Molten Salt Reactor
PROGRAM

Impact of Radiation on Noble Gas Performance

Praveen K. Thallapally, Keerthana Krishnan, Matthew J. Hurlock, Mark K. Murphy & Maddison A. Rex

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Radiation Exposure Experiments:

- Mark K. Murphy & Maddison A. Rex

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MSR Milestone Progress

WP#	Deliverable Description	Due Date	On schedule? Y/N
M3AT-26PN0702063	Complete analysis of irradiated MOF engineered particles in collaboration with ORNL and NSLS-II	2/28/2026	Y
M3AT-26PN0702064	Construct and Test a modular off-gas system to treat MSR off-gases Xenon and Krypton	9/30/2026	N

Publications:

1. Krishnan, K., *al.”* Mechanisms Governing Noble Gas Adsorption in a Copper-Based Metal–Organic Framework” *Langmuir* **2025**, *41*, 33, 22193–22199
2. Krishnan, K., *al.”* Impact of Radiation on noble gas adsorption in Metal Organic Frameworks” *in preparation, 2026*
3. Hurlock, K., *al.”* Metal Organic Composites as Alternate Radiation Tolerant Materials, In prep, 2026

Invention Disclosure:

1. Thallapally., *al.,* ”Metal Organic Composites for Noble Gas Adsorption” in prep.

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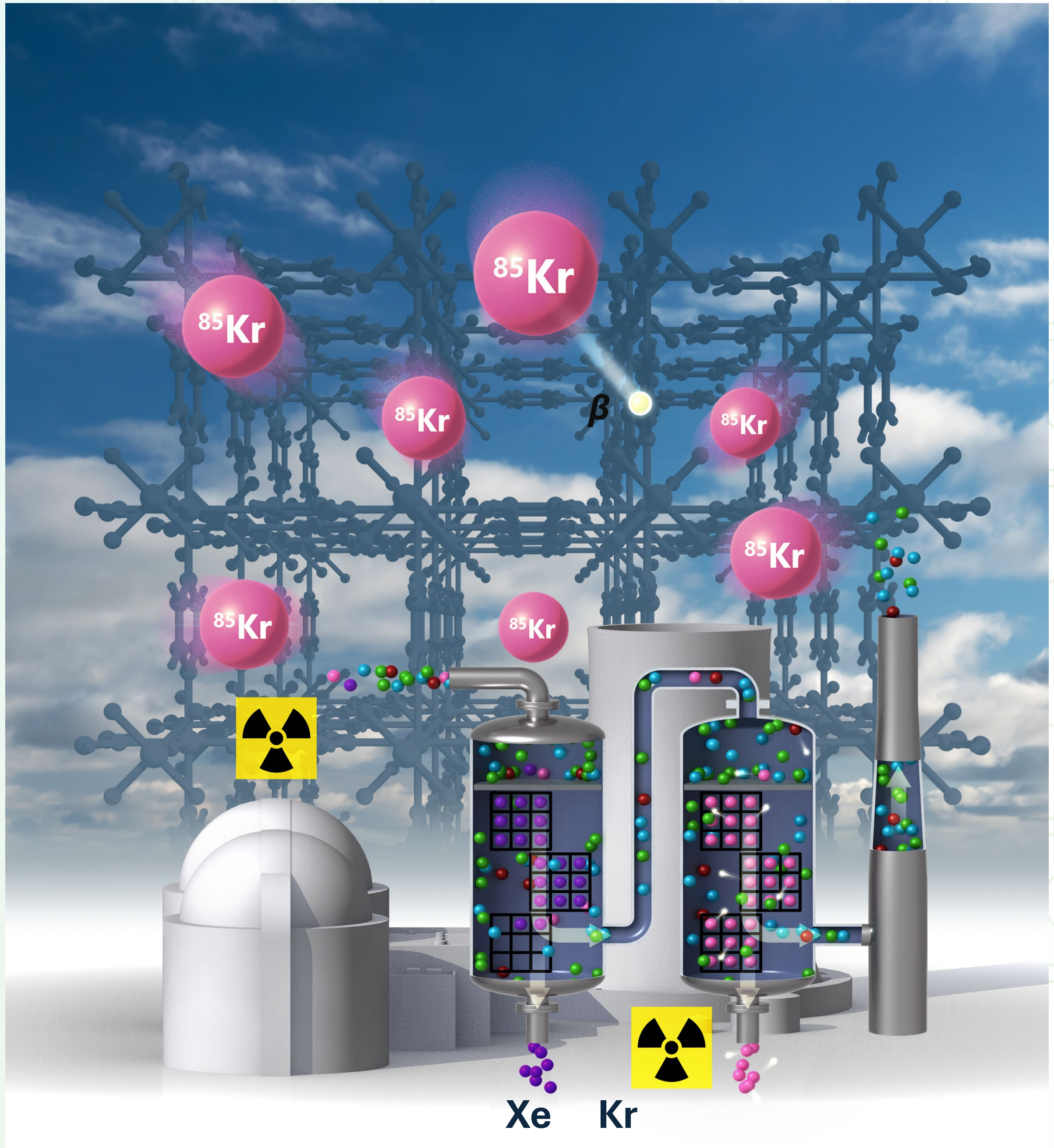
Driving Factors

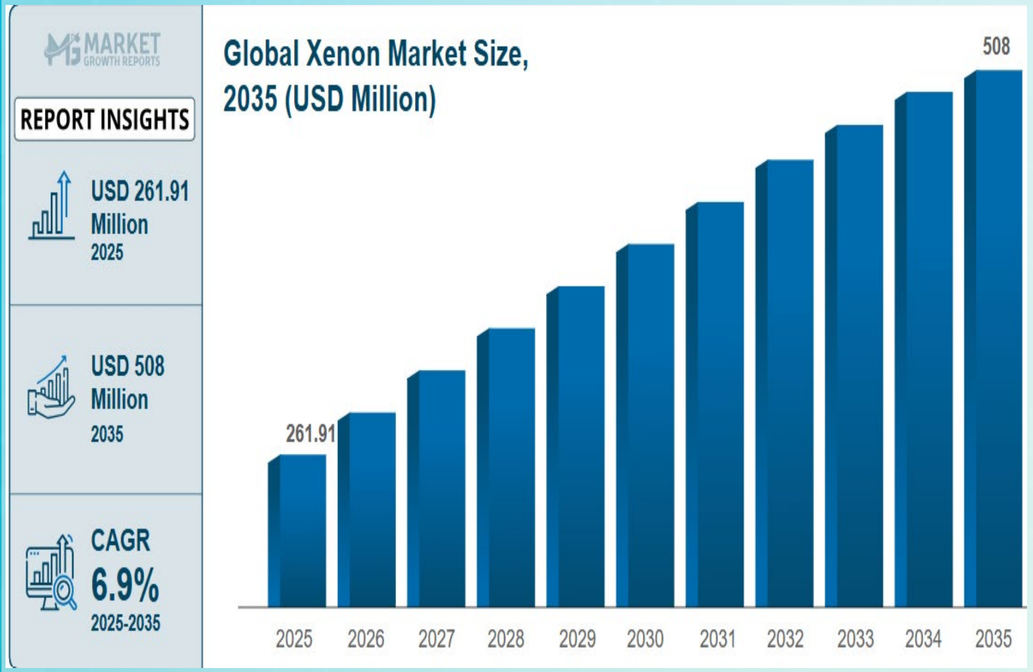
❑ **Why**

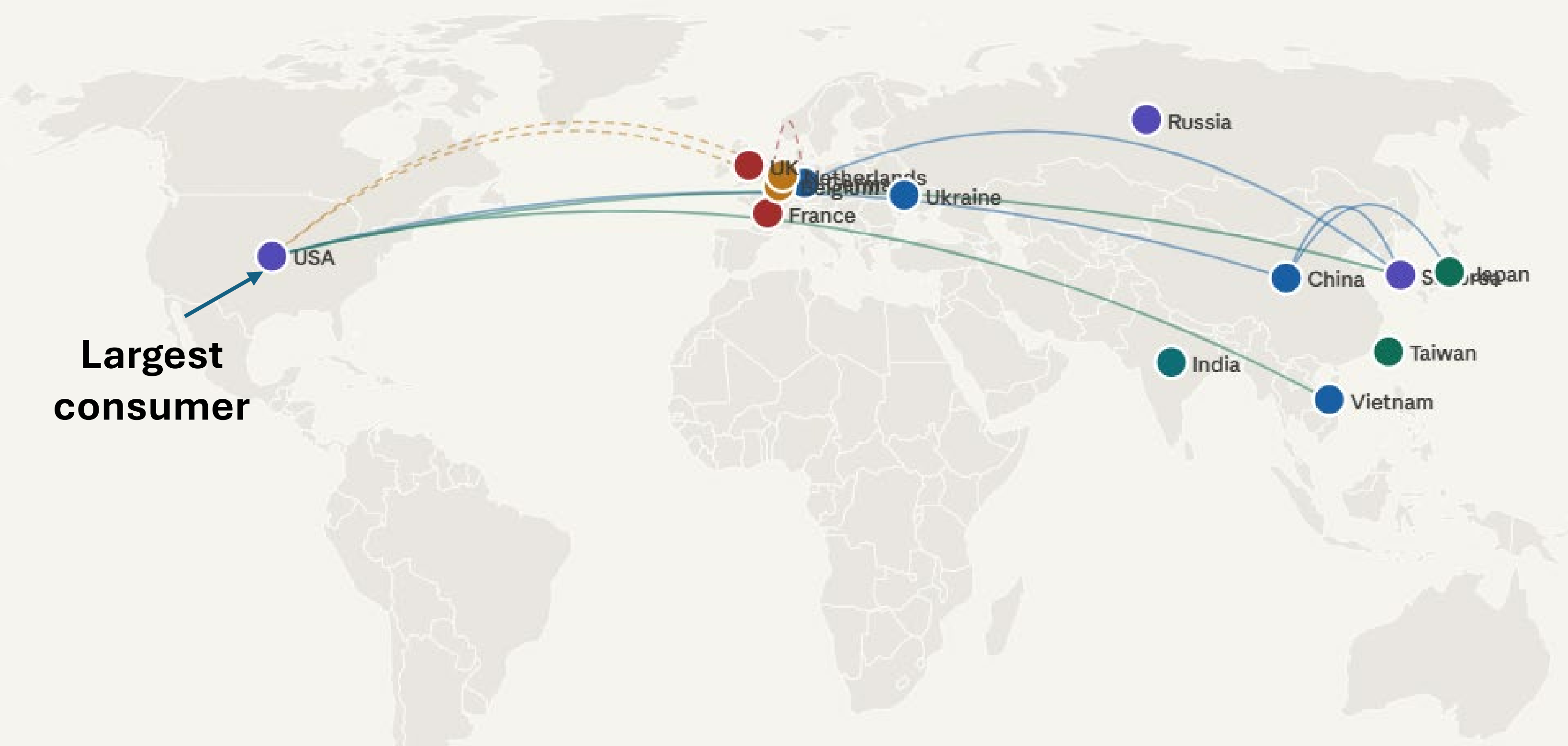
- U.S. EPA 40 CFR 190 and NRC regulation requires volatile radio nuclides (^{14}C, ^{3}H, ^{131}I, ^{133}Xe and ^{85}Kr) must be captured and sequestered
- Noble gas capture is the most difficult to capture as they are inert by definition
- Potential economic incentive if captured
- Impact of radiation will help develop compact off-gas system using sorbents to meet developer (MSR) needs and support licensing activities.
- 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.



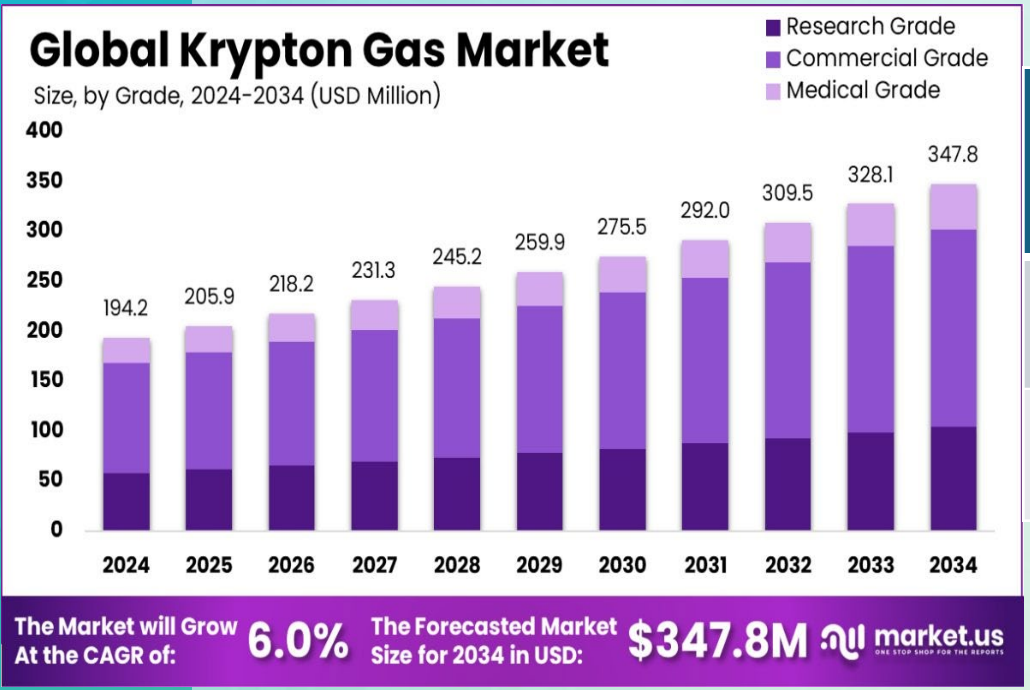
Elsaidi SK., Thallapally PK *et al.* Radiation-resistant metal-organic framework enables efficient separation of krypton fission gas from spent nuclear fuel. *Nat Commun* 11, 3103 (2020).

Noble Gas and Its Isotope Supply Chain





Stable and Radio Xe and Kr Exporters



Market Type	Estimated Value	Primary Drivers
Kr-85	~$25 – $45 Million	Leak detection, thickness gauging, and medical diagnostics
Xe-133 and 131	~$200 – $400 Million	Nuclear medicine for lung ventilation, Lung MRI

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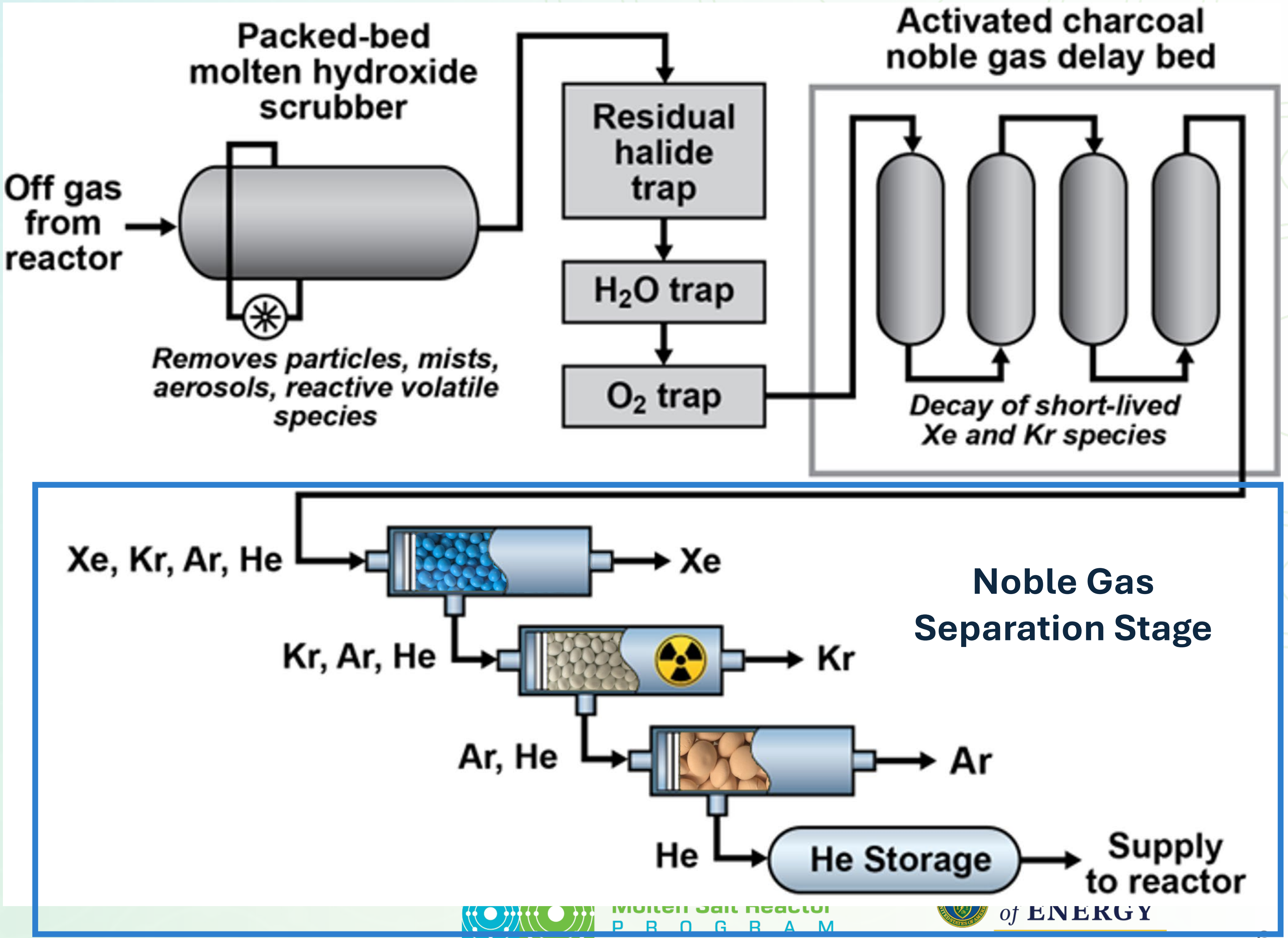
Nuclear Industry Offers Unique Sources for Xe and Kr

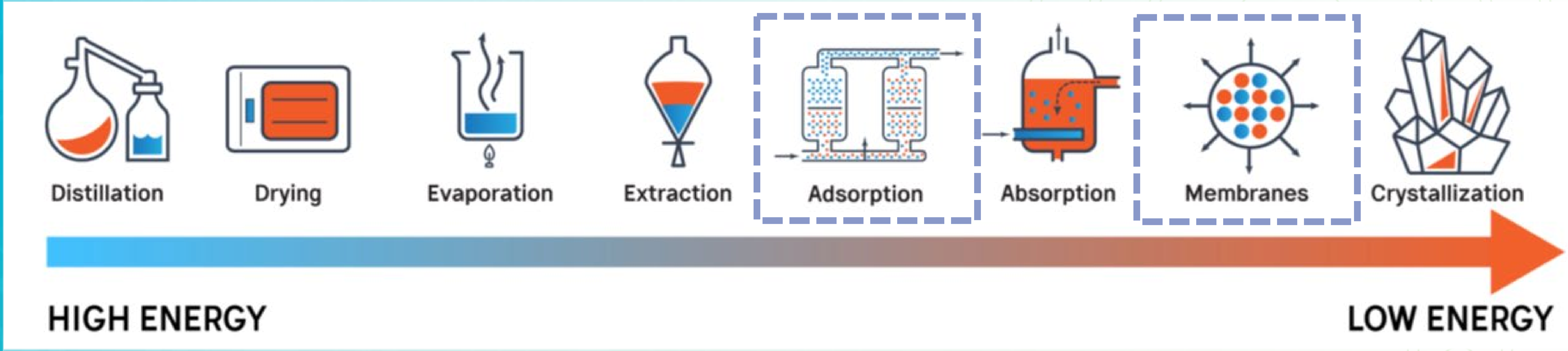
- Advanced reactors produce gaseous waste streams (**off-gas**)
- Unique features of these gas streams
  - High concentrations of Xe and Kr
  - Contains unique radioisotopes
  - Complex process dependent mixtures

Traditional Xe/Kr separation and purification methods are not necessarily most economical for these sources

Off-Gas Proposed Management System



Current Technologies



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

1) Complex
2) Large footprint
3) Costly
4) Hazardous and safety issues

➢ **Need advanced materials and membranes to develop a modular/compact off-gas system**

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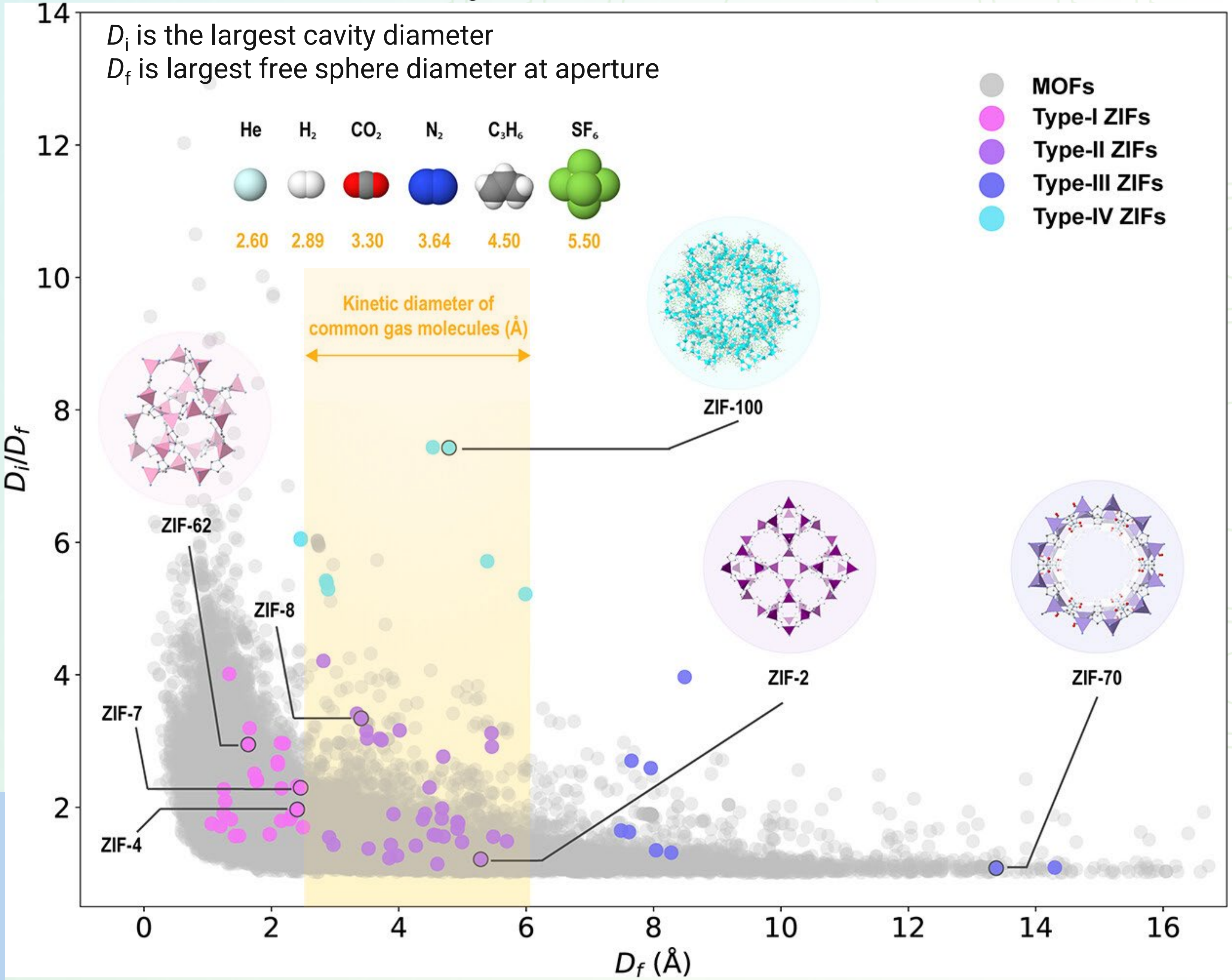
Adsorptive Separation is a Promising Approach for Noble Gas Capture

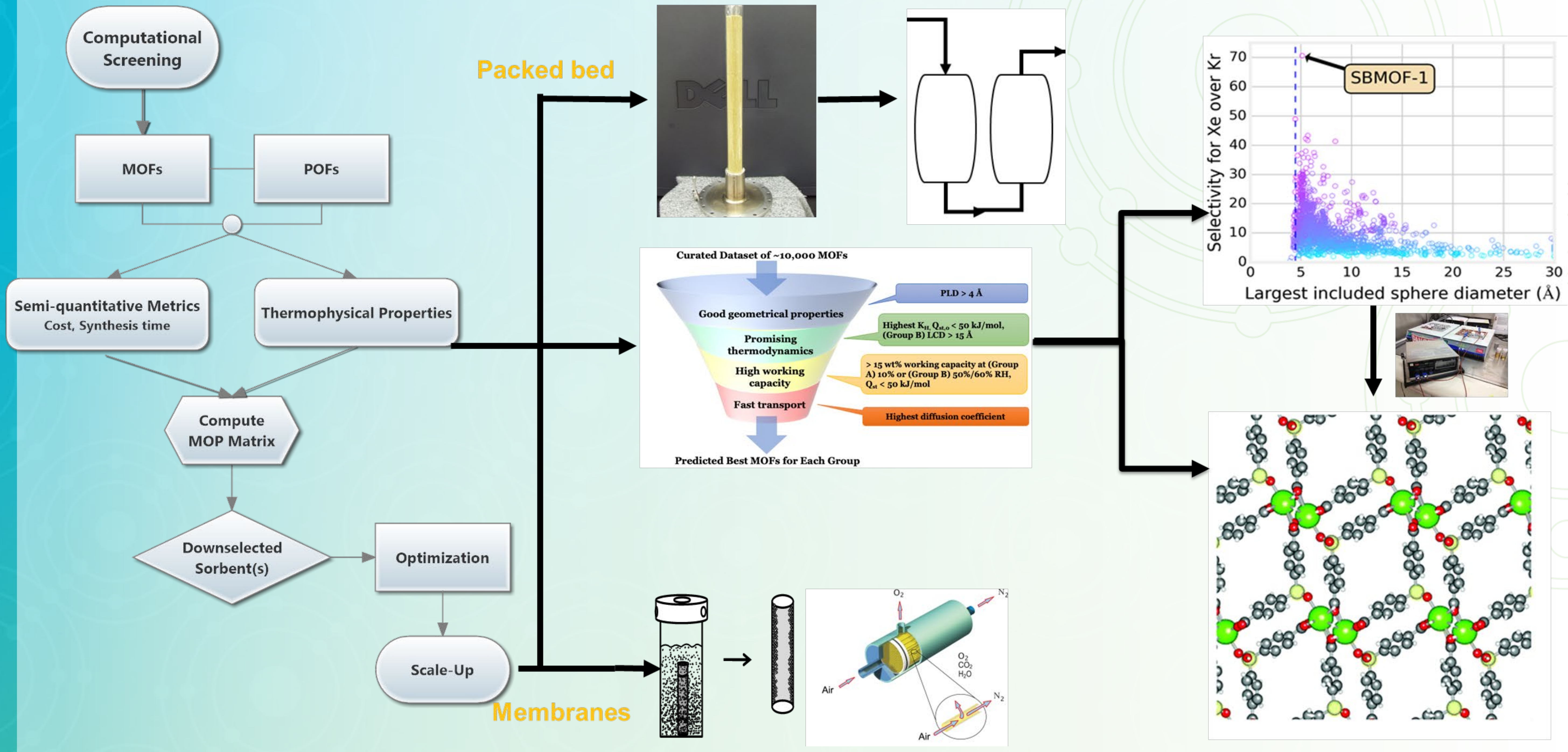
- Sorbents include porous carbons, zeolites, and metal–organic frameworks (MOFs)
- Limited chemical interactions make noble gas adsorption challenging
- Due to their unique features MOFs offer the best separation and capture performance

A gap exists between fundamental testing and large-scale implementation of MOFs for noble gas separations

Inorg. Chem. **2023**, *62*, 51, 20861–20873

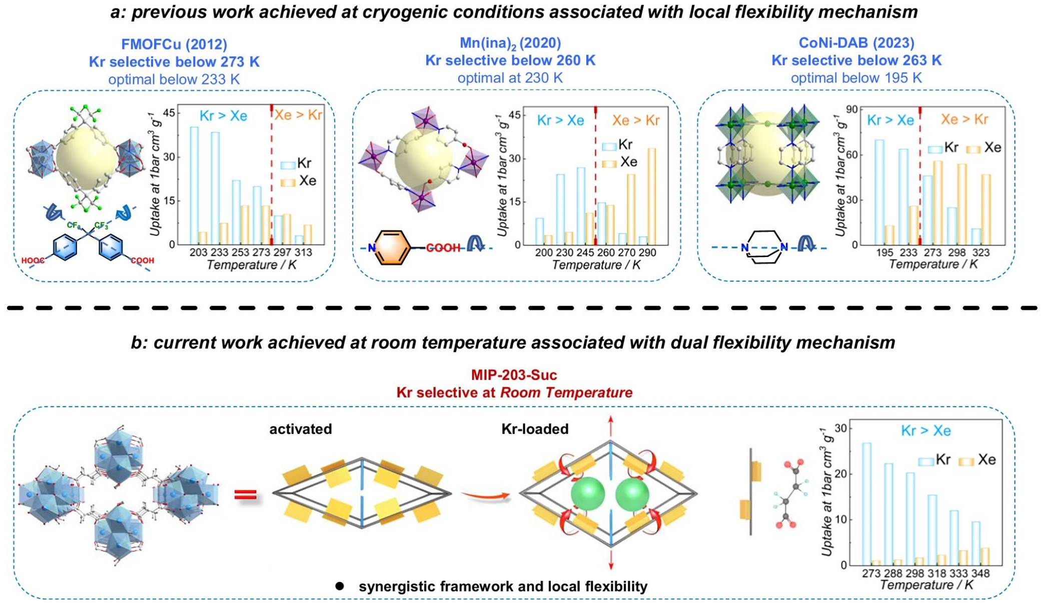


Sorbent Down Selection



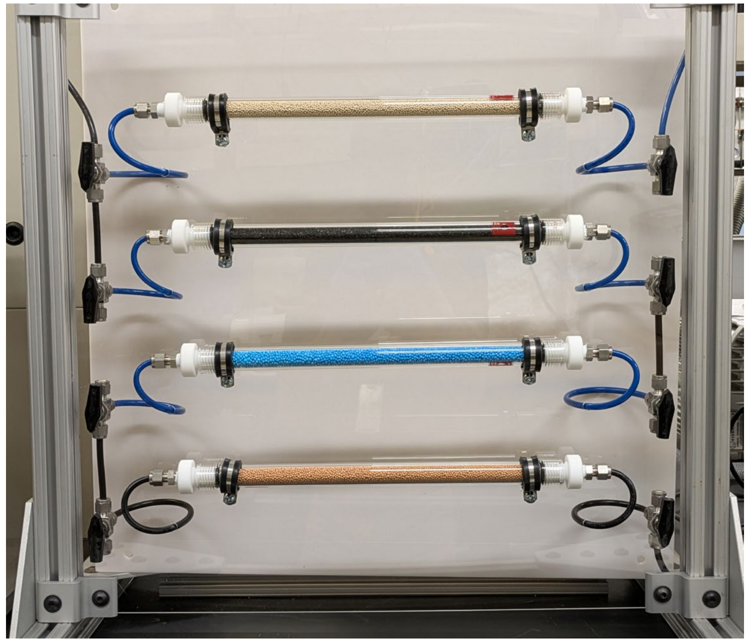
Where are MOFs for Noble Gas Capture at Scale?

Kr Capture



Nat. Commun. **2026**, 17, 1065

Xe Capture



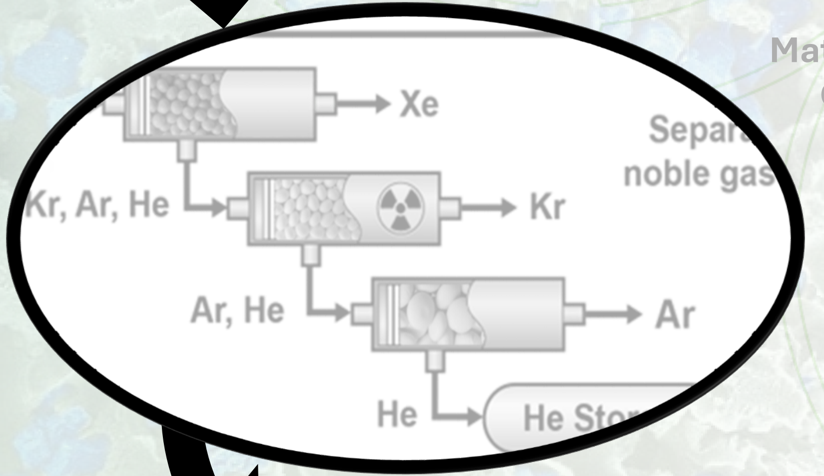
Materials and Systems Design Approach to Sorbent Development

Testing and Evaluation

Material property determination and validation of performance criteria

Process Modeling

Mathematical and Computational modeling of materials and systems



Techno-Economic Analysis

Sorbent material production and adsorption process cost analysis

Sorbent Processing

Recipe development and form processing of bulk powder solids

Material Synthesis

Small to large (kilogram) scale production of porous materials

Develop and Demonstrate Sorbent Technologies Under Relevant Conditions

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Materials and Systems Design Approach to Sorbent Development

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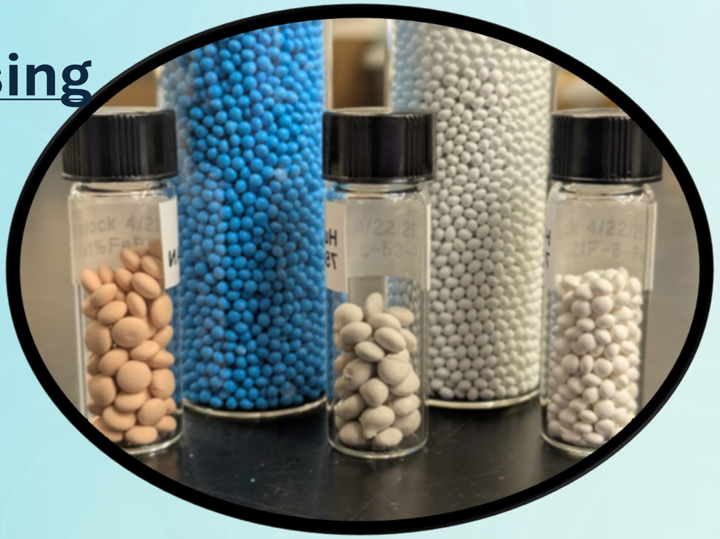

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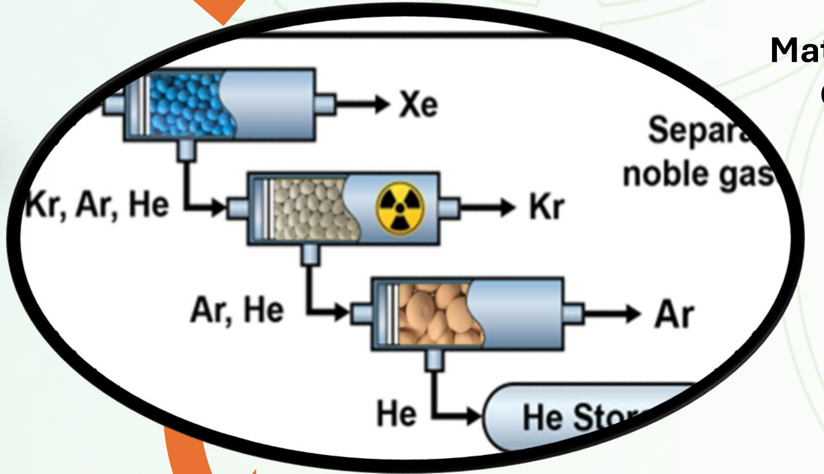
Process Modeling



Mathematical and Computational modeling of materials and systems

Techno-Economic Analysis

Sorbent material production and adsorption process cost analysis

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Develop and Demonstrate Sorbent Technologies Under Relevant Conditions

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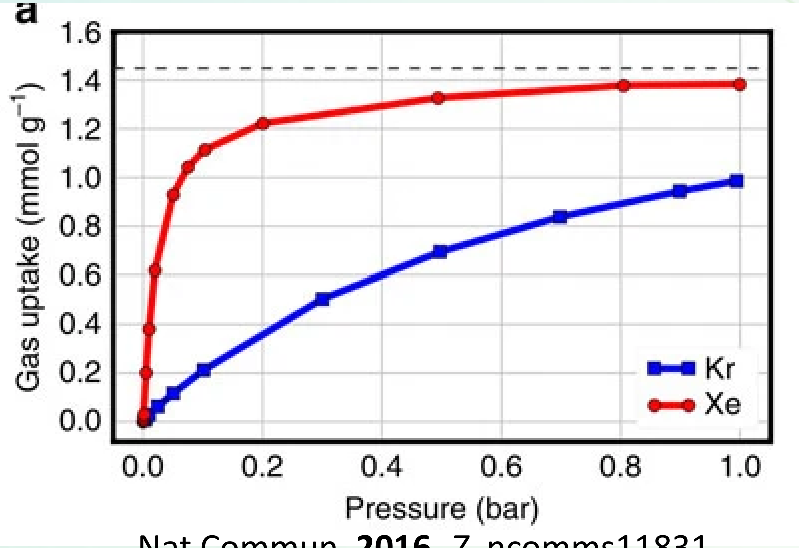
Off-Gas Relevant Evaluation Necessary to Develop and Compare Sorbents

Current Challenges:

- **Limited data under process conditions**
  - *Developing and standardizing testing under relevant conditions*
- **Long-term sorbent performance unknown**
  - *Automating data collection*
- **Radiation tolerance of materials unknown**
  - *Ex situ performance testing post-irradiation*
- **Lacking *in situ* testing approaches**
  - *Leverage PNNL facilities to develop new testing methods*

Single Component Isotherm Evaluation

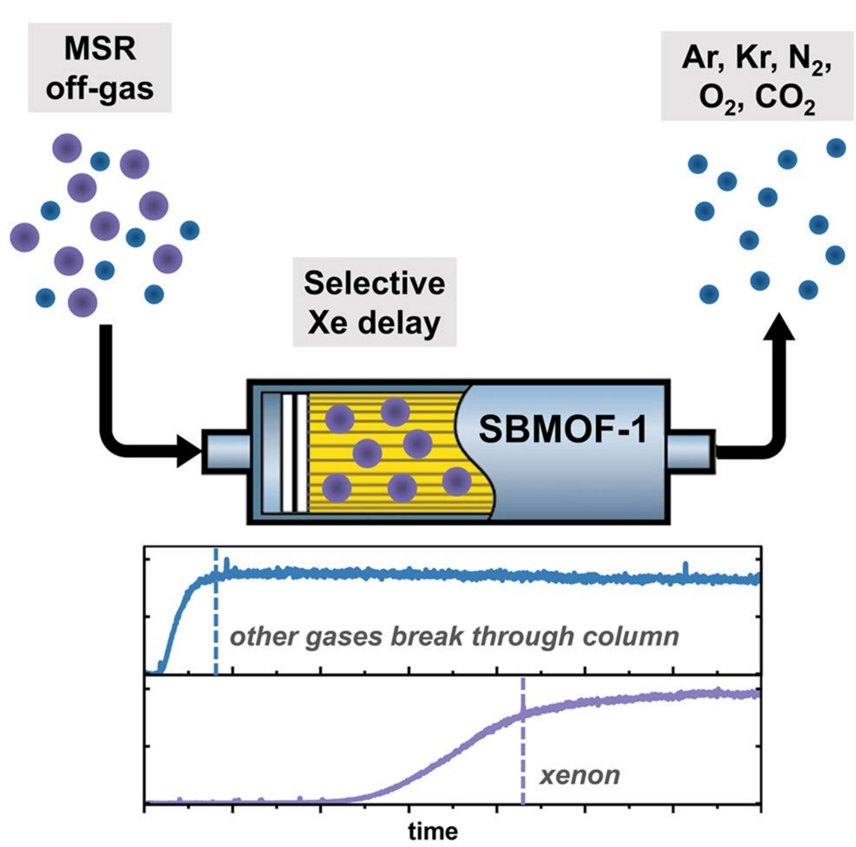


Nat Commun, **2016**, *7*, ncomms11831

Gas Capacity

$$q_i = \frac{p_i v t_s}{RTm}$$

Breakthrough Testing of a Packed Bed



Cell Rep Phys Sci, **2024**, *5* (2), 101829

Gas Selectivity

$$S_{BT} = \frac{q_i/q_j}{p_i/p_j}$$

Langmuir **2012**, *28* (31), 11584–11589

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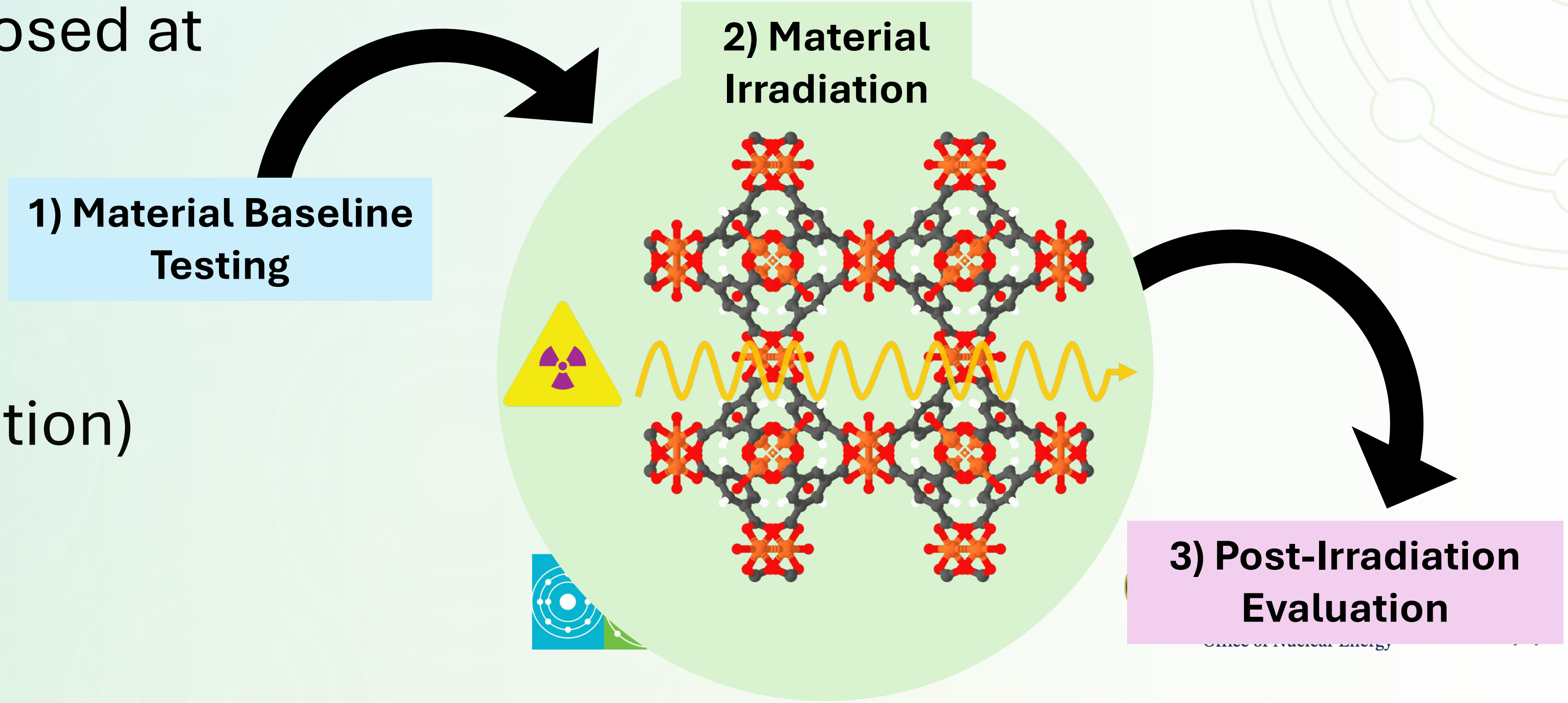
Nuclear Energy Applications Require Radiation Stable Sorbent Materials

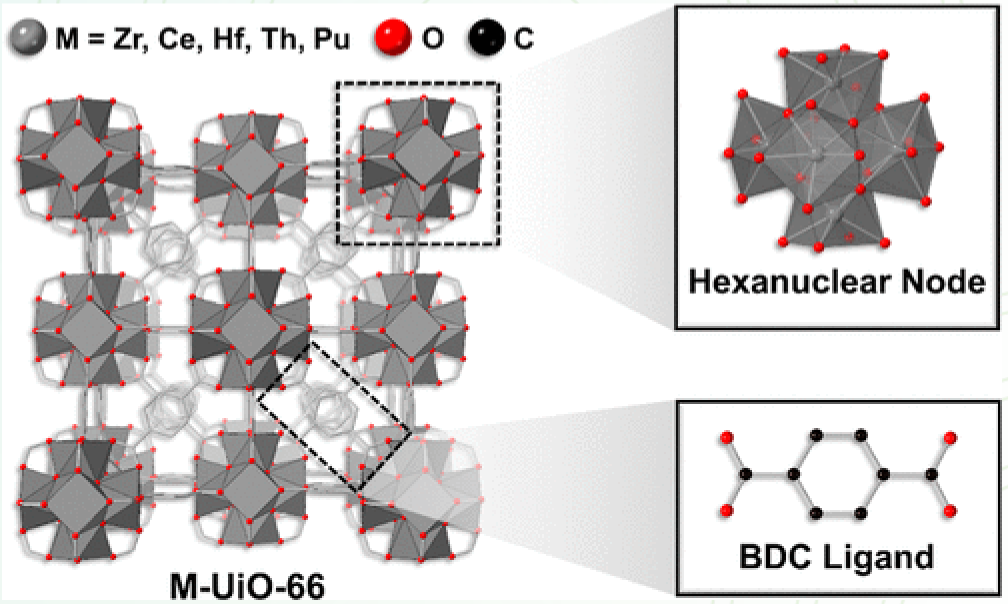
- Radiation tolerance required for sorbents used for noble gas separation of off-gas
- Tolerance impacted by several factors (e.g., composition, metal centers, linkers, dose rate)
- Exemplar sorbent candidates exposed at PNNL radiation facilities
  - ^{60}Co gamma source
  - Cumulative does was 1 MGy
- Material performance (gas adsorption) analyzed before and after

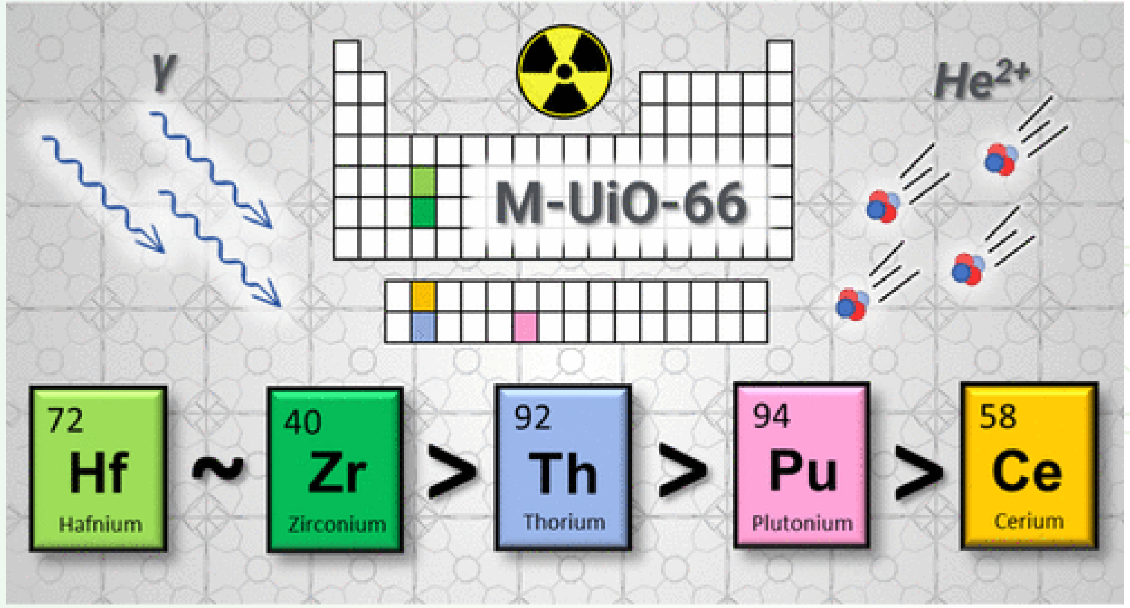
Samples for Irradiation



Impacts of Radiation on MOFs

- ❑ MOFs provide an opportunity to study impact of radiation in a systematic manner
- ❑ Absorption cross section is an important factor, but it is not sufficient to understand radiation stability
- ❑ MOFs with organic struts with extended π systems have shown improved radiation stability
- ❑ Presence of electron-donating groups in MOFs shows higher radiation stability.
- ❑ Presence of defects can facilitate energy dissipation, potentially enhancing the radiation stability.
- ❑ MOFs decorated with single functional groups are less stable than dual functional group

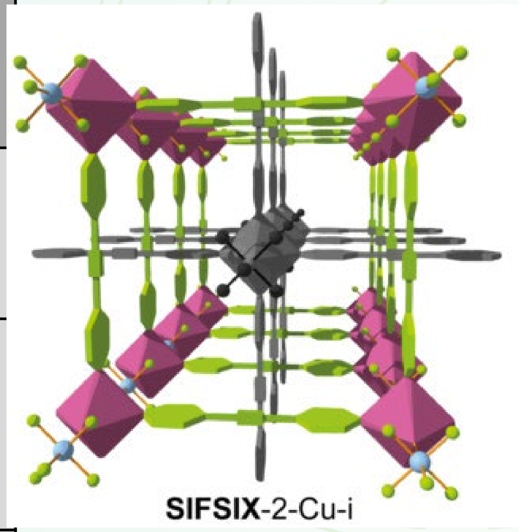


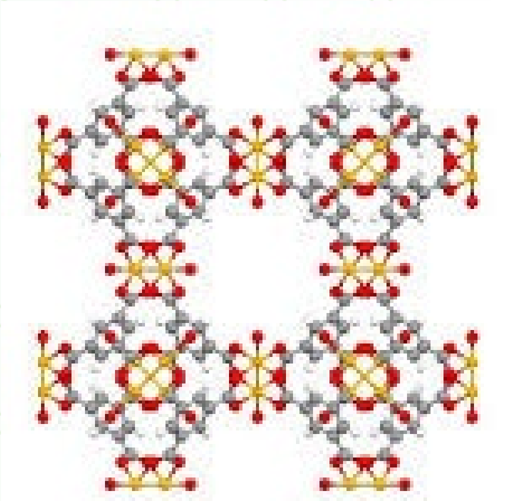


Chem.Mater.2022,34,8403−8417

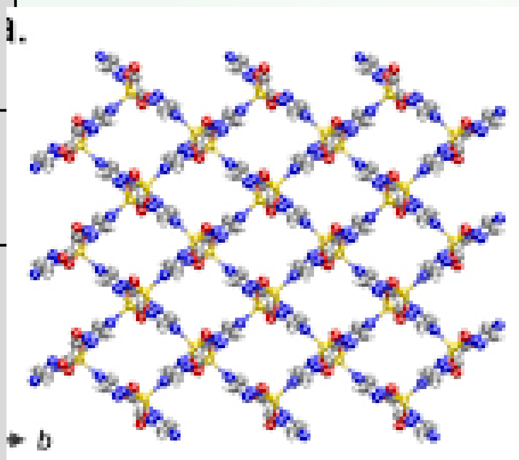
MOFs Studied for Radiation Studies

	SIFSIX-2-Cu-i	HKUST-1	CALF-20	SBMOF-1
Metal Node	Cu^{2+}	Cu^{2+}	Zn^{2+}	Ca^{2+}
Organic Lineker	4,4′-dipyridylacetylene	Benzene-1,3,5-tricarboxylate	1,2,4-triazolate + oxalate	4,4′-sulfonyldibenzoate
BET (m^2g^{-1})	~735	1,000–1,800	~520–550	~240–470
Pore size (Å)	~5.15	~9, 1.1 and 5	~4	~5.1
Moisture stability	Moderate	Poor	Excellent - >450,000 steam cycles	Stable
Thermal stability (°C)	170	~240–300	350	450
Scale up	Lab-scale	Commercial	Industrial	Lab scale
Radiation	Unknown	Unknown	unknown	unknown

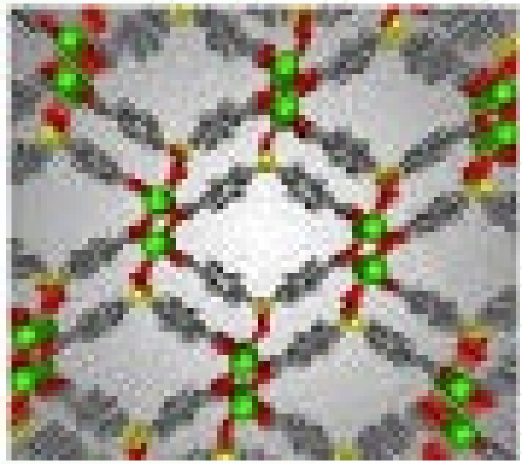




HKUST-1



CALF-20

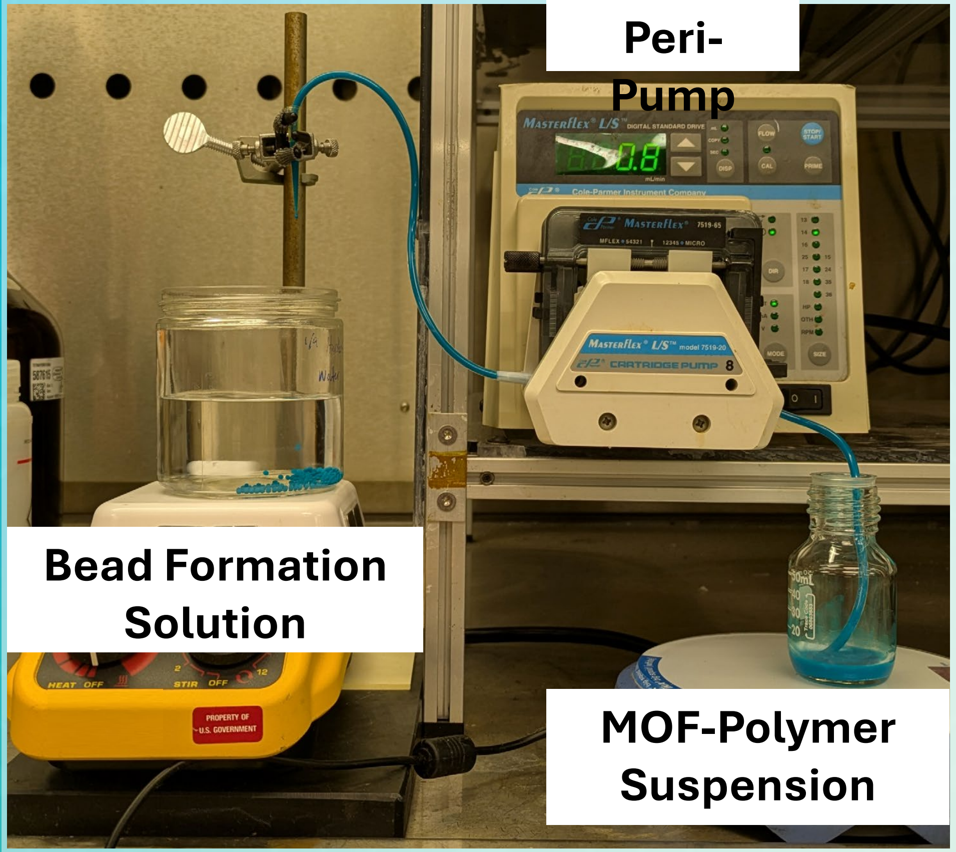


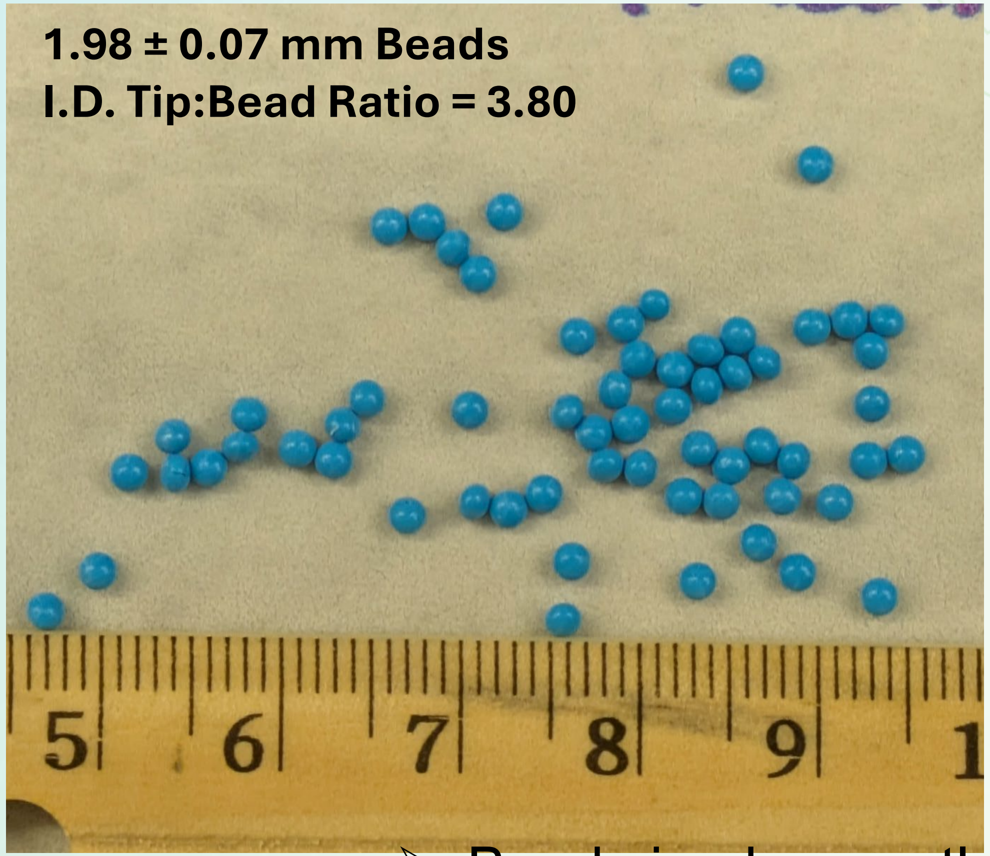
SBMOF-1

Banerjee, Nat. Comm, 2016,
Shekhah, O., et. al., *Nat Comm* 2014.
JB Lin · Science 2021

Processing Methods Impact Radiation Stability

1. MOF powders → Irradiation (1 MGy) → Characterization
2. MOF beads without polymers → Irradiation (1 MGy) → Characterization
3. MOF beads with polymer (composites) → Irradiation (1 MGy) → Characterization





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

- ➢ 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

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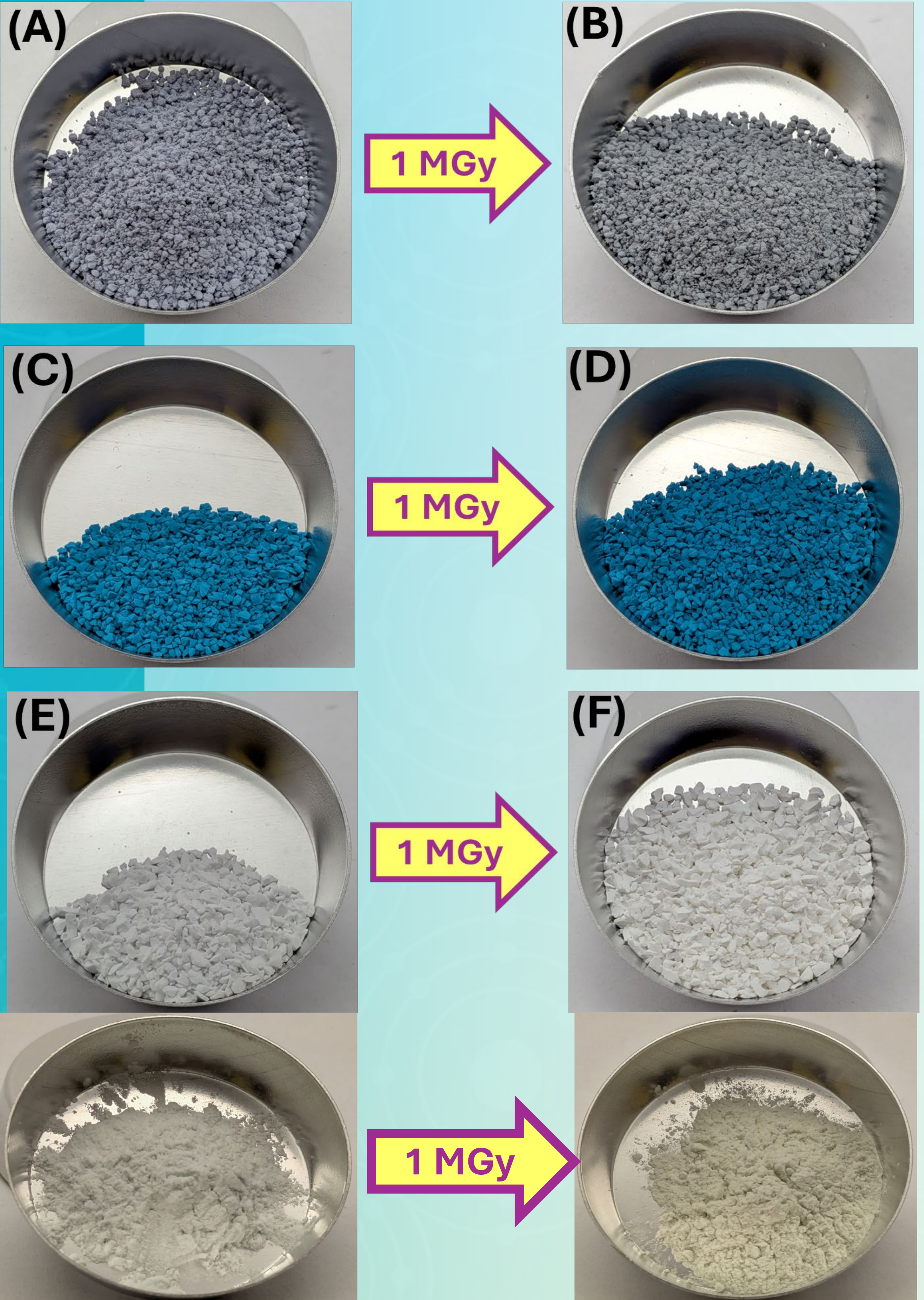
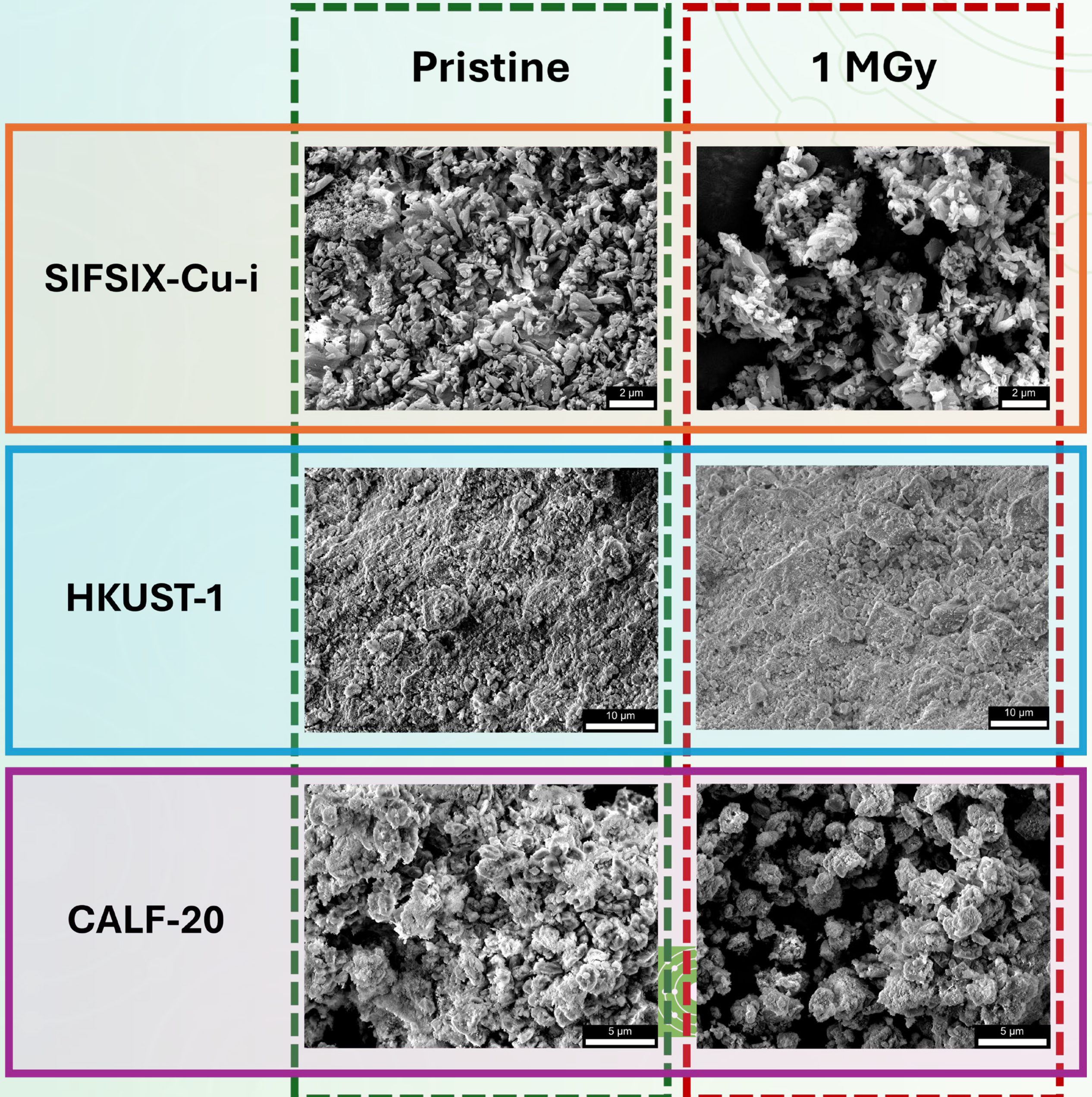
All Material Types Showed Morphological and Structural Radiation Tolerance





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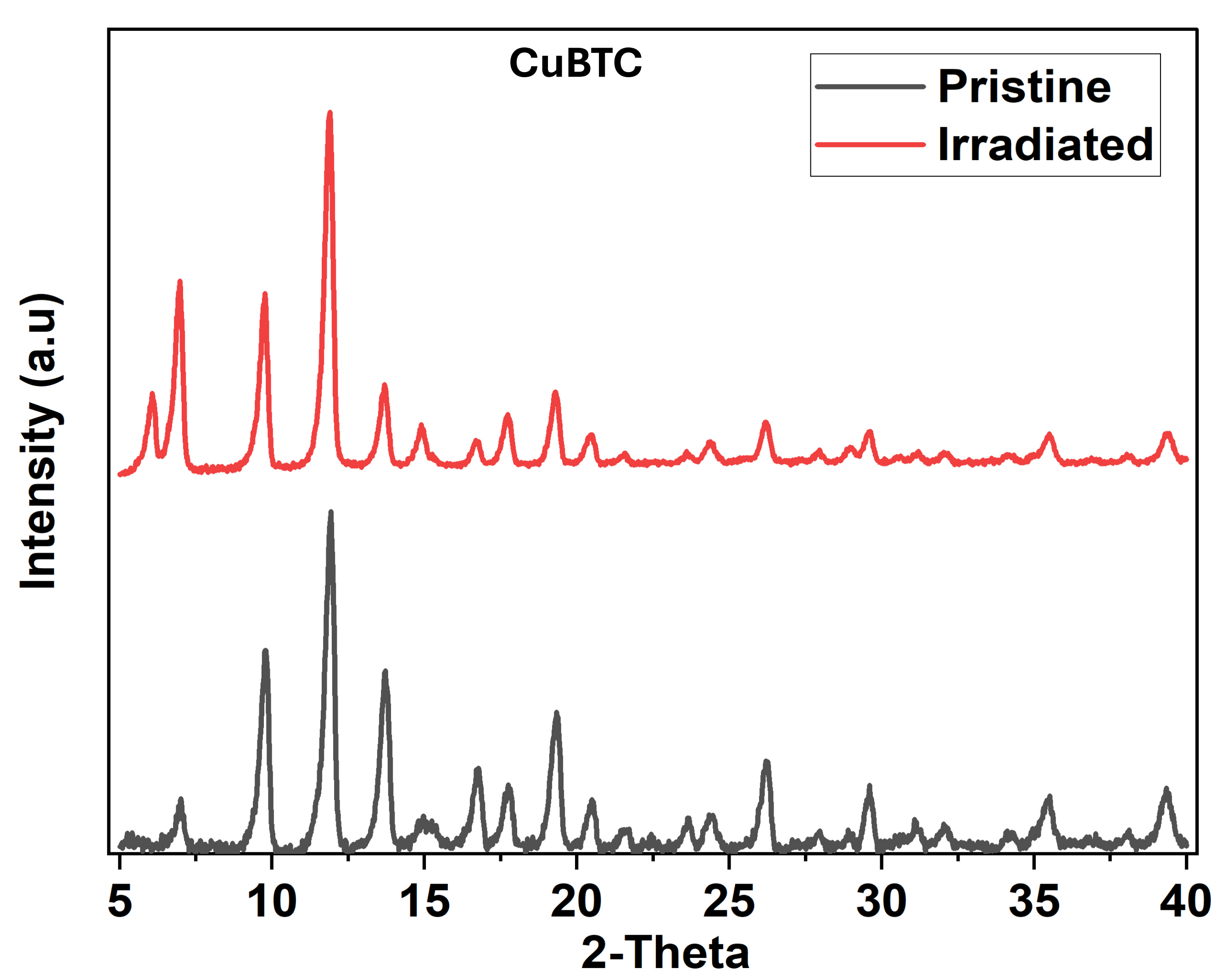

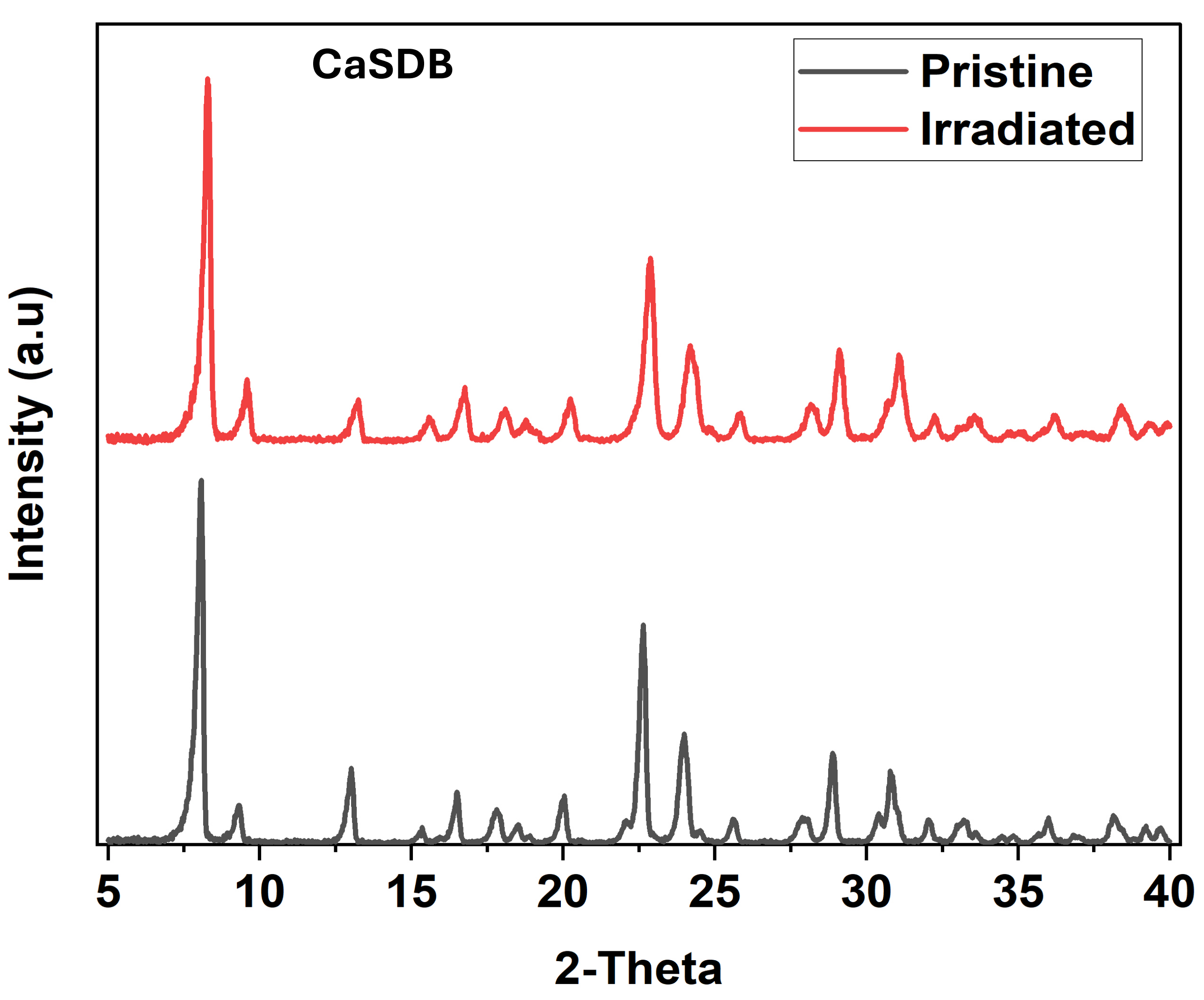

Sorbents showed little change in XRD patterns (i.e. no additional phases and limited increased in amorphous phase) post-irradiation

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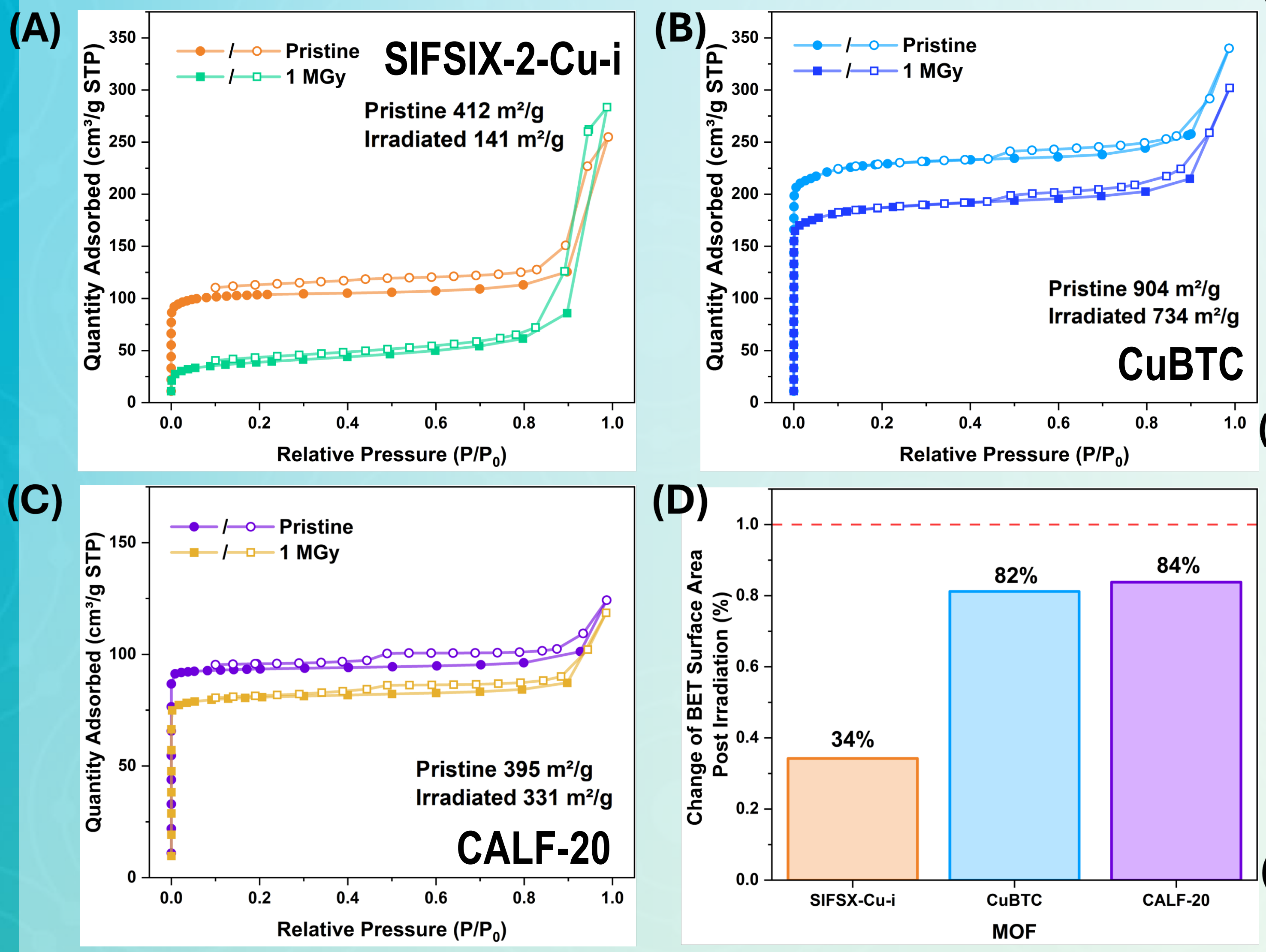
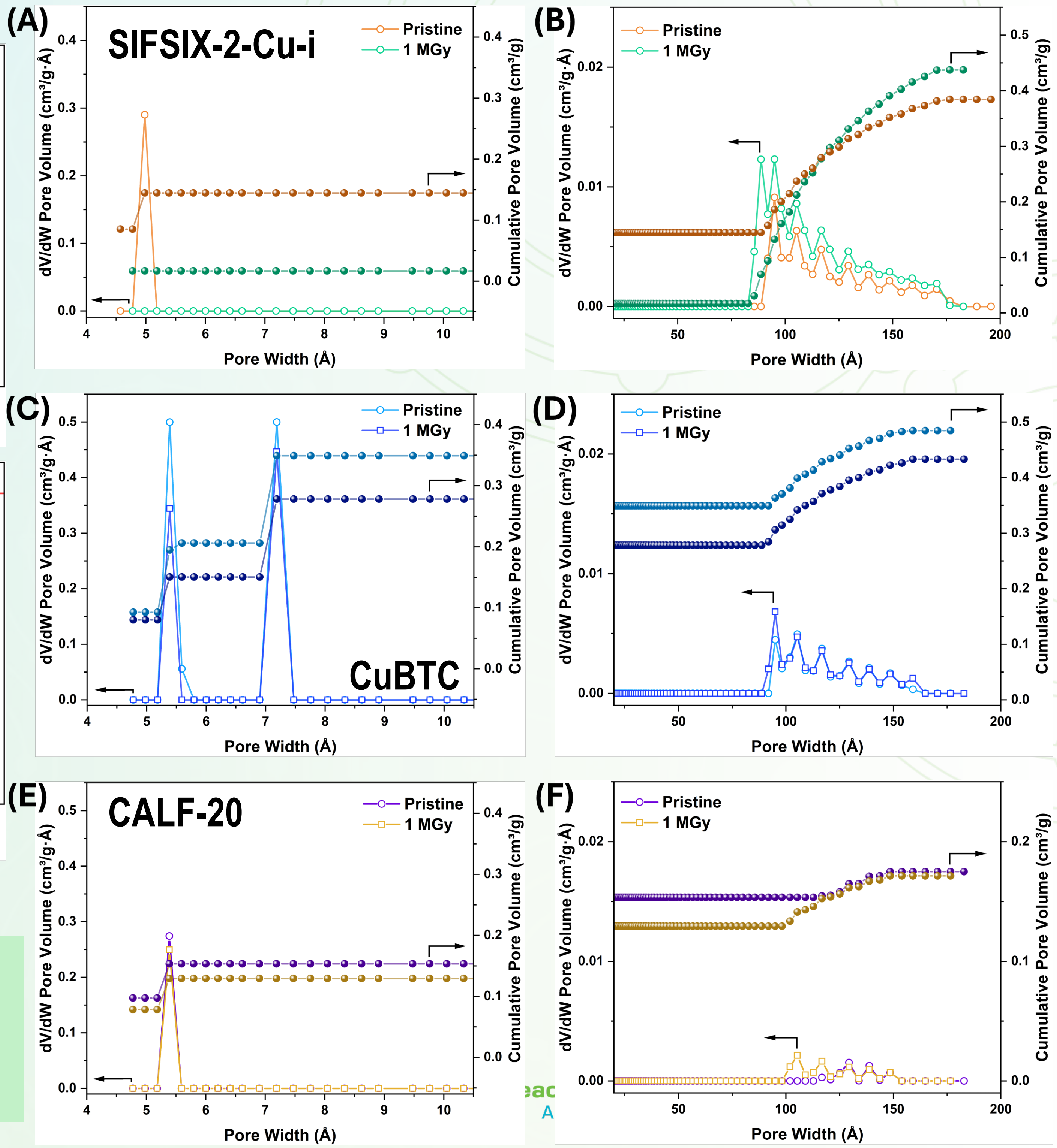
Textural Properties Post-Irradiation





N_2 Adsorption Isotherms Showed:

- Decreased surface areas* and micropore volume distribution
- Increased mesopore volume and distribution

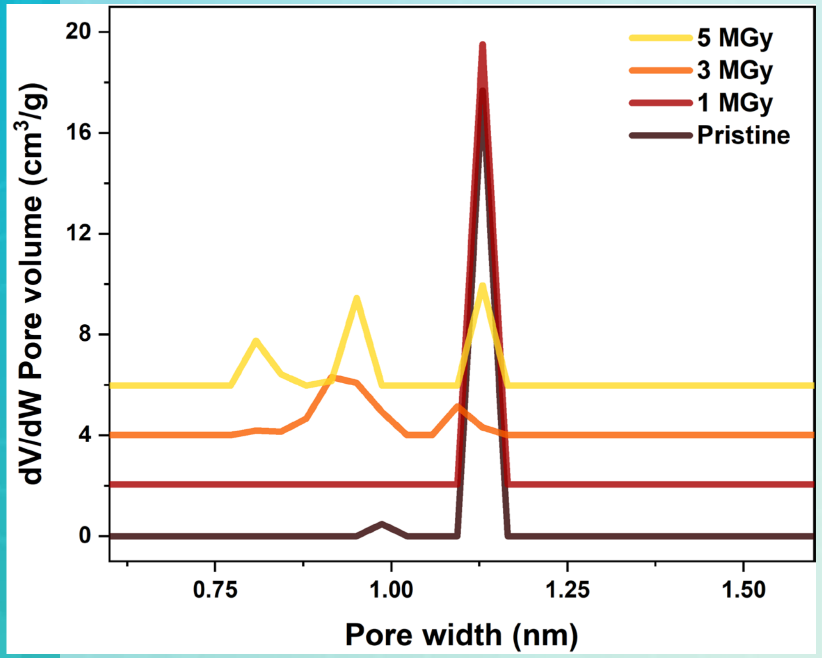
BETSI Used to calculated BET surface areas (DOI: 10.1002/adma.202201502)

Non-Monotonic Degradation Behavior Likely Result of Walk-on Radiolysis

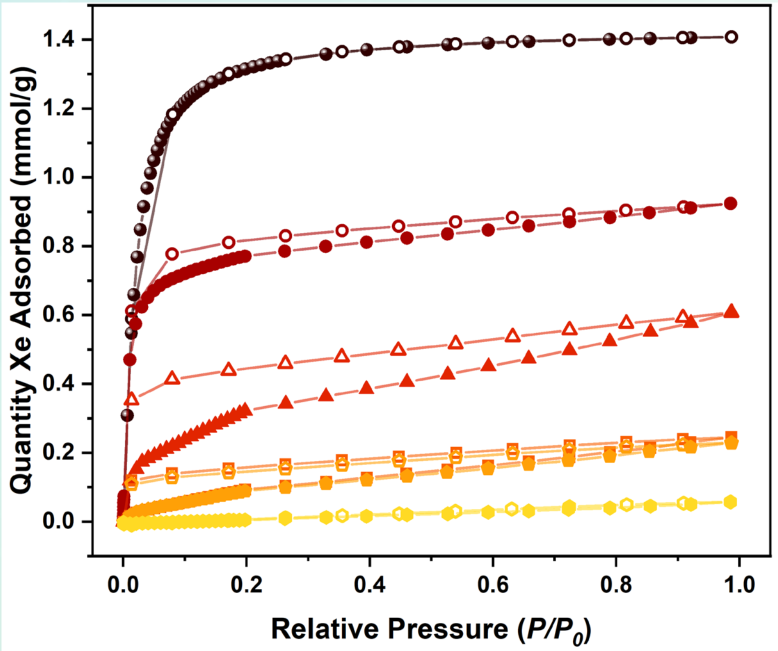
Hypothesis:

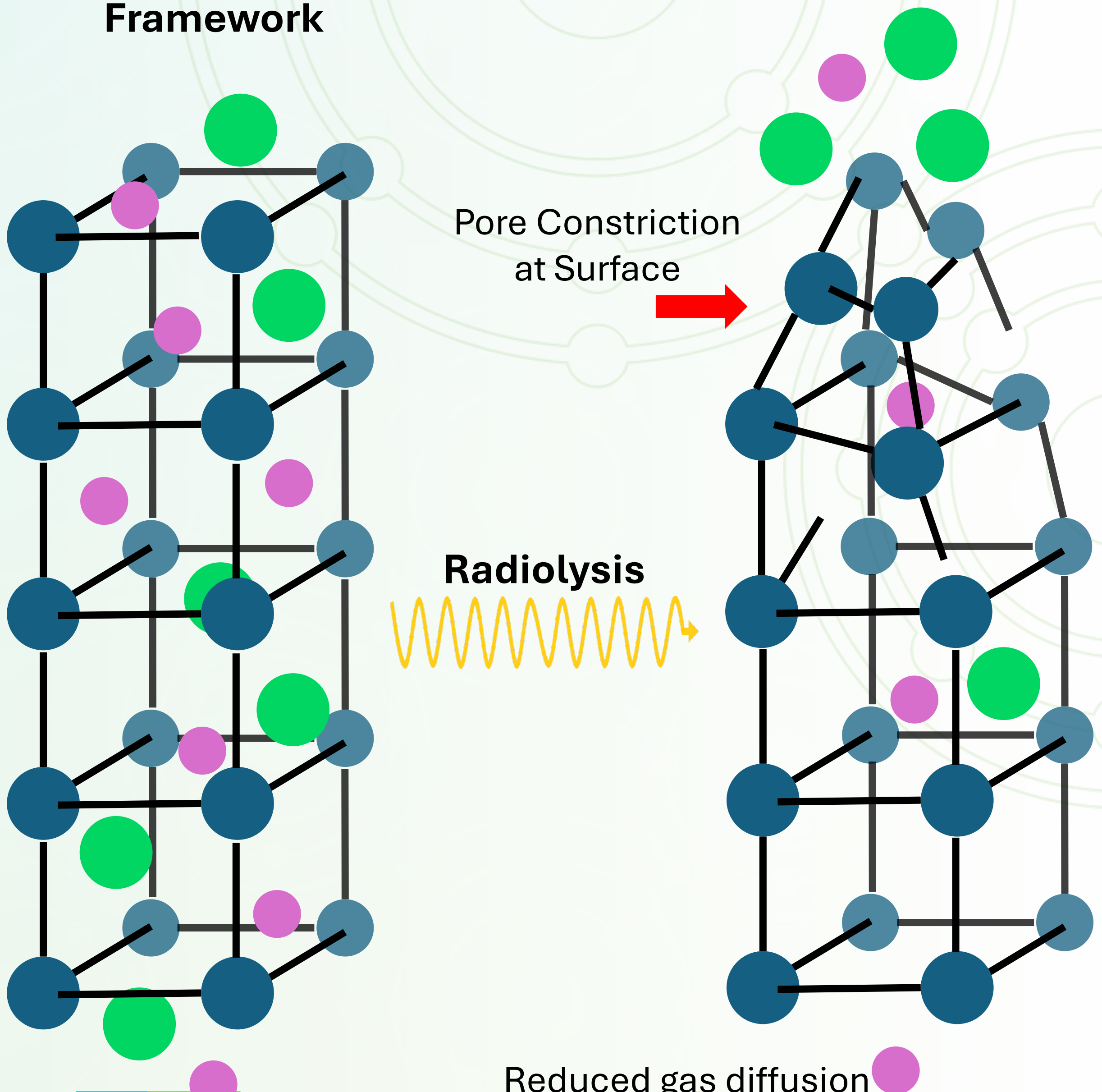
Radiation induced degradation of local structure is site dependent and differs between external surface and bulk

Wider Micropore Size Distribution Post-Irradiation



Xe Adsorption at –80°C





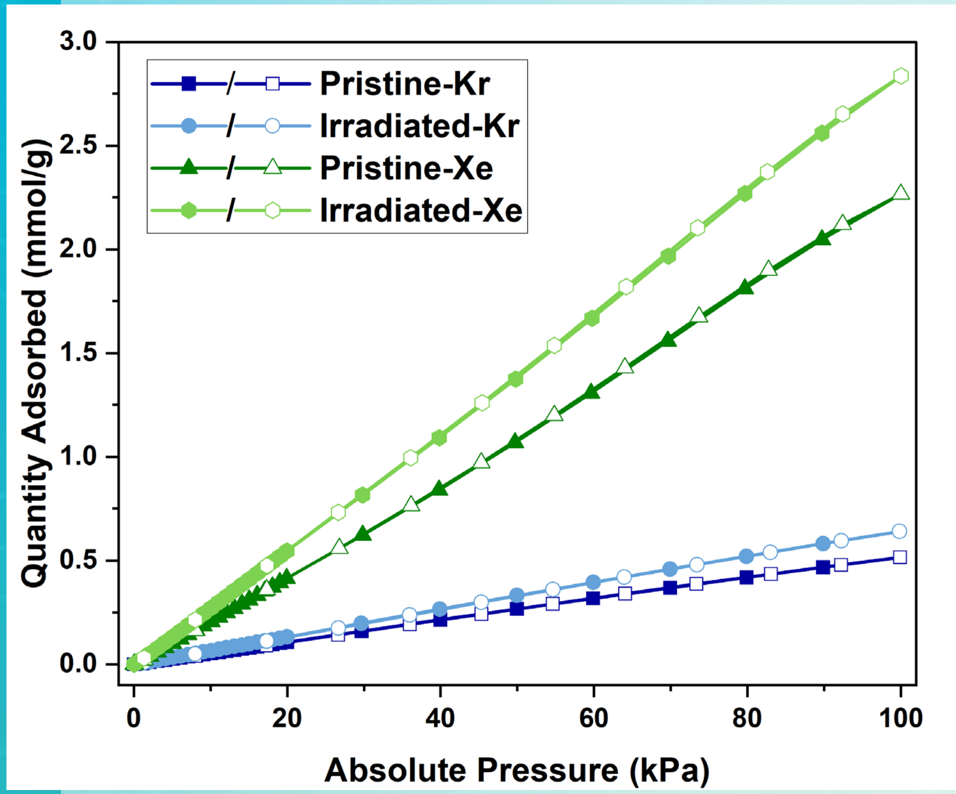
Degradation Pathway:

Radiolysis Induced Pore Contraction

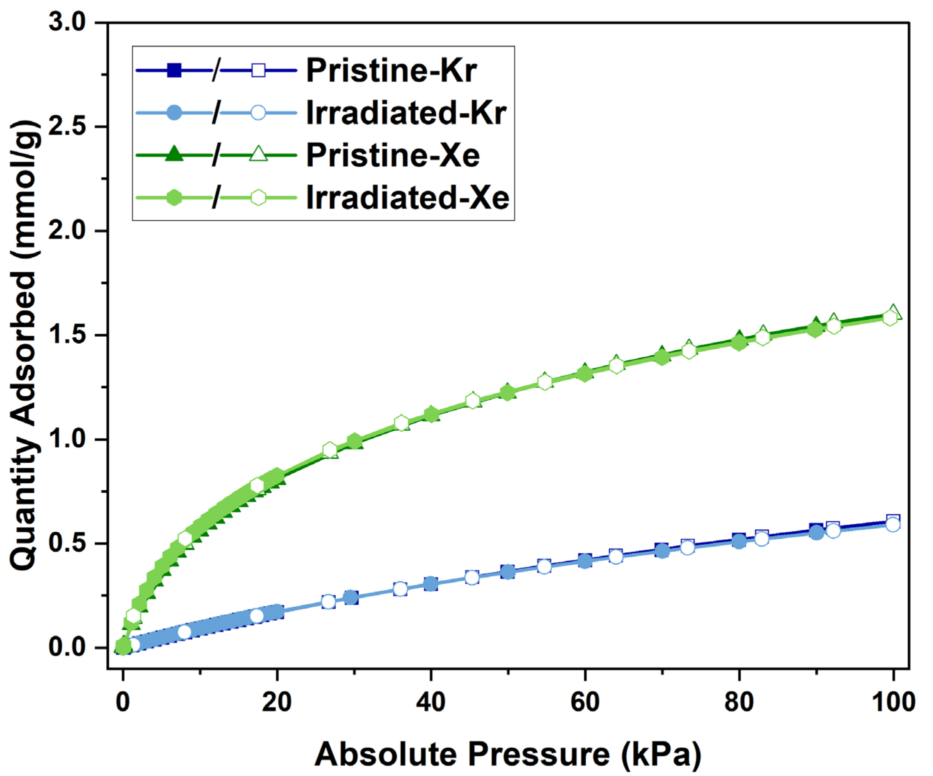
Krishnan, Hurlock, *et al. Langmuir* **2025**, *41*, 33, 22193–22199

Single Component Noble Gas Isotherms: Xe and Kr at 298 K (Composites)

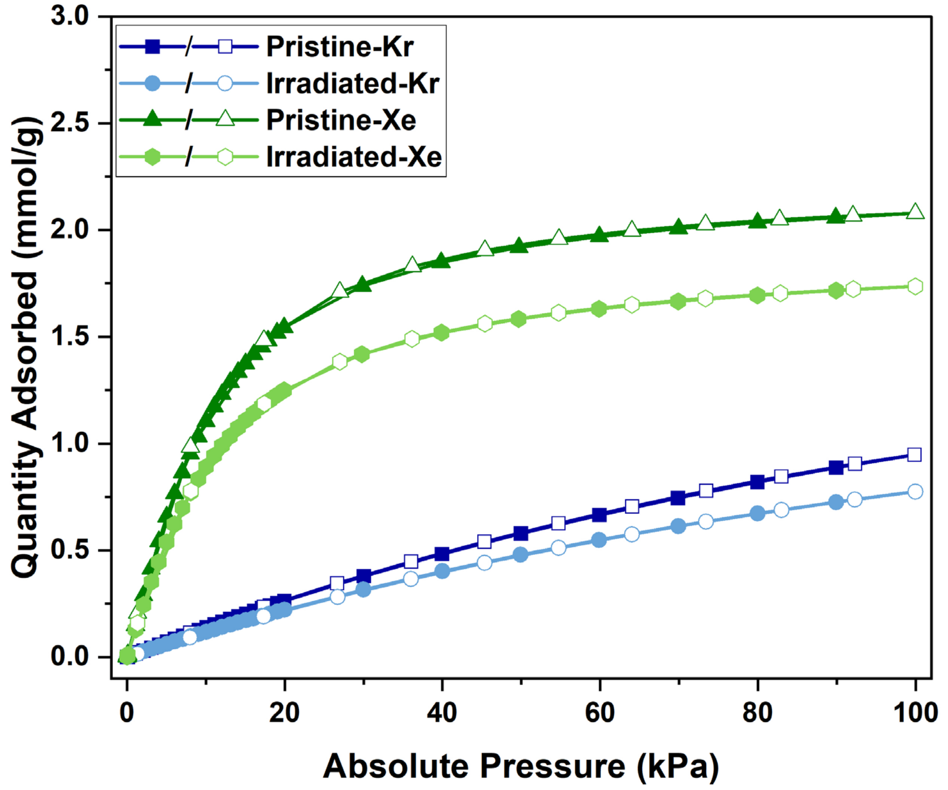
SIFSIX-2-Cu-i



CuBTC



CALF-20



Activation conditions:

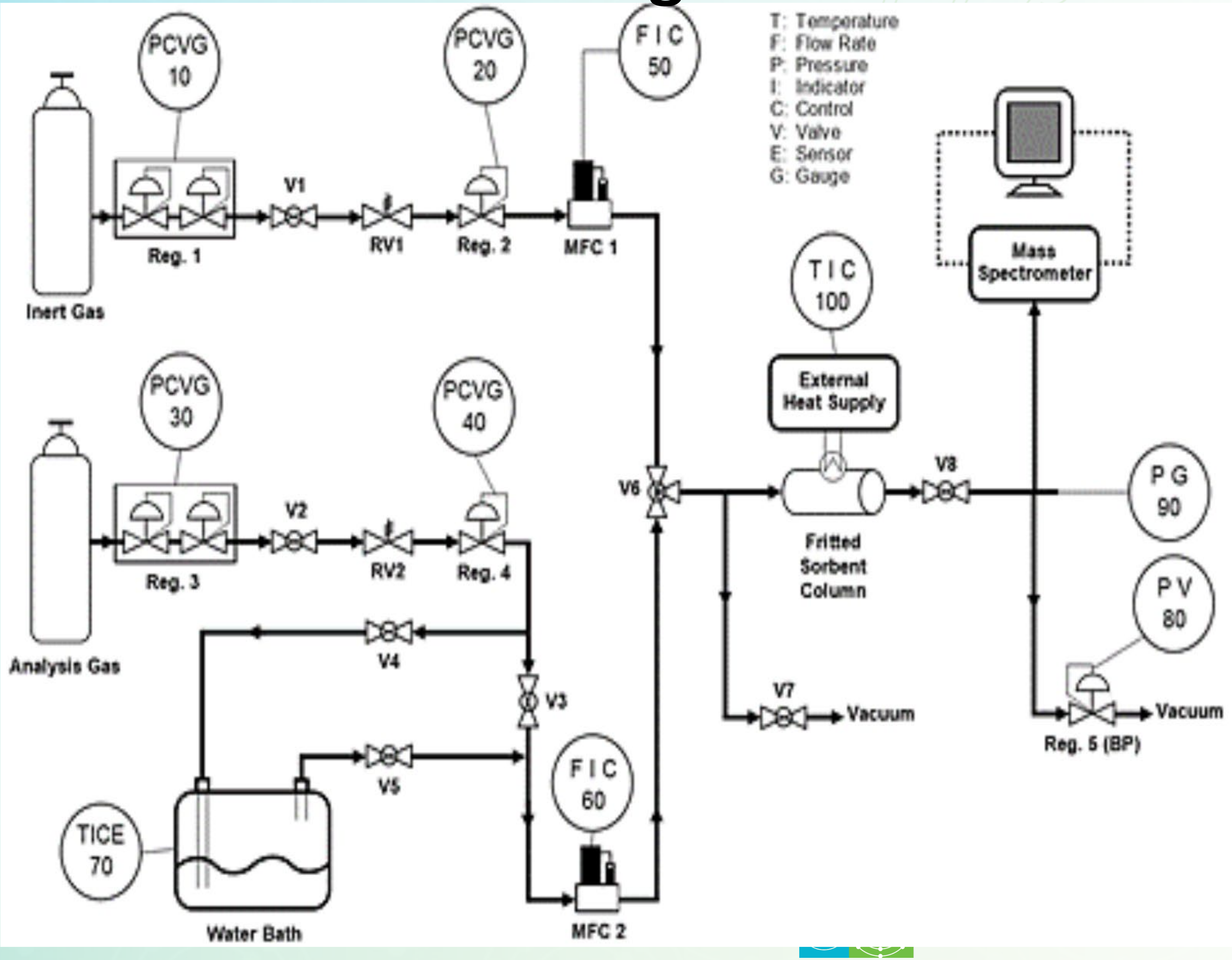
- SIFSIX-2-Cu-i: 16 hours at ambient temp. (about 24°C)
- CuBTC composite: 16 hours at 150°C
- CALF-20: 16 hours at 150°C

298 K Isotherm Results Showed:

- SIFSIX-2-Cu-i: *Increase* in both Xe and Kr uptakes across pressure range
- CuBTC composite: No substantial change post-irradiation, isotherms unchanged
- CALF-20: *Decrease* in uptake for Xe and Kr across pressure range

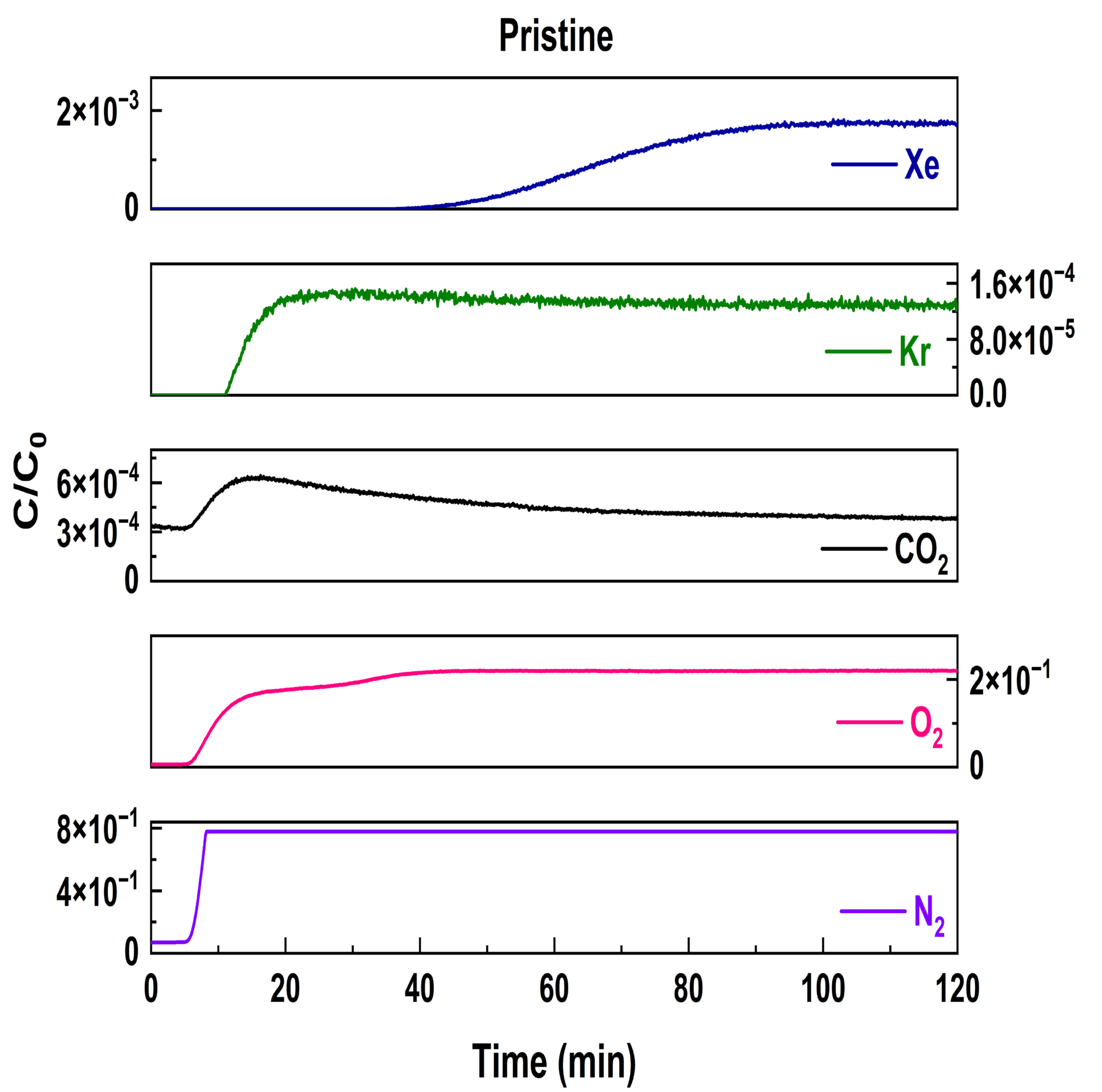
Differences observed likely result of difference in structure and binder

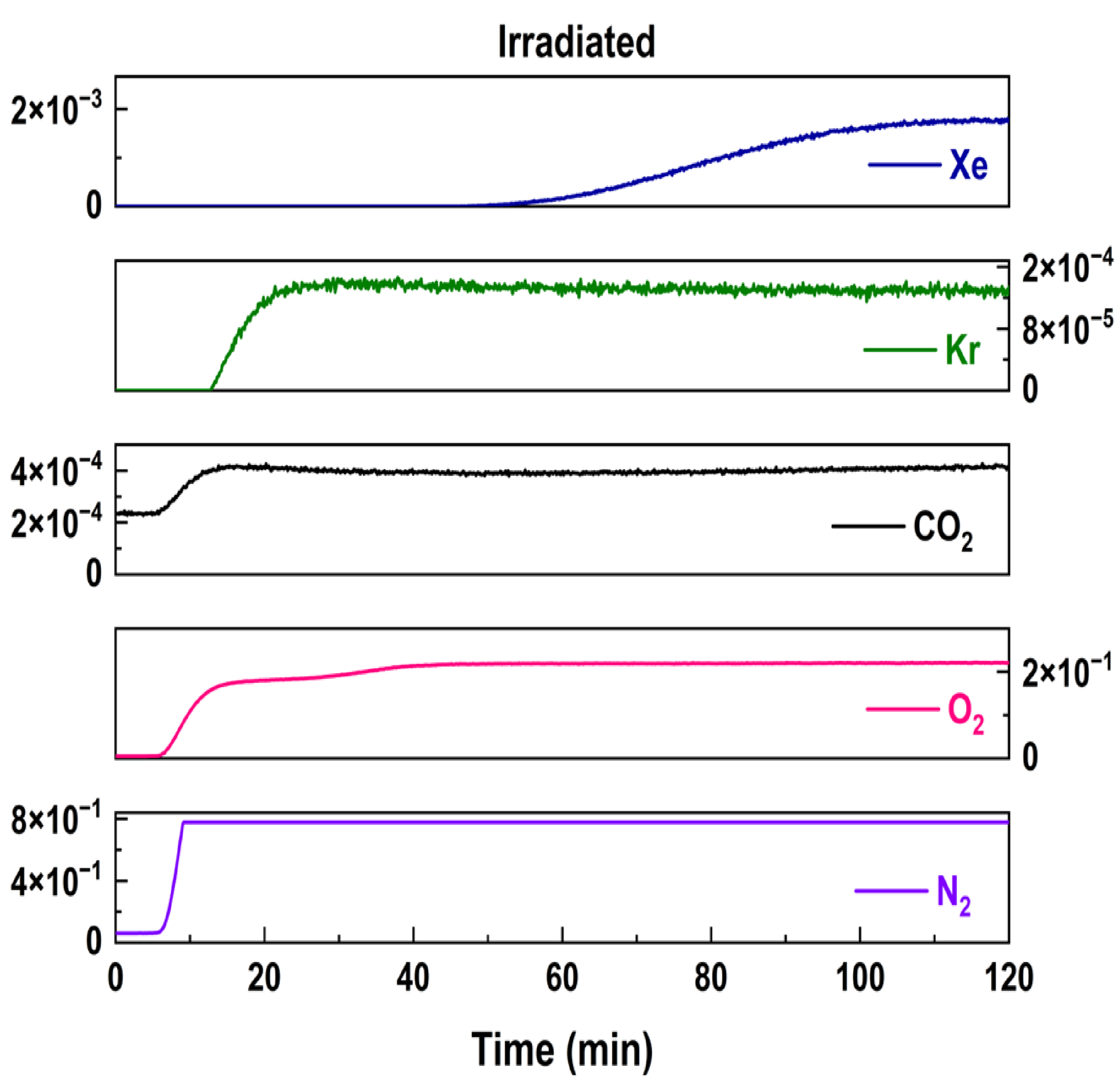
Noble Gas Performance Testing Before and After Irradiation



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

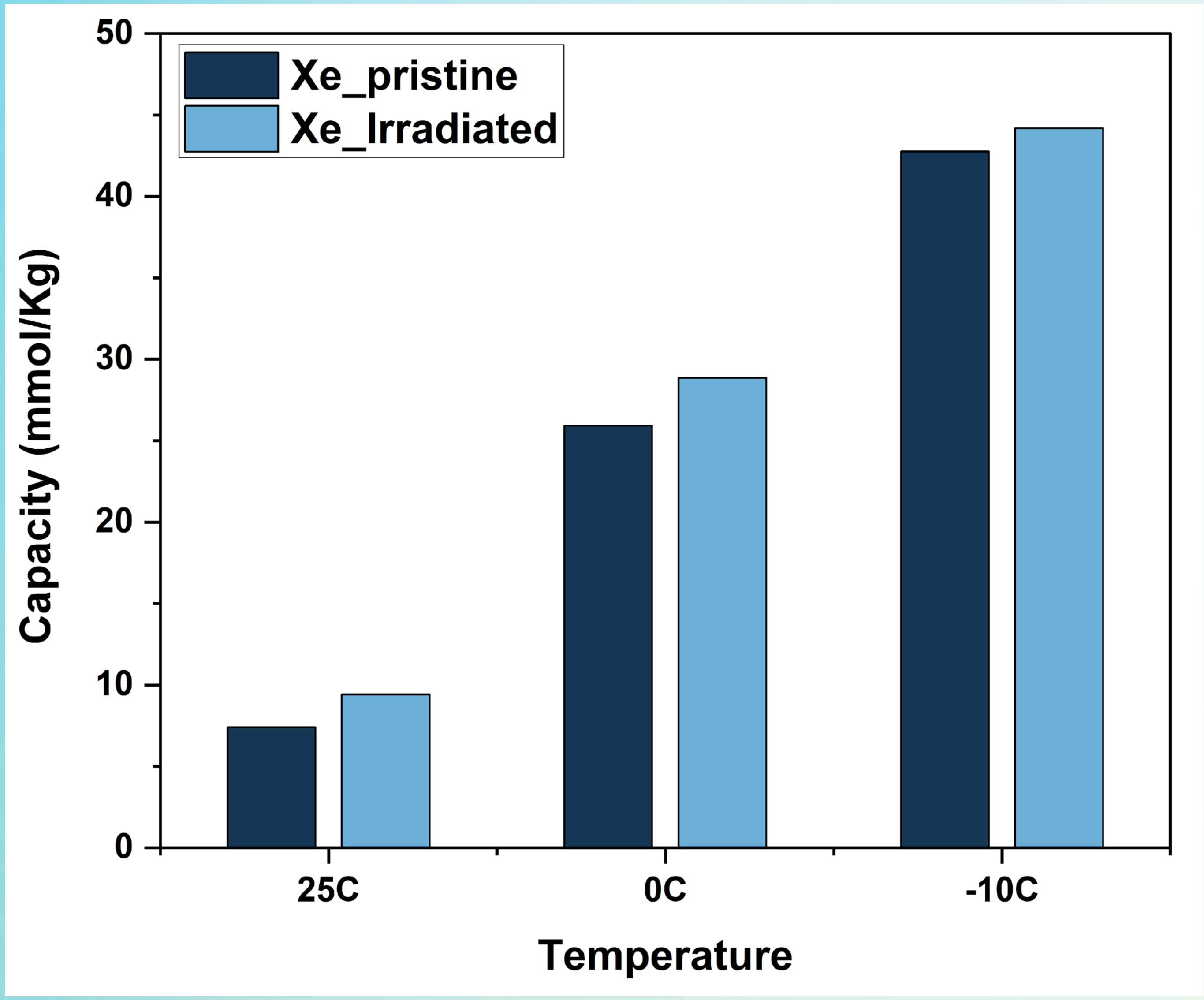
Breakthrough Analysis-CALF20

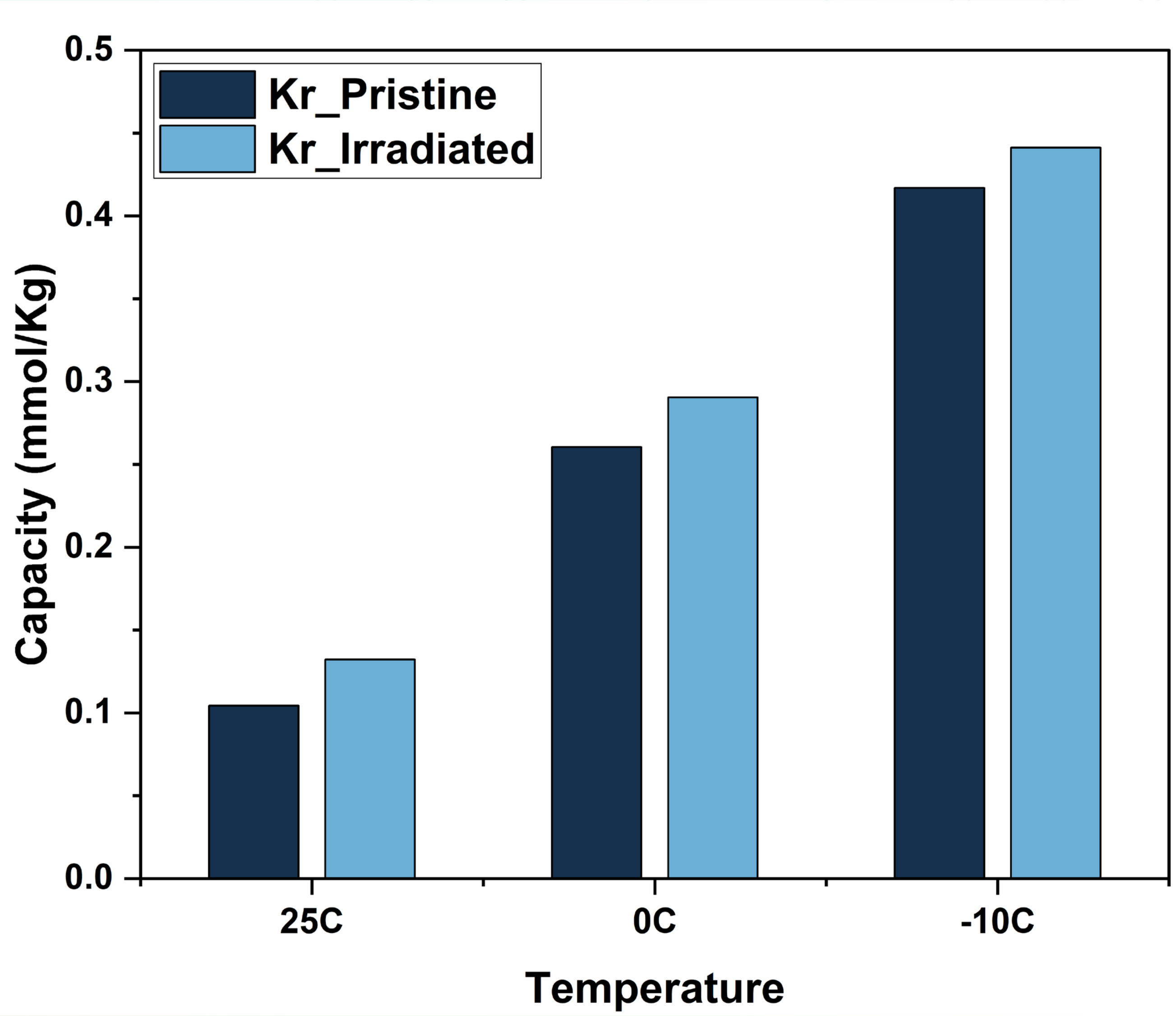




Activation conditions: 16 hours at 150°C

Breakthrough analysis-CALF20





Breakthrough results showed:

- Slight increase in Xe and Kr **saturation** capacity post irradiation.
- Overall, the material integrity is preserved post irradiation

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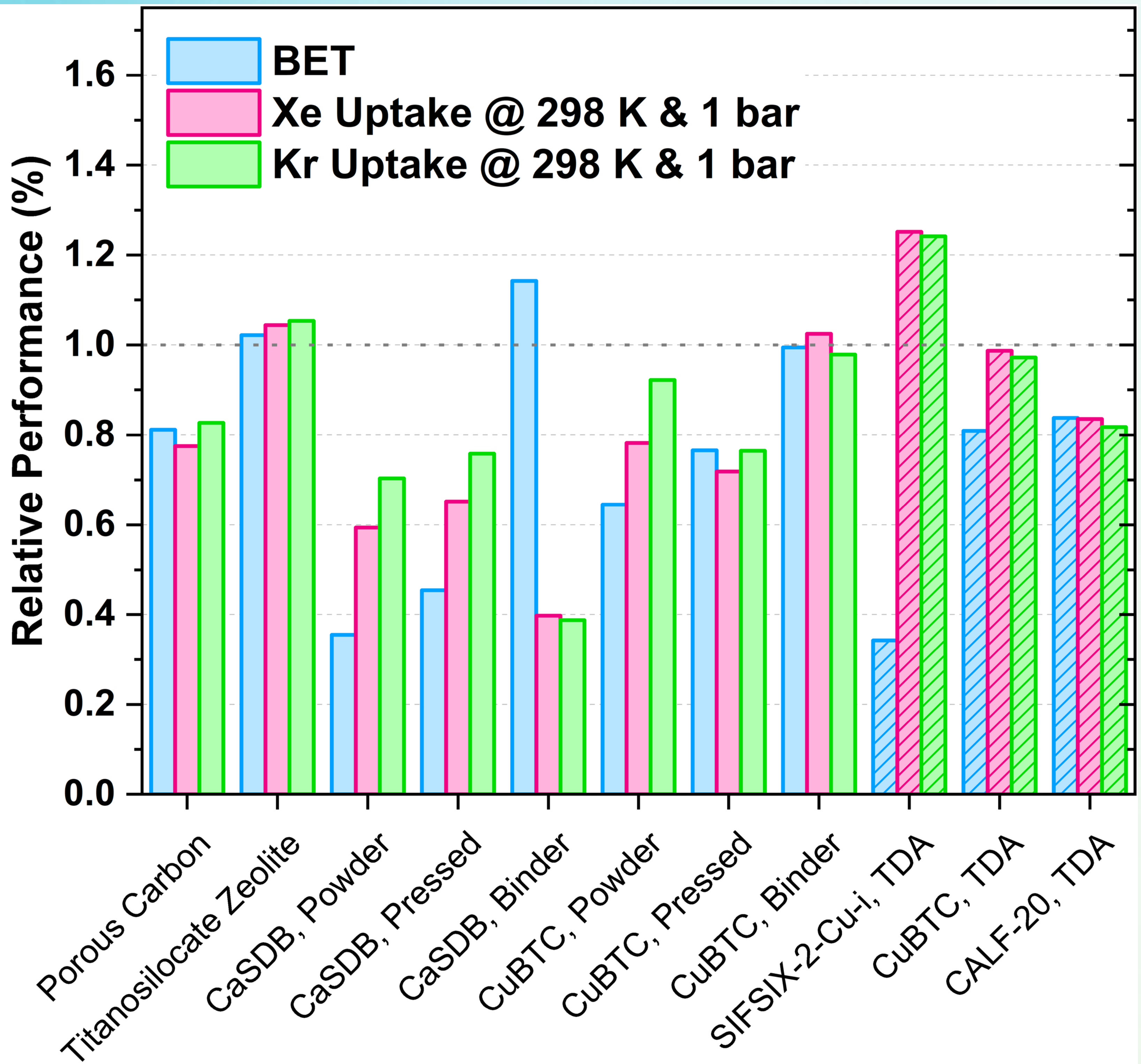
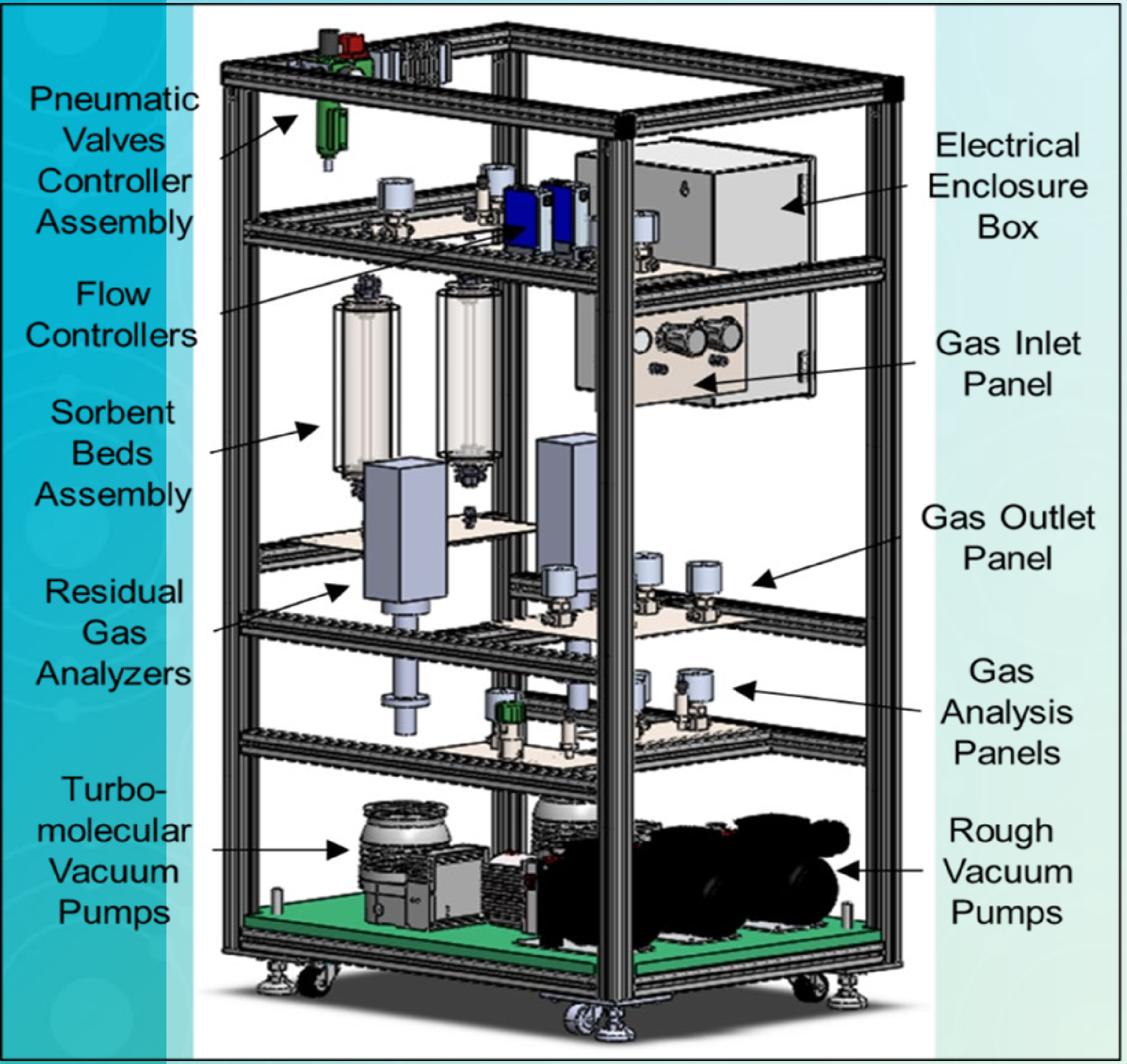
Material Comparison Before and After Irradiation

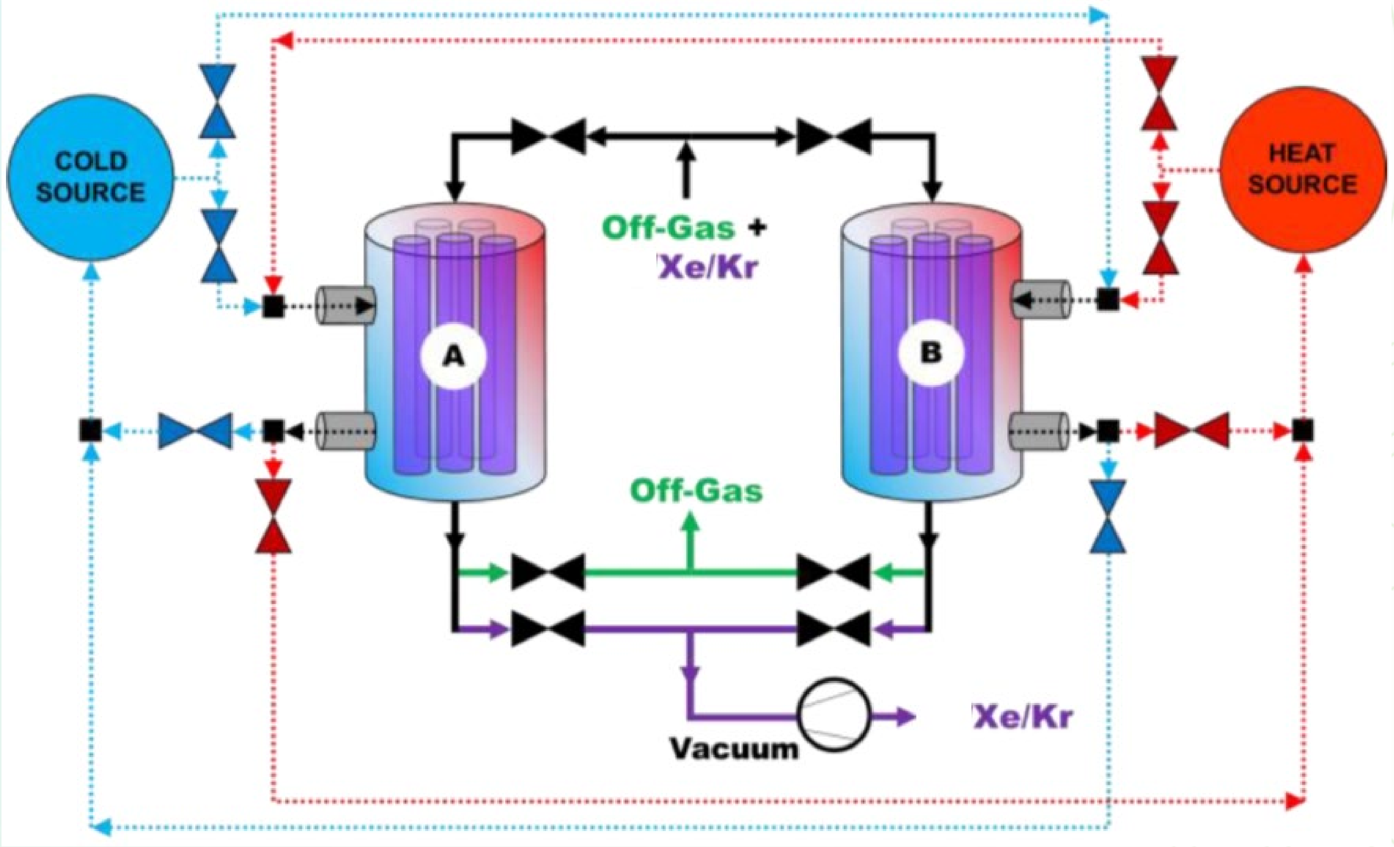


MOF-composite samples performing at or better than porous carbons post-irradiation

What Next?



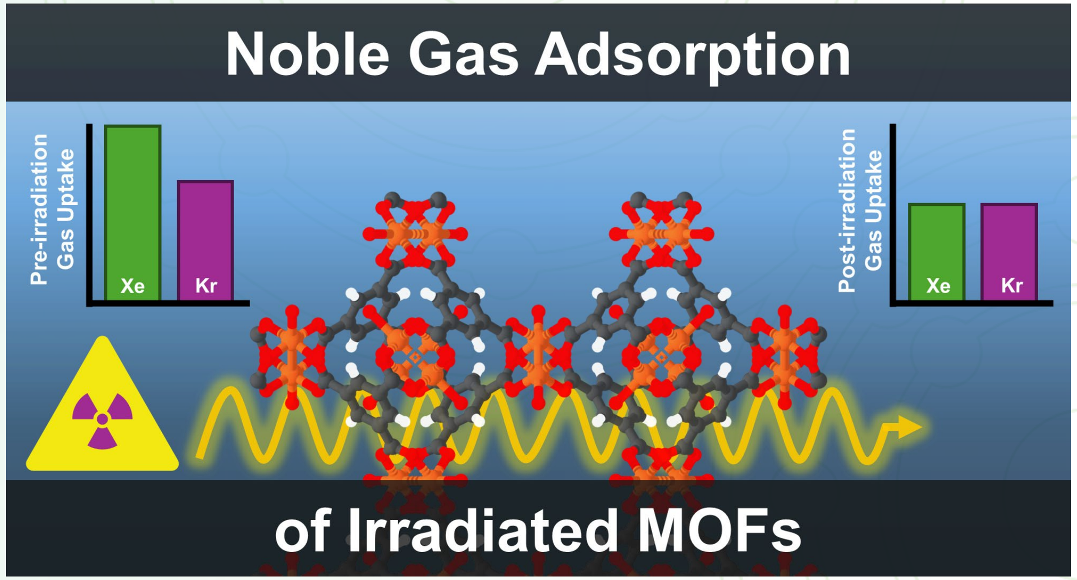
Pressure, Temperature Swing Adsorption Process



- **Designing the upstream controls to ensure the Noble gas system operational ranges are satisfied:**
  - Does delay bed require before noble gas system?
  - Impact of halide, oxygen and water on noble gas system?
  - Develop an integrated off-gas system flow sheet
  -

Summary and Conclusions

- Illustrated the holistic approach starting from fundamental material discovery to performance testing to economic analysis and implementation
- Showed that
  - Depending on the MOF, and its composition with and without binder affects its radiation stability
  - Zeolites and MOFs show similar trends and tolerance
  - Sorbent processing with binder can help



Krishnan, Hurlock, *et al.* *Langmuir* **2025**, *41*, 33, 22193–22199

<u>Ongoing and Future Work</u>

- Develop an Off-gas system to evaluate the performance at the bench scale
- Demonstration of large-scale noble gas separation from simulated process streams
- Optimization and automation of sorbent synthesis and testing
- Development and testing using *in situ* methods

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Molten Salt Reactor PROGRAM

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Office of Nuclear Energy