



Evaluation of solid sorbents as a retrofit technology for CO₂ capture

Sharon Sjostrom*, Holly Krutka

ADA Environmental Solutions, 8100 Southpark Way, Unit B, Littleton, CO 80120, USA

ARTICLE INFO

Article history:

Received 30 June 2009

Received in revised form 27 October 2009

Accepted 13 November 2009

Available online 4 December 2009

Keywords:

Adsorption

CO₂ adsorbents

Carbon capture

ABSTRACT

Processes based upon solid sorbents are currently under consideration for post-combustion CO₂ capture. Twenty-four different sorbent materials were examined on a laboratory scale in a cyclic temperature swing adsorption/regeneration CO₂ capture process in simulated coal combustion flue gas. Ten of these materials exhibited significantly lower theoretical regeneration energies compared to the benchmark aqueous monoethanolamine, supporting the hypothesis that CO₂ capture processes based upon solids may provide cost benefits over solvent-based processes. The best performing materials were tested on actual coal-fired flue gas. The supported amines exhibited the highest working CO₂ capacities, although they can become poisoned by the presence of SO₂. The carbon-based materials showed excellent stability but were generally categorized as having low CO₂ capacities. The zeolites worked well under dry conditions, but were quickly poisoned by the presence of moisture. Although no one type of material is without concerns, several of the materials tested have theoretical regeneration energies significantly lower than that of the industry benchmark, warranting further development research.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Approximately one-third of all anthropogenic CO₂ emissions are created when generating electricity [1]. Therefore, in a carbon-constrained future the emissions from stationary point sources, such as coal-fired power plants, must be addressed. Carbon capture and sequestration (CCS) will be an important component of reducing worldwide CO₂. Specifically, for post-combustion CO₂ capture, solvent-based removal such as aqueous amines or chilled ammonia can be utilized in a temperature swing cyclic process. However, studies have shown that use of aqueous monoethylamine (MEA) for 90% CO₂ 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 CO₂ removed [2]. To reduce the costs associated with commercial-scale CCS technology, developers must continue to evaluate and improve options.

Similar to aqueous amines, solid sorbents can also be used in a temperature swing process, but have the potential to drastically reduce the energy required to release the CO₂ due to higher CO₂ loading, lower material heat capacity and/or lower heat of reaction. Many different types of solid materials for CO₂ capture have been or are currently being investigated, including supported amines [3–9], carbon-based sorbents [10–13], supported carbonates [14,15], and zeolites [16]. These materials are being developed and tested at universities, government laboratories and by private

institutions worldwide. However, during the testing of these materials, the adsorption and regeneration conditions are often highly varied, leading to difficulty in comparing material performance.

ADA Environmental Solutions is examining available sorbents as well as process equipment options to assess the viability and accelerate development of solid sorbents as a CO₂ capture option. This work is being completed through a DOE Cooperative Agreement and supplemental funding from EPRI and power producers. During the first phase of this program, ADA is evaluating materials from top sorbent developers throughout the world. These materials are being tested under the same adsorption conditions in the laboratory using simulated coal-fired flue gas, typical of that observed downstream of a wet scrubber at a conventional pulverized coal-fired power plant. Materials demonstrating the most promise from the initial tests were then screened using actual flue gas at a lignite coal-fired electric generating unit (EGU). The goal of this phase of the research is to help clarify each sorbents' performance under realistic operating conditions. In a parallel effort, large-scale process options are being reviewed and evaluated. The results of this equipment-related phase of work will be presented in future publications.

2. Experimental

2.1. Classification of materials

All materials submitted under this program have been given a non-identifying alphabetic identifier. This precaution has been

* Corresponding author. Tel.: +1 303 339 8856; fax: +1 303 734 0330.

E-mail addresses: sharons@adaes.com (S. Sjostrom), hollyk@adaes.com (H. Krutka).

taken to protect the identities of the sorbent developers and in the hopes of obtaining the widest array of samples.

2.2. Sorbent screening equipment and procedure

All lab-scale sorbent screening was conducted 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 0.4 to 2.5 g. The sorbent was held in a fixed bed for all tests. Although it is likely that a fixed bed does not represent the final contactor design for a large-scale system, this configuration allowed fast and efficient lab-scale sorbent screening. Fig. 1 is a schematic of the sorbent screening testing unit when set-up for laboratory testing (only minor modifications are necessary for field testing). Note that the CO₂ monitor's 90% response time was 10 s. 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 quantities less than 1.0 g more extensively than it did for those tested in 2.5 g quantities. It is preferable to use greater quantities of sorbent for evaluation, however, in many cases small particle size resulted in a high pressure drop across the fixed bed. A large pressure drop could alter the CO₂ removal due to the relationship between CO₂ partial pressure and working CO₂ capacity. In addition, in several cases the sorbent developer was unable to provide a 2.5 g sample, so testing a smaller sample size was necessary.

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 otherwise recommended by the sorbent developer. A thermocouple on the outside of the glass fixed bed was used to determine when the bed reached the flushing temperature, at which point the sorbent was flushed with dry N₂ for 10 min. Then the simulated flue gas, composed by mixing compressed gases from tanks, was sent through the bypass line (i.e., the gas was not contacting the sorbent). The composition of the laboratory sample gas on a volumetric basis was approximately 10–14% CO₂,

4% O₂ and a balance of N₂. The relative humidity, set at either 0%, 45%, or 90%, was controlled using a peristaltic pump; addition of moisture resulted in a simulated flue gas that was 0%, 6%, or 17.5% (by volume) of the gas composition, respectively. When the CO₂ monitor reading was stable, the datalogger was enabled and a baseline CO₂ concentration was established. This step was especially important during field testing where the CO₂ concentration was not controlled, but was a function of coal type, plant configuration, operating conditions, etc. After the baseline CO₂ concentration was measured, the gas flow was directed through the sorbent. After the CO₂ levels returned to their original levels (i.e., the sorbent was saturated with CO₂), the gas was redirected through the bypass, which marked the end of the capture step.

A temperature swing with N₂ flushing was used to regenerate the sorbents and desorb the CO₂. First, the sorbent was heated with no gas flow. When the thermocouple on the fixed bed indicated the desired regeneration temperature had been reached, dry N₂ was sent through the bed to flush out the CO₂. 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. For most materials, a parametric evaluation of the regeneration temperature was completed. After discussing any issues related to thermal stability, a low regeneration temperature was initially used, often 80 °C. Then, during each subsequent adsorption/regeneration cycle, the regeneration temperature was increased by 10 °C (i.e., cycle 2 regeneration was at 90 °C, cycle 3 regeneration was at 100 °C, etc.). Testing the sorbents at multiple regeneration temperatures helped to identify optimal cyclical operating conditions. Note that a minimum regeneration temperature of 80 °C and a maximum regeneration temperature of 120 °C were used unless otherwise specified by the sorbent developer. For instance, in some cases thermal stability was of concern so the maximum regeneration temperature was limited to 100 °C.

Integration of either the adsorption profile (i.e., breakthrough curve) or the regeneration profile can be used to calculate the working CO₂ capacity (i.e., delta loading). The working capacity is the difference in the CO₂ immobilized on the sorbent after regeneration versus that after sorption. It is important to use the working capacity rather than the absolute capacity when comparing materials for use in a CO₂ capture process. As an example of a typ-

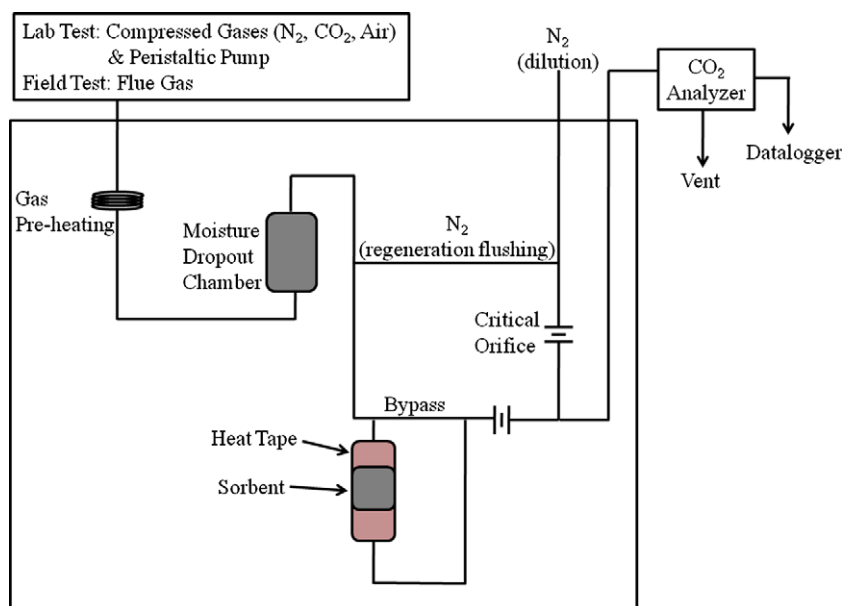


Fig. 1. Schematic of sorbent screening unit.

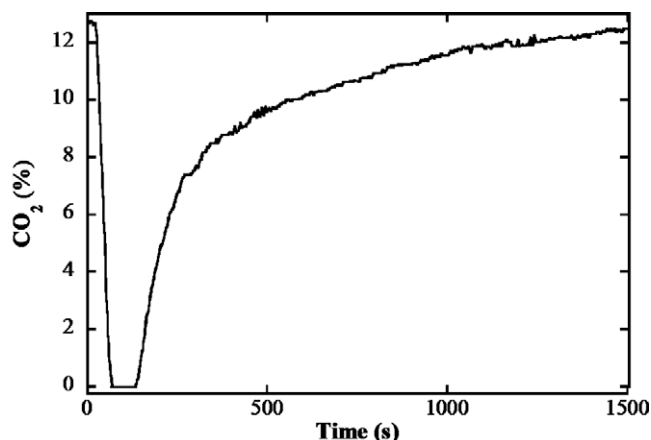


Fig. 2. Sorbent R CO₂ breakthrough curve.

ical breakthrough curve, the CO₂ concentration during sorption for sorbent R is provided in Fig. 2.

One key issue that would limit the use of commercial-scale fixed beds for this application is the heat management. Since all the sorbents evaluated under this study have exhibited an exothermic reaction with CO₂, regardless if the reaction is physical or chemical in nature, the sorbents heat up as they react with CO₂. Unfortunately, in most cases the sorbent's CO₂ 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 CO₂ capture. Similarly, if the sorbent is allowed to cool due to the endothermic release of CO₂, all the CO₂ 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 was high, the residence time was low (~1 s) and some CO₂ may have passed through the fixed bed unreacted, even when adsorption/reaction 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.

2.3. 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 laboratory screening. Then, the best materials were selected for field tests and were used for many adsorption/regeneration cycles carried out at 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 (°C)	55–60
CO ₂ concentration (%)	10–12
Moisture	Saturated
O ₂ (%)	5–6
NO _x (ppm)	100–120
SO ₂ (ppm)	50–250

The field testing location was downstream of a wet scrubber for SO₂ removal at a plant firing lignite coal. Because the sample port was downstream of the scrubber, the SO₂ levels were low (typically less than 200 ppm), the temperature was reduced, and the gas stream was saturated with moisture.

For the field testing, there was one significant issue with sample flue gas. The sample was excess gas from the plant's existing continuous emissions monitoring system. This system included a sintered metal extraction probe installed into the duct. To prevent excessive build-up of deposits, the plant periodically back-flushed the probe. During this blowback, the sample gas was unavailable for testing. This led to increased error in the adsorption profiles during field testing, which in turn increased the error involved with calculating the working capacity based on integration of the adsorption profile. Therefore, to minimize the impact of the error on results, many adsorption/regeneration cycles were completed, and the working capacities were averaged.

The testing procedure was modified between the two field tests, based on preliminary results and feedback from the sorbent developers. Two important modifications were made to the experimental apparatus and procedures for the second round of field testing. 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 N₂ flush gas began to flow as the materials were heating. The second change was based on concerns that decreases in CO₂ capacity observed during the first field test may be attributed to heating the sorbent while flue gas was present in the interparticle void spaces.

3. Theory/calculation

When evaluating and comparing sorbents for use in a commercial-scale CO₂ capture and sequestration system, one of the most important evaluation criteria is the energy required for regeneration. This allows for direct comparison of sorbents with different regeneration temperatures, working CO₂ capacities, heat capacities, etc., Eq. (1) shows the energy balance for regeneration

$$\frac{Q}{m_c} = \frac{m_e}{m_c} C_e \Delta T + \frac{B}{L} C_s \Delta T + C_{p,c} T_2 - C_s T_1 + \frac{Q_r}{m_c} [17] \quad (1)$$

where Q is the regeneration heat input (kJ), m_c is the mass of adsorbed CO₂ (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 CO₂ loading, kg CO₂/kg sorbent, C_s is the sorbent specific heat (kJ/kg K), $C_{p,c}$ is the constant pressure specific heat for CO₂ (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 CO₂).

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 Eq. (1) can be neglected because no equipment heating will be required during regeneration (i.e., the regeneration system will be maintained at the regeneration temperature and the sorbent will be moved). The second term on the right hand side of Eq. (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. Note that the sorbent loading is the working capacity/100% when the working capacity is reported as a weight percent. The third and fourth term on the right hand side of Eq. (1) can be combined to determine the energy required for the phase change of CO₂ from a free gas to one adsorbed on a solid. The final term on the right

hand side of Eq. (1) is the energy required to overcome the endothermic reaction associated with desorbing the CO₂ from the sorbent. For physical adsorbents, this term is usually an order of magnitude lower than sorbents that chemically react with the CO₂. However, the loading is also lower.

For all the sorbents tested in this program, the theoretical energy required for regeneration was calculated using Eq. (1). The result of this calculation can be used to compare different materials and assess their respective viability for use in a commercial-scale CO₂ capture system. Note that from previous reports, a liquid MEA CO₂ capture system requires approximately 4530 kJ/kg CO₂ (1934 BTU/lb CO₂) [18]. This value is used as a benchmark against which the sorbents can be compared. The regeneration energy is the preferred term for comparison because it takes into account working capacity, heat capacity, regeneration temperature, and heat of reaction.

4. Results and discussion

Table 2 lists 24 sorbents that exhibited CO₂ removal properties during laboratory screening using simulated flue gas. The sorbent type, mass tested, minimum regeneration temperature, maximum regeneration temperature, maximum, minimum, and average CO₂ working capacities for each material are presented in this table. In addition, the theoretical regeneration energy calculated using Eq. (1) for each of the materials is also given, which is a preferable means of comparison because the working capacities are based on the optimal regeneration temperature. This theoretical regeneration energy was calculated by using the average working capacity for the tests that include moisture (when available). In addition, the highest regeneration temperature was used. For this reason, these are not the best-case values, but are characteristic of the measured sorbent performance under moist simulated flue gas conditions.

Carbon-based sorbents A, B, C, G, H, I, P and AA rely primarily on physical adsorption. Sorbent A was composed of carbon nanotubes

with limited amine functionalization. All the other carbon-based sorbents were varieties of activated carbon. Except for sorbent A, these materials were not treated with chemicals after activation (i.e., no amine or carbonate loading). With the exception of sorbent A, the CO₂ capacities of the carbon-based sorbents were lower than the CO₂ capacities of supported amines. For physical adsorbents, the energy required during regeneration to counteract the endothermic reaction is low, ~3 kJ/mol CO₂ [12]. However, if the CO₂ capacity is also low, more sorbent must be heated during regeneration. In addition, more material would have to be moved, which is an important consideration in a full-scale system. Based on the laboratory results, sorbent A was the only physical adsorbent that was competitive with the theoretical regeneration energy of aqueous MEA (~4530 kJ/kg CO₂). Since the physical adsorbents are expected to have longer lives and may not require additional SO₂ scrubbing, they continue to be viable options, especially if further improvements in working CO₂ 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 (see Table 2 for actual zeolite type) tested during this program showed signs of CO₂ removal from simulated flue gas. Note that sorbents T and U were 13× treated with a hydrophobic liquid in the attempt to reduce the hydrophilic nature of these materials. Unfortunately, this material blocked the pores and actually decreased the working CO₂ capacity. Sorbent O was included in the field tests because it had exhibited the highest capacity of the zeolites tested prior to the first field test. It was able to remove CO₂ during all adsorption cycles. Sorbent M, which was evaluated in the laboratory after the first round of field tests, exhibited a superior capability to remove CO₂ from dry, simulated flue gas. However, based on the poor performance of all zeolites in the presence of moisture, it was not included in the second round of field testing. To improve the CO₂ capture potential of zeolites the effect of moisture must be addressed.

Sorbents D, E, F, Q, R, S, V, W, X, and Y were variations of supported amine materials. The exact composition of specific materi-

Table 2
CO₂ working capacities during laboratory tests.

Laboratory		Testing conditions				Working CO ₂ capacity (wt%)			Q _{regen} (kJ/kg CO ₂)
Sorbent ID	Sorbent type	Mass (g)	T _{regen-min.} (°C)	T _{regen-max.} (°C)	# Cycles	Max.	Min.	Average	
A	Carbon nanotubes ^a	0.6	90	130	5	5.05	2.05	4.10	1700
B	Carbon-based ^b	2.5	80	120	10	0.58	0.38	0.48	13,600
C	Carbon-based	2.5	80	120	10	0.54	0.43	0.47	13,900
D	Supported amine	2.5	80	120	10	7.48	3.92	7.01	2600
E	supported Amine	2.5	90	90	10	1.34	0.72	0.95	6100
F	Supported amine ^{a,b}	0.5	90	120	7	4.71	3.70	4.23	3400
G	Carbon-based	2.0	80	120	10	0.97	0.28	0.38	17,200
H	Carbon-based	2.5	80	120	15	1.07	0.66	0.75	8700
I	Carbon-based	2.5	80	120	15	1.09	0.57	0.68	9600
J	Zeolite (13X)	2.5	200	250	10	3.37	0.69	0.80	18,800
M	Zeolite (5A)	2.5	200	250	10	5.14	0.22	1.28	12,000
N	Zeolite (HiSiv 3000)	2.5	80	150	5	0.40	0.33	0.37	26,400
O	Zeolite (NaY)	2.5	200	250	18	1.61	0.83	1.12	13,300
P	Carbon-based	2.5	80	120	10	0.81	0.61	0.63	7200
Q	Supported amine	0.5	80	130	9	4.22	1.13	3.27	3550
R	Supported amine	2.5	80	100	10	13.43	8.44	9.80	1900
S	Supported amine	2.5	80	100	10	3.29	1.82	2.60	2700
T	Zeolite (13× treated)	2.5	100	200	10	0.83	0.23	0.43	3440
U	Zeolite (13× treated)	2.5	100	200	10	0.93	0.13	0.42	35,200
V	Supported amine	0.5	80	120	10	4.21	1.11	2.87	4300
W	Supported amine	0.4	80	120	10	5.22	1.44	3.86	3500
X	Supported amine	2.5	80	100	10	9.09	5.92	6.66	2200
Y	Supported amine	2.5	80	100	8	9.39	3.63	4.16	3400
AA	Carbon-based	2.5	80	120	10	0.61	0.38	0.48	13,600

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

^b Test did not include 90% relative humidity.

als cannot be provided due to the terms of the test materials agreements. However, generalities can be provided. Most of these materials contained approximately 40–50 wt% amine. In several cases this reactant was polyethyleneimine. The substrates included several mesoporous silicas as well as clays, frameworks, and other high surface area supports. Details regarding the performance of individual materials are widely available in the public literature. Several of these materials were powders and could only be tested in quantities of 0.5 g or less. In general, supported amines exhibited high CO₂ working capacities. It should be noted that the 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. D, F and Q were included in the first round of field testing based on their positive results in the laboratory (i.e., low theoretical regeneration energy). Fig. 3 shows the maximum, minimum, and average laboratory working CO₂ capacities of all the sorbents.

Based on the laboratory testing results, the theoretical regeneration energy was calculated for all sorbents that were able to remove CO₂ from the simulated flue gas. Fig. 4 shows the theoretical regeneration energy for all the materials and also includes a dotted line for the benchmark aqueous MEA value. The values in Fig. 4 are based on the average working CO₂ capacity at the highest regeneration temperature tested (i.e., not optimized values). Based on the laboratory tests, eleven materials included in the screening program exhibited significantly lower theoretical regeneration energies compared to the benchmark. In addition, several more showed promise and may reach the benchmark with slight improvements.

To complete the most comprehensive evaluation of solid sorbents for post-combustion CO₂ capture, at least one material from each sorbent classification tested in the program to date (i.e., car-

bon-based, zeolites, and supported amines) was selected for field testing. Within each sorbent type, the selections for field testing were made based on the theoretical regeneration energy. Out of all of the sorbents tested in the laboratory, five were selected for the first round of field testing. One carbon-based material, three supported amines, and one zeolite were tested for multiple CO₂ adsorption/regeneration cycles using actual flue gas. Table 3 lists the sorbents that were included, the mass tested, the regeneration temperatures, the number of field cycles run and key results from these experiments. The theoretical regeneration energy provided in Table 3 is based on the average working capacity at the regeneration temperature, which was constant during field tests.

The minimum, maximum, and average working capacities recorded during the field test are also shown in Fig. 5. The three supported amines (D, F, and Q) exhibited the highest working capacities, with averages ranging from approximately 2.5 to greater than 6%. The carbon-based material had an average working CO₂ capacity of nearly 1 wt%, while the zeolite, sorbent O, had an average capacity of approximately 0.5 wt%.

Although the CO₂ 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 CO₂ capture system, sorbents must retain their capacity for long periods of time, likely thousands of cycles. Therefore, the field tests included testing the sorbents for many cycles to identify any consistent loss of capacity.

A fresh bed of sorbent D was used for 11 cycles during field tests. Although this material continued to exhibit high CO₂ capacity, the field tests showed significantly reduced CO₂ removal compared to the laboratory results. In addition, a slow decrease in the CO₂ 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, the performance of sorbent D decreased the most during field testing.

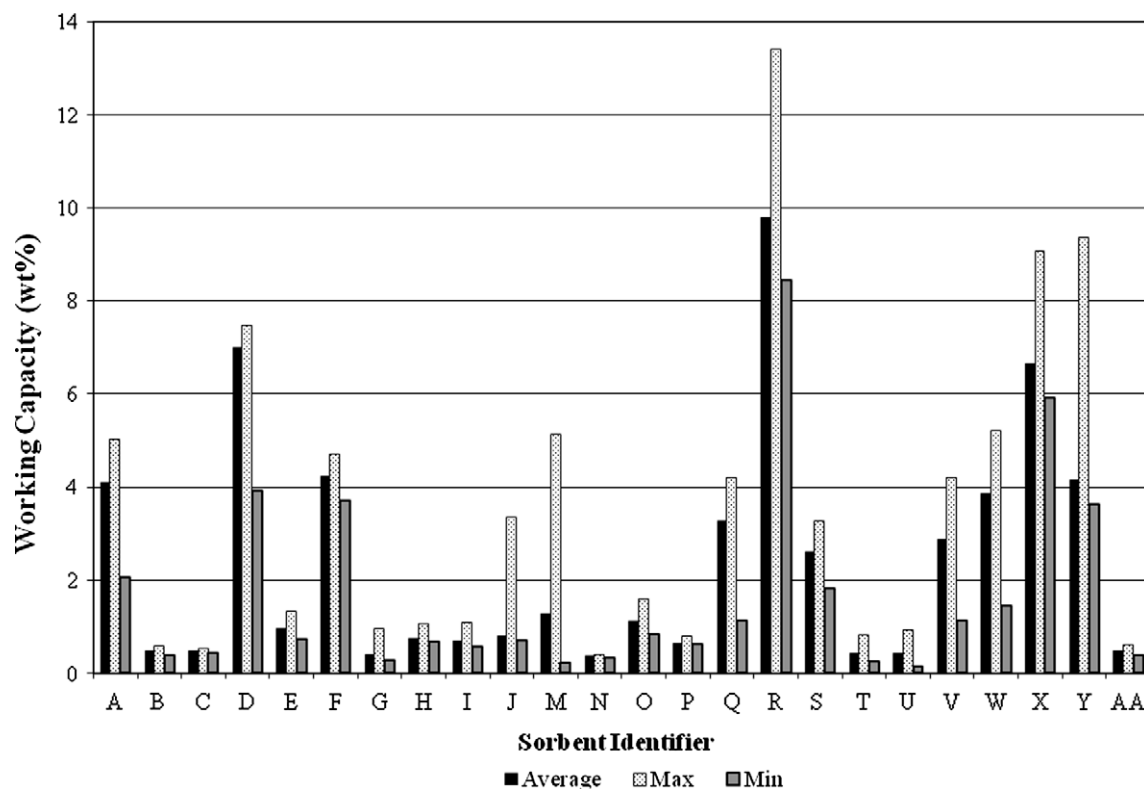


Fig. 3. CO₂ working capacity during laboratory tests.

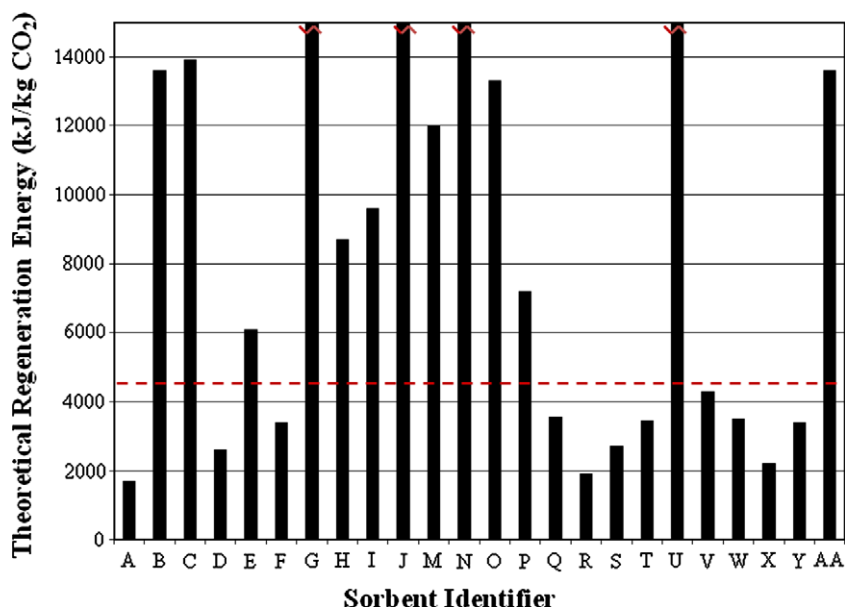


Fig. 4. Theoretical working capacity based on laboratory screening.

Table 3

Field testing round 1 results.

Field 1							
Sorbent ID	Testing conditions			Working CO ₂ capacity (wt%)			Q _{regen} (kJ/kg CO ₂)
	Mass (g)	T _{regen} (°C)	# Cycles	Max.	Min.	Average	
D	2.5	120	11	8.2	4.8	6.2	2700
F	0.5	120	34	5.4	3.0	4.1	3500
H	2.5	120	18	1.1	0.7	0.9	7200
O	2.5	200	18	0.8	0.3	0.5	29,700
Q	0.5	120	17	3.5	1.2	2.4	4900

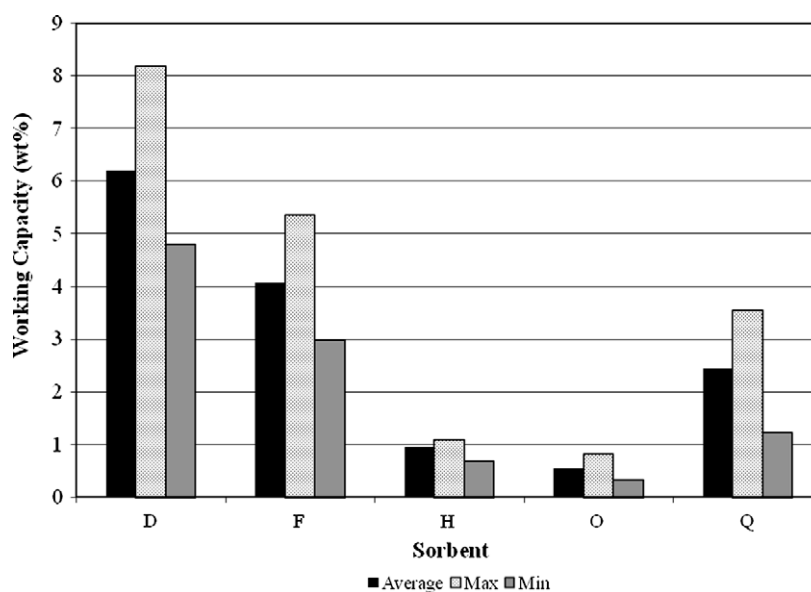


Fig. 5. Working capacity during first round field testing.

Sorbent F was also included in field tests due to its high CO₂ capacity and complete cyclic stability during laboratory testing. This material was tested in 34 adsorption/regeneration cycles on actual flue gas. Fig. 6 contains the working CO₂ capacity for each

cycle completed during the first round of field testing. A trendline was used on Fig. 6 to fully illustrate the decrease in working CO₂ capacity. Between the first cycles and the last cycles, the CO₂ capacity had decreased by approximately 20%. Based on a SO₂

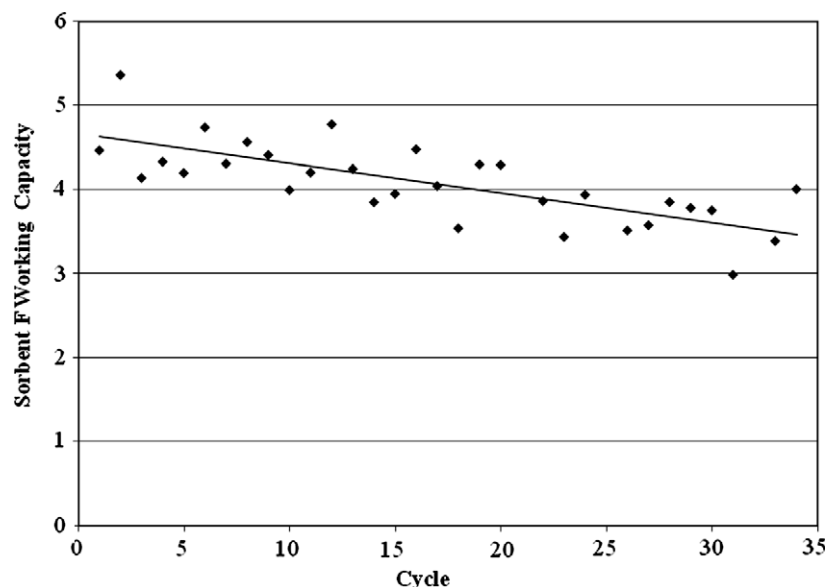


Fig. 6. Sorbent F working capacity during second round field tests.

concentration of 50–250 ppm in the flue gas, a mass balance reveals that if indeed this deactivation can be attributed to reaction with SO_2 , it was reacting with the active amine sites in a 1:1 ratio (i.e., little to no SO_2 passed through the bed unreacted). Running long breakthrough tests in a fixed bed will exaggerate this behavior because the sorbent is exposed to flue gas for longer adsorption times than possible in a larger-scale system. However, similar to aqueous amines, SO_2 will most certainly need to be reduced below the 50 ppm level in a commercial-scale system utilizing supported amine sorbents. For a retrofit aqueous amine system, developers have suggested that it will be necessary to add a second SO_2 scrubber, rather than losing the amine. The proposed acceptable SO_2 control is less than 10 ppm [2].

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 was 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 18 cycles that were completed in the field. Although low loadings and selectivity are concerns for any physical adsorbent, the cyclic stability in actual flue gas exhibited by sorbent H was superior when compared to all other materials examined.

Sorbent O was a zeolite sorbent that was included in the field testing. For the ten cycles following the initial flushing, the working capacity of sorbent O decreased dramatically. In fact, between the first cycle and cycle 10, sorbent O lost nearly half its CO_2 working capacity. This was attributed to the 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 3, only sorbents D and F had lower theoretical regeneration energy than the reported value for aqueous MEA. However, two others were close and may surpass this goal with a slight change in sorbent composition or operating conditions (i.e., regeneration temperature).

After additional laboratory screening, several materials were selected for the second round of field testing. The materials included in the second round of field testing were sorbents F, R, and V due to their low theoretical regeneration energy during laboratory tests. As is shown in Table 2 sorbents F, R and V are different supported amines. 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 in part 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. Table 4 is a list of the mass tested, regeneration temperature, maximum, minimum, and average working capacities as well as the theoretical regeneration temperature during the second round of field testing. Similar to the first field test, the theoretical regeneration energy was calculated based on the average working capacity at the field test regeneration temperature. Although the system was automated, a different analyzer was used to measure the CO_2 concentration, and the regeneration procedure was changed, the average working capacity of sorbent F was nearly identical to that measured during the first round of field testing.

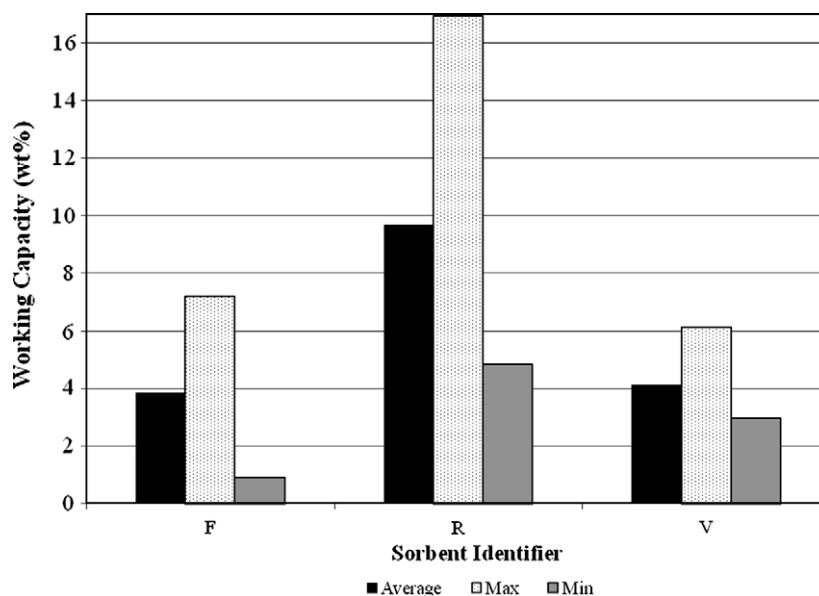
The average, maximum, and minimum working capacities measured during the second round of field testing are shown in Fig. 7. For all three of these supported amines, there was a significant difference between the maximum and minimum values measured, although some of this difference could be attributed to the error introduced during probe blowback. As described previously, the flue gas was unavailable during probe blowback (see Section 2).

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 be attributed, at least in part, to reaction with SO_2 to form heat-stable salts. With the new automated system, a greater number of cycles can be com-

Table 4

Field testing round 2 results.

Field 2							
Sorbent ID	Testing conditions			Working CO ₂ capacity (wt%)			Q _{regen} (kJ/kg CO ₂)
	Mass (g)	T _{regen} (°C)	# Cycles	Max.	Min.	Average	
F	0.5	120	34	7.2	0.9	3.9	3500
R	2.5	100	43	16.9	4.8	9.7	2000
V	0.5	100	120	6.1	3.0	4.1	3400

**Fig. 7.** Working capacity during second round field testing.

pleted. Future studies will evaluate cyclic stability without the presence of SO₂ to quantify the contribution of SO₂ to sorbent degradation.

5. Conclusions

Many different materials have been tested thus far in the ADA CO₂ sorbent screening program. All materials that were contributed to the program either have been or will be tested for multiple CO₂ adsorption/regeneration cycles. This paper discussed in detail 24 materials that showed any signs of CO₂ removal from either simulated or actual flue gas. Based on the theoretical regeneration energy, several sorbents were superior to the current state-of-the-art CO₂ capture technologies. Further testing will be performed to determine whether these materials are stable enough to be used in a commercial-scale CO₂ capture system. Pre-pilot scale testing, which will be conducted in a system more representative of the full-scale process, will help to reveal more about the effect of heat removal, attrition, pressure drop, etc. The first round of bench-scale tests are scheduled for late 2009. In addition, as part of the overall effort, ADA is developing a conceptual design for a 500 MW-scale system including the projected capital and operating costs.

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.

Acknowledgements

The authors gratefully acknowledge the organizations that provided both financial and technical support for this project. Support for this work was provided by the US Department of Energy National Energy Technology Laboratory (DE-NT0005649) with additional cost share from American Electric Power, Ameren, EPRI, Luminant, North American Power Group, Southern Company, Xcel Energy.

References

- [1] IEA Greenhouse Gas R&D Programme. CO₂ capture and storage. See <http://www.co2captureandstorage.info/whatisccs.htm>; 2009 [accessed 14.05.09].
- [2] Ramezan M, Skone TJ, Nsakala N, Liljedahl GN. Carbon dioxide capture from existing coal-fired power plants. Final Report DOE/NETL-401/110907, December; 2007.
- [3] Birbara PJ, Filburn TP, Nalette TA. United Technologies Corporation. Regenerable Solid Amine Sorbent. US 5,876,488; 1999.
- [4] Gray ML, Champagne KJ, Fauth D, Baltrus JP, Pennline H. Performance of immobilized tertiary amine solid sorbents for the capture of carbon dioxide. Int J Greenhouse Gas Control 2008;2:3–8.

- [5] Drage TC, Arenillas A, Smith KM, Snape CE. Thermal stability of polyethyleneimine based carbon dioxide adsorbents and its influence on selection of regeneration strategies. *Micropor Mesopor Mater* 2008;116:506–12.
- [6] Siriwardane RV. The United States Department of Energy, solid sorbents for removal of carbon dioxide from gas streams at low temperatures. US 6,908,497; 2005.
- [7] Harlick PJE, Sayari A. Applications of pore-expanded mesoporous silica. 5. Triamine grafted material with exceptional CO₂ dynamic and equilibrium adsorption performance. *Ind Eng Chem Res* 2007;45:446–58.
- [8] Kim S, Ida J, Gulians VV, Lin JYS. Tailoring pore properties of MCM-48 silica for selective adsorption of CO₂. *J Phys Chem B* 2005;109:6287–93.
- [9] Hicks JC, Drese JH, Fauth DJ, Gray ML, Qi G, Jones CW. Designing adsorbents for CO₂ capture from flue gas – hyperbranched aminosilicas capable of capturing CO₂ reversibility. *J Am Chem Soc* 2008;130:2902–3.
- [10] Drage TC, Arenillas A, Smith KM, Pevida C, Piippo S, Snape CE. Preparation of carbon dioxide adsorbents from the chemical activation of urea-formaldehyde and melamine-formaldehyde resins. *Fuel* 2007;86:22–31.
- [11] Plaza MG, Pevida C, Arenillas A, Rubiera F, Pis JJ. CO₂ capture by adsorption with nitrogen enriched carbons. *Fuel* 2007;86:2204–12.
- [12] Radosz M, Hu X, Krutkramelis K, Shen Y. Flue-gas carbon capture on carbonaceous sorbents: toward a low-cost multifunctional carbon filter for “Green” energy producers. *Ind Eng Chem Res* 2008;47:3783–94.
- [13] Lu C, Bai H, Wu B, Su F, Hwang JF. Comparative study of CO₂ capture by carbon nanotubes, activated carbons, and zeolites. *Energy Fuels* 2008;22:3050–6.
- [14] Nelson T, Coleman L, Anderson M, Herr J, Pavani M. The dry carbonate process: carbon dioxide recovery from power plant flue gas. Annual NETL CO₂ capture technology for existing R&D meeting, Pittsburgh, PA; 2009.
- [15] Shigemoto N, Yanagihara T, Sugiyama S, Hayashi H. Material and energy consumption for CO₂ recovery from moist flue gas employing K₂CO₃-on-activated carbon and its evaluation for practical adaptation. *Energy Fuels* 2006;20:721–6.
- [16] Siriwardane RV, Shen MS, Fisher EP, Poston JA. Adsorption of CO₂ on molecular sieves and activated carbon. *Energy Fuels* 2001;15:279–84.
- [17] Hoffman JS, Richards GA, Pennline HW, Fischer D, Keller G. Factors in reactor design for carbon dioxide capture with solid, regenerable sorbents. Clearwater Coal Conference, Clearwater, FL; 2008.
- [18] Tarka TJ, Ciferno JP, Gray ML, Fauth D. CO₂ capture systems using amine enhanced solid sorbents. In: Proceedings of the 5th annual conference on carbon capture and sequestration. Pittsburgh, PA; 2006.