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Molten Salt Reactor PROGRAM

Update on Radiation Tolerant Metal Organic Frameworks

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Annual MSR Campaign Review Meeting April 16 -17 2024

Objective

Objective was to study the impact of radiation on Xe-selective sorbents (MOFs) to develop a compact off-gas treatment technologies to meet developer (MSR) needs and support licensing activities.

Milestone: Level 3

Title: Radiation stability of xenon selective sorbent under gamma irradiation

Date: September 20th, 2024 (on-schedule)

- Based on calculation a 600 MW reactor is expected to deliver a dose of ~64 Gy to the sorbent from beta decay of Xe radioisotopes and 132.7 Gy from decay of Kr

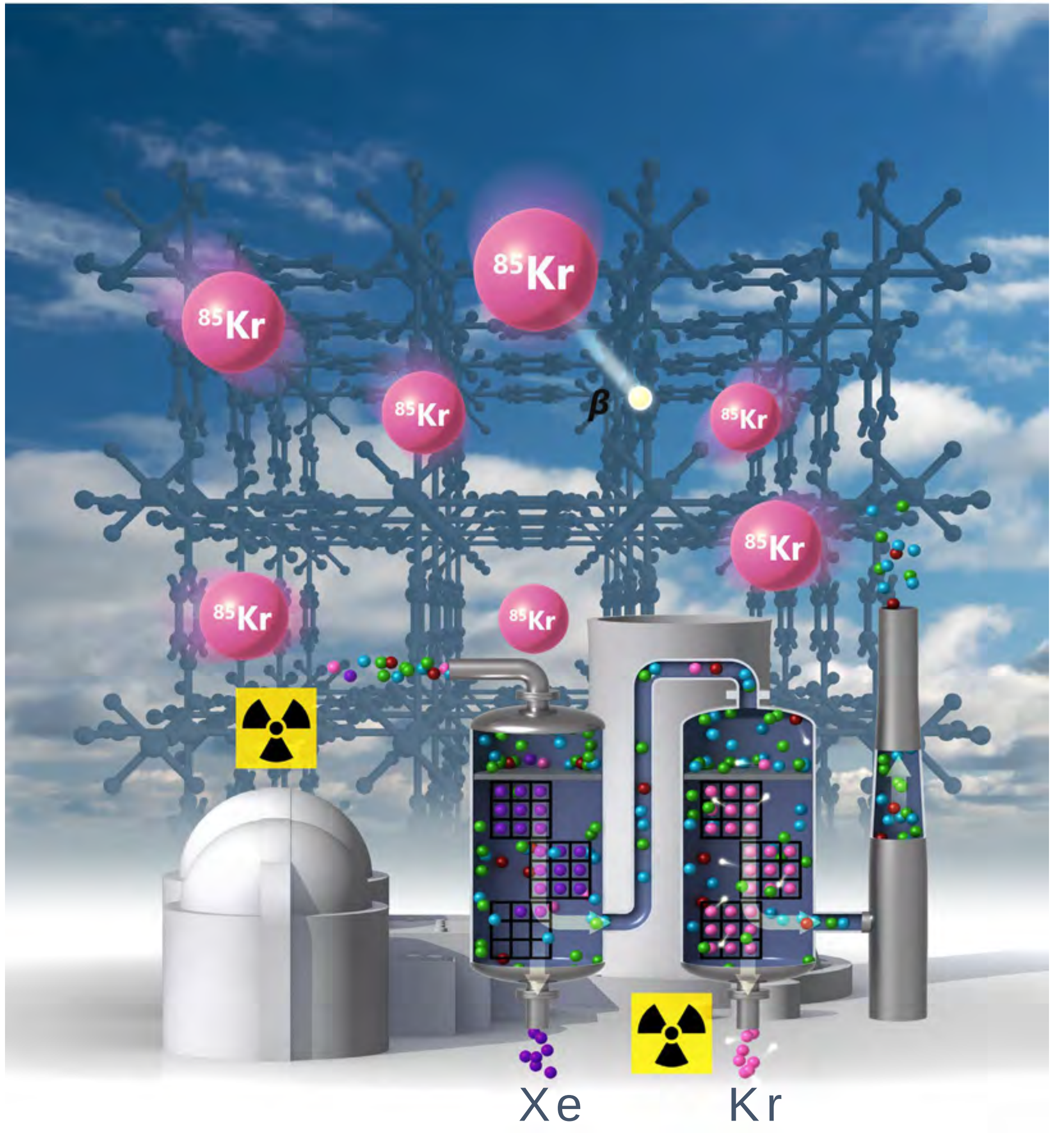
Driving Factors

❑ Why

- U.S. EPA 40 CFR 190 and NRC regulation requires volatile radio nuclides (^{14}C, ^{3}H, ^{131}I, ^{133}Xe and ^{85}Kr) must be captured and sequestered
- Noble gas capture is the most difficult to capture as they are inert by definition
- Potential economic incentive if captured

❑ Major sources of emissions:

- Regular operation of nuclear power plant
- Advanced reactors
- Reprocessing of spend nuclear fuel
- Nuclear accidents
- Medical isotope facilities



Applications of Noble Gases

❖ Fortune Business Insights reported ”The noble gases market size stood at **USD 40.34 billion in 2020** and continue to grow

➢ High purity of Xe

❑ Space Industry – Propellant

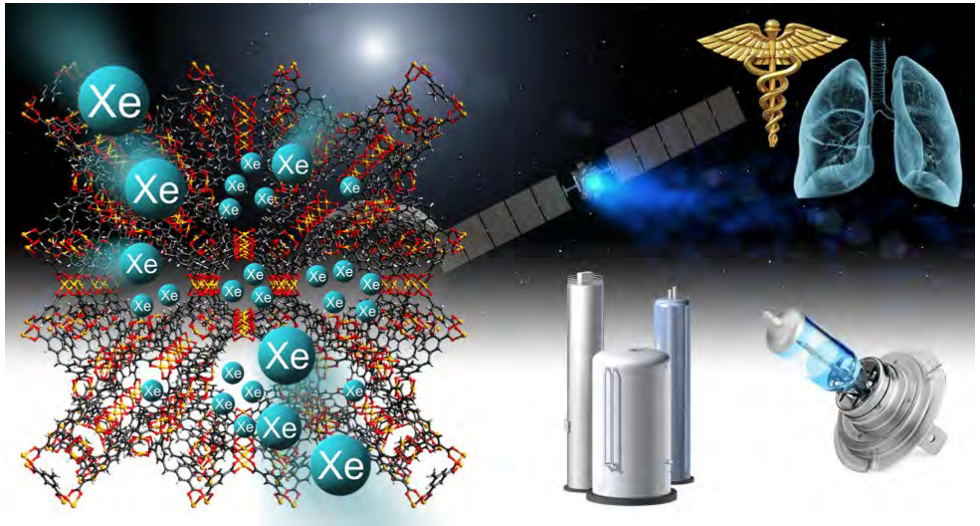
- NASA Xe-ion-thrusters is projected to use approximately 16 metric tones of Xe, for a cost ranging between $81–100 million at today's market price

❑ Medical – Anesthesia, Imaging

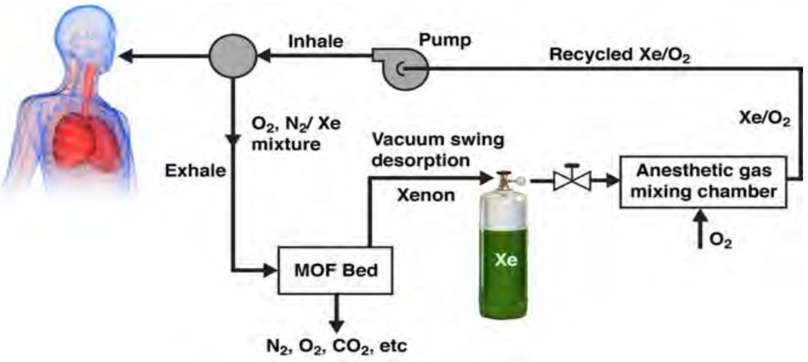
- Approximately 313.4 million major surgical procedures were performed around the world in 2012.
- Due to the supply issues and cost of Xe makes it prohibitive to use. Could open-up huge market

❑ Semiconductor – Plasmas in deposition and etch

- Demand for chips increase so as noble gases (~multi billion-dollar industry)



Elsaidi, Thallapally et. al., *ACS. Mat. Lett.*, 2020



Elsaidi, Thallapally et. al., *Chem. Eur. J.*, 23, 10758 – 10762, 2017

➢ High purity of Kr

❑ Buildings – Window insulation

❑ Automotive – Head lights, Laser lights

❑ Geoscience – to detect the age of ancient ground water

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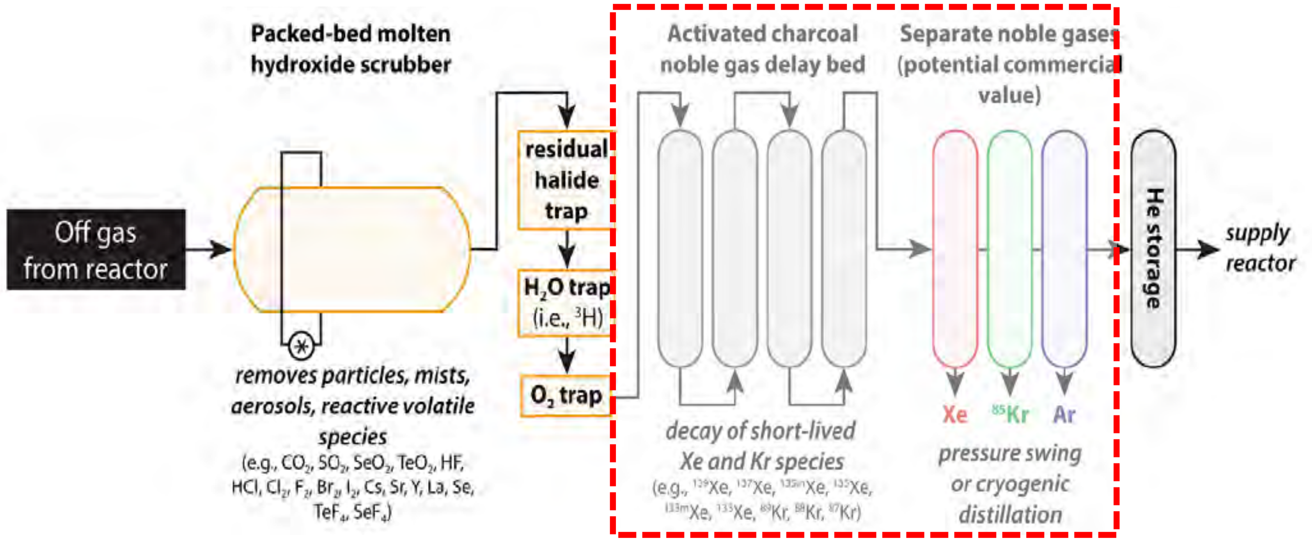
Current Technologies and Alternatives

Current Technology

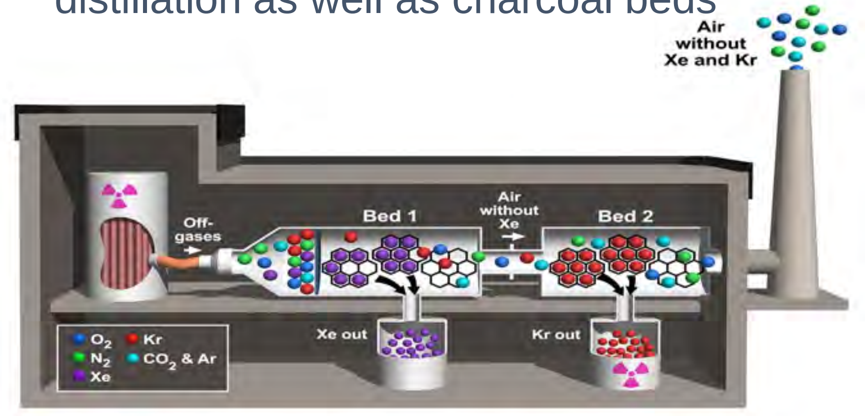
- Cryogenic removal of Xe and Kr
  - Projected to be expensive
  - Potential for O_3 accumulation
  - Hazardous conditions

➢**Charcoal** delay beds (MSR)

- o Requires 4-5 charcoal tanks with 6 – 9 foot in diameter and 50 foot long
- o Fire hazard: Presence of oxygen and heat production due to radioactive decay
- o 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



➢MOFs as Alternate Technology

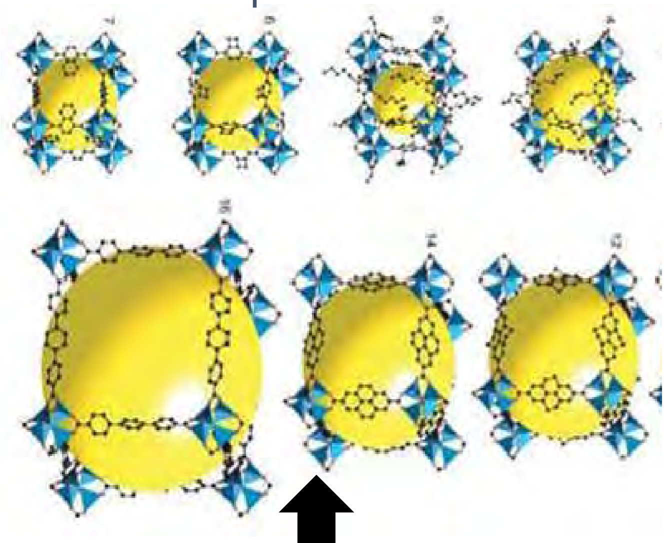
- o Higher capacity and selectivity represents significant cost reduction compared to cryogenic and charcoal beds
- o Smaller size columns, reduced footprint and no fire hazard
- o Remove Xe (non-radioactive) and Kr in separate steps at near RT
  - o Recover process costs by selling Xe?
- o Remove Kr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

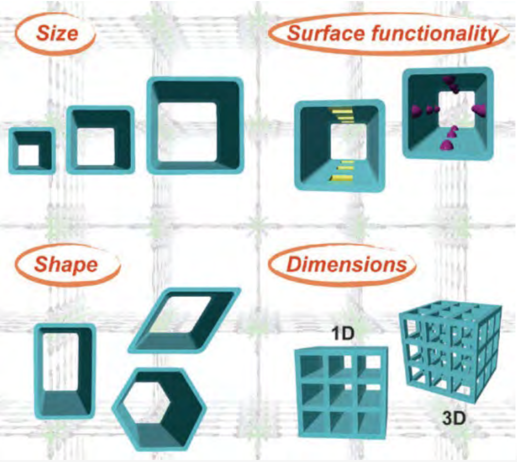
Liu *et. al., Ind. Eng. Res. & Chem.,* 53, 12893-12899, 2014
Thallapally, Vienna et. al., USPTOWO/2017/218346A1
Thallapally, Patricia et. al., Compact and Modular Integrated Off-Gas System and Sensors." Invention Disclosure e-IDR 18117

Metal Organic Frameworks

	Zeolites/Charcoal	MOFs
Safety	Potential bed fires (charcoal)	NA
Type	Inorganic/Organic	Hybrid
Diversity	Limited	Infinite
Pore Size	Fixed	Fine-tunable 0.3 to 10 nm
Surface Area	Up to 1000 m^2/g	Up to 8000 m^2/g
Capacity*	Moderate	High
Selectivity	Need to remove CO_2, and Water	Not required (CaSDB) Yes for water (for some MOFs)
Cycle	200	>2000 (PNNL) (water adsorption n desorption)
Stability	Up to 1 x 10^7 RAD	1.75MGy PNNL and SNL Study Recent literature shows even higher stability
Cost	Varies	Varies;

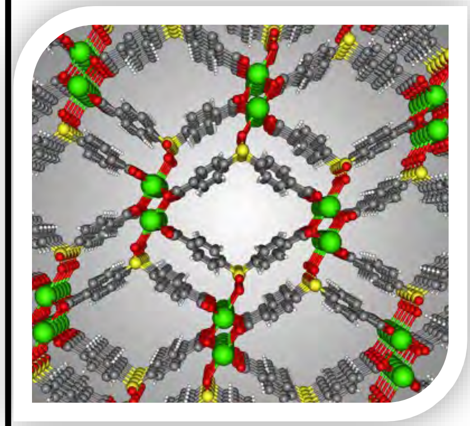
- ►MOFs with higher adsorption capacity, and selectivity represents significant cost reduction compared to existing technology
- ►Smaller-size columns and reduced footprint





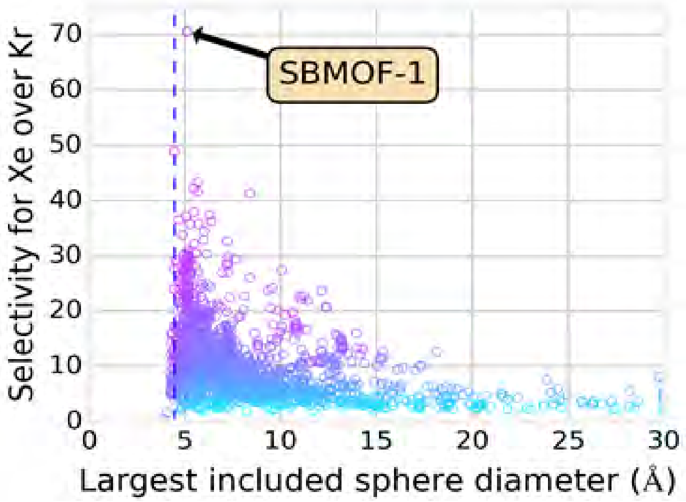
Yaghi *et. al.,* Science 2013, 974; Kitagawa *et. al.,* Angew Chem. 2002; Ferey *et. al.,* Science 2002

Leading Sorbent for Noble Gas Management



- ❑ 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

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



- ❑ A rare example of computationally inspired material discovery

Thallapally, Ali Z. Riley, BJ., Paviet, P., Matyas, J., Vienna, J., Compact and Modular Integrated Off-Gas System and Sensors." Invention Disclosure e-IDR 18117

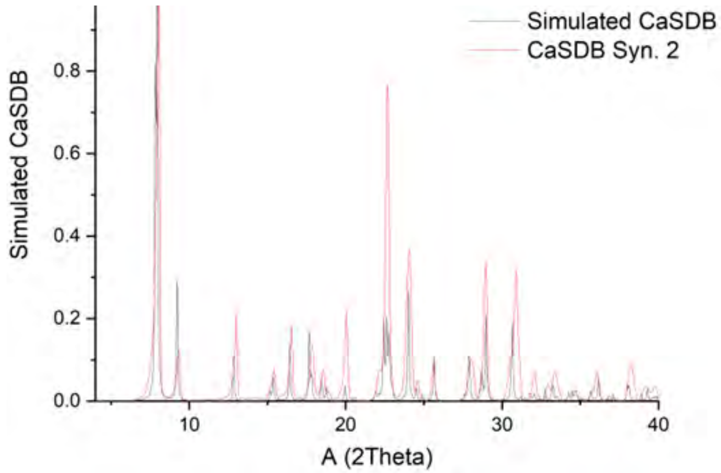
Thallapally, PK., Vienna et. al., USPTO WO/2017/218346A1

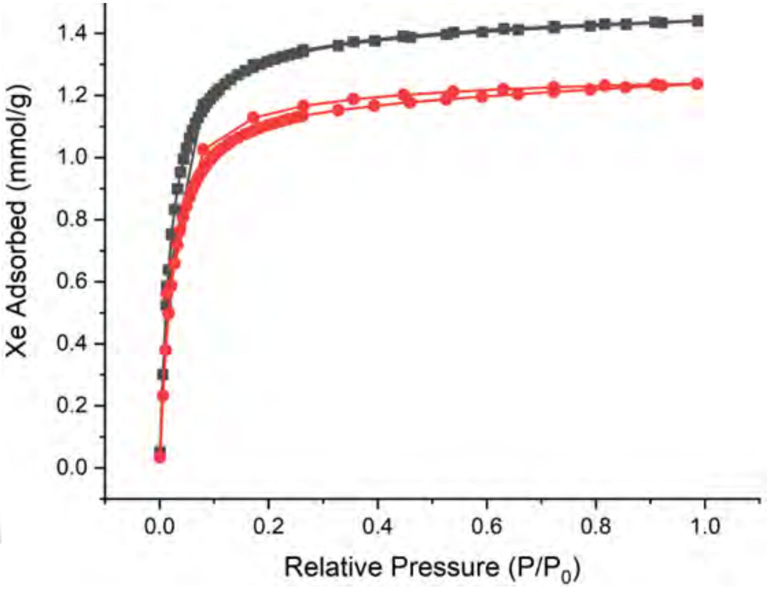
Banerjee, D, Thallapally, PK, Kunapuli R., McGrail, BP, Liu J et al., Surface acoustic wave sensors for refrigerant leak detection., *USPTO WO2021/041359 A1*

Identified a CaSDB MOF as part of DOE MRWFD Campaign

MOF Synthesized at PNNL

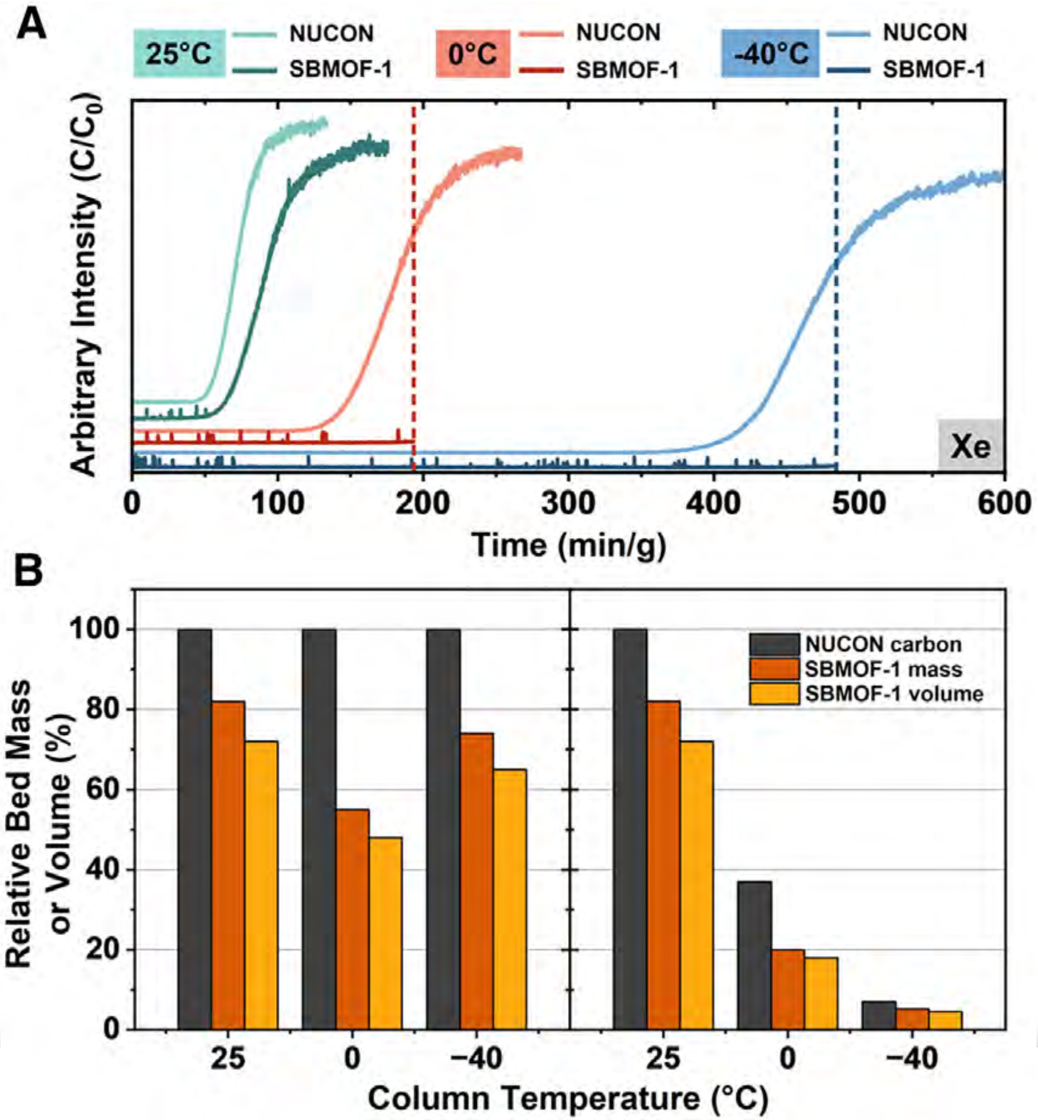
- Identical PXRD confirmed (powder to pellet)
- No amorphous phase
- Reduced BET surface area

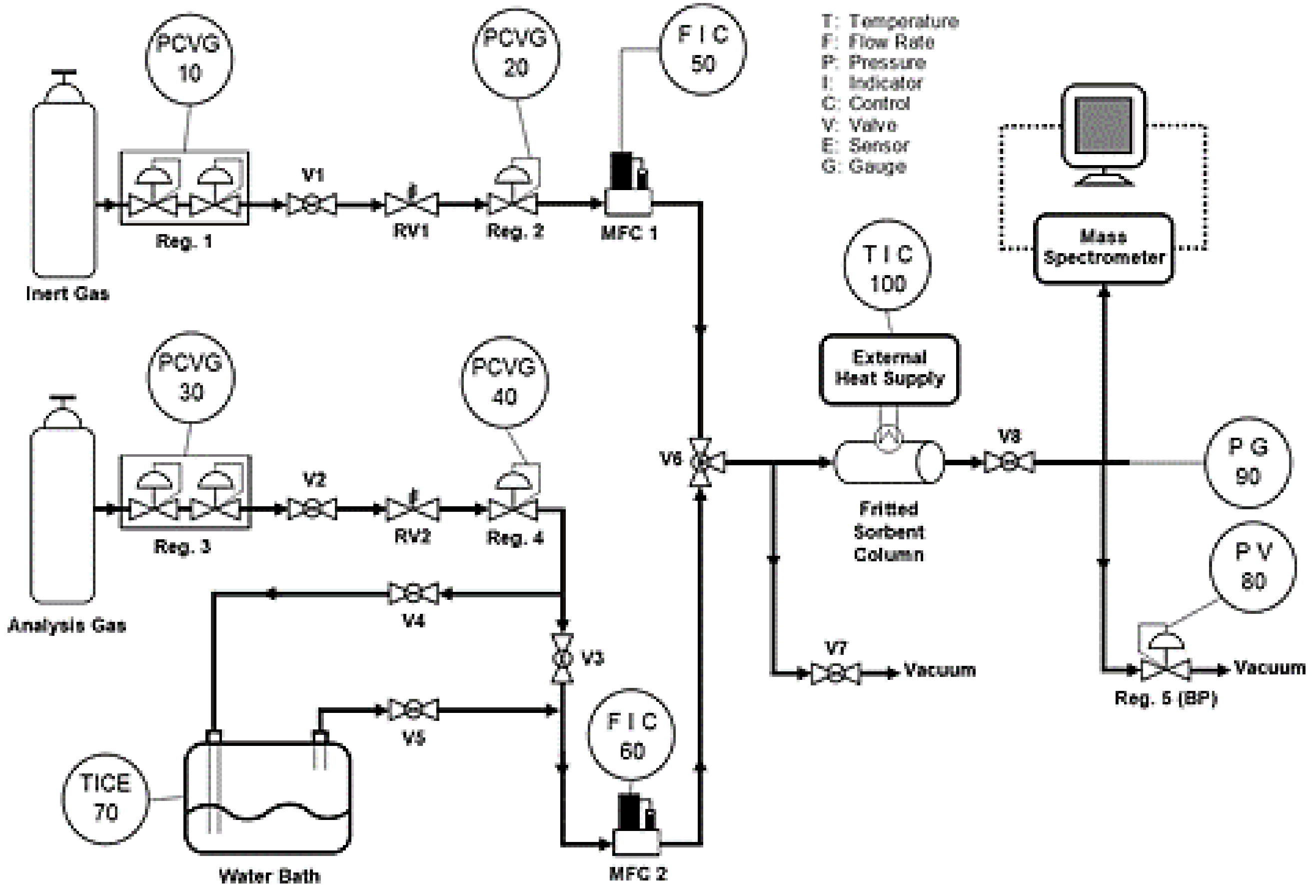




Property	Value
Pressed Pressure	2000 psi for 3 min
Size	600 – 850
BET Surface area	15 m^2/g
BET Surface area, Po	120 m^2/g

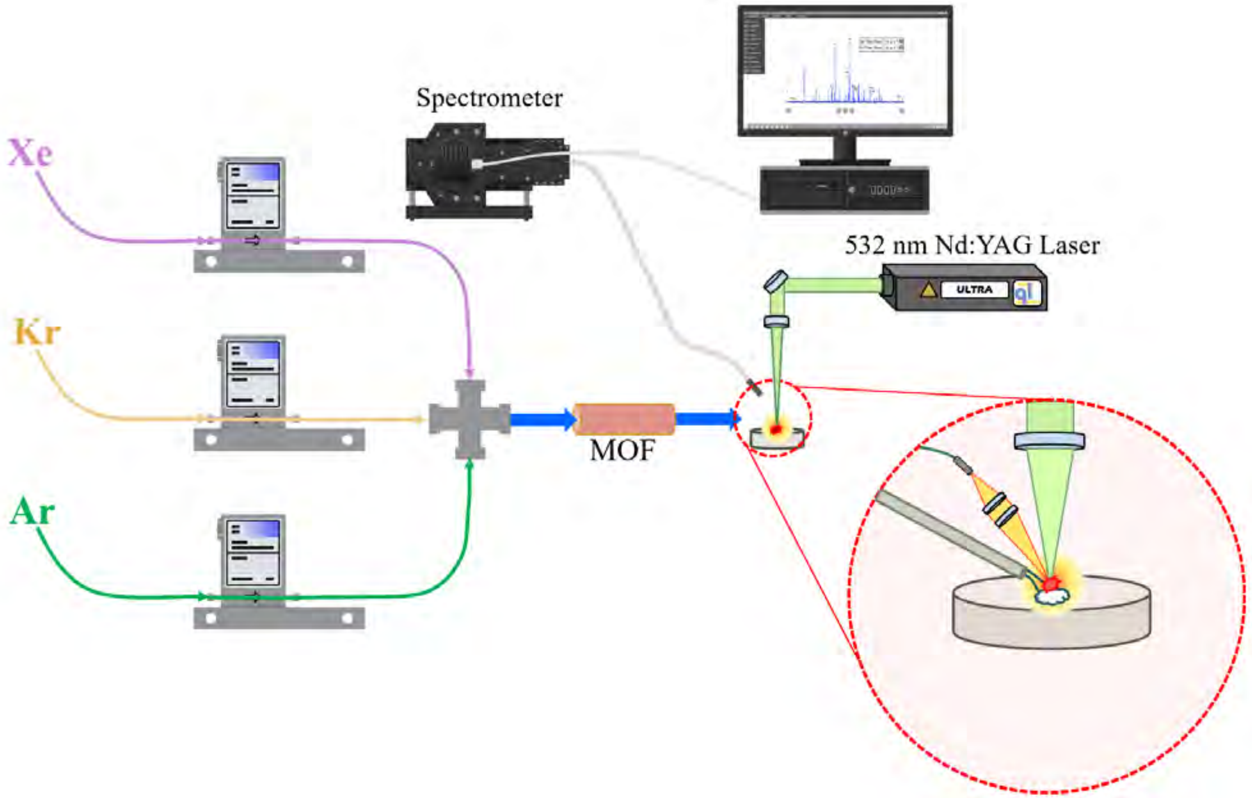
Xe/Kr Capture and Monitoring using RGA

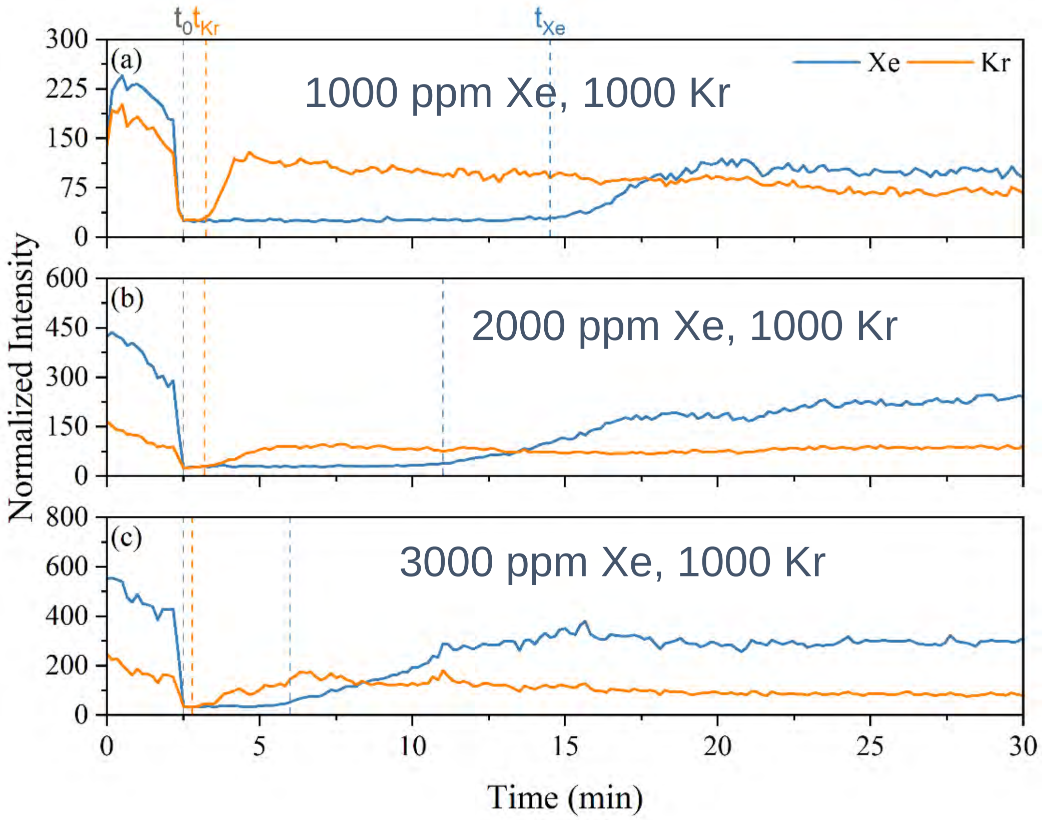




Robinson et al., Cell Reports Physical Science 5, 101829 February 21, 2024 ª 2024).
https://doi.org/10.1016/j.xcrp.2024.101829

MOF-LIBS in Collaboration with ORNL





In collaboration Dr. Andrew Hunter in ORNL (last FY)

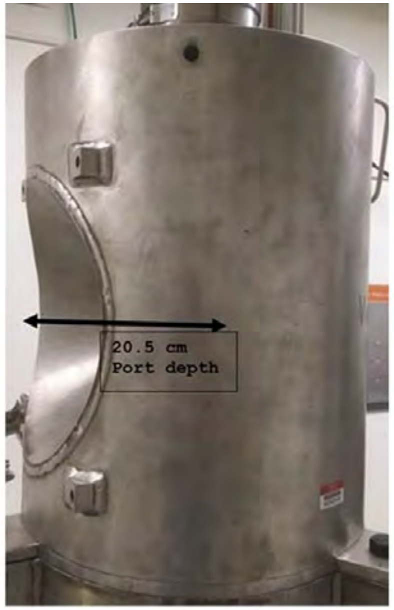
Xe over Kr selectivity = 16

Current FY: Radiation Stability of MOFs

- A wire mesh was concavely shaped into a geometry of ~5.2 cm radius, then taped within the HEF collimator.

- A micro-volume ionization chamber (Exradin Model A16) was used to map the dose rate at various locations across the wire grid for Co-60 source 318-548 (~8000 curies).

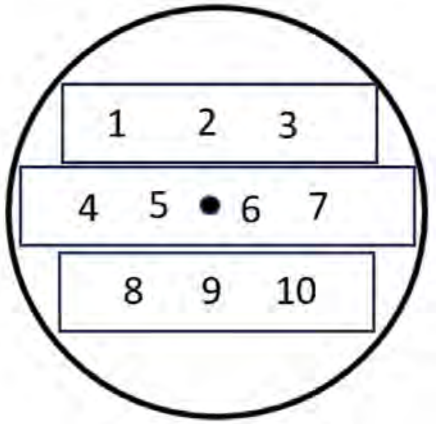
- 5 pairs of locations within 1-2% dose rates were identified (provided in the graphic on the right).



Current FY: Radiation Stability Cont.

- The Grid locations where the labeled vial samples were secured/positioned are shown in the image.

- Table below shows the associated dose rates and irradiation durations to achieve the 100-500 Mrad dose levels.
  - Note the dose rates are associated with the estimated center of volume of the powder within the glass vials, which was ~4mm out from the surface of the wire grid.



Grid Pair Locations	Vial Samples at these Locations	Dose Rate (Mrad/hr)	Irradiation Time (hours)	Total Dose (Mrad)
8/9	1A/2A	2.36	42.45	100
4/5	1B/2B	2.13	94.03	200
2/10	1C/2C	2.07	145.08	300
1/6	1D/2D	2.04	196.24	400
3/7	1E/2E	1.93	42.45	82.145
8/9	1E/2E	2.36	177.37	417.86

Samples 1A and 2A: 100 Mrad
Samples 1B and 2B: 200 Mrad
Samples 1C and 2C: 300 Mrad
Samples 1D and 2D: 400 Mrad
Samples 1E and 2E: 500 Mrad

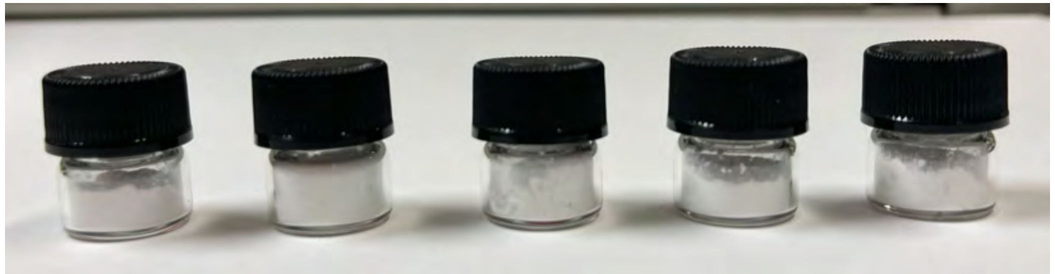
Samples 1A-E CuMOF
Samples 2A-E: CaSDB

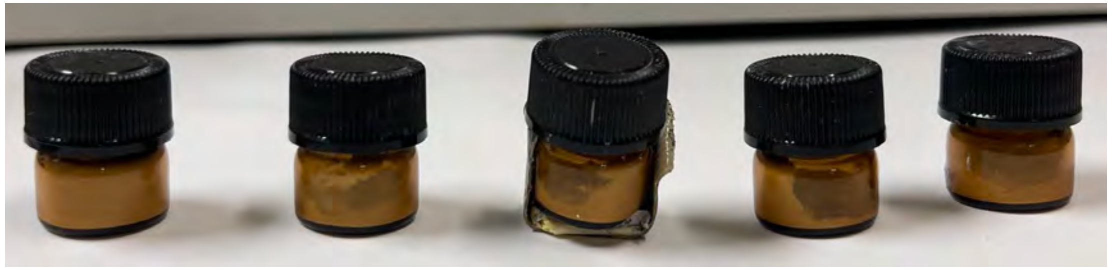
Current FY: Radiation Stability Cont.

Pre-Radiation

From left to right:2A:2E

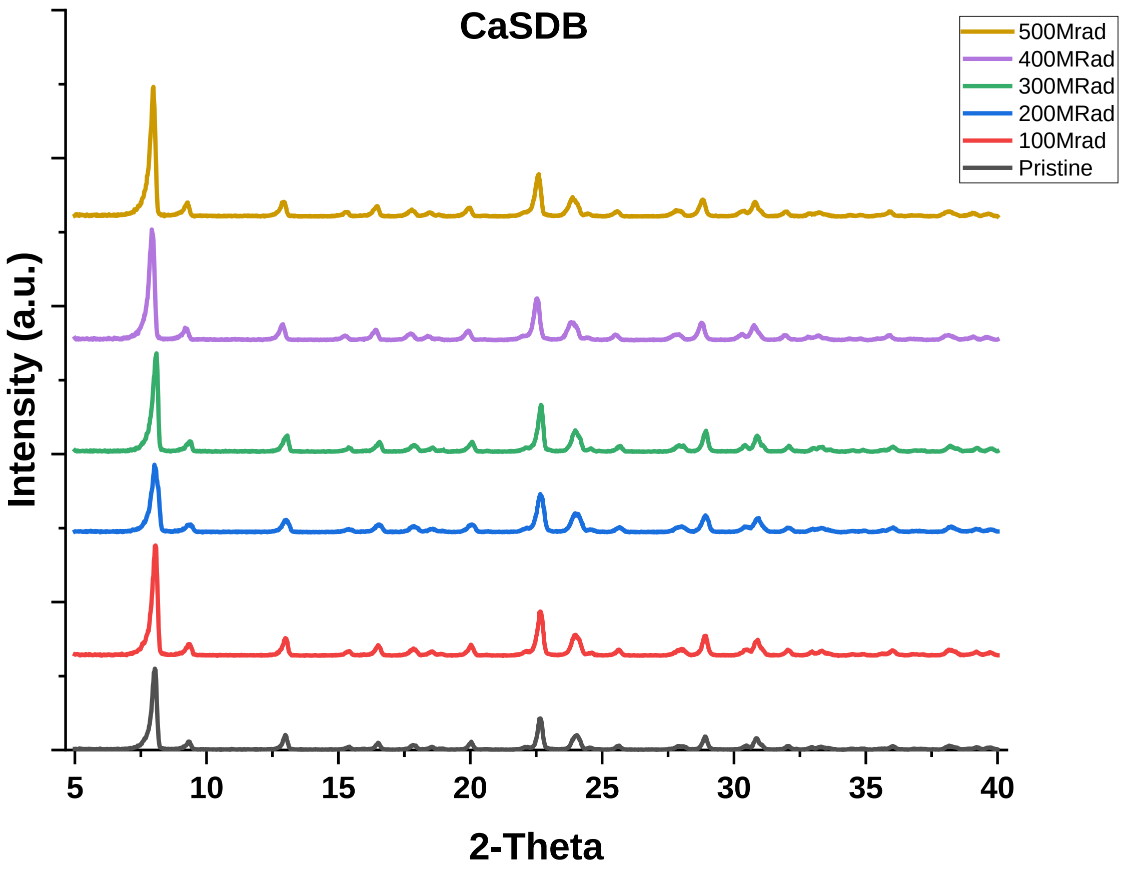
Post-Radiation

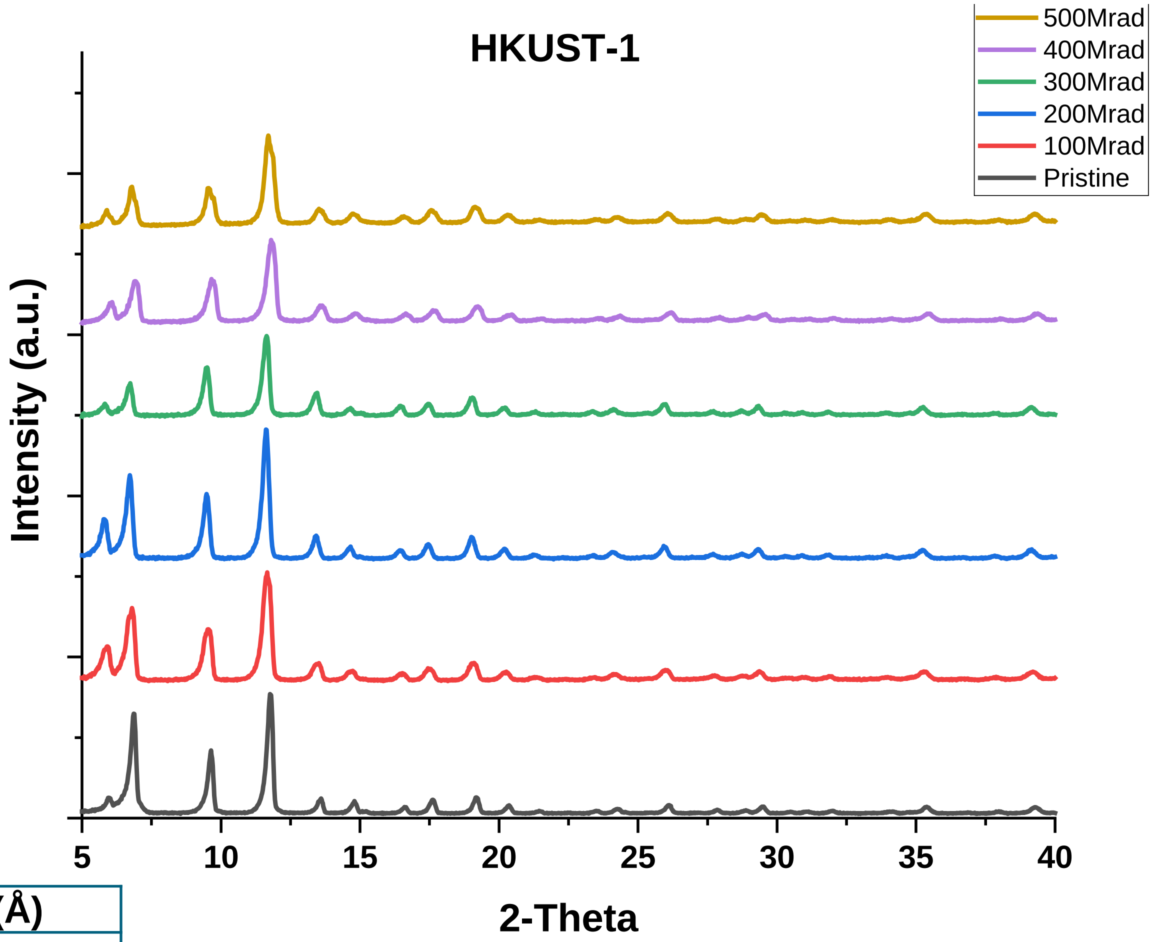




From left to right:1A:1E

XRD Patterns Post Irradiation

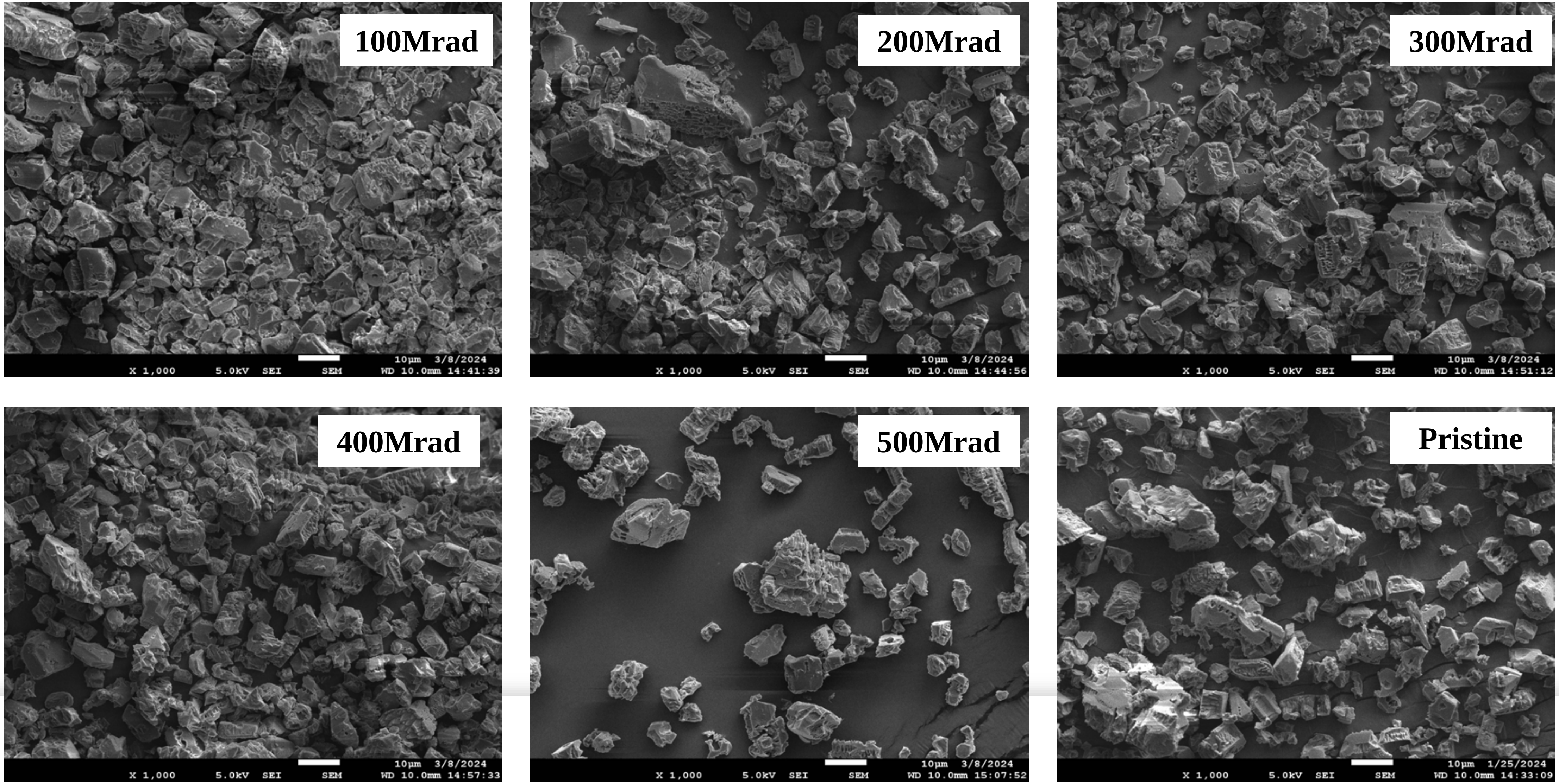




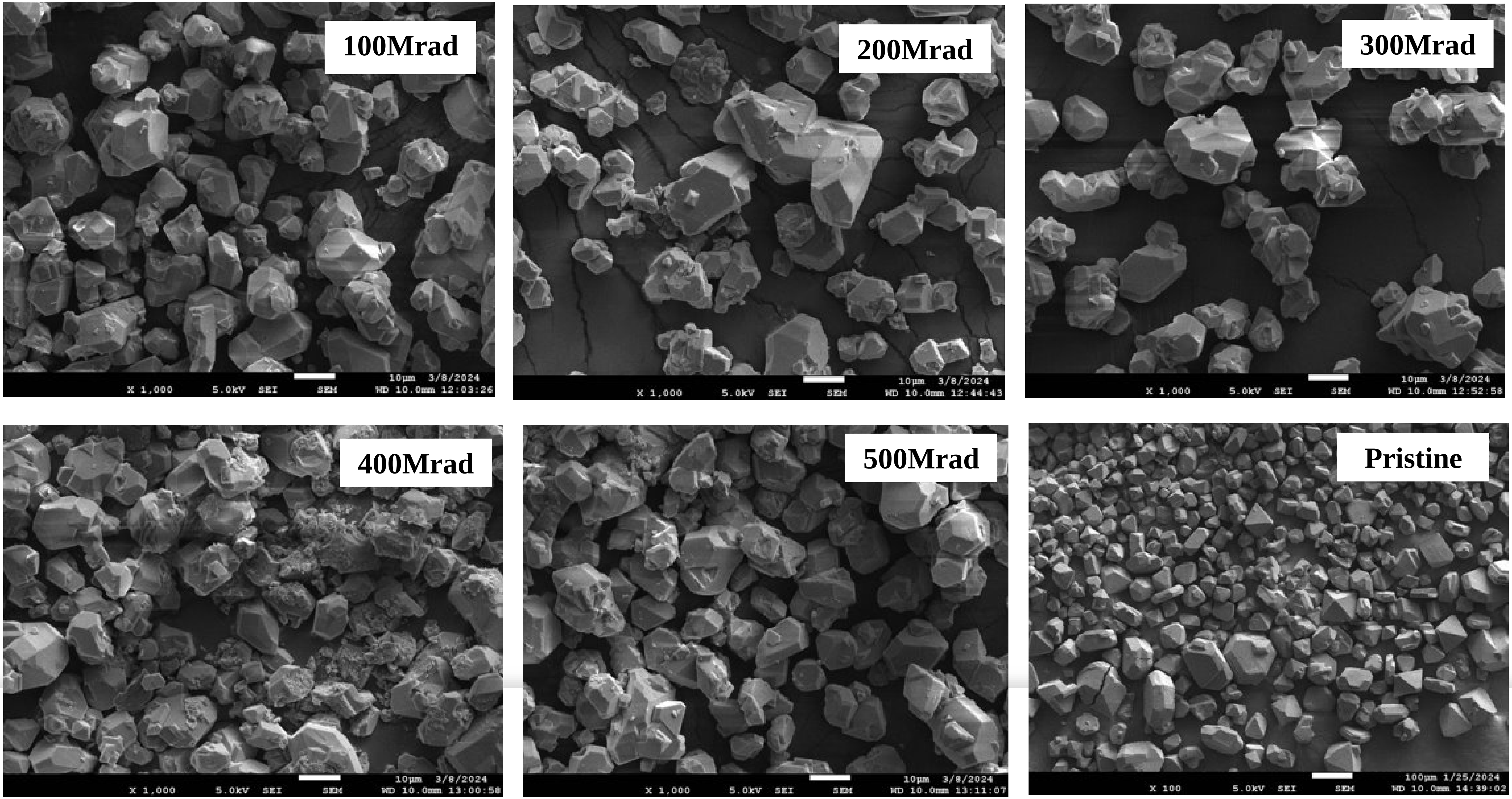
CaSDB	a (Å)	b (Å)	c (Å)
Pre-irradiated	11.832	5.585	22.846
100Mrad	11.841	5.591	22.857
200Mrad	11.852	5.590	22.844
300Mrad	11.861	5.589	22.827
400Mrad	11.864	5.592	22.846
500Mrad	11.863	5.592	22.853
% change in unit cell parameter	-0.3	-0.1	-0.1

Dr. Jarrod Crum (PNNL) for fitting the XRD data

SEM Images Pre and Post Irradiation: CaSDB



SEM Images Pre and Post Irradiation: HKUST-1



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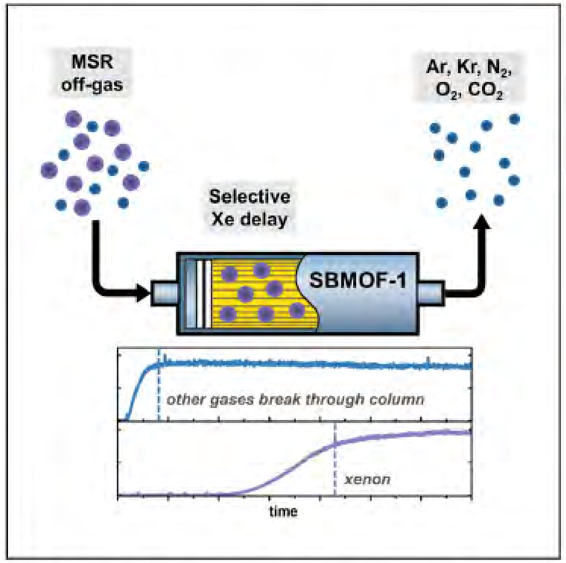
Noble gas management with radiation-tolerant MOF for molten salt reactors



MSRs are one of the advanced generation IV reactors capable of meeting modern energy demands. However, engineered solutions are still required for the continuous online mitigation of radioactive noble gas byproducts. As reported by Robinson et al., developing selective sorbents would accelerate the widespread adoption of MSR technology and progress the global decarbonization of energy production.

Alexander J. Robinson, Hannah M. Johnson, Saehwa Chong, Brian J. Riley, Mark K. Murphy, Parker Okabe, Praveen K. Thallapally

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Highlights

- MSRs are seeking more effective sorbent technology for processing noble gases
- SBMOF-1 selectively adsorbs Xe over Kr and Ar in dynamic breakthrough experiments
- SBMOF-1 pellets outperform the current activated carbon sorbent for MSRs
- More suitable pellet binder materials are still required for industrial application

Robinson et al., Cell Reports Physical Science 5, 101829
February 21, 2024 © 2024 The Author(s).
https://doi.org/10.1016/j.xcrp.2024.101829

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Monitoring Xenon Capture in a Metal Organic Framework Using Laser-Induced Breakdown Spectroscopy

by Hunter B. Andrews [1,*], Praveen K. Thallapally [2] and Alexander J. Robinson [2]

1 Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA
2 Pacific Northwest National Laboratory, Richland, WA 99352, USA

What Next in FY'25?

- XRD results show no change before and after irradiation.
- Continue to characterize the post-irradiated MOF samples to demonstrate the radiation stability (FY'24).
- Set-up parallel experiments using the irradiated and the non irradiated MOF (engineered form) to trap Xe (FY'25).
  - Can we capture same amount of Noble gas Xe?
  - Vary the irradiation dose from low to high and each time measure the Xe capture using RGA (PNNL) and LIBS (ORNL)
- Integrate MOF capture technology with molten salt test loop and LIBS in collaboration with ORNL

Acknowledgements

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- **Dr. Stephen Kung (DOE, NE-4)**

Dr. John Vienna (PNNL)
Dr. Brian Riley (PNNL)
Dr. Joseph Matyas (PNNL)
Mr. Jarrod Crum (PNNL)
Dr. Keerthana Krishnan (PNNL)

Thank you

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