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

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**Abstract**
This project focuses on development of new metal-organic framework (MOF) materials for carbon capture. An important part of the project is complementary process-leveling modeling to design processes that take advantage of the new materials. A new MOF functionalization technique, solvent assisted ligand incorporation (SALI), was used 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 functional groups that improve the water stability of the MOF. We also installed "complementary organic motifs" designed to selectively bind $CO_2$ and demonstrated improved $CO_2/N_2$ selectivity compared to the parent MOF. High-throughput computational screening techniques are being developed to identify new or existing MOFs with increased ability to capture $CO_2$. Process-level modeling indicates that reducing the concentration of water prior to capturing $CO_2$ from flue gas should be economically and technically feasible. Process modeling also suggests that pressures up to ~3 bar (total pressure) may be reasonable for carbon capture by P/VSA. Most researchers have focused on 1 bar, so this information may open 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 project 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 in tandem with 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

### Materials Development

The materials portion of the project is currently focused on designing, synthesizing, characterizing, and functionally evaluating nanoporous materials that feature the following properties: a) excellent water vapor 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. These properties are being addressed mainly via metal node functionalization within MOFs. Molecular modeling is used in a close interaction between experiment and theory.
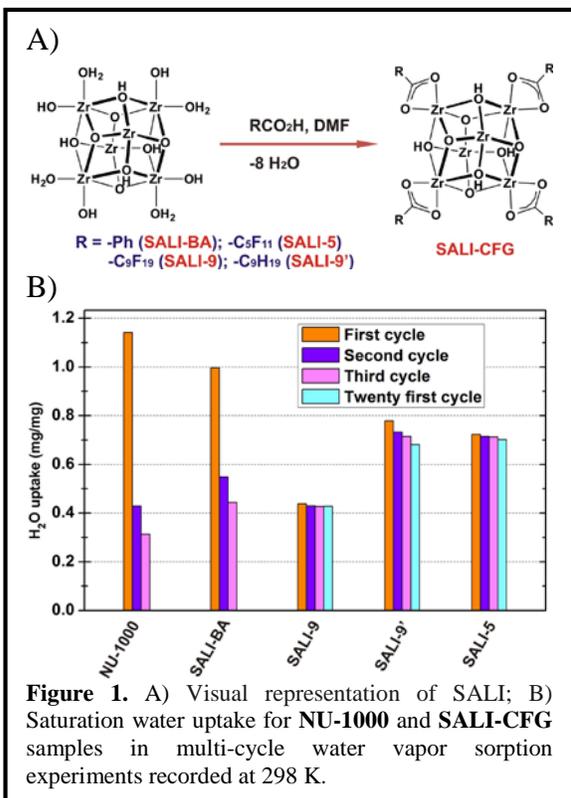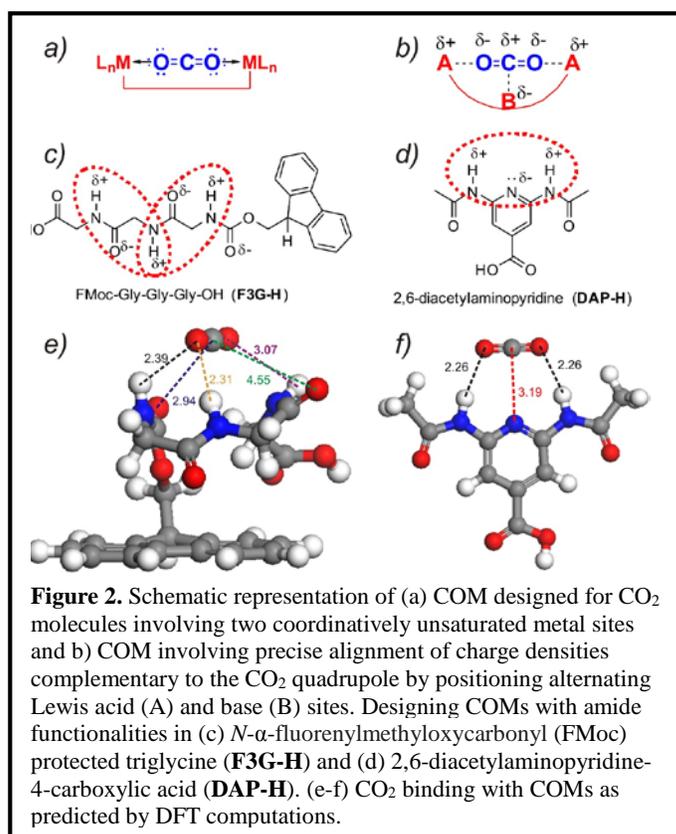
**S̲olvent-A̲ssisted L̲igand Incorporation (SALI):** This technique was developed to efficiently install various carboxylate-derived functionalities into the Zr-based MOF **NU-1000** as channel-tailoring moieties that are strongly bound to the $Zr_6$ nodes *via* the terminal –OH and aqua groups (Figure 1A).[1,2,3] We have established that the large hexagonal channels of **NU-1000** (> 30 Å width) can be systematically tailored with various chemical entities *via* SALI, which relies upon an acid-base reaction between an incoming carboxylic acid-containing functional group (**CFG**) and a pair of



**Figure 1.** A) Visual representation of SALI; B) Saturation water uptake for **NU-1000** and **SALI-CFG** samples in multi-cycle water vapor sorption experiments recorded at 298 K.

terminal –OH and aqua ligands of the $Zr_6$ node.  As a result, the charge-compensating CFG ligands in **SALI-CFG** daughter materials are strongly bound to the **NU-1000** nodes.

**Water Stabilization of $Zr_6$-Based MOFs via SALI:** Frameworks constructed from Zr(IV)-carboxylate connections are inherently robust, and this class of materials was shown to withstand wide ranges of pH and hot water.[3-6]  However, it has been shown that these materials lose porosity upon exposure and activation from water, mainly due to capillary-forces-driven channel collapse during activation from water and not as a result of energetically uphill hydrolytic cleavage of strong $Zr^{IV}$-carboxylate connections ($\Delta G \approx$ +26 kcal mol$^{-1}$ with $\Delta G^{\ddagger} \approx$ +38 kcal mol$^{-1}$).[6]  The water-exposed MOF samples, when exchanged with a solvent having lower capillary force, were shown to retain permanent porosity by thermal activation under dynamic vacuum.[7]  Application of MOFs in CCS, under flue gas condition, however, would not allow such a recycling process.  Therefore, we focused on an alternative and general stabilization method by understanding the origin of such capillary-force-driven collapse and then devising a strategy that would allow high recyclability for such MOFs under direct thermal activation processes.

We studied, as a proof of principle, several SALI-CFG materials (Fig 1A) using water vapor sorption experiments.  Our study finds that a strong interaction of the condensed water with the polar node within the framework can exert strain during activation or removal of the water from the pores.  While replacement of the polar hydroxyl and aqua ligands with aprotic, non-polar organic carboxylates can reduce the effective interaction of the water with the node, a flexible alkyl chain can further limit the accessibility by the water vapors (see Figure 1B).  MD simulations revealed that a longer and flexible carboxylate-based ligand indeed provides more limited access of the water molecules to the $Zr_6$ nodes.  This study suggests that MOF-node functionalization, such as SALI, can be a powerful strategy towards highly water stable and recyclable framework materials.  Note that we previously reported that both SALI-9 and SALI-5 are superior $CO_2$ capture materials compared to the unmodified NU-1000.[2]



**Figure 2.** Schematic representation of (a) COM designed for $CO_2$ molecules involving two coordinatively unsaturated metal sites and b) COM involving precise alignment of charge densities complementary to the $CO_2$ quadrupole by positioning alternating Lewis acid (A) and base (B) sites. Designing COMs with amide functionalities in (c) *N*-α-fluorenylmethyloxycarbonyl (FMoc) protected triglycine (**F3G-H**) and (d) 2,6-diacetylaminopyridine-4-carboxylic acid (**DAP-H**). (e-f) $CO_2$ binding with COMs as predicted by DFT computations.

**Complementary Organic Motifs for $CO_2$ Binding:** Some of our recent work was inspired by the hydrophobic pocket at the
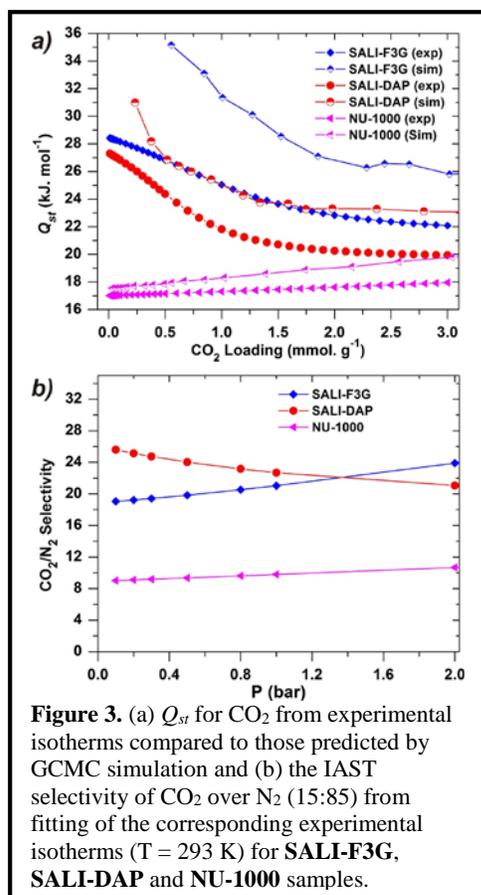
**Figure 3.** (a) $Q_{st}$ for $CO_2$ from experimental isotherms compared to those predicted by GCMC simulation and (b) the IAST selectivity of $CO_2$ over $N_2$ (15:85) from fitting of the corresponding experimental isotherms (T = 293 K) for **SALI-F3G**, **SALI-DAP** and **NU-1000** samples.

carbonic anhydrase II active site, which has a $CO_2$ binding constant of $10^8$ M$^{-1}$ s$^{-1}$, a TON ~ 106 s$^{-1}$ and $K_m$ ~10 mM. $CO_2$ binds *via* an interaction with the backbone amide of Thr-199, but the $CO_2$ does not coordinate to the zinc.[8] To implement this structural insight into MOFs, we designed small complementary organic motifs (COMs; Figure 2; L= **F3GH** and **DAP**) that take advantage of precise alignment of charge densities that are complementary to those in a $CO_2$ molecule. We reasoned that COMs (Fig 2c,d) with precisely aligned charge densities in their polar functionalities ($\delta^+\cdots\delta^-\cdots\delta^+$) that complement the quadrupolar charge orientation in O=C=O ($\delta^-\cdots\delta^+\cdots\delta^-$) could provide selective binding of $CO_2$ (Figure 2b). These promising COMs were post-synthetically incorporated into NU-1000 using SALI. In this study, we demonstrated that these COM-functionalized MOFs exhibit selectivity for capturing $CO_2$ compared to other reported motifs. Figure 3a shows isosteric heats of adsorption, $Q_{st}$, for $CO_2$, and it can be seen that the heats of adsorption are increased significantly compared to the unfunctionalized NU-1000. The selectivities for $CO_2$ adsorption over $N_2$ were calculated from the single-component isotherms using ideal adsorbed solution theory (IAST), and Figure 3b shows a significant improvement in selectivity upon functionalization of NU-1000. The performance of the MOFs with integrated COMs predicted by GCMC simulation, including the performance trend in $CO_2$ and $N_2$ adsorption isotherms as well as the $Q_{st}$ plots for the **SALI-F3G** and **SALI-DAP** samples are in good agreement with the corresponding experimental data. This work highlights the potential of synergistic theoretical design and experimental study to identify and develop new organic functionalities for $CO_2$ capture and separation. Based on the knowledge gained from this work, we are currently designing better motifs with a facile strategy for incorporation into MOFs for $CO_2$ capture.

**High-throughput Computational Screening of Water-Resistant Metal-Organic Frameworks for $CO_2$ Capture:** In addition to modeling of individual materials of interest, we are also using high-throughput computational screening to identify MOFs with the ability to adsorb $CO_2$ over $N_2$ in the presence of high humidity. In particular, we screened the Computation-Ready Experimental (CoRE) MOF database of Chung et al.[9] The CoRE MOF database contains 5195 crystal structures from the published experimental literature. First, we calculated the $CO_2/H_2O$ selectivity based on the ratio of the simulated Henry's constants using an approximate method[10] for obtaining the MOF atomic charges. Over 30 candidates with the highest $CO_2/H_2O$ selectivity were selected,

and the calculations were repeated using a more accurate (but much slower) quantum mechanical method to obtain the MOF atomic charges. In addition, the selectivities were calculated based on full GCMC mixture simulations, rather than the simpler ratio of Henry's constants. The various methods do not give identical results, but the faster methods are effective in identifying top performing materials and thus may be used for initial screening. Finally, $CO_2/H_2O/N_2$ mixtures were simulated to provide additional detail about the top candidates. Further analysis is underway.

*Process-level Modeling*

Process-level modeling is an important complement to materials development. 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.

During the past year, the pressure/vacuum swing adsorption (P/VSA) model developed last year in MATLAB was used to investigate several potential adsorbent materials in order to determine the minimum cost for capturing $CO_2$. Two zeolites and two MOFs were investigated: zeolite 13X, zeolite 5A, HKUST-1, and Ni-MOF-74. The standard 4-step Skarstrom cycle, while operationally simple, was unable to achieve the desired purity and recovery for $CO_2$ capture. Therefore, a two-stage configuration was developed in order to achieve the required purity and recovery. Using this P/VSA model, the process parameters were optimized using the nondominant sorting genetic algorithm (NSGA-II) proposed by Deb et al.[11] For the NSGA-II, a population of 10 times the number of decision variables was used. The algorithm was run for at least 60 generations or until no visible improvement was seen in the objective functions for 5 generations.

This optimization algorithm was used along with the P/VSA simulation to determine the maximum purity and recovery achievable for each of the adsorbents, along with the minimum cost of capturing $CO_2$ and pressurizing it for pipeline transportation. This was done for both dry and wet flue gas. The two-stage P/VSA cycle with post-separation compression is shown in Figure 4.
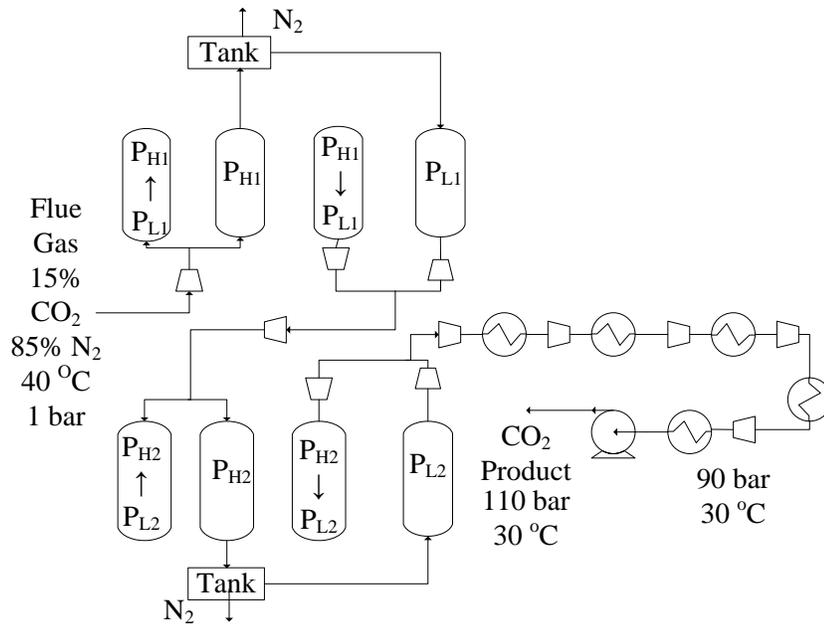
**Figure 4.** P/VSA cycle with post-separation compression.  H and L indicate high and low pressures.

As a starting point, we determined the capabilities of each material in a single-stage Skarstrom cycle.  A Pareto front for each material was calculated to see the maximum purity and recovery.  The results are shown in Figure 5.  It is seen that the best performing material was zeolite 13X, which was able to attain a purity of 78% while maintaining 90% recovery.  It was also seen that HKUST-1 was the worst performing material of the four, unable to achieve even 30% purity at 90% recovery.  The



**Figure 5.** Pareto curves for multi-objective optimization of purity and recovery.

internal column profiles for the mole fraction of $CO_2$, the $CO_2$ and $N_2$ loadings, and the temperature are shown in Figure 6 for zeolite 13X and HKUST-1 for the highest purity points.
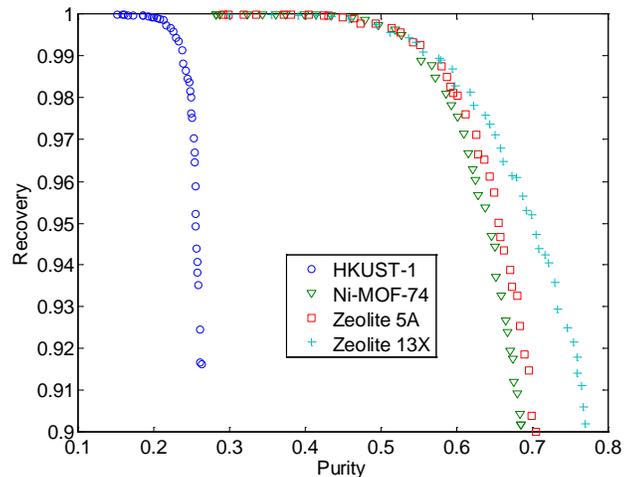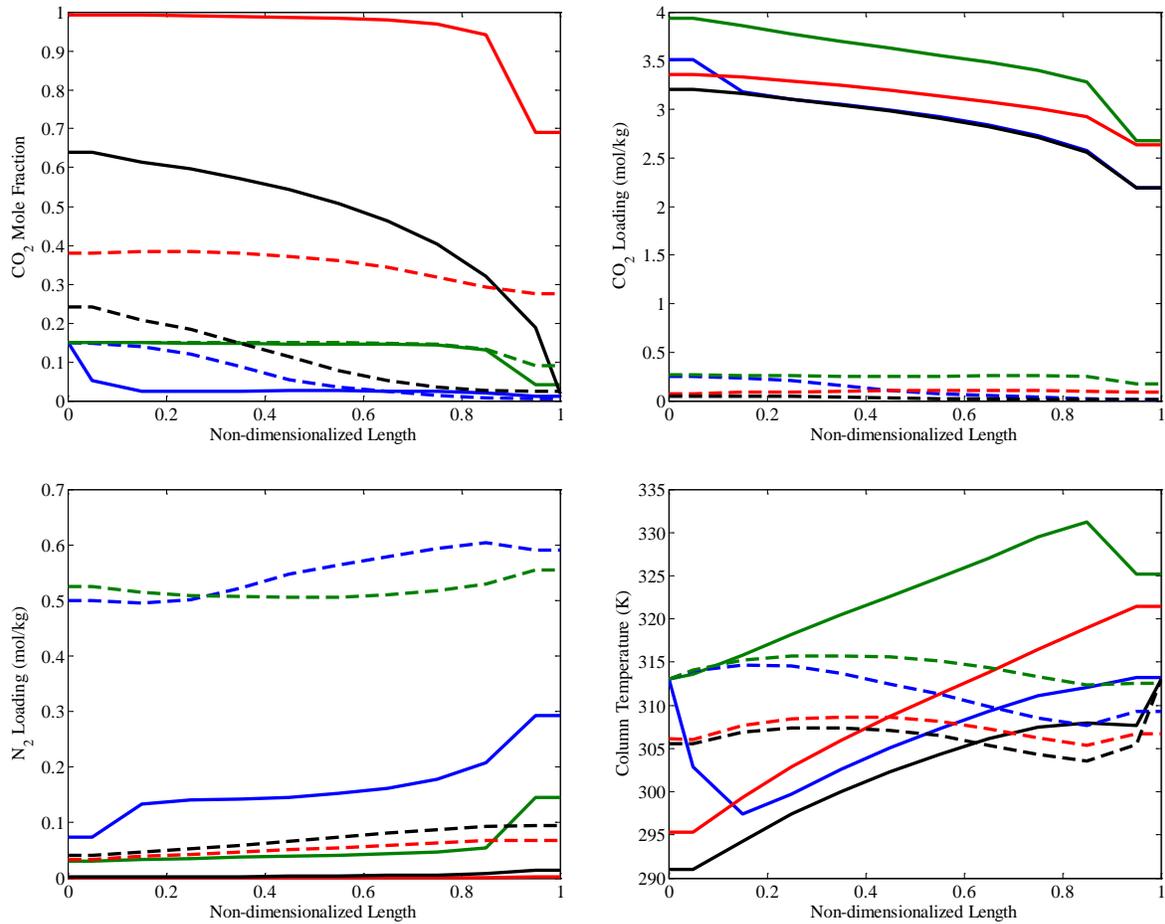
**Figure 6.** Solid lines correspond to zeolite 13X: $P_0$=4.46 bar, $t_{ads}$=794 s, $t_{pur}$= 789 s, L=4.28 m, cycle time=1945 s. Dashed lines correspond to HKUST-1: $P_0$=1.5 bar, $t_{ads}$= 680 s, $t_{pur}$= 646 s, L= 4.81 m, cycle time=1642 s. For both materials, the profiles correspond to the bed at the end of each step with the colors corresponding to Pressurization (Blue), Adsorption (Green), Depressurization (Red), and Purge (Black) steps.

In determining the minimum cost of capturing the $CO_2$ from dry flue gas, the total cost of the process was calculated including the capital and operating cost of the P/VSA system itself and the cost of pressurizing the flue gas to 110 bar for pipeline transportation. Of the three materials examined, zeolite 13X had the lowest minimum cost of $5.19 million per year or $32.10 per ton of $CO_2$. The minimum costs for each material are shown Table 1, and the operating parameters for each material are shown in Tables 2 and 3. It should be noted that the higher capital costs of Ni-MOF-74 compared to the two zeolites are due to the estimated cost of the MOF itself ($7/kg for Ni-MOF-74 versus $1/kg for the zeolites).

**Table 1.** Optimal cost breakdown for dry flue gas.

| Material | Operating Costs ($ million /year) | Capital Costs ($ million /year) | Post-Separation Costs ($ million /year) | Total Costs ($ million /year) |
|---|---|---|---|---|
| Zeolite 13X | 2.47 | 0.27 | 2.44 | 5.19 |
| Zeolite 5A | 2.68 | 0.26 | 2.47 | 5.41 |
| Ni-MOF-74 | 3.16 | 0.86 | 2.42 | 6.44 |

**Table 2.** Optimal operating parameters for the first stage of the PSA system.

| Material | Adsorption Pressure (bar) | Purge Pressure (bar) | Adsorption Time (s) | Purge Time (s) | Length (m) | Cycle Time (s) |
|---|---|---|---|---|---|---|
| Zeolite 13X | 1.00 | 0.10 | 726 | 382 | 1.73 | 1173 |
| Zeolite 5A | 1.27 | 0.10 | 520 | 291 | 1.69 | 879 |
| Ni-MOF-74 | 1.36 | 0.10 | 657 | 418 | 1.50 | 1145 |

**Table 3.** Optimal Operating Parameters for the second stage of the PSA system.

| Material | Adsorption Pressure (bar) | Purge Pressure (bar) | Adsorption Time (s) | Purge Time (s) | Length (m) | Cycle Time (s) |
|---|---|---|---|---|---|---|
| Zeolite 13X | 1.26 | 0.10 | 589 | 249 | 3.81 | 1120 |
| Zeolite 5A | 1.30 | 0.10 | 664 | 449 | 4.95 | 1520 |
| Ni-MOF-74 | 2.66 | 0.10 | 330 | 215 | 3.22 | 939 |

In determining the minimum cost of capturing $CO_2$ in the presence of water, it was necessary to determine the detrimental effects of water on the performance of the capture materials and accurately model this. Based on work in the literature,[12,13] a correction factor was added to the simulation to account for the section of the column that would experience a decrease in adsorption capacity due to the presence of water. This correction factor was tested by performing a simulation using flue gas containing 5.5 mol% water using the operating parameters determined for zeolite 13X in the dry flue gas scenario. The column profiles are shown in Figure 7. In the dry flue gas scenario, a purity of 49.7% was achieved with a recovery of 97.5%. In the wet flue gas scenario, the purity increased to 52.1% and the recovery decreased to 93.1%, which is consistent with other work.[14]

Using the correction factors, the minimum cost of capturing $CO_2$ from wet flue gas was determined for each material. Zeolite 13X was determined to have the lowest cost of $5.63 million per year or $34.82 per ton of $CO_2$, using cooling and condensing technology to reduce the water level of the flue gas to 3.85 mol%. The optimal costs for each material are shown in Table 4, and the operating parameters for both stages are shown in Tables 5 and 6.
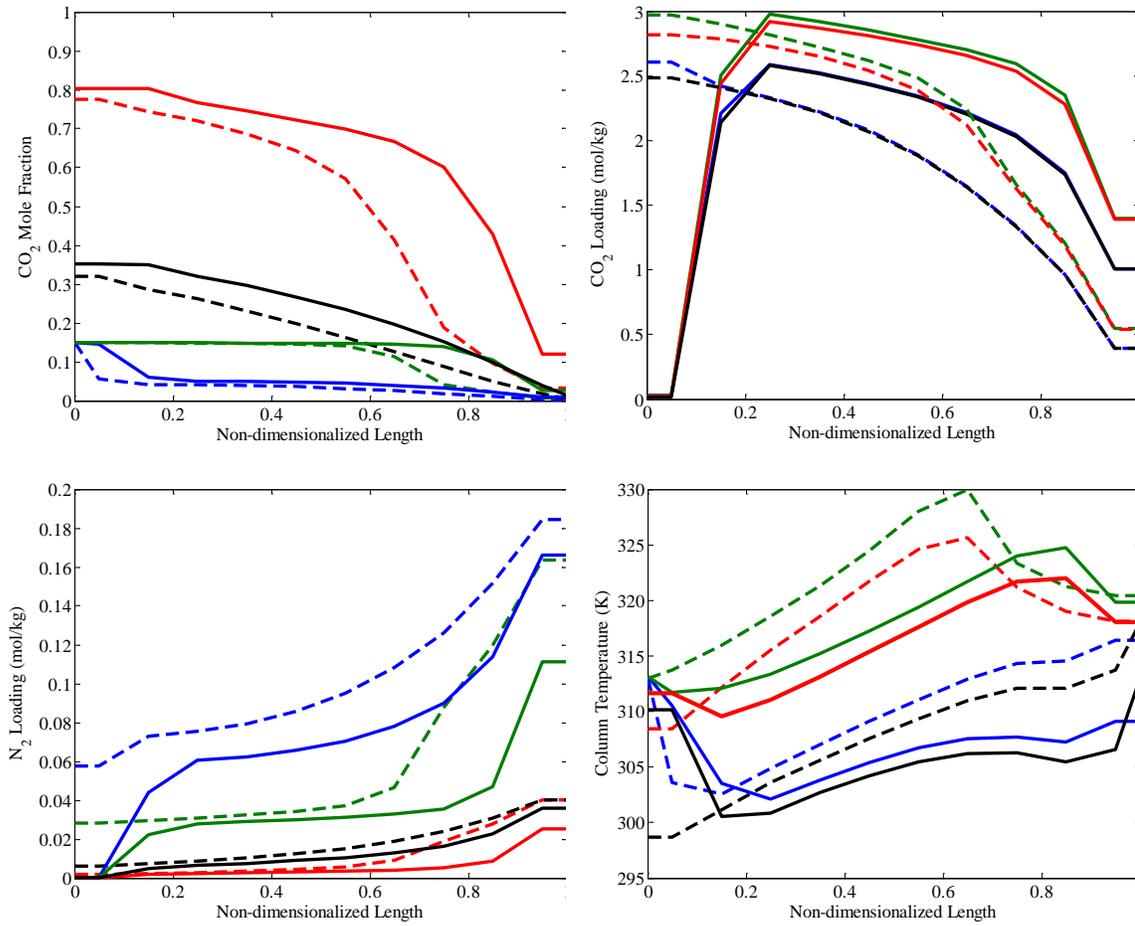
**Figure 7.** Profile of the zeolite 13X P/VSA bed at the end of each step comparing wet and dry flue gas. The colors correspond to Pressurization (Blue), Adsorption (Green), Depressurization (Red), and Purge (Black) steps. Dashed Lines correspond to the dry flue gas conditions, while the solid lines correspond to the wet flue gas conditions.

**Table 4.** Optimal cost breakdown for wet flue gas, costs are in $ million per year. C&C is cooling and condensation, and TEG is absorption with triethylene glycol.

| Material | Operating Costs | Capital Costs | Post-Separation Costs | Dehydration Costs | Total Costs | Dehydration Technology |
|---|---|---|---|---|---|---|
| Zeolite 13X | 2.65 | 0.394 | 2.45 | 0.129 | 5.63 | C&C |
| Zeolite 5A | 2.83 | 0.248 | 2.48 | 0.815 | 6.37 | TEG |
| Ni-MOF-74 | 3.49 | 0.826 | 2.46 | 0.084 | 6.86 | C&C |

**Table 5.** Optimal Operating Parameters for the first stage of the PSA system.

| Material | Adsorption Pressure (bar) | Purge Pressure (bar) | Adsorption Time (s) | Purge Time (s) | Length (m) | Water Level (%) | Cycle Time (s) |
|---|---|---|---|---|---|---|---|
| Zeolite 13X | 1.21 | 0.10 | 677 | 264 | 3.23 | 3.85 | 1056 |
| Zeolite 5A | 1.48 | 0.10 | 561 | 315 | 2.12 | 0.33 | 955 |
| Ni-MOF-74 | 1.81 | 0.10 | 709 | 553 | 1.90 | 4.34 | 1354 |

**Table 6.** Optimal Operating Parameters for the second stage of the PSA system.

| Material | Adsorption Pressure (bar) | Purge Pressure (bar) | Adsorption Time (s) | Purge Time (s) | Length (m) | Water Level (%) | Cycle Time (s) |
|---|---|---|---|---|---|---|---|
| Zeolite 13X | 1.68 | 0.10 | 389 | 258 | 3.54 | 3.85 | 895 |
| Zeolite 5A | 1.44 | 0.10 | 301 | 250 | 3.58 | 0.33 | 783 |
| Ni-MOF-74 | 2.90 | 0.14 | 300 | 154 | 3.90 | 4.34 | 773 |

**Progress**

Development of the SALI technique allows for rapid synthesis of a wide range of variants for a single parent MOF material.  Development of MOFs with complementary organic motifs for capturing $CO_2$, 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.  High-throughput computational screening has the potential to drastically increase the speed of identifying promising materials for $CO_2$ capture.

Our process-level modeling indicates that reducing the concentration of water prior to capturing $CO_2$ from flue gas should be economically and technically feasible.  Note that the concentration of water does not need to be reduced to zero, and the final water concentration is an interesting design variable.  This issue has not received much attention in the literature and could simplify the materials requirements.  The process-level modeling also indicates that the standard 4-step Skarstrom cycle is not adequate for $CO_2$ capture and more complex cycles (or 2-stage systems) are needed. Process modeling also suggests that pressures up to ~3 bar (total pressure) may be reasonable for carbon capture by P/VSA.  Most materials researchers are focused on 1 bar as the upper pressure, so this should be very useful information to researchers trying to develop new materials for $CO_2$ capture.

**Future Plans**

We will complete the high-throughput computational screening for MOFs with high $CO_2/H_2O$ selectivity.  We have also started developing a database of MOFs with three types of linkers to test whether the additional tunability provided by three linkers (versus one or two) is advantageous for $CO_2$ capture.  We currently have a set of such structures with no functionality, and we will now add various chemical functional groups and analyze the performance computationally.  The experimental effort in the coming year

will focus on synthesis, characterization, and testing of top materials identified by molecular modeling.

Process-level modeling will continue in two directions. First, we will determine the adsorbent properties that lead the highest $CO_2$ purity and recovery and the lowest cost for capturing $CO_2$. Second, we will examine (and possibly develop) improved cycles that will lead to lower operating costs while meeting the required recovery and purity.

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