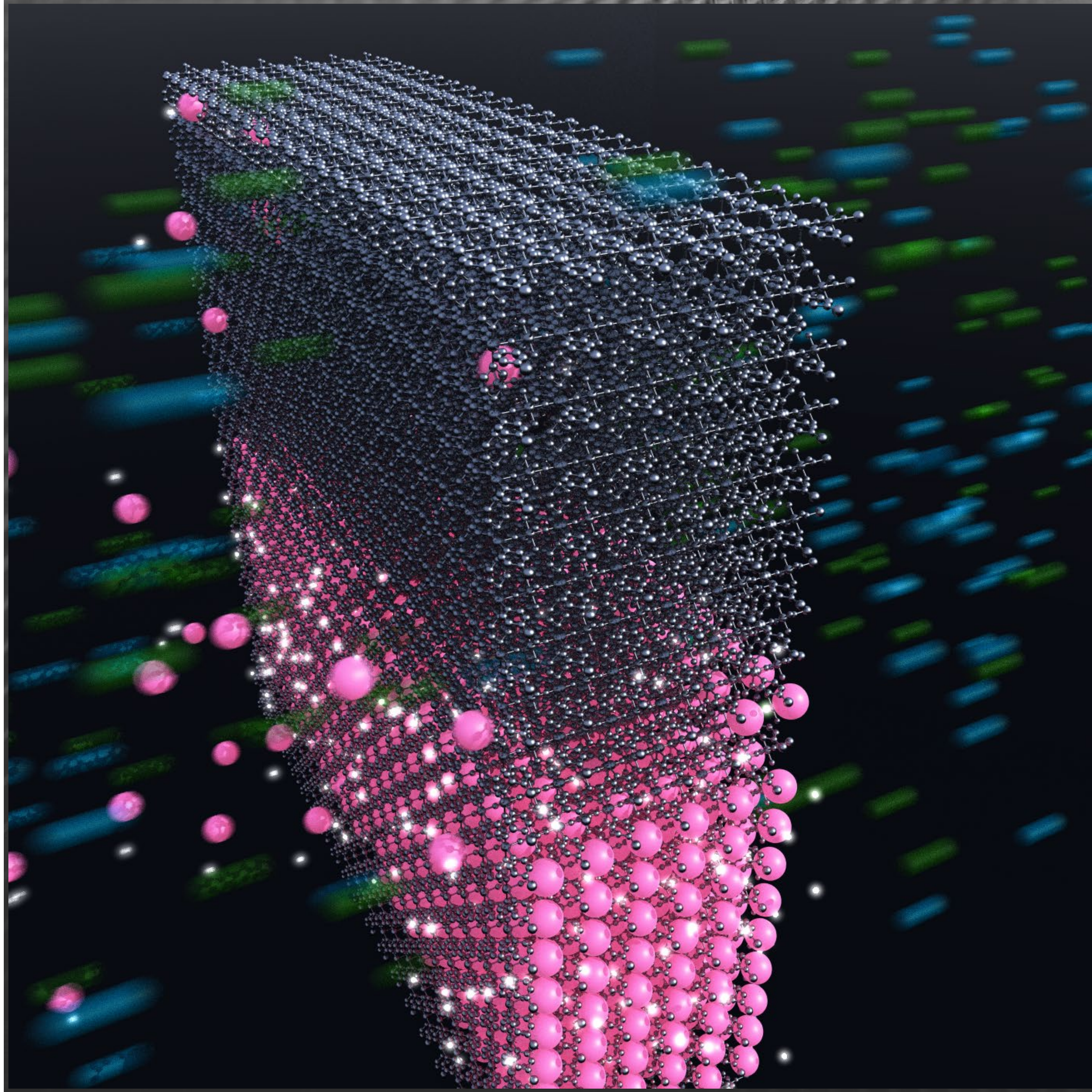
Metal organic frameworks for noble gas capture



Praveen K. Thallapally

WOSMIP Remote 2 at
Pacific Northwest National Laboratory
Richland, Washington 99352
May 25th to 26th 2021

MOF Capabilities at PNNL

- Computationally inspired material discovery
- Porous material characterization and testing
- Milligram to kilogram scale synthesis
- Bench scale demonstration
- Full Patent on noble gas separation using MOFs and related materials USPTO WO/2017/218346A1
- Filed a provisional patent on making mechanically robust particles using PNNL proprietary approach
- Licensed the large-scale synthesis of material technology to Inna Venture, LA

Current Technologies and Alternatives

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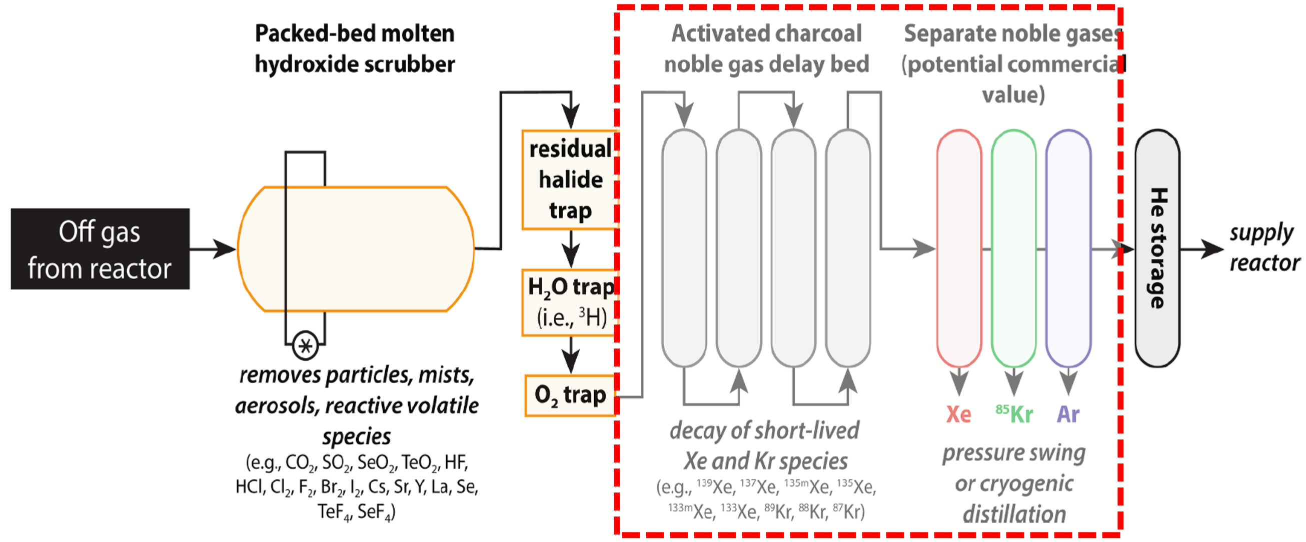
Current Technology

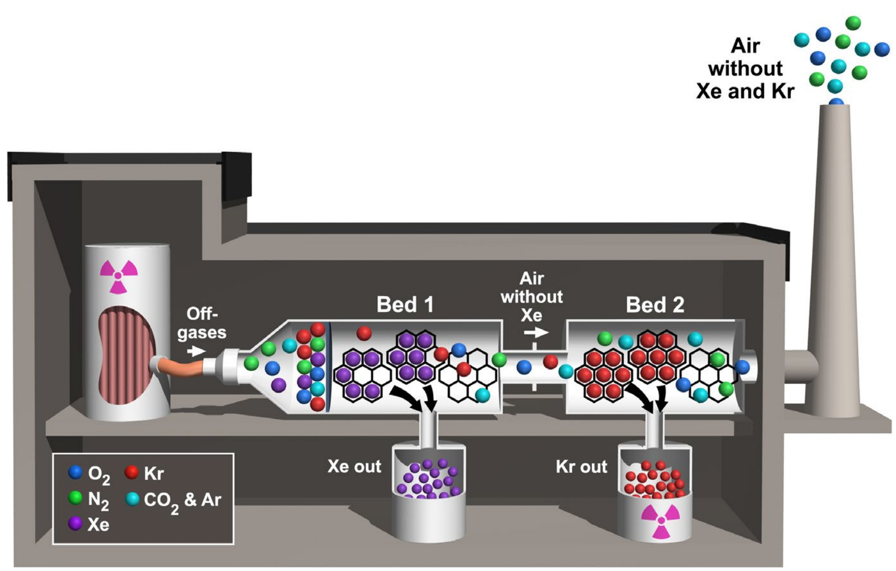
- Cryogenic removal of Xe and Kr
  - Projected to be expensive
  - Potential for O_3 accumulation
  - Hazardous conditions

➢ **Charcoal** delay beds (MSR)

- ○ Requires 4-5 charcoal tanks with 6 – 9 foot in diameter and 50 foot long
- ○ Fire hazard: Presence of oxygen and heat production due to radioactive decay
- ○ Oxygen needs to be removed upfront from cryogenic distillation as well as charcoal beds



Riley, B. J et. al., Nuclear Engineering and Design., 2019, 345, 94.
Nichols J. P., Status of noble gas removal and disposal report, 1971, ORNL-TM-3515

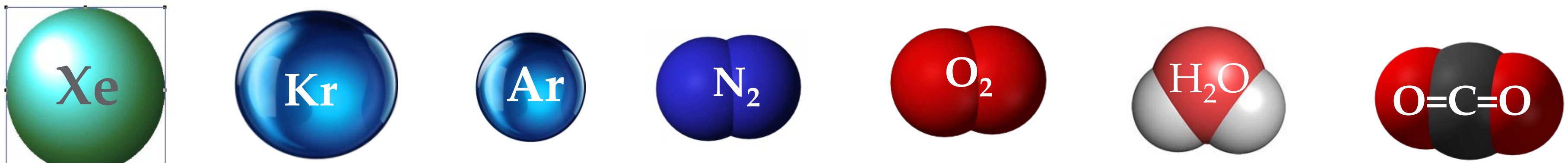


Liu *et. al.*, *Ind. Eng. Res. & Chem.*, 53, 12893-12899, 2014
Thallapally, Vienna et. al., USPTOWO/2017/218346A1

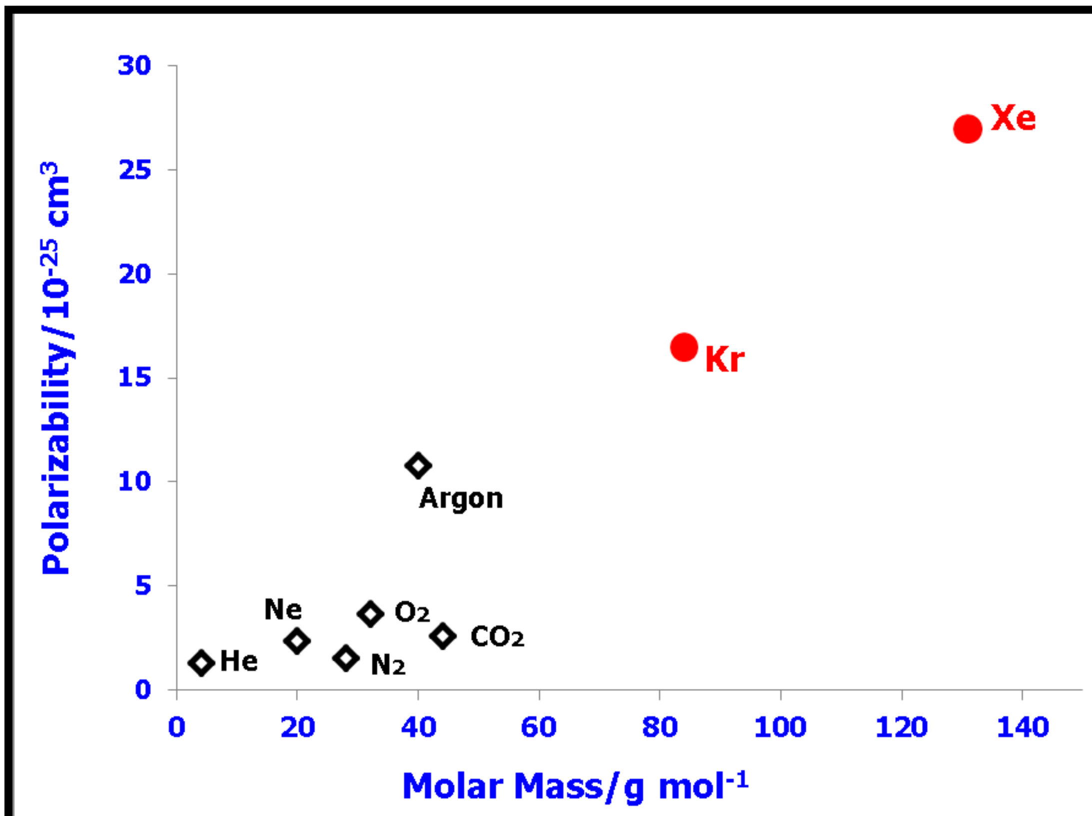
➢MOFs as Alternate Technology

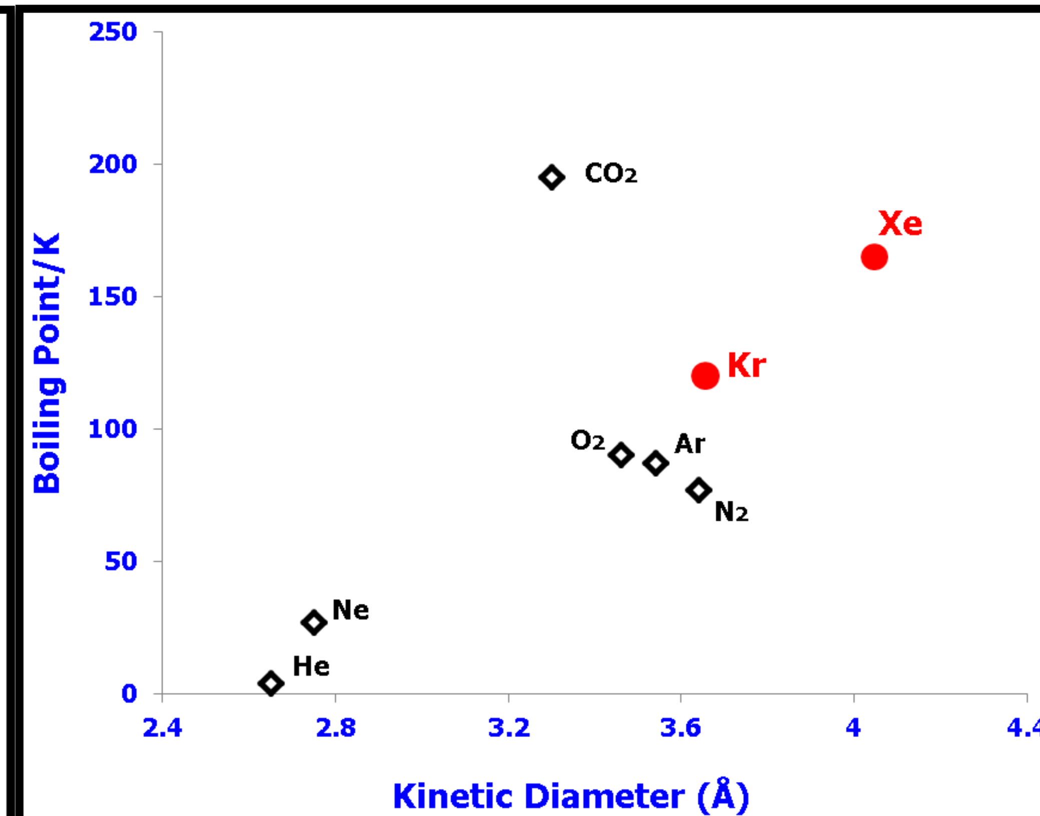
- ○ Higher capacity and selectivity represents significant cost reduction compared to cryogenic and charcoal beds
- ○ Smaller size columns, reduced footprint and no fire hazard
- ○ Remove Xe (non-radioactive) and Kr in separate steps at near RT
  - ○ Recover process costs by selling Xe?
- ○ Remove Kr in single step

Gas Composition in Air



87 ppb | 1 ppm | 0.9% | 78% | 21% | variable | 0.03%

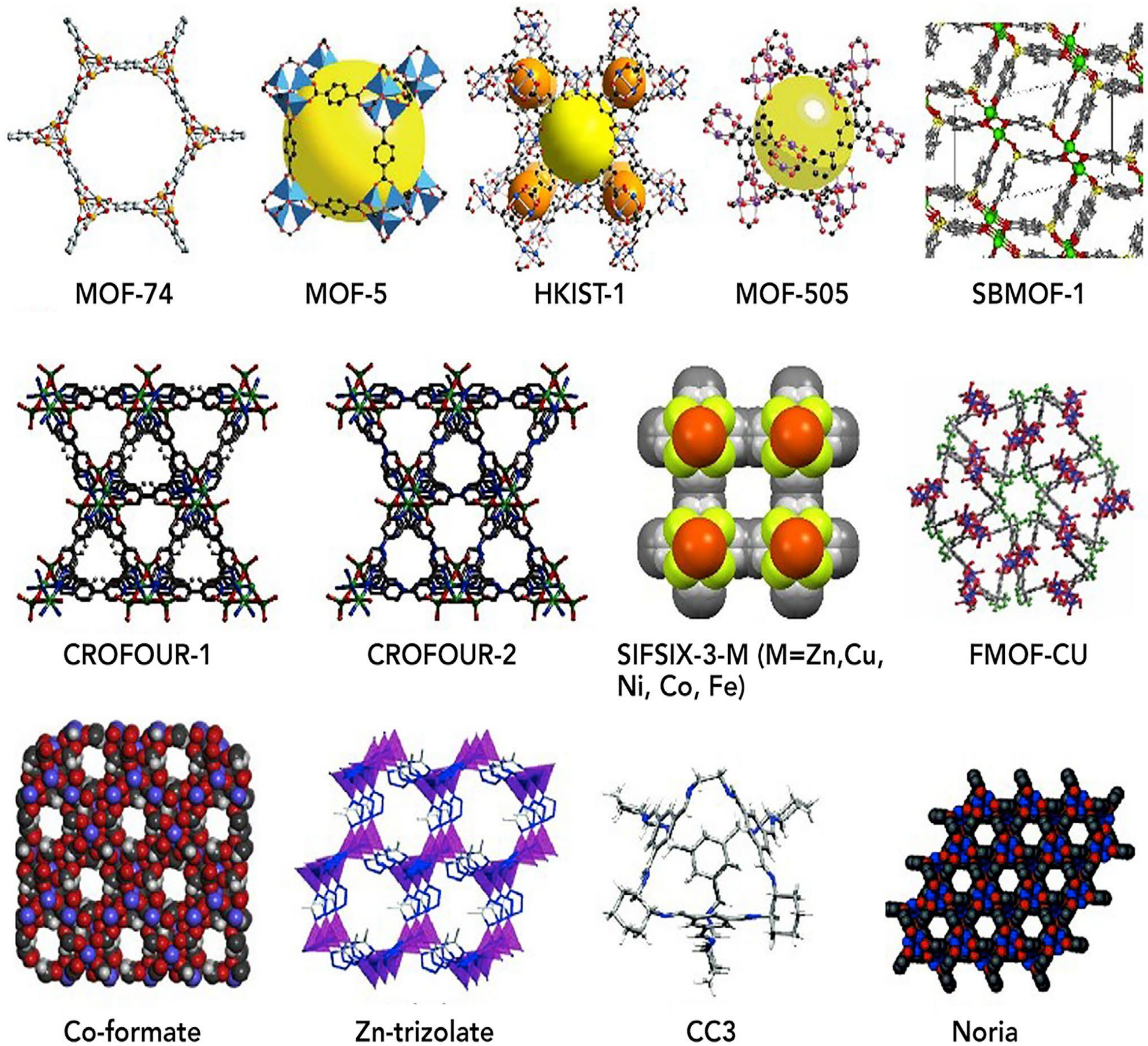




Banerjee et. al., *Acc. Chem. Res.*, 48, 211, 2015

Adsorbents Studied at PNNL

Organic, Inorganic and Hybrid (MOFs)



Debasis *et. al., CHEM.,* 4, 466-494, 2018
Debasis et. al., *Acc. Chem. Res.*, 48, 211–219, 2015
Chen et. al., *Nature Materials,* **13,** 954–960, 2014
Debasis et. al., *Nature Communications.*, **7**, 11831, 2016
Elsidi Et. al., *Nature Communications.*, **11**, 3103, 2020

- Pore diameter close to the KD of Xe/Kr
  - Chen et. al., *Nat. Mat.,* 2014
  - Debasis et. al., *Nat. Comm*., 2016
  - Elsaidi et. al., *Chem. Eur J.*, 2017
- High density of open metal sites
  - Thallapally et. al., *Chem. Commun,* 2012
  - Liu et. al., *Chem. Commun*, 2014
  - Ghose et. al., *J. Phys. Chem C.*, 2016
- Polar functional groups within pore surface
  - Chen et. al., *J. Am. Chem. Soc.*, 2015
  - Elsaidi et. al., *Angew Chem. Int. Ed.*, 2016
- Temperature switching selectivity
  - Fernandez et al., *J. Am. Chem. Soc.*, 2012
- High surface area, KD smaller than Xe/Kr and Impregnation with silver Nanoparticles
  - Liu et. al., *Chem. Commun.*, 2013
  - Feng et. al., *J. Am. Chem. Soc.* 2016
  - Elsaidi et. al., *Chem. Sci.,* 2017

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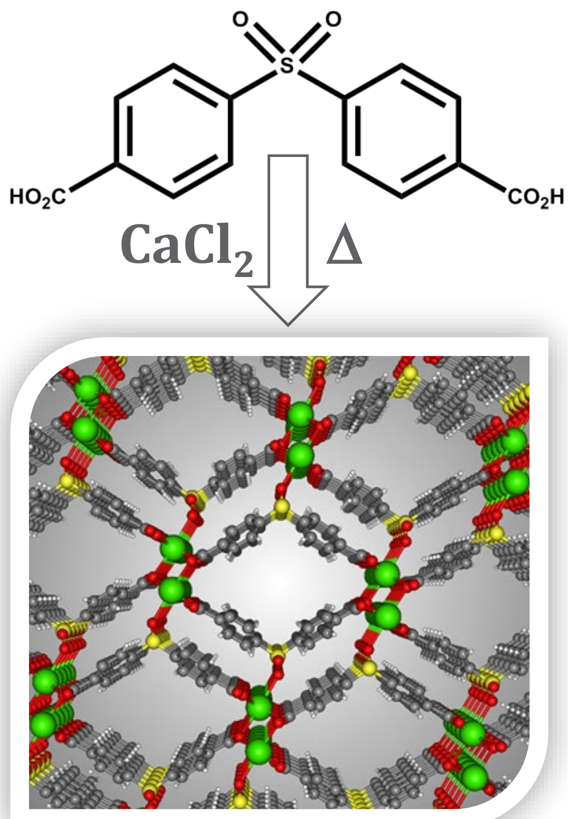
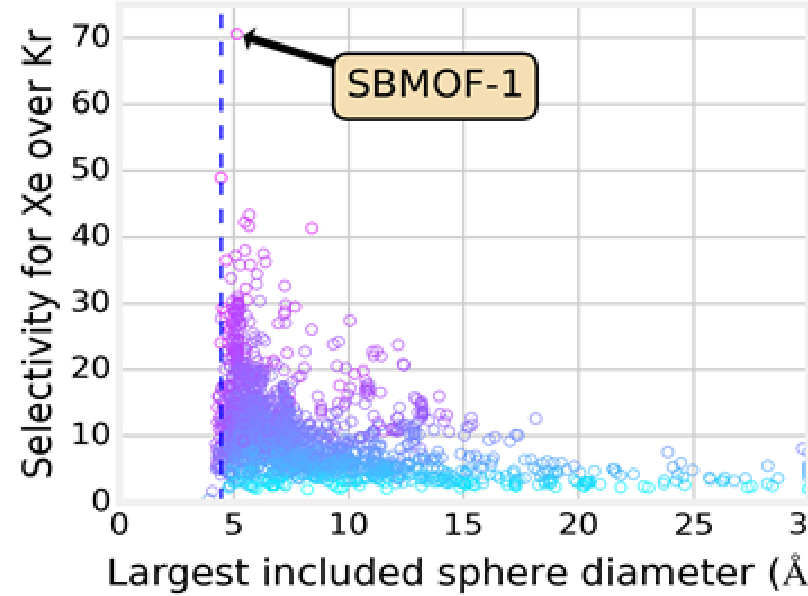
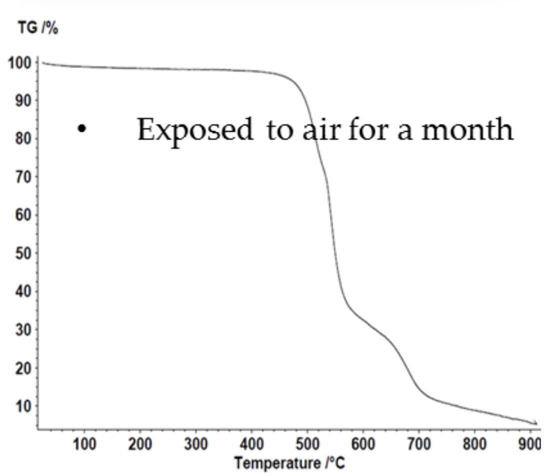
CaSDB Leading MOF Material at Room Temperature Adsorption



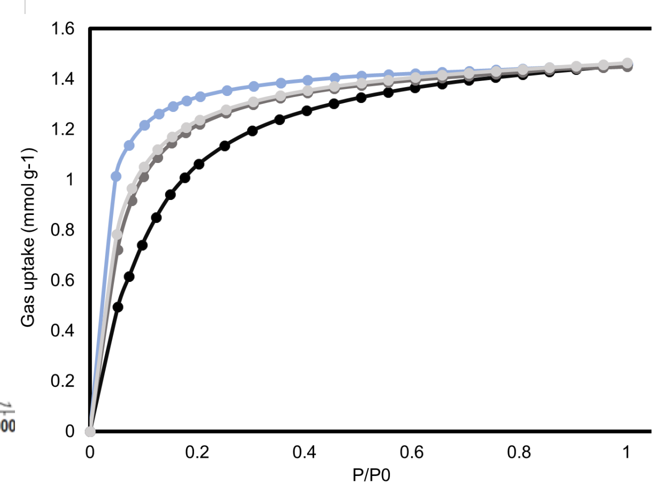
- ❑ Modelling predicts the CaSDB (SBMOF-1) is the best among 5000 experimental and 125,000 hypothetical MOFs.
- ❑ 3D network structure connected with CaO units
- ❑ Small pore diameter (4.1 Å) with surface area of 120 m^2/g
- ❑ Very stable in air
- ❑ Very selective to Xe even in presence of CO_2

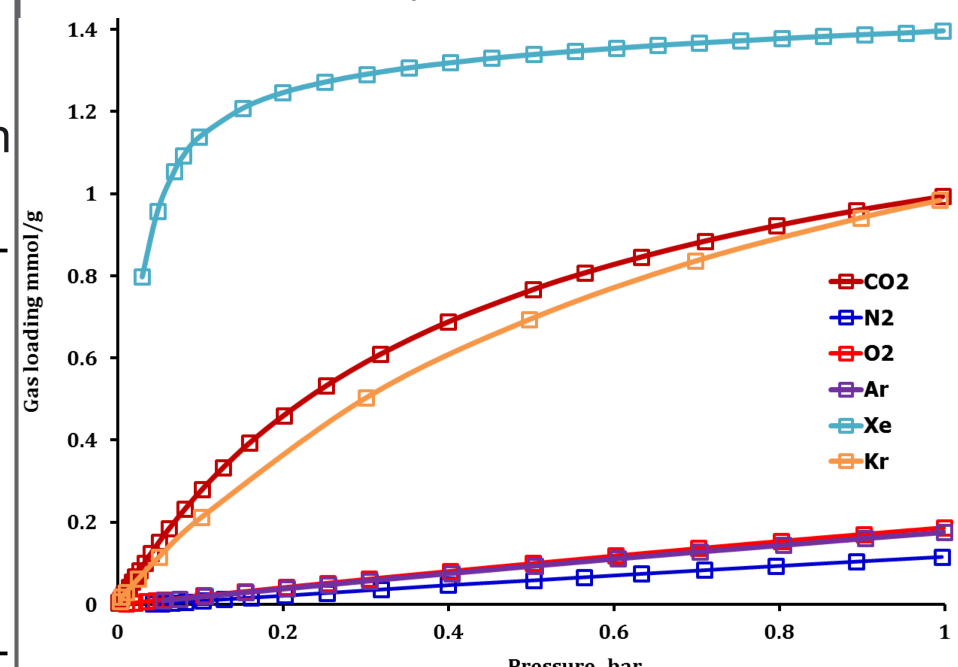


- ❑ A rare example of computationally inspired material discovery



Thermo-gravimetric analysis

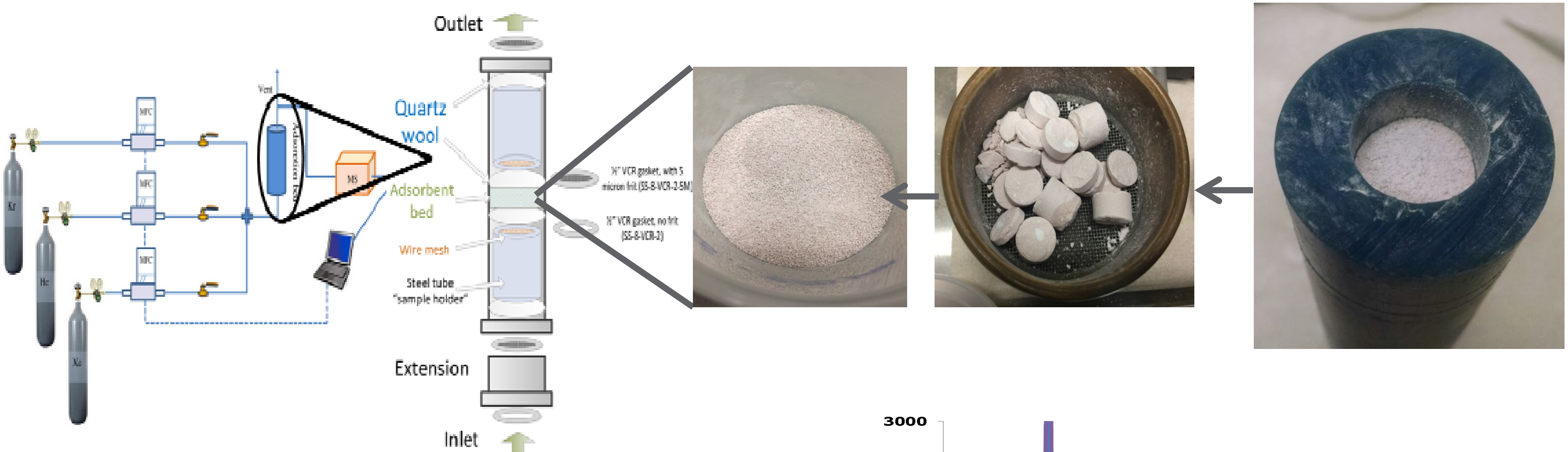




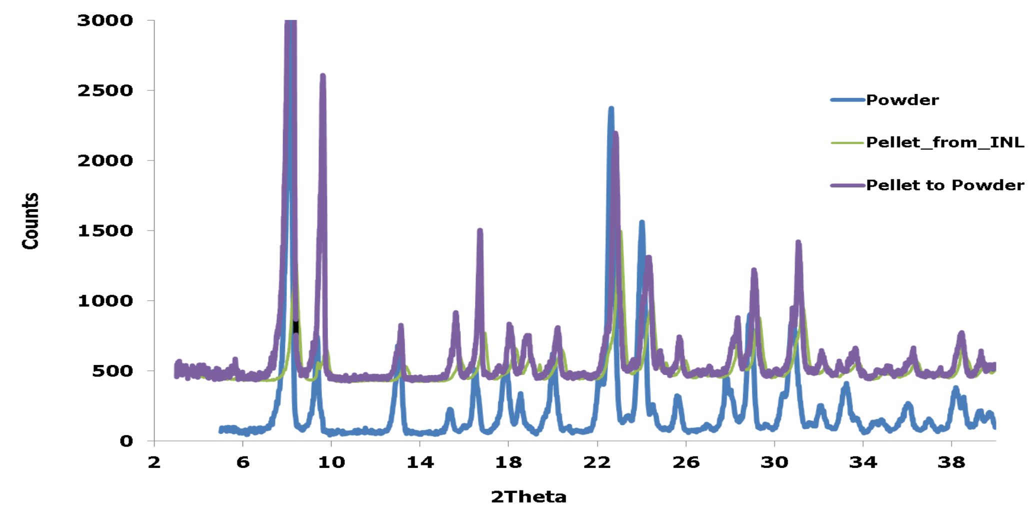
Banerjee *et. al.*, *Nature Communications*, 2016

Thallapally, Vienna et. al., USPTO WO/2017/218346A1

Breakthrough Measurements Apparatus



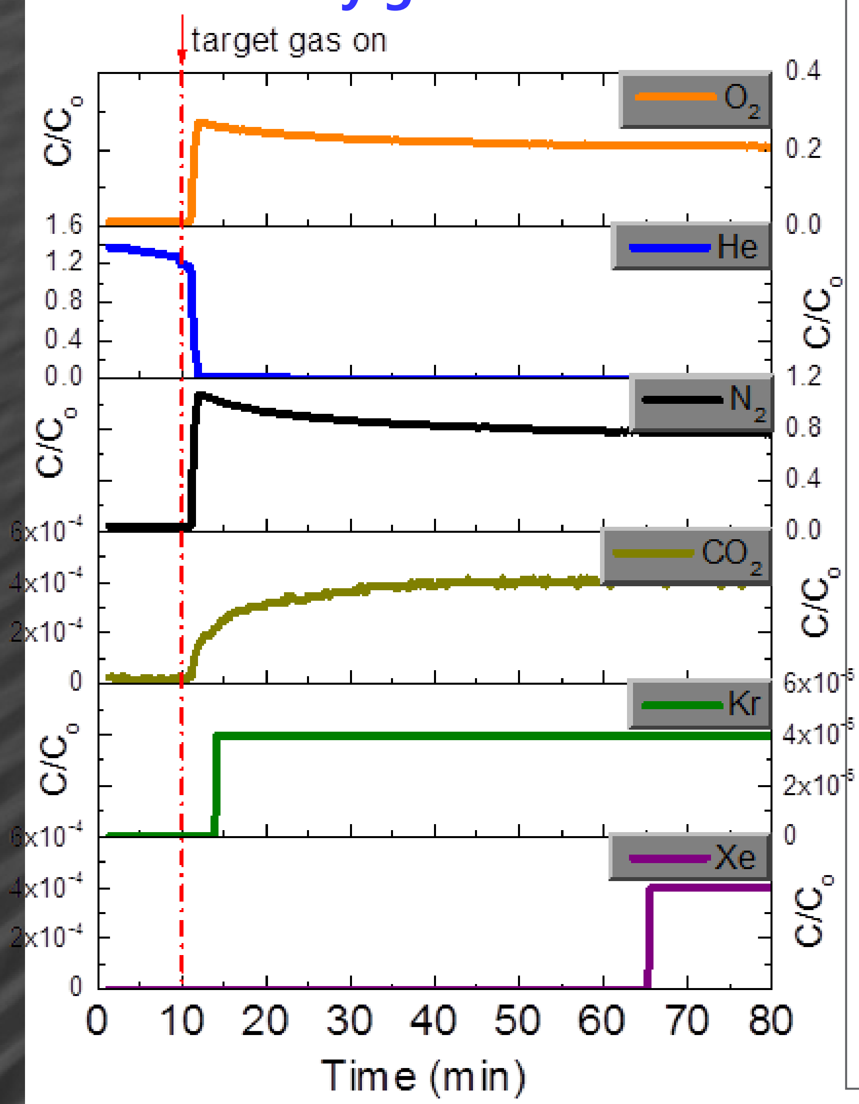
Property	Value
Pressed Pressure	75 MPa
Size	500 – 850
BET Surface area	15 m^2/g
BET Surface area, Po	120 m^2/g



- Identical PXRD confirmed (powder to pellet)
- No amorphous phase
- Reduced BET surface area

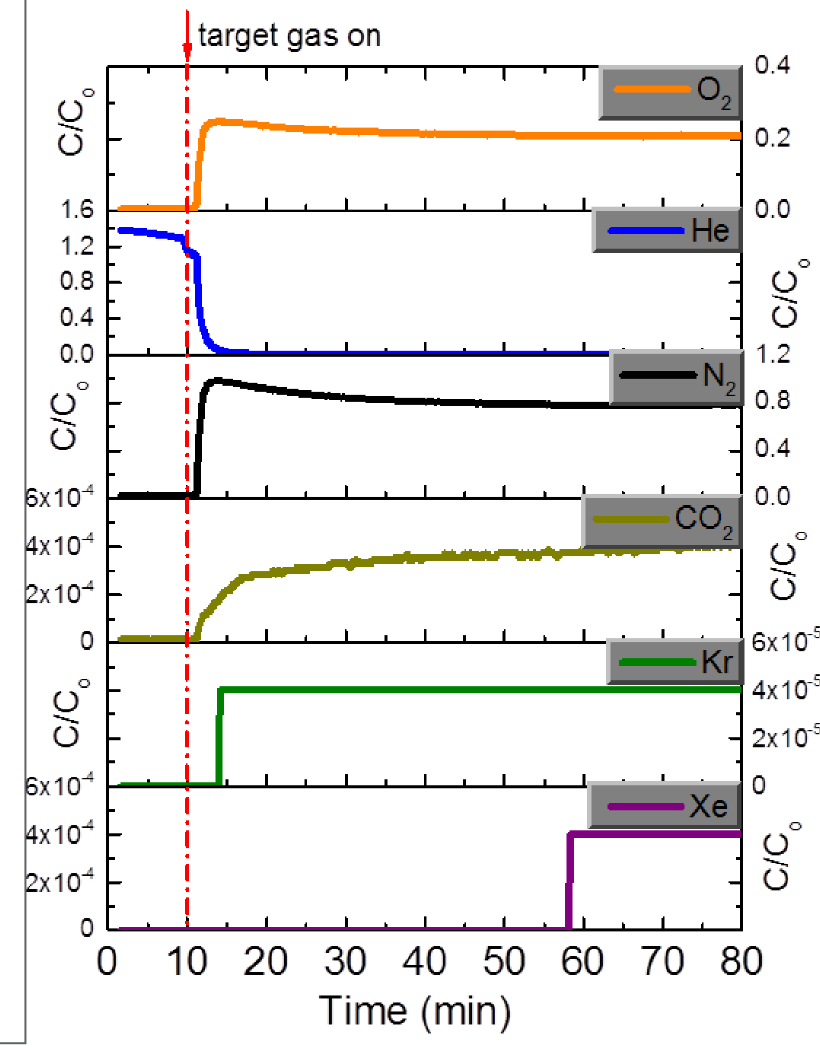
Single Column Breakthrough Experiments using CaSDB MOF at Room Temperature

dry gas



- **Conditions**
- Air = 78% N_2, 21% O_2, 0.9% Ar, 0.03% CO_2, 1300 ppm Xe, 130 ppm Kr
- Flow rate = 20 cm^3/min
- T = 25 °C (298K)
- MOF = CaSDB
- **Results**
- Xe capacity@RT = 30 mmol/kg
- Xe capacity@5 °C = 60 mmol/kg
- No need to remove, O_2, CO_2 or trace water vapor
- Capacity from single component gas adsorption ~159 mmol/kg
- >99% of the Xe captured from air
- Xe/Kr (selectivity) = 15 under simulated off-gas

Wet gas (RH 48%)



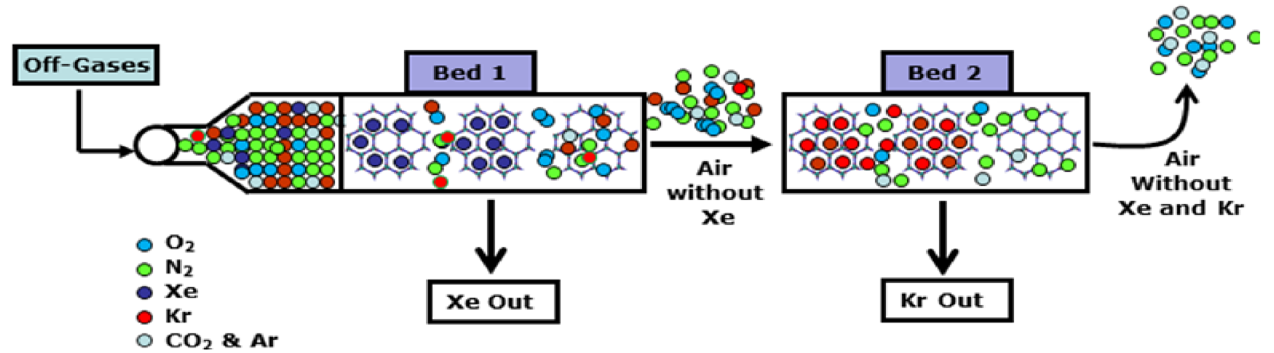
- CaSDB falls in the optimal pore size and shape, making it stand out among other MOFs

Banerjee *et. al., Nature Communications*, 2016

Thallapally, Vienna et. al., USPTO WO/2017/218346A1

Two-Column Breakthrough and Co-Adsorption at RT using CaSDB MOF

- **A two-bed technique to remove and separate**
  - Bed 1 remove Xe from air
  - Bed 2 remove Kr
    - ✓ Yields air without Xe and Kr
    - ✓ Off-gas can be released

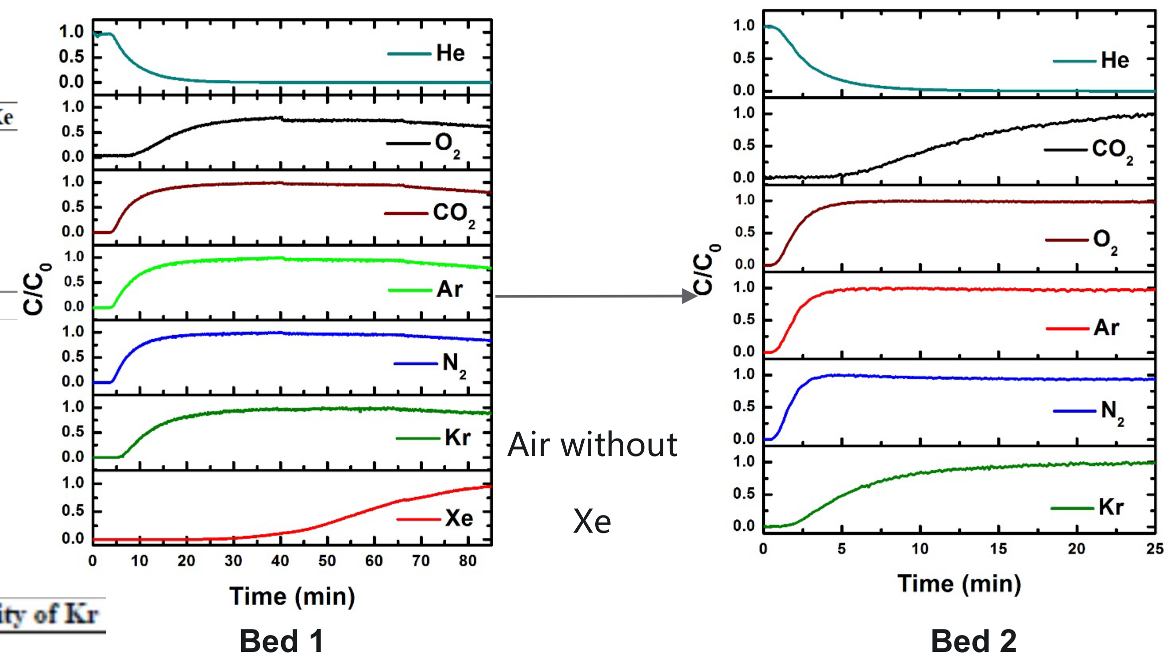


Results:

- **Bed - 1**

Gas	Breakthrough Time (min)	Capacity (mmol/kg)	Selectivity of Xe
Xe	18	16 (33.8)[a]	
Kr	1	0.11 (0.75)[a]	14
CO_2	5	1.2	3
N_2	0.08	47	209
Ar	0.08	5.28	210
O_2	0.08	12	206

[a] Capacity at equilibrium

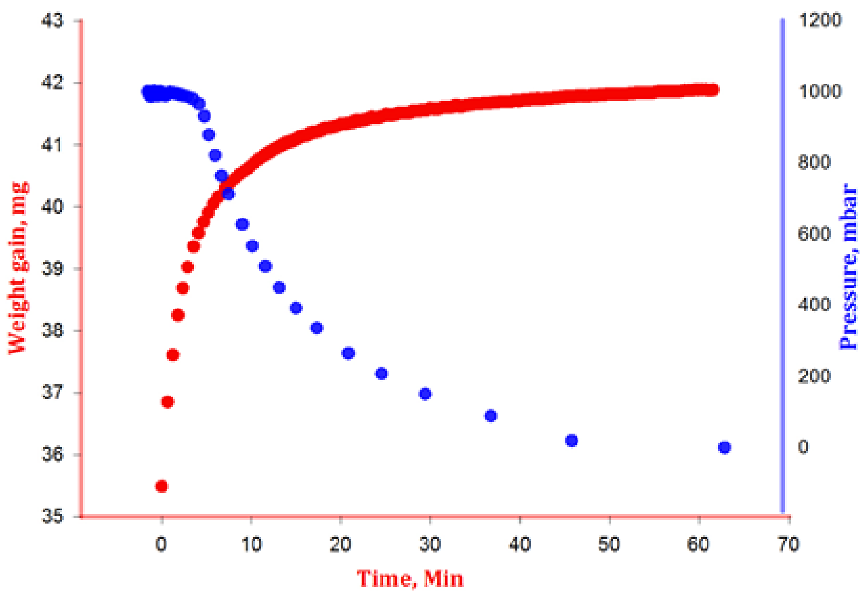


- **Bed - 2**

Gas	Breakthrough Time (min)	Capacity (mmol/kg)	Selectivity of Kr
Kr	2.5	0.13	
CO_2	7.5	0.90	0.3
N_2	0.25	80.8	9.9
Ar	0.25	9.09	9.3
O_2	0.25	21.2	9.3

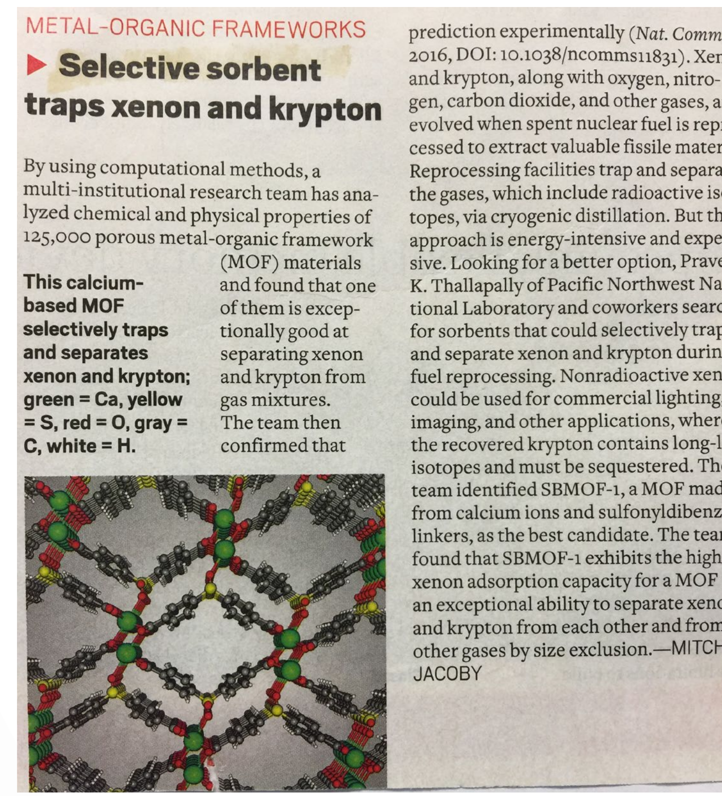
Thallapally, Vienna et. al., USPTO WO/2017/218346A1

Kinetics and Cycle Experiments using CaSDB at Room Temperature



- Faster kinetics, 80% of Xe adsorbed within 10 minutes.
- Cycling study indicate no loss of capacity even after 20 cycles.

Chemical & Engineering News., 94, 26, June 27, 2016

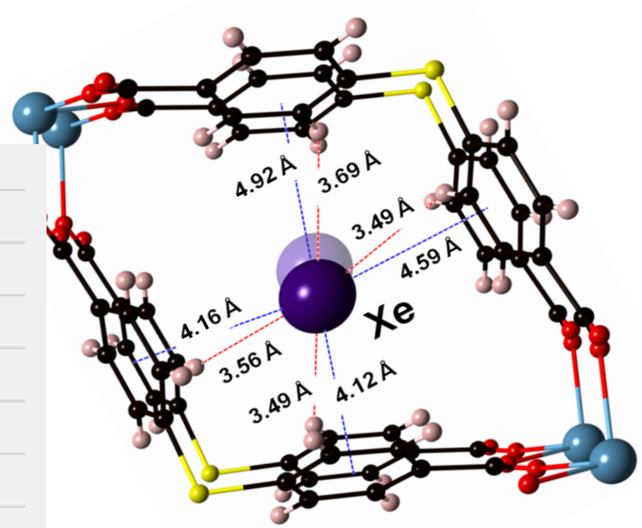


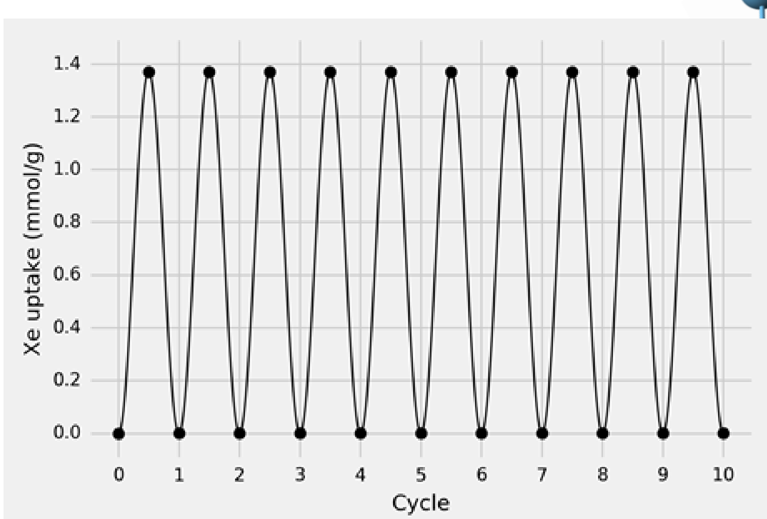
METAL-ORGANIC FRAMEWORKS

Selective sorbent traps xenon and krypton

By using computational methods, a multi-institutional research team has analyzed chemical and physical properties of 125,000 porous metal-organic framework (MOF) materials and found that one of them is exceptionally good at separating xenon and krypton from gas mixtures. The team then confirmed that prediction experimentally (*Nat. Commun* 2016, DOI: 10.1038/ncomms11831). Xenon and krypton, along with oxygen, nitrogen, carbon dioxide, and other gases, are evolved when spent nuclear fuel is reprocessed to extract valuable fissile material. Reprocessing facilities trap and separate the gases, which include radioactive isotopes, via cryogenic distillation. But that approach is energy-intensive and expensive. Looking for a better option, Praveen K. Thallapally of Pacific Northwest National Laboratory and coworkers searched for sorbents that could selectively trap and separate xenon and krypton during fuel reprocessing. Nonradioactive xenon could be used for commercial lighting, imaging, and other applications, whereas the recovered krypton contains long-lived isotopes and must be sequestered. The team identified SBMOF-1, a MOF made from calcium ions and sulfonyldibenzoa linkers, as the best candidate. The team found that SBMOF-1 exhibits the highest xenon adsorption capacity for a MOF an an exceptional ability to separate xenon and krypton from each other and from th other gases by size exclusion.—MITCH JACOBY

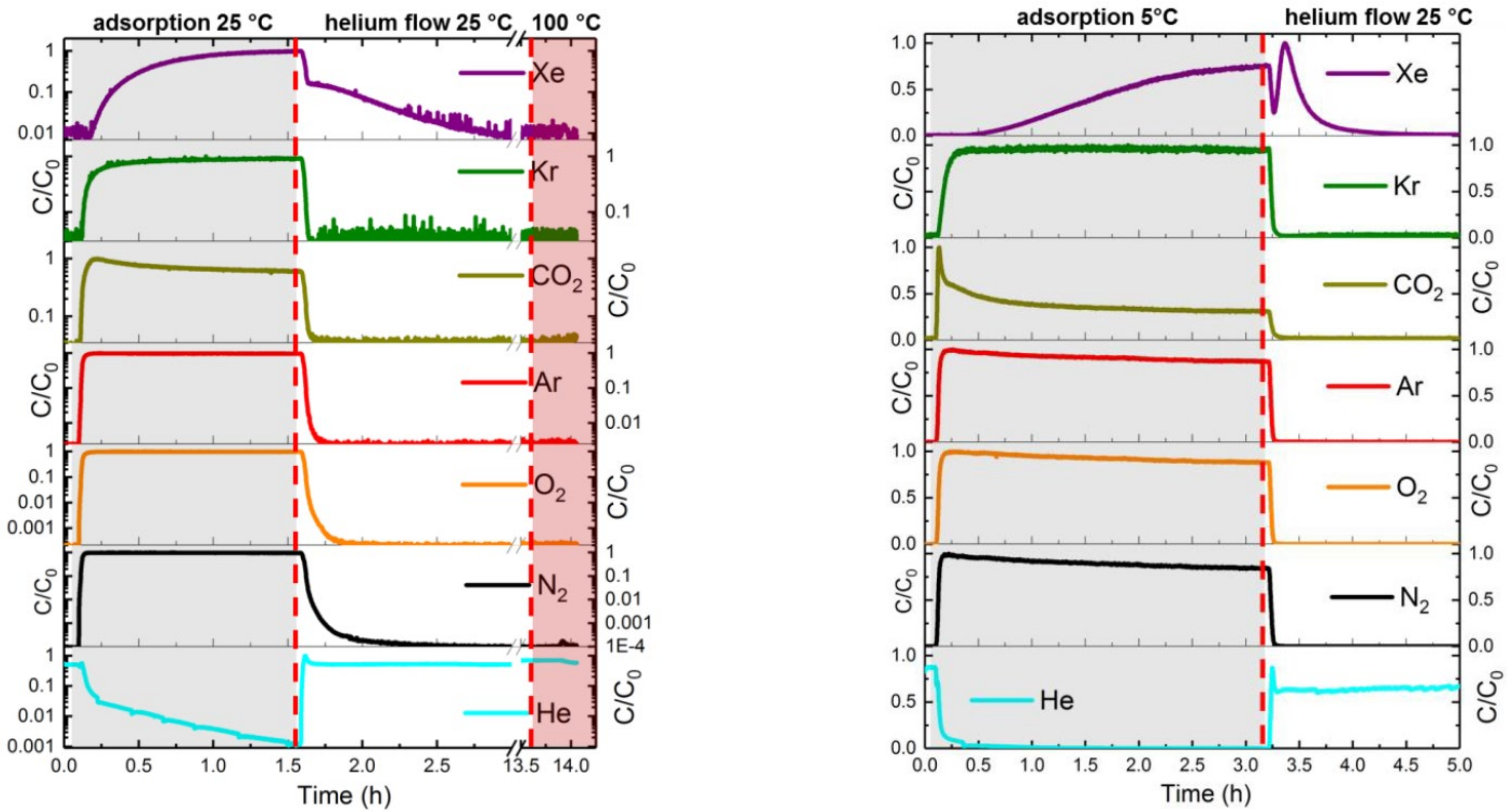
This calcium-based MOF selectively traps and separates xenon and krypton; green = Ca, yellow = S, red = O, gray = C, white = H.





Banerjee and co-workers *Nature Communications,* 2016

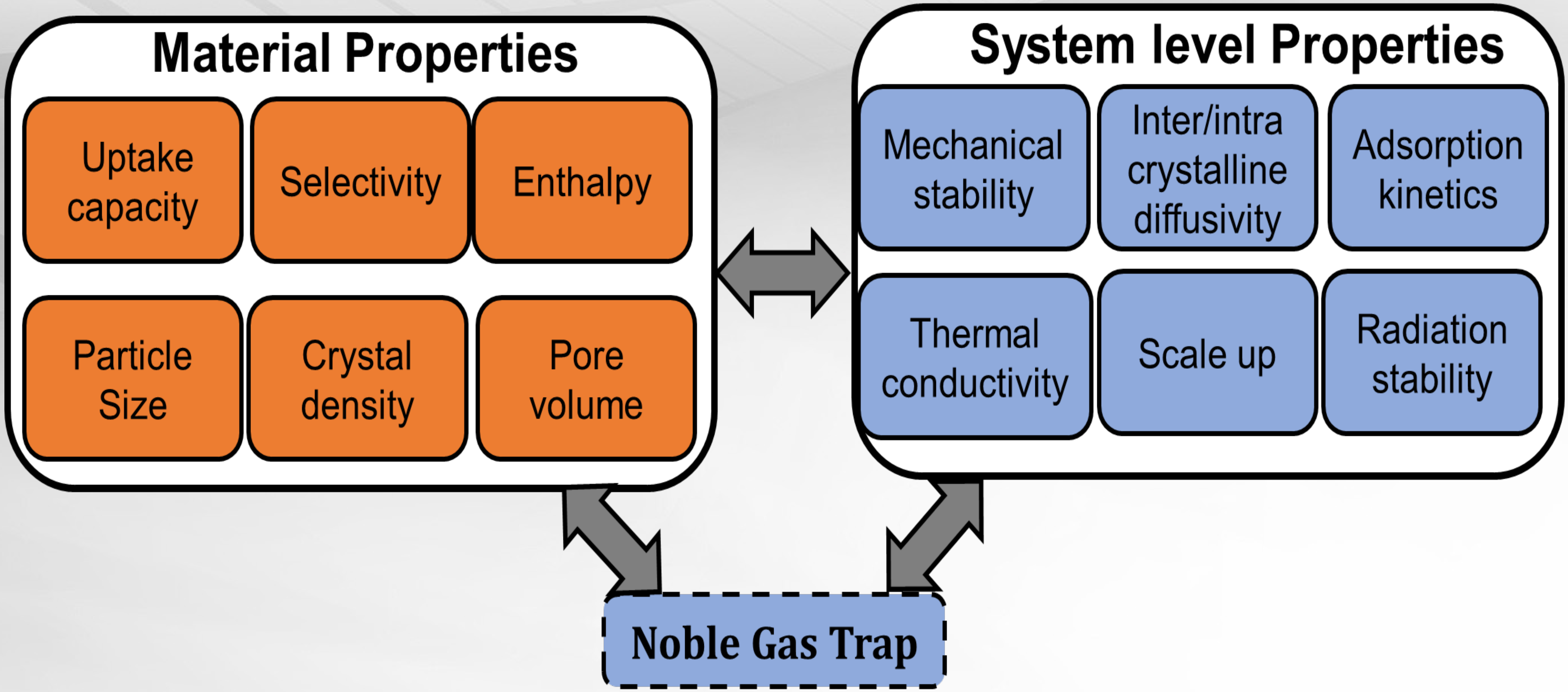
Desorption Process using CaSDB



- Adsorption at 5 C
- 220 mmol/kg of Xe at 5 C, 8 times higher than at RT.
- Desorption at 25 C by He purge
- Desorb within 2 hr with He purge

Thallapally P. K. *et. al.,* DOE NE NTRD report (PNNL 2864), 2019

Noble Gas Devise



1. Thallapally, P. K. Riley., B. J "POLYACRYLONITRILE-METAL-ORGANIC-FRAMEWORK COMPOSITES FOR XE-KR CAPTURE." Pacific Northwest National Laboratory, Richland, WA, 31691-E, Patent pending, **2019**.
2. Thallapally, P. K., Sinnwell, M. S., Shaping crystalline powder materials into engineered bodies, Pacific Northwest National Laboratory, Richland, WA, 31606-E, Patent pending, **2019**
3. Thallapally P.K., S., K. L., Kuang, W., , Develop Engineered forms of MOF with polymers. DOE MRWFD, Pacific Northwest National Laboratory, Richland, WA PNNL-28497 **2019**.
4. Thallapally P.K., S., M.A. Liu, J. and Motkuri, R. K.,, Desorption process of Krypton using Engineered MOF. DOE MRWFD, Pacific Northwest National Laboratory, Richland, WA PNNL-28654. **2018**
5. Thallapally P.K., Perform column breakthrough measurments on best performing sorbent to characterize the co-adsorbed gases. DOE MRWFD, Pacific Northwest National Laboratory, Richland, WA PNNL-26506 **2017**.
6. Thallapally, P. K., Scale up of CaSDB MOF for deep bed measurements. Pacific Northwest National Laboratory, Richland, WA PNNL-27179 **2017**.
7. Thallapally, P. K., Perform Cycle Testing to Measure the Stability and Performance of Sorption Material. pacific Northwest National Laboratory, Richland, WA PNNL-25962 **2016**.

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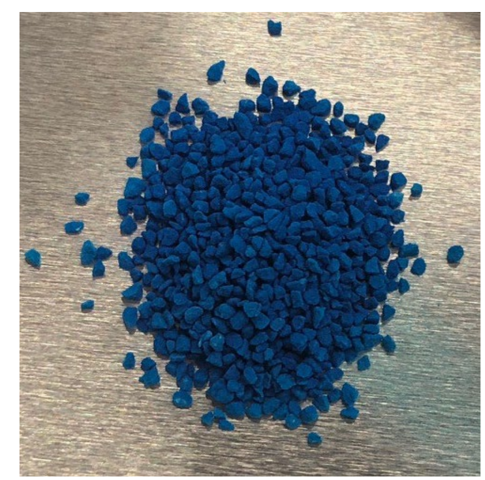
Wet Granulation Method

CaSDB MOF

CuBTC MOF

CuBTC MOF

- Converted CaSDB (RT sorbent) and CuMOF powders into MOF composites using PMMA as a binder.

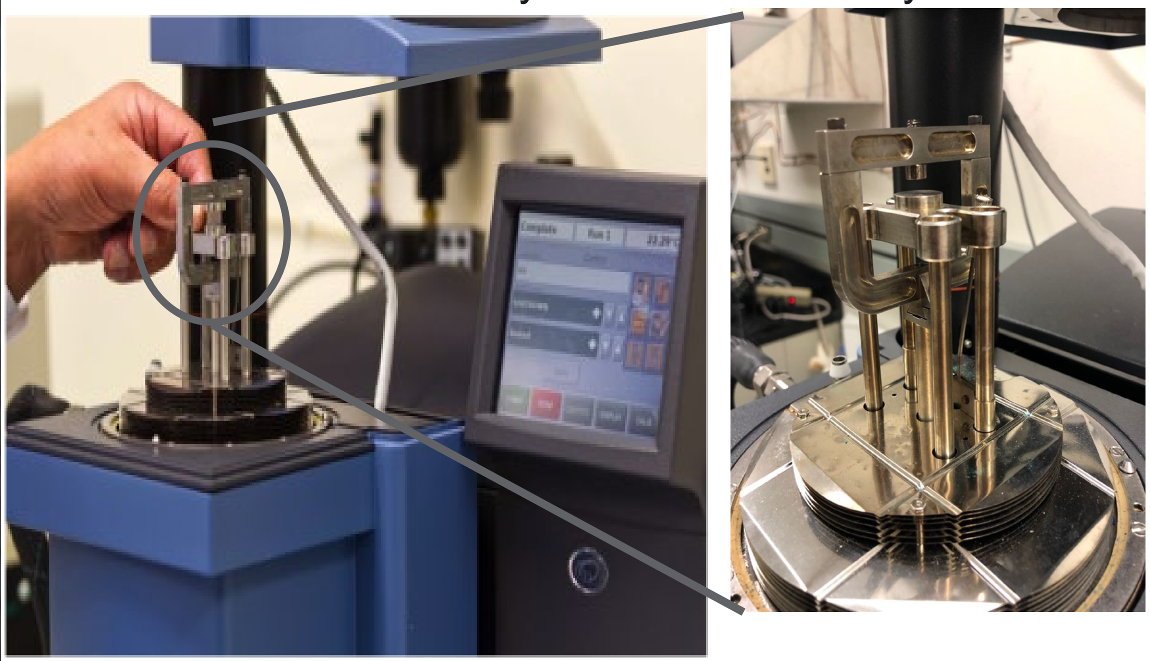


Thallapally et. al., Patent Pending

Thallapally P. K. *et. al.,* DOE NE NTRD report (PNNL 2864), 2019

Mechanical Stability Testing

Dynamic Particle Analyzer



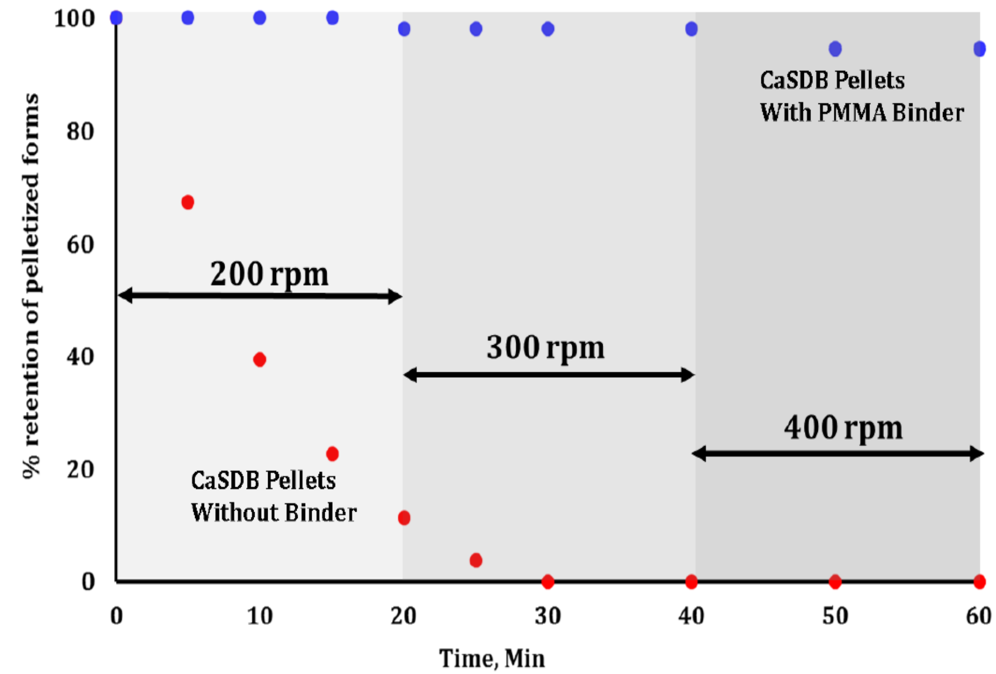


Table 2. Mechanical Properties of CaSDB MOF With and Without Binder in Comparison with Nuclea Grade Activated Carbon Material

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

- 3X higher mechanical stability with minimal loss in capacity compared to nuclear grade activated carbon

Thallapally P. K. *et. al.*, DOE NE NTRD report (PNNL 2864), 2019

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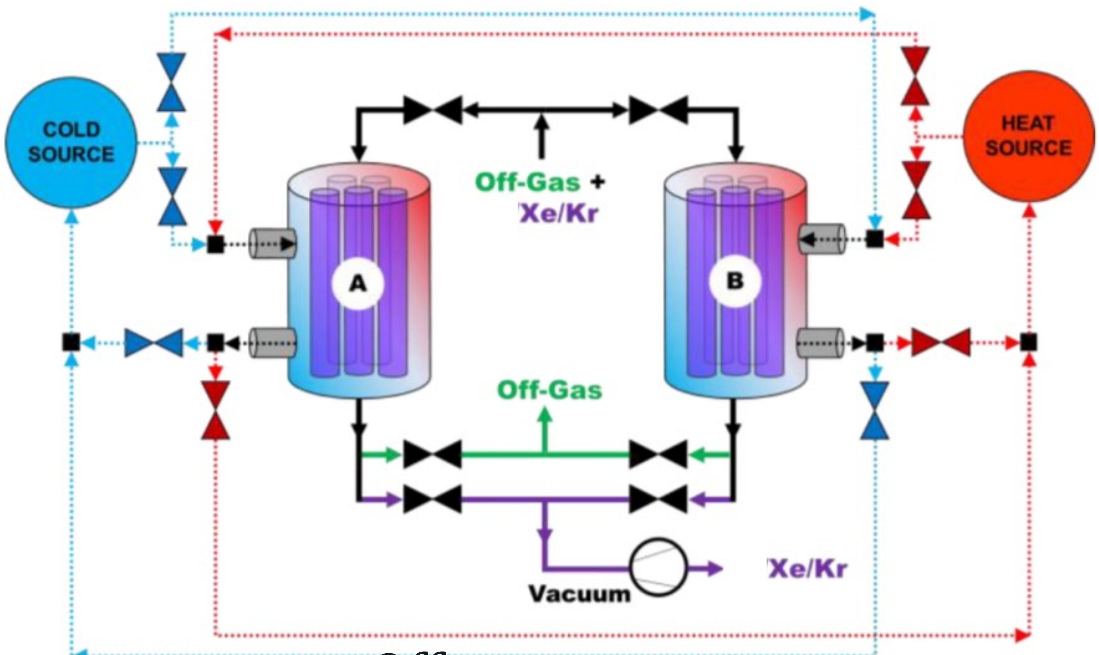
Conclusions

- For Nuclear Energy needs, MOFs are being developed and tested with success.
- More research is necessary to evaluate if MOFs are beneficial to collection of Xe from air.
- MOFs with small pore morphology seems to outperform for Xe/Kr separation.
- CaSDB MOF can selectively remove Xe over CO_2 and water compared to Zeolite.
- Economic analysis suggest RT separation is more economical than commercial cryogenic separation.
- Preliminary radiation stability on CaSDB suggest radiation stable.

Chen *et. al., Nat. Mat.*, 2016



Off-gas system