatively affected by flue gas constituents such as SO_2. Overall, laboratory sorbent screening has been used to successfully identify the most promising sorbents for CO_2 capture and draw general conclusions about different sorbent families.

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APPENDIX E: JENIKE & JOHANSON SORBENT ATTRITION TESTING REPORT

JENIKE & JOHANSON
INCORPORATED
Bulk Solids: Science/Engineering/Design

Attrition Testing of Sorbent Material

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Reviewed by: Tom Troxel

ADA ES
10616-1

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JENIKE & JOHANSON

June 3, 2009

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1 BACKGROUND

ADA ES is developing a method of removing CO_2 from coal fired power station flue gas. The system will involve entraining sorbent in the flue gas and then removing it to remove the CO_2. One of the factors that will determine the utility of the sorbent is its ability to resist attrition. Jenike & Johanson was asked to test the attrition of two samples of sorbent to compare them.

Two sorbent materials were received for testing. They were both labeled as CARIACT from Fuji Silysia Chemical Ltd. The first was labeled Grade G-10, 75 – 500 μm and the second, Grade Q-10, 75 – 500 μm. A particle size analysis was run on both samples using a laser diffraction analyzer from Malvern Instruments Ltd.

2 TEST SETUP

A new tester was built to measure attrition due to conveying and re-circulating in an entrained fluidized bed (basically a pneumatic conveyor). A diagram of the test setup is shown in Figure 1. Details are also shown in the attached pictures.

The test was run with the sorbent and the tester kept at a constant 140°F. The vacuum system was adjusted to make the air velocity in the riser leg approximately15 fps. The air-to-solids ratio in the riser varied widely as the filters were blinded by fines and then cleaned by the pulsejet system. The filters were cleaned by a back pulse approximately every 15 seconds. The average air-to-solids ratio was 4.41.

Test procedure

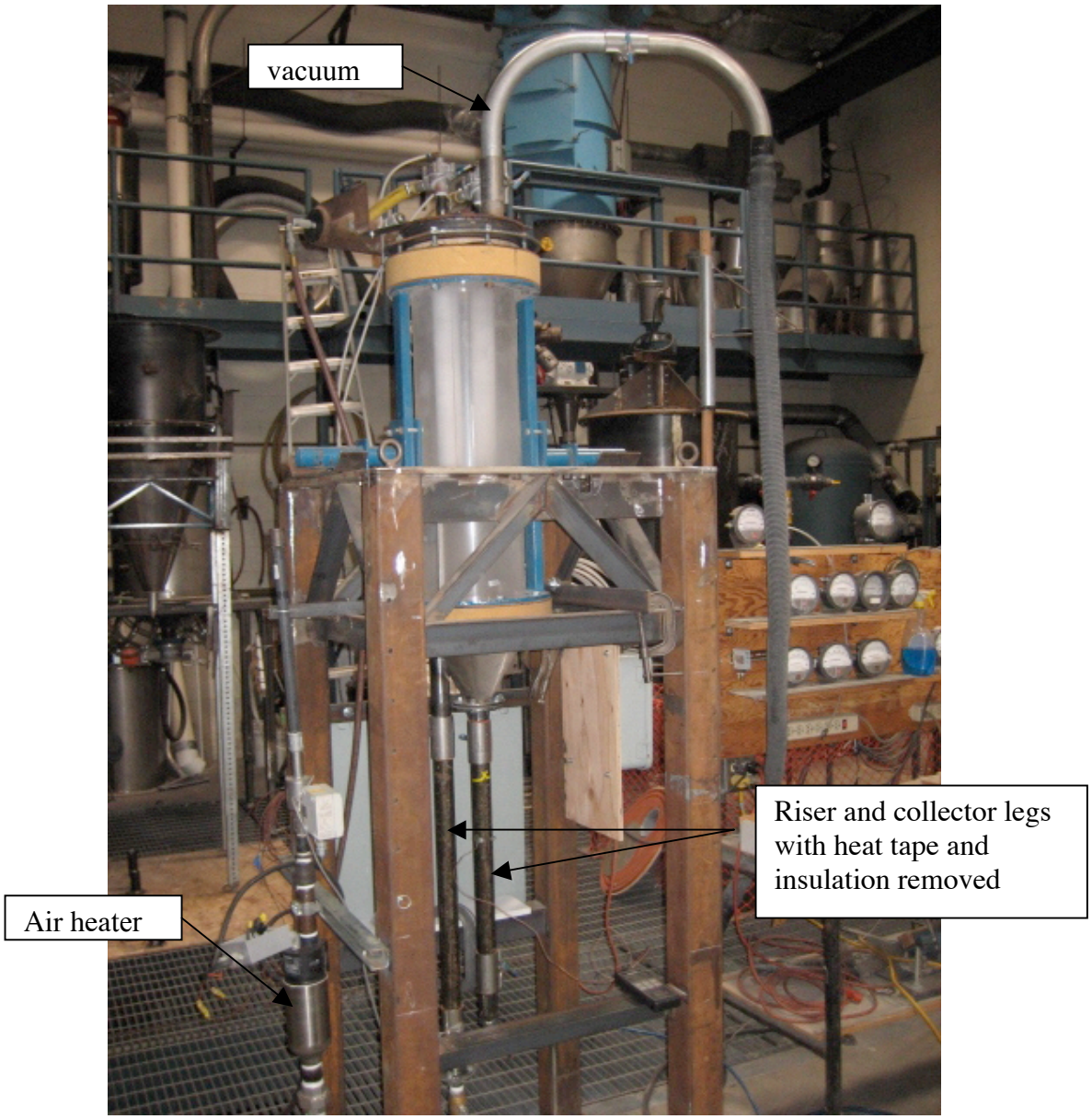
The collector leg was filled with fresh sorbent and with the heaters on, the vacuum system was started. The test was run for six hours and then all the material was collected. Samples of the recirculated material were taken for particle size analysis.

Test results

The results of the attrition tests are shown in the attached figures. Figures 2 and 3 show the particle size distributions of the original “G” and “Q” samples. Figures 4 and 5 show the distributions after recirculation in the tester.

The terms d(0.1), d(0.5), and d(0.9) refer to the particle sizes at which 10%, 50%, and 90% of the sample are smaller, respectively. The value for d(0.5) is also referred to as the mass median diameter.

As an example of the test results, the d(0.5) size of the "G" sample changed from 184.484 μm to 155.072 μm. The d(0.5) size of the "Q" sample changed from 211.776 μm to 190.725 μm.



Picture 1 Test Setup

Picture 2 Details of Recirculation Mechanism

Picture 3 Details of Curved Deflector

Conclusions

There is an obvious change in particle size of the sorbent material as a result of "entrained fluidization". It is expected that the attrition will continue with time and the particle sizes will get smaller with longer test runs.

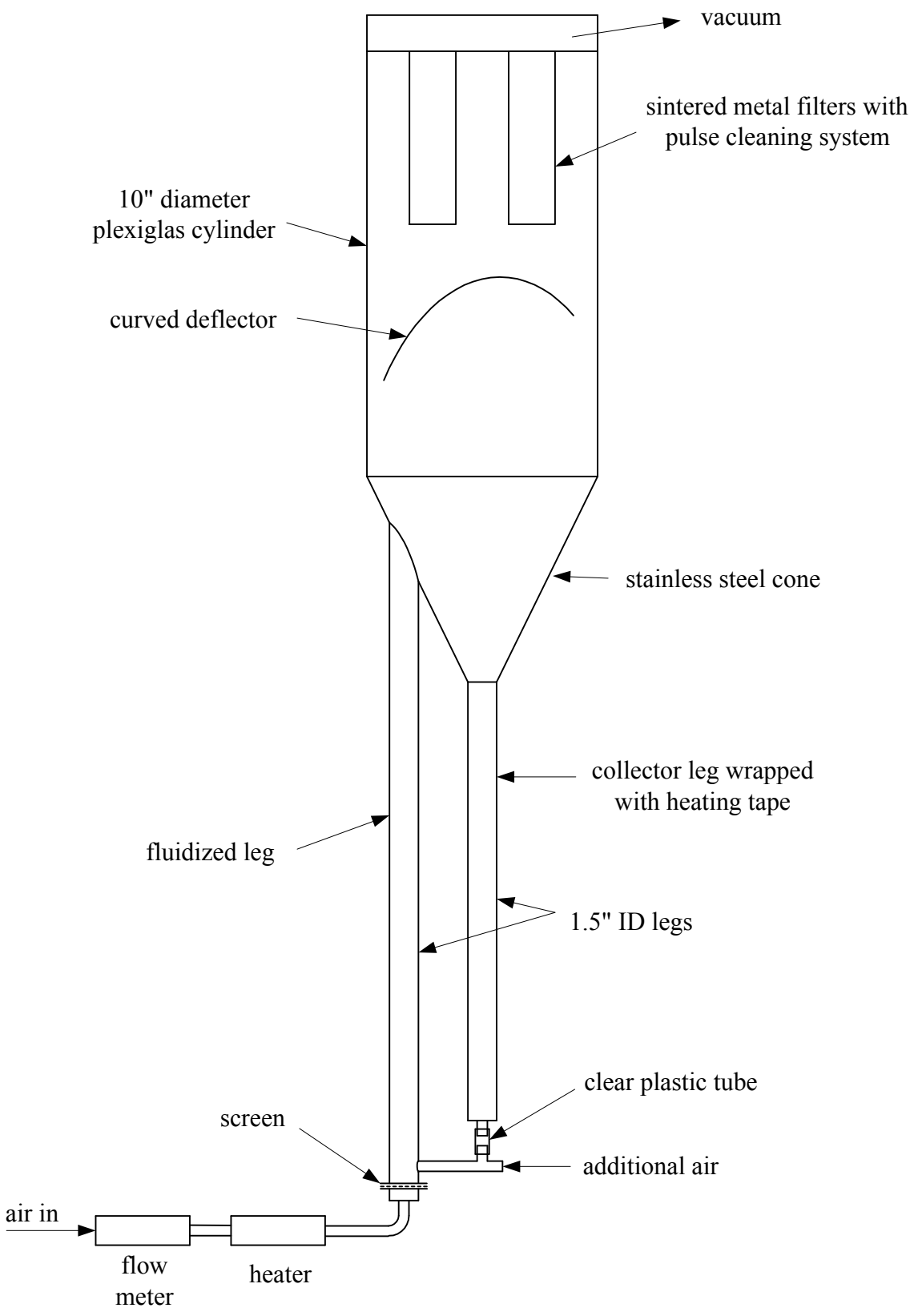


Figure 1 Layout of Fluidized Attrition Tester

Job No. 10616
Date: 6/2/09
Engineer: DSD

JENIKE & JOHANSON

Particle Size Distribution Analysis
Figure 2

Sample Name:

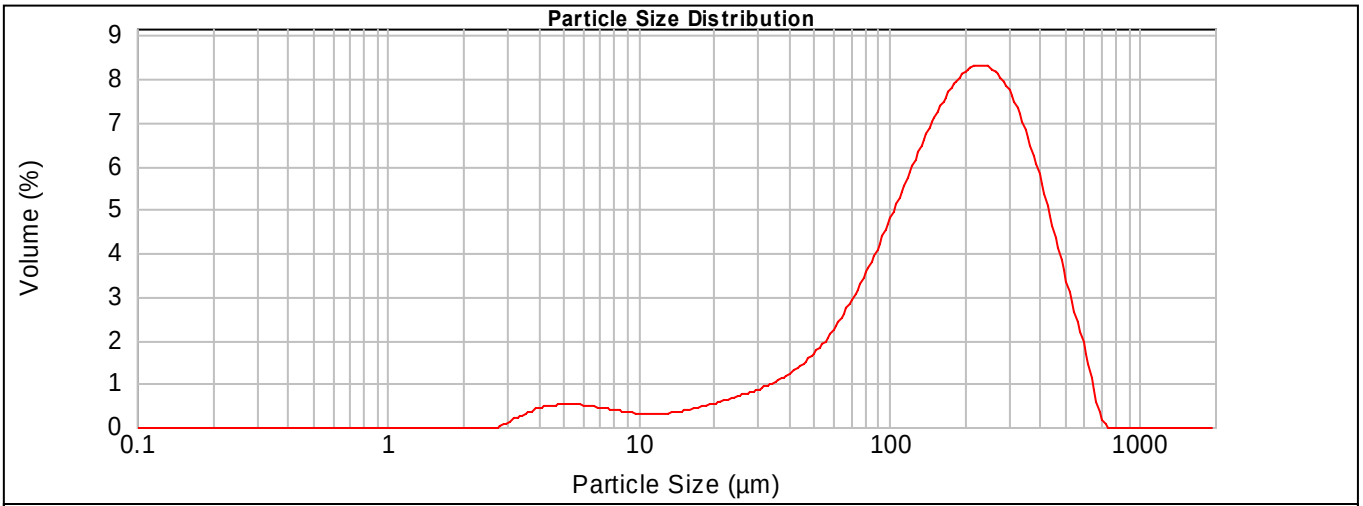
ADAES_G_3bar_grab_Avg

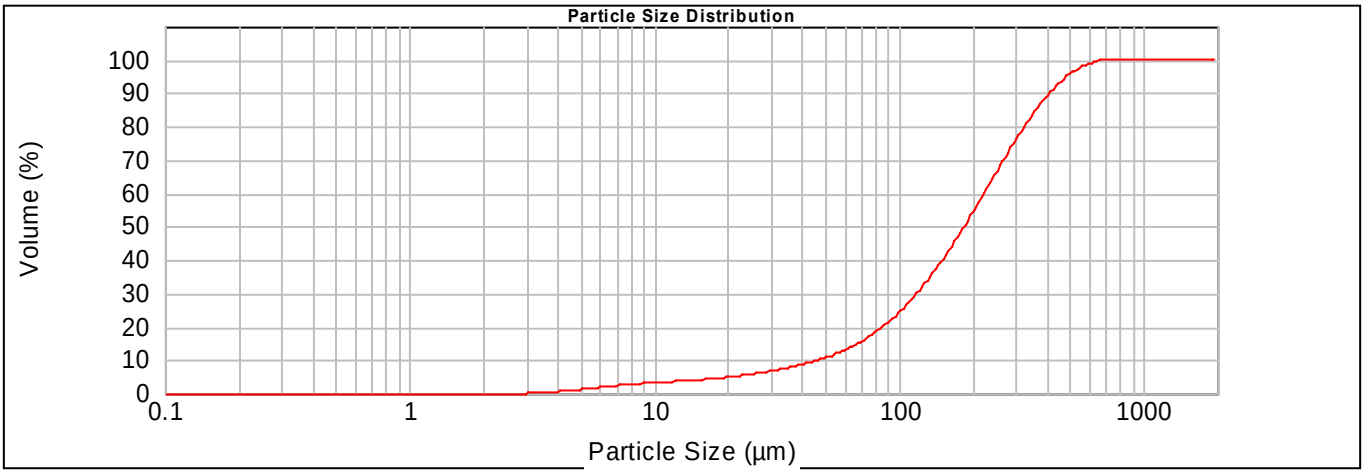
Jenike & Johanson ID: Supplier = Malvern

Measured: Monday, May 18, 2009 1:09:23 PM

Notes: Average of 3 measurements from 3bar grabs.mea

Vol. Weighted Mean D[4,3]:	**210.264**	**um**
Surface Weighted Mean D[3,2]:	**69.547**	**um**
d(0.1):	**46.666**	**um**
d(0.5):	**184.484**	**um**
d(0.9):	**412.246**	**um**





Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.300	0.00	1.803	0.00	10.840	3.37	65.156	14.30	391.651	88.08
0.353	0.00	2.123	0.00	12.759	3.69	76.695	17.36	461.012	93.62
0.416	0.00	2.499	0.00	15.019	4.05	90.278	21.28	542.656	97.43
0.489	0.00	2.941	0.00	17.679	4.49	106.266	26.16	638.761	99.62
0.576	0.00	3.462	0.20	20.810	5.03	125.085	32.07	751.885	100.00
0.678	0.00	4.075	0.59	24.495	5.69	147.238	38.99	885.043	100.00
0.798	0.00	4.797	1.10	28.833	6.50	173.314	46.81	1041.784	100.00
0.939	0.00	5.646	1.65	33.939	7.46	204.008	55.31	1226.283	100.00
1.106	0.00	6.646	2.18	39.950	8.63	240.137	64.14	1443.457	100.00
1.301	0.00	7.823	2.64	47.025	10.08	282.665	72.89	1699.092	100.00
1.532	0.00	9.209	3.04	55.353	11.92	332.725	81.04	2000.000	100.00

Optical particle model: Default
Particle RI: 1.520
Absorption: 0.1
Dispersant: Dry dispersion

Analysis model: General purpose
Obscuration: 3.42 %
Weighted Residual: 0.656 %
Measurement int. time: 1813 mS

Christian

Particle Size Distribution Analysis
Figure 3

Sample Name:

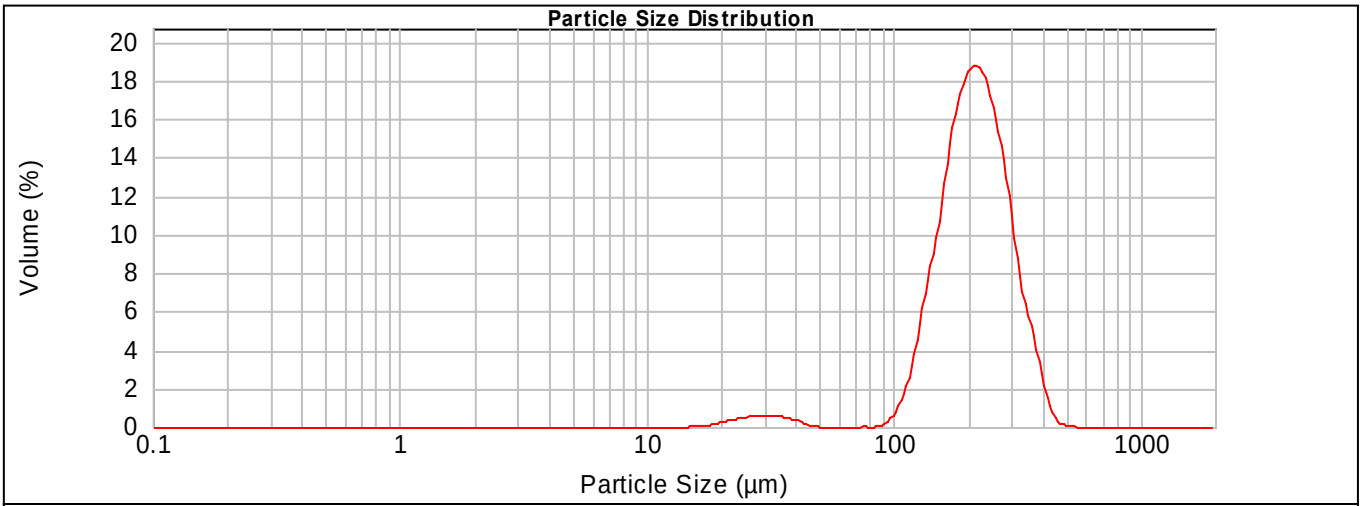
ADAES_Q_3bar_grab_Avg

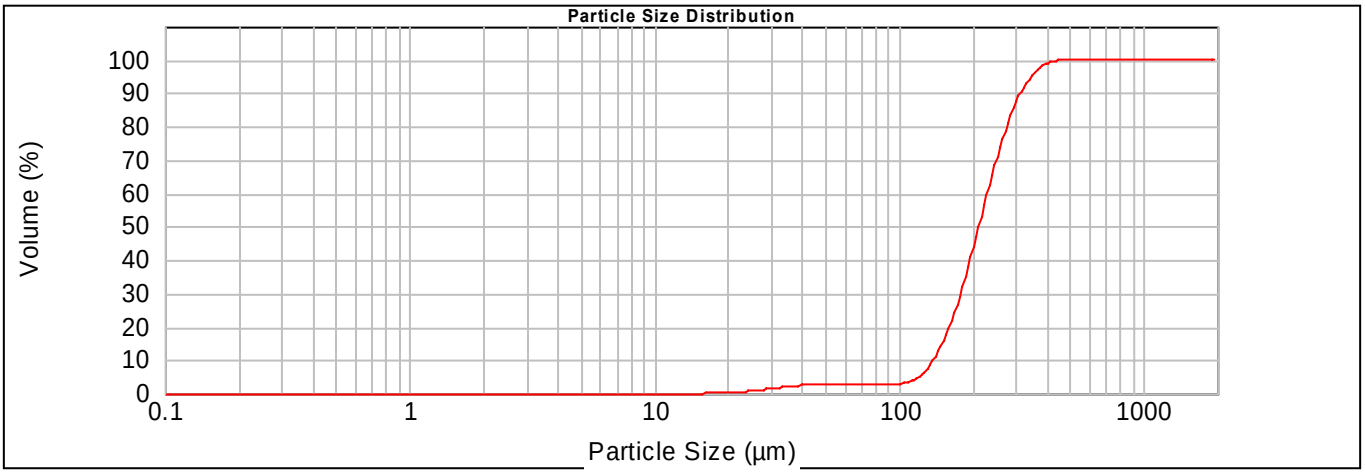
Jenike & Johanson ID: Supplier = Malvern

Measured: Monday, May 18, 2009 1:13:25 PM

Notes: Average of 3 measurements from 3bar grabs.mea

Vol. Weighted Mean D[4,3]:	**218.346**	**um**
Surface Weighted Mean D[3,2]:	**175.673**	**um**
d(0.1):	**138.312**	**um**
d(0.5):	**211.776**	**um**
d(0.9):	**313.353**	**um**





Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.300	0.00	1.803	0.00	10.840	0.00	65.156	2.62	391.651	98.53
0.353	0.00	2.123	0.00	12.759	0.00	76.695	2.62	461.012	99.91
0.416	0.00	2.499	0.00	15.019	0.00	90.278	2.61	542.656	100.00
0.489	0.00	2.941	0.00	17.679	0.04	106.266	3.17	638.761	100.00
0.576	0.00	3.462	0.00	20.810	0.24	125.085	5.89	751.885	100.00
0.678	0.00	4.075	0.00	24.495	0.66	147.238	13.55	885.043	100.00
0.798	0.00	4.797	0.00	28.833	1.25	173.314	26.79	1041.784	100.00
0.939	0.00	5.646	0.00	33.939	1.89	204.008	45.40	1226.283	100.00
1.106	0.00	6.646	0.00	39.950	2.41	240.137	65.33	1443.457	100.00
1.301	0.00	7.823	0.00	47.025	2.62	282.665	82.19	1699.092	100.00
1.532	0.00	9.209	0.00	55.353	2.62	332.725	93.04	2000.000	100.00

Optical particle model: Default
Particle RI: 1.520
Absorption: 0.1
Dispersant: Dry dispersion

Analysis model: General purpose
Obscuration: 2.56 %
Weighted Residual: 0.961 %
Measurement int. time: 2798 mS

Christian

Particle Size Distribution Analysis
Figure 4

Sample Name:

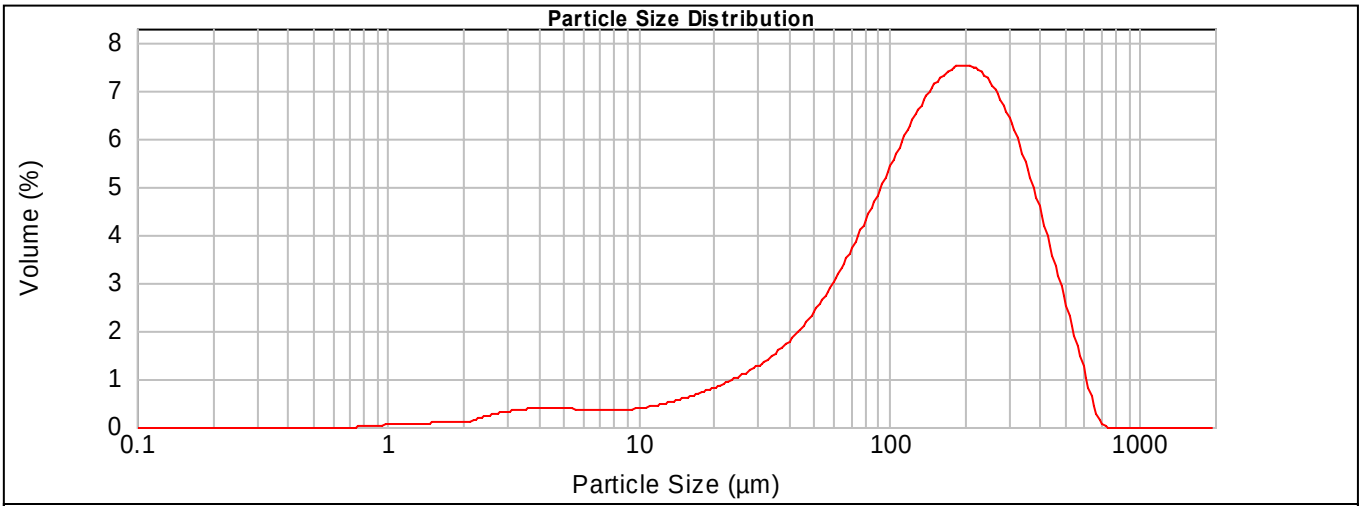
ADAES_G10_Silica_Recirculated_3bar_Avg

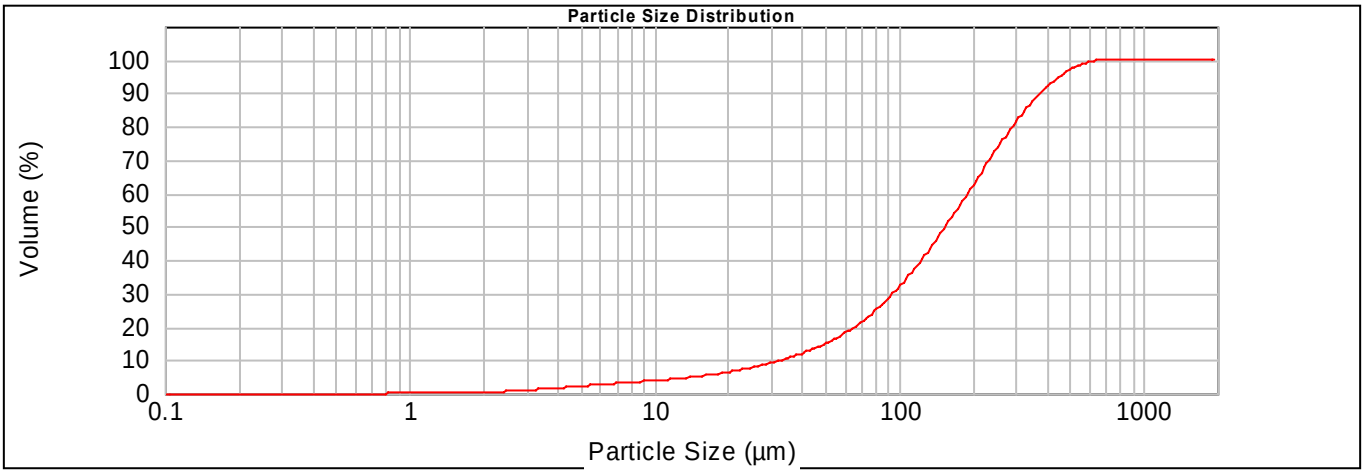
Jenike & Johanson ID: Supplier = Malvern

Measured: Tuesday, June 02, 2009 1:28:06 PM

Notes: Average of 3 measurements from 3bar grabs.mea

Vol. Weighted Mean D[4,3]:	**183.847**	**um**
Surface Weighted Mean D[3,2]:	**47.906**	**um**
d(0.1):	**33.222**	**um**
d(0.5):	**155.072**	**um**
d(0.9):	**377.603**	**um**





Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.300	0.00	1.803	0.33	10.840	4.05	65.156	19.80	391.651	91.15
0.353	0.00	2.123	0.43	12.759	4.53	76.695	23.71	461.012	95.48
0.416	0.00	2.499	0.62	15.019	5.10	90.278	28.44	542.656	98.37
0.489	0.00	2.941	0.91	17.679	5.78	106.266	34.02	638.761	99.81
0.576	0.00	3.462	1.28	20.810	6.61	125.085	40.44	751.885	100.00
0.678	0.00	4.075	1.69	24.495	7.60	147.238	47.60	885.043	100.00
0.798	0.00	4.797	2.10	28.833	8.78	173.314	55.30	1041.784	100.00
0.939	0.03	5.646	2.51	33.939	10.20	204.008	63.28	1226.283	100.00
1.106	0.08	6.646	2.90	39.950	11.92	240.137	71.22	1443.457	100.00
1.301	0.15	7.823	3.27	47.025	14.02	282.665	78.75	1699.092	100.00
1.532	0.24	9.209	3.64	55.353	16.61	332.725	85.50	2000.000	100.00

Optical particle model: Default
Particle RI: 1.520
Absorption: 0.1
Dispersant: Dry dispersion

Analysis model: General purpose
Obscuration: 3.10 %
Weighted Residual: 0.596 %
Measurement int. time: 5613 mS

Christian

Particle Size Distribution Analysis
Figure 5

Sample Name:

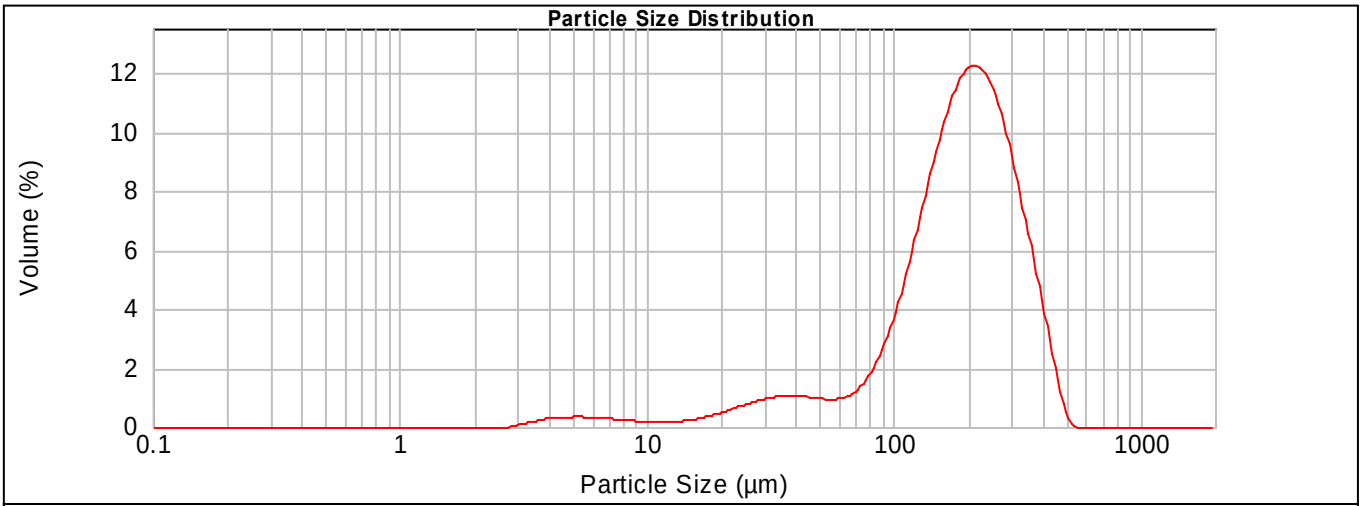
ADAES_Q10_Silica_Recirculated_3bar_Avg

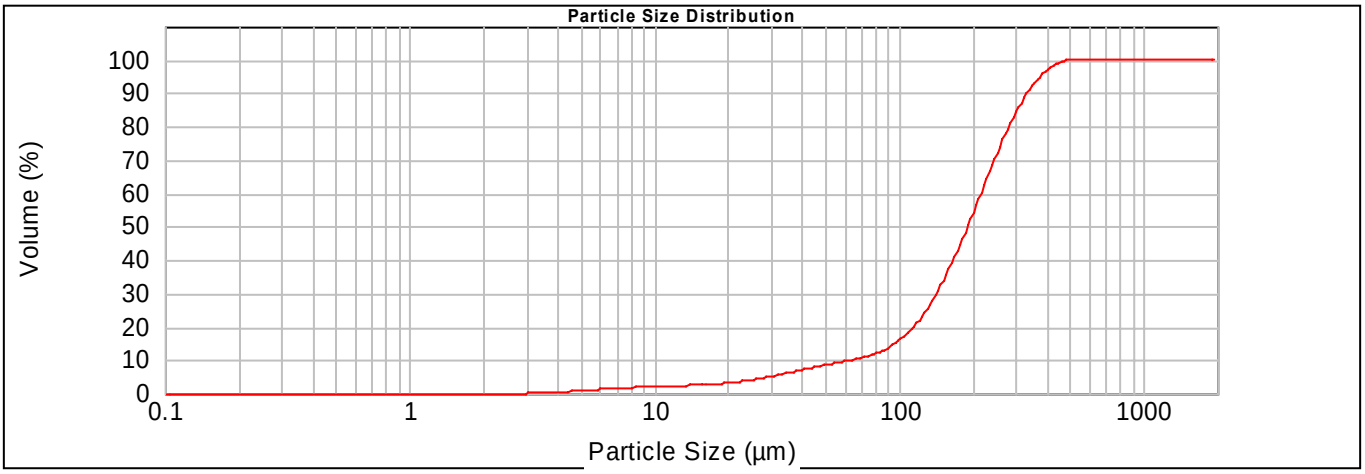
Jenike & Johanson ID: Supplier = Malvern

Measured: Tuesday, June 02, 2009 1:32:51 PM

Notes: Average of 3 measurements from 3bar grabs.mea

Vol. Weighted Mean D[4,3]:	**197.823**	**um**
Surface Weighted Mean D[3,2]:	**86.770**	**um**
d(0.1):	**63.578**	**um**
d(0.5):	**190.725**	**um**
d(0.9):	**334.774**	**um**





Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.300	0.00	1.803	0.00	10.840	2.14	65.156	10.16	391.651	96.14
0.353	0.00	2.123	0.00	12.759	2.30	76.695	11.48	461.012	99.45
0.416	0.00	2.499	0.00	15.019	2.51	90.278	13.64	542.656	100.00
0.489	0.00	2.941	0.00	17.679	2.82	106.266	17.32	638.761	100.00
0.576	0.00	3.462	0.13	20.810	3.29	125.085	23.22	751.885	100.00
0.678	0.00	4.075	0.39	24.495	3.96	147.238	31.73	885.043	100.00
0.798	0.00	4.797	0.72	28.833	4.84	173.314	42.70	1041.784	100.00
0.939	0.00	5.646	1.08	33.939	5.89	204.008	55.35	1226.283	100.00
1.106	0.00	6.646	1.43	39.950	7.01	240.137	68.36	1443.457	100.00
1.301	0.00	7.823	1.72	47.025	8.11	282.665	80.23	1699.092	100.00
1.532	0.00	9.209	1.95	55.353	9.14	332.725	89.70	2000.000	100.00

Optical particle model: Default
Particle RI: 1.520
Absorption: 0.1
Dispersant: Dry dispersion

Analysis model: General purpose
Obscuration: 3.40 %
Weighted Residual: 0.857 %
Measurement int. time: 3871 mS

Christian

APPENDIX F: ADSORPTION RESEARCH, INC. PARTICLE DENSITY AND CRUSH STRENGTH TEST REPORT

Draft Report

Adsorbent Characterization: AX and BN

Submitted to:
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ADA-ES, Inc.
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Littleton, CO 80120-4525

Submitted by:
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Adsorption Research, Inc.
6175 Shamrock Court, Suite D
Dublin, Ohio 43016-1200
614-798-9090
Fax: 798-9091

May 3, 2011

Project Overview

The purpose of this study was to determine the particle density and crush strength of the provided adsorbents labeled AX and BN. Adsorbent AX was delivered as a powder while BN was small beads. Particle densities were measured for both, but crush strength was only measured for the BN material, as it is impractical to measure the crush strength of a powder.

Results: Adsorbent Properties

The particle density, ρ_P, is the mass of the adsorbent per unit volume of a particle, i.e., once the intraparticle voids have been deducted. The particle density for AX – as delivered – was found to be 0.835, 0.804, and 0.824 for an average of 0.821± 0.016 g/cm^3. Values for BN were 0.651, 0.632, and 0.655 g/cm^3 for an average of 0.646 ± 0.012 g/cm^3. The values for BN after pretreating at 55°C at high humidity were: 0.580, 0.597, 0.581 g/cm^3 for an average of 0.586 ± 0.009 g/cm^3 (error = 1.616%). There was a (76.415 - 46.713) g / 76.415 g = 38.9% mass loss during pretreatment. The change in particle density, however, was only 9.3%.

Crush strength values were found for BN. They ranged from 232 to 1019 g. The average mass required was 412.5 ± 175.8 g. The median of the masses was 363.3 g. The distribution of measured values is shown in Figure 1. The lowest masses required were for the smallest particles and the particle was determined to be "crushed" when the particle audibly cracked.

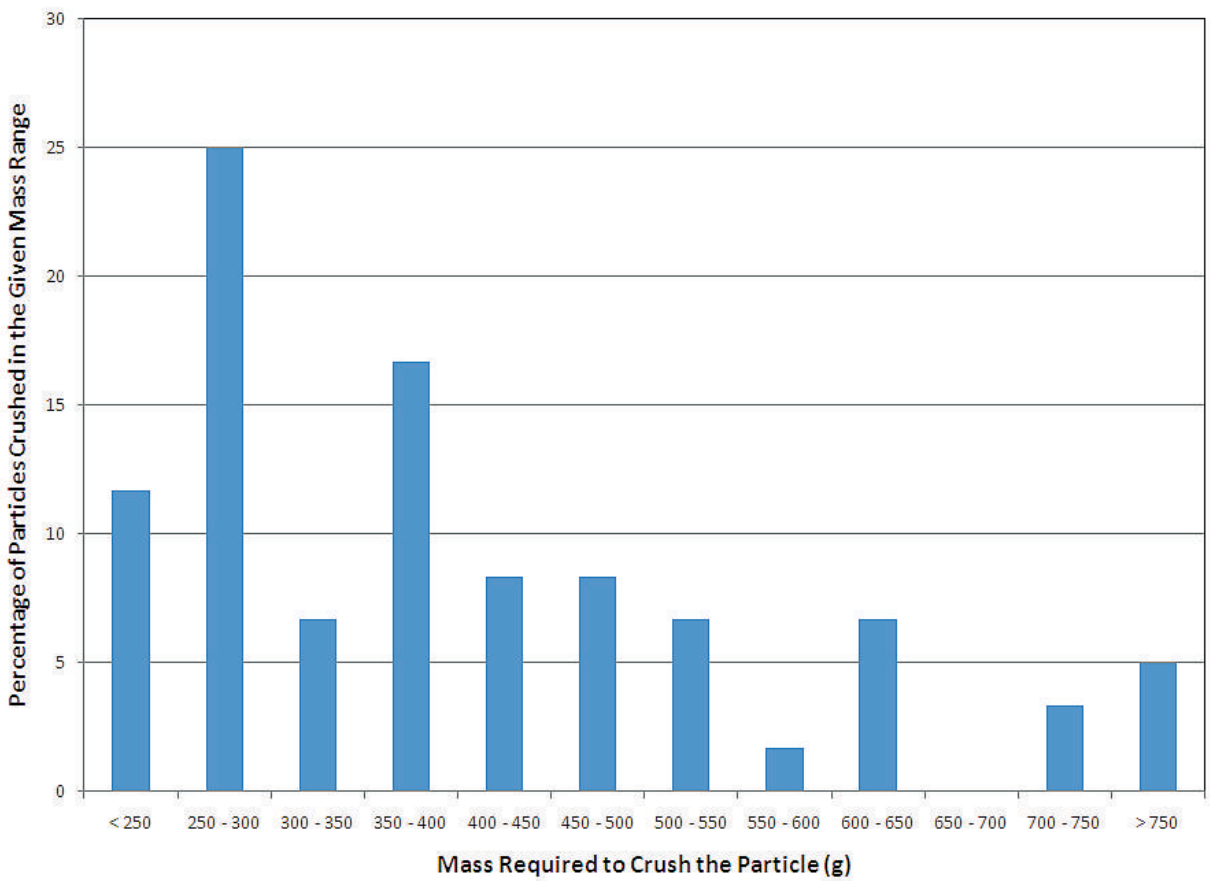

Figure 1. Crush Strength Results