Initial Evaluation of CaSDB MOF Xe and Kr Capacities

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SUMMARY

Idaho National Laboratory (INL) and Pacific Northwest National Laboratory (PNNL) have been conducting parallel research, as part of the off-Gas Sigma Team, producing and testing sorbents for the selective capture of xenon and krypton from surrogate nuclear fuel recycling off-gas streams. Sorbents showing promise during initial evaluations are tested further at INL in a system designed to emulate anticipated plant process conditions. This report summarizes INL's initial testing of CaSDB MOF developed and produced at PNNL.

Previous testing of the same base CaSDB MOF material, conducted at INL in 2016, indicated good saturation capacity for xenon, but a low xenon capacity at initial breakthrough. Additionally, the material displayed a propensity to break down into fine powder during use and handling. The current test series looks at the same base material, but with refinements to production and activation techniques.

A series of ambient temperature tests were conducted to determine capacities of CaSDB MOF for krypton and xenon at initial breakthrough as well as at saturation. Adsorption tests were run in triplicate at superficial velocities of 21 and 53 cm/min, along with a single test at 373 cm/min. Saturation capacity across all tests was 30.7 mmol/kg +/- 1.4, with capacity at initial breakthrough of 7.0 mmol/kg +/- 1.8.

It should be noted that while the usable portion of the material has a much tighter size distribution than that previously tested, propensity to physically break down into very fine powder with use and handling continues to be problematic. An improved engineered form is recommended prior to further testing.

CONTENTS

FIGURES

TABLES

ACRONYMS

BET	Brunauer-Emmet-Teller
CaSDB	calcium-4,4’-sulfonyl dibenzoate
GC-TCD	Gas Chromatograph with Thermal Conductivity Detector
INL	Idaho National Laboratory
K	Kelvin
MOF	Metal-Organic Framework
PNNL	Pacific Northwest National Laboratory
PPMV	Part per million volume
SCCM	Standard Cubic Centimeters per Minute

INITIAL EVALUATION OF CASDB-MOF XE AND KR CAPACITIES

1. INTRODUCTION

The Off-Gas Sigma Team is focused on mitigation of environmental emissions from used nuclear fuel recycling. Ongoing research at both INL and PNNL has resulted in development of several innovative sorbents that effectively capture and selectively separate krypton (Kr) and xenon (Xe) from air.

Calcium-4, 4’-sulfonyl dibenzoate (CaSDB) metal organic framework (MOF), developed and produced at PNNL was tested at INL in 2016. That testing indicated good saturation capacity for Xe, but a low Xe capacity at initial breakthrough. The breakdown of the material to fine dust during handling and use was of concern as well (Welty, Garn, & Greenhalgh, 2016).

This test series examines Xe capacity of the same base material with modification to production and activation techniques. The purpose of the preliminary testing is to gather sufficient information to determine the type of extended testing that may be warranted.

2. MATERIAL PHYSICAL CHARACTERISTICS

Upon receipt, the CaSDB MOF was weighed, activated, and screened for size in preparation for testing. The as received sample was labeled as 600-850 μm, but the material appeared very dusty (Figure 1). Most likely, the sorbent material was damaged during shipping. As seen previously with this material, abrasion from handling causes it to break down to powder (Welty, Garn, & Greenhalgh, 2016).

Figure 1. CaSDB MOF as-received

Initial weight of the sample was 18.99 g. The entire sample was carefully transferred to a one inch diameter column for activation. It was then placed in a 200 °C oven for 10 hours under a vacuum of 20 inches Hg, according to instructions from PNNL (Thallapally, 2018). Post-activation weight was 17.52 g, a loss of 0.47 g of water as well as fine powder that remained on the walls of the activation column.

Following activation, the CaSDB MOF was gently screened to remove powder and fines, ensuring appropriately sized material for deep bed testing. Screening resulted in 9.5 g (55%) of material ≥425 μm and 7.7 g (45%) of material <150 μm, all of which appeared to be fine powder.

Bulk density of the ≥425 μm material was measured at 0.633 g/mL. Brunauer-Emmet-Teller (BET) surface area was measured using a Micromeritics ASAP 2020 and found to be 81 m^2/g. Previous CaSDB MOF had a BET surface area of 4 m^2/g and a density of 0.740 g/mL (Welty, Garn, & Greenhalgh, 2016).

3. INITIAL CaSDB MOF TESTING AT INL

All testing was conducted at ambient temperature, nominally 295K in a stainless steel column with 11 mm internal diameter and 152 mm in length. The column was fitted with glass 150 micron screens and glass frits at both inlet and outlet. A total of 9.05 g of CaSDB MOF ≥425 μm was was installed in the column using a light tap material packing technique to minimize void space in the packed column while minimizing damage to the sorbent material. All adsorption tests were conducted with 150 ppm Kr and 1000 ppm Xe in a balance of air.

3.1 Test Results

A series of seven capacity tests were conducted; three at nominally 20 sccm, three at 50 sccm and one at 350 sccm, corresponding to superficial velocities of 21, 53, and 374 cm/min, respectively. The first test, at 17 sccm, resulted in a saturated capacity of 48 mmol Xe/kg CaSDB, a higher capacity than that previously measured on this material. However, this number was not duplicated on subsequent tests (Table 1). There are two possible explanations for the discrepancy: 1) The mass flow controller used for this test had a full range of 2500 sccm and, with a setpoint of 20 sccm, was being asked to operate at 0.8% of range where accuracy and precision may be poor. Although initial flow was independently measured at 17 sccm, that measurement was merely a spot-check, and it is possible the flow drifted down over the course of the test. A mass flow controller with 0-50 sccm range was used for subsequent low flow tests. 2) It is possible the sorbent did have a higher initial capacity. It had not, up to that point, been exposed to air for any extended period of time. Given results of previous testing, as well as the consistency of subsequent tests in this series, this possibility is considered remote.

Table 1. CaSDB-MOF Initial Test Results

			XENON (mmol/kg)		**KRYPTON** (mmol/kg)		**AIR** (mmol/kg)	
Test	Temp (K)	Flow Rate (sccm)	Initial Breakthrough	Saturated	Initial Breakthrough	Saturated	Initial Breakthrough	Saturated
1(1)	295	17	8.94	48.25	0.23	0.64	571	2109
5	295	20	6.10	29.39	0.04	0.47	212	1203
7	295	20	8.50	28.93	0.24	0.26	487	1188
2	295	50	8.50	31.32	0.19	0.29	1006	570
3(2)	295	50	1.17	31.65	0.18	0.20	927	55
4	295	50	8.03	32.66	0.48	0.48	595	632
6	295	350	4.01	31.14	0.60	0.43	3165	1426
20 sccm		Avg	7.84	35.53	0.17	0.46	423	1500
		StD	1.25	9.00	0.09	0.16	153	431
20 sccm (without outliers)		Avg	7.30	29.16	0.14	0.37	350	1195
		StD	1.20	0.23	0.10	0.11	138	8
50 sccm		Avg	5.90	31.88	0.28	0.32	842	419
		StD	3.35	0.57	0.14	0.12	178	259
50 sccm (without outliers)		Avg	8.27	31.99	0.33	0.38	800	601
		StD	0.23	0.67	0.14	0.09	205	31
ALL sccm		Avg	6.46	33.33	0.28	0.40	995	769
		StD	2.70	6.21	0.19	0.14	920	524
ALL sccm (without outliers)		Avg	7.03	30.69	0.24	0.39	575	751
		StD	1.75	1.36	0.16	0.09	285	452

(1) Considered inaccurate due to mass flow controller

(2) Considered inaccurate due to inadequate reactivation after desorption

This sorbent is intended to remove the Xe from the air stream so that Kr may then be removed downstream and stored. Consequently, Kr and air saturation capacity should be minimized while Xe breakthrough capacity is maximized in order to allow reasonably sized adsorption columns with the longest possible run time between desorption cycles. During the first three tests, desorption was accomplished by flowing 25 sccm helium (He) through the sorbent while heating to 420K until Kr and Xe were non-detectable, then holding for one more hour at 420K. It was noted that breakthrough capacity decreased with each subsequent test, to the point where breakthrough was nearly immediate. After consultation with PNNL (Thallapally, 2018), a decision was made to alter the desorption technique to include the same conditions used to initially activate the sorbent. Remaining tests were desorbed at 473K with He flow, until no Kr and Xe were detected, then a vacuum was applied while temperature was held at 473K. Tests 3 and 4 were held under vacuum for 10 hours each, which successfully restored the initial breakthrough capacity. Since excessively long desorption cycles could be detrimental to plant operability, time under vacuum was decreased to four hours in order to determine if reactivation time could be decreased without detrimental effect on performance. There may have been a slight decrease in initial breakthrough capacity, but this was not explored further as there was inadequate time for more testing. More extensive testing is necessary to optimize desorption/reactivation of this material.

The primary criteria for this sorbent is its ability to capture Xe. In that regard, it displayed good average saturated capacity of 30.7 mmol Xe/kg sorbent (Figure 2). However, initial breakthrough occurs at a much lower capacity of 7.0 mmol Xe/kg sorbent. While this is nearly double that of this same material prior to modifying production and activation techniques, it remains problematic for adsorption system design.

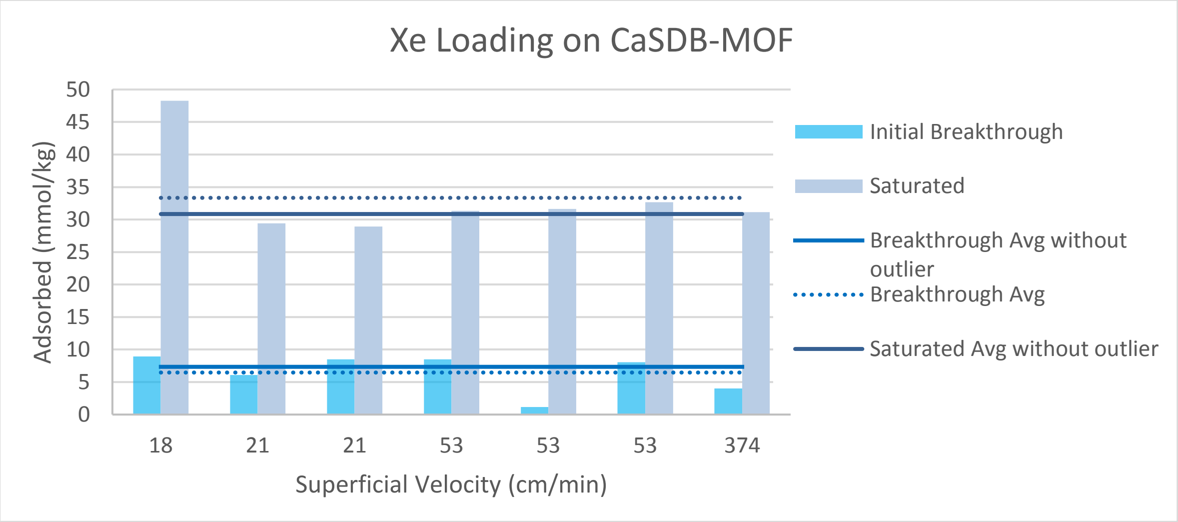

Figure 2. Xe Capacity of CaSDB-MOF at ambient temperature

It is also important for this sorbent to have low capacity for Kr and other contaminants that may be present in the off-gas stream. In this regard, CaSDB results are quite good, consistently adsorbing very little Kr compared to Xe. In the case of Kr, saturation capacity is the important number to note, as it is desirable for the vast majority of the Kr to pass through this sorbent for capture downstream. There appears to be more scatter in the data due to low concentrations (Figure 3) and a higher-resolution graph, but saturated capacity averaged a low 0.24 mmol Kr/kg sorbent.

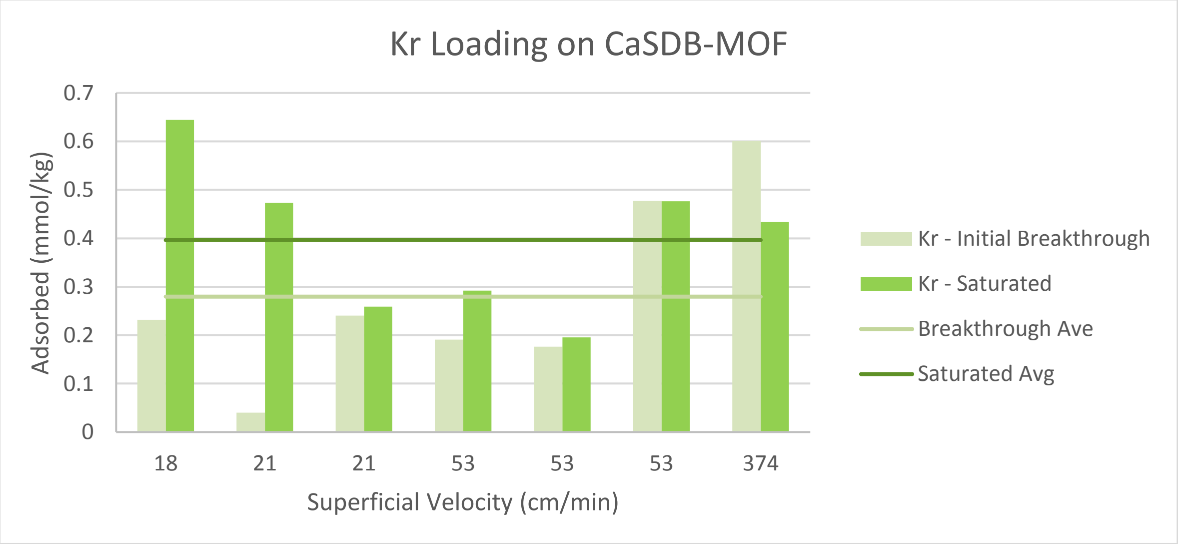

Figure 3. Kr Capacity of CaSDB-MOF at ambient temperature

An attempt was made to quantify air adsorption. There is, however, a high degree of scatter in the data. This error can be attributed to the overwhelming concentration in the feed gas, effectively 100%. A few seconds of difference in the time to turn valves results in a large calculated capacity difference. Even so, there is indication that this sorbent is highly selective for Xe over air.

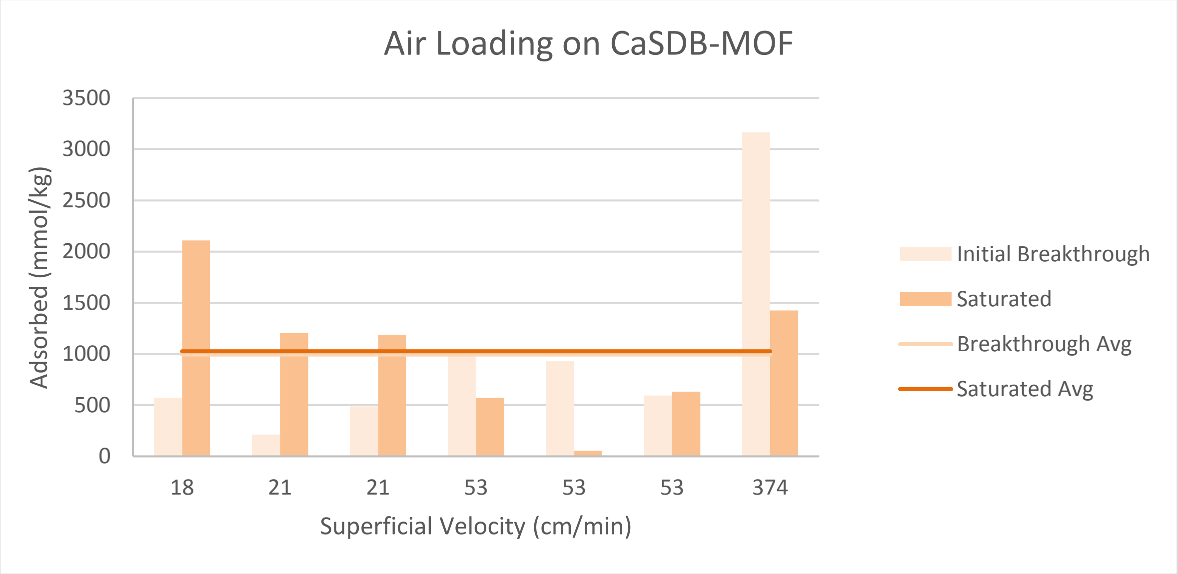

Figure 4. Air Capacity of CaSDB-MOF at ambient temperature

3.2 Post-Testing Material Evaluation

After tests were concluded, bulk material weight was 8.78, a loss of 0.27 g, or 3%. The weight loss is attributed to fine powder evolving off of the surface of the bulk sorbent. A glass frit was installed on the outlet side of the column to catch fines. It did manage to contain some of the fines, ending the testing caked with fines and powder (Figure 5).

Figure 5. Glass frit from column outlet

However, much of the powder was fine enough to pass through the glass frit and into the column effluent tubing. After knocking out as much accumulated powder as possible, a fair amount of it still remained in the column screen (Figure 6), requiring sonication to remove.

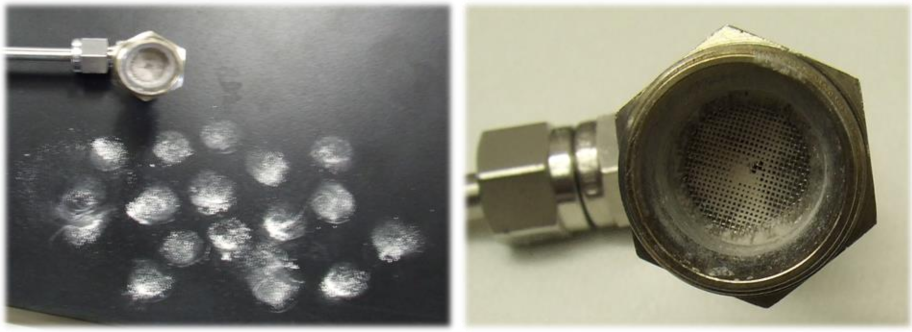

Figure 6. Column effluent screen after knocking out accumulated powder

4. CONCLUSIONS AND RECOMMENDATIONS

Modifications in CaSDB-MOF production and activation techniques resulted in improved breakthrough capacity. This should be further optimized, if possible, with the goal of moving breakthrough capacity as close to saturation capacity as possible, preferably while maintaining the low Kr and air capacities of the material.

Desorption techniques for CaSDB-MOF should be explored further. While desorption with heat and He flow followed by 10 or more hours with heat and under vacuum reactivates the material consistently, those conditions may be prohibitive in a process situation. This series of tests provides some indication that desorption and reactivation time may be decreased but there is insufficient data to draw hard conclusions.

While production modifications resulted in usable material with more uniform size distribution, structural delicacy continues to be an issue. The propensity of this material to turn to powder presents some problems for testing. Allowing the powder to escape into effluent and analysis tubing contaminates the system, requiring significant down-time for disassembly and cleaning. More importantly, there is risk of damage to the GC. Installation of filters capable of capturing the powder may impact test results due to back pressure across the column system. Given the problematic nature of containing easily fluidized dusts and powders, it is recommended that a more physically stable engineered form be developed. A sturdier engineered form will have benefits for extended testing of the material and, more importantly, result in a material with more favorable handling and operational characteristics for process utilization.

5. REFERENCES

Thallapally, P. K. (2018, January). Personal communication.

Welty, A. K., Garn, T. G., & Greenhalgh, M. (2016). *Multi-Column Experimental Test Bed Using CaSDB MOF for Xe/Kr Separation.* FCRD-MRWD-2016-0000260.