# High-performance sorbents for carbon dioxide capture from air

## **Final Technical Report**

Reporting period: 12/1/2009 – 3/31/2013

Principal Authors Names: Prof David S. Sholl, School of Chemical & Biomolecular Engineering, Georgia Institute of Technology (david.sholl@chbe.gatech.edu); Prof Christopher W. Jones, School of Chemical & Biomolecular Engineering, Georgia Institute of Technology (christopher.jones@chbe.gatech.edu)

Date of report: 6/30/2013

**DOE** Award #: DE-FE0002438

#### 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.

#### **Abstract**

This project has focused on capture of CO<sub>2</sub> from ambient air ("air capture"). If this process is technically and economically feasible, it could potentially contribute to net reduction of CO<sub>2</sub> emissions in ways that are complementary to better developed techniques for CO<sub>2</sub> from concentrated point sources. We focused on cyclic adsorption processes for CO<sub>2</sub> capture from air in which the entire cycle is performed at moderate temperatures. The project involved both experimental studies of sorbent materials and process level modeling of cyclic air capture processes.

In our experimental work, a series of amine-functionalized silica adsorbents were prepared and characterized to determine the impact of molecular architecture on  $CO_2$  capture. Some key findings were:

- Amine functionalized silicas can be prepared with high enough CO<sub>2</sub> capacities under ambient conditions to merit consideration for use in air capture processes.
- Primary amines are better candidates for CO<sub>2</sub> capture than secondary or tertiary amines, both in terms of amine efficiency for CO<sub>2</sub> adsorption and enhanced water affinity.
- Mechanistic understanding of degradation of these materials can enable control of molecular architecture to significantly improve material stability.

Our process modeling work provided the first publically available cost and energy estimates for cyclic adsorption processes for air capture of CO<sub>2</sub>. Some key findings were:

- Cycles based on diurnal ambient heating and cooling cannot yield useful purities or amounts of captured CO<sub>2</sub>.
- Cycles based on steam desorption at 110 °C can yield CO<sub>2</sub> purities of ~88%.
- The energy requirements for cycles using steam desorption are dominated by needs for thermal input, which results in lower costs than energy input in the form of electricity.

Cyclic processes with operational costs of less than \$100 tCO<sub>2</sub>-net were described, and these results point to process and material improvements that could substantially reduce these costs.

The most critical conclusions from our work are that (i) CO<sub>2</sub> capture from ambient air using moderate temperature cyclic adsorption processes is technically feasible and (ii) the operational costs of realistic versions of these processes are moderate enough to encourage future development of this technology. Because of the very modest net investment that has been made in R&D associated with this approach from all sources worldwide (relative to the massive public and private investment that has been made in technologies for CO<sub>2</sub> from concentrated point sources), our results strongly suggest that continued development of air capture is justified.

## **Table of Contents**

Abstractp	). 3
Summary of Key Findings p	). 4
Topical Report on Synthesis, Characterization, Adsorption Methodology, and Results	p. 5
Topical Report on Cycle Strategy and Economic Assessment of End-Uses	p. 10
Topical Report on MOF Capture Materials	p. 16
Publications and Presentations	p. 18

#### **Summary of Key Findings**

This project has focused on capture of CO<sub>2</sub> from ambient air ("air capture"). If this process is technically and economically feasible, it could potentially contribute to net reduction of CO<sub>2</sub> emissions in ways that are complementary to better developed techniques for CO<sub>2</sub> from concentrated point sources. We focused on cyclic adsorption processes for CO<sub>2</sub> capture from air in which the entire cycle is performed at moderate temperatures. The project involved both experimental studies of sorbent materials and process level modeling of cyclic air capture processes.

In our experimental work, a series of amine-functionalized silica adsorbents were prepared and characterized to determine the impact of molecular architecture on  $CO_2$  capture. Some key findings were:

- Amine functionalized silicas can be prepared with high enough CO<sub>2</sub> capacities under ambient conditions to merit consideration for use in air capture processes.
- Primary amines are better candidates for CO<sub>2</sub> capture than secondary or tertiary amines, both in terms of amine efficiency for CO<sub>2</sub> adsorption and enhanced water affinity.
- Mechanistic understanding of degradation of these materials can enable control of molecular architecture to significantly improve material stability.

A more detailed discussion of our process modeling work is given below in a *Topical Report on Synthesis, Characterization, Adsorption Methodology, and Results*.

Our experimental work focused primarily on amine-functionalized silica materials as adsorbents. We also, however, investigated the potential of using metal organic framework (MOF) materials as adsorbents for air capture of CO<sub>2</sub>. The results of this work are summarized below in a *Topical Report on MOF Capture Materials*.

Our process modeling work provided the first publically available cost and energy estimates for cyclic adsorption processes for air capture of CO<sub>2</sub>. Some key findings were:

- Cycles based on diurnal ambient heating and cooling cannot yield useful purities or amounts of captured CO<sub>2</sub>.
- Cycles based on steam desorption at 110 °C can yield CO<sub>2</sub> purities of ~88%.
- The energy requirements for cycles using steam desorption are dominated by needs for thermal input, which results in lower costs than energy input in the form of electricity.
- Cyclic processes with operational costs of less than \$100 tCO<sub>2</sub>-net were described, and these results point to process and material improvements that could substantially reduce these costs.

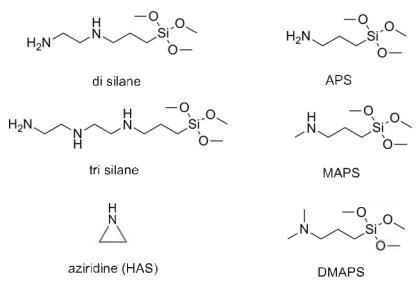
A more detailed discussion of our process modeling work is given below in a *Topical Report on Cycle Strategy and Economic Assessment of End-Uses*.

The most critical conclusions from our work are that (i) CO<sub>2</sub> capture from ambient air using moderate temperature cyclic adsorption processes is technically feasible and (ii) the operational costs of realistic versions of these processes are moderate enough to encourage future development of this technology. Because of the very modest net investment that has been made in R&D associated with this approach from all sources worldwide (relative to the massive public and private investment that has been made in technologies for CO<sub>2</sub> from concentrated point sources), our results strongly suggest that continued development of air capture is justified.

### Topical Report on Synthesis, Characterization, Adsorption Methodology, and Results

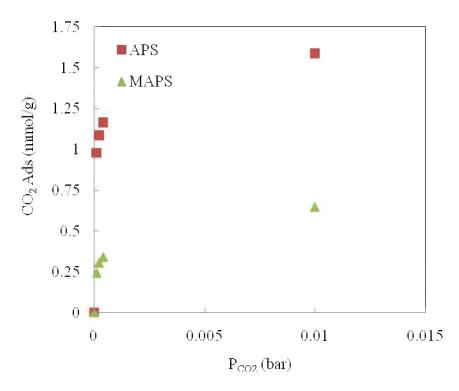
The goal of these studies was to perform a series of tests on various amine sorbents to evaluate their potential for use in air capture applications; both through experimental and modeling results. In much of our work we used a silica support in the form of a mesocellular foam (MCF) which is then functionalized with one of the following silanes: (3-Aminopropyl)trimethoxysilane (APS), (N-Methylaminopropyl)trimethoxysilane (MAPS) and (N,N-Dimethylaminopropyl)trimethoxysilane (DMAPS). The purpose of using these silanes is to evaluate whether primary, secondary or tertiary amines have a higher capacity at air capture

Dimethylaminopropyl)trimethoxysilane (DMAPS). The purpose of using these silanes is to evaluate whether primary, secondary or tertiary amines have a higher capacity at air capture conditions. A representative set of the silanes used to functionalize our silica materials (currently and previously) are shown below in Fig. 1.1.



**Figure 1.1:** Amines and silanes used in the synthesis of our adsorbent materials.

We acquired a TA Instruments Q500 TGA that was solely dedicated to measuring adsorption isotherms of our materials. Initially, various tests were performed to determine the optimum measurement conditions to ensure consistency and comparability between measurements. The most important of which was determining how long to measure adsorption for to ensure equilibrium had been attained. This enabled measurements of equilibrium capacity at various concentrations of CO<sub>2</sub> in an inert gas. We primarily focused on primary and secondary amines for these measurements because the tertiary amine should not adsorb CO<sub>2</sub> in the dry case. Sample isotherms for APS and MAPS-functionalized silica are shown in Figure. 1.2. A significant difference in capacity can be seen between the two materials.



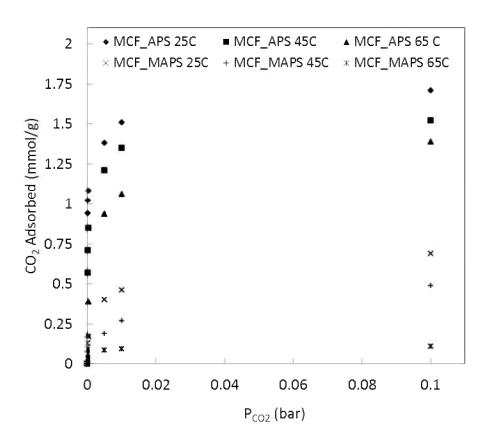
**Figure 1.2:** CO<sub>2</sub> adsorption isotherm at 25 °C for primary and secondary amine sorbents.

Our initial results led us to hypothesize that impurities may be introduced from the silane agent used in the synthesis of these materials, as MAPS and DMAPS are produced by methylating APS. Therefore if the reaction does not go to 100% completion and the resulting silane is not fully purified, there may be a minimal amount of other amine species in the commercial silane that can be functionalized on the surface of all materials. Furthermore, since primary amines have the highest efficiency, presence of a primary amine impurity, in particular, could artificially inflate the adsorption capacities of the other materials.

Due to the hypothesis that primary amine impurities may exist in some materials, a method for observing the presence of primary amine and subsequently deactivating them was used. This technique uses the fact that primary amines in solid aminosilicas will react with aldehydes to form imines. Therefore, by reacting an aldehyde such as 3,4-dihydroxybenzaldehyde with MAPS and DMAPS (shown in figure 2.2) we can assess if there are any impurities present. Impurities can be observed visually as well as experimentally. A color change from white to yellow powder takes place when the aldehyde reacts. Additionally, the CO<sub>2</sub> adsorption capacity will decrease once the primary amines are deactivated to imines. This process was performed with MAPS and DMAPS functionalized silicas and impurities were detected in both materials. The powder changed color from white to a pale yellow for both materials. The adsorption capacity for MAPS at 25 °C and 400 ppm CO<sub>2</sub> in dry conditions decreased from 0.34 to 0.19 mmol CO<sub>2</sub>/g material after aldehyde reaction.

To complete our amine structure studies we synthesized another batch of materials whereby the silanes are first purified before grafting to the silica surface. This method allows for "pure" secondary or tertiary amine coverage at comparable loadings to that of the primary amine material so that meaningful comparisons can be made with adsorption data. To achieve this, the aminosilane is first reacted with an excess of benzaldehyde at elevated temperatures; the resulting product is distilled to recover the pure secondary or tertiary silane component. Afterwards, MCF is functionalized with the purified silane to obtain pure secondary and tertiary amine adsorbents.

Figure 1.3 shows multiple adsorption isotherms at different temperatures while Table 1.1 shows amine efficiencies for MCF\_APS and MCF\_MAPS, the primary and secondary amine materials. From this data, the heat of adsorption was calculated assuming Langmuir-type adsorption with the Toth equation. For MCF\_APS and MCF\_MAPS, ΔH<sub>ads</sub> is 77 kJ/mol and 56 kJ/mol, respectively. Heat of adsorption results as well as comparing amine efficiencies clearly indicate that primary amines have a stronger interaction with CO<sub>2</sub> at low partial pressures and are therefore a good candidate for air capture.



**Figure 1.3:** CO<sub>2</sub> adsorption isotherms for MCF\_APS and MCF\_MAPS at varying temperatures.

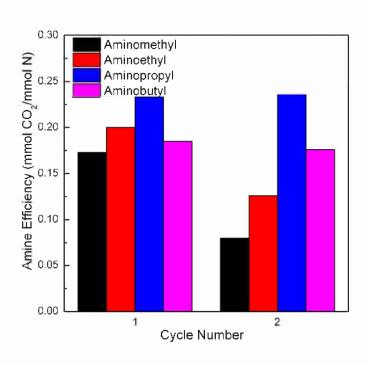
**Table 1.1:** Amine efficiencies of primary and secondary amines at 25 °C.

	Amine efficiency					
P <sub>CO2</sub> (bar)	(mmol CO <sub>2</sub> /mmol N)				(mmol CO <sub>2</sub> /mmol N	
	MCF_APS	MCF_MAPS				
$1.1 \times 10^{-4}$	0.25	0.04				
$2.2 \times 10^{-4}$	4 0.27 0.05					
$4 \times 10^{-4}$	0.29	0.07				

0.005	0.37	0.17
0.01	0.4	0.19
0.1	0.46	0.29

Following the experiments above, additional experiments were performed with materials that systematically varied the linker length in the functionalizing species. Cyclic CO<sub>2</sub> adsorption capacity measurements were performed to see if any differences in adsorption capacity/amine efficiency were present as a result of linker length. From Figure 1.4 it can be seen that there is an observable difference in amine efficiency for different linker length materials, with an optimal efficiency at 3 carbons between the silane and amine. This can be attributed to varying degrees of flexibility in the amine group for interactions with other amines or the silica support. However, the most interesting result from this study is the fact that there appears to be degradation of the aminomethyl and aminoethyl adsorbents after a single round of CO<sub>2</sub> adsorption, as evidenced by the dramatic decrease in amine efficiency during the second adsorption cycle. Aminopropyl and aminobutyl remained stable. The materials used in these studies are shown schematically in Fig. 1.5.

The conclusions of our work varying the size and type of amine-containing functionalizing species on adsorbent performance have been described more fully in Stephanie A. Didas, Ambarish R. Kulkarni, David S. Sholl, and Christopher W. Jones, ChemSusChem 5 (2012) 2058-2064.



**Figure 1.4:** Amine efficiency for aminosilicas with different linker length during 2 cycles of adsorption and desorption at 25 °C and 400 ppm CO<sub>2</sub>.

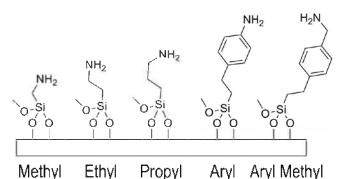


Figure 1.5: Materials used for linker length studies.

The experimental work discussed above focused on the CO<sub>2</sub> capacity of a variety of adsorbents. In practical applications, the stability of these materials is also crucial. Initial experiments were done to examine the oxidative stability of a number of materials. These experiments motivated quantum chemistry calculations to attempt to understand the mechanisms that can lead to instability of amine-functionalized adsorbents. These calculations indicate that the single step carbamic acid formation mechanism is not the physically dominant mechanism for oxidative degradation. Instead, a self-catalyzed (from two amine groups) or proton catalyzed (from surface silanols) mechanism appears to be dominant. These preliminary results suggest that further understanding of these mechanisms and subsequent control of molecular architecture in amine-functionalized adsorbents could yield significant improvements in the stability of these materials.

### Topical Report on Cycle Strategy and Economic Assessment of End-Uses

A key objective of this project was to perform process-level modeling of cyclic adsorption processes for air capture of CO<sub>2</sub> that could be used to generate meaningful cost estimates for these processes. At the outset of this project, no information on this topic was publically available. A report commissioned by the American Physical Society had made costs estimates for a very different process involving capture via carbonate formation and regeneration of these materials at very high temperatures. Not surprisingly given the large temperature variation required in this process, the estimated process costs were very high (more than \$1000/t-CO<sub>2</sub>). It is important to note that these estimates only apply to the specific process considered in that report, not to moderate temperature cyclic adsorption processes. The aim of our work was to provide meaningful costs estimates using publically available information and full disclosure of any assumptions made in our models. This approach facilitates useful debate and future improvement of our models. Our results have been described in great detail in A. R. Kulkarni and D. S. Sholl, Ind. Eng. Chem. Res. 51 (2012) 8631-8645, so only the key conclusions and concepts are described below.

Our models focus on using an amino-modified silica adsorbent, TRI-PE-MCM-41, and a structured monolithic contactor unit. This adsorbent was chosen because of the availability of dry gas isotherms from the work of Sayari et al. at the time we were performing our modeling. Monolithic contactors are appropriate because they can be operated with very low pressure drop, therefore greatly reducing pumping costs, and are commercially available. We studied several different temperature swing adsorption processes using the purity of CO<sub>2</sub> and annual product throughput as metrics for comparing process performance. This analysis identifies some of the operational parameters, adsorbent characteristics and other factors that have a significant effect on the performance of the process. One assumption inherent in our work is that we used adsorption isotherms for dry CO<sub>2</sub>. We certainly do not anticipate that air will be dried prior to adsorption in a practical process, but no firm data on CO<sub>2</sub> from humid air was available at the time of our work. The presence of humidity is generally expected to enhance CO2 adsorption in amine-based adsorbents, however, to neglecting the effect of ambient humidity is likely to underestimate the cyclic adsorption capacity of these materials. All estimates were made in terms of adsorption "units", which are groups of monolithic contactors with the same volume as a standard shipping container.

We first examined a process in which adsorption of  $CO_2$  occurs at ambient temperatures and desorption is accomplished purely by diurnal heating in the same location. This concept is superficially very appealing, since it require no energy input apart from energy for flowing gases in and out of the monolith. Quantitative analysis of this approach, however, indicates it will not be useful in practice. We performed modeling for 6 different geographic locations in the US using actual weather data. Our models indicate that at best, a shipping container sized unit would capture  $CO_2$  at a rate of  $\sim 3$  kg/year at a purity of only  $\sim 0.3\%$ . This performance was so minimal that no further work on cycles based on diurnal heating was pursued.

The majority of our models of cyclic adsorption examined a cycle in which  $CO_2$  is desorbed using steam at 110  $^{\circ}$ C. This process generates a concentrated  $CO_2$  stream that is saturated with water. Drying of this stream would be necessary if the  $CO_2$  stream was to be used delivered to traditional sequestration sites via pipelines, but this step would not necessarity be required in applications where  $CO_2$  is used in a bioreactor (e.g. algae growth or enzymatic catalysis). A cyclic adsorption process was considered that yields  $CO_2$  purities of ~88%, that is, a concentration of  $CO_2$  by a factor of over 2000 from the ~400 ppm level in ambient air. Results

for a typical version of this process are summarized in Table 2.1. The results in this table are for the very conservative approach of performing just a single adsorption/desorption cycle per day. This approach captures 90-116 tCO<sub>2</sub> unit<sup>-1</sup> year<sup>-1</sup>.

**Table 2.1** Cyclic adsorption process performance at different locations for one adsorption-desorption cycle per day.

Location $t_{ads}^{a}$ (min)		Purity CO <sub>2</sub>	CO <sub>2</sub> throughput	Product throughput
		(percent)	(tCO <sub>2</sub> unit <sup>-1</sup> year <sup>-1</sup> )	(t-product unit <sup>-1</sup> year <sup>-1</sup> )
FL	91.3	88.7	92.0	103.8
AL	101.5	88.6	104.1	117.5
UT	113.9	88.5	119.4	135.0
GA	103.0	88.6	106.1	119.8
WA	111.4	88.5	116.5	131.5
TX	104.4	88.6	107.8	121.7

 $<sup>^{\</sup>rm a}$   $t_{\rm ads}$  calculated for a pressure drop of 100 Pa.

Table 2.1 includes a calculated adsorption time,  $t_{ads}$ , for each geographic location. This time was calculated to provide an estimate for the equilibration time required for the adsorption portion of the cyclic adsorption/desorption cycle. It was clear from these calculations that an approach using multiple cycles per day is both reasonable and desirable. Table 2.2 summarizes results for the same process but using varying numbers of cycles per day. It can be seen that with this approach, capture of more than 600 tCO<sub>2</sub> unit<sup>-1</sup> year<sup>-1</sup> is possible.

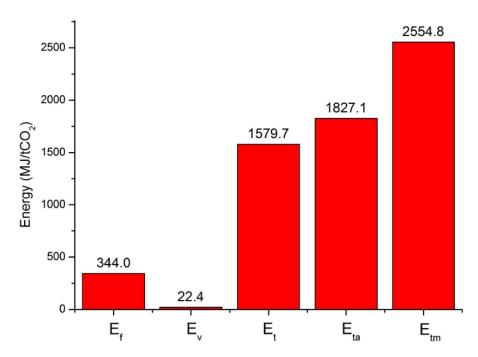
**Table 2.2** Cyclic adsorption process performance for different cycles per day using steam at the UT location. The units for yield are in metric tons/unit/year.

Cycles per day	Cycle time	t <sub>ads</sub> <sup>a</sup> (min)	CO <sub>2</sub> throughput	Product throughput	
		(IIIII)	(tCO <sub>2</sub> unit <sup>-1</sup> year <sup>-1</sup> )	(t-product unit <sup>-1</sup> year <sup>-1</sup> )	
1	24	113.9	119.4	135.0	
2	12	101.1	207.0	234.0	
3	8	101.9	313.8	354.5	
4	6	100.6	411.7	465.1	
6	4	100.5	616.9	696.9	

<sup>&</sup>lt;sup>a</sup> t<sub>ads</sub> calculated for a pressure drop of 100 Pa.

Although the process modeling outlined above can be used to optimize process performance, it was deemed more important to generate useful cost estimates and energy requirements for these processes. In these estimates, only the operational cost of the process was considered. Capital costs for these processes are also clearly important, but insufficient data is currently available on the manufacturing cost at scale of relevant adsorbents-coated monoliths and, critically, the lifetime of these adsorbents is currently available to make meaningful estimates of capital costs.

Figure 2.1 shows that energy requirement calculated for a cyclic process based on steam desorption using 4 cycles per day. At the UT location used for these calculations, this process captures  $1.1 \text{ tCO}_2$ /unit/day at a yearly-averaged purity of 88.5%. These energy requirements include the energy for flowing air through the monolith,  $E_f$ , the removal of gases from the monolith using a partial vacuum,  $E_v$ , the sensible heat requirements for the adsorbent,  $E_{ta}$ , and monolith,  $E_{tm}$  and energy for providing steam,  $E_f$ . It can be seen that in the configuration considered, the thermal energy components dominate the overall energy requirement. This is an important observation, because the cost of providing thermal energy via steam is considerably lower than the cost of providing energy in the form of electricity. A recent analysis of a generic air capture process by House et al. (K. Z. House et al., Proc. Natl. Acad. Sci. 108(2011) 20428-20433) assumed that all energy input the process comes from electricity. This unrealistic assumption led to very high cost estimates that, in our view, have little bearing on the real cost of a cyclic adsorption process.



**Fig. 2.1** Energy requirements of a cyclic adsorption process (four cycles per day) at the UT location. Energy required for air flow, E<sub>f</sub>, is calculated for a pressure drop of 100 Pa across the contactor.

The operational cost of a cyclic adsorption process was estimated for several different scenarios. In Scenario I ("no steam"), all energy was assumed to come from electricity. This is essentially the scenario described by House et al. which, as stated above, is quite unrealistic. In Scenarios II-IV, the cost of thermal energy was determined by assuming this energy comes from steam, with the scenarios different by the source of steam. In the most optimistic scenario, Scenario IV, waste steam is assumed to be available from a nearby source at no cost. For each scenario, cost estimates were made based on a wide range of electricity sources, as shown in Table 2.3. In every case, cost was assessed based on net CO<sub>2</sub> capture. That is, when the electricity sources in question produce CO<sub>2</sub>, the CO<sub>2</sub> produced to generate the requisite electricity was subtracted from the overall CO<sub>2</sub> captured by the cyclic adsorption process.

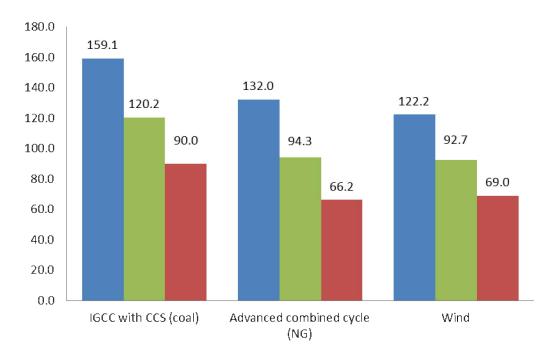
**Table 2.3** Cost of cyclic adsorption process with steam desorption (four cycles per day at UT) for different scenarios

	Monetary cost (\$/tCO <sub>2</sub> -net) <sup>a</sup>			
Electricity source	Scenario I	Scenario II	Scenario III	Scenario IV
	No Steam <sup>c</sup>	Dedicated Steam	Purchased Steam	Waste Steam
Coal				
Conventional coal	N/A <sup>b</sup>	162.8	138.2	58.6
IGCC	N/A <sup>b</sup>	161.3	138.5	
IGCC with CCS	408.1	120.2	108.3	60.9
Natural Gas				57.3
Conventional combined cycle	494.3	95.9	85.5	42.2
Advanced combined cycle	471.9	94.3	84.1	43.3
Advanced CC with CCS	196.8	92.5	83.8	42.6
Other				45.4
Advanced nuclear	213.4	100.0	90.9	
Wind	181.7	92.7	84.2	50.0
Wind—offshore	455.7	156.4	142.1	46.3
Solar PV	394.8	142.2	129.2	78.1
Solar thermal	584.2	186.3	169.3	71.0
Biomass	337.1	108.9	98.1	93.0
Hydro	161.9	88.0	80.0	51.9
11,410	101,2	00.0	55.0	44.0

<sup>a</sup> electricity requirement = 783.6 MJ/tCO<sub>2</sub>, steam requirement = 5961.6 MJ/tCO<sub>2</sub>, <sup>b</sup> the net amount of CO<sub>2</sub> captured is negative and results in net emission of CO<sub>2</sub>, <sup>c</sup> similar to the analysis of House et al.

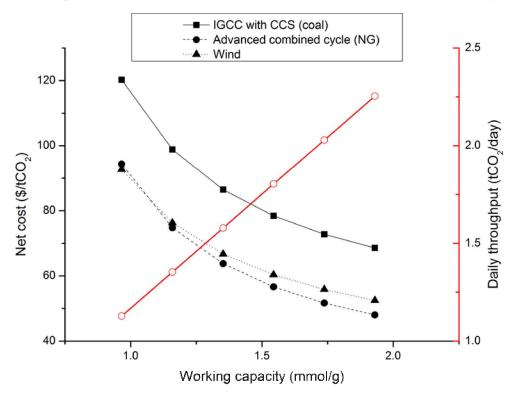
The key conclusion from Table 2.3 is that multiple plausible scenarios exist where the operational cost of capturing  $CO_2$  using cyclic adsorption is less than \$100/t $CO_2$ . It is important to note that this estimate comes from an unoptimized adsorption process. It is therefore reasonable to expect that this cost can be reduced with further process optimization. Thus, although these cost is higher than current estimates for  $CO_2$  capture from large point sources (e.g. coal fired power plants), they are not so high that the concept of air capture of  $CO_2$  can be rejected out of hand.

The cost estimates outlined above suggest several useful directions for improving process performance. It can be seen from Fig. 2.1 that a significant fraction of the thermal energy required for the process is associated with sensible heat of the monolith. This thermal energy cannot be avoided, but it can readily be reduced by using monoliths with thinner walls. In the model above, a monolith with 2.86 mil thick walls was assumed, simply because of the ready commercial availability of monoliths of this type. Reducing the wall thickness to values that seem readily achievable can significantly reduce the overall process cost. An example of this idea is shown in Fig. 2.2, which shows the estimated cost in the same units as Table 2.3 for three sources of electricity with Scenario II. Reducing the wall thickness to 1.5 mil reduces the  $CO_2$  capture by  $\sim$ \$30 t $CO_2$ -net, and gives net operational costs < \$70 t $CO_2$ -net for two of the electricity sources.



**Fig. 2.2** Monetary cost of four cycles per day of process B at UT for a 1.5 mil (red), 2.86 mil (green) and 4 mil (blue) channel wall thickness of the contactor.

An alternative means of reducing the net cost of the cyclic adsorption process is to increase the working capacity of the adsorbent. Fig. 2.3 shows sample results for processes similar to those in Fig. 2.2. Increasing the working capacity of the adsorbent from 1.0 to 1.5 mmol/g reduces the process cost by  $\sim$ \$40 tCO<sub>2</sub>-net. This observation creates a strong motivation to continue development of adsorbents for this process with higher working capacity than existing materials, provided that these materials can be shown to have suitable stability.



**Fig. 2.3** Daily throughput of CO<sub>2</sub> (red, open) and cost capture (black) as a function of increasing working capacity of the process.

We emphasize that this topical report has only described key results from our work and that a detailed discussion of the modeling assumptions and outcomes is available in A. R. Kulkarni and D. S. Sholl, Ind. Eng. Chem. Res. 51 (2012) 8631-8645. These results have significantly advanced the state of the art for understanding these processes relative to the information that was publically available at the outset of this project. As such, our results provide a useful foundation for future development of cyclic adsorption processes for air capture of CO<sub>2</sub>.

#### **Topical Report on MOF Capture Materials**

Although the experimental work in this project focused primarily on the use of amine-functionalized silica materials, we also examined the potential use of metal-organic framework (MOF) materials as adsorbents for air capture of CO<sub>2</sub>. MOFs are crystalline, ultra-high surface area materials that have received considerable attention for a variety of adsorption applications (and other potential technical applications). In cooperation with Dr. Sunho Choi, a postdoctoral scholar at Georgia Tech not directly funded by this project, we developed a MOF material with significant adsorption capacity for CO<sub>2</sub> under ambient conditions following a strategy of post-synthesis modification of a MOF with amine groups. This work is described in detail in S. Choi et al., J. Phys. Chem. Lett. 3, (2012) 1136-1141, so only the principal observations and conclusions are described here.

We synthesized Mg/DOBDC, a relatively large pore MOF that has a high density of undercoordinated Mg sites in its initial state. We then introduced ethylene diamine into this MOF, leading to the complexation of the diamine molecules with the undercoordinated metal sites. Density Functional Theory (DFT) calculations confirmed the expectation that this functionalization creates a material in which a significant number of amine groups are sterically accessible in the MOF's pores. A combination of these DFT calculations and experimental nitrogen physisorption and thermogravimetric analysis indicated that on average, one ethylene diamine molecule was added to the MOF per crystallographic unit cell.

The  $CO_2$  capture capacity of the diamine-functionalized MOF was assessed over four adsorption-desorption cycles with adsorption using dry simulated air (400 ppm  $CO_2$  with balance Ar) at room temperature and desorption with pure Ar. The adsorption capacity of the MOF was stable over the four cycles at ~1.5 mmol/g adsorbent. This adsorption capacity was considerably larger than the ~0.25 mmol/g capacity that was measured under the same conditions with silane grafting of N-(2-(trimethoxysilyl)-propylethylene-diamine onto mesoporous silica. High adsorption capacities where observed in a PEI-impregnated mesoporous silica, but the capacity of this material showed a steady decrease over four cycles.

At the same time this work was being performed, a group led by Prof. Jeff Long (UC Berkeley) produced an amine-functionalized MOF via a similar strategy. This work is reported in detail in T. M. McDonald et al., J. Am. Chem. Soc. (2012) DOI:10.1021.ja300034j. Comparison of this report with our results highlights one of the potential advantages of MOFs relative to other porous supports, namely the possibility of rationally designing the pore architecture. McDonald et al. used a material similar to Mg/DOBDC but with an expanded pore size. This made it possible to achieve a higher CO<sub>2</sub> capacity under conditions relevant to air capture of CO<sub>2</sub> than in our work.

The results from our work constitute a useful initial exploration of the potential for using MOFs for air capture of CO<sub>2</sub>. At the outset of our work, no information was available on this topic. Now, there are two demonstrations in the literature that MOFs can have adsorption capacities for CO<sub>2</sub> under ambient conditions that are competitive with many more traditional mesoporous adsorbents. Future work on MOFs in this application should most urgently address the stability of these materials with respect to exposure to humid air. Although not all MOFs are stable under these conditions, a variety of MOFs that have good water and temperature stability are now known. Information to assess these issues directly in the context of cyclic processes for air capture of CO<sub>2</sub> is critical for future development of these materials in this application. A secondary need for further consideration of MOFs as adsorbents is work on scale up and economical manufacturing of these materials. Although a small number of MOFs are available

commercially from BASF, little is known about the scale up and cost at scale of the vast majority of MOFs that have been described in the research literature. Some efforts to tackle this issue directly are being made (e.g. by a startup company spun off from Georgia Tech recently, Inmondo Tech), but further work on this topic is needed.

#### **Publications and Presentations**

This project led to a number of published papers in peer-reviewed journals and invited presentations at technical meetings. These papers and presentations are listed below. *Papers* 

Analysis of equilibrium-based TSA processes for direct capture of CO<sub>2</sub> from air, Ambarish Kulkarni and David S. Sholl, Ind. Eng. Chem. Res. 51 (2012) 8631-8645

Role of Amine Structure on Carbon Dioxide Adsorption from Ultrafilute Gas Streams such as Ambient Air, Stephanie A. Didas, Ambarish R. Kulkarni, David S. Sholl, and Christopher W. Jones, ChemSusChem 5 (2012) 2058-2064

Tuning Cooperativity by Controlling the Linker Length of Silica-supported Amines in Catalysis and CO<sub>2</sub> Capture, Nicholas A. Brunelli, Stephanie A. Didas, Krishnan Venkatasubbaiah, and Christopher W. Jones, J. Am. Chem. Soc. 134 (2012) 13950-13953 *Invited Presentations* 

Symposium on CO<sub>2</sub> Capture and Utilization, 245<sup>th</sup> ACS National Meeting, New Orleans, LA, March 2013 (invited talk by David Sholl)

Air Capture: Developing Technologies for Carbon Recycling and Negative Emissions, Institution of Mechanical Engineering, London, UK, October 2012 (invited talk by David Sholl)