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Impact of Radiation on Metal Organic Frameworks

Noble Gas Capture and Monitoring

Praveen K. Thallapally, Matthew Hurlock, Keerthana Krishnan and Mark Murphy,

Pacific Northwest National Laboratory, Richland, WA

Argonne NATIONAL LABORATORY · INL Idaho National Laboratory · Los Alamos NATIONAL LABORATORY · OAK RIDGE National Laboratory · Pacific Northwest NATIONAL LABORATORY · Sandia National Laboratories · U.S. DEPARTMENT of ENERGY Office of Nuclear Energy

FY Status Update

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.

- M3AT-25PN0702071: Gamma radiation study on CaSDB and CuBTC MOF Powders – Feb 28th 2025 – **Completed**
- Under the radiation spotlight: Effect of radiation dose on a copper-based MOF, "*Keerthana Krishnan†, Matthew J. Hurlock†, Sun Hae Ra Shin†, Mark K. Murphy, Praveen K. Thallapally* ACS App Mat and Int. 2025 Submitted.*

Upcoming Milestone:

- M3AT-25PN0702072: Scale up and fabricate MOF engineered particles to support FY25 irradiation experiments – 9/30/2025 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. See Cell Reports Physical Science 5, 101829, February 21, 2024
  - Two MOF powder samples (CuBTC and CaSDB) were irradiated up to 5000 kGy of Gamma Radiation. An order of magnitude higher than observed

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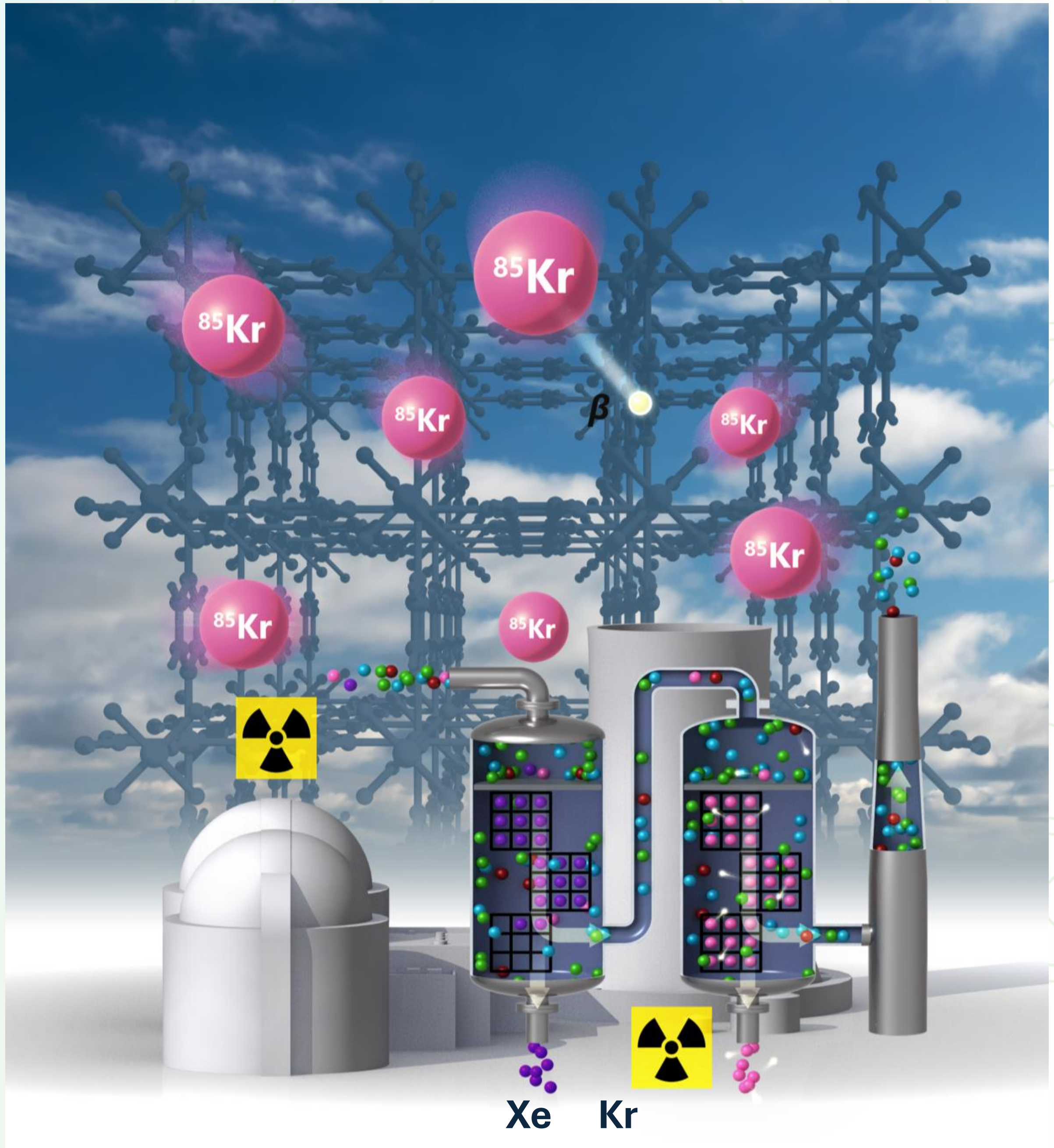
Driving Factors

❑ 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



Elsaidi SK., Thallapally PK *et al.* Radiation-resistant metal-organic framework enables efficient separation of krypton fission gas from spent nuclear fuel. ***Nat Commun*** **11**, 3103 (2020).

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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

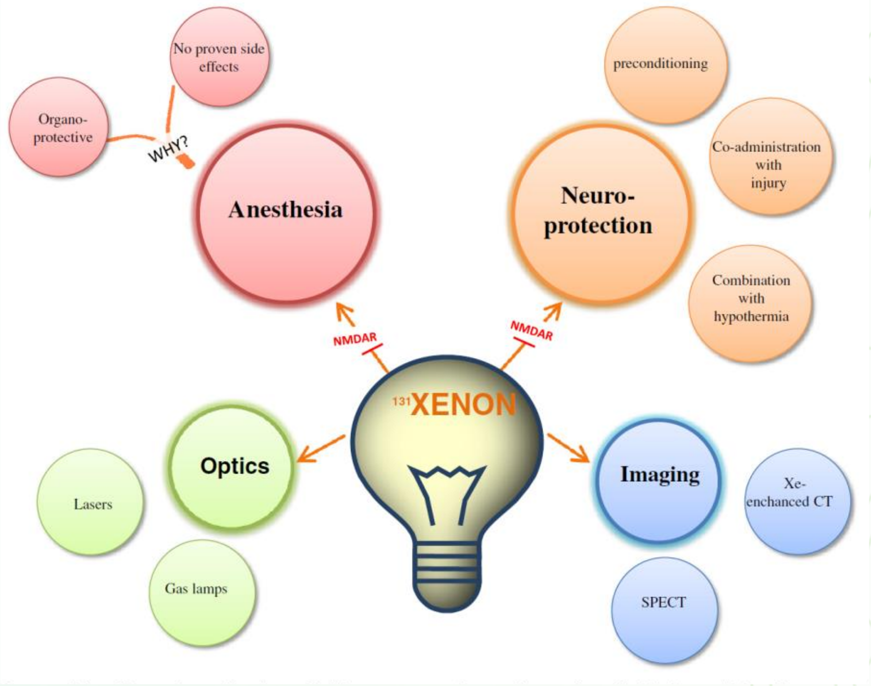
- NASA Xe-ion-thrusters is projected to use approximately 16 metric tones of Xe, for a cost ranging between $81–100 million at today's market price

❑ Medical – Anesthesia, Imaging

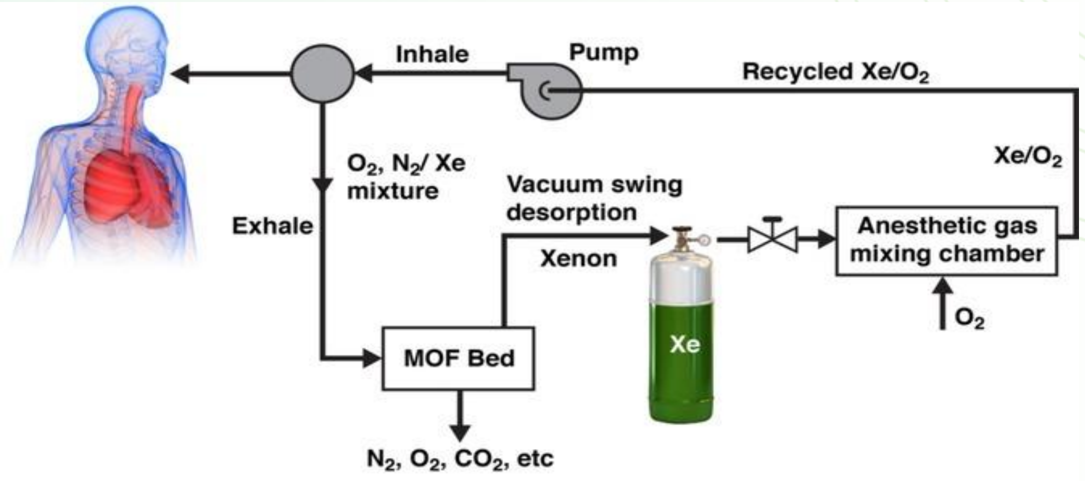
- Approximately 313.4 million major surgical procedures were performed around the world in 2012.
- Due to the supply issues and cost of Xe makes it prohibitive to use. Could open-up huge market

❑ Semiconductor – Plasmas in deposition and etch

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



Esencan et al. Medical Gas Research 2013, 3:4



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

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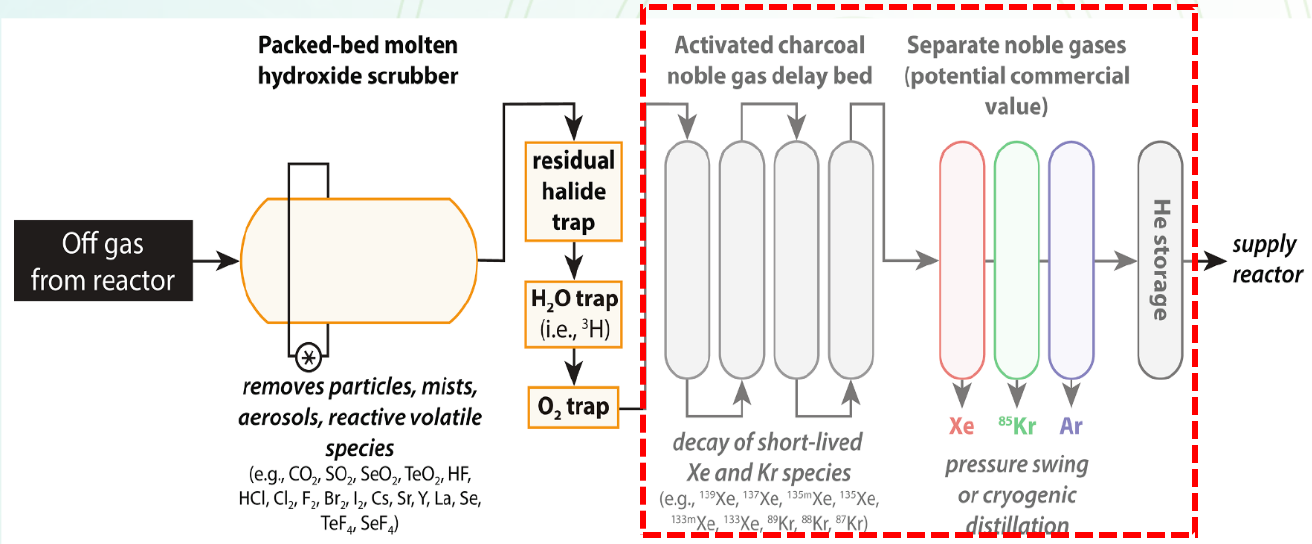
Current Technologies and Alternatives

Current Technology

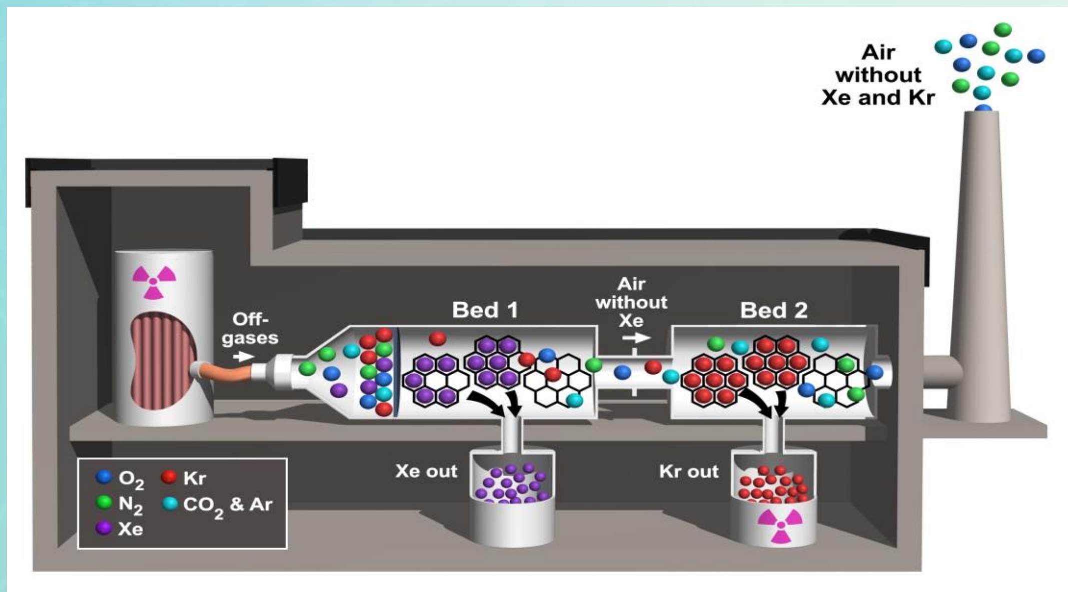
- Cryogenic removal of Xe and Kr
  - Projected to be expensive
  - Potential for O_3 accumulation
  - Hazardous conditions

➢**Charcoal** delay beds (MSR)

- 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, J and Thallapally P.K *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

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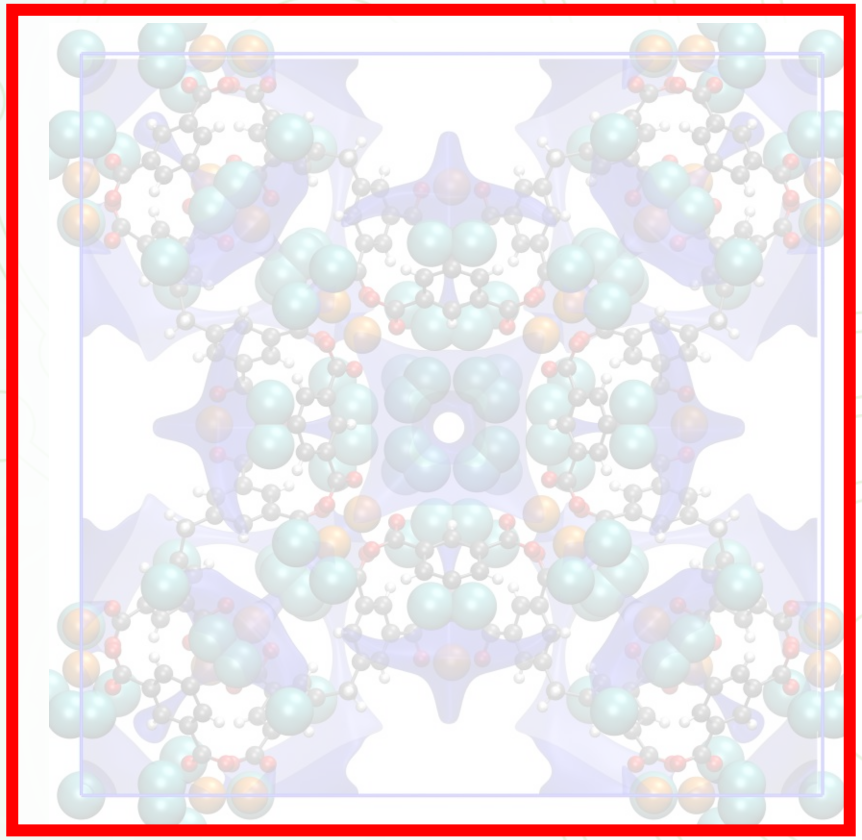
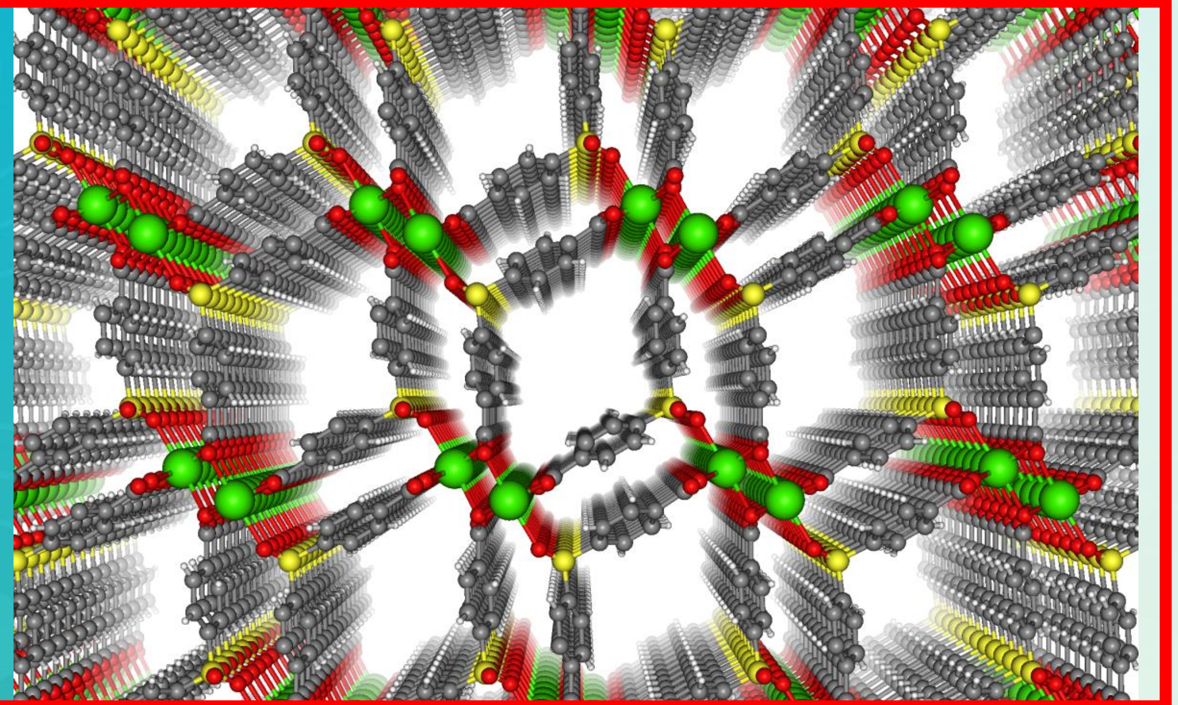
Sorbent Selection for Radiation Experiments

- Previous work on advanced functional materials for noble gas capture (DOE NE-4)
  - AI/ML simulations
  - Lessons from biological molecules
- Sorbents that are easy to scale up
- Sorbents that have exceptional Xe capacity and selectivity



CuBTC loaded with Xe



CaSDB MOF

- Identified CuBTC and CaSDB for radiation experiments
- Surface are – 2200 and 250 m^2/g
- CuBTC with 3 different cavities *Vs* CaSDB 1D channels

Elsaidi, S, Thallapally, PK et. al., **ACS Materials Lett**. 2020, 2, 3, 233–238

CaSDB is going though exhaustive testing under ARPA-E program

Banerjee, D., Thallapally PK. *et al.* Metal–organic framework with optimally selective xenon adsorption and separation. ***Nat Commun* 7**, ncomms11831 (2016).

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Radiation Stability Testing

- PNNL's Radiological Exposures and Metrology Lab (REM Lab) contains highly characterized beta, neutron, X-ray and gamma-ray fields.
- Support a wide range of applications, including radiation effects on materials and electronics.
- Within the higher energy photon fields, PNNL can provide elevated temperatures (up to 200 °C), humidity (20 – 90%), and vacuum environments.
- These fields are calibrated in terms of either *Exposure*, *Absorbed Dose or Dose Equivalent.*

Radiation experiments are planned during FY'25

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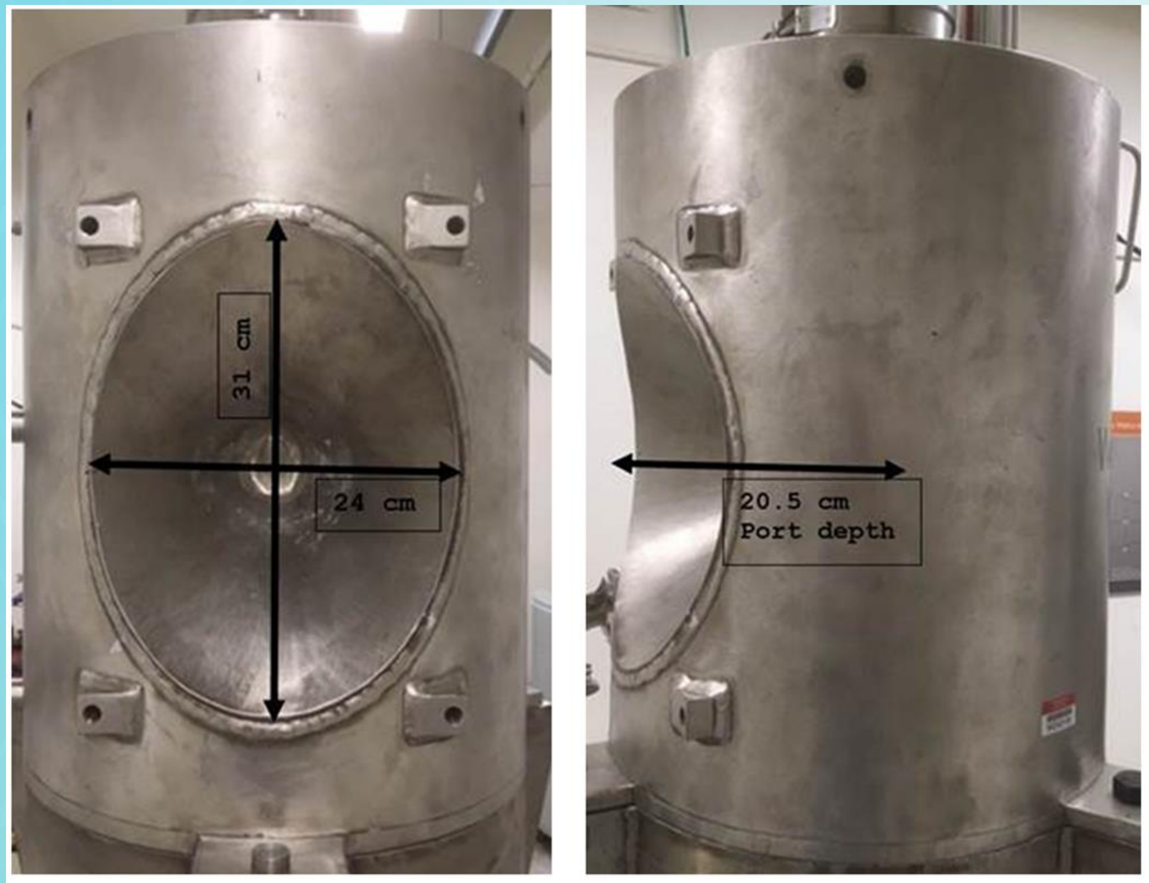
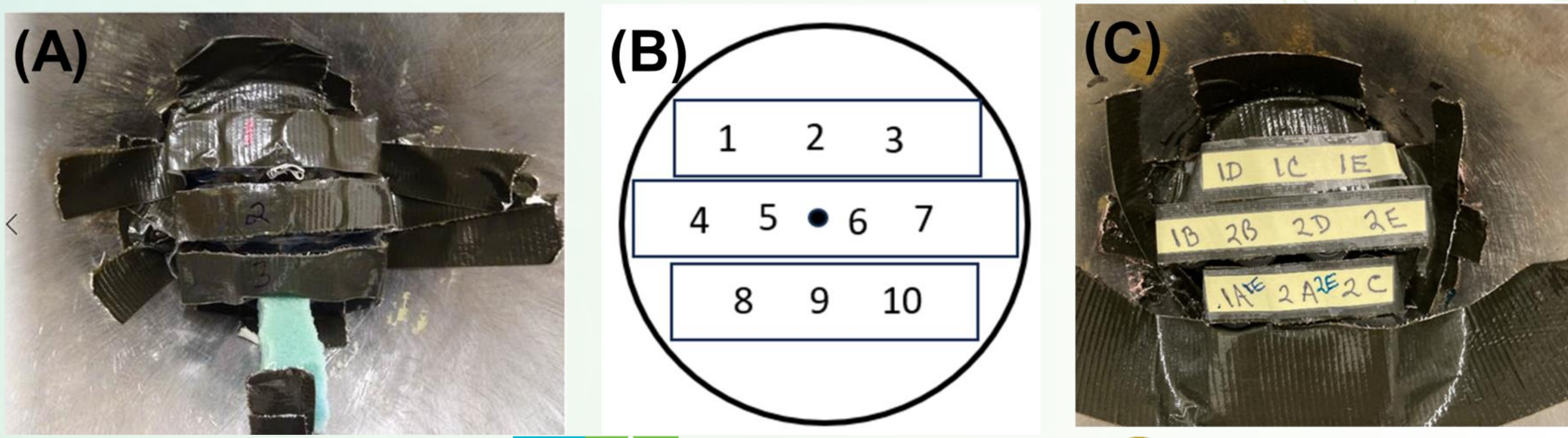
Radiation Experiments

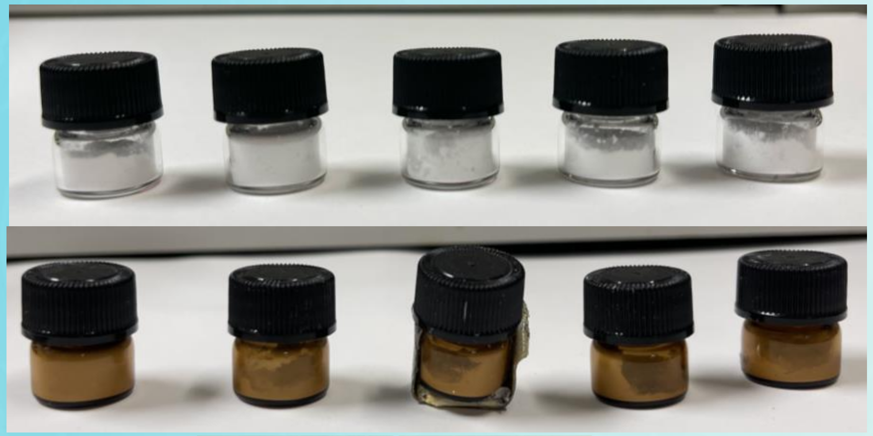


MOF	Sample ID	Dose (Mrad)
CuBTC	1A	100
	1B	200
	1C	300
	1D	400
	1E	500
CaSDB	2A	100
	2B	200
	2C	300
	2D	400
	2E	500

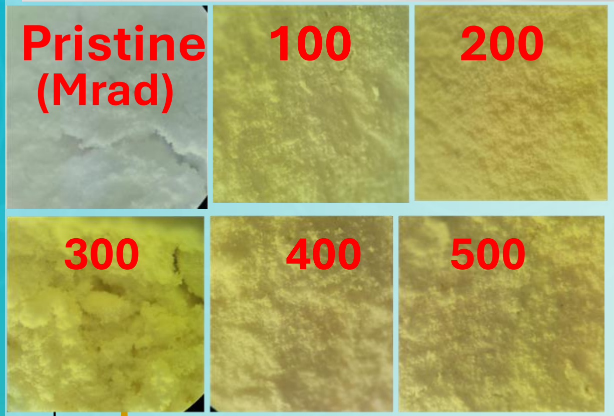
Grid Pair	Sample ID at Location	Dose Rate (Mrad/h)	Irradiation Time (h)	Total Dose (Mrad)
1/6	1D/2D	2.04	196.2	400
2/10	1C/2C	2.07	145.1	300
3/7	1E/2E	1.93	42.5	82
4/5	1B/2B	2.13	94.0	200
8/9	1A/2A	2.86	42.5	100
8/9	1E/2E	2.36	177.4	418

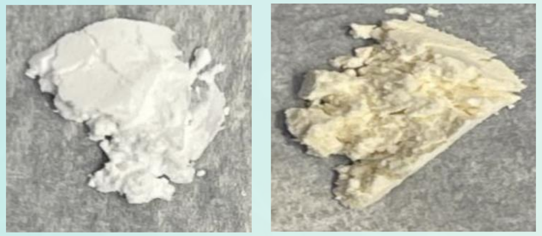


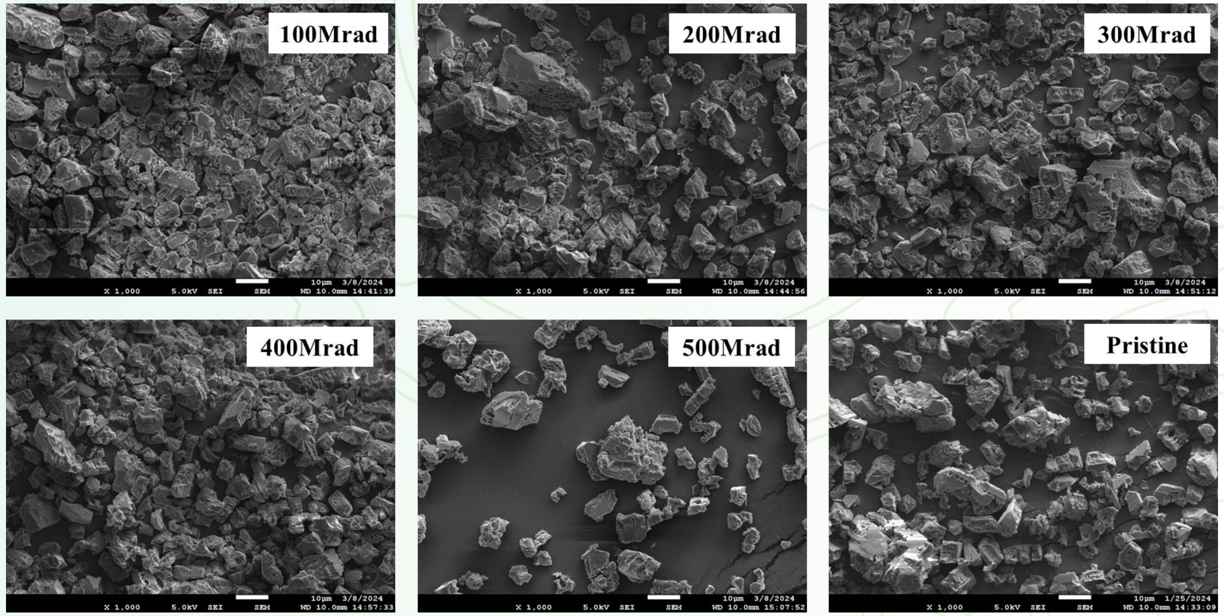
Characterization of Irradiated CaSDB MOF

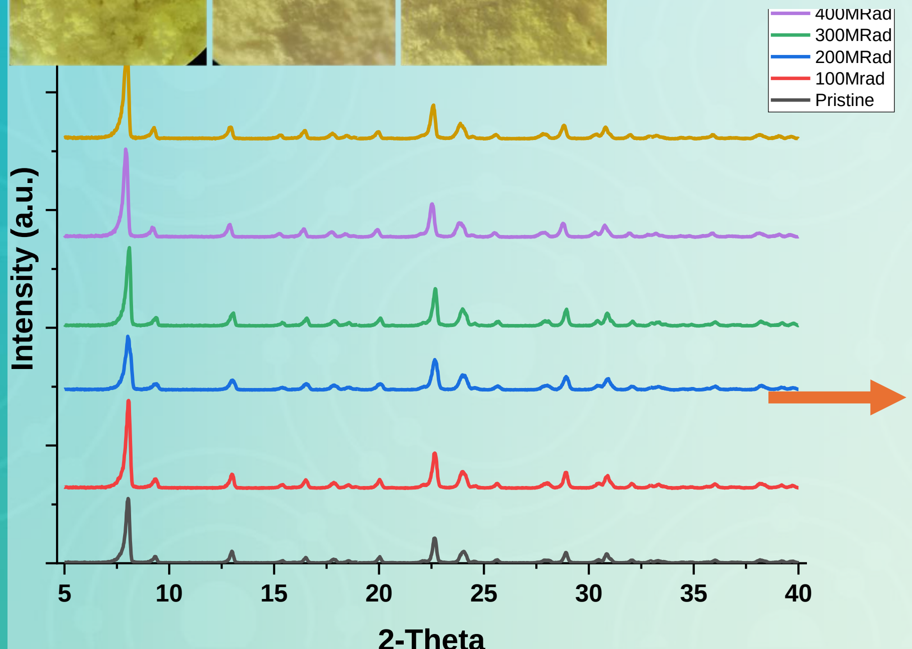


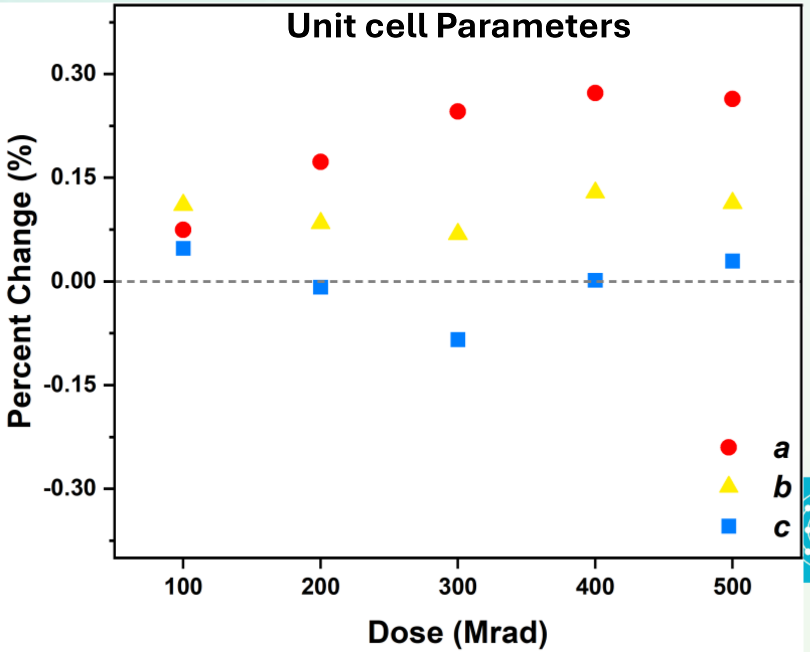
- Optical images suggest color change
- No changes in XRD, SEM (sintering) and IR
- No changes in unit cell parameters

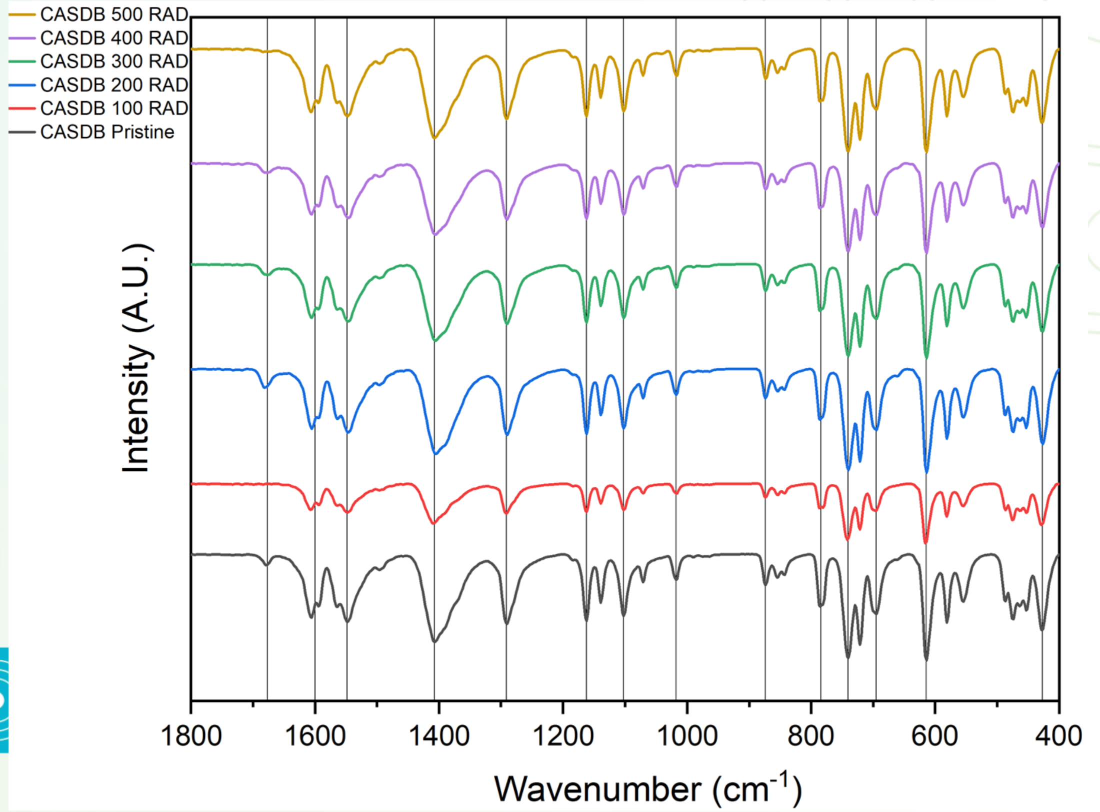












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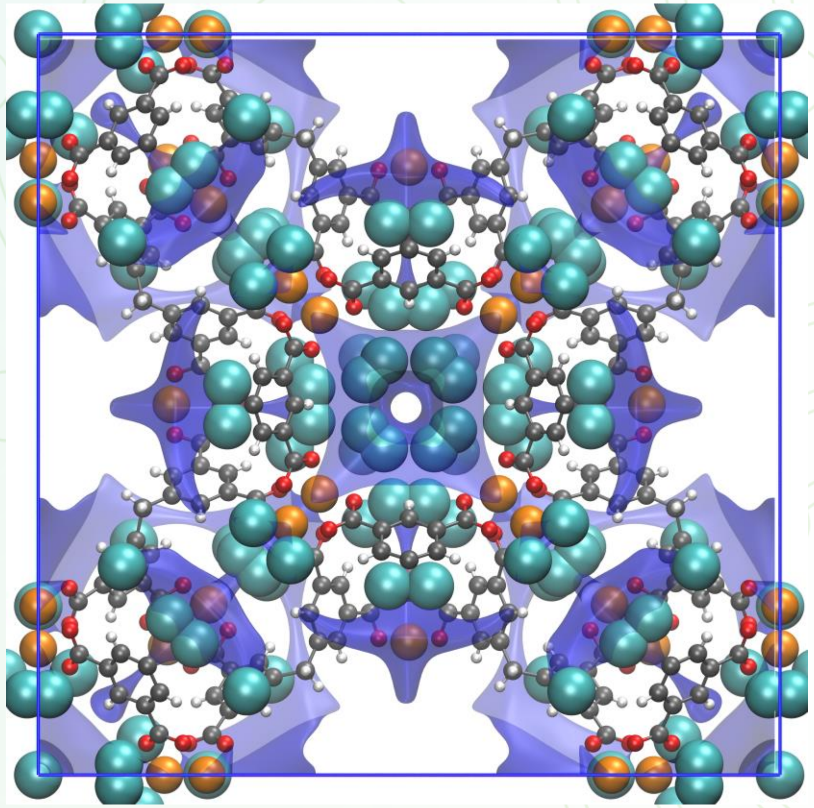

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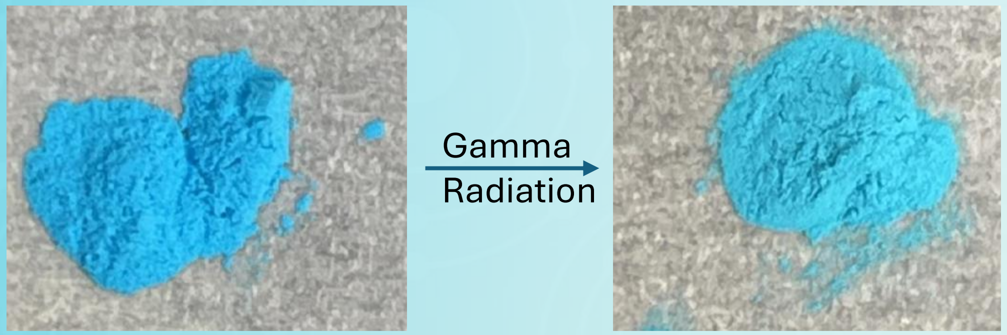
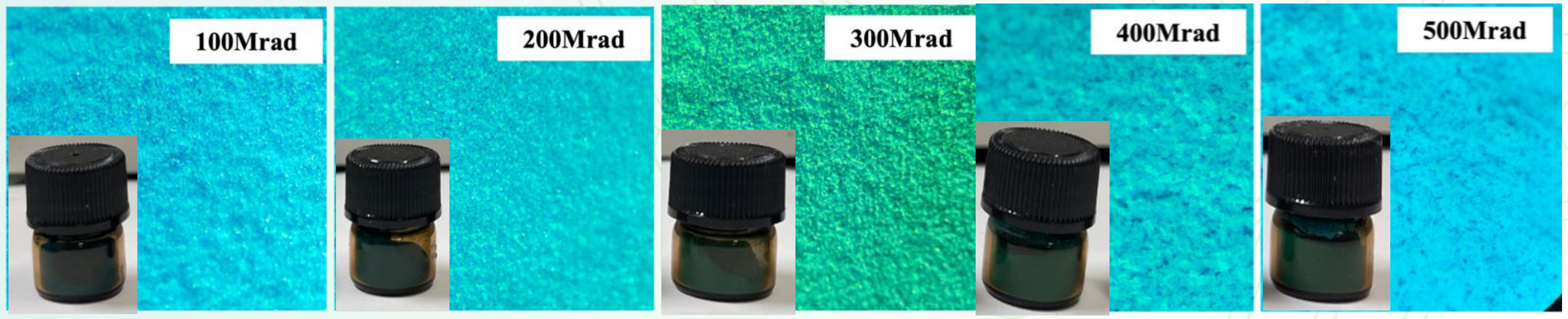
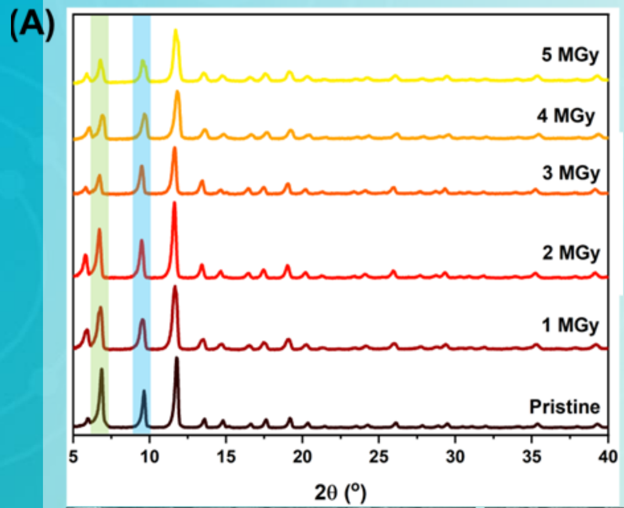
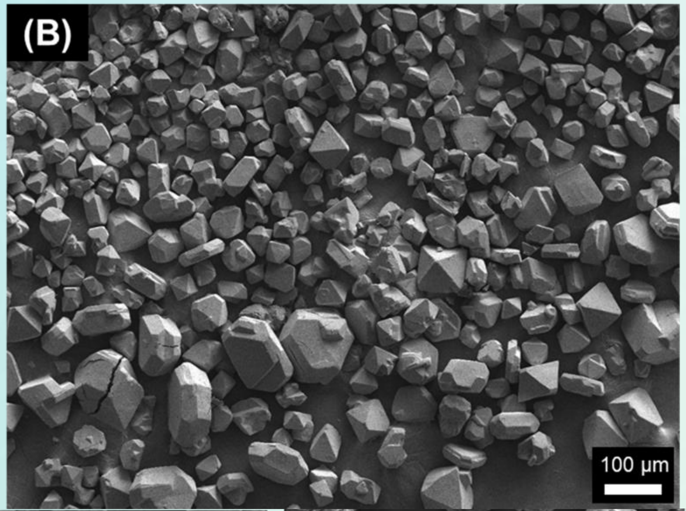
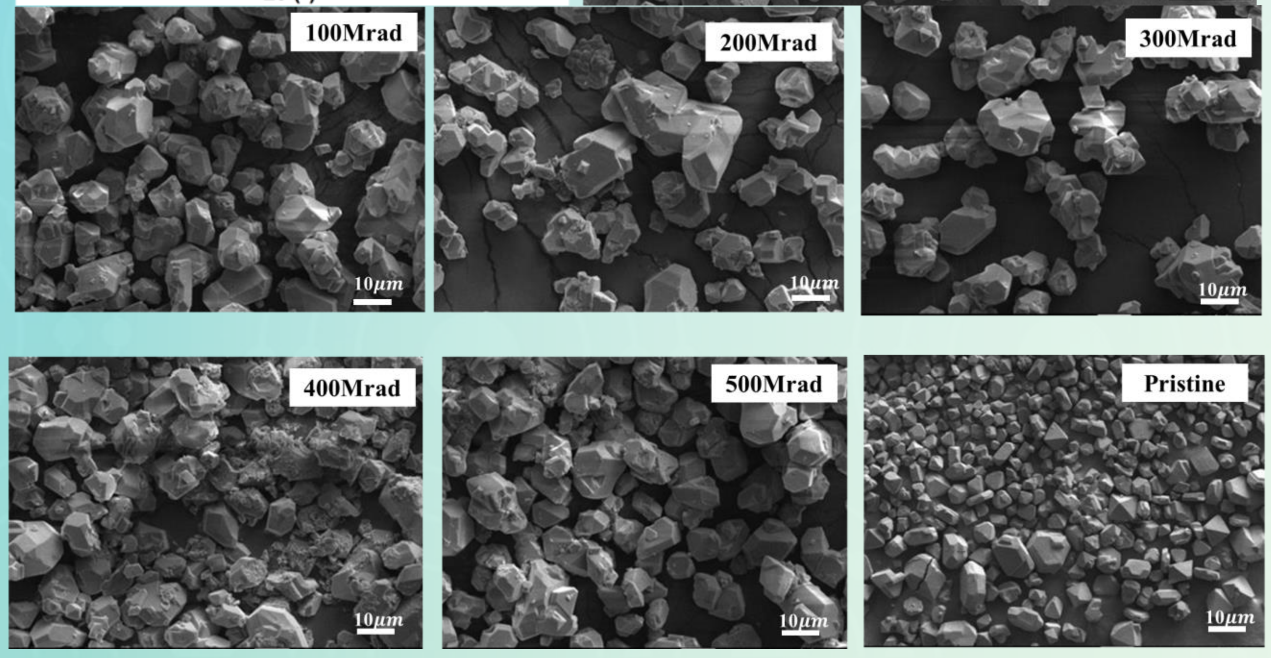
Characterization of Irradiated CuBTC MOF (FY'25)



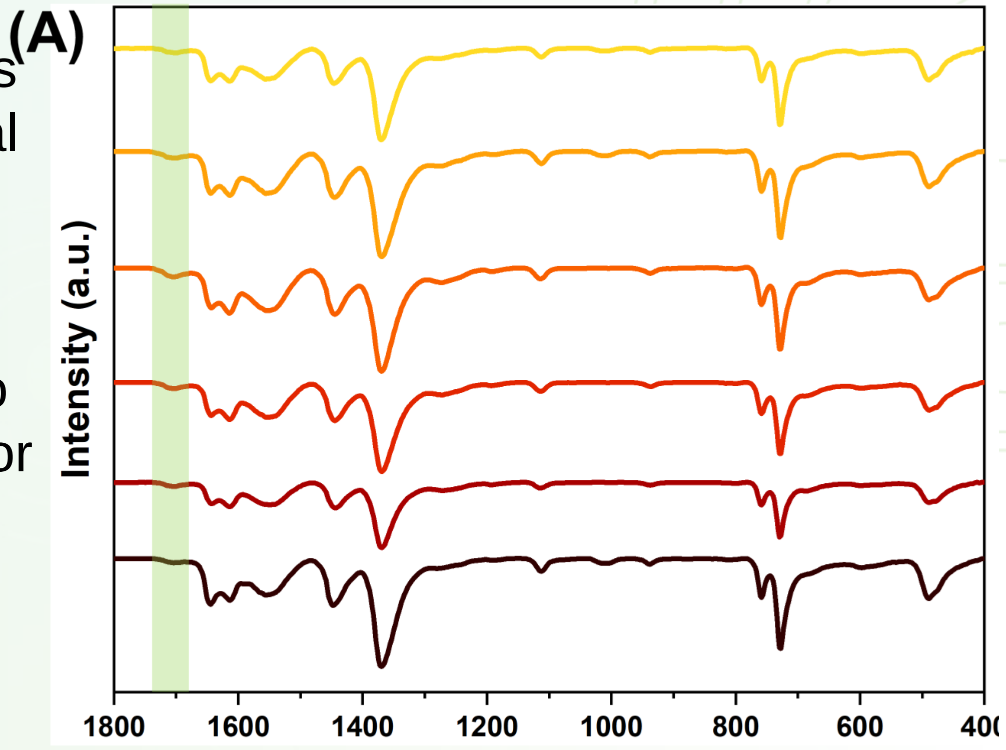








- PXRD, SEM (sintering), IR patterns showed no substantial changes to the framework.
- This illustrates that no additional crystalline or amorphous phases formed.



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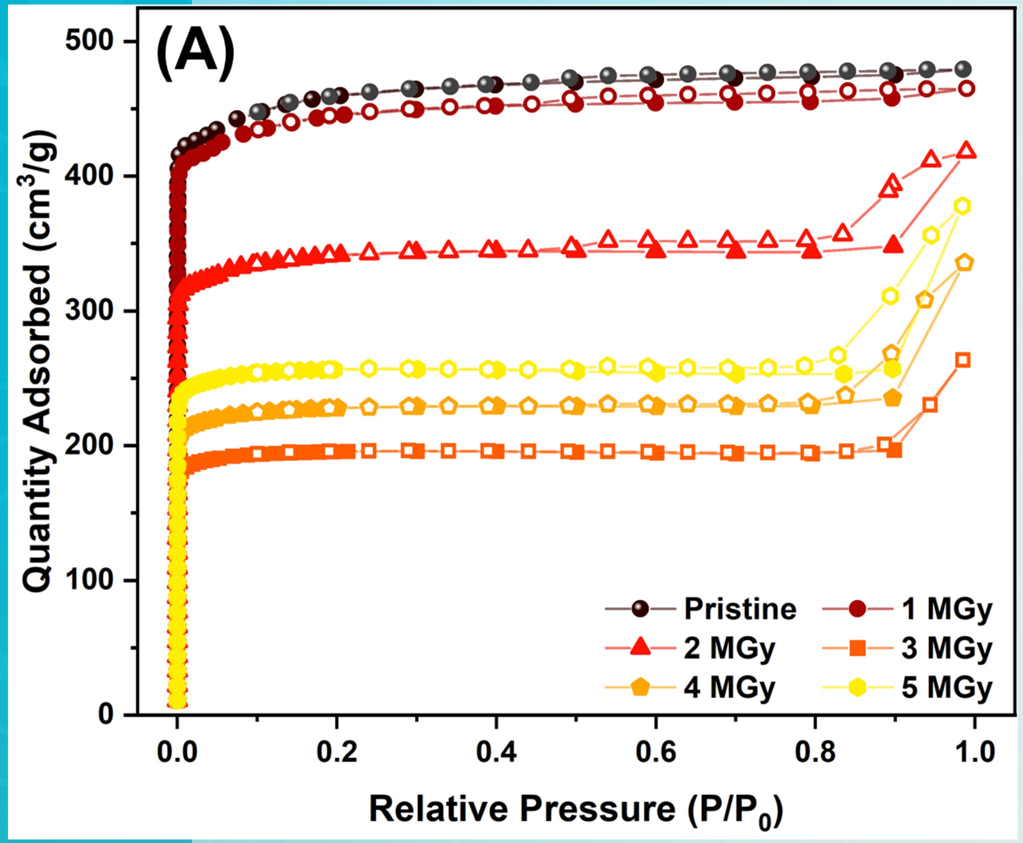
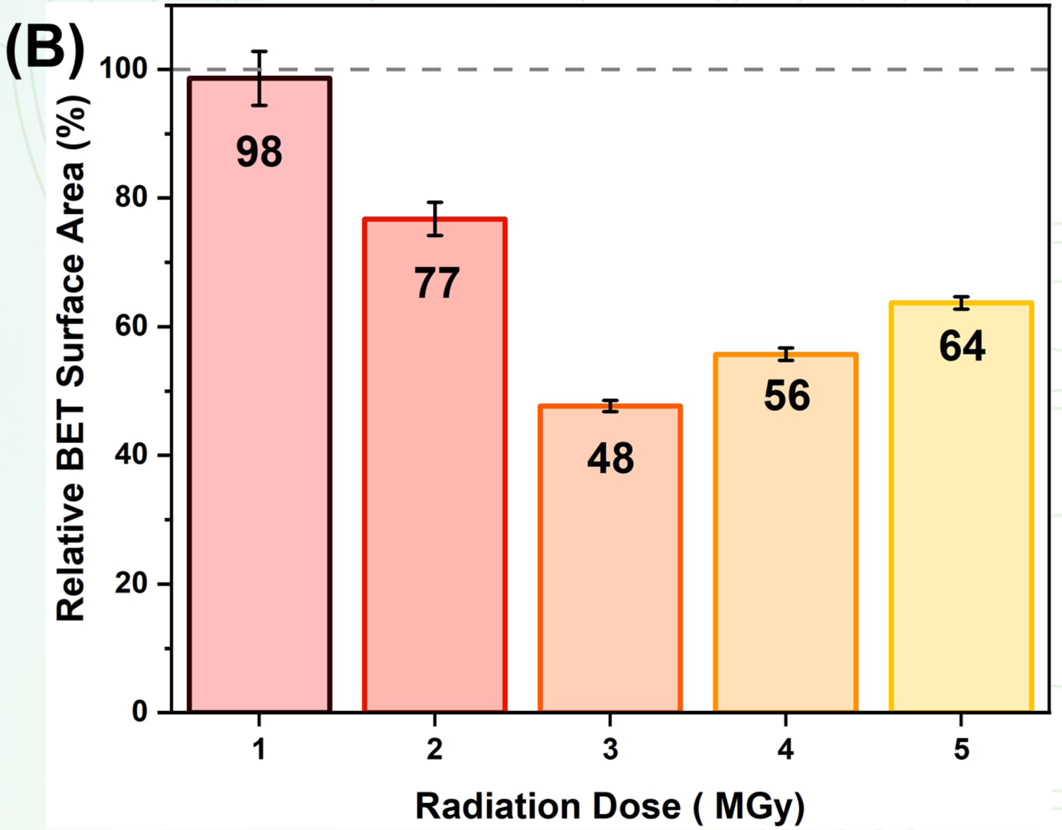
Surface Area of Irradiated CuBTC MOF (FY'25)



- ➢ Surprisingly, the BET surface area of CuBTC decreases with increasing dose



- ➢ The 3 MGy exposed sampled showed the largest decrease (50%) surface area but increases after 300 Mrad

- ➢ The pores of CuBTC blocked at lower gamma doses (300). Then at higher doses the pores free up.

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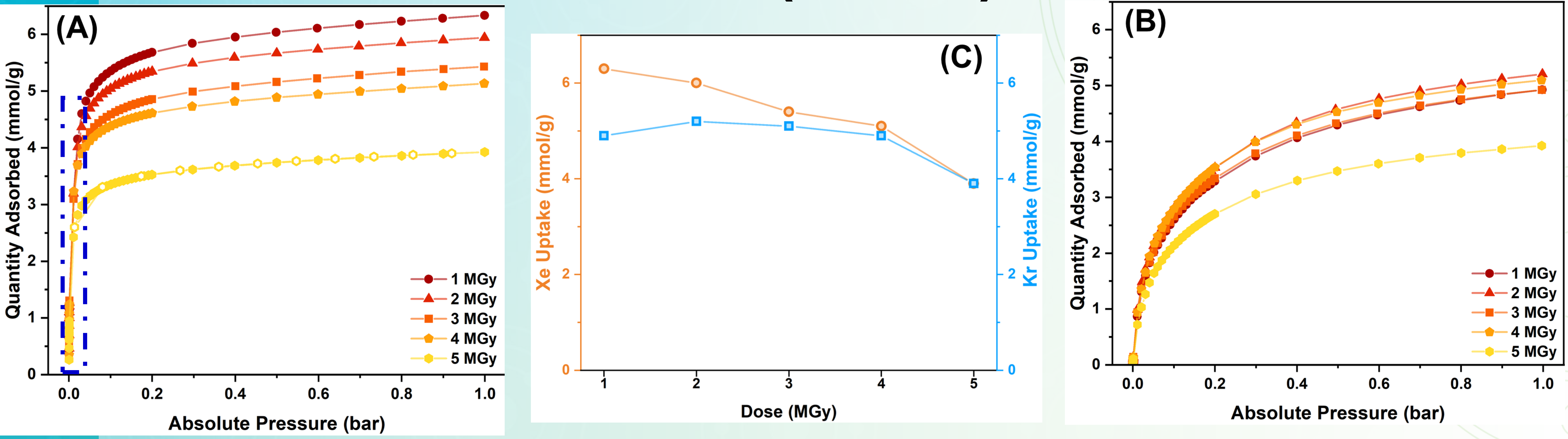
Noble Gas Adsorption of Irradiated CuBTC MOF (FY'25)



- The noble gas adsorption and BET differed however they both suggest reduced pore accessibility caused by radiation.
- The decreased Xe uptake while maintaining Kr uptake until high doses indicated a constriction of the pore size.
- CuBTC still has an exceptional Xe loading at low pressure region

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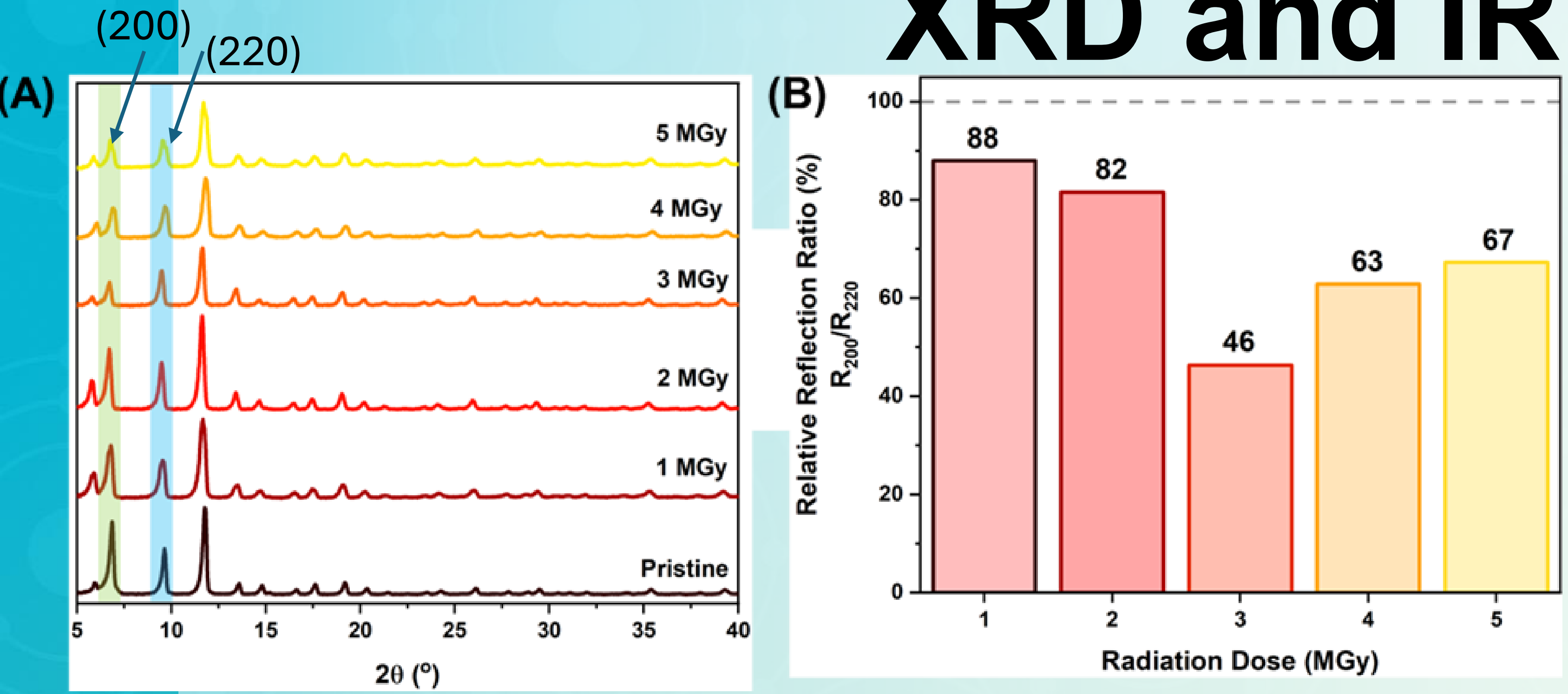
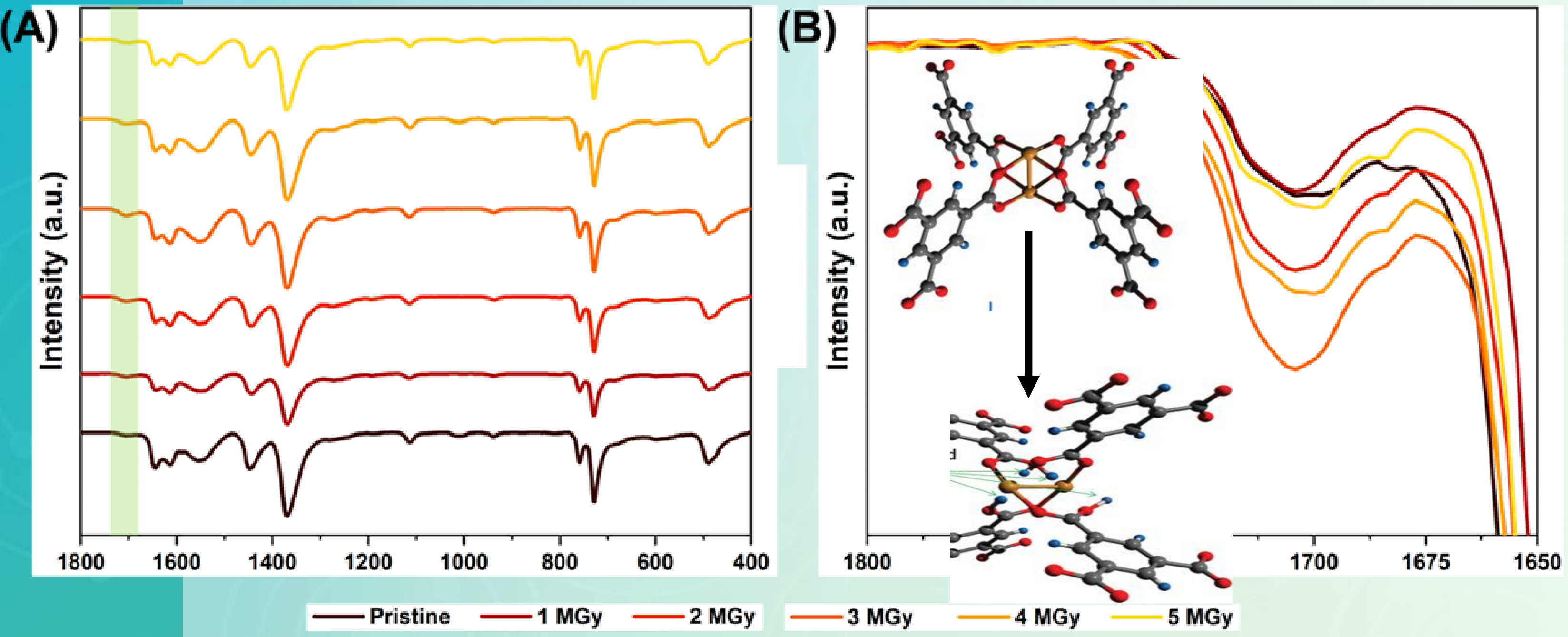
Re-investigation of Irradiated CuBTC MOF: XRD and IR (FY'25)





- The relative ratio of the (200) and (220) reflections decrease gradually until at 3 MGy dose
- The reflection ratio then began to increase at doses of 4 and 5 MGy
- The decrease in (200) reflection intensity suggested possible occupancy of the pores by organic linkers
- Subtle changes in the IR spectra near 1700 cm^{-1} represents a free (i.e., non-coordinated) carboxylic acid vibrational mode
- The presence of free acid indicates either a coordination defect or residual extra-framework BTC within the pores from synthesis
- More radiation experiments on MOF (CuBTC and CaSDB) engineered particles are planned end of next May
- Collaborating with Prof. Maik Lang, UTK (synchrotron XRD)

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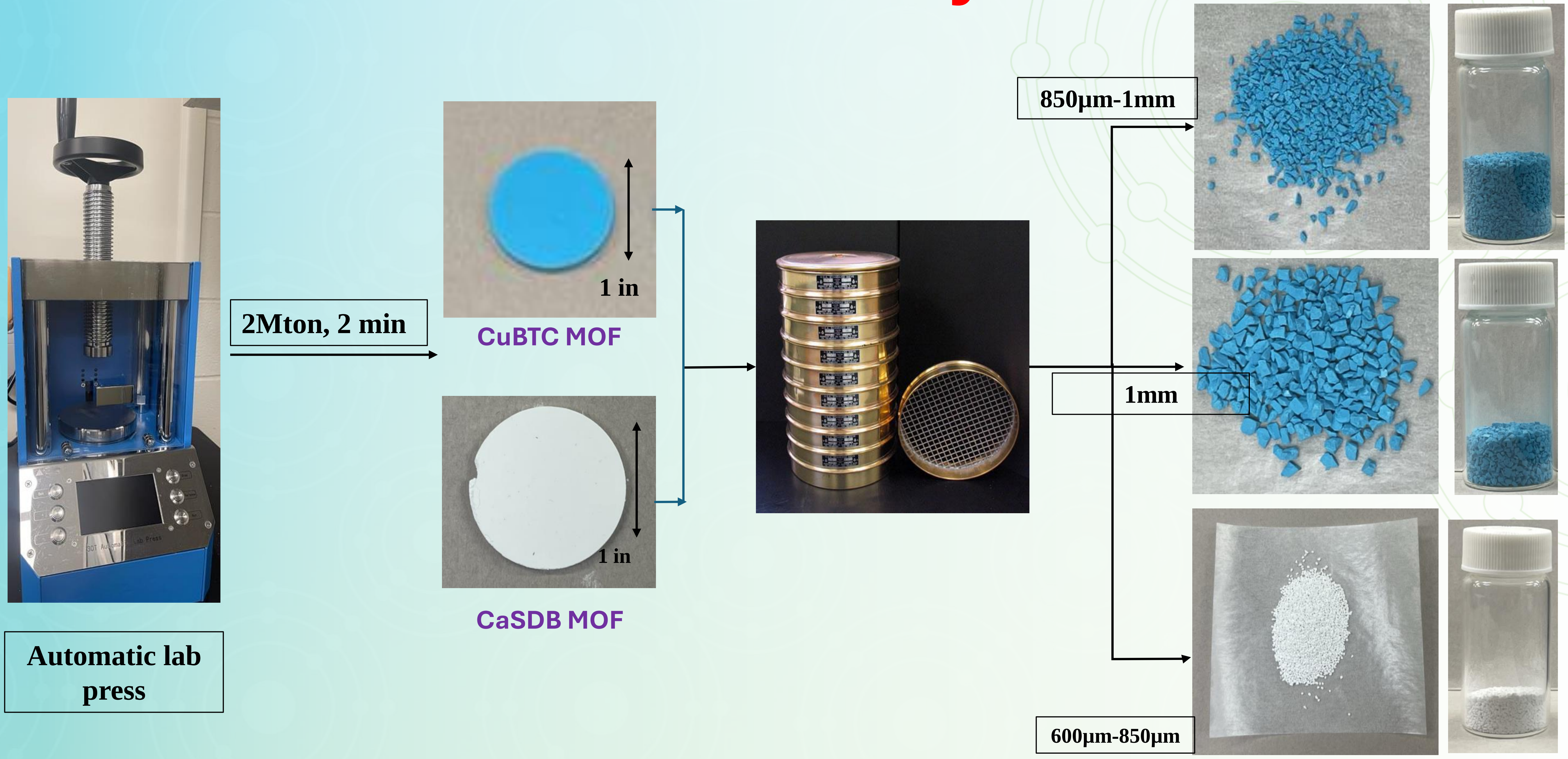
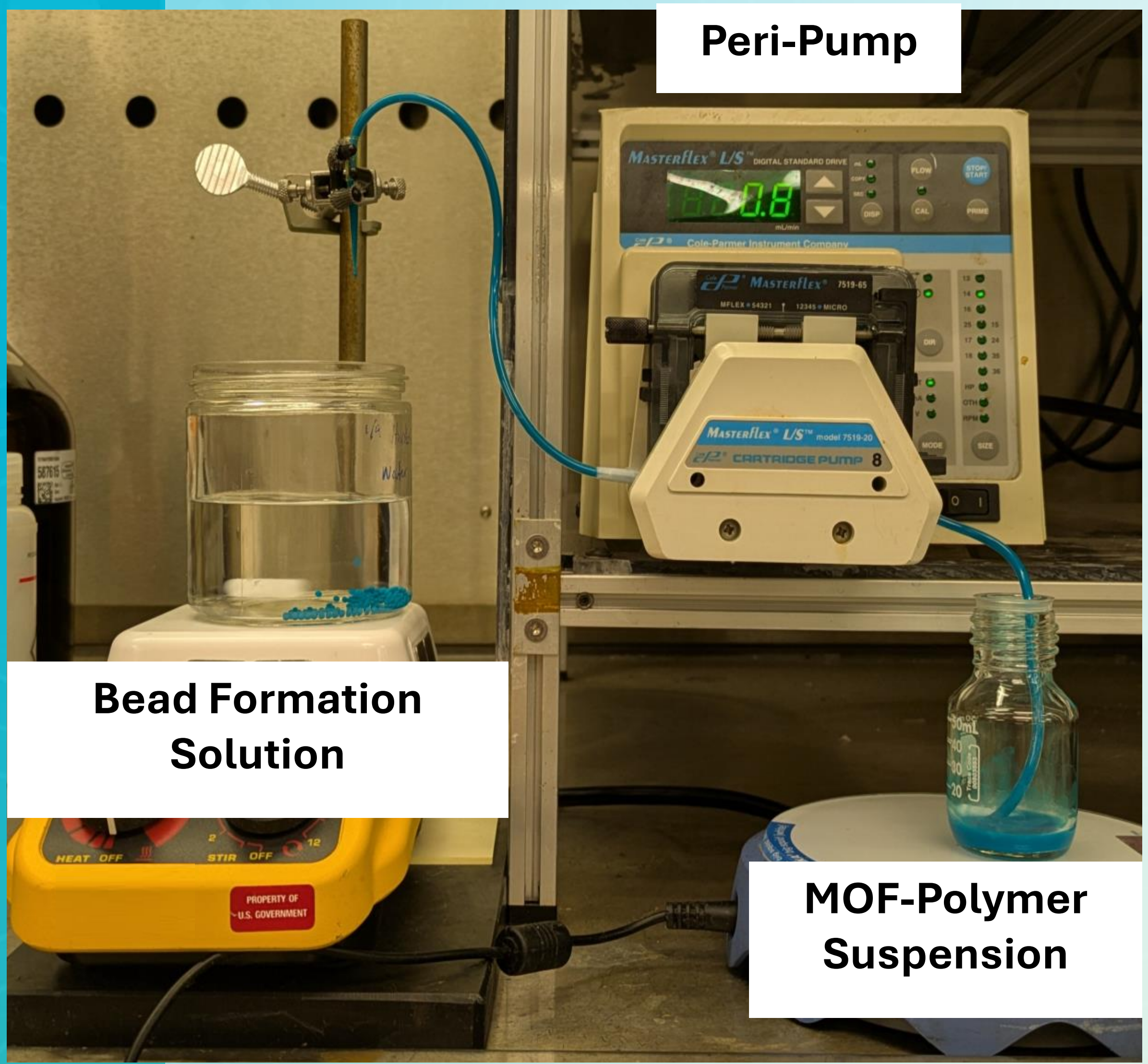
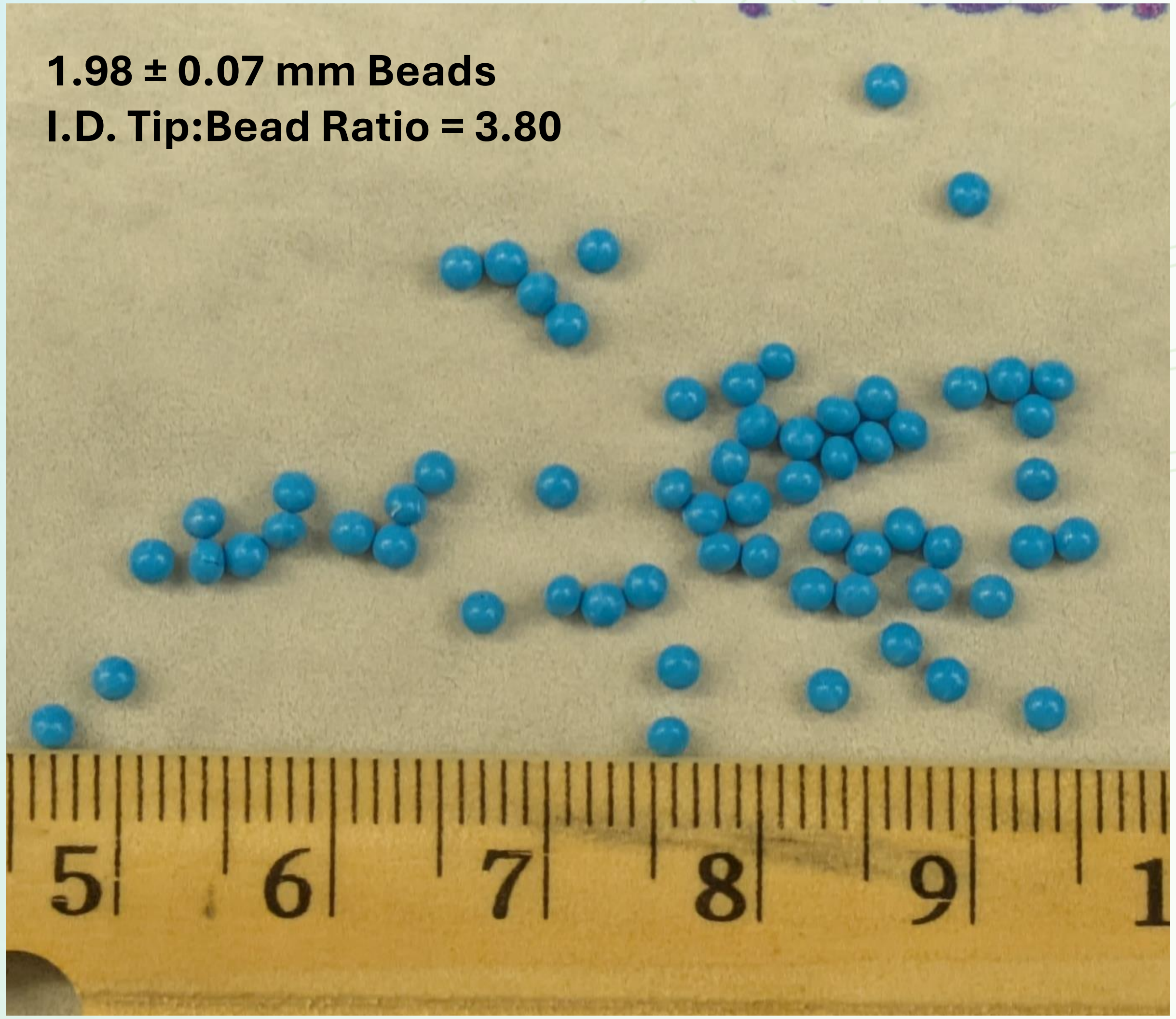
CuBTC Bead without Polymer Fabrication



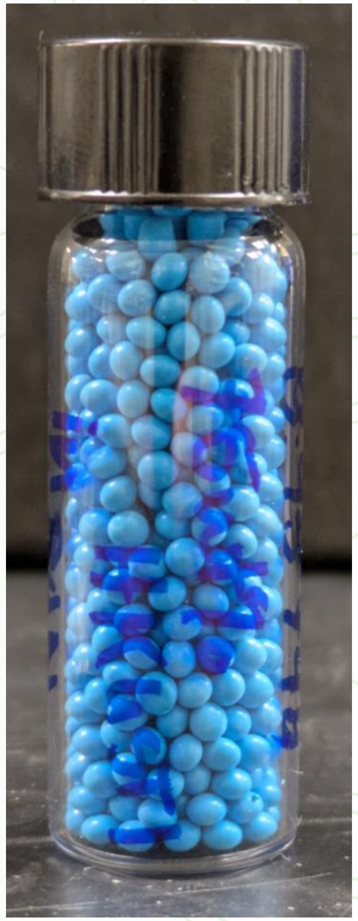
CuBTC-Polymer Bead Fabrication (FY'25)



- Peristaltic Pump set-up for high throughput production of MOF-Polymer composite beads
- Currently makes about 15 g/h of final sorbent beads

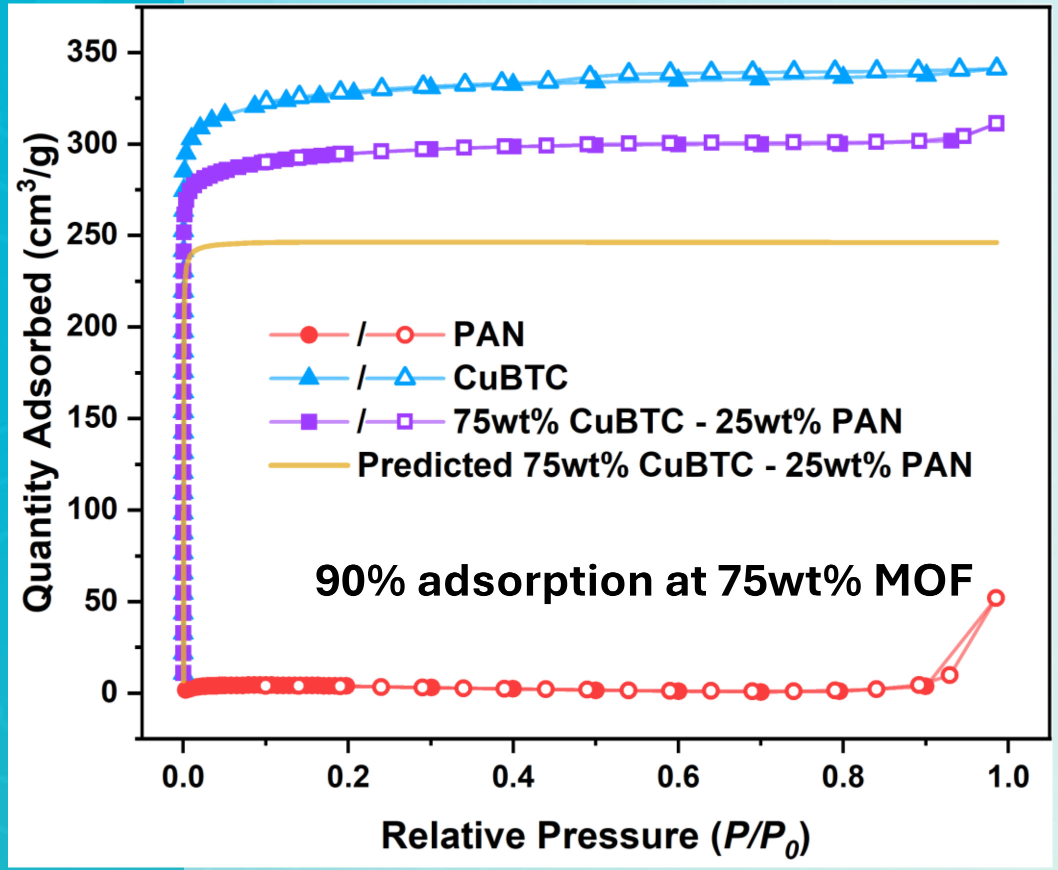


- Bead sized currently controllable from 1.7 mm to 4 mm
- Readily controllable with tip used



1 g of final 75wt% CuBTC 25wt% PAN Sorbent Beads

Surface Area: CuBTC-Polymer (FY'25)

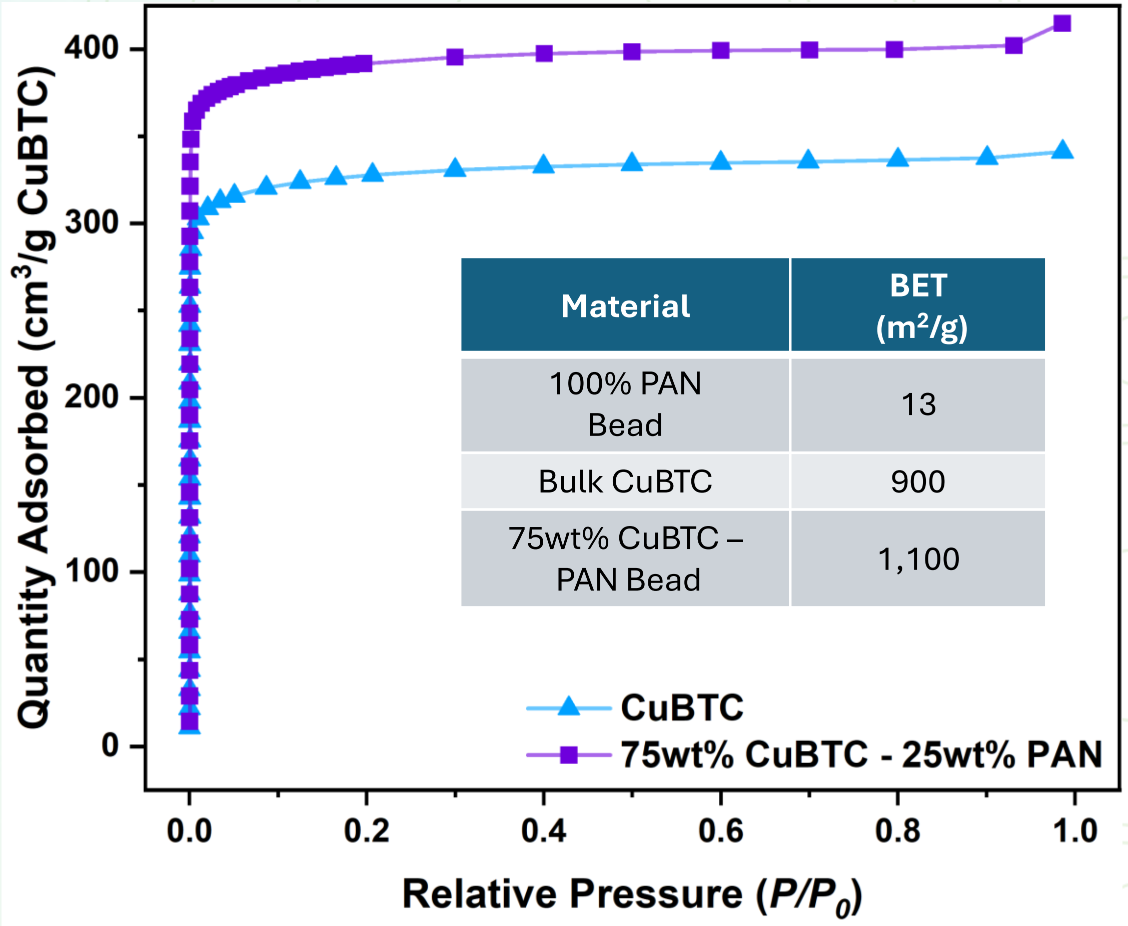


Prediction Calculation:

$$n_{Bead} = (\omega_{poly} \cdot n_{poly}) + (\omega_{MOF} \cdot n_{MOF})$$

Adjustment Calculation:

$$n_{Bead}/_{g\ MOF} = \frac{n_{Bead} - \omega_{poly} n_{poly}}{\omega_{MOF}}$$



Material	BET (m^2/g)
100% PAN Bead	13
Bulk CuBTC	900
75wt% CuBTC – PAN Bead	1,100

- Apparent decrease in gas adsorption by 10% upon polymer bead formation
- Compared to predicted was 22% larger, while predicted was 73% of bulk CuBTC
- Adjusted to uptake per g of MOF in polymer bead 20% larger uptake compared to bulk powder
- IP analysis and patent disclosure ongoing at PNNL

New method means ***MORE*** gas capacity with ***LESS*** MOF

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Conclusions and What's Next

Irradiated CuBTC MOF show short- and long-range order is retained even at 500 Mrad

The surface area has significantly impacted by the radiation including noble gas adsorption

Successfully scaled-up MOF-Polymer composite for gamma radiation experiments (FY'25)

Characterize post-irradiated MOF samples using synchrotron XRD experiments to demonstrate the radiation stability (FY'25).

- 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

DOE – Office of Nuclear Energy - Molten Salt Reactor Campaign

Dr. Patricia Paviet – MSR NTD

DOE NE – 5 Molten Salt Reactor Campaign

- Dr. Patricia Paviet (PNNL) - NTD
- Dr. Joanna McFarlane (ORNL)
- Dr. Andrew Hunter (ORNL)
- Dr. Kevin Rob (ORNL)

DOE NE-4 Materials Research and Waste Form Campaign:

- Dr. Ken Marsden (INL) - NTD
- Dr. Robert Jubin (ORNL)
- Mrs. Amy Welty (INL)
- Mrs. Kimberly Gray (DOE, NE-4)

PNNL

- Dr. John Vienna (PNNL)
- Dr. Brian Riley (PNNL)

DOE ARPA-E ONWARDS

- Dr. Robert Ledoux (DOE – ARPA-E)
- Dr. Christina Leggett

Industry

- Dr. Sven Bader, (ORANO)
- Mr. Carl Perez (Exodys)
- Mr. Vik Singh (Curio)

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