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# Development and Test Evaluations for Ni-DOBDC Metal Organic Framework (MOF) Engineered Forms

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# SUMMARY

A joint effort to prepare engineered forms of a Ni-DOBDC metal organic framework (MOF) was completed with contributions from PNNL, SNL and the INL. Two independent methods were used at INL and SNL to prepare engineered form (EF) sorbents from Ni-DOBDC MOF powder developed and prepared at PNNL. Xe and Kr capacity test evaluations were performed at ambient temperature with the cryostat experimental setup at INL. The initial INL EF MOF test results indicated a Xe capacity of 1.6 mmol/kg sorbent and no Kr capacity. A large loss of surface area also occurred during minimal testing rendering the INL EF MOF unusable. Four capacity tests were completed using the SNL EF MOF at ambient temperature and resulted in Xe capacities of 1.4, 4.2, 5.0 and 3.8 mmol/kg sorbent with no Kr capacity observed in any ambient temperature tests. Two additional capacity tests were performed at 240 K to further evaluate SNL EF MOF performance. Xe capacities of 50.7 and 49.3 mmol/kg of sorbent and Kr capacities of 0.77 and 0.69 mmol/kg of sorbent were obtained, respectively. Following the adsorption evaluations, the SNL EF MOF material had lost about 40 % of the initial mass and 40 % of the initial surface area. In general, the Xe capacity results at ambient temperature for the INL and SNL EF Ni-DOBDC MOF's were lower than 9.8 mmol Xe/kg sorbent test results reported by INL in FY-12 using PNNL's inital EF supplied material.

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# ACRONYMS

| | |
|---|---|
| BET | Brunauer, Emmett, and Teller theory |
| EF | engineered form |
| GC-MS | gas chromatography mass spectrometer |
| GC-TCD | gas chromatograph with thermal conductivity detector |
| INL | Idaho National Laboratory |
| K | Kelvin (°C + 273.15) |
| Kr | krypton |
| MOF | metal organic framework |
| PNNL | Pacific Northwest National Laboratory |
| PXRD | powder x-ray diffraction |
| SNL | Sandia National Laboratory |
| SPME | solid phase microextraction |
| Xe | xenon |

# 1. Development and Test Evaluations for Ni-DOBDC Metal Organic Framework (MOF) Engineered Forms

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PNNL Contributors: Praveen Thallapally

SNL Contributors: Tina Nenoff and Ina Sava

## 1.1 Introduction

In support of the DOE sponsored Off-Gas Sigma Team collaborative efforts, a joint effort to prepare engineered forms of a Ni-DOBDC metal organic framework (MOF) was completed with contributions from PNNL, SNL and the INL. PNNL team members prepared the powdered MOF material and then submitted material samples to both SNL and INL for preparation into two individual engineered forms. The engineered forms were then evaluated for krypton (Kr) and xenon (Xe) capacity at ambient temperature with the INL cryogenic experimental setup. Physical characteristics of the engineered forms were also noted throughout the evaluations including robustness and surface area changes. This report provides details for preparing an engineered form MOF at INL and test evaluations for engineered form MOF's prepared at both INL and SNL. Information for engineered form development completed at SNL is not included. The delivery of this report to PNNL team members satisfies milestone M3FT-13IN0312023.

## 1.2 Purpose and Scope

Materials being evaluated for use in off-gas treatment systems are required to be in engineered forms (EF) to facilitate ease of material handling as well as to prevent over pressurization of system components during processing. The preparation of engineered forms from powdered material can be achieved by methods including the addition of binding components, extrusion or a combination of both.

Two engineered forms of Ni-DOBDC MOF material were prepared respectively at INL and SNL. Individual preparatory methods were used at each facility and the resultant materials were then evaluated for adsorption performance. Capacity measurements for Kr and Xe were obtained at ambient temperature using the cryostat experimental setup at the INL. Surface area measurements, powdered x-ray diffraction (PXRD) analyses and visual observations of both engineered forms were performed throughout the testing regime.

## 1.3 Engineered Form (EF) Preparation at INL

An initial shipment containing newly prepared Ni-DOBDC MOF was received at INL and SNL in December 2012. SNL researchers indicated that a PXRD analysis of the material revealed a disagreement with expected PXRD spectra. A PXRD analysis was performed on the "as received" material at INL as well with results indicating that the material was not prepared as desired. The PXRD results are shown in Figure 1. This material was returned to PNNL and a second shipment of MOF in three individual tubes at ~ 10 grams each was received at the INL in February 2013. A PXRD analysis was completed on each tube with spectra results agreeing well with those supplied by PNNL. The PXRD results for a selected tube (Ni74SU) are included in Figure 2. Surface area analyses were also supplied

from PNNL for each tube reporting BET results of 1158, 1218, and 1039 $m^2/g$. Communications with PNNL staff resulted in agreement that this material was properly prepared and ready for EF development studies.

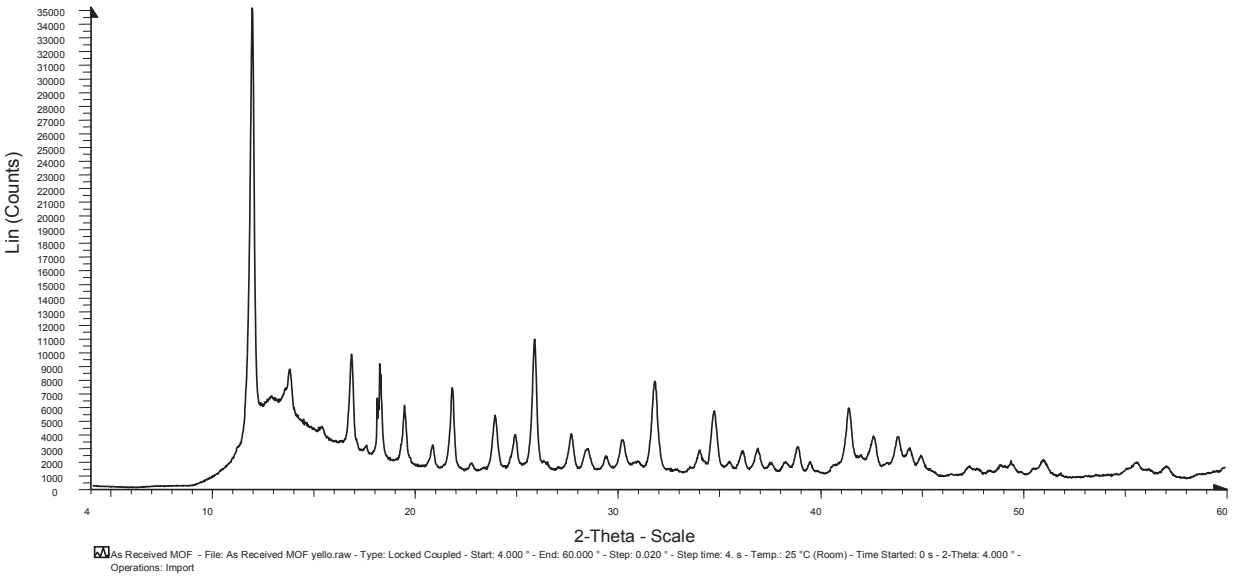


**Figure 1. PXRD of initial MOF received 12/2012.**

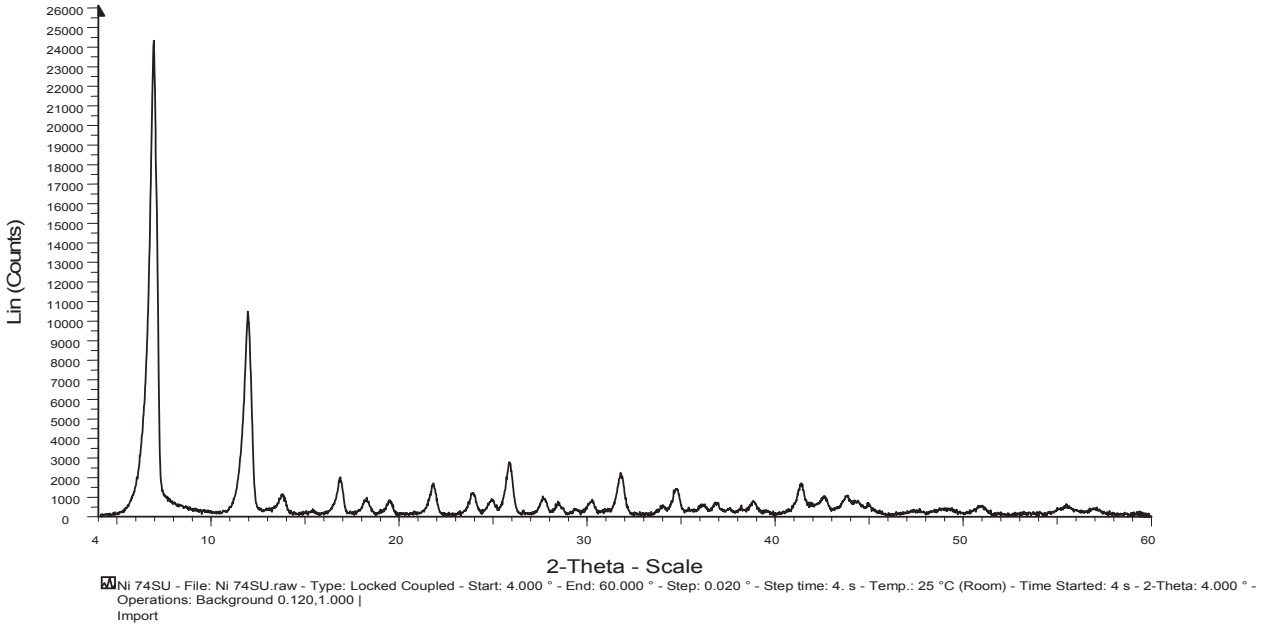


**Figure 2. PXRD of second MOF material (Ni74SU) received at INL 2/2013.**

A small-scale batch of INL EF MOF material was initially attempted to investigate the feasibility of using the INL sorbent development procedure. One gram of MOF (Ni 74SU) was used to prepare a final 80 wt% material with the macroporous binder. This scoping effort resulted in a completed EF material which was labeled as MOF-EF1. Surface area and PXRD analysis was performed on this material to verify that no changes to the MOF crystalline structure occurred during preparation. The PXRD spectra for the INL EF MOF is shown in Figure 3. A surface area of 477 $m^2/g$ was obtained at degas conditions of 150 °C for 4 hours.

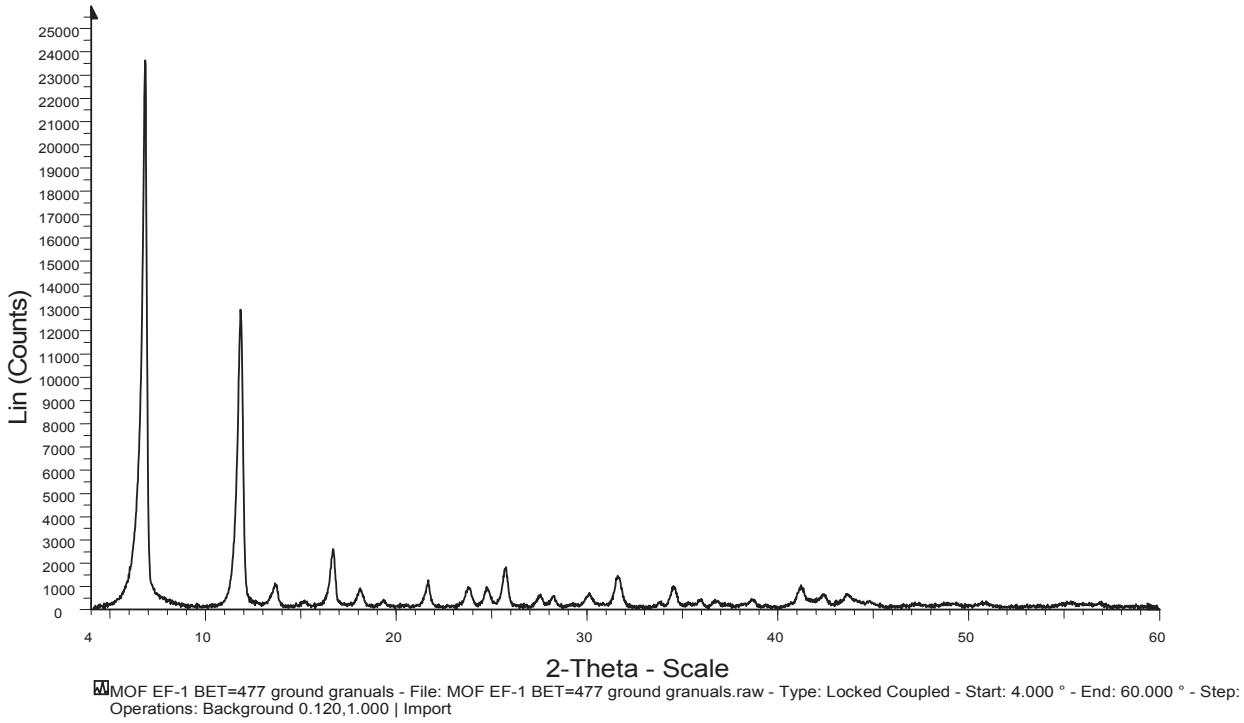


**Figure 3. PXRD MOF-EF1.**

The MOF-EF1 PXRD results indicated relatively no change compared to original powder PXRD in Figure 2 suggesting that an EF MOF utilizing the INL sorbent development procedure could be prepared and evaluated for use in the cryostat experimental setup.

Three individual ~ 10 gram batches of INL EF MOF were prepared. BET surface area analyses were completed for each batch using degas conditions of 150 °C for 4 hours with results of 778, 718 and 773 $m^2/g$, respectively, being obtained. These surface area results, although slightly lower than 80 % of the initial powder MOF BET values due to lower degas temperatures used, were more on the order of what was expected when preparing sorbents with the INL procedure. The surface area results indicate the INL EF MOF was suitable for further adsorption evaluations. The sorbent material from each batch was combined and sieved to a particle range of 0.3-3 mm diameter for final test preparation.

## 1.4 INL EF MOF Xe/Kr Capacity Evaluations

A combined 22.44 grams of the prepared INL EF MOF was placed into the cold column nearly filling it. Figure 4 includes a picture of the INL EF MOF in the cold column prior to placement into the cryostat and activation. The material was activated at 150°C for 18 hours with helium flowing at 50 sccm. During this activation, a substantial amount of water was observed at the outlet of the cryostat. A Kr/Xe adsorption test was performed with this activated material utilizing a test gas of 150 ppmv Kr and 1000 ppmv Xe with the balance consisting of air at ambient temperature. A capacity of 1.6 mmol Xe/kg sorbent was obtained and no capacity for Kr was observed. This unanticipated Xe capacity was about 5 times lower than previous capacities reported in FY-12 by PNNL of 9.3 mmol Xe/kg sorbent and INL of 9.8 mmol Xe/kg sorbent with PNNL prepared EF material.

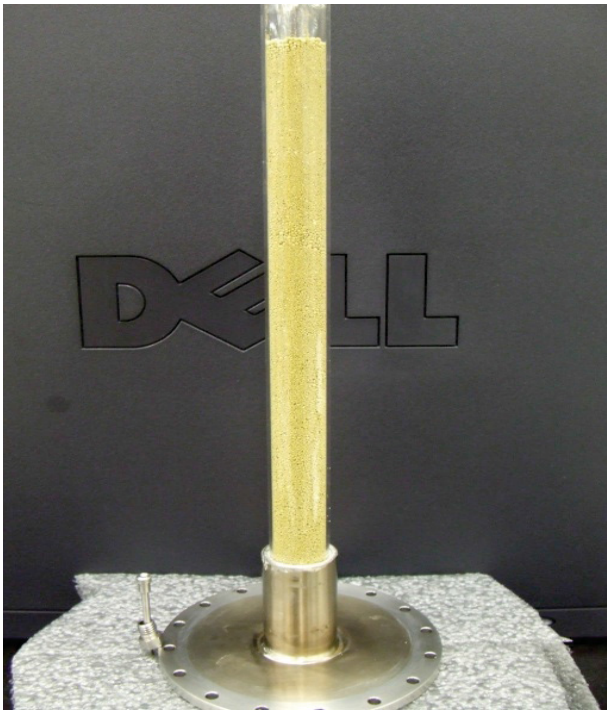

**Figure 4. INL EF MOF loaded into cold column.**

The Xe and any Kr were desorbed at 150 °C with helium flowing at 50 sccm until their respective peaks were no longer observed on the GC spectra. During desorption cycles, a large peak was observed at 4.5 minutes on the GC spectra and was initially assumed to be water. It was concluded at this time, the 18 hour activation had been insufficient for the complete removal of the water from the pores of the material. An additional activation of the material was attempted for over 120 hours utilizing either helium flow or vacuum at 150 °C while monitoring the effluent gas with the GC. The 4.5 minute peak on

the GC was never observed to be completely removed during this activation process. It was later analytically determined that this 4.5 minute peak was actually carbon dioxide ($CO_2$), which will be addressed later.

An additional adsorption test was performed using the INL EF MOF with the same test gas and conditions and no measurable capacity for either Xe or Kr was observed. The material was removed from the cryostat with 18.37 grams of material recovered resulting in a mass loss of 4.07 grams or about 20 %. Surface area analysis of the material indicated a large loss of surface area decreasing from an average of 756 $m^2/g$ to less than 30 $m^2/g$, rendering the material unusable for continued testing. PXRD analysis was also performed on the material after the activation treatments with the spectra obtained shown in Figure 5. It can be seen from the spectra that a shift of the peaks had occurred when compared to the PXRD spectra (Figure 2) of the original material.

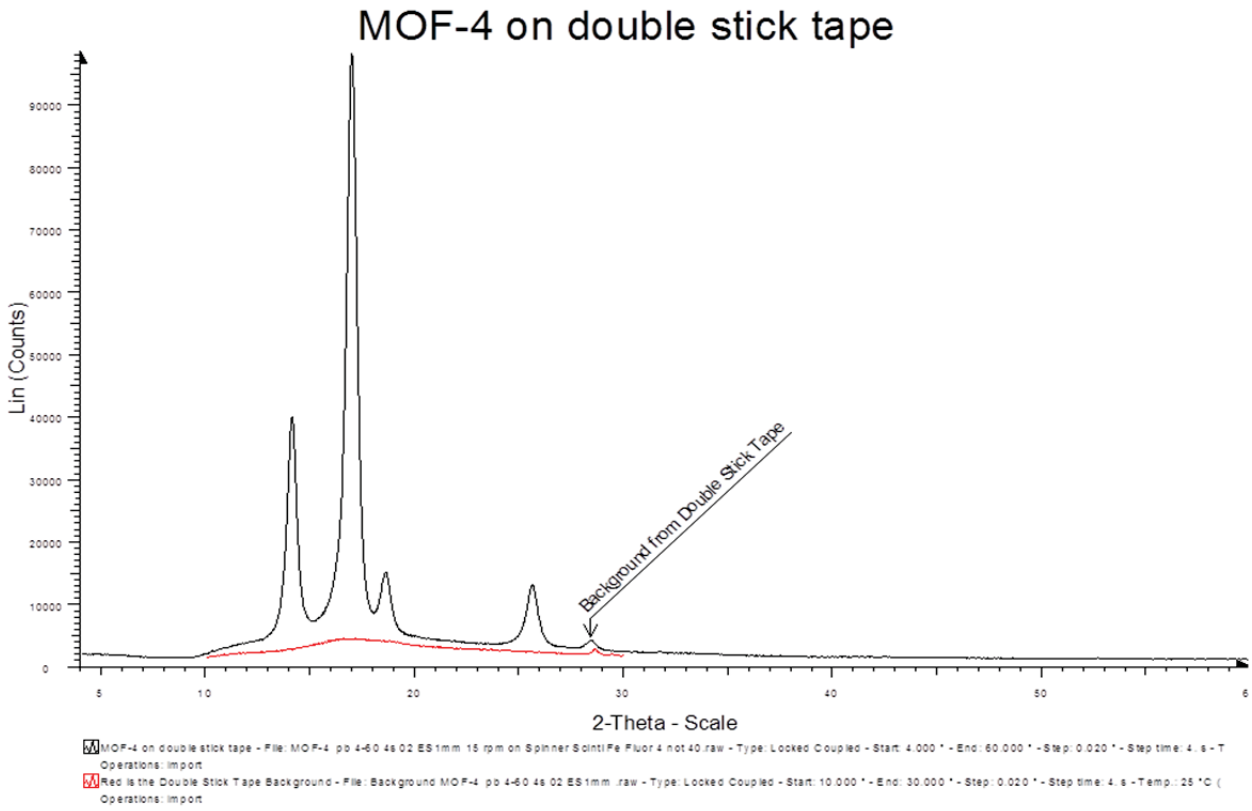


**Figure 5. PXRD soectra of INL EF MOF after testing.**

## 1.5 SNL EF MOF Xe/Kr Capacity Evaluations

In May 2013 the INL received ~30 grams of the SNL prepared EF MOF Ni-DOBDC. This material was very uniform in shape as small cylinders or pellets approximately 2 mm in diameter with varying length averaging about 6 mm. A BET surface area analysis was performed on the material following a 250 °C

degas for 12 hours under vacuum. The resulting BET surface area was 945 $m^2/g$, which was slightly lower than the surface area reported by SNL of 1152 $m^2/g$.

Initially, 21.78 grams of SNL EF MOF was loaded in the cryostat column; however, due to the higher activation time and temperature required per SNL, the column with material was removed and placed into a vacuum oven at 250 °C for 18 hours under 6.3 inches of mercury vacuum. After activation, the column containing the material was removed from the oven and re-installed in the cryostat. The material had undergone a color change from green to almost black as a result of the activation. Figure 6 shows a photo of the SNL EF MOF following activation.

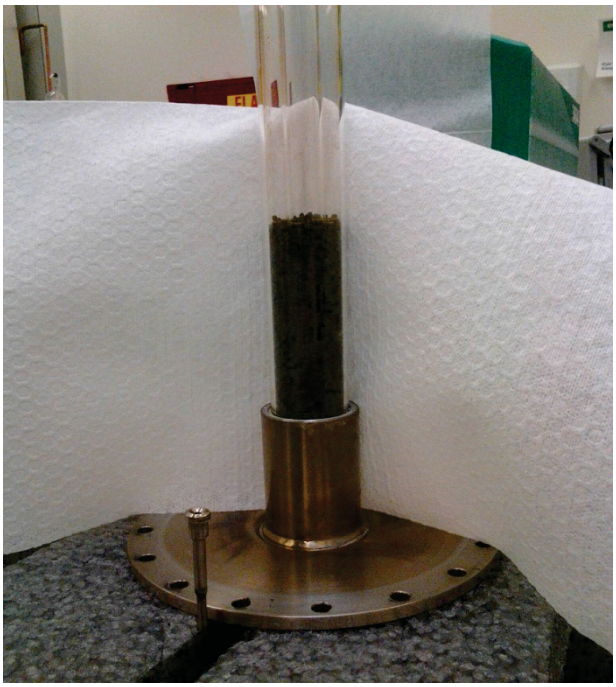

**Figure 6. SNL EF MOF following activation.**

All ambient temperature tests used the same test gas and conditions as was used for the INL EF MOF testing. The initial test resulted in a capacity of 1.4 mmol Xe/kg of sorbent with no capacity for Kr observed. Three more tests were performed at the same test conditions with the addition of a 150 °C preceeding test desorption. Xe capacities of 4.2, 5.0 and 3.8 mmol/kg sorbent were obtained respectively, with no measurable Kr capacity for the test series. During the 150 °C desorption phase following each test, a relatively large peak would form on the GC spectra at 4.5 minutes as was observed with INL EF MOF testing. A sample of the cryostat effluent was taken and analyzed by solid phase microextraction (SPME) on a Shimadzu 2010 GC/MS with an Rtx-5 column and helium carrier. The resultant spectra was library defined as carbon dioxide (m/z = 44). A second analysis was performed with a Hewlett Packard 5890 Series II GC/TCD with a Poraplot Q column and helium carrier. A $CO_2$ standard was analyzed and compared to the effluent sample. Both spectra indicated a peak at the same retention time. A third and final analysis was performed using the GC/TCD utilized for all capacity

testing with the $CO_2$ standard; again the retention peak matched the peak observed at 4.5 minutes. These three analyses provide very strong evidence that $CO_2$ gas was being generated in the cryostat at 150 °C during the desorption cycles.

As a follow-on to the four ambient temperature tests, two capacity tests were also performed at 240 K, using the same test gas. Xe capacities of 50.7 and 49.3 mmol/kg of sorbent and Kr capacities of 0.77 and 0.69 mmol/kg of sorbent were obtained, respectively. At the conclusion of the SNL EF MOF evaluations, the column and material were removed from the cryostat for further physical evaluations. Figure 7 includes a photo of the SNL EF MOF after testing.

**Figure 7. SNL EF MOF removed from cryostat following testing.**

As is depicted in Figure 7, the SNL EF had physically started to breakdown. There was substantially more powder present, presumably from physical decomposition, than observed before testing began. It was found that just by attempting to pick up pellets with tweezers resulted in the pellets collapsing back into powder form. The measured mass of the sorbent removed from the cryostat was 12.99 grams, corresponding to a mass loss from testing of 8.79 grams or ~40%. A BET was performed on the tested material using degas conditions at 250 ° C for 12 hours resulting in a surface area of 567 $m^2/g$, nearly a 40% reduction from the initial surface area of 945 $m^2/g$ measured prior to testing. The presence of $CO_2$, mass loss and surface area reduction does provide evidence that the SNL EF MOF may have experienced decomposition. More testing is warranted.

Figure 8 provides the spectra for the PXRD analysis that was performed on the SNL EF material removed from the cryostat for comparison to original powder spectra (reference Figure 2). The SNL EF

MOF spectra indicate no crystalline structure changes resulting from the six thermal cycles it was subjected to.

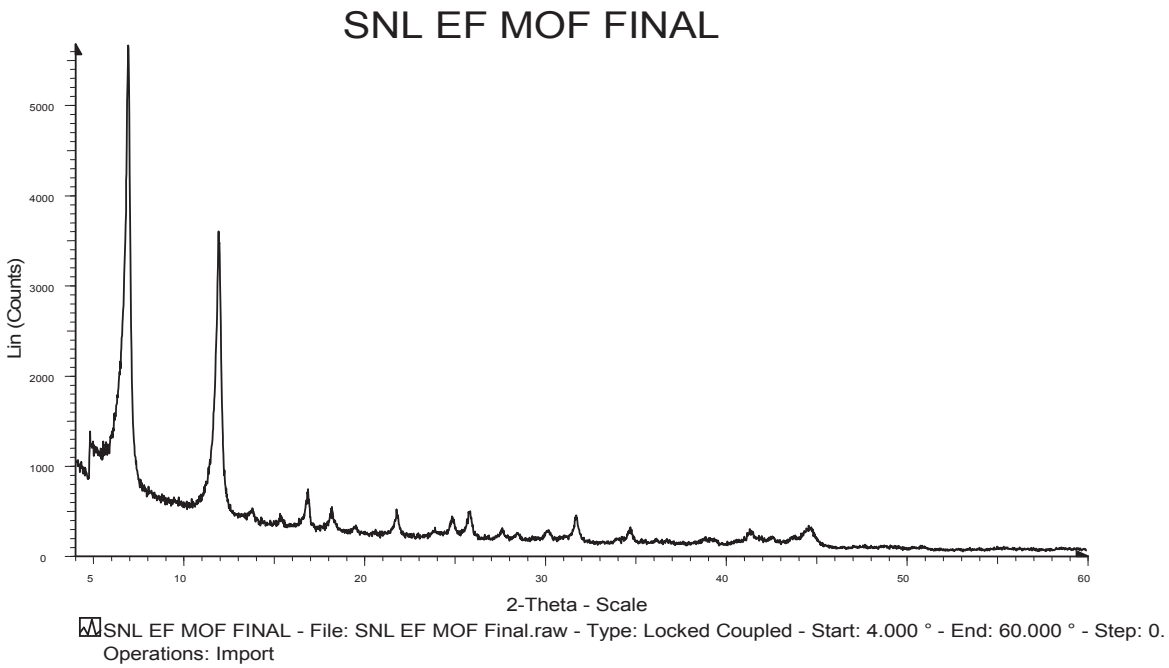


**Figure 8. PXRD spectra for SNL EF MOF after testing.**

## 1.6 Conclusions

Two independent methods were used at INL and SNL to prepare engineered form sorbents from Ni-DOBDC MOF powder developed and prepared at PNNL. Xe and Kr capacity test evaluations were performed at ambient temperature with the cryostat experimental setup at INL. The initial INL EF MOF test results indicated a Xe capacity of 1.6 mmol/kg sorbent and no Kr capacity. A second test indicated no capacity for Xe or Kr. The PXRD spectra obtained following the testing revealed a shift in the peaks relative to original spectra indicating the crystalline structure had changed. The material change was presumably due to the continuous 120 hour 150 °C activation effort where an ever present 4.5 minute peak on the GC spectra was initially incorrectly assumed to be water. The peak was later analytically determined to be $CO_2$. A large loss of surface area also occurred during the minimal testing rendering the INL EF MOF unusable for continued testing.

Four capacity tests were completed using the SNL EF MOF at ambient temperature and resulted in Xe capacities of 1.4, 4.2, 5.0 and 3.8 mmol/kg sorbent with no Kr capacity observed in any ambient temperature tests. Two additional capacity tests were performed at 240 K to further evaluate SNL EF MOF performance. Xe capacities of 50.7 and 49.3 mmol/kg of sorbent and Kr capacities of 0.77 and 0.69 mmol/kg of sorbent were obtained, respectively. Throughout the thermal cycling, specifically the desorption cycles at elevated temperature, the 4.5 minute peak was present and ultimately determined to be $CO_2$ using three separate analytical techniques. Following the adsorption evaluations, the SNL EF

MOF material had lost about 40 % of the initial mass and 40 % of the initial surface area. PXRD analysis of the material after testing indicated little crystalline structure change when compared to the original MOF powder (Figure 2) material. The mechanical stability of the SNL EF MOF appeared to be compromised during thermal cycling of the adsorption evaluations. This loss of stability was indicated by simply attempting to pick single pellets up with tweezers and they would collapse into powder.

In general, the Xe capacity results at ambient temperature for the INL and SNL EF Ni-DOBDC MOF's were lower than 9.8 mmol Xe/kg sorbent test results obtained in FY-12 using PNNL EF material. Capacity results with the SNL EF for both Xe and Kr did increase when tested at 240 K as expected. The data suggest that the tested EF MOF sorbents do not provide capacities at the level the FY-12 MOF exhibited.