

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

Investigators

All investigators are at Northwestern University.

Randall Q. Snurr, Professor, Chemical & Biological Engineering

Joseph T. Hupp, Professor, Chemistry

Omar K. Farha, Research Professor, Chemistry

Fengqi You, Assistant Professor, Chemical & Biological Engineering

David Chen, Graduate Student, Chemical & Biological Engineering

Pravas Deria, Post-doctoral Researcher, Chemistry

Olga Karagiari, Graduate Student, Chemistry

Karson T. Leperi, Graduate Student, Chemical & Biological Engineering

Song Li, Post-doctoral Researcher, Chemical & Biological Engineering

Peyman Z. Moghadam, Post-doctoral Researcher, Chemical & Biological Engineering

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-level 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 CO₂. 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 CO₂ capture and new, optimal process configurations for these sorbents would be a step-out development in CCS.

Background

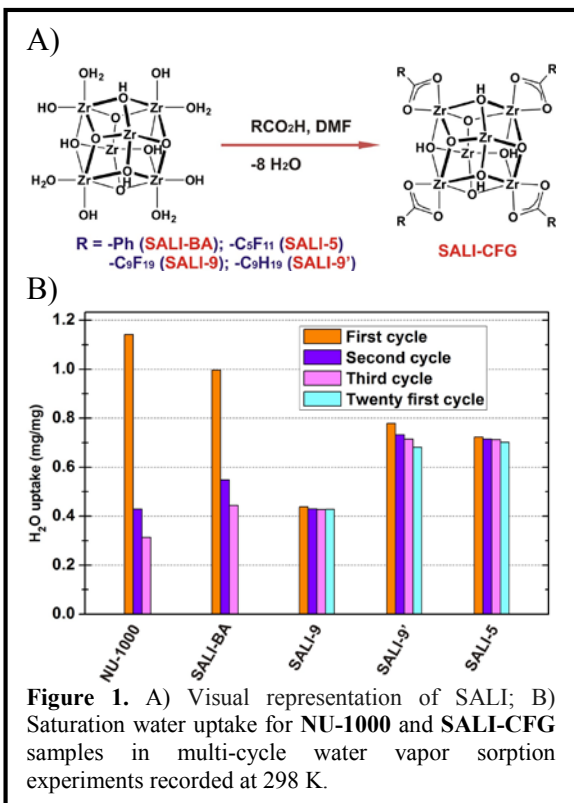
Research on MOFs continues to explode. Many research groups are investigating MOFs for separation of CO₂/N₂ mixtures, motivated by carbon capture. However, very few papers report results that take water into account. A small number of papers have appeared recently on the stability of MOFs, including 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 CO₂ 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.

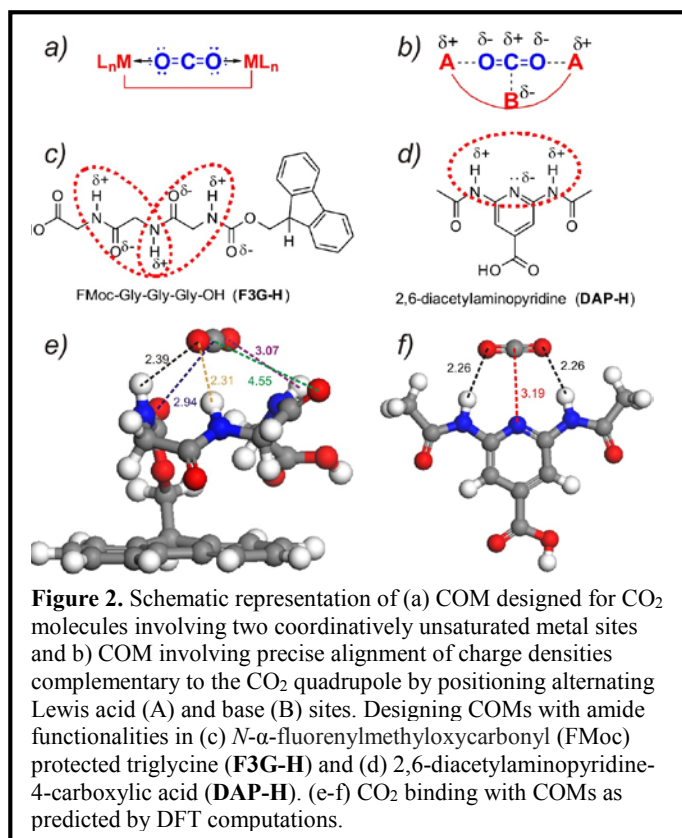


Solvent-Assisted Ligand Incorporation (SALI): This technique was developed to efficiently install various carboxylate-derived functionalities into the Zr-based MOF NU-1000 as channel-tailoring moieties that are strongly bound to the Zr₆ nodes via the terminal -OH and aqua groups (Figure 1A).^{1,2,3} 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

terminal –OH and aqua ligands of the Zr₆ 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 Zr₆-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 ($\Delta G \approx +26 \text{ kcal mol}^{-1}$ with $\Delta G^\ddagger \approx +38 \text{ kcal mol}^{-1}$).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 Zr₆ 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 CO₂ capture materials compared to the unmodified NU-1000.²

Complementary Organic Motifs for CO₂ Binding: Some of our recent work was inspired by the hydrophobic pocket at the

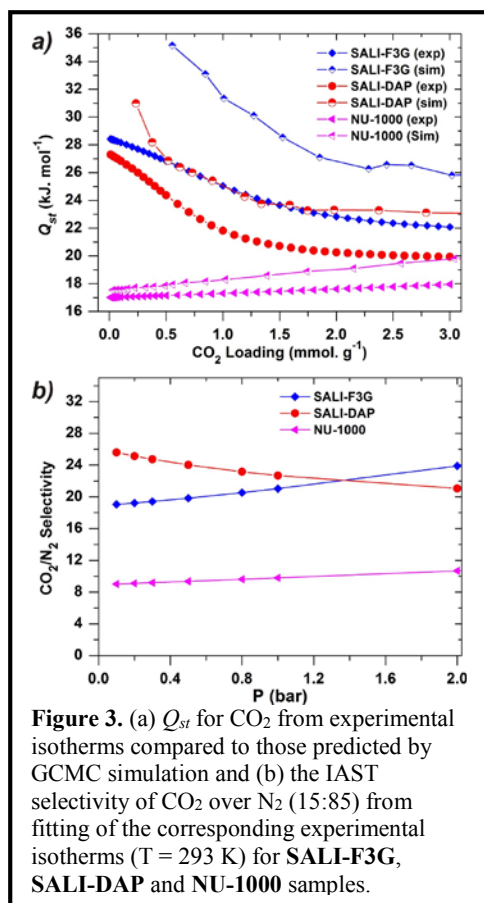


Figure 3. (a) Q_{st} for CO_2 from experimental isotherms compared to those predicted by GCMC simulation and (b) the IAST selectivity of CO_2 over N_2 (15:85) from fitting of the corresponding experimental isotherms ($T = 293 \text{ K}$) for **SALI-F3G**, **SALI-DAP** and **NU-1000** samples.

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 $\text{CO}_2/\text{H}_2\text{O}$ selectivity based on the ratio of the simulated Henry's constants using an approximate method¹⁰ for obtaining the MOF atomic charges. Over 30 candidates with the highest $\text{CO}_2/\text{H}_2\text{O}$ selectivity were selected,

carbonic anhydrase II active site, which has a CO_2 binding constant of $10^8 \text{ M}^{-1} \text{ s}^{-1}$, a $\text{TON} \sim 106 \text{ s}^{-1}$ and $K_m \sim 10 \text{ mM}$. 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 $\text{O}=\text{C}=\text{O}$ ($\delta^- \cdots \delta^+ \cdots \delta^-$) 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

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, CO₂/H₂O/N₂ 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 CO₂. 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 CO₂ 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 CO₂ 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.

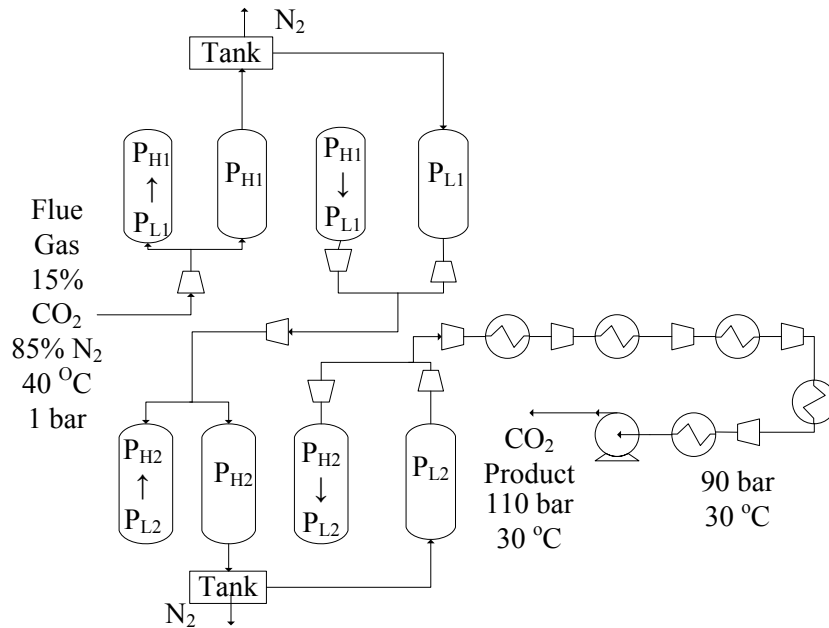


Figure 4. P/VSA cycle with post-separation compression. H and L indicate high and low pressures.

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 internal column profiles for the mole fraction of CO₂, the CO₂ and N₂ loadings, and the temperature are shown in Figure 6 for zeolite 13X and HKUST-1 for the highest purity points.

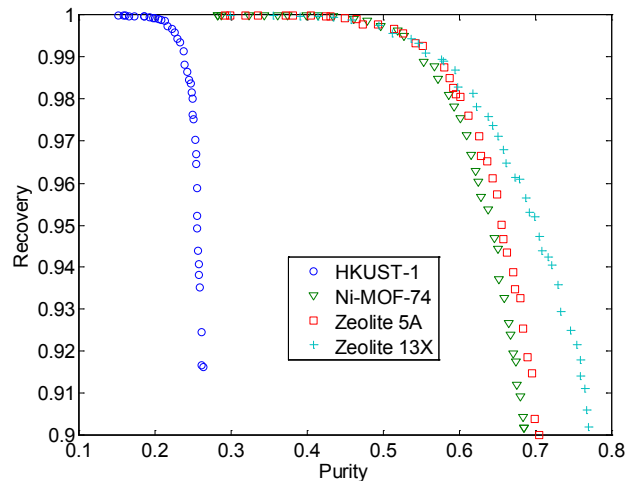


Figure 5. Pareto curves for multi-objective optimization of purity and recovery.

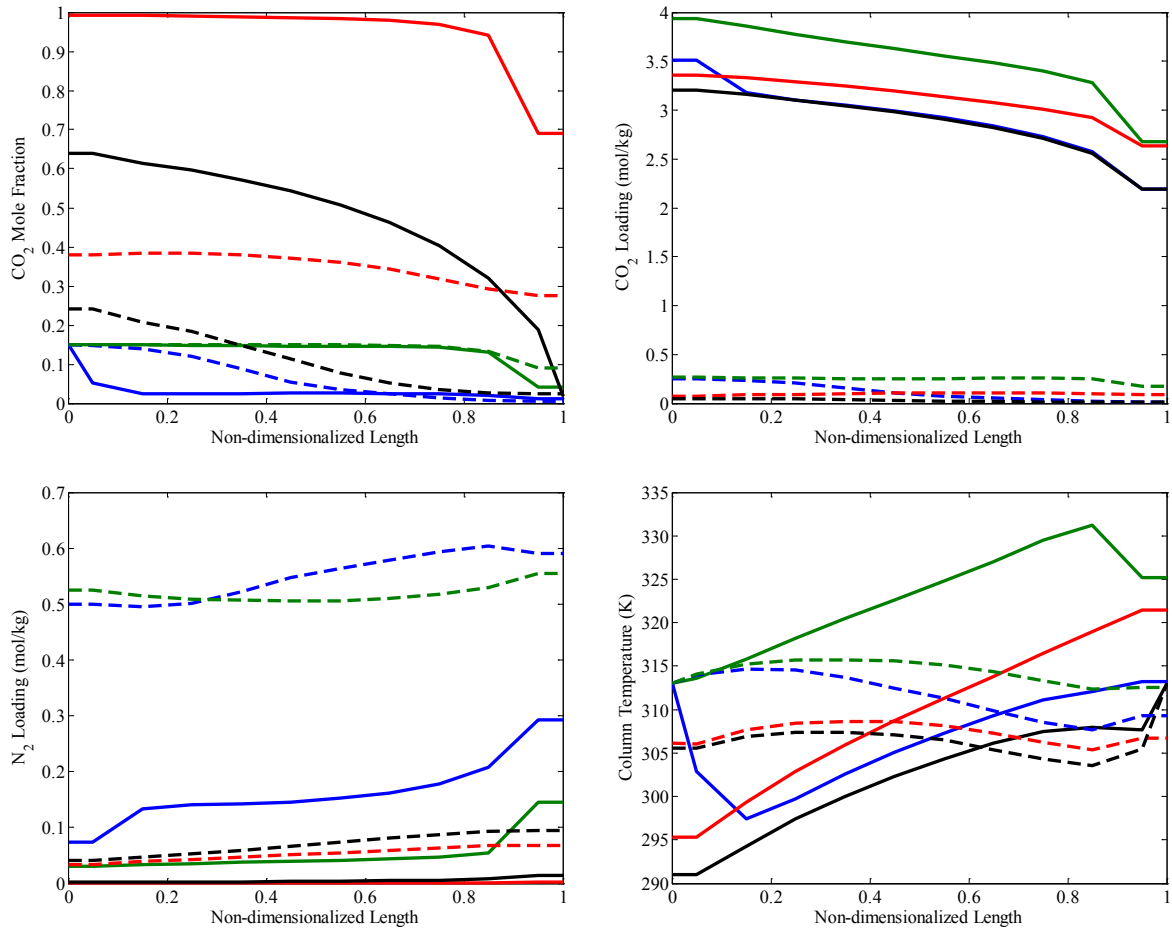


Figure 6. Solid lines correspond to zeolite 13X: $P_0=4.46$ bar, $t_{ads}=794$ s, $t_{pur}=789$ s, $L=4.28$ m, cycle time=1945 s. Dashed lines correspond to HKUST-1: $P_0=1.5$ bar, $t_{ads}=680$ s, $t_{pur}=646$ s, $L=4.81$ m, cycle time=1642 s. For both materials, the profiles correspond to the bed 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 CO₂ 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 CO₂. 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 CO₂ 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 CO₂ 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 CO₂, 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.

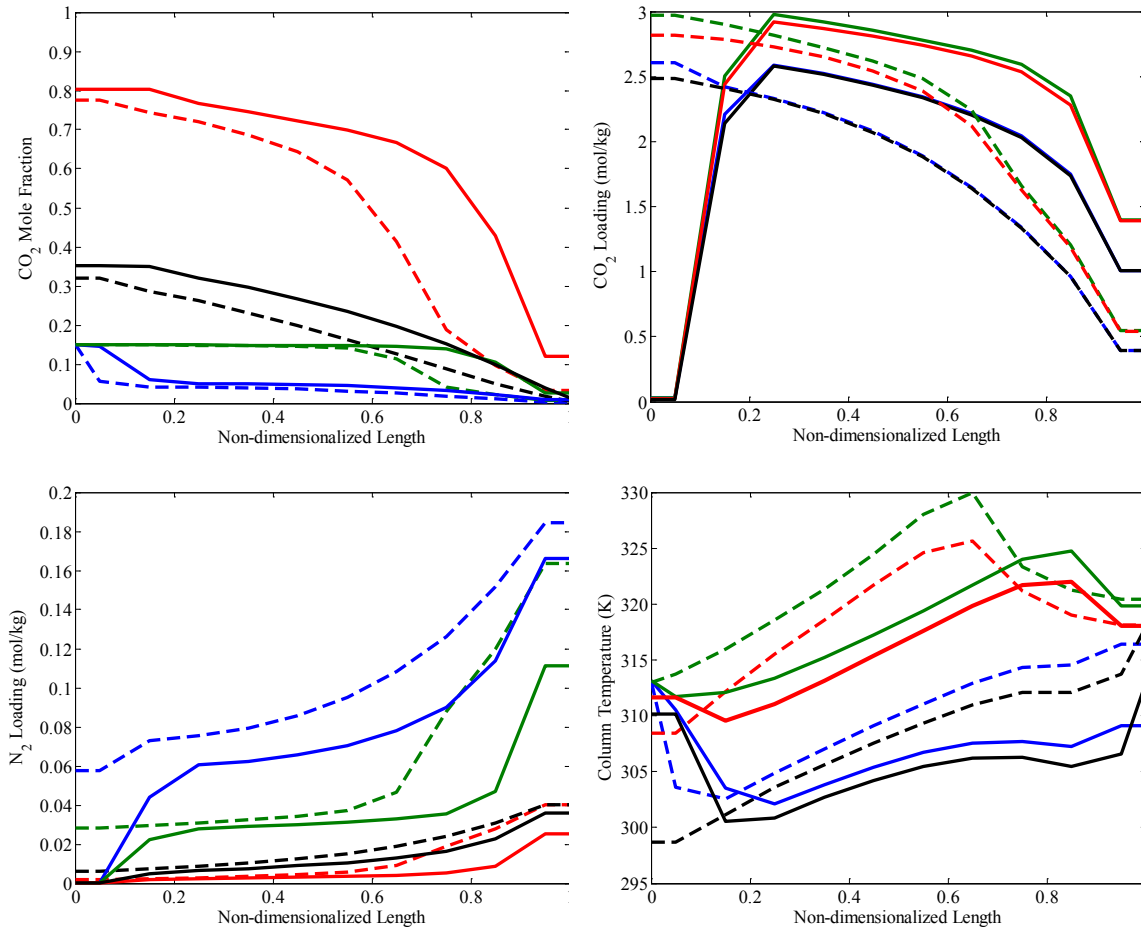


Figure 7. Profile of the zeolite 13X P/VSA bed at the end of each step comparing wet and dry flue gas. The colors correspond to Pressurization (Blue), Adsorption (Green), Depressurization (Red), and Purge (Black) steps. Dashed Lines correspond to the dry flue gas conditions, while the solid lines correspond 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 CO₂, through SALI or other methods, may provide a solution to the difficult problem of selectively adsorbing CO₂ over N₂ in the presence of water vapor. High-throughput computational screening has the potential to drastically increase the speed of identifying promising materials for CO₂ capture.

Our process-level modeling indicates that reducing the concentration of water prior to capturing CO₂ 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 CO₂ 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 CO₂ capture.

Future Plans

We will complete the high-throughput computational screening for MOFs with high CO₂/H₂O 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 CO₂ 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 CO₂ purity and recovery and the lowest cost for capturing CO₂. 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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Contacts

Randall Q. Snurr, snurr@northwestern.edu
Joseph T. Hupp, j-hupp@northwestern.edu
Omar K. Farha, o-farha@northwestern.edu
Fengqi You, you@northwestern.edu