# *Develop Engineered Forms of MOF with Polymers*

## Nuclear Technology Research and Development

***Prepared for***
***U.S. Department of Energy***

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***February 28th, 2019***
**PNNL-28497**

# Summary

At Pacific Northwest National Laboratory, mechanically robust composite materials were developed and tested from a gas mixture relevant to potential future nuclear reprocessing applications. Several composite materials were produced using a wet granulation method, which is very scalable. Metal-organic framework (MOFs) composite materials were produced using a well-known polymer as a binder (poly(methyl methacrylate)) to convert a fine microcrystalline powder into shaped bodies while preserving the intrinsic properties of the MOFs. The resulting MOF composite shows an improved mechanical stability (>100% compare to MOF beads without polymer and 3X higher compared to nuclear grade activated carbon pellets) in comparison with nuclear-grade activated-carbon pellets and with minimal loss of adsorption capacity (~10% reduction) at room temperature.

This document completes the milestone (M5FT-19PN0301070312) to prepare a Pacific Northwest National Laboratory document summarizing the results on “develop engineered forms of MOF using polymers.”

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# Acronyms and Abbreviations

| | |
|---|---|
| CaSDB | calcium sulfonyldibenzoate |
| CuATC | copper adamantine tetracarboxylate |
| HKUST-1 | copper 1,3,5-benzene-tricarboxylate (also called CuBTC) |
| MOF | metal-organic framework |
| NiPYC | nickel pyridine carboxylate |
| PAN | polyacrylonitrile |
| PMMA | poly methyl methacrylate |
| PNNL | Pacific Northwest National Laboratory |

# 1. Introduction

We at Pacific Northwest National Laboratory (PNNL) tested a large number of materials including metal-organic frameworks (MOFs), zeolites, and porous organic cage-like materials for the selective removal of xenon and krypton at room temperature using a similar composition as the nuclear reprocessing industry (Banerjee et al. 2016, 2018). Among all the microporous materials, MOFs have shown to be a very promising class of materials because the pore size, shape, and specific surface area can be manipulated with the choice of organic building blocks and metal clusters. As a result, over the past decade, > 20,000 MOF structures were reported with significant porosity; therefore, it is extremely difficult to synthesize and screen all the materials reported in the literature. As part of this program, we screened and tested MOFs with small to large pore diameters, specific surface areas ranging from 100–3000 $m^2/g$, functionalized with polar and non-polar functional groups, and different topologies to understand the roles of surface functionalization and confinement. Among all of those materials evaluated, it was found that materials with small-pore sizes, i.e., just enough to accommodate a single xenon, would be ideal for separation; the same was true for krypton. These observations were supported by recent molecular modeling and our own work.

As part of this work, we identified three potential candidate MOFs (i.e., CaSDB, CuATC, and NiPYC) for xenon/krypton separation at room based on their pore size (Banerjee et al. 2016; Garn et al. 2013; Thallapally et al. 2017, 2018). For low temperature applications, we identified MOFs with high specific surface areas, pore volumes, availability in large scale (HKUST-1) and ability to separate xenon and krypton from other gases (Elsaidi et al. 2018). Among the four MOFs, CuATC was ignored due to synthetic difficulties in obtaining the linker. Based on single-component gas adsorption, single- and two-column breakthrough experiments suggest all these materials were selective for xenon over other gases present in off-gas. The krypton can be captured in the second column with the same, or a different, MOF selectively from off-gases (without xenon). Table 1 provides some details about these MOFs in terms of xenon and krypton loading capacity and impact of other gases and vapors present in off-gas.

**Table 1. Physical and Chemical Properties of MOFs Identified for Room Temperature Application**

| Metric | CaSDB | CuATC | NiPYC |
|---|---|---|---|
| Xenon uptake | 33.7 mmol/kg[1] | ~70 mmol/kg[1] | ~70 mmol/kg[1] |
| Krypton capacity | 0.75 mmol/kg[1] | 1.7 mmol/kg[1] | Not investigated |
| Impact of $CO_2$ | No | Yes<br>(need to be removed) | No |
| Impact of water | No | Yes<br>(need to be removed) | Yes<br>(need to be removed) |
| Synthesis | Straight forward | Difficult (precursors need to obtain from China) | Easier than CaSDB |
| Mechanical stability | High (current report) | Not investigated | Not investigated |
| Co-adsorption | Very minimal | Can be higher compared to CaSDB | Might be close to CaSDB |
| Desorption | Not investigate | Not investigated | Not investigated |

[1] Single-column breakthrough experiments using 1300 ppm xenon and 130 ppm krypton balanced with air at room temperature.

Though MOF materials were shown to be very promising for removal of xenon and krypton from off-gas, one fundamental issue impeding the large-scale deployment of MOFs in commercial and industrial applications is the high pulverulent properties. Thus, the shaping of MOFs on a macroscopic level (i.e., converting a fine microcrystalline powder into a shaped body while preserving the intrinsic properties of the MOF) is a vibrant area of research (Semino et al. 2018). Strategies to overcome this problem involve the evaluation of various binders and processes to produce MOF bodies with different shapes including: pressing, extrusion, and granulation to produce pellets, granules, and spheres (Thallapally et al. 2017; Kalaj et al. 2018). In general, shaping of sorbents for off-gas processes improves handling and reduces the pressure drop for flow systems. Several industries produce shaped bodies of various adsorbent materials (e.g., zeolites) for applications in catalysis, separation, and adsorption.

Our recent off-gas report identifies that mechanical stability is one of the data gaps, which needed to be addressed going forward (Jubin et al. 2016). As part of this effort, PNNL worked with an industrial partner to produce mechanically stable MOF-epoxy composites. The process was developed to form commercial zeolitic-resin cartridges used to dry liquid refrigerants. *Importantly, this method has been demonstrated to be extremely scalable.* Based on the results, the MOF composites produced undoudtdedly improved the mechanical stability but significantly reduced the xenon/krypton loading capacity. As part of this report, we looked at various polymeric binders to improve the mechanical stability of MOFs including CaSDB, HKUST-1, and NiPYC. Due to the limited data on HKUST-1 and NiPYC, we will restricted our discussion to CaSDB; however, the same approach is applicable to other MOFs and experiments are ongoing with additional materials.

# 2. Shaping of Metal Organic Framework Granules

To prepare the MOF-polymer composite, a wet granulation method was used. Wet granulation is a conventional method where granules are formed by the addition of a liquid onto a powder bed undergoing agitation. The primary powder combines with a binder material to produce a wet material that, once dried, forms robust particles. The granulation liquid can be any volatile liquid. Typical liquids include water, organic solvents, or a combination thereof. Although aqueous solutions have the advantage of being safer, the choice of granulation liquid depends on the inherent chemical stability of the MOF and the solubility of the binder. Importantly, this method of granulation has been demonstrated to be extremely scalable, with manufacturers of polyacrylonitrile (PAN)-type granulators reporting tons of granules (mostly fertilizers) being produced per hour. Herein, we sought to investigate the employment of a wet granulation process in shaping the CaSDB MOF powder using various polymers. Large numbers of polymers were considered as part of this milestone, including polyacrylonitrile (PAN), poly methyl methacrylate (PMMA), graphene, alumina, and sugar. The effects of pressure, temperature, and percentage of binder for making the beads were also considered. Similarly, efforts were also made to produce MOF composites using 3D printing. Given the large numbers of methods to prepare the composites and experimental conditions available to control the mechanical stability of the composites, we focused our efforts on PMMA as the polymer choice and wet granulation as a possible method for scale up.

PMMA is economical, structurally flexible, transparent, ultraviolet tolerant, as well as chemically and heat resistant. Fabrication of the MOF pellets was achieved as follows. First, a known amount of PMMA (~10% by weight) and the CaSDB powder were sonicated in dichloromethane to solubilize the polymer and disperse the MOF powder. Dichloromethane was chosen because of its volatility and PMMA's solubility. The dispersed MOF was added to a custom, small, pan-type granulator shown in **Figure 1**; a) early stages of particle formation, b) particles taking shape, c) and final 600-850 μm pellets.

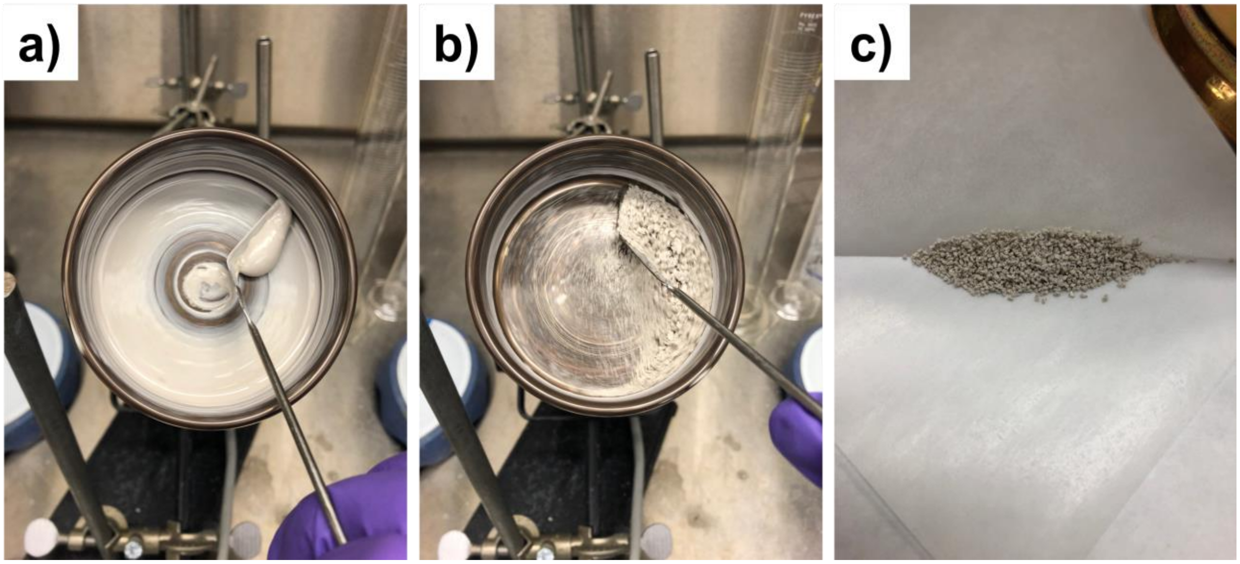

**Figure 1. PNNL Pan Granulator for Wet Granulation of MOFs**

During the mixing process, dichloromethane evaporated and the resulting paste was agitated to achieve the desired particle growth. Granules with a wide size distribution were produced and sieved to yield 600-850 μm pellets. Fine and larger particles can be reprocessed to improve the yield by spraying dichloromethane into the pan. The particles were dried at 100°C for 12 hours in a vacuum oven. Powder X-ray diffraction studies confirmed the chemical stability of CaSDB MOF towards the binders and the wet granulation process. **Figure 2** shows, from bottom to top: simulated pellets of CaSDB obtained from single-crystal data, pressed CaSDB pellets, and CaSDB pellets with 10% wt PMMA. No noticeable degradation was observed.

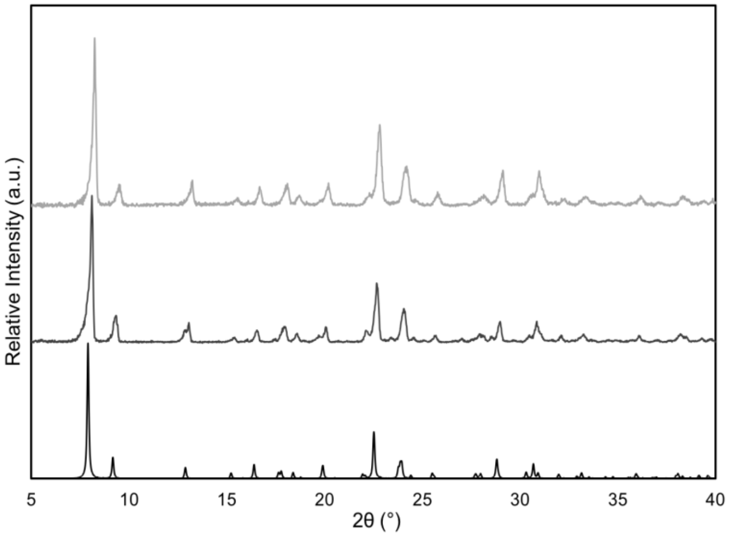

**Figure 2. Powder X-ray Diffractograms of CaSDB MOF**

# 3. Evaluating Mechanical Stability

To measure the ability of the dried pellets to remain intact during handling, we vigorously shook pellets on a shaker table. We compared the attrition rate of the pellets formed with PMMA binders to unaltered CaSDB MOF pellets formed via pressure (2000 psi). A typical experiment involved adding 100 mg of pellets to a 20 mL vial and shaking at a rate of 300 rpm for an hour. At this rate, the pellets were striking the sides, top, and bottom vigorously. After an hour, the material was screened for intact 600-850 µm pellets.

The simulated handling method resulted in significant powderization of the unaltered pellets formed via pressure (i.e., no intact 600-850 µm pellets remained). The particles formed with the PMMA binder were much more robust, with all the pellets remaining after handling (i.e., 100 mg of 600-850 µm CaSDB pellets were recovered). In addition to pellets, a larger sphere was formed from the CaSDB/PMMA paste described above to demonstrate the macroscopic mechanical stability, weight bearing capacity, and robustness. As shown in **Figure 3**, a) CaSDB with PMMA binder and without, b) shaker table, c) pellets after shaking, and d) and e) recovered 600-850 µm pellets. Notice the difference in the amount of powder formed. Further, mechanical stability of the CaSDB particles pressed at 13 MPa without binder was compared with PMMA binder using shaker table as a function of time at variable speed. Pristine CaSDB and CaSDB composite pellets (PMMA) were shaken at 200 rpm for 20 minutes followed by 300 rpm for next 20 minutes, and finally 400 rpm for additional 20 minutes. As shown in **Figure 4**, 80% of the CaSDB pellets pressed at 13 MPa were powderized (200 rpm). Whereas CaSDB composite with PMMA binder remained intact even after 1 hour with less than 5% powdered. These experiments clearly demonstrate the improved mechanical stability of CaSDB with PMMA binder; however, we cannot explain improved stability at this time.

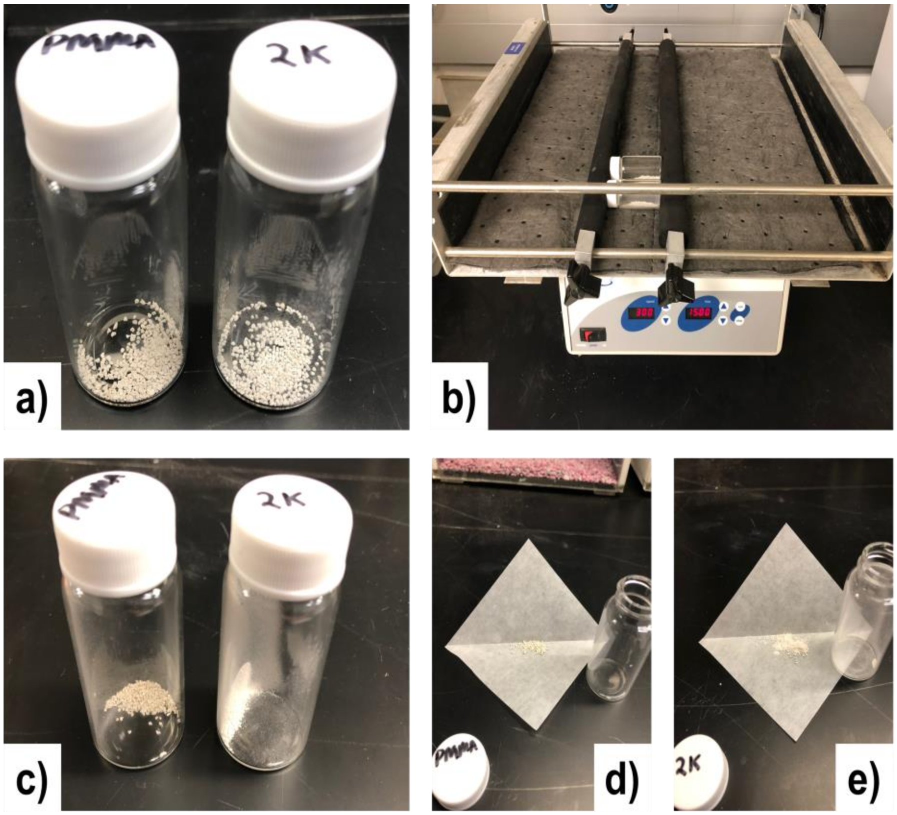

**Figure 3. Mechanical Stability Test of Particles**

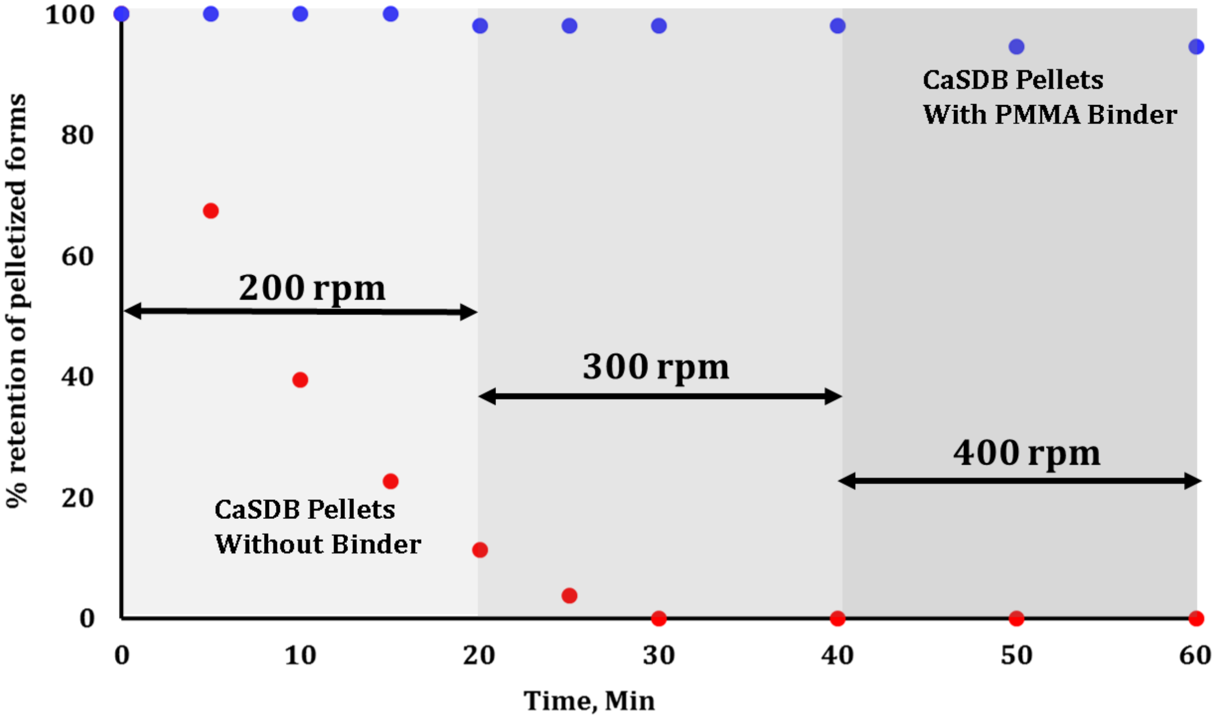

**Figure 4. Percentage of pellet retention as a function of time**

**Figure** shows the dried ~1 cm sphere before and after a ~400 g weight was placed onto it where a) shows a 1 cm sized CaSDB MOF composite sphere, b) before and c) after ~400 grams of weight on 1-cm sphere. Notice very little deformation of the sphere as show in c). The weight did deform the sphere and cause some material fragmentation, but the overall size and shape of the MOF sphere remained intact. In conclusion, PMMA was effective as a binder under the described wet granulation conditions as significant amounts of the formed pellets remained intact after handling.

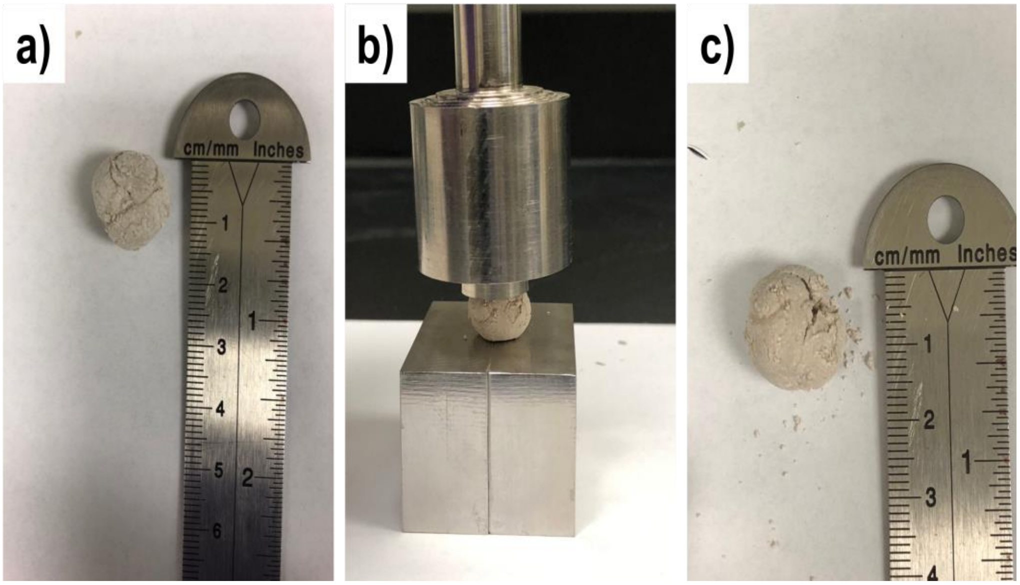

**Figure 5. Mechanical Stability of CaSDB Particles with PMMA Binder**

To further demonstrate the mechanical stability of the engineered particles, a TA instruments Q800 dynamic mechanical analyzer was used to investigate the mechanical properties of the MOF-based composites, including Young's modulus, ultimate compressive strength, toughness, and strain at breaking (**Figure** ). The testing was performed using a compression setup under the controlled force mode. A preloading force of 0.001 N and frequency of 1 Hz were adopted. Each sample was previously measured in diameter and mounted into fixtures by 5 in-lb torque force. Then, the sample was pressed at room temperature by ramping force at a rate of 0.5 N/min until breakage or 50% diameter of displacement was reached if they did not break, during which stress and strain data were recorded (**Figure** ).

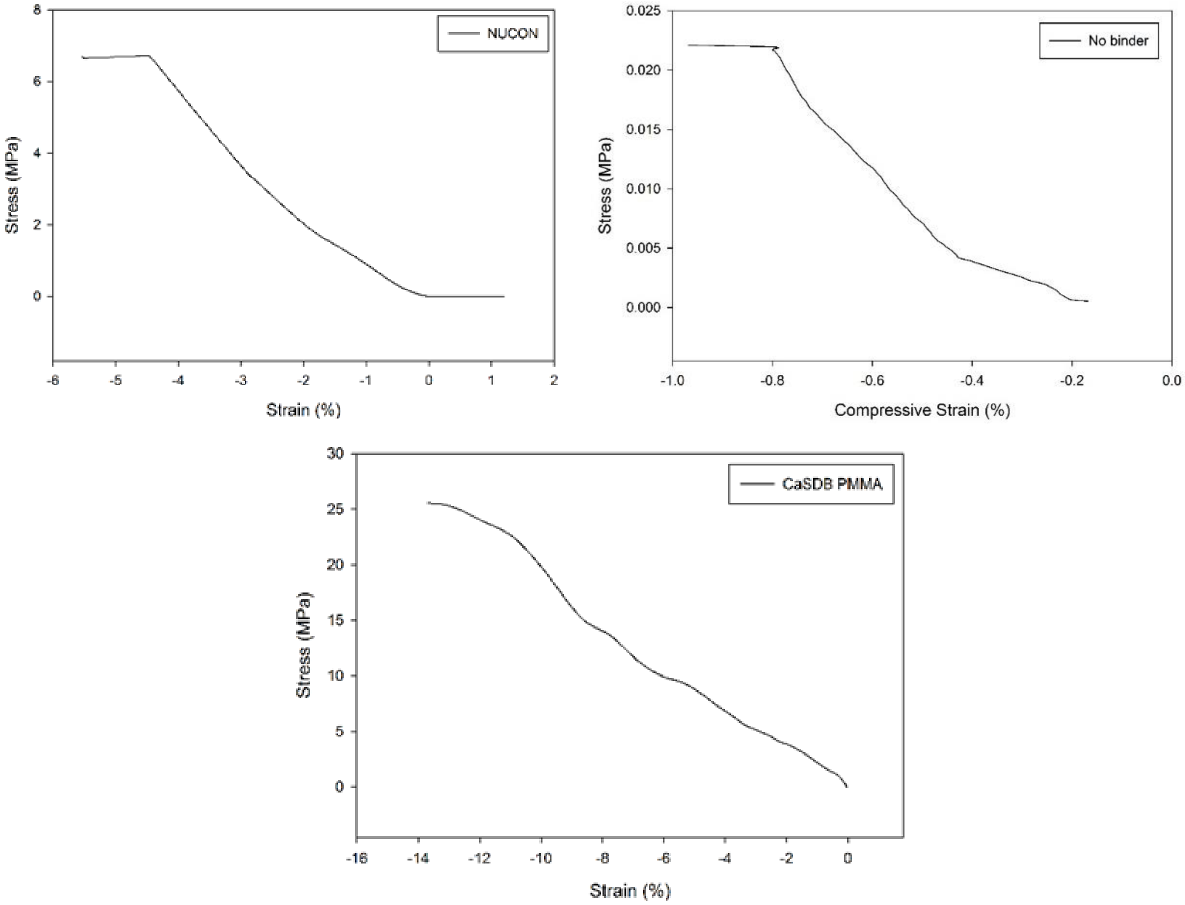

**Figure 6. Stress-Strain Curves Obtained for Nucon Activated Carbon Pellets, CaSDB MOF Without Binder, and With Binder (PMMA)**

Young's modulus was calculated by taking the slope of the elastic region of the stress-strain curve. Ultimate compressive strength represents the highest stress in compression achieved prior to total failure or severe deformation. Toughness values were obtained by integrating the area underneath the stress-strain curve, indicating the measure of how well the samples were resistant to deformation. Strain at breaking refers to the strain at which the sample breaks or deforms at least 50%. The mechanical stability of CaSDB MOF with and without binder in comparison with nuclear-grade activated carbon pellets indicate that CaSDB with polymer composite (PMMA) has higher mechanical stability than pristine CaSDB MOF and activated carbon under identical conditions (**Table 2**).

**Table 2. Mechanical Properties of CaSDB MOF With and Without Binder in Comparison with Nuclear-Grade Activated Carbon Material**

| Sample | Young's Modulus (MPa) | Ultimate Compressive Strength (MPa) | Toughness (MPa) | Strain at breaking (%) |
|---|---|---|---|---|
| NUCON Activated carbon | 116 | 6.713 | 19.352 | 4.623 |
| CaSDB pellets without binder | 4.45 | 0.022 | 0.005 | 0.096 |
| CaSDB PMMA | 185.51 | 25.547 | 176.076 | 13.752 |

## 4. Xenon Adsorption

To gain insights into the effect shaping had on xenon adsorption, we conducted adsorption experiments using a Quantachrome Autosorb IQ 2 instrument. Samples were activated at 100°C under vacuum at a rate of 5°C/min for 12 hours on the outgassing side of the instrument. The sample was then cooled to room temperature and the dry mass was measured. The experimental temperature was maintained by a water bath. The pressure points were set beforehand using the Quantachrome software. Volumetric changes, resulting from adsorption at each pressure step, were plotted against the pressure.

As shown in **Figure** , an average 17% reduction in the capacity was observed over the total pressure range; however at lower pressure, which is of interest for off-gas capture, only 10% reduction was observed. This was expected and the reduction in capacity can be attributed to the amount of PMMA binder used. Further, we are exploring the applicability of PMMA binder with other leading room-temperature and low-temperature MOFs. For comparison, **Figure**  shows the single component xenon adsorption isotherms of all the four leading adsorbent materials at room temperature, which clearly shows the MOFs have an improved performance at low pressure and room temperature. If successful, converting the MOF powders into shaped bodies would provide a clear path for large-scale implementation of these materials. The PMMA binders show improved mechanical stability with minimal reduction in capacity at room temperature using single-component gas adsorption isotherms. We are currently investigating the relationship between the amount of binder used and associated adsorption properties including single-column breakthrough experiments.

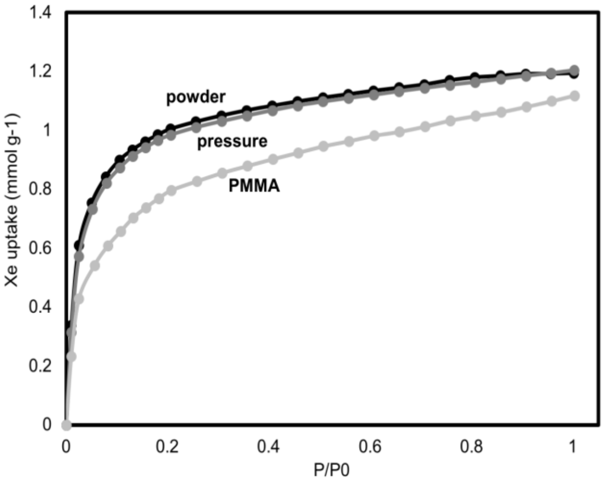

**Figure 7. Adsorption Isotherms of Xenon at 298K for CaSDB MOF Powder and Pellets Form at Pressure with PMMA Binder**

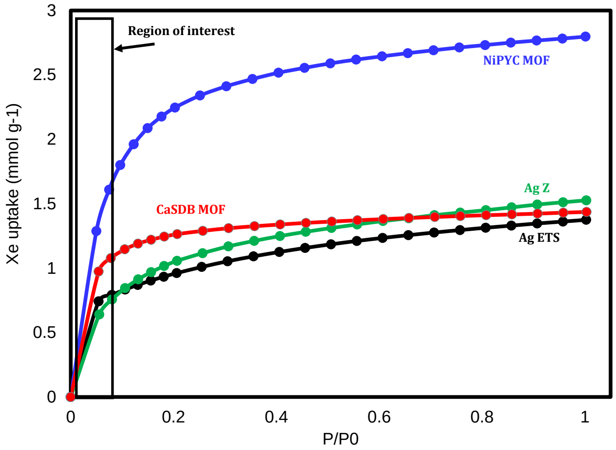

**Figure 8. Adsorption Isotherms of Xenon at 298K for CaSDB, NiPyC MOF, AgZ, and AgETS at 1 Bar Pressure and Room Temperature**

## 5. Future Work

Given the improved mechanical stability with minimal loss in adsorption capacity of CaSDB MOF with PMMA binder, further experiments are necessary in moving forward. First, experiments with percentage of PMMA binder (current report used 10 wt%) and MOF composition are needed to optimize the high mechanical stability with minimal loss of capacity. Second, single-column and two-column breakthrough experiments need to be performed with newly engineered particles. Third, the use of PMMA as a binder for other low- and room-temperature MOFs needs to be explored. Fourth, fundamental understanding of PMMA interaction with MOFs using a combination of experiments and theory needs to be investigated to design a better composite material. Fifth, detailed investigation of why certain polymers (PAN, polyacrylic acid, alumna, and sugar) resulted in reduced capacity and mechanical stability. Finally, scale up of newly engineered forms is needed for testing at Idaho National Laboratory for deep beds. On top of the above fundamental understanding of polymer interaction with MOF is necessary to design a better composite material.

## 6. Conclusions

In conclusion, we have successfully identified a polymer to demonstrate the significant improvement in mechanical stability (>100% compared to MOF beads without polymer, 3X higher compared to nuclear grade activated carbon pellets) of the resulting MOF composite using a wet granulation method. The resulting MOF composite shows minimal loss in xenon adsorption capacity (10% at low pressure) at room temperature and 1 bar pressure. Further single-column experiments are needed to be performed to evaluate the performance under realistic conditions.

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