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Ongoing Research Activities at PNNL in Support of MSR Development

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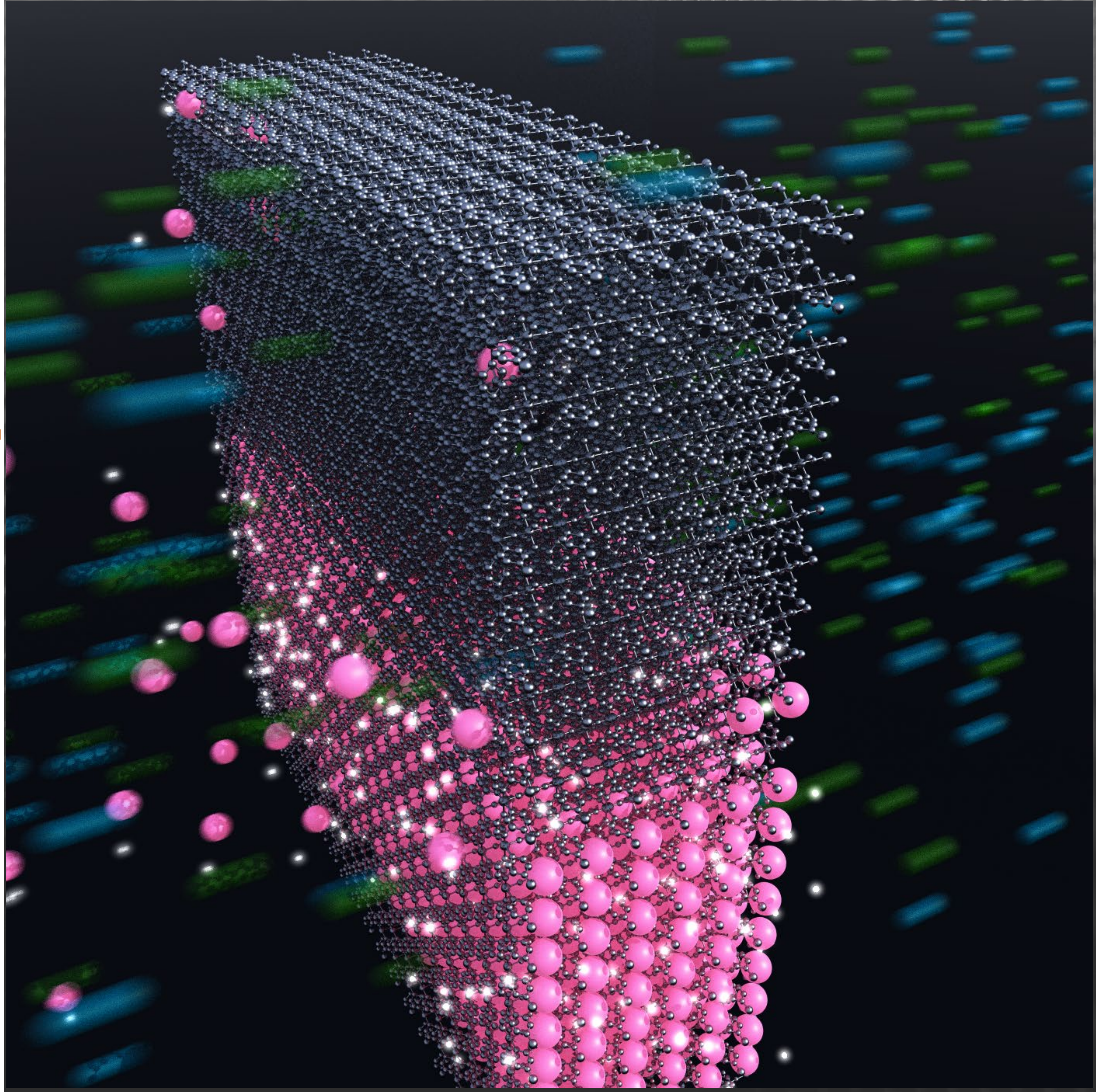
U.S. DEPARTMENT OF ENERGY BATTELLE



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Acknowledgements

DOE, NE-5, NE-4 ARPA-E and NNSA Offices

Dr. Patricia Paviet (NE-5) and Dr. Ken Marsden (NE-4), NTDs

- Dr. Manh-Thuong Nguyen –Ab initio calculations
- Dr. Huber, Zachary F - Structure-transport relationship in $NaCl$-$PuCl_3$ molten salts
- Dr. Bruce McNamara, Parker Okabe, Elizabeth Schoenberg, Zach Huber - Actinide Salt Synthesis
- Zach Huber, Bruce McNamara, Mike Powell - Cl-35/37 Separations through Thermal Diffusion Isotope Separation
- Dr. Tatiana G Levitskaia – Easy-XAFS
- Dr. Thomas Hartmann - Corrosion
- Dr. Heather Felmy, Dr. Amanda Lines and Dr. Samuel Bryan - OLM
- Dr. Praveen K. Thallapally, and Dr. Heinrik Goettsche – Off-gas management and gas sensors
- Dr. Mark Murphy – Radiation testing

DOE's 17 national laboratories tackle critical scientific challenges

Radiochemical Processing Laboratory (RPL)

Built in 1953 to support the Hanford production mission

1960 High-Level Radiochemistry Facility (HLRF) added

1963 Shielded Analytical Laboratory (SAL) added

1996-present Tritium Target Program

2001-present Support to Hanford Waste Treatment Plant

2017-present High Burnup Spent Fuel Performance Eval

2018-present Tank Side Cesium Removal

2022-2035 RPL Extended Life Program

2022-present Advanced Fuel Cycle R&D

A national asset with multiple missions—

- Nuclear nonproliferation
- Nuclear forensics
- Carbon-free nuclear power
- Legacy nuclear waste disposal
- Medical isotopes

Hazard Category **2** Non-Reactor Nuclear Research Facility

87 Radiological Laboratory Research Spaces

16 Hot Cells

22 Gloveboxes

160 Rad Fume Hoods

- Only radionuclide monitoring lab in the U.S. certified by the Comprehensive Nuclear-Test-Ban Treaty Organization to process air particulate samples
- Microgram-to-kilogram quantities of fissionable materials; megacuries of other radionuclides

MSR@PNNL

- Predict fundamental properties of molten salts using computational tools
- Validate models by synthesis and characterization of molten salts
- On-line monitoring, off-gas management, and isotope separation
- Waste-form development
- Materials Corrosion
- Prototype development and testing in collaboration with industrial partners
- Commercialization and technology transfer

Thermophysical and structural properties of $MgCl_2$-KCl

ab initio molecular dynamics

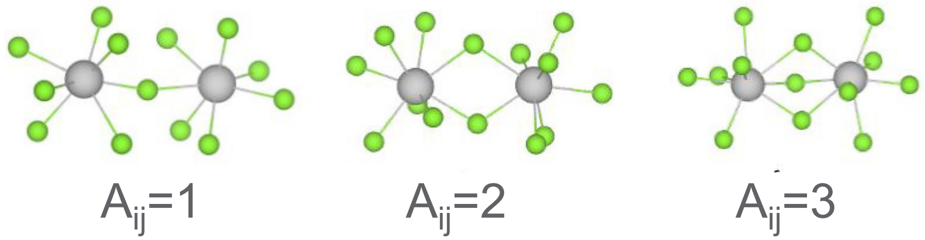
- Five compositions, four temperatures.
- Density increased with $MgCl_2$ concentration.
- Viscosity is dependent on the composition:
  - higher at 900 K and constant at 1200 K.
- Coordination number increased with $MgCl_2$ concentration and decreased with temperature.

Nguyen et al., in preparation

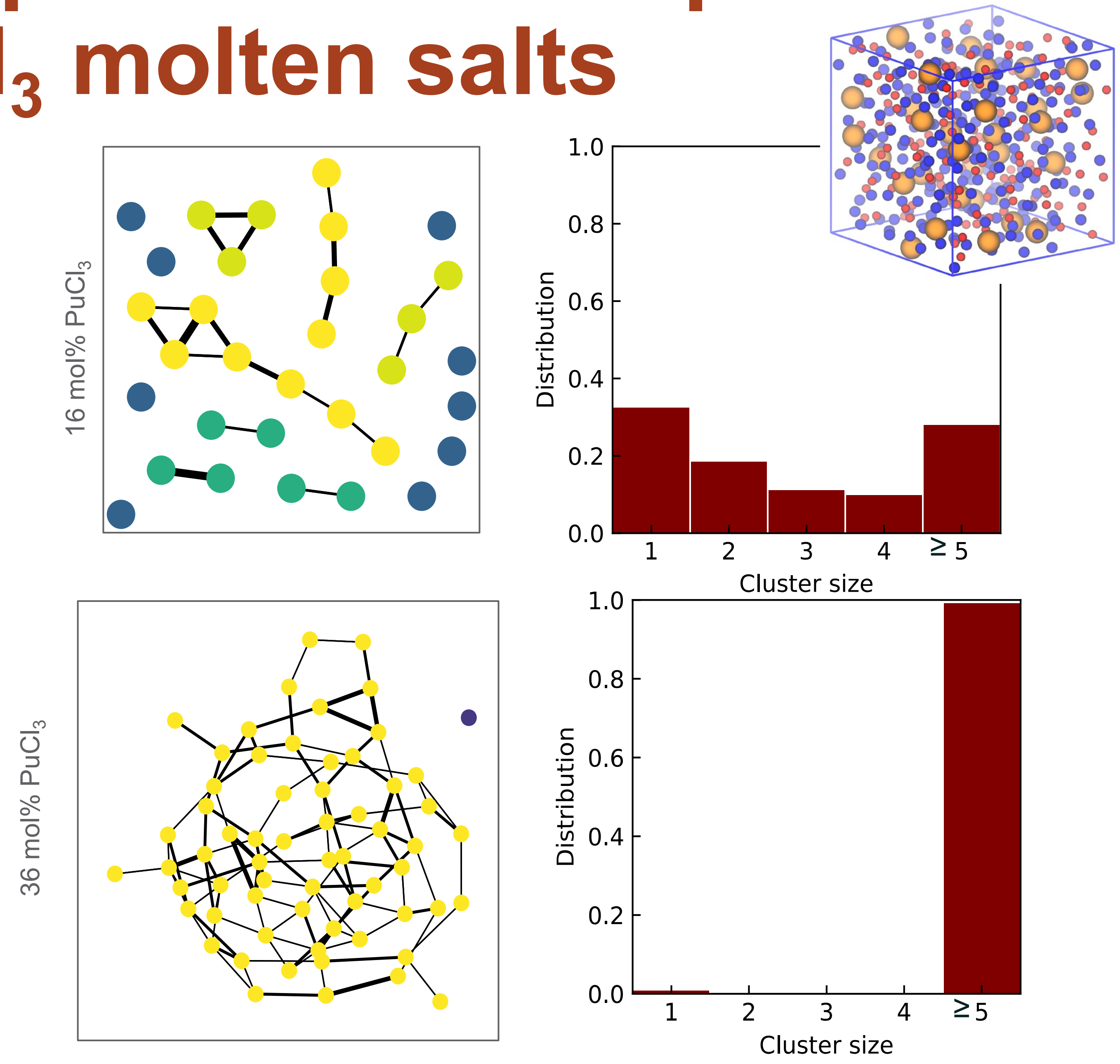
Exp.: Janz J. Phys. Chem. Ref. Data 4, 871 (1975)

Structure-transport relationship in NaCl-$PuCl_3$ molten salts

A_{ij} = number of shared Cl ions



- Molecular dynamics based on machine learning interatomic potentials.
- Each Pu^{3+} ion represented by 1 circle; thickness of each link represented by the link thickness.
- Different Pu^{3+} oligomers formed; Pu^{3+} network developed by $PuCl_3$ concentration.
- Lower diffusion coefficient in high $PuCl_3$ concentration systems due to network formation.



Nguyen et al., *Applied Materials Today* 35, 101951 (2023)

Thermophysical Property Measurement

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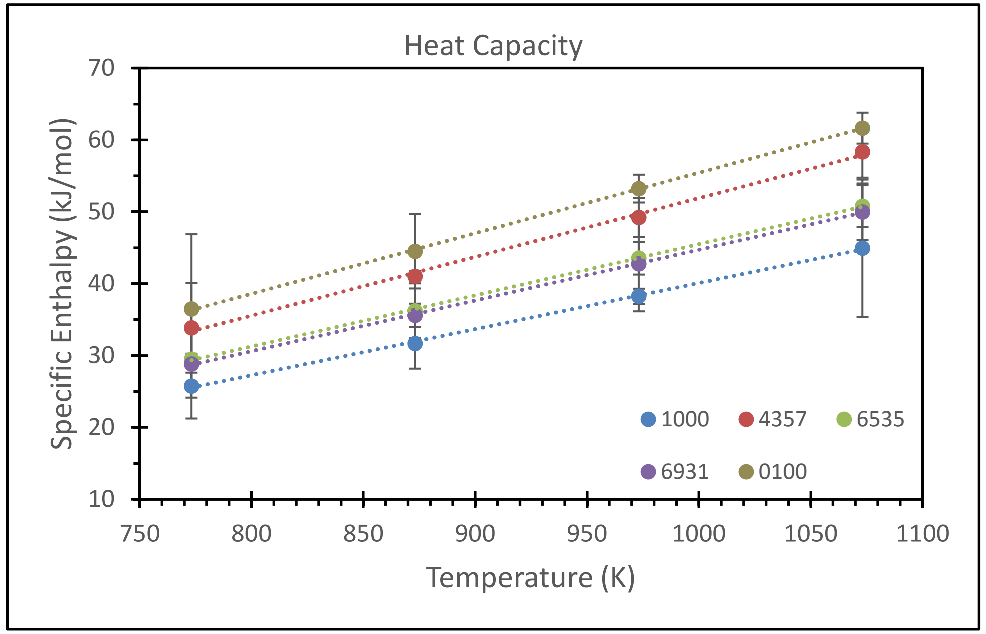
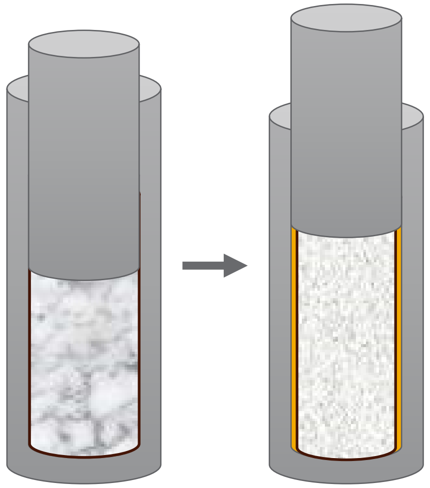
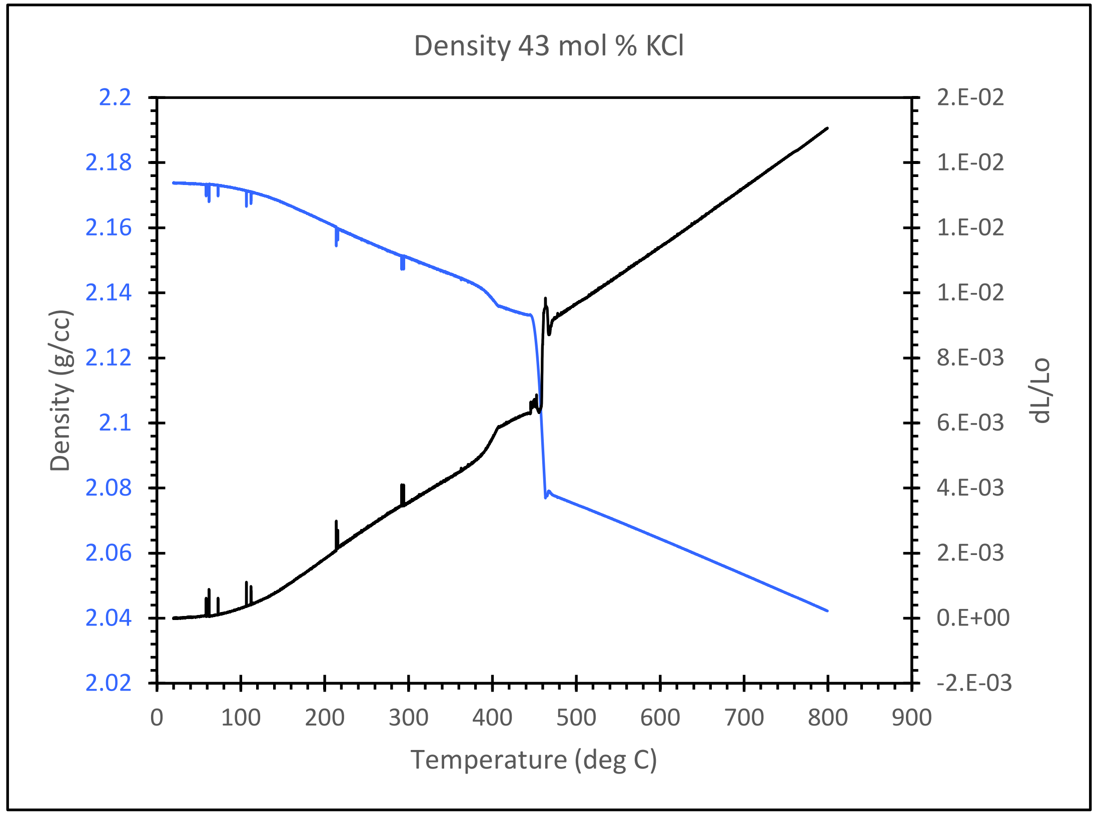
- Active Capabilities at PNNL
  - Specific Enthalpy/Heat Capacity (Drop Calorimetry)
  - Melting Point/Density (TMA)
  - Volatility

- FY24 focus on KCl-$MgCl_2$

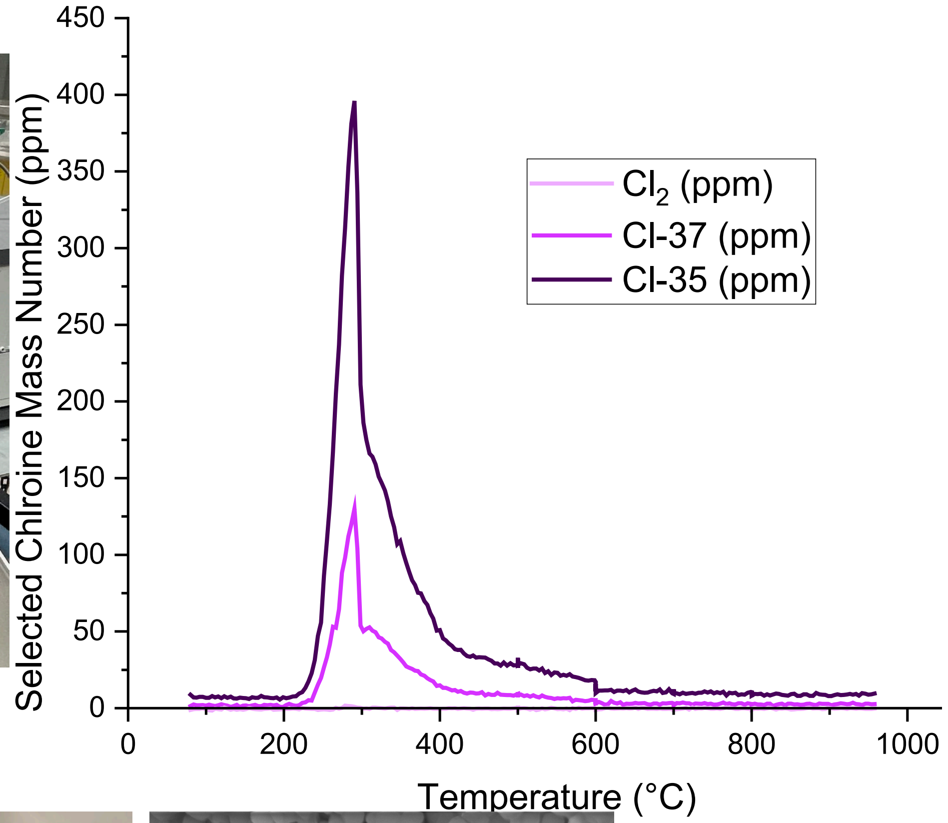


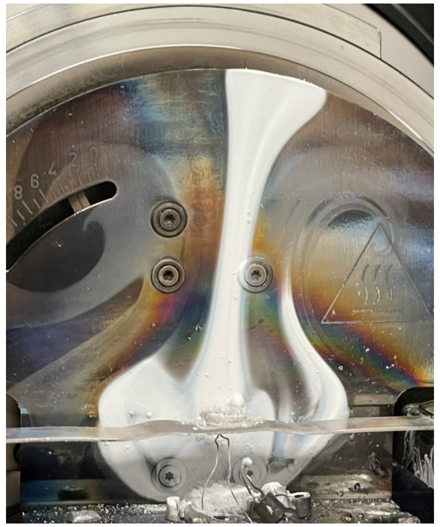


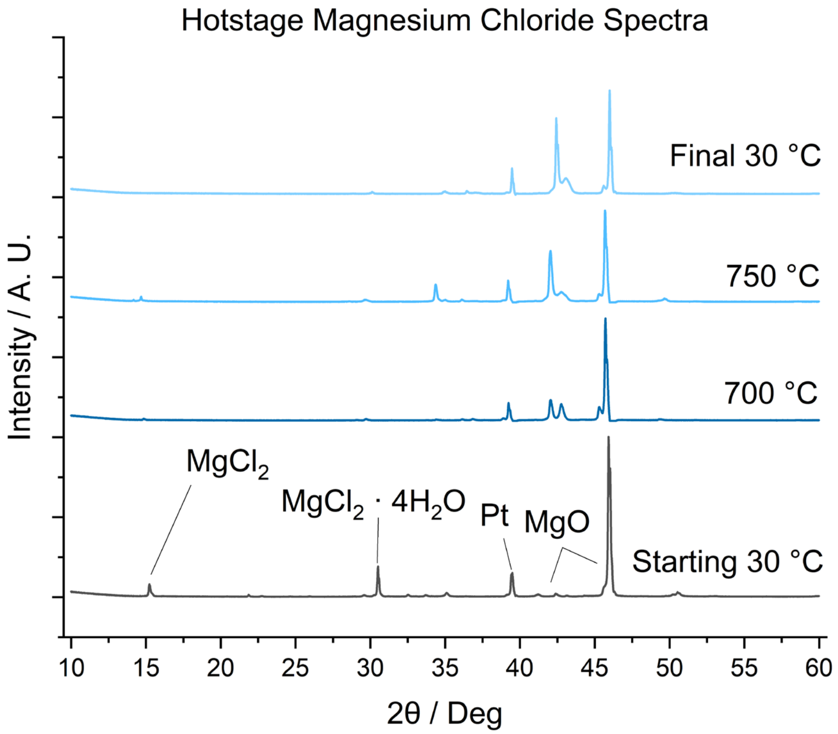


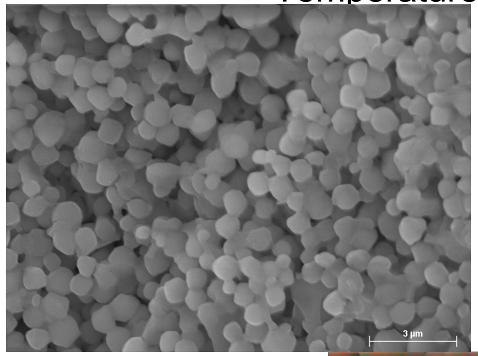
Thermophysical Property Measurement

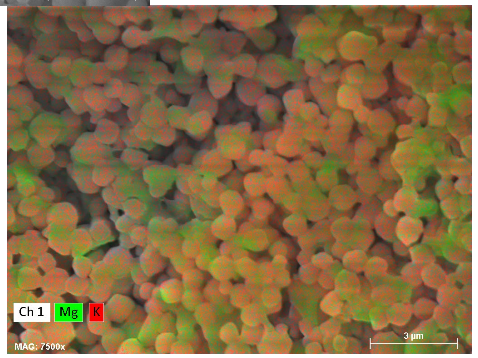
- Active Capabilities at PNNL
  - ➢ Volatility (EGA-MS; XRD; Cold Trap)
- Several methods developed to better understand the volatile nature of KCl-$MgCl_2$ salt at melt temperatures
- Preliminary results suggest incongruent volatilization of eutectic compositions











Thermophysical Property Measurement

- Characterization of commercial salts
  - ➢ Fluid inclusions are formed at imperfections on the surface of the growing crystal
  - ➢ Although individual inclusions are small, they are voluminous. Thus, can account for significant volume of water (i.e., >0.1% by vol.)
  - ➢ Vacuum oven experiment shows they survive 8 hours at both 100 and 200 °C

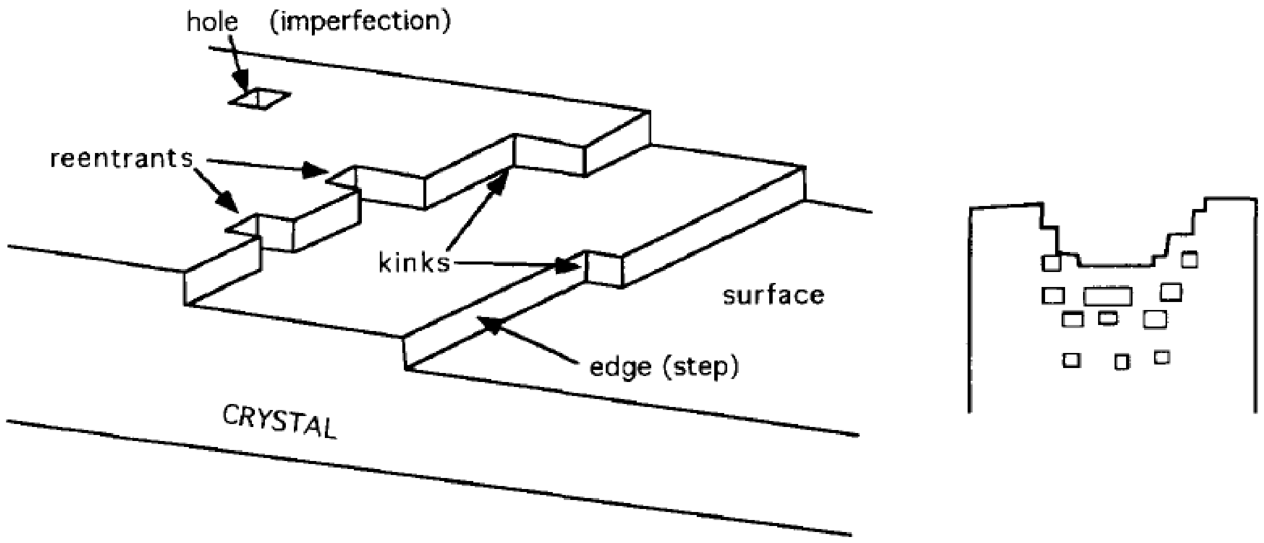
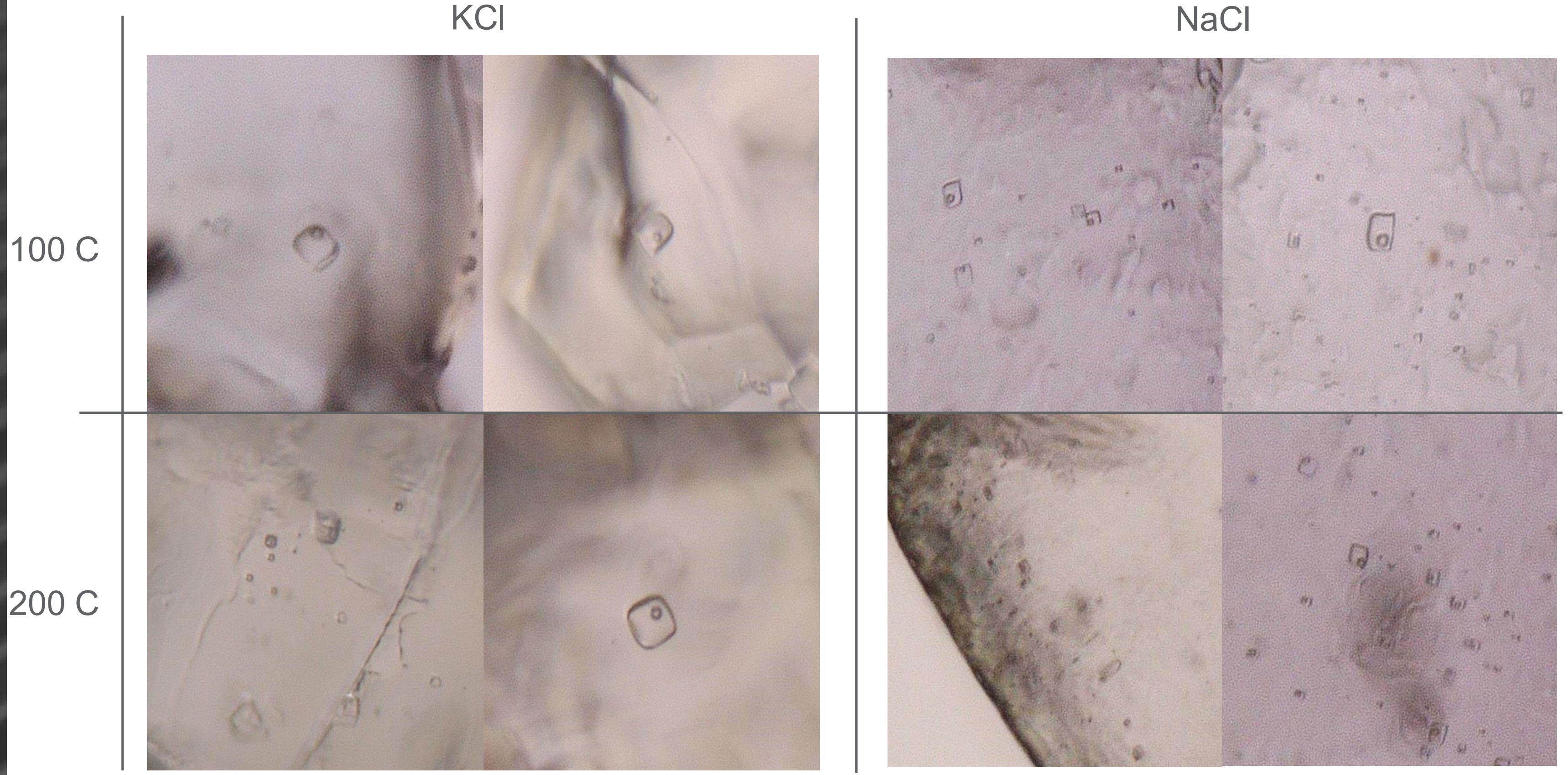
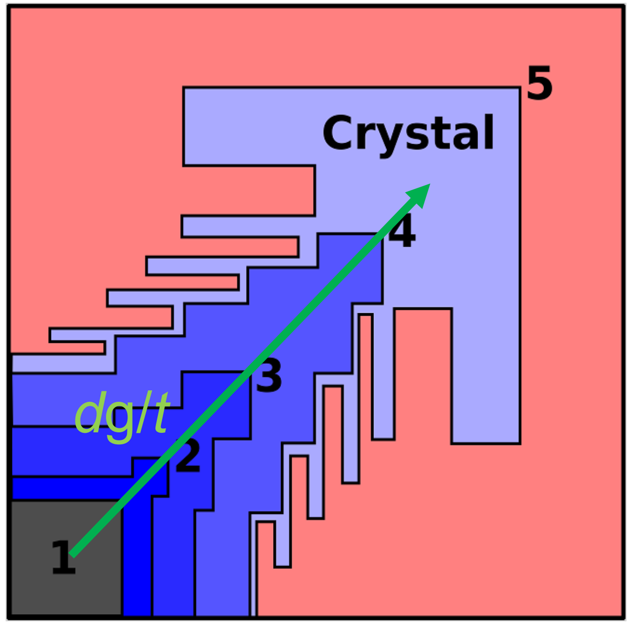


Figure from Goldstein and Reynolds (1994)

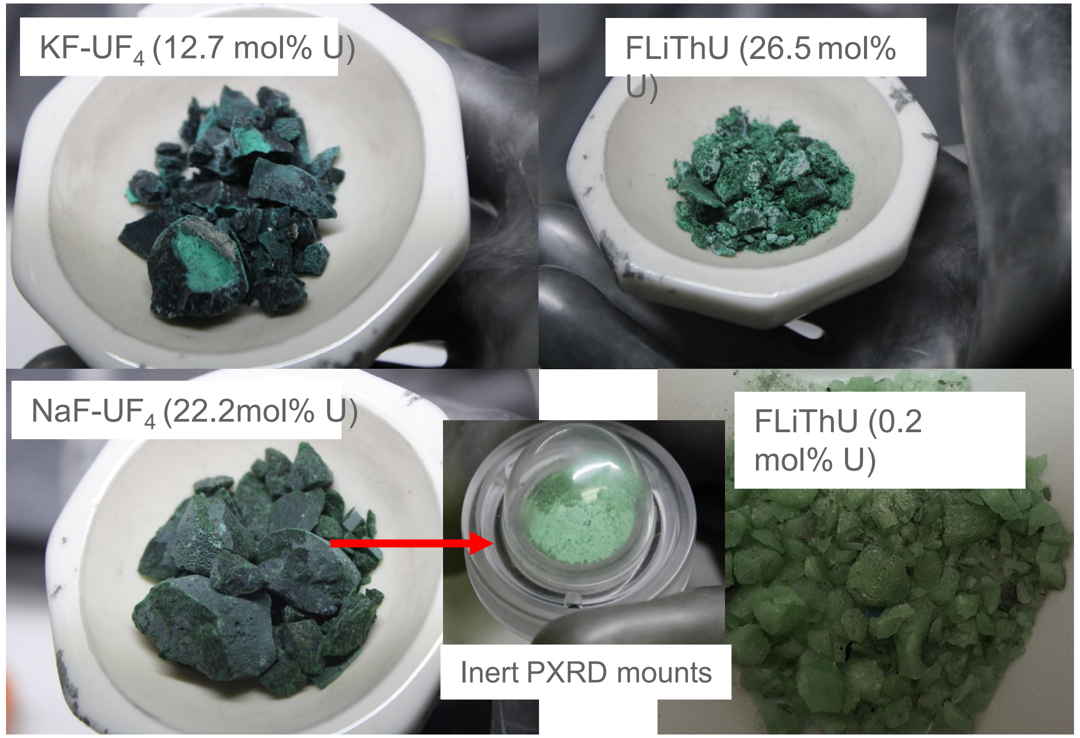




Modified from Kretz (2003) and https://www.alexstrekeisen.it/english/vulc/skeletal.php

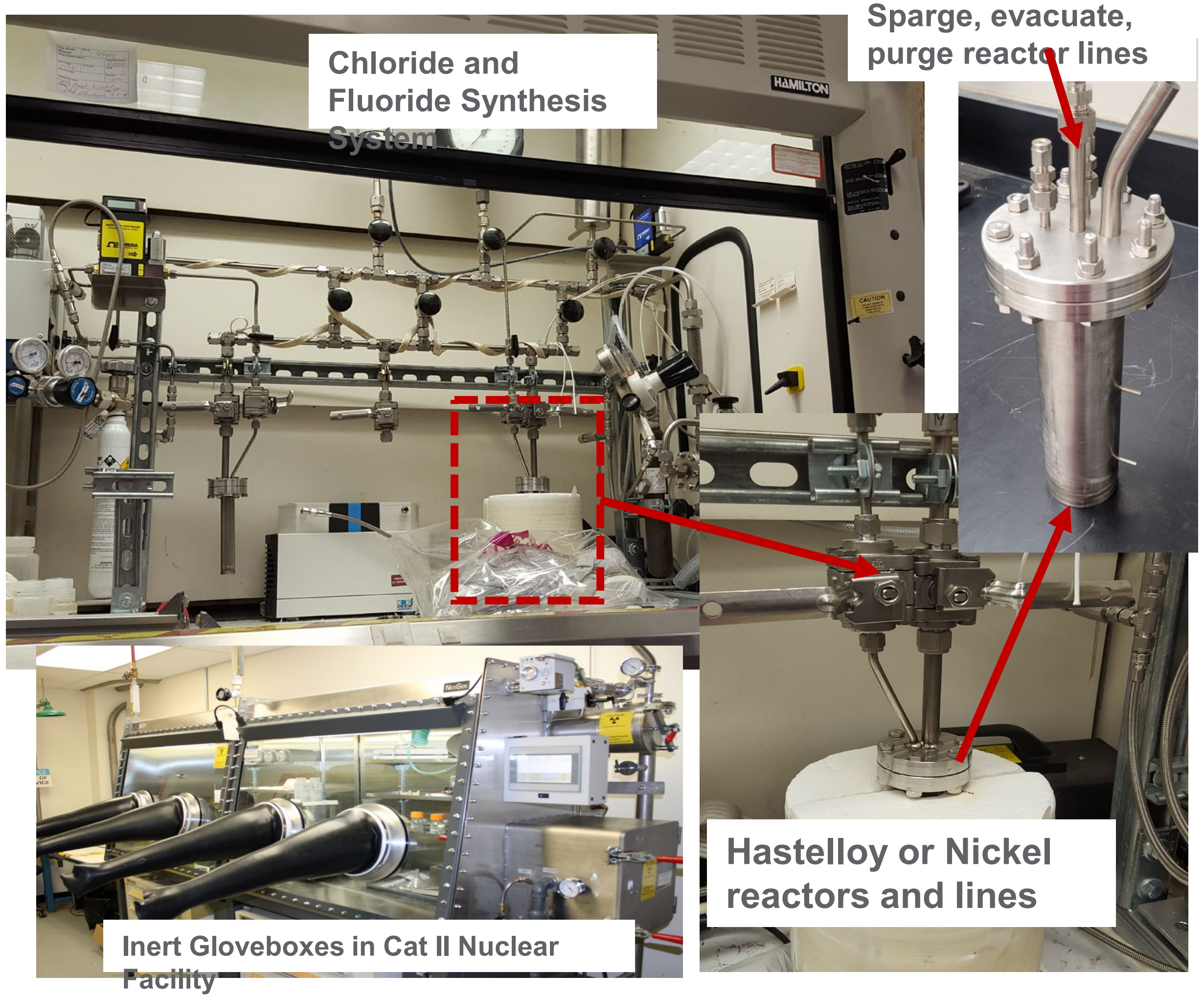
Actinide Salt Synthesis

- Synthesis and purification of chloride and fluoride U/Th/Pu salts
  - HF/F_2 /NF_3 / HCl /Cl_2 sparging or static atmosphere
- XRD, DSC, TIMS/ICPMS, Polarized Light Microscopy
- Salts being provided to Nat'l Labs (i.e. ORNL) and to industry partners for study
- Effusion and transpiration vapor pressure measurement system being built



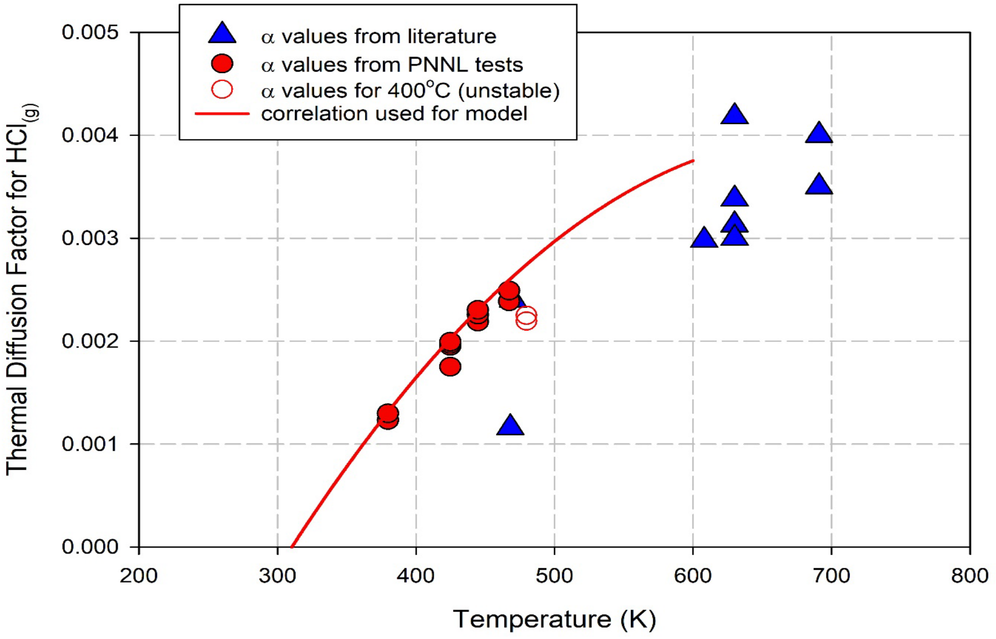
*2024 salts synthesized included (**First Pu salt made!**):*

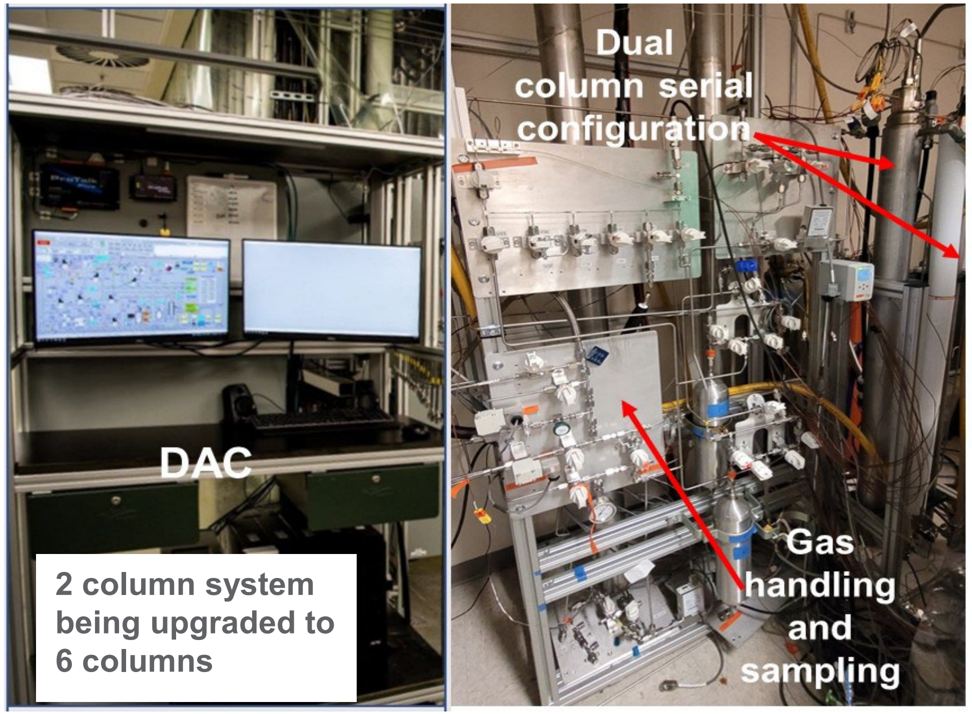
- FLiTh-U
- FLiNa-U
- ClNaK-U
- LiF-UF_4
- NaF-UF_4
- KF-UF_4
- NaF-ZrF_4-UF_4
- LiF-ThF_4-UF_4-PuF_3

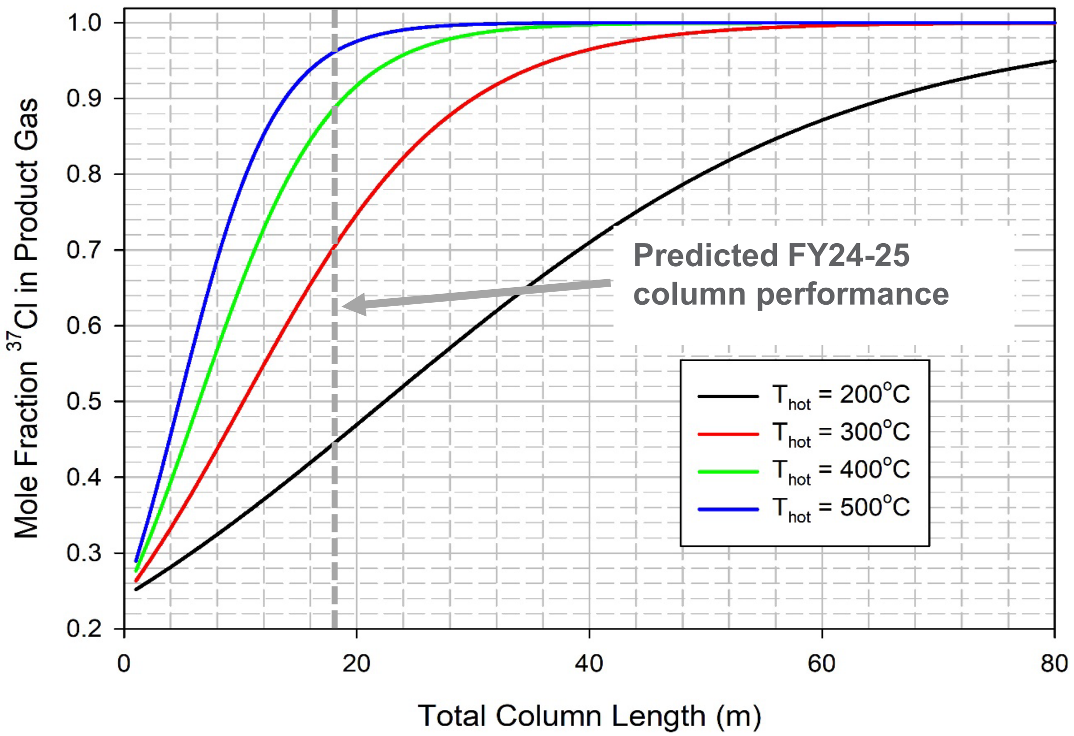


Cl-35/37 Separations - Thermal Diffusion Isotope Separation

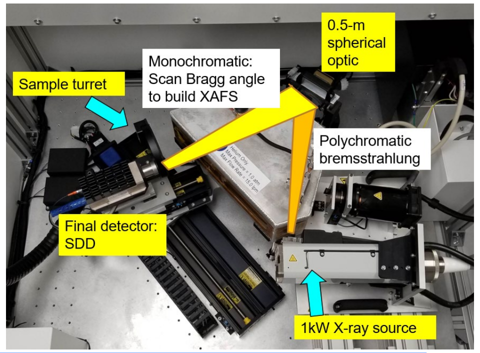
- Work in 2023 demonstrated successful separation of Cl-35/37 in $HCl_{(g)}$ matrix and predictive model validation
- FY24 system is being upgraded to 6 serial columns for 18m of column length – predicted for single pass~85% Cl-37 enrichment
- Limiting factor is laboratory space and $HCl_{(g)}$ corrosion at temperatures above 400C



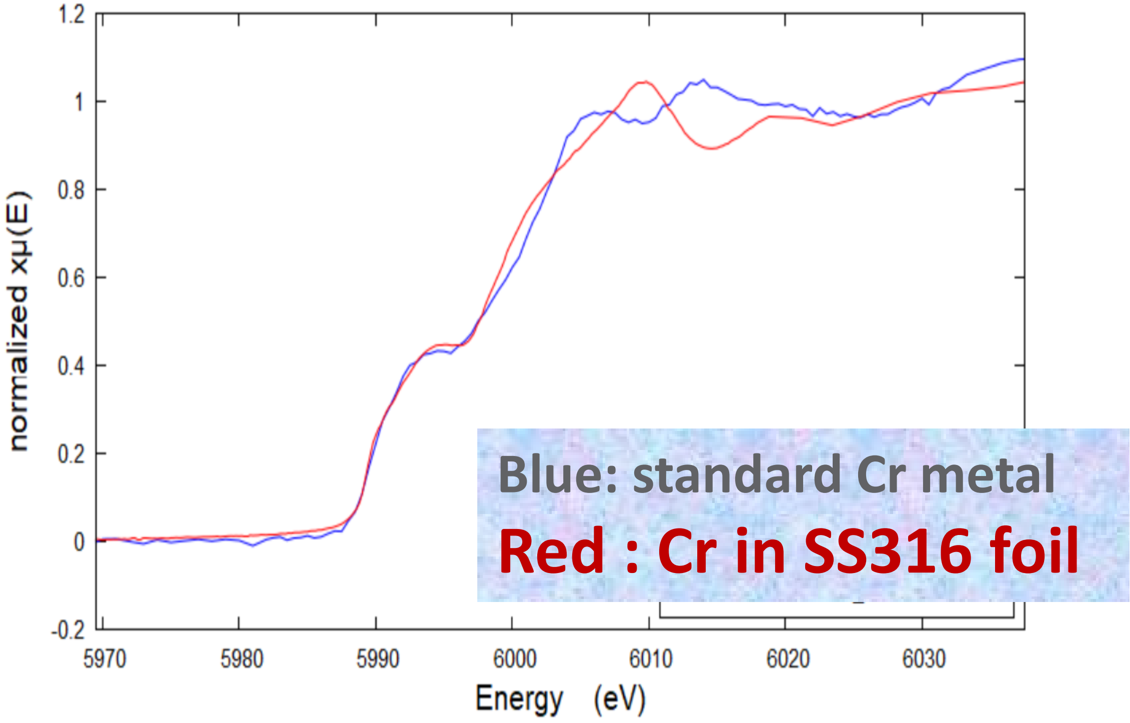




EasyXAFS300 for *in-situ* Cr Measurements: Proof of Concept

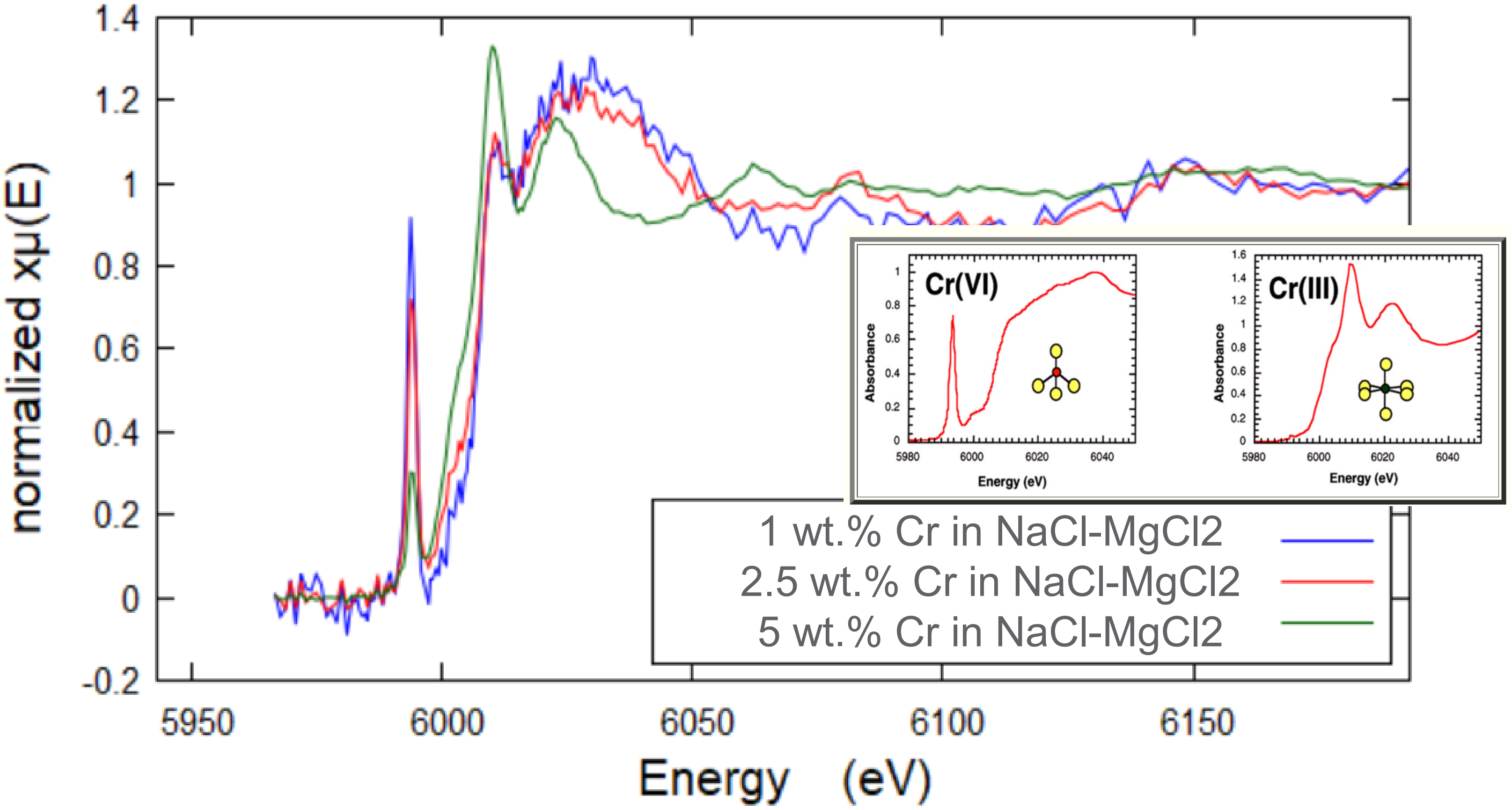


Cr K-edge XAFS measurements in solid metal



- XAFS indicate different local environment of Cr in SS316 and in pure metals
  - Structural changes are observable

Cr K-edge XAFS measurements in NaCl-$MgCl_2$ eutectic



- XANES: determination of Cr oxidation state possible
  - 1 and 2.5 wt% Cr samples: mostly Cr(VI)
  - 5 wt% Cr sample: about equal mixture of Cr(III) and Cr(VI)

On-line Monitoring of MSR Off-gases

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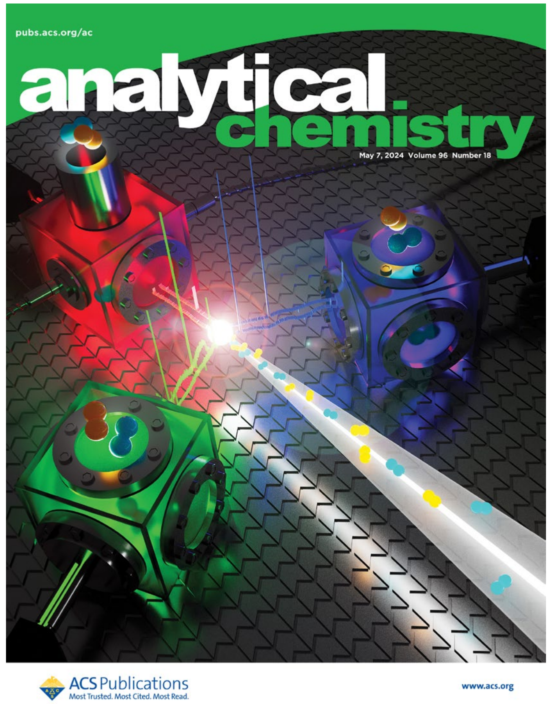
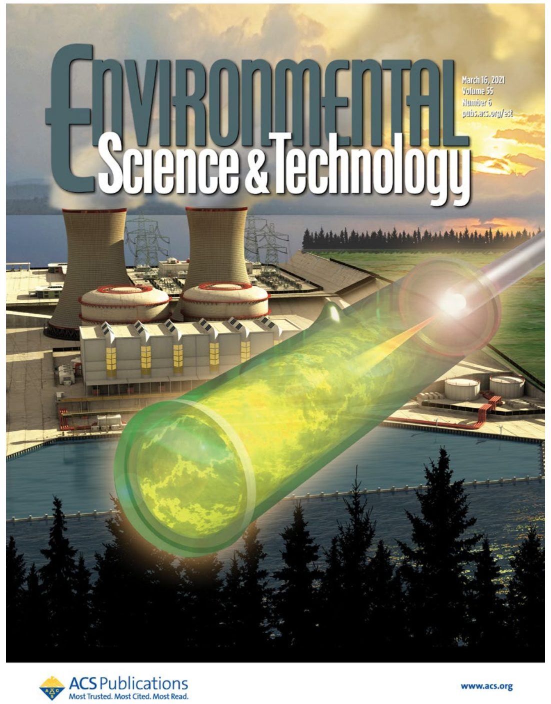
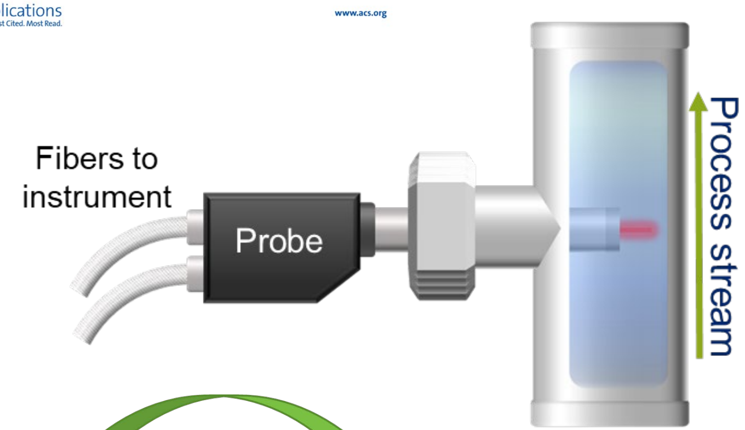
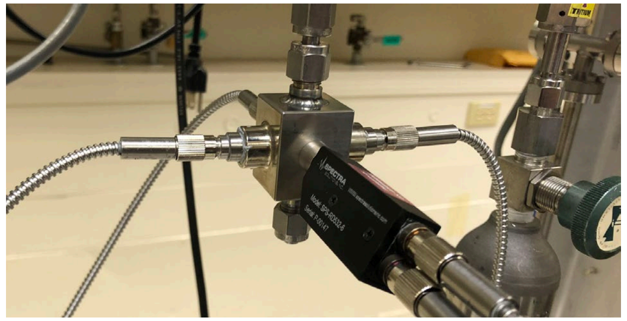
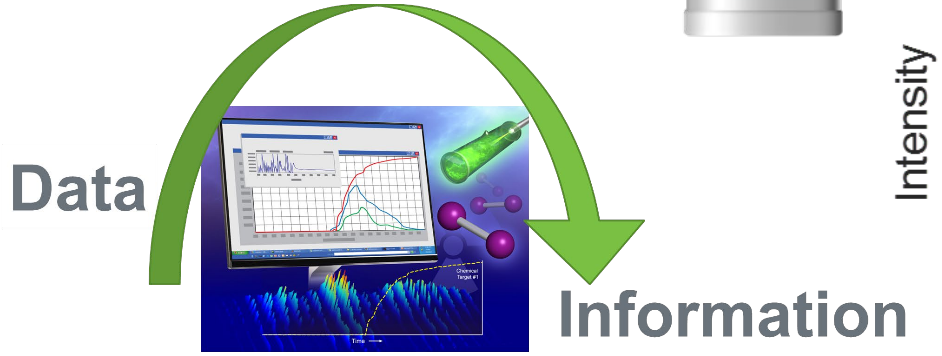
- Building tools, and sensors that enable **safe**, **cost effective**, and **near-term deployment** of MSRs
- OLM to support:
  - Sensor development:
    - Overcoming COTS (commercial off-the-shelf) limitations to build sensors capable of surviving processes which are:
      - Highly corrosive, high temperatures, radiation
  - Building advanced data processing tools
    - Real-time identification and quantification of chemical targets
    - Robust models capable of being applied across systems

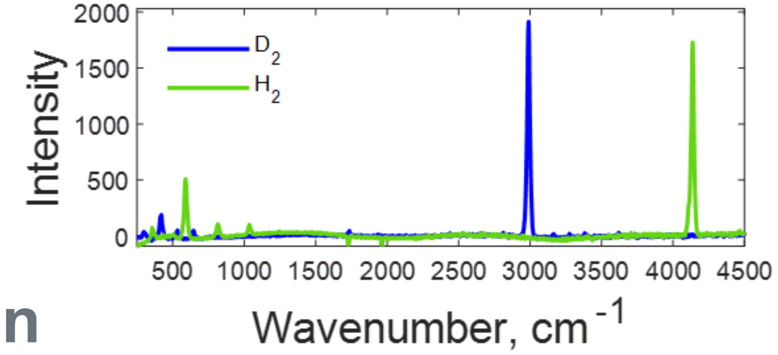










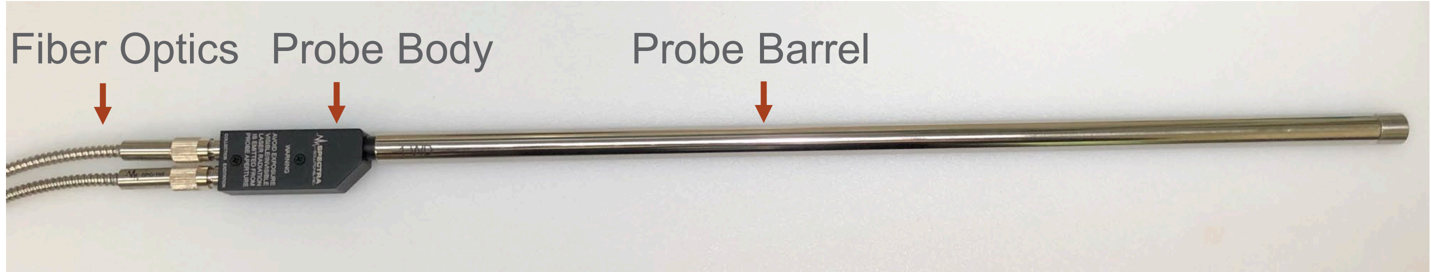


Optical Spectroscopy Tools

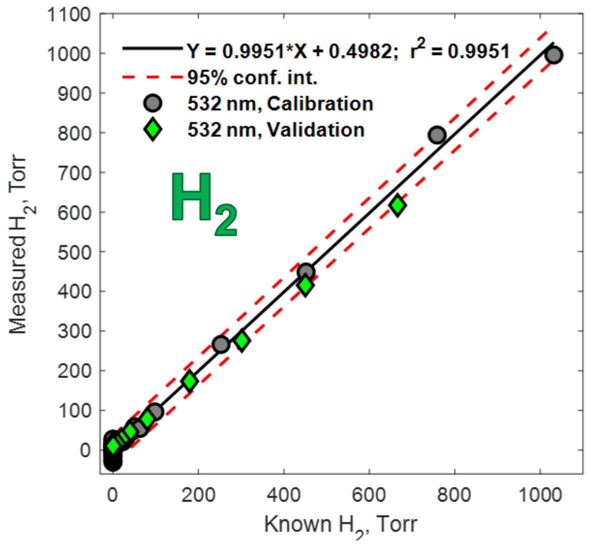
- Can provide detailed chemical composition information:
    - Identification and quantification, oxidation state, speciation
- Highly flexible, fast, robust, and versatile
- Chemical targets:
    - Iodine and hydrogen isotopes

- **Collaboration between ORNL and PNNL**
    - Supporting system development and demonstrations
    - Laying foundation for tools that enable cost effective and near-term deployment of technology

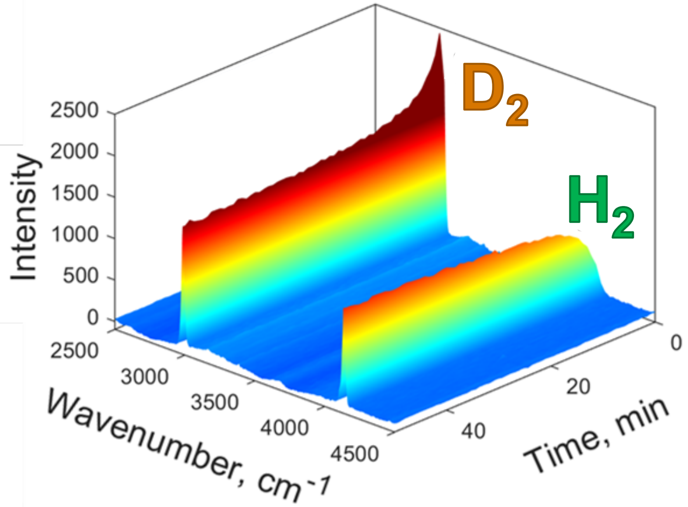
- **Opportunities for Collaboration between PNNL and INL** on tritium monitoring
- **Additional industry collaborations**

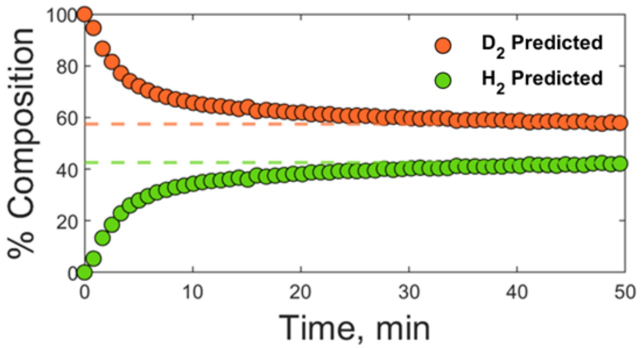


Testing probe components in ORNL LSTL



Monitoring of hydrogen isotopes





Heather M. Felmy, Richard M. Cox, Alyssa F. Espley, Emily L. Campbell, Bethany R. Kersten, Hope E. Lackey, Shirmir D. Branch, Samuel A. Bryan, Amanda M. Lines, *Analytical Chemistry* 2024, 96 (18), 7220-7230. DOI: 10.1021/acs.analchem.4c00802.

Shirmir Branch, Heather Felmy, Adan Schafer Medina, Samuel Bryan, Amanda Lines, *Industrial & Engineering Chemistry Research*, 2023, 62, 37, 14901–14909.

Adan Schafer Medina, Heather M. Felmy, Molly E. Vitale-Sullivan, Hope E. Lackey, Shirmir D. Branch, Samuel A. Bryan, and Amanda M. Lines *ACS Omega* 2022 7 (44), 40456-40465. DOI: 10.1021/acsomega.2c05522

Heather M. Felmy, Andrew J. Clifford, Adan Schafer Medina, Richard M Cox, Jennifer M. Wilson, Amanda M. Lines, Samuel A. Bryan, *Environmental Science & Technology* 2021. DOI: 10.1021/acs.est.0c06137.

Creating Value from MSR Off-gases

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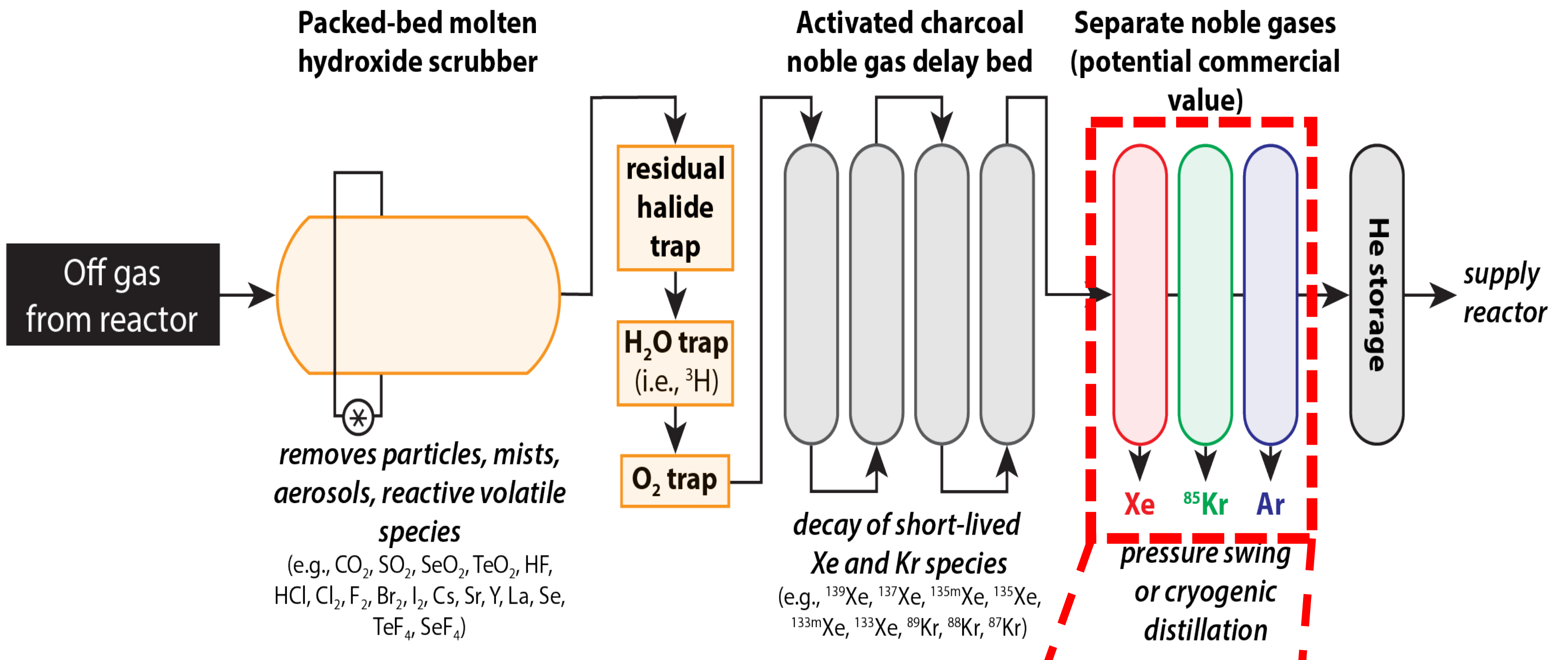
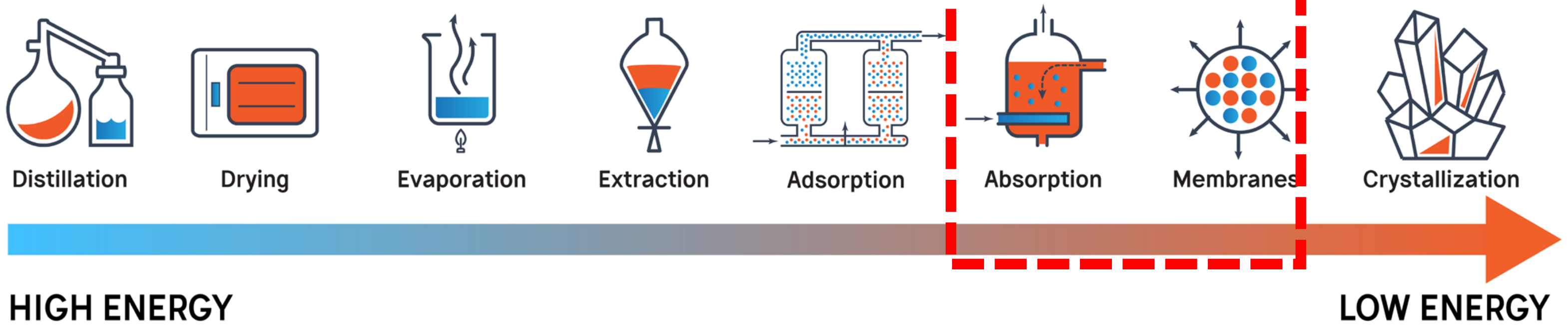
- Noble gas (Xe, Kr and Ar) market projected to be $40B in 2030
- MSR provide cleaner gas feed for noble gas recovery
- MSR plant operation enable growing noble gas needs
- Cost of operations and capital reduced with each product recovered
- Sequential removal of volatile gases improves noble gas recovery processes



Mcfarlane, J.; Ezell, N.; Del Cul, G.; Holcomb, D. E.; Myhre, K.; Chapel, A.; Lines, A.; Bryan, S.; Felmy, H. M.; Riley, B. *Fission Product Volatility and Off-Gas Systems for Molten Salt Reactors*; Oak Ridge National Lab.(ORNL), Oak Ridge, TN (United States): 2019.

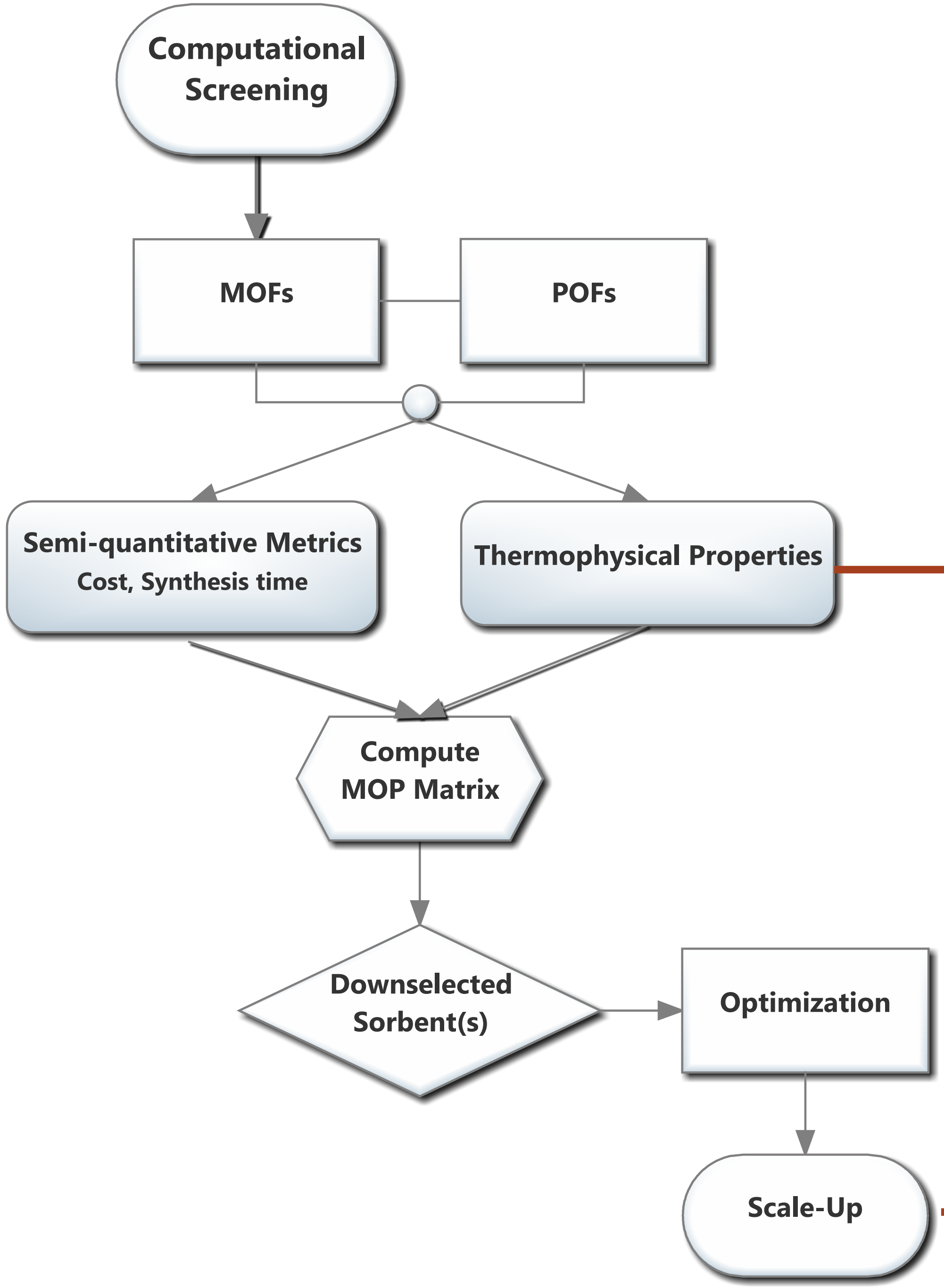
1) Too complex, 2) Large footprint, 3) Costly, 4) Hazardous and safety issues

- Need advanced materials and membranes to develop a modular/compact off-gas system to meet vendor needs in support of licensing and deployment activities

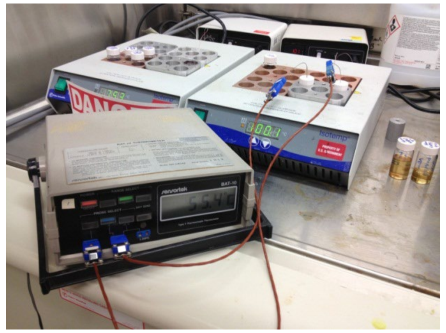


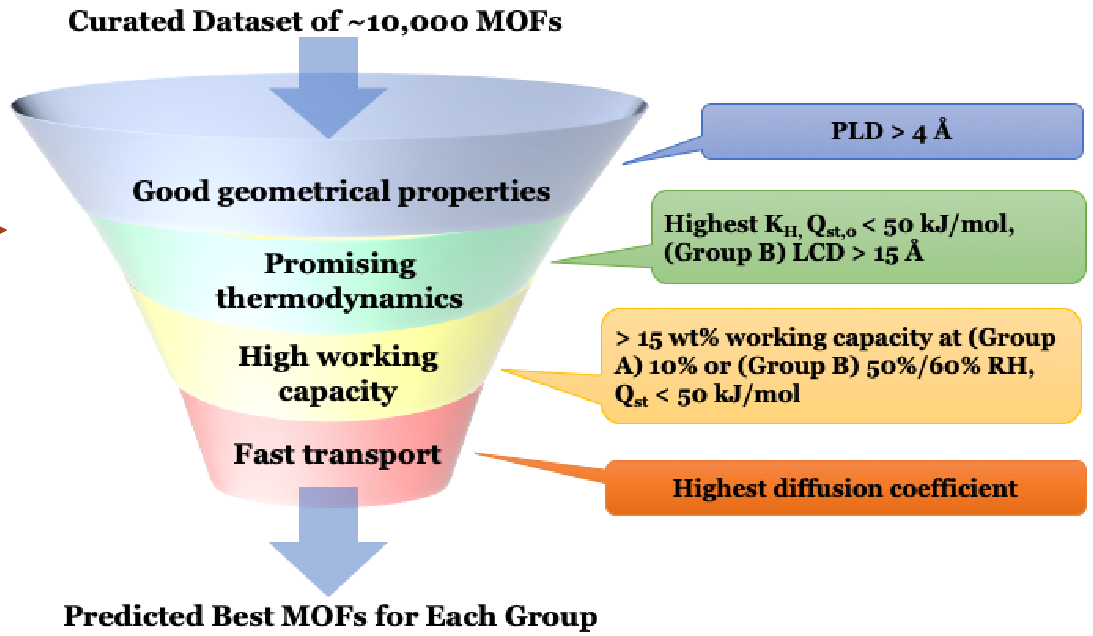
to start commissioning SIPF gas centrifuges (GC) to produce enriched Xenon-129. Xenon-129 is the newest isotope to show its effectiveness in polarized lung imaging; there is no U.S. production capability. This isotope has also garnered the interest of the medical community in monitoring lung function and damage from infectious disease such as COVID-19. The FY 2022

Sorbent (MOF) Down Selection Process for Off-gas

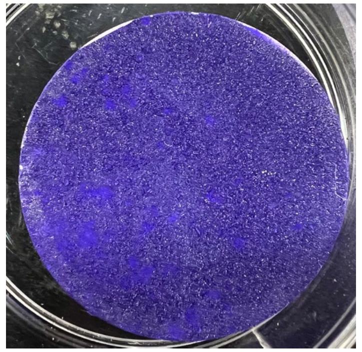


Adsorbent



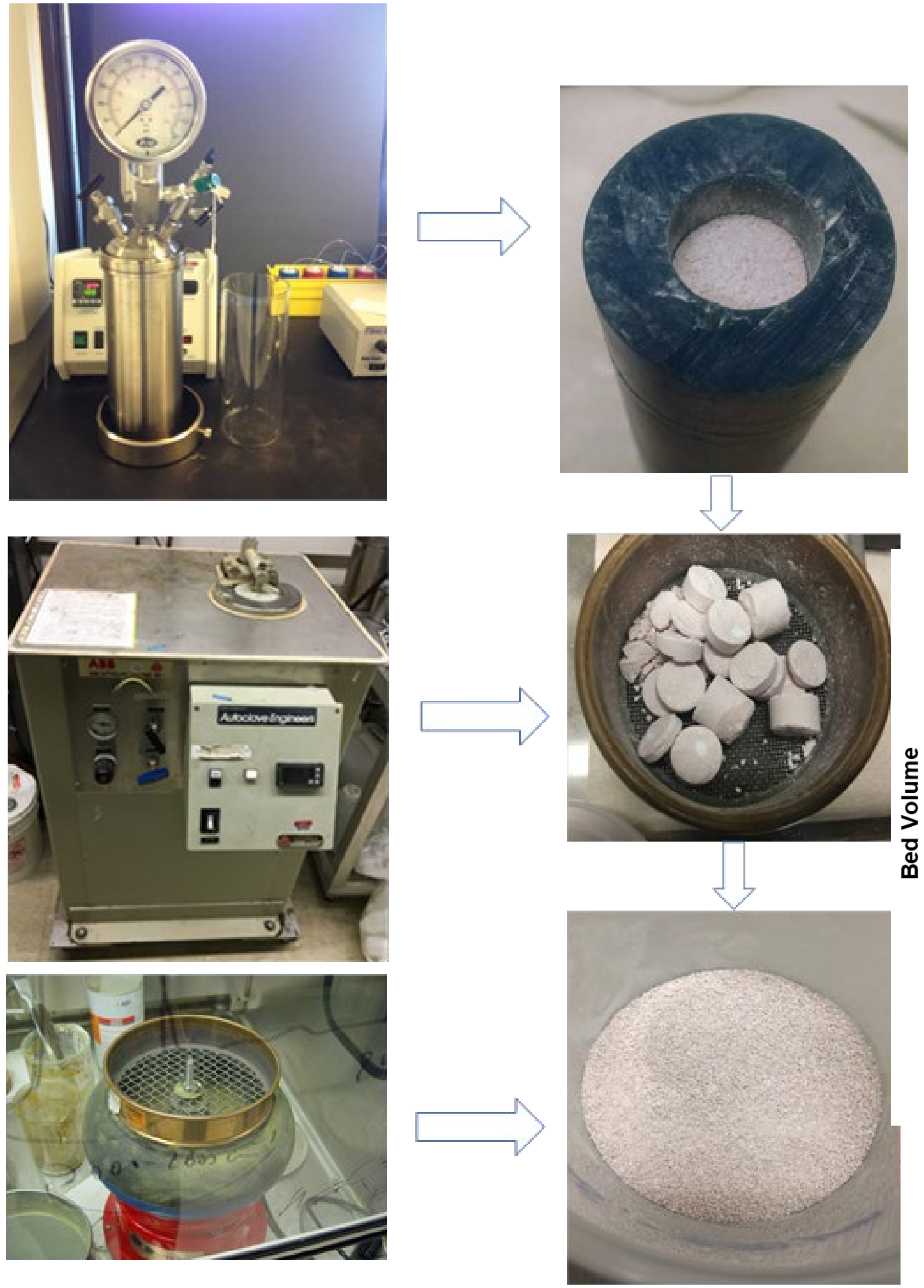


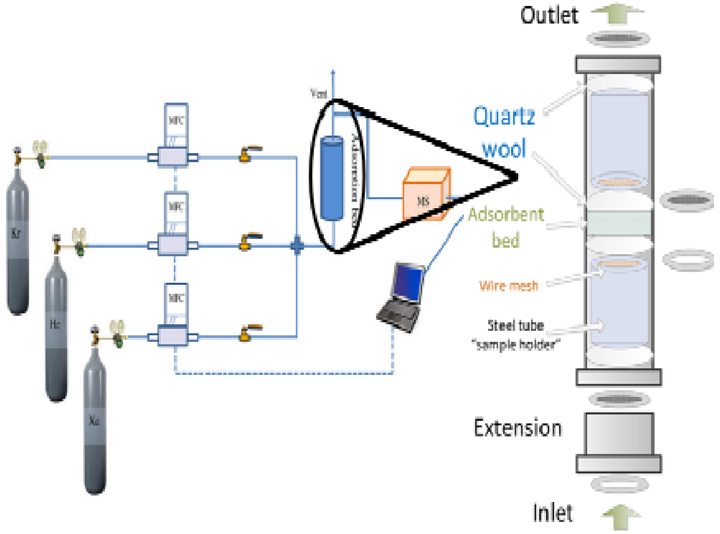
Membranes

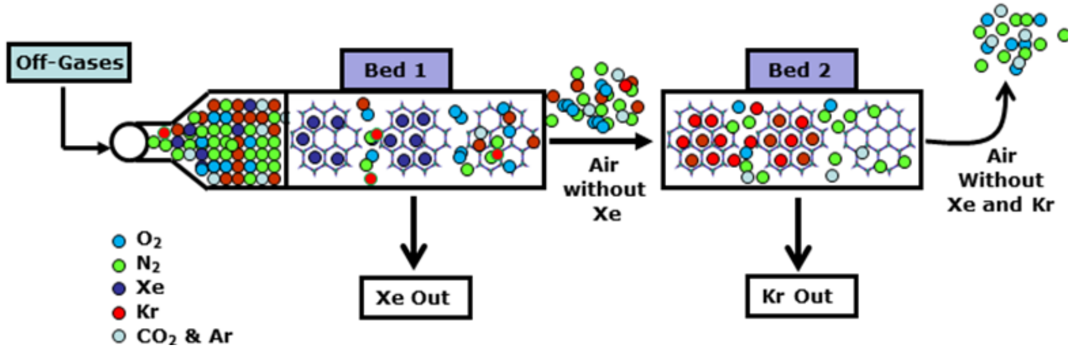


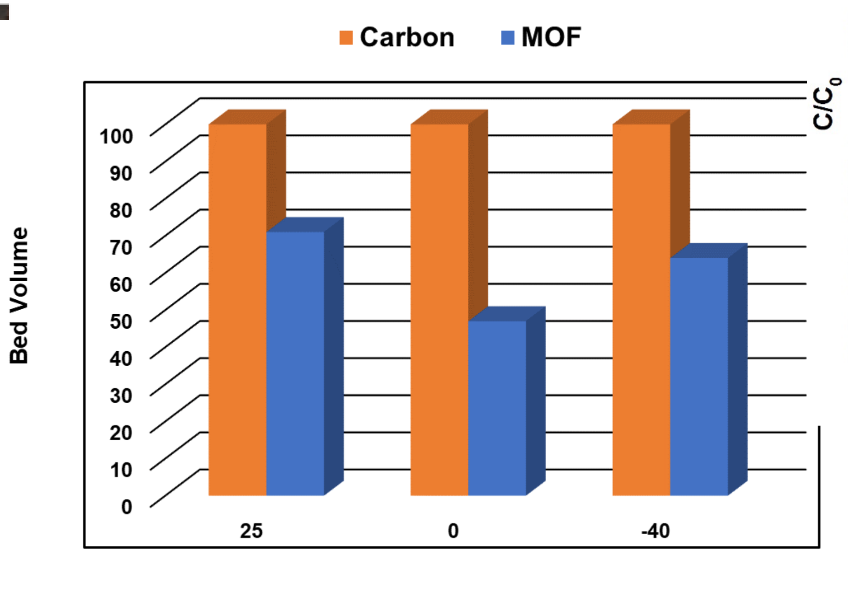
Sorbent testing for Noble Gas Separation

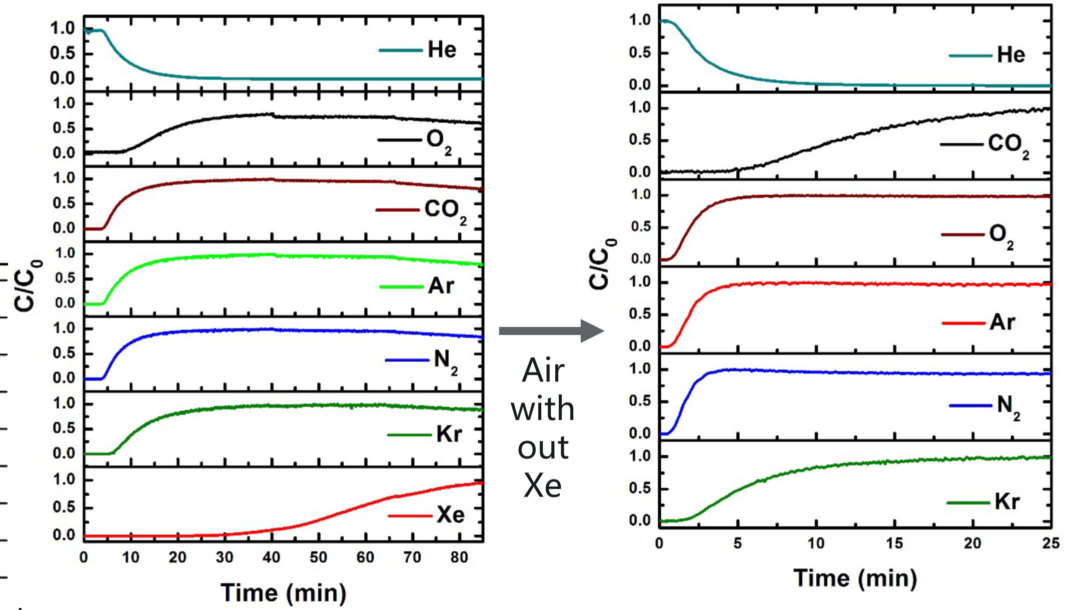
Engineered Particles (FY'24)









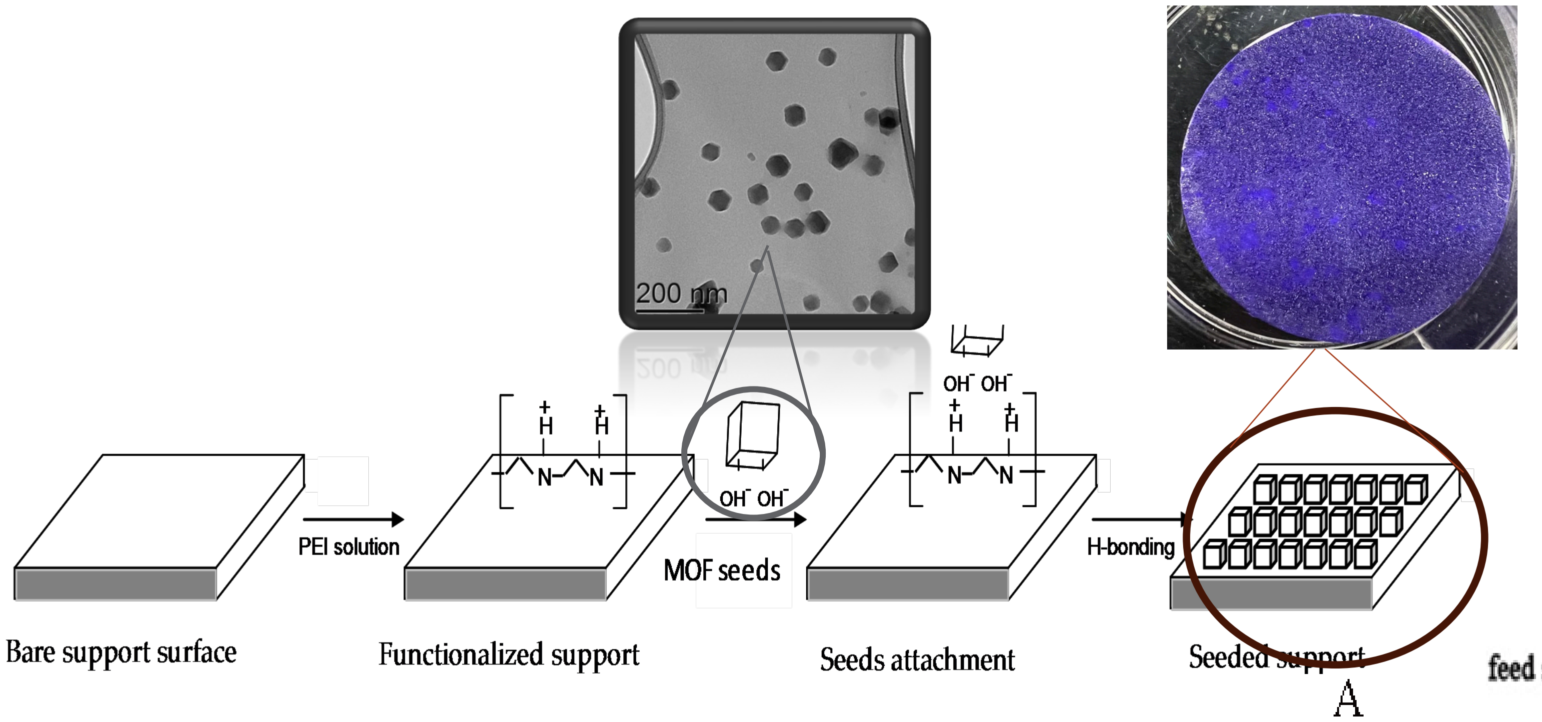


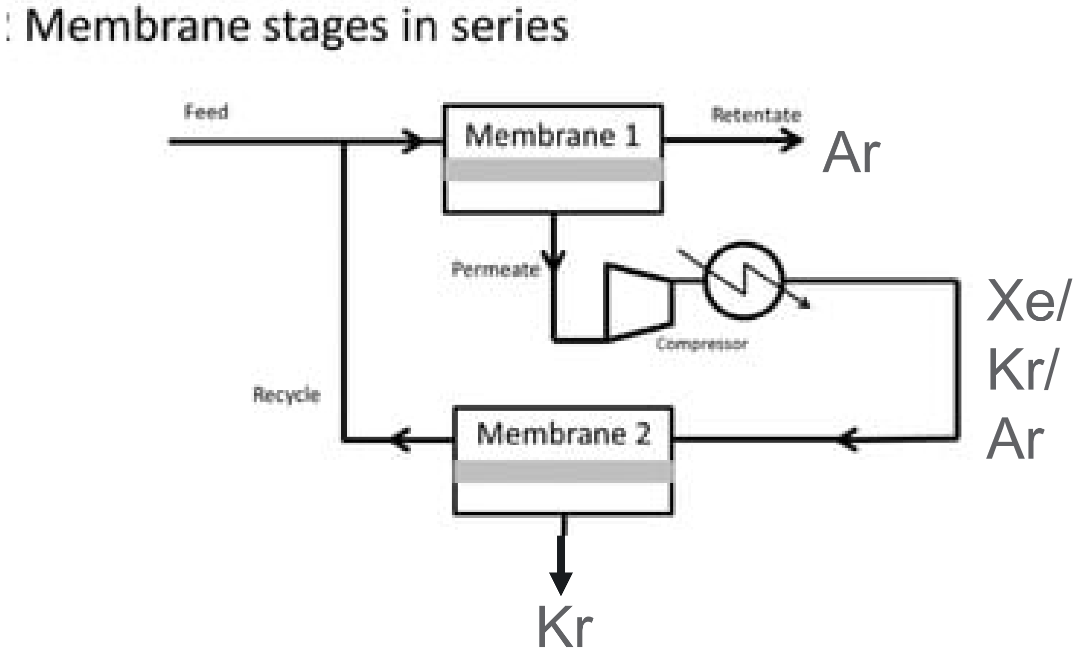
- Xe and Kr separation in 2 step at RT

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

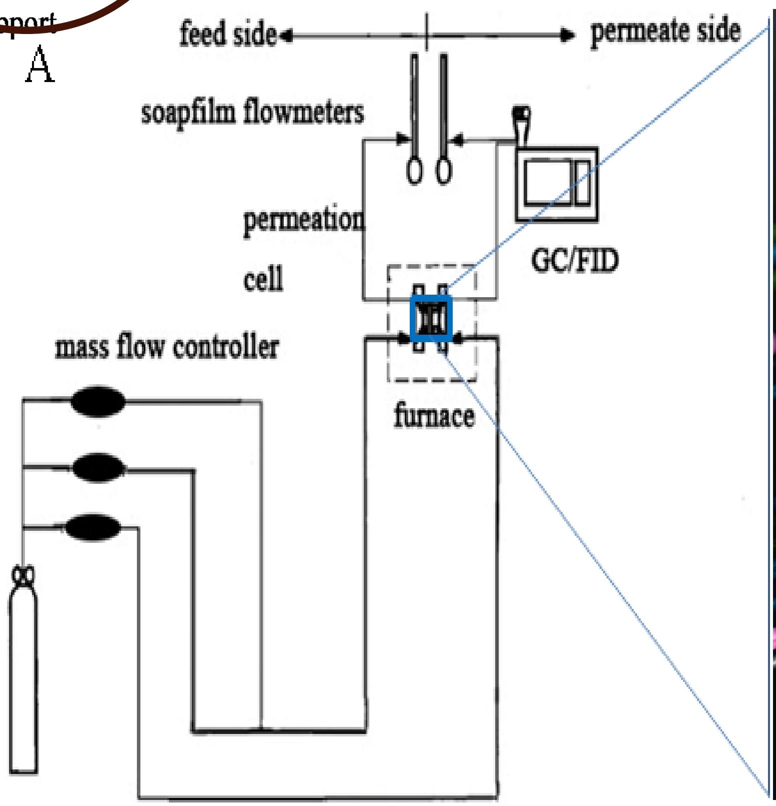
- **Continue to collaborate with ONRL on integrating MOF technology with LIBS and LSTL test loop**
- **Additional collaborations with INL and industry**

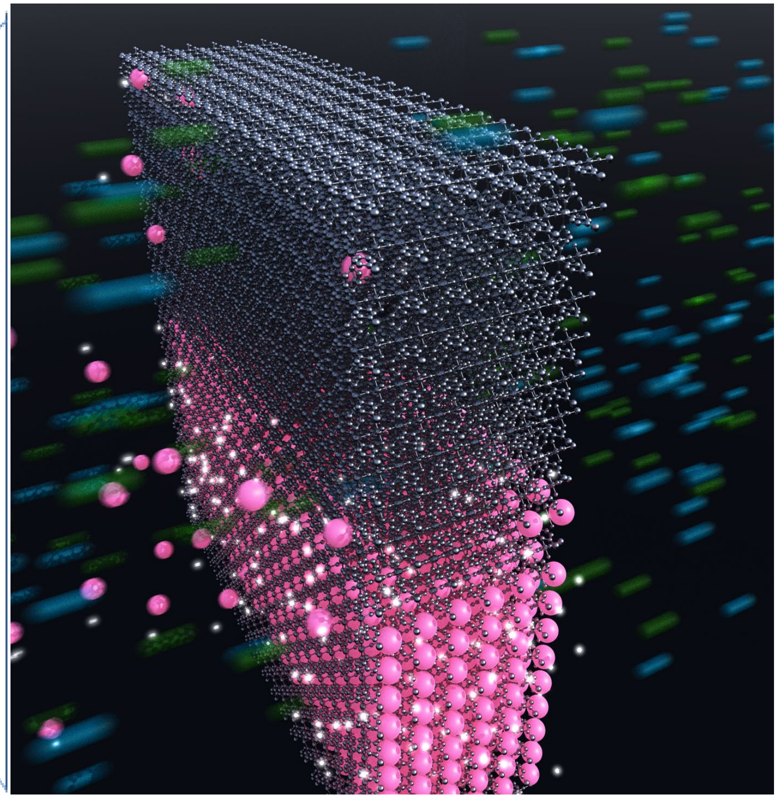
Capabilities in Membrane Fabrication and Testing





Time	Xe	Kr	Ar
48	27.37	32.62	13.46





- First experimental evidence to separate Ar from MSR off-gas using a membrane at RT
- Need further experiments and modelling to support our observation

Thallapally et. al., US Patent Pending

Part of GAIN Voucher

Radiation Stability Testing

- PNNL's Radiological Exposures and Metrology Lab (REM Lab) contains highly characterized beta, gamma-ray, neutron, and X-ray fields
- Supported a wide range of applications, including radiation effects on materials and electronics
- PNNL can simulate a wide variety of temperature (from -60 to 200 °C), humidity (20 – 90%), and vacuum environments within these radiation fields.

Radiation experiments are planned during FY'25

Characterization of Irradiated MOF Sample (FY’24)

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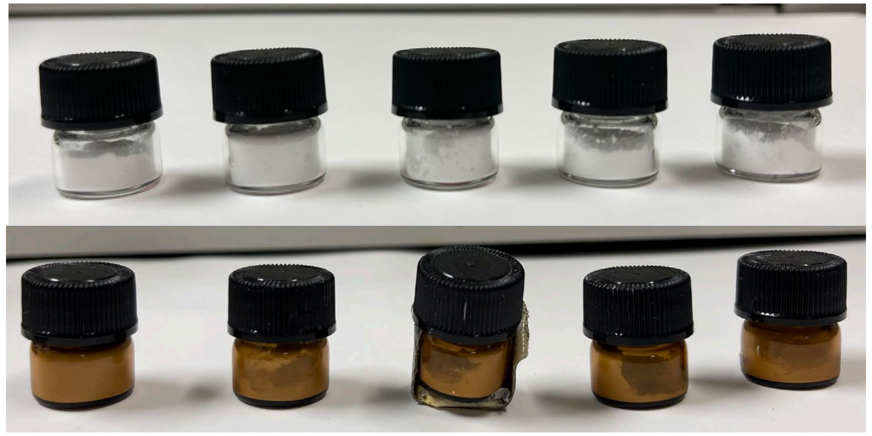
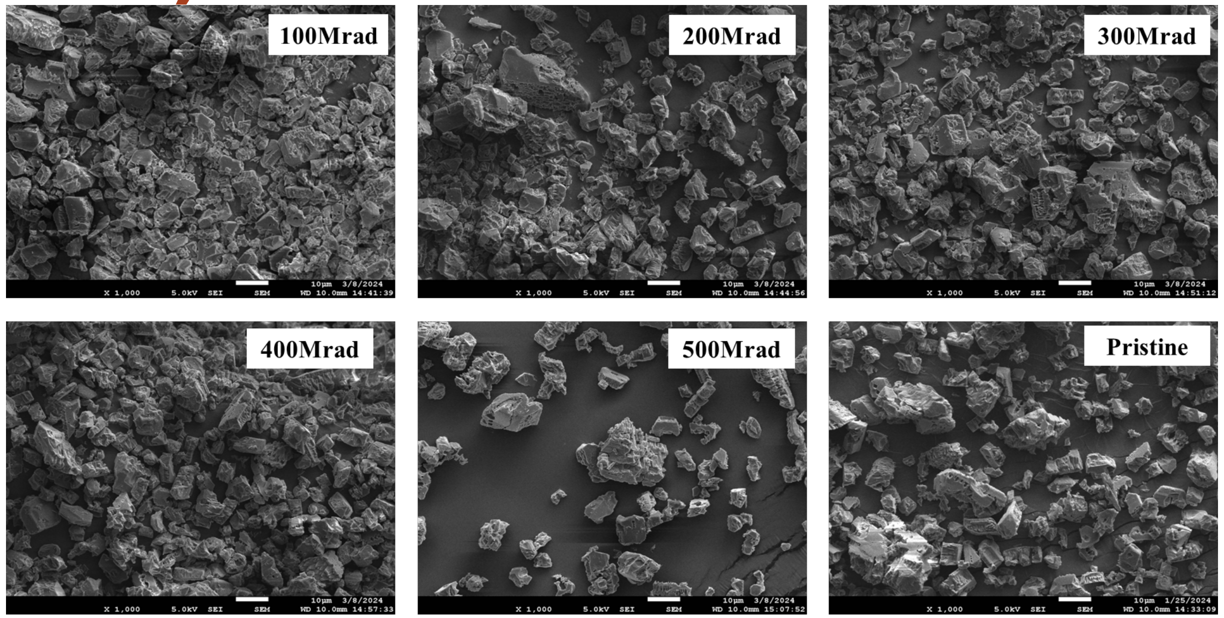
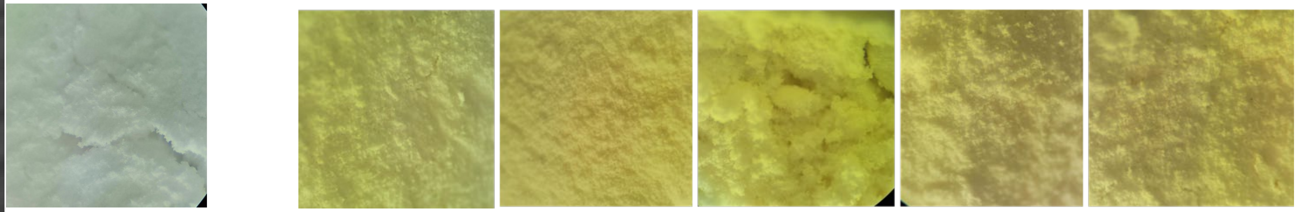
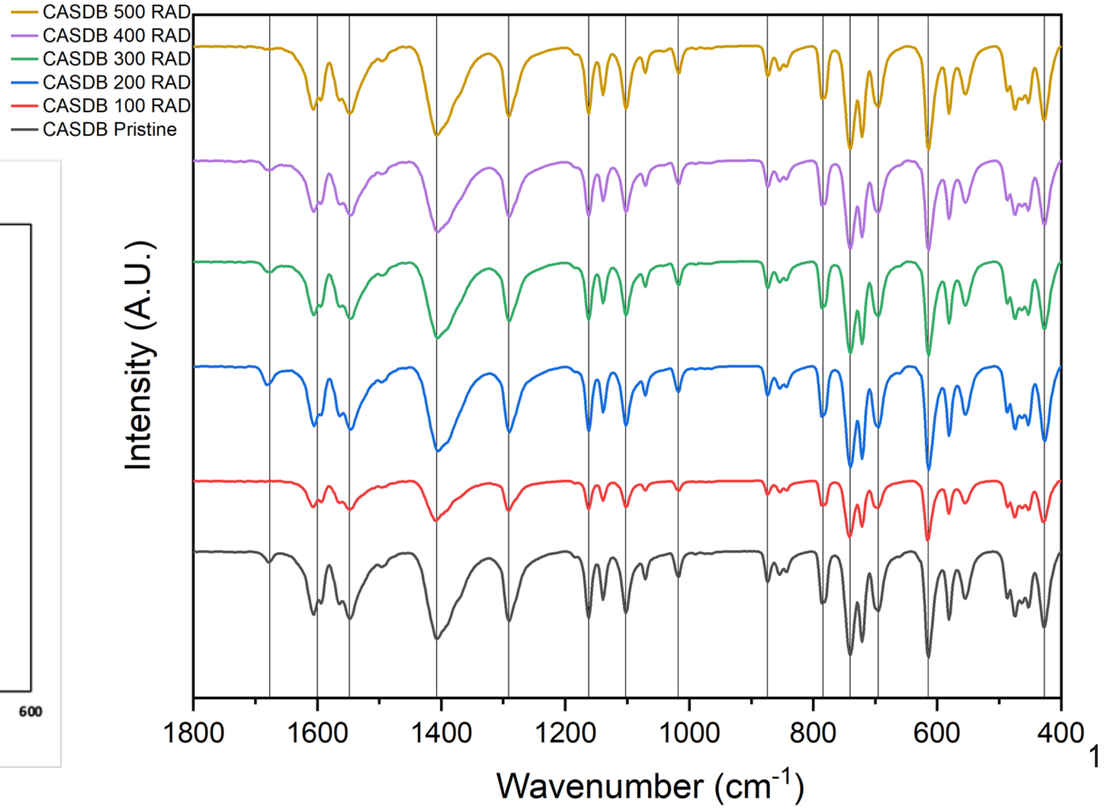


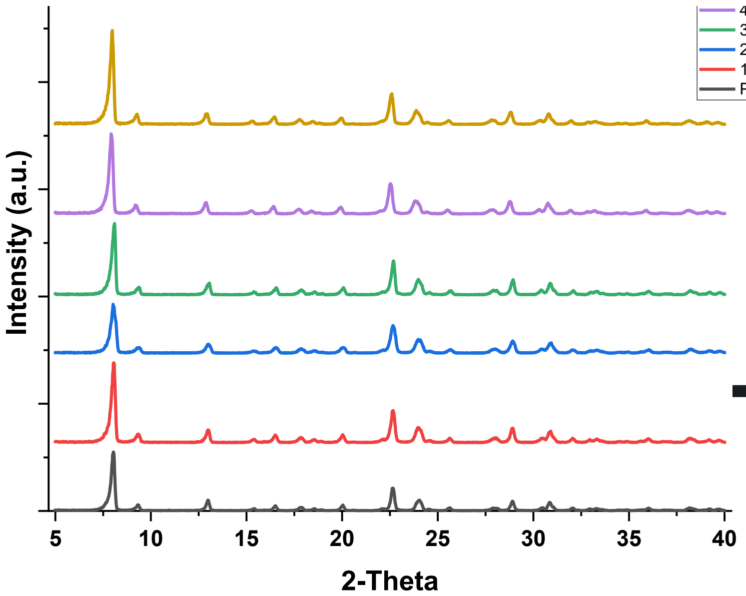
- Optical images suggest color change
- No changes in XRD, SEM (sintering) and IR
- No changes in unit cell parameters

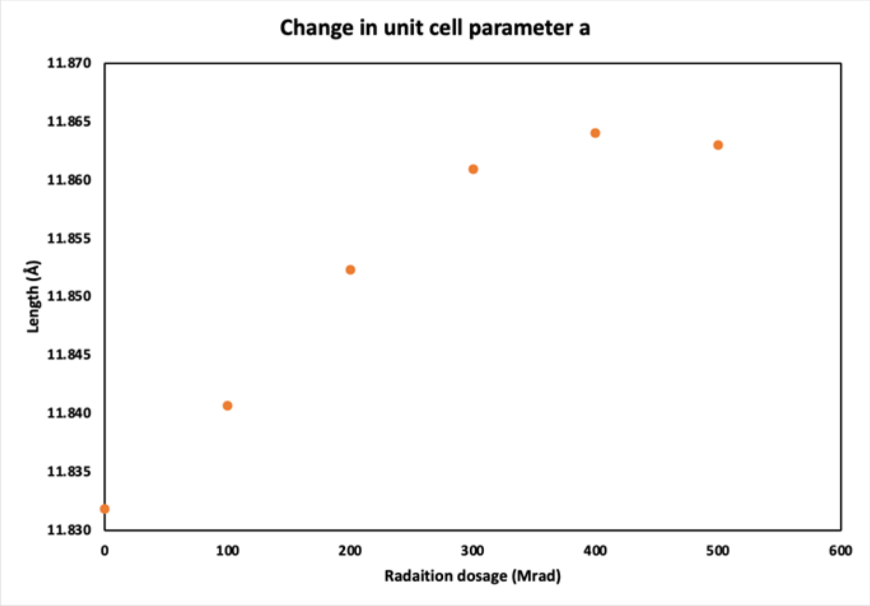




Pristine 100 200 300 400 500 MRad







Non-silver Loaded Sorbents for I_2 adsorption

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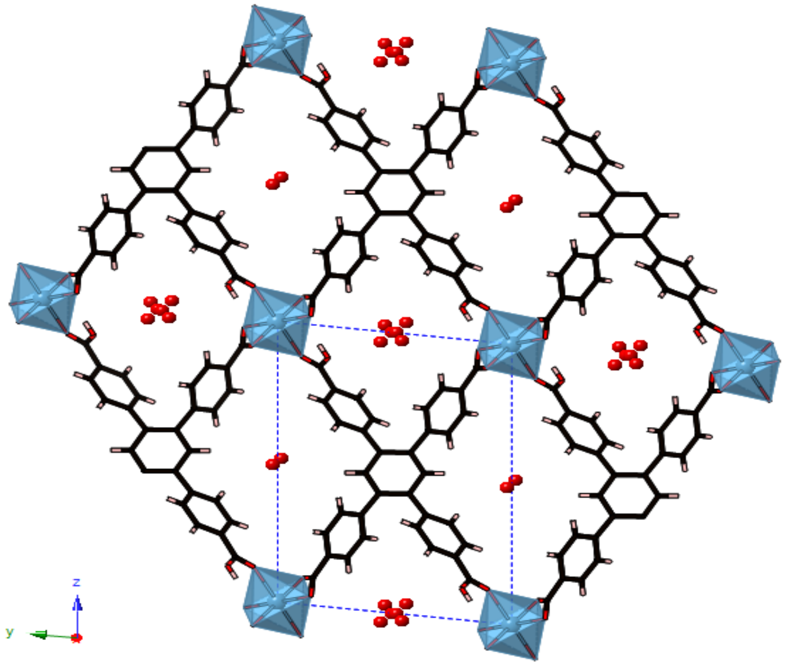
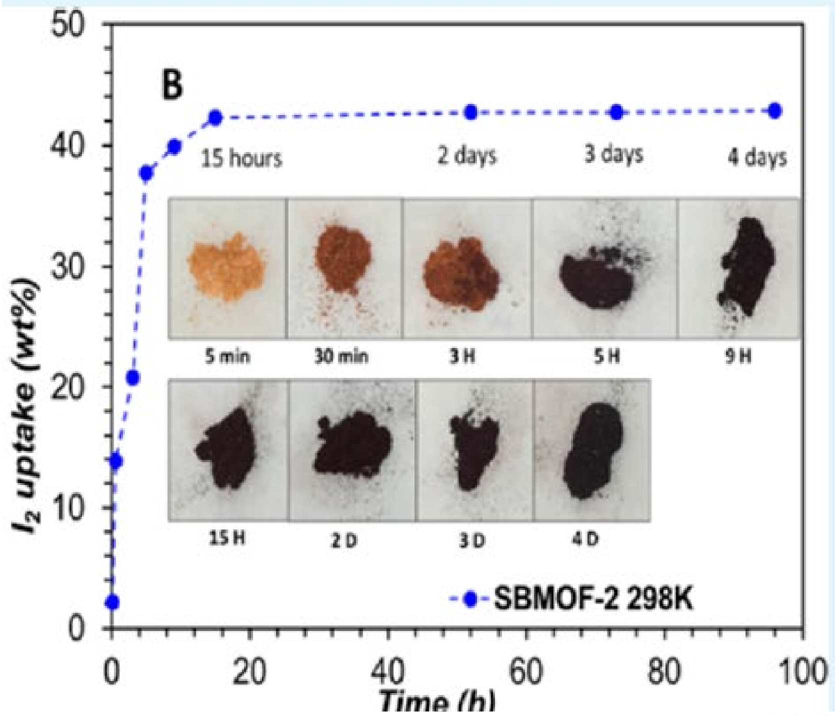
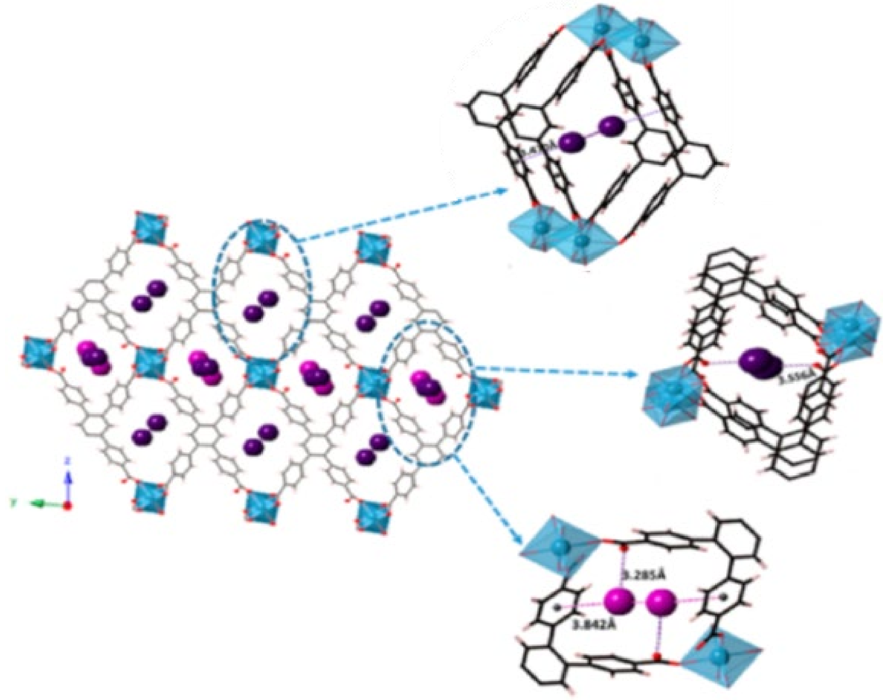
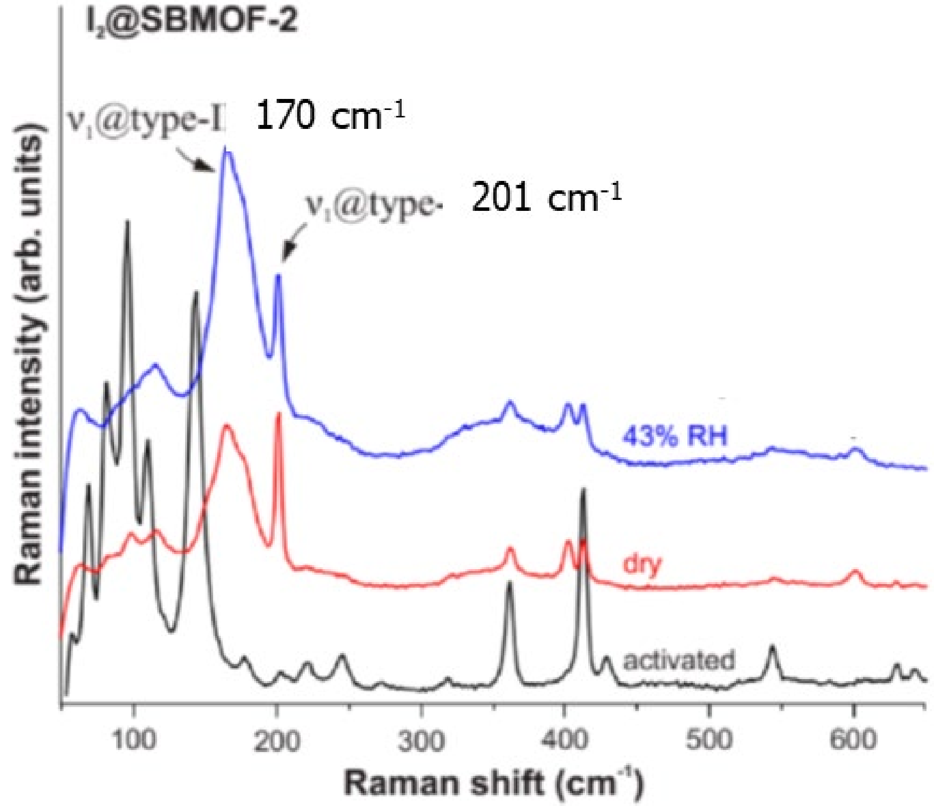






- Change in color of the sorbent as a function of I2 concentrations
- The prominent adsorbate−adsorbent interactions are I··· π (phenyl ring) and I···O, the occupancy of I_2 is higher in channel II compared to channel I.
- The H – I and O – H stretching in Raman spectra were absent suggest preferential adsorption of I_2 under humid environment



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- Industrial Partners