New Materials and Process Development for Energy-Efficient Carbon Capture in the Presence of Water Vapor

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Abstract
   A new functionalization technique, solvent assisted ligand incorporation (SALI), was developed to efficiently incorporate carboxylate-based functionalities in the Zr_6-based metal-organic framework, **NU-1000**. Unlike previous metal node functionalization strategies, which utilize dative bonding to coordinatively unsaturated metal sites, SALI introduces functional groups as charge compensating and strongly bound moieties to the Zr_6 node. Utilizing SALI, we have efficiently attached perfluoroalkane-carboxylates of various chain lengths (C_1–C_9) on the Zr_6 nodes of **NU-1000**. These fluoroalkane functionalized mesoporous MOFs were studied experimentally and theoretically as potential CO_2 capture materials. Molecular simulations were also used to study adsorption of CO_2, N_2, and water in the fluorinated metal-organic framework FMOF-1. The results support the idea that perfluorinated nanopores are promising for CO_2 capture under humid conditions. Preliminary process-level modeling has shown that if materials are not available for capturing CO_2 from humid flue gas, it may be economically feasible to remove much of the water from the flue gas prior to CO_2 removal. This opens up a wider range of material and process combinations for cost-effective CO_2 capture.

Introduction
   Adsorption processes based on porous solids are a promising technology for removing CO_2 from power plant flue gas. The premise of this proposal is that game-changing improvement of adsorption separation processes for carbon capture and storage (CCS) will require *simultaneous development of new materials and specially designed processes that take advantage of these new materials*. Competitive adsorption of water is regarded as the single greatest technical hurdle to adsorption-based CCS, but there is very little research on new water-tolerant CCS adsorbents. One goal of this project is to develop new metal-organic framework (MOF) materials with extraordinarily high selectivity for CO_2 over nitrogen and water, together with suitably high absolute capacity for CO_2. Several related strategies are being explored, and molecular modeling is being used to guide the synthetic effort. In addition, we are using state-of-the-art process-level modeling to optimize adsorption processes around the new class of sorbents and explore
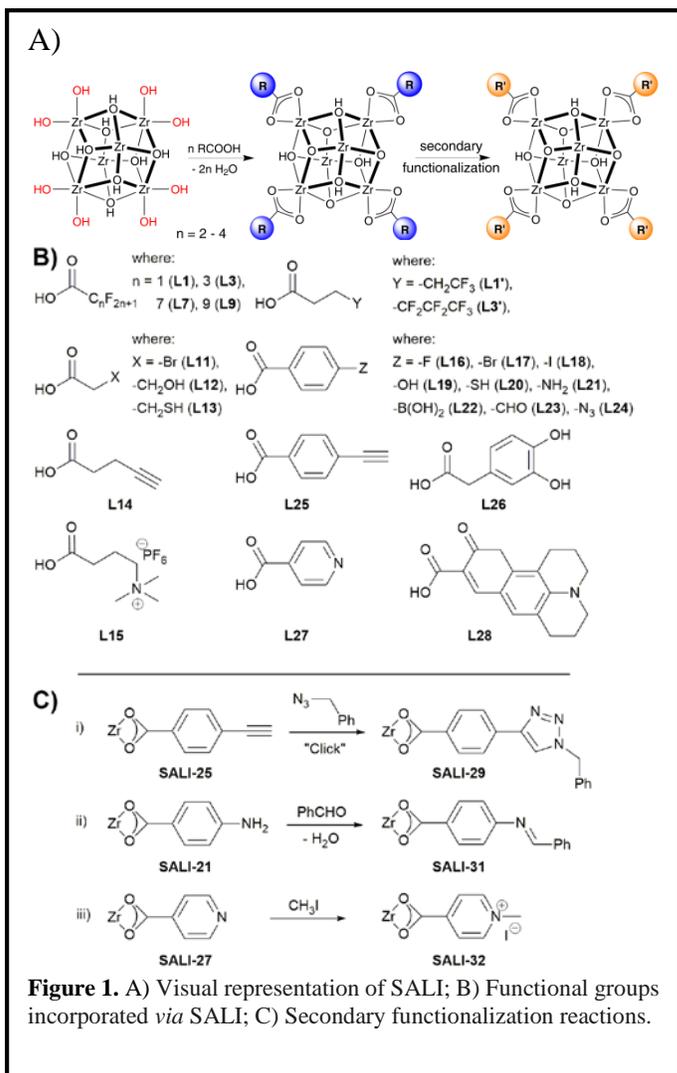
the real efficiency limits of MOF-based adsorption processes that meet desired CCS technical and economic criteria, while minimizing the life-cycle environmental impact. Adsorption processes are already used in large-scale applications, such as air separation, with high reliability. Discovery of new, water-stable and water-tolerant adsorbents for CO_2 capture and new, optimal process configurations for these sorbents would be a step-out development in CCS.

Background

Research on MOFs continues to explode. Many research groups are investigating MOFs for separation of CO_2/N_2 mixtures, motivated by carbon capture. However, very few papers report results that take water into account. A small number of papers have appeared recently on the stability of MOFs, including their stability in water or humid gas streams. Many groups are now starting to study MOFs based on zirconium nodes due to their superior stability.

Results

Experimental Materials Research

Figure 1. A) Visual representation of SALI; B) Functional groups incorporated *via* SALI; C) Secondary functionalization reactions.

The experimental portion of the project is currently focused on designing, synthesizing, characterizing, and functionally evaluating nanoporous materials that feature the following properties: a) excellent stability under conditions encountered in flue-gas environments, b) high capacity for gas uptake, c) ability to capture CO_2 at pressures found in flue gas, and d) ability to inhibit competitive adsorption of water.

Solvent-Assisted Ligand Incorporation (SALI): This technique was developed to efficiently insert various carboxylate-derived functionalities into the Zr-based MOF **NU-1000** as channel-tailoring moieties that are strongly bound to the Zr_6 nodes *via* the eight terminal –OH groups (Figure 1A).[1,2] We have found that the large channels of **NU-1000** (> 30 Å width) can be systematically tailored with an enormous variety of chemical entities *via* SALI, an acid-base reaction between a carboxylic

acid-containing functional group (**CFG**) and a pair of terminal -OH ligands of the Zr_6 node. As a result, **SALI-CFG** daughter materials were synthesized, where the charge-compensating CFG ligands are strongly bound to the **NU-1000** nodes. Furthermore, the chemical generality and functional group tolerance of the SALI approach were explored (see Figure 1B). Interestingly, by using SALI we have successfully incorporated a catechol moiety into **NU-1000**, thus opening new opportunities for the synthesis of metal-catecholates based on different M^{2+} ions with prospective catalytic activity or the ability to adsorb CO_2 selectively. Moreover, we have found that the large cavities and chemical robustness of the **NU-1000** framework permit newly installed functional groups to be subsequently derivatized *via* various secondary functionalization reactions For example, acetylide/azide "click" chemistry (**SALI-25**), imine formation (**SALI-21**), and quaternization of a nitrogen base (**SALI-27**) were successfully carried out in good to excellent (i.e. quantitative) yield (Figure 1C). These widely used, secondary functionalization reactions can be used to: a) incorporate new functionalities that are not compatible with a free carboxylate moiety, b) facilitate introduction of various metal-Schiff base catalysts, and c) demonstrate incorporation of ionic species.
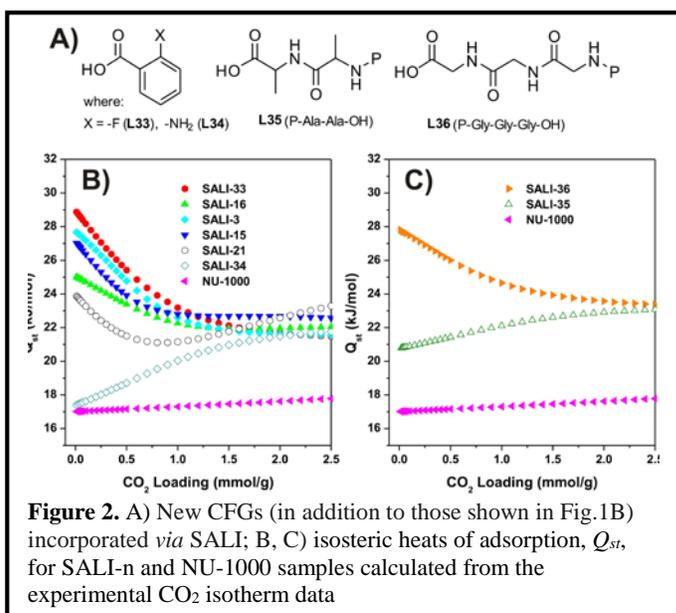

Figure 2. A) New CFGs (in addition to those shown in Fig.1B) incorporated *via* SALI; B, C) isosteric heats of adsorption, Q_{st}, for SALI-n and NU-1000 samples calculated from the experimental CO_2 isotherm data

Various **SALI-CFG** daughter materials were screened for their ability to capture CO_2 at pressures relevant to flue gas conditions. Figure 2B shows isosteric heats of adsorption, Q_{st}, for CO_2 in SALI-n samples as a function of various chemical entities relative to the unfunctionalized NU-1000 platform. This approach not only enables us to choose chemical functionality suitable for CO_2 capture but also highlights the position of the functionality relative to the channel direction (for example **SALI-33** *vs* **SALI-16** and **SALI-34** *vs* **SALI-21**).

From the literature, it is known that the hydrophobic pocket at the carbonic anhydrase II active site binds CO_2 (at 10^8 M^{-1} s^{-1}, TON~ 106 s^{-1} and K_m ~10 mM.) *via* hydrogen bonding interaction with the backbone amide of Thr-199, where the CO_2 does not coordinate to the zinc.[3] To implement this structural insight into MOFs, small peptides (Figure 2A; **L35** and **L36**) were incorporated into NU-1000 channels via SALI. As shown in Figure 2C, a glycine based peptide provides better binding of CO_2 compared to an alanine based peptide. Though detailed investigations are underway, it can be hypothesized that glycine units offer better hydrogen bonding accessibility of their unhindered amides relative to that in alanines.

Molecular-level Modeling

We are using molecular-level modeling 1) to screen new candidate materials and 2) to obtain insights into the structures that provide the best performance.
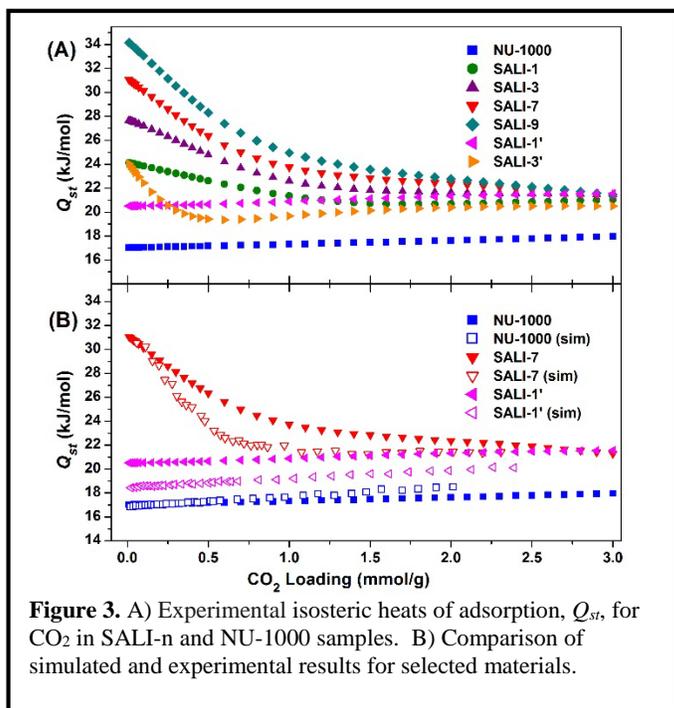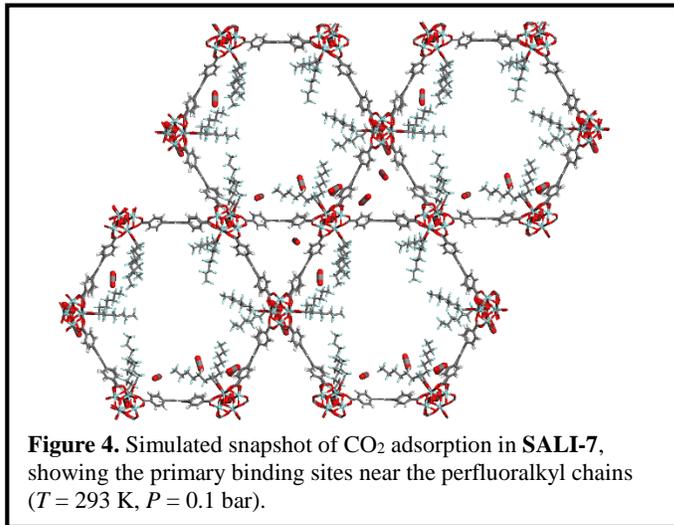

Figure 3. A) Experimental isosteric heats of adsorption, Q_{st}, for CO_2 in SALI-n and NU-1000 samples. B) Comparison of simulated and experimental results for selected materials.

Molecular modeling was used to confirm some of the experimental observations for SALI-modified NU-1000 and to provide additional insights. As shown in Figure 3B, the simulations capture the dependence of the isosteric heat of adsorption, Q_{st}, as a function of CO_2 loading quite well.[2] The simulations predict that CO_2 molecules adsorb preferentially near the Zr_6 nodes of the MOF. In addition, we found that the perfluoroalkyl chains are fairly rigid and treating them as rigid or treating them as flexible makes little difference on the predicted adsorption properties.[2]

We also performed extensive simulations of CO_2, water, and other molecules in FMOF-1,[4] which is a completely fluorinated material known to be very hydrophobic. Initial simulations were used to validate the model by comparing with experimental data from the literature for n-hexane, benzene, water, N_2, and O_2 adsorption. In agreement with experiment, the simulations predict no adsorption of water at pressures below the bulk saturation pressure. Single-component CO_2 isotherms were then predicted, as well as adsorption of CO_2/H_2O mixtures. The simulations predict that the CO_2 capacity of FMOF-1 is unaffected by the presence of water. While the CO_2 capacity of FMOF-1 is rather low, the results suggest that other hydrophobic MOFs could be a good choice for CO_2 capture under humid conditions. The simulations also provide very interesting insights about the relative importance of van der Waals and Coulombic interactions in the adsorption of water and CO_2 in nanopores lined with fluorine groups.

Another focus this year was to wrap up a series of quantum mechanical calculations started last year for screening of candidate functional groups that could be incorporated into MOFs or other sorbents for selective adsorption of CO_2 over N_2 in the presence of water vapor. We are currently writing up these results for publication.

Figure 4. Simulated snapshot of CO_2 adsorption in **SALI-7**, showing the primary binding sites near the perfluoralkyl chains ($T = 293$ K, $P = 0.1$ bar).

Process-level Modeling

There are two main objectives of the process-level modeling in this project: first, to design a system that utilizes materials discovered in the project and, second, to provide feedback to the materials discovery effort on the desired material properties. While our primary focus is the development of materials that can adsorb CO_2 in the presence of water, we thought it worthwhile also to investigate how much it would cost to remove water vapor from the flue gas prior to the CO_2/N_2 separation.

During the past year, a MATLAB code for modeling the pressure-swing adsorption units was developed. The model consists of nonlinear algebraic and partial differential equations and considers a multi-component adsorption system with temperature effects.[5] This code was used to simulate a four-step Skarstrom cycle, shown in Figure 5. In this cycle, the adsorption column is first pressurized and then the flue gas is fed into the column, where both CO_2 and N_2 are adsorbed. The adsorbent preferentially adsorbs CO_2 over N_2, enriching it in the solid phase. The column is then depressurized, allowing both components to be desorbed from the adsorbent. Finally, the column is purged by feeding N_2 gas (the product from the adsorption step), allowing enriched CO_2 to be collected from the front of the column.

The model was developed by adopting a finite volume method for spatial discretization, transforming the partial differential equations (PDEs) into ordinary differential equations (ODEs).[6,7] These ODEs were then solved through numerical integration using the ODE15s solver in MATLAB.
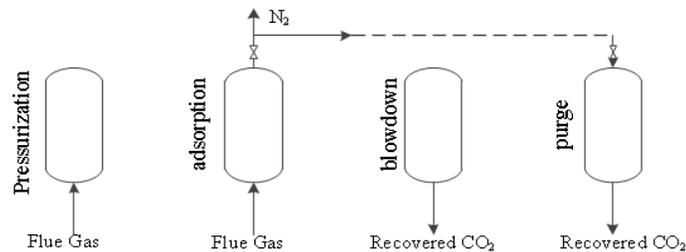

Figure 5. 4-step Skarstrom Cycle

After the model was developed, it was desired to develop a code for optimizing the process parameters of the model in order to maximize the purity of the CO_2 recovered from the column or minimize the overall cost of the system. Although the Skarstrom

cycle is preferred for its simplicity, it has been shown to be unable to achieve high CO_2 purity and recovery.[6] We also observed this issue through our process dynamic simulation study. In order to overcome this problem, a two-stage Skarstrom cycle was used where the product from the first stage is used as the feed for the second stage as shown in Figure 2. In addition, we wanted the optimization to select the most effective material from a selection of zeolites and metal-organic framework (MOFs) materials, as well as the desired level of water in the flue gas coming into the adsorption process. Binary 0-1 variables were introduced to model the "yes-no" decision of material selection and water level selection. The optimization problem was developed by fully discretizing the PDEs from the model, both in space and in time, forming a mixed-integer non-linear programming (MINLP) problem. The finite volume method was used for spatial discretization, while a Radau collocation method was used for temporal discretization.[8,9] The initial point of the MINLP problem was found using the solution of the MATLAB model. The MINLP problem was solved using GAMS with SBB as the MINLP solver and CONOPT as the nonlinear programing solver.
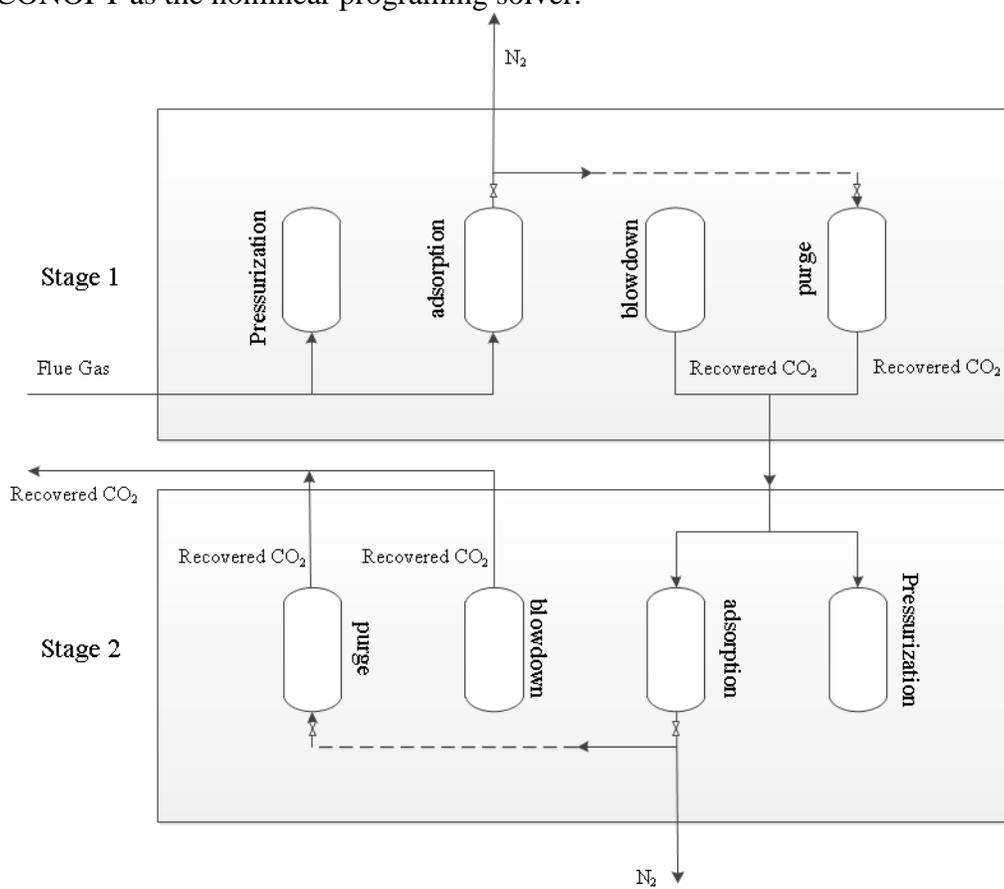

Figure 6. Two stage PSA/VSA system

The optimization code was used to determine the maximum purity of CO_2 that could be recovered from the two-stage PSA system and also the minimum cost for the two-stage system. In both cases, the overall recovery of CO_2 from the two stages was set to be at least 90%. For the minimum cost, the purity of CO_2 recovered from the second stage was set to be at least 80%.

For the maximum CO_2 purity calculations, the adsorbent material was fixed as ZIF-78. With a two-stage PSA system, it was determined that 90.3% was the maximum achievable purity. The CO_2 mole fraction profiles for the second stage are shown in Figure 7 and the values of the operating parameters for the optimal purity are shown in Table 1.
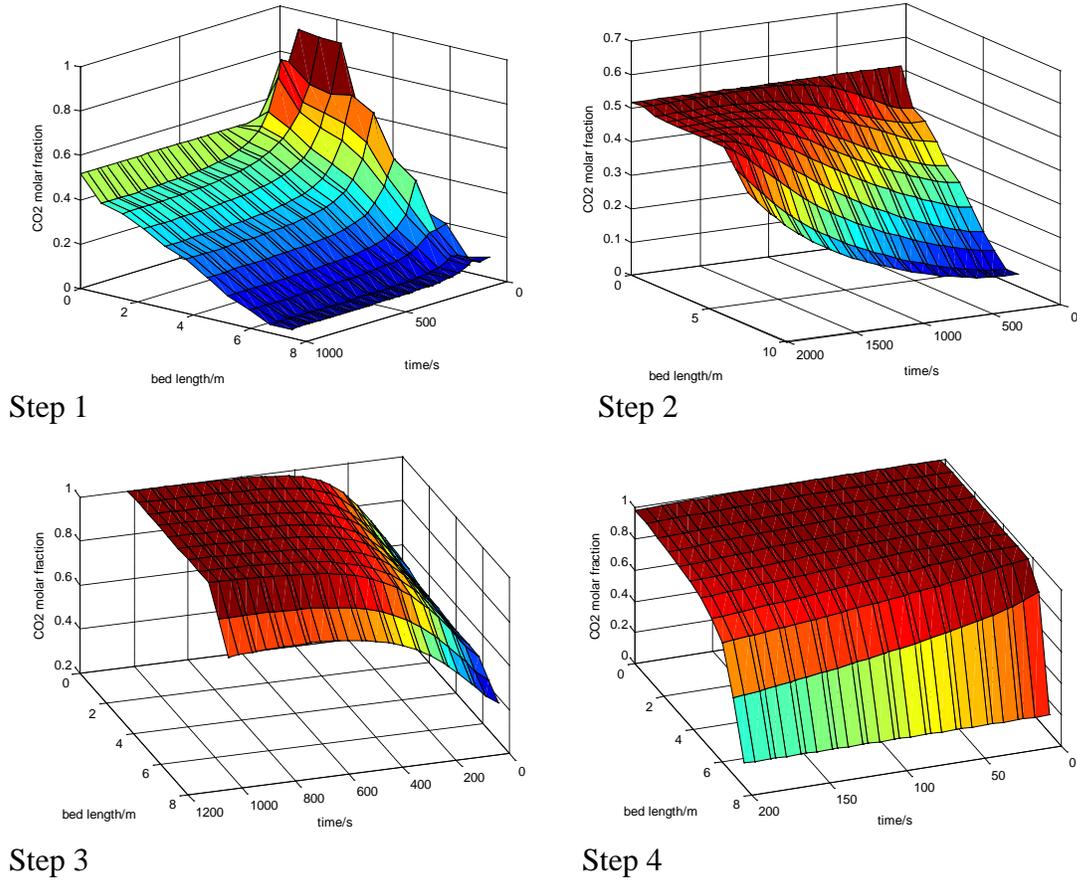

Step 1

Step 2

Step 3

Step 4

Figure 7. CO_2 mole fraction profiles of the second-stage PSA/VSA

Table 1: The optimal operating conditions when CO_2 purity is maximized

	Stage 1	Stage 2
t_{pres} (s)	117.8	1000
t_{ads} (s)	2000	2000
t_{bd} (s)	785.1	939.1
t_{pur} (s)	1062.1	200
L (m)	7.71	7.50
P_H (Pa)	3.33×10^5	1.22×10^5
P_L (Pa)	10000	10956
CO_2 Purity	51.7%	90.3%

For the minimum cost, the total cost of the process was calculated as the sum of the annualized investment cost (AIC) and the annual operating cost (AOC). The AIC was estimated from the equipment purchase cost and the AOC was calculated from the utilities required for operation of the process. Three adsorbent materials were considered, ZIF-78, zeolite 13X, and zeolite 5A. ZIF-78 was determined to be the best performing adsorbent material among these three, with a total cost of $6.42 million per year. A breakdown of the costs is shown in Table 2. The cost per year with ZIF-78 is estimated to be more than $1 million less than with either of the zeolites.

Table 2: Cost (million $ per year)

	ZIF-78	Zeolite 5A	Zeolite 13X
AIC compressor	1.12	1.07	1.13
AOC compressor	2.30	0.45	0.42
AIC vacuum	0.32	2.16	2.28
AOC vacuum	1.47	2.30	2.08
AIC everything else	1.20	1.59	1.51
Total	**6.42**	**7.58**	**7.40**

After the optimal adsorbent material was determined, dehydration costs were taken into account. The material was fixed to ZIF-78 and the model was run accounting for the effect of water on the process performance using some simple estimates of the effect of water on the material performance. With these assumptions, the optimal water level was determined to be 3.0% for ZIF-78 with using Cooling & Condensing technology for water removal upstream of the adsorption system.

Progress
Development of the SALI technique allows for rapid synthesis of a wide range of variants for a single parent MOF material. Development of fluorinated MOFs, through SALI or other methods, may provide a solution to the difficult problem of selectively adsorbing CO_2 over N_2 in the presence of water vapor.

Our preliminary process-level modeling indicates that removing water prior to capturing CO_2 from flue gas may be economically and technically feasible. The question of how much of the water to remove requires an integration of the process modeling and the materials development and will be one focus in the coming year.

Future Plans
Computational screening of MOFs will continue in close association with the experimental effort, as described in the original proposal. One new direction is suggested by the process-level modeling, namely, an assessment of how MOFs perform in the presence of a small amount of water vapor (as opposed to a stream that is essentially saturated with water vapor). The process modeling also suggests that pressures up to around 3 bar (total pressure) may be reasonable for screening candidate materials.

We will finish our assessment of the cost of water removal and investigate possible improvements to the adsorption cycle by adding additional steps, such as heavy reflux and pressure equilization steps, in order to further reduce the process cost.

Publications and Patents Acknowledging GCEP

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