Evaluation of an Engineered Form MOF CaSDB

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Summary

Under the Off-Gas Sigma Team, Idaho National Laboratory (INL) and Pacific Northwest National Laboratoory (PNNL) have been able to study various sorbents for the separation of krypton (Kr) and xenon (Xe). PNNL has researched and prepared various metal-organic frameworks (MOFs) to use for the separation. Calcium–4,4’–sulfonyl dibenzoate (CaSDB), a high surface area MOF, was synthesized and sent to INL for deep bed testing. The CaSDB – MOF showed an acceptable saturation capacity, but a low breakthrough capacity; However, the received CaSDB – MOF was deemed unusable in a flow through system because of its powdery nature.

In 2018, PNNL sent a sample of CaSDB powder to INL with the goal to incorporate it into an engineered form that maintained adsorption properties comparable to the original MOF. It was anticipated that the engineered form of the sorbent would possess sufficient mechanical strength to be used in a column, and eliminate the dustiness of the raw material to improve handling and operability.

An engineered from of CaSDB (CaSDB – EF1) was produced at INL by incorporating the raw powder into a polyacrylonitrile (PAN) binder. The PAN binding material eliminated the dustiness of the raw MOF and provided a robust matrix that prevented damage from handling and use in a column. Xe adsorption testing of the sorbent revealed that it performs as well or better than previous CaSDB samples tested at INL, with an initial breakthrough capacity of 14 mmol/ kg at ambient temperature. Reducing the operating temperature to 253 K resulted in an increased breakthrough capacity of Xe.

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Acronyms

CaSDB	Calcium–4,4’–sulfonyl dibenzoate
CaSDB – EF1	INL’s 2018 CaSDB PAN engineered form
CaSDB – MOF	PNNL’s compressed engineered form sent to INL for testing
CaSDB powder	CaSDB powder that was sent to INL to produce CaSDB – EF1
INL	Idaho National Laboratory
MOF	Metal–organic framework
PAN	Polyacrylonitrile
PNNL	Pacific Northwest National Laboratory
sccm	standard cubic centimeters per minute

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1. Introduction

INL, as part of the Off-Gas Sigma Team, has conducted research focused on the separation and capture of Kr and Xe in gas effluents generated from nuclear fuel reprocessing. INL and PNNL have been researching the viability of sorbents to perform the separation. Unfortunately, commercially available engineered form sorbents typically are not conducive to physisorption of noble gases primarily due to the pelletization manufacturing process. This resulted in the development of new sorbent manufacturing techniques to prepare engineered forms that retain the characteristic high surface areas contained in the active ingredients by incorporating them into a PAN binder. PNNL has been preparing and researching various MOFs, with reported characteristics that suggest optimal separation of Xe and Kr.

PNNL synthesized CaSDB powder and produced an engineered form by compressing it into a puck and then grinding it to size, herein referred to as CaSDB – MOF (Banerjee, et al., 2016). This MOF material was intended to capture Xe at ambient temperature. The PNNL engineered form was sent to INL for deep bed testing. CaSDB – MOF testing concluded that Xe capacity at saturation was high, but low at initial breakthrough (Welty, Garn, & Greenhalgh, 2018). Physical examination of the material in the 2016 report refers to CaSDB – MOF as being easily friable resulting in a fine dust, which can lead to issues like blockage and over pressurization in flow through systems.

In order for CaSDB materials to be viable in a flow through system they must be converted into a robust engineered form. In 2018 INL received CaSDB powder from PNNL. INL utilized its patented method of forming a composite PAN material to make an engineered form of CaSDB (CaSDB – EF1) (USA Patent No. 8,686,083, 2013) (Fujimoto, Welty, Garn, & Greenhalgh, 2019). Physical tests on the new material concluded that the process of converting the CaSDB into an engineered form lowered the surface area compared to the initial powdered form. However, the reduced surface area was still higher than previously received CaSDB – MOF materials (Fujimoto, Welty, Garn, & Greenhalgh, 2019). A rotational robustness test concluded that the material was significantly more stable than the original CaSDB – MOF (Fujimoto, Welty, Garn, & Greenhalgh, 2019). The improved physical characteristics of CaSDB – EF1 suggested that the material could be used for deep bed testing. This report contains the results of the CaSDB – EF1 deep bed testing of Xe adsorption.

2. Experimental Setup

In order to evaluate the adsorption abilities of CaSDB – EF1, a packed column was assembled to perform deep bed tests. The column was a 20 cm length piece of 0.77 cm I.D., stainless steel tubing. Both ends of the column were connected to elbows encasing wire screens to ensure the bed material would not migrate through the flow system during testing. Sieved CaSDB – EF1 particles between 425 and 1400 µm were slowly added to the column with light intermittent tapping to ensure that interstitial spaces were minimized. The final column contained 2.28 grams of CaSDB – EF1.

2.1 Test Conditions

A calibrated feed gas consisting of 150 ppm Kr and 1000 ppm Xe in air was used to determine the capacity of CaSDB – EF1. Capacity tests were performed at two temperatures, 295 K and 253 K. Each temperature test was completed at two flow rates, 50 sccm and 25 sccm. All tests were performed at atmospheric pressure. Before each test the sorbent was activated to ensure the column was void of any entrained water or other impurities. Activation consisted of 50 sccm He flow while the column temperature was maintained at 400 K for 2 hours. The sorbent was then allowed to cool to ambient temperature under constant He flow.

In addition to simple capacity tests, two tests were performed on the column to see how the presence of air affected the capacity. These tests were performed by exposing the sorbent to 50 sccm air while heat cycling from 400 K to 310 K a total of three times. The sorbent was then activated using 50 sccm He and heat as described previously. Finally, the sorbent was tested using the Xe/Kr feed gas at 50 sccm, 295 K, and atmospheric pressure.

3. Results

Capacity results at initial breakthrough and saturation were obtained for Xe, Kr, and air adsorption on CaSDB – EF1 (Table 1. CaSDB – EF1 capacities for Xe, Kr, and air at initial breakthrough and saturation.Table 1). The data obtained for CaSDB – EF1 shows consistent Xe saturation capacity for tests at each respective temperature, regardless of flow rate. Tests 1 to 4 were performed at room temperature. Test 3 and 4 were completed to assess the effect on Xe capacity at room temperature after the sorbent was exposed to air. Tests 5 and 6 were performed at 253 K to increase initial breakthrough capacities.

Table 1. CaSDB – EF1 capacities for Xe, Kr, and air at initial breakthrough and saturation.

Test	Temp (K)	Flow Rate (sccm)	Xenon (mmol/kg)		Krypton (mmol/kg)		Air (mmol/kg)	
			Initial Breakthrough	Saturated	Initial Breakthrough	Saturated	Initial Breakthrough	Saturated
1	295	25	22	32	0.33	0.56	1000	1100
2	295	50	14	33	0.39	0.47	1800	1500
3	295[a]	50	15	32	0.39	0.44	2000	1700
4	295[a]	50	15	32	0.40	0.46	2000	2000
5	253	25	140	220	0.38	0.31	190	1000
6	253	50	120	220	0.74	1.3	2100	9700
Average	295	50	14	33	0.39	0.46	1900	1700
Std			0.22	0.39	0.00	0.0	94	205

a. Capacity tests performed after air flow and heat cycling

3.1 Tests: 295 K

The average Xe saturation capacity at 295 K and 50 sccm was 33 mmol/kg. Data from the previous report showed that at 50 sccm and 295 K the average saturation capacity for CaSBD – MOF from PNNL was 32 mmol/ kg (Welty, Garn, & Greenhalgh, 2018). It should be noted that though both materials have the same saturation capacity CaSDB – EF1 is approximately 80 wt.% CaSDB, suggesting that the CaSDB powder in CaSDB – EF1 is 20% more efficient than the CaSDB – MOF samples previously tested.

The average Xe initial breakthrough capacity of the CaSDB – MOF was 6 mmol/ kg (Welty, Garn, & Greenhalgh, 2018). Though CaSDB – EF1 demonstrated an initial breakthrough capacity two times greater than that of the CaSDB – MOF, Xe still broke through the column almost immediately. Figure 1 clearly shows the immediate breakthrough of Kr and air through the CaSDB – EF1 column. Xe broke through after processing less than 0.3 liters of feed gas. A low initial breakthrough capacity of Xe is not ideal for complete separation of Xe and Kr because Xe could negatively affect the adsorption of Kr in downstream processes.

Average air adsorption on the column at 50 sccm and room temperature was 1700 mmol/ kg, much larger than 419 mmol/ kg observed in previous testing (Welty, Garn, & Greenhalgh, 2018). It should be noted that as the balance gas, air produces a large peak in the gas chromatogram. Minute differences in such a large peak area can integrate a large error into that measurement. Nonetheless, an increase in air adsorption or an incomplete desorption of air could greatly affect the Xe capacity of the sorbent.

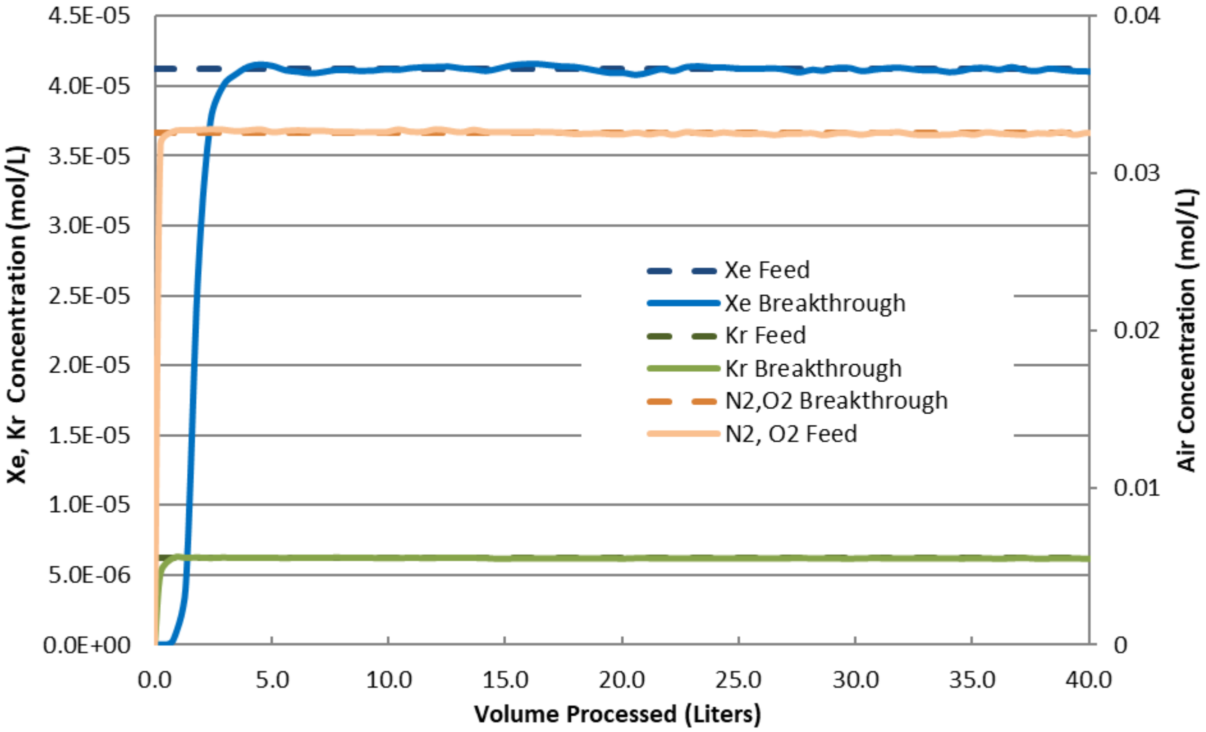

Figure 1. Xe, Kr, air breakthrough curves for CaSDB – EF1 in a 0.77 cm I.D. and 20 cm length column at 295 K. Feed gas 1000 ppm Xe and 150 ppm Kr in a balance of air was fed at 50 sccm.

The potential effect of repeated exposure to air was tested by exposing the CaSDB – EF1 column to an air flow of 50 sccm. The sorbent underwent heat cycling where the temperature was ramped from 295 K to 400 K over 1 hour, held at 400 K for 2 hours, then cooled to 310 K over 4 hours. This heat cycle was repeated for a total of three times. After exposure to air the sorbent underwent a He desorption cycle. The desorption included 50 sccm He and a temperature ramp to 400 K. The CaSDB – EF1 column was cooled to 295 K then exposed to 50 sccm feed gas flow. Both the initial breakthrough and saturation capacity results indicated that air cycling with proper desorption did not diminish the performance of the sorbent.

3.2 Capacity Tests: 253 K

To increase the Xe initial breakthrough capacity of CaSDB – EF1, the sorbent was cooled to 253 K. At this temperature the Xe initial breakthrough capacity and saturation capacity of the sorbent increased to 120 mmol/ kg and 220 mmol/ kg respectively. These Xe capacities were approximately seven times higher than the average room temperature capacities. Figure 2 shows the breakthrough curves for feed gas at 50 sccm and bed material at 253 K. Xe initial breakthrough occurs after 6.6 liters of feed gas were processed, nine times longer than the column at ambient temperature. Figure 2 clearly shows that at 253 K Kr and air almost immediately breakthrough the CaSDB – EF1 column.

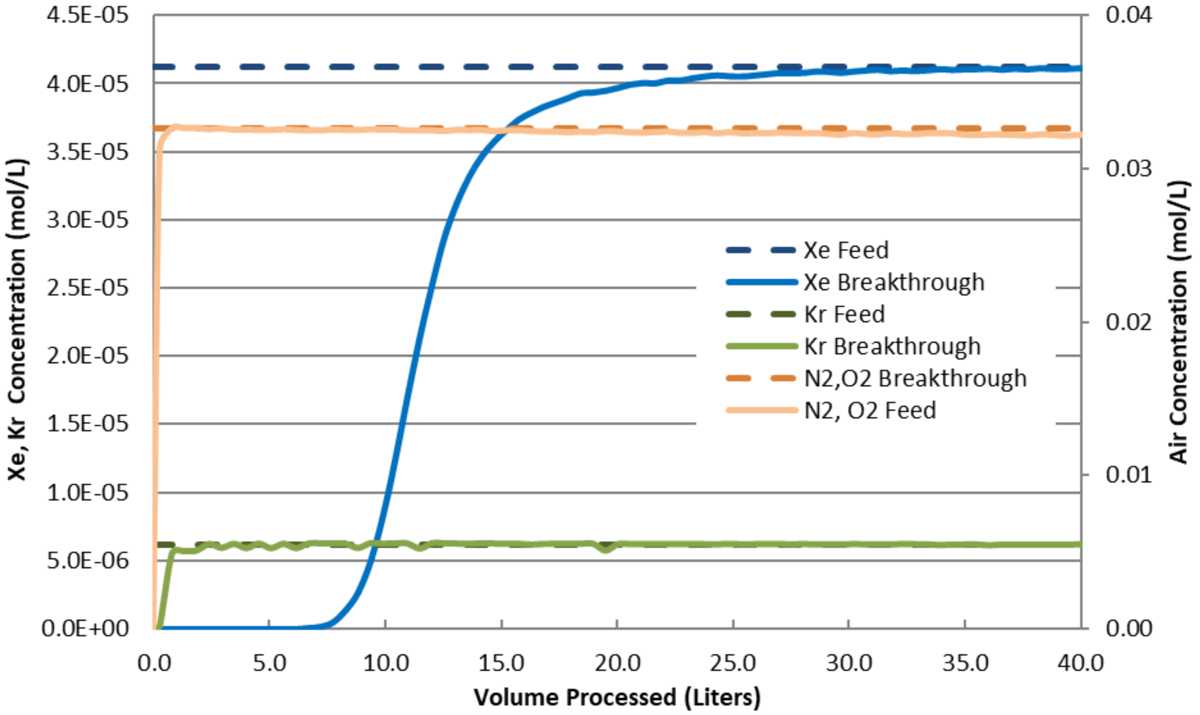

Figure 2. Xe, Kr, air breakthrough curves for CaSDB – EF1 in a column 0.77 cm I.D. and 20 cm length at 253 K. Feed gas 1000 ppm Xe and 150 ppm Kr in a balance of air was fed at 50 sccm.

4. Conclusions

The more robust form of CaSDB, CaSDB – EF1 exhibited very similar saturation capacities at room temperature to the previous tested CaSDB – MOF. Though the initial breakthrough capacity of the CaSDB – EF1 was two times higher than CaSDB – MOF, Xe broke through after only processing 0.3 liters. Almost immediate breakthrough is suboptimal because Xe can negatively affect the separation of Kr in downstream processes. This issue could be resolved by integrating several columns in series, effectively simulating one very long column or reducing the operating temperature. Cooling the sorbent material to 253 K increased the initial breakthrough and saturation capacity by about seven times.

Moving forward, it is important to think about the operability and economics of the process. Though the capacities were similar for the CaSDB materials, the approximate 80 wt% CaSDB content would mean that a CaSDB – EF1 column would need 20% less active sorbent than previously tested CaSDB – MOF forms. This could potentially reduce material costs, assuming the same raw material source, but the difference between this material and those previously tested is suspected to relate more to the CaSDB raw material quality than the engineered form production. As with previous CaSDB samples tested, the issue of rapid breakthrough of Xe remains. Using multiple columns in series to effectively simulate one really long column would most likely be impractical in terms of cost to procure large quantities of sorbent, large footprint for multiple columns, and high pressure drop. Cooling the sorbent material is likely a better option to overcome the rapid breakthrough problem. An economic sensitivity analysis would provide some insight regarding economic viability, but is outside the scope of this report.

5. References

Banerjee, D., Simon, C. M., Plonka, A. M., Motkuri, R. K., Liu, J., Chen, X., . . . Thallapally, P. K. (2016, June 13). Metal-Organic Framework with Optimally Selective Xenon Adsorption and Separation. *Nature Communications*. Retrieved from https://doi.org/10.1038/ncomms11831

Fujimoto, M. S., Welty, A. K., Garn, T. G., & Greenhalgh, M. R. (2019). *Developing an Engineered Form of MOFs CaSDB and HKUST-1*.

Garn, T. G., Law, J. D., Greenhalgh, M. R., & Tranter, T. J. (2013, May 9). *USA Patent No. 8,686,083*.

Welty, A. K., Garn, T. G., & Greenhalgh, M. R. (2018). *Initial Evaluation of CaSDB MOF Xe and Kr Capacities*. INL/EXT-18-44890.