INL/MIS-21-62308-Revision-1

Kr/Xe Separation and Capture Overview - US/UK collaboration

April 2021

Changing the World's Energy Future

Amy K Welty, Mitchell Greenhalgh, Troy G Garn, Meghan S Fujimoto

Idaho National Laboratory

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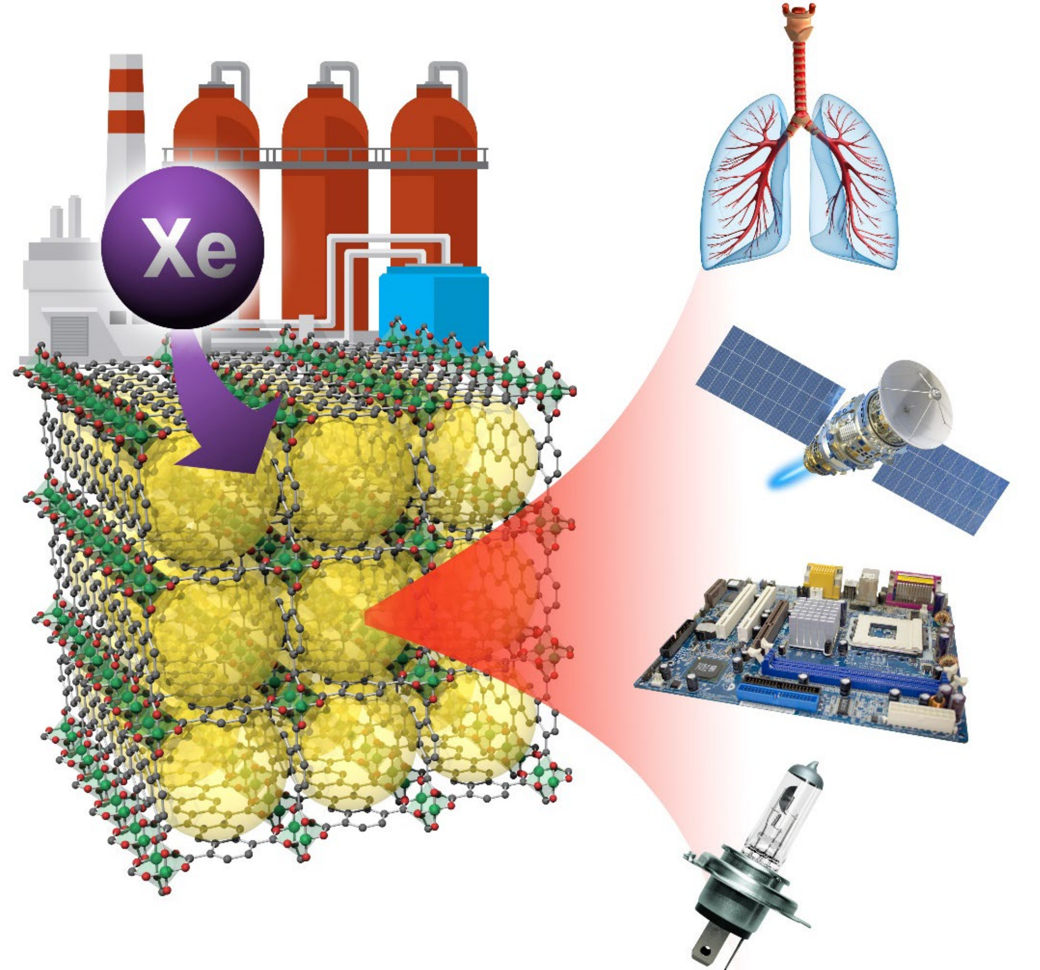
Kr/Xe Separation and Capture from Used Nuclear Fuel Reprocessing Off Gas

Praveen K. Thallapally, Alex Robinson, Jian Liu (PNNL)
Mitchell Greenhalgh, Troy Garn, Meghan Fujimoto, Amy Welty (INL)
April, 2021



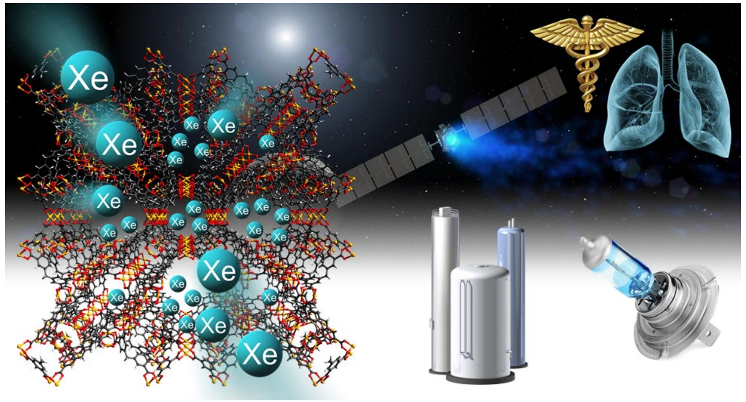
CHEM., 4, 466-494, 2018

U.S. DEPARTMENT OF ENERGY

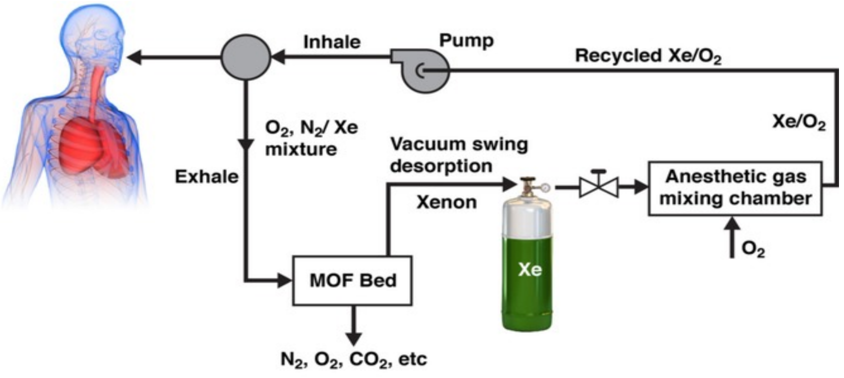
Current technology

- **Current Technology**
  - Cryogenic removal of Xe and Kr
    - Projected to be expensive
    - Potential for O_3 accumulation ⇒ hazardous conditions
    - ^{85}Kr decay product Rb is a liquid at storage temperatures and corrosive
    - corrosion of storage canisters

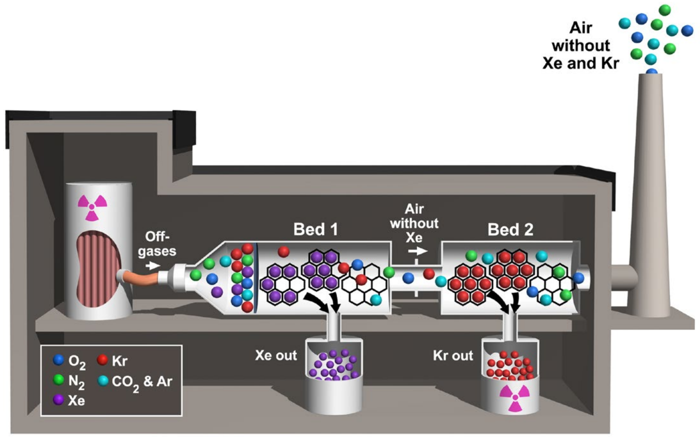
- **Porous materials**
    - Remove Xe and Kr in separate step:
    - Remove Xe at ambient or low temperatures
      Recover process costs by selling Xe?
    - Remove Kr at near room temperature
    - MOFs and COFs (PNNL)
    - AgZ and HZ (INL)



ACS. Mat. Lett., 2020, 3, 233–238

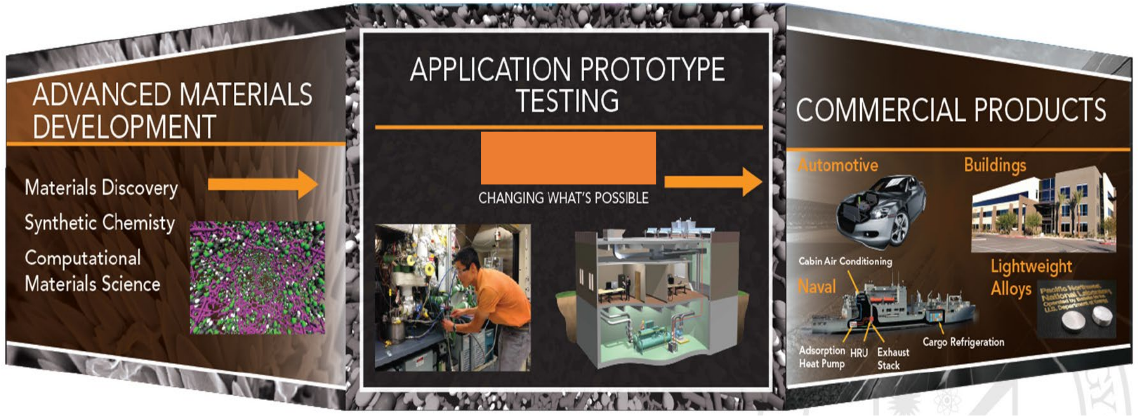


Chem. Eur. J., 23, 10758 – 10762, 2017



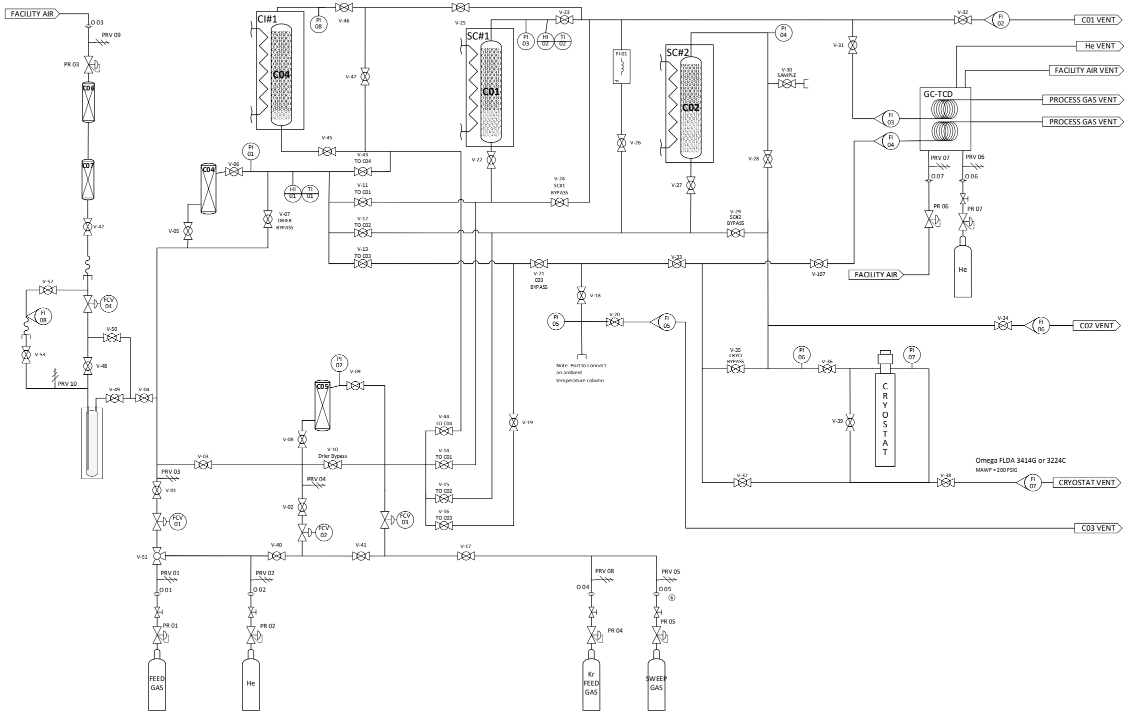
Acc. Chem. Res. 2015, 48, 2, 211–219

Capabilities@PNNL and INL



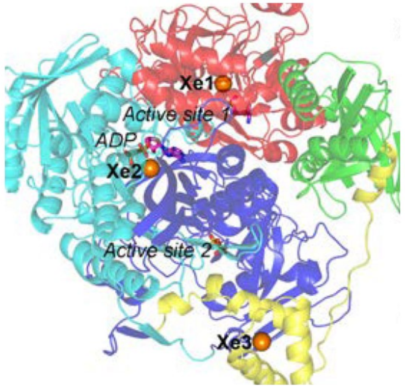
- Computationally inspired material discovery
- Porous material characterization and testing
- Milligram to kilogram scale synthesis
- Bench scale demonstration – in collaboration with industrial partners

- Full Patent on noble gas separation using MOFs and related materials USPTO WO/2017/218346A1
- Filled a provisional patent on making mechanically robust particles using PNNL proprietary approach
- Licensed the large-scale synthesis of material technology to Inna Venture, LA



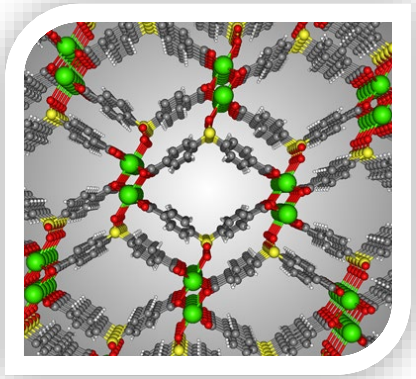
- Flexible test system designed to emulate real-world conditions
  - Operates at nearly any applicable temperature, pressure, or flow condition
  - Dual-stream, continuous gas analysis
- Zeolite sorbent production: Patent awarded 2014 (US 8,686,083 B2)
- Customer/partner sorbent testing

Bio-inspired Material Discovery: Room Temperature Sorbent



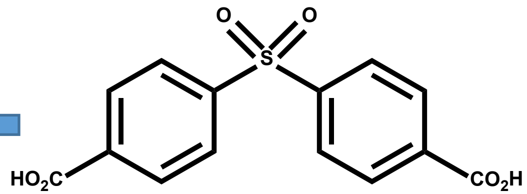
Insights from biology

Schoenborn, B. P., et. al., *Nature,* 207, 28, 1965

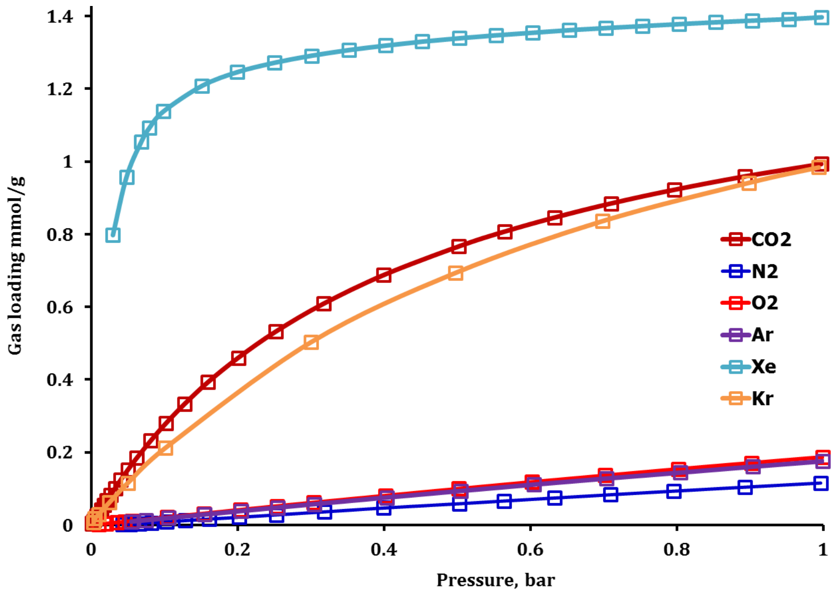


$CaCl_2$

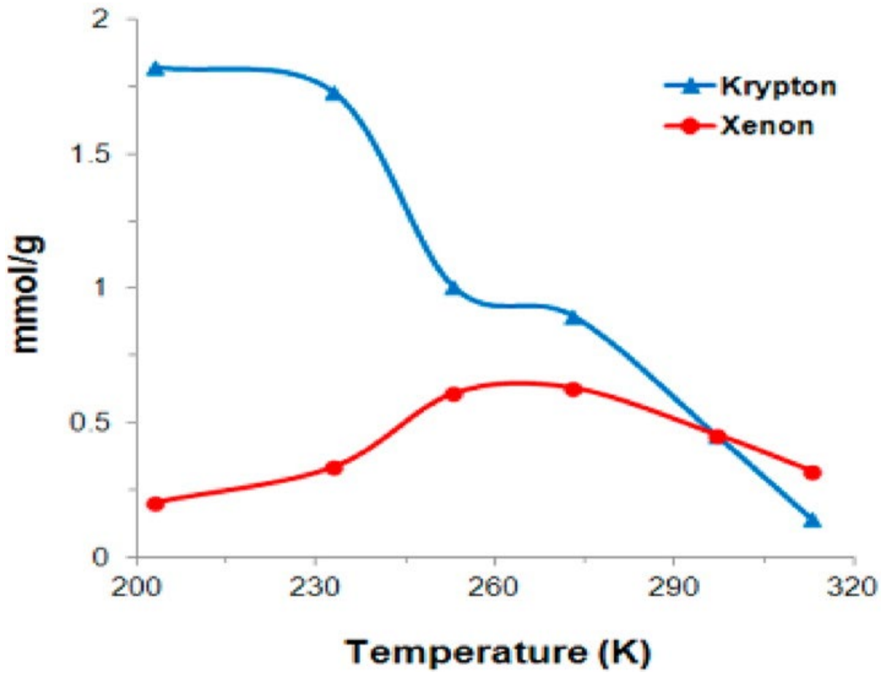
Solvent/heating



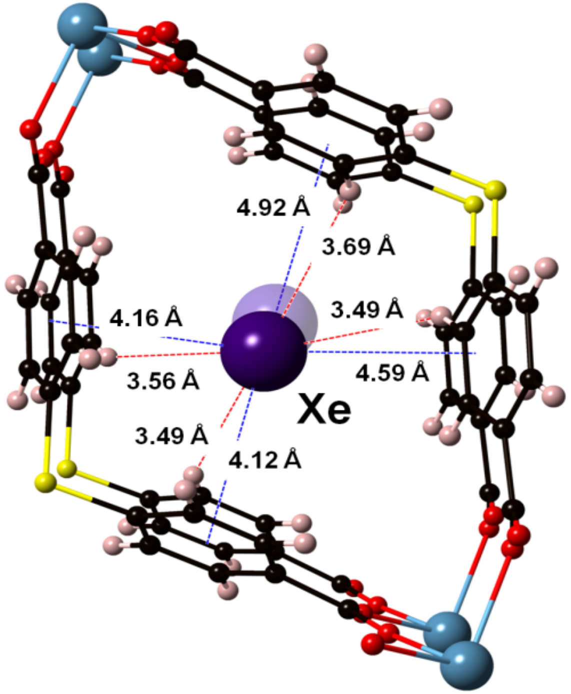
Banerjee et. al., Nature Communications, 2016
Chemical Engineering New, 94, 26, June 27, 2016, highlight



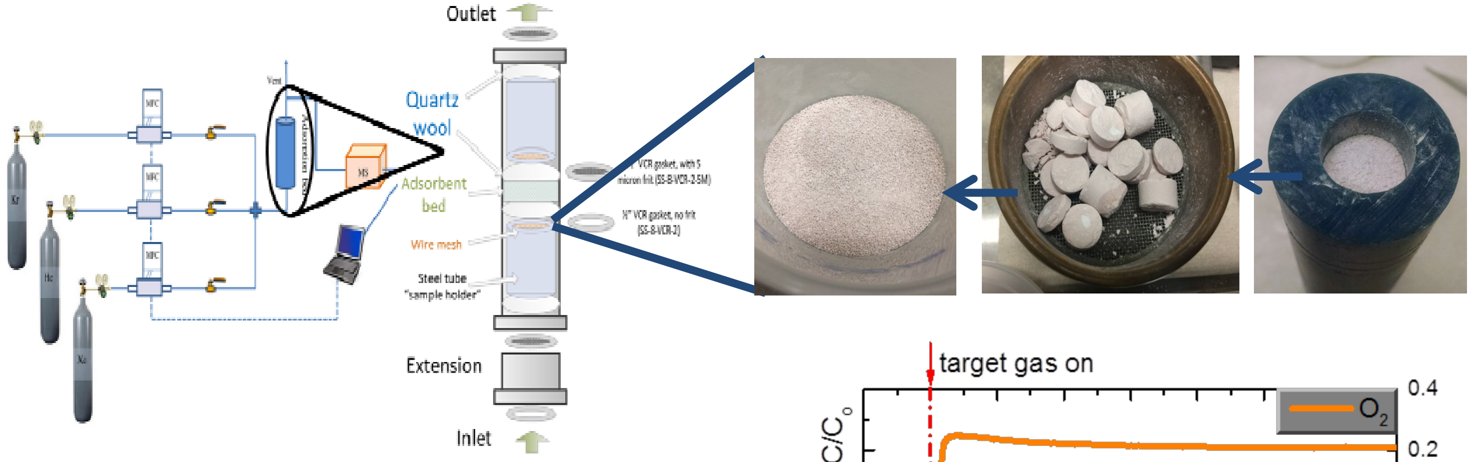
Very selective to Xe over other gases present in air



Xe/Kr selectivity switch as a function of temp

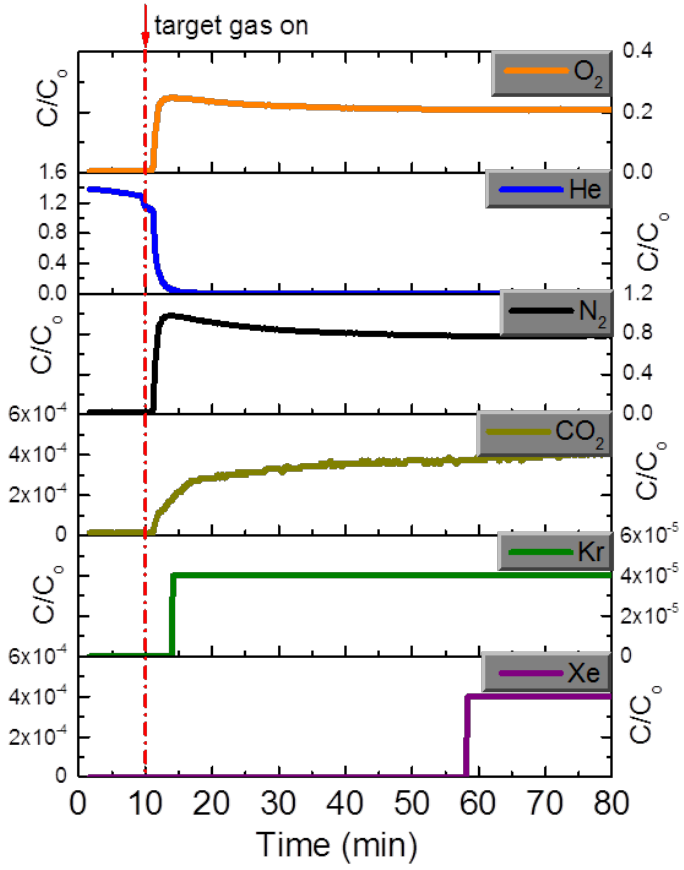


Single Column Breakthrough Experiments and Desorption



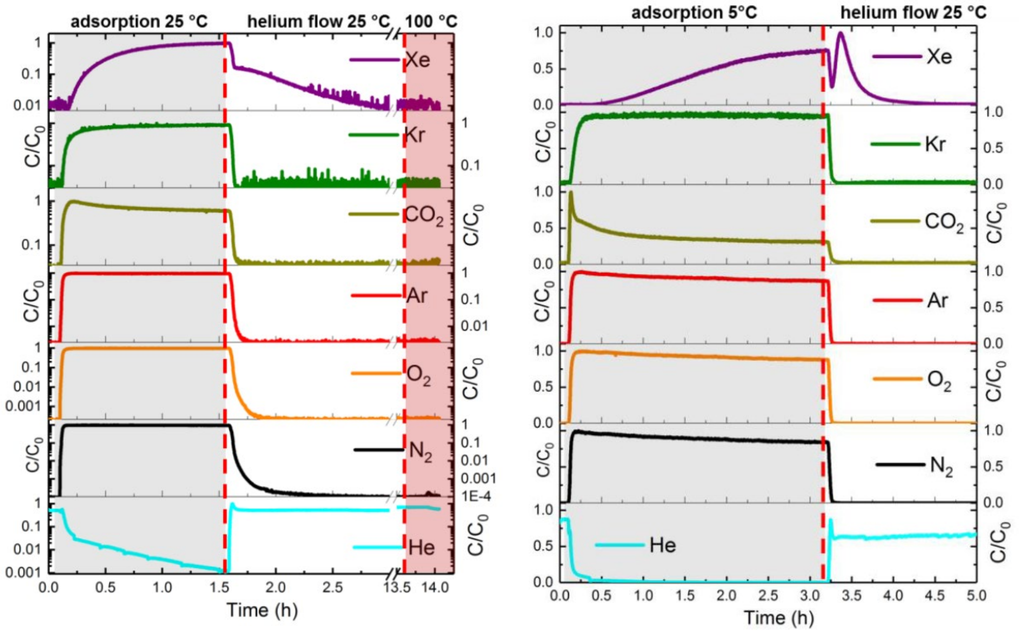
Property	Value
Pressed Pressure	75 MPa
Size	500 – 850
BET Surface area	15 m²/g
BET Surface area, powder	120 m²/g

- **Conditions**
  - Air = 78% N_2, 21% O_2, 0.9% Ar, 0.03% CO_2, 1300 ppm Xe, 130 ppm Kr
  - Flow rate = 20 cm³/min
  - T = 25 °C (298K)
  - MOF = CaSDB
- **Results**
  - Xe capacity = ~30 mmol/kg *vs* 8 mmol/kg (NiMOF) and 22 mmol/kg (CC3)
  - >95% of the Xe captured from air
  - Xe/Kr (selectivity) = 15

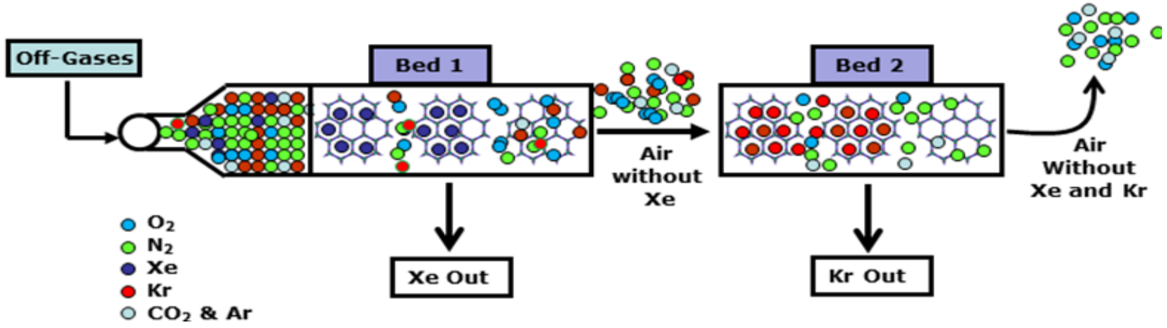


Wet gas (RH 48%)

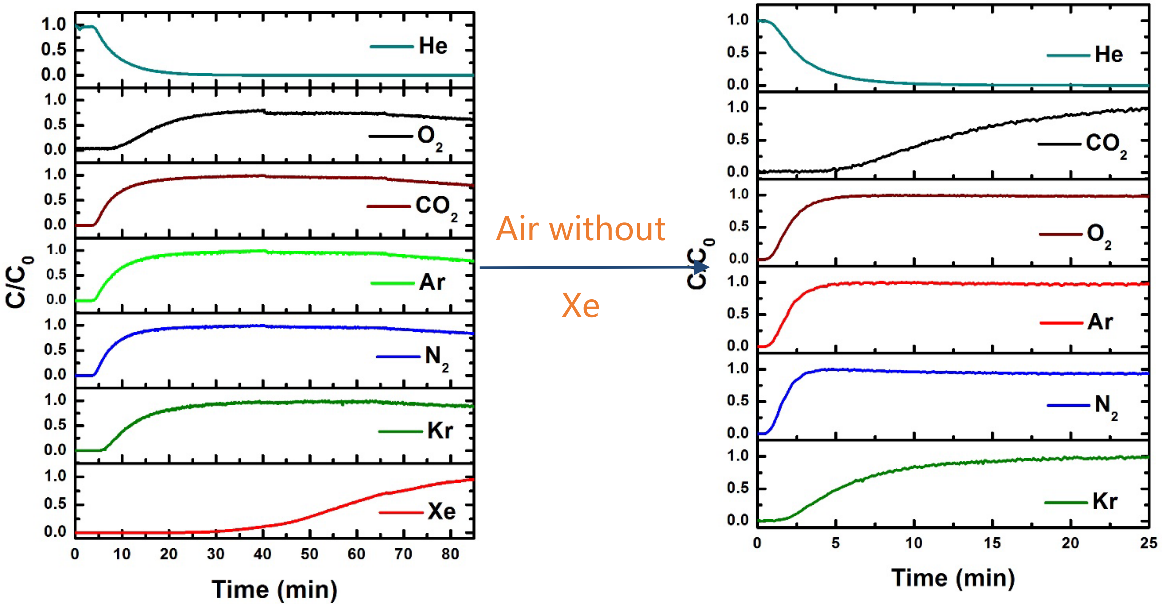
Desorption experiments



Two Column Breakthrough Experiments



- **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



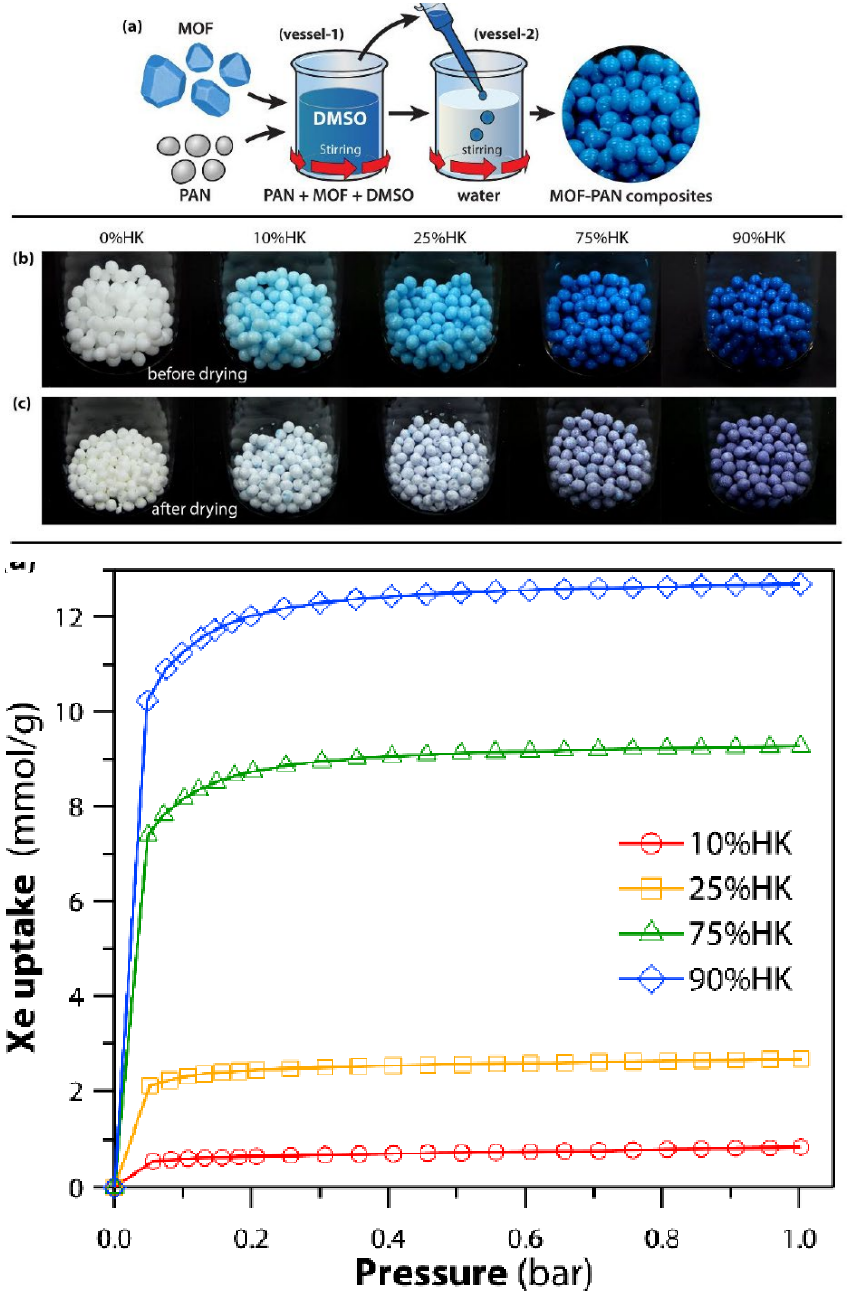
Gas	Breakthrough Time (min)	Capacity (mmol/kg)	Selectivity of Xe
Xe	18	16 (33.8)[a]	
Kr	1	0.11 (0.75)[a]	14
CO_2	5	1.2	3
N_2	0.08	47	209
Ar	0.08	5.28	210
O_2	0.08	12	206

[a] Capacity at equilibrium

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

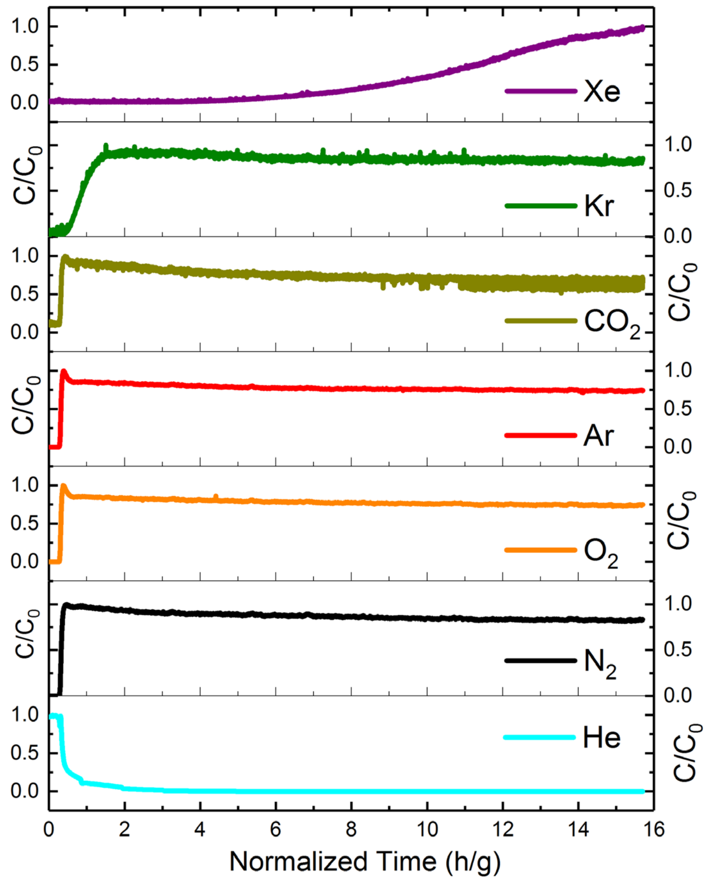
Thallapally, et. al., USPTO WO/2017/218346A1

Low Temperature MOF Sorbent for Xenon



- **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 = -78 °C
  - MOF = CuBTC
- **Results**
  - Xe capacity = ~900 mmol/kg;
  - >99% of the Xe captured from air;
  - 12 times higher capacity than CaSDB MOF

Low temperature (-78 C)

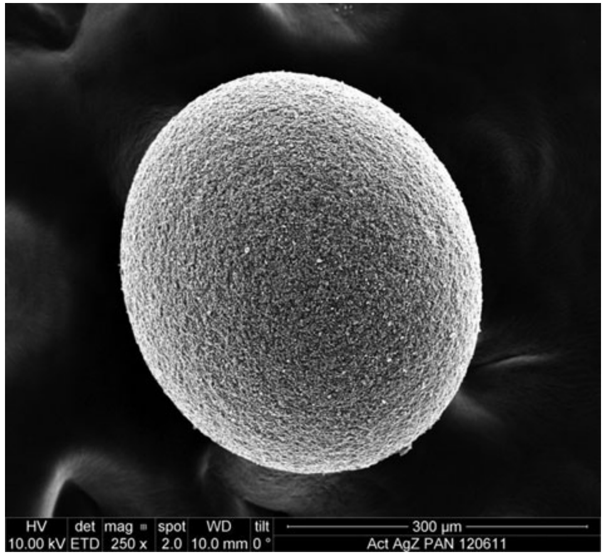


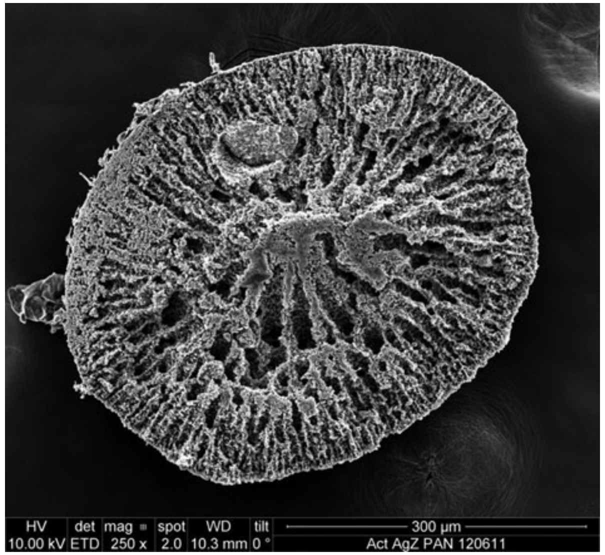
Major Accomplishments

- Developed novel engineered form sorbents
  - AgZ-PAN and HZ-PAN
  - Patent awarded for the process
- Designed custom adsorption system
- Evaluated solid phase adsorption of Xe/Kr
- **Published two journal articles**
  - Journal of Nuclear Science and Technology, 51:4, 476-481, DOI: 10.1080/00223131.2014.877404
  - Journal of Nuclear Science and Technology, DOI:10.1080/00223131.2015.1126205
- Investigated sorbent cycling effects
- Demonstrated separation of Xe from Kr in a dual column system
- Produced a pure Kr stream from a Kr/Xe/Air mixture
- **Evaluated desorption of Kr and Xe**
- Performed other adsorption testing for external customers

Engineered from sorbent development

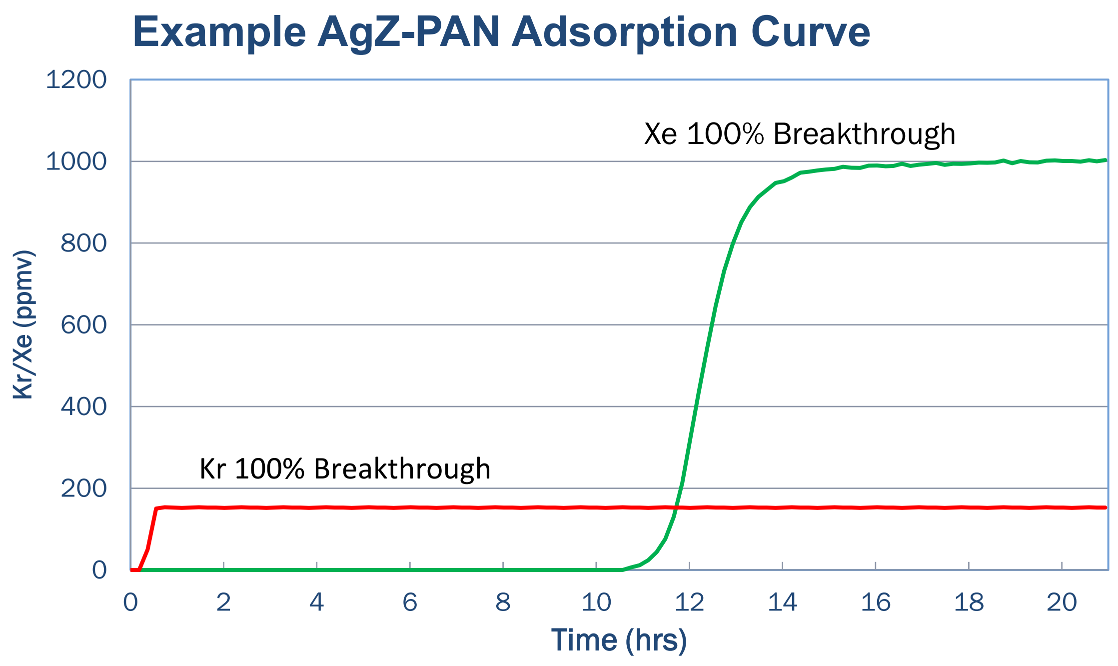
- **Mordenite powders incorporated into a macroporous polymer (PAN)**
  - H and Na powders ~80 wt. %
  - Spherical beads 0.3-1.4 mm diameter
  - Bulk density 0.3-0.4 g/mL
  - Na form converted to silver form
  - Patent awarded 2014 (US 8,686,083 B2)
- **HZ-PAN Sorbent**
  - BET surface area = 336 m^2/g
  - Micropore area (0.4-1.0 nm) = 250 m^2/g
- **AgZ-PAN Sorbent**
  - BET surface area = 250 m^2/g
  - Micropore area (0.4-1.0 nm) = 190 m^2/g





INL Adsorption Testing

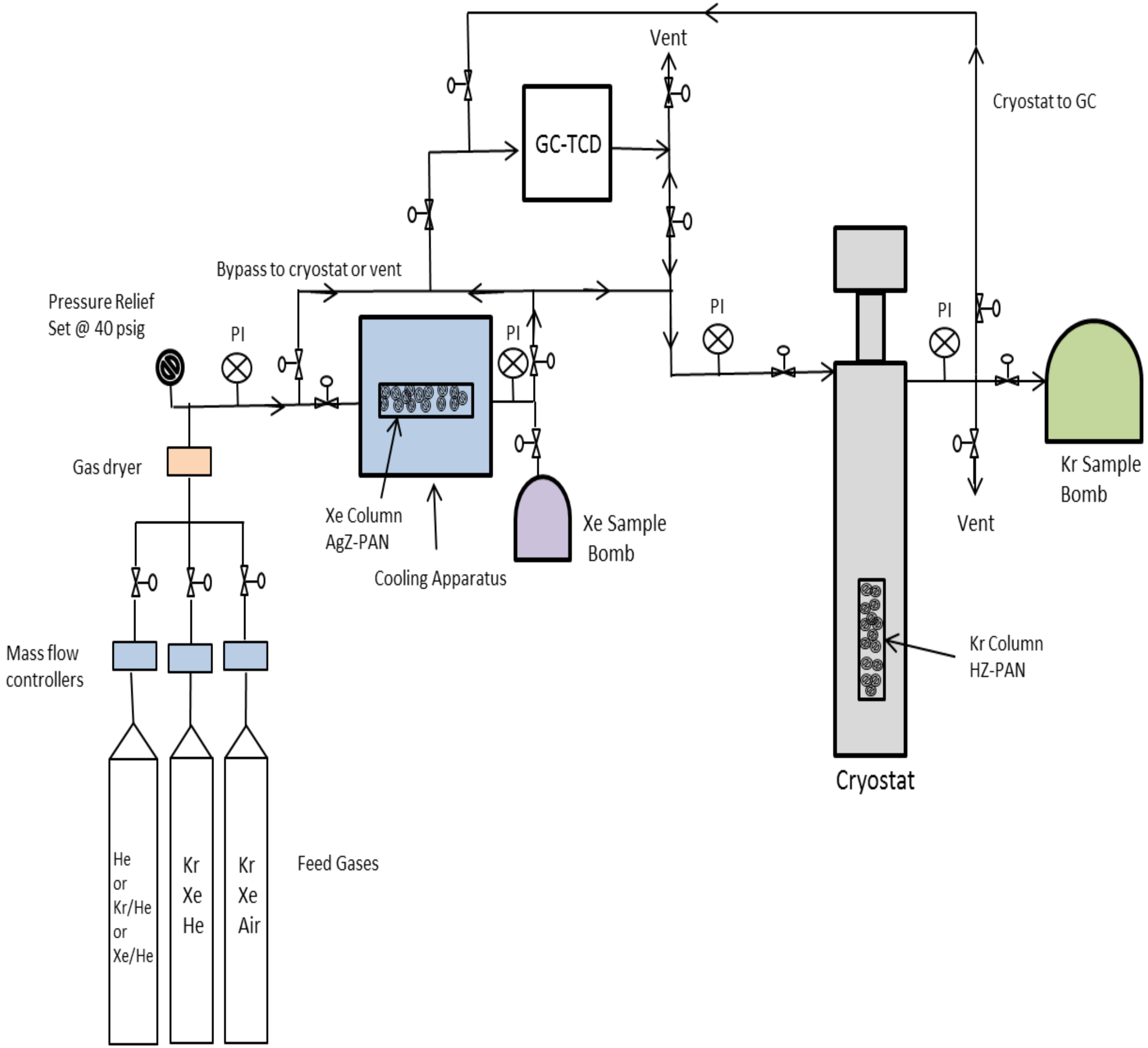
- AgZ-PAN
  - Highly selective for Xe over Kr
  - Temperatures 295 to 220 K
- HZ-PAN
  - High capacity for Kr in air
  - 191 K temperature
- Removal of Xe from Kr
  - Reduction in captured Kr volume



- Demonstrate feasibility of Xe removal with solid phase sorbents
- Produce pure Kr waste stream
- Determine adsorbed phase composition of both columns

FY-15 Dual Column Tests

- Test Conditions
  - 1000 ppmv Xe, 150 ppmv Kr
  - Flow rate 50 sccm
  - 18.3 grams AgZ-PAN
  - 4.45 grams HZ-PAN
  - Superficial velocity
    - Xe column 23.0 cm/min
    - Kr column 18.7 cm/min
  - Column temperatures
    - Xe column 295 or 253 K
    - Kr column 191 K
  - Test times (stop
    - 55 minutes (295 K)
    - 105 minutes (253 K)

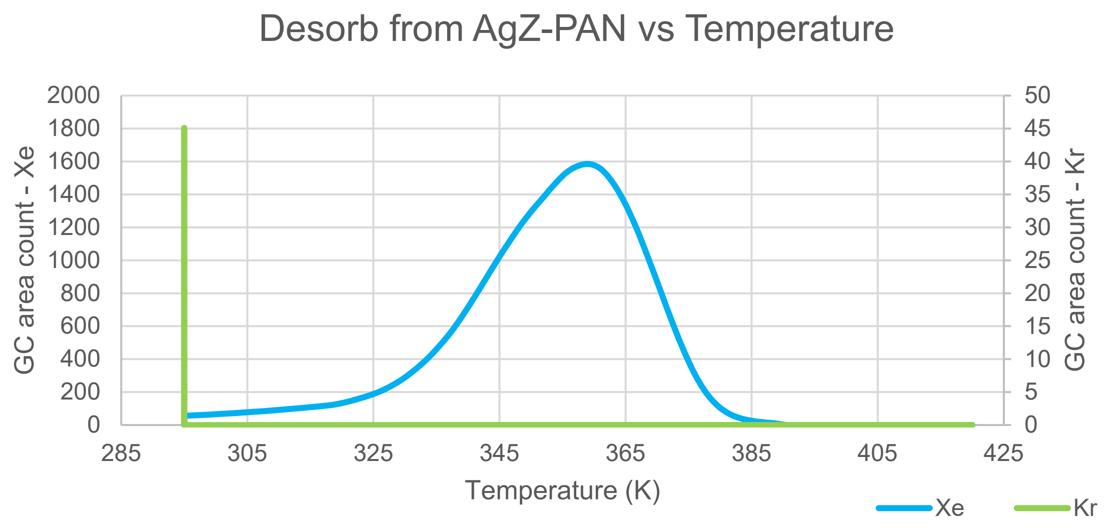


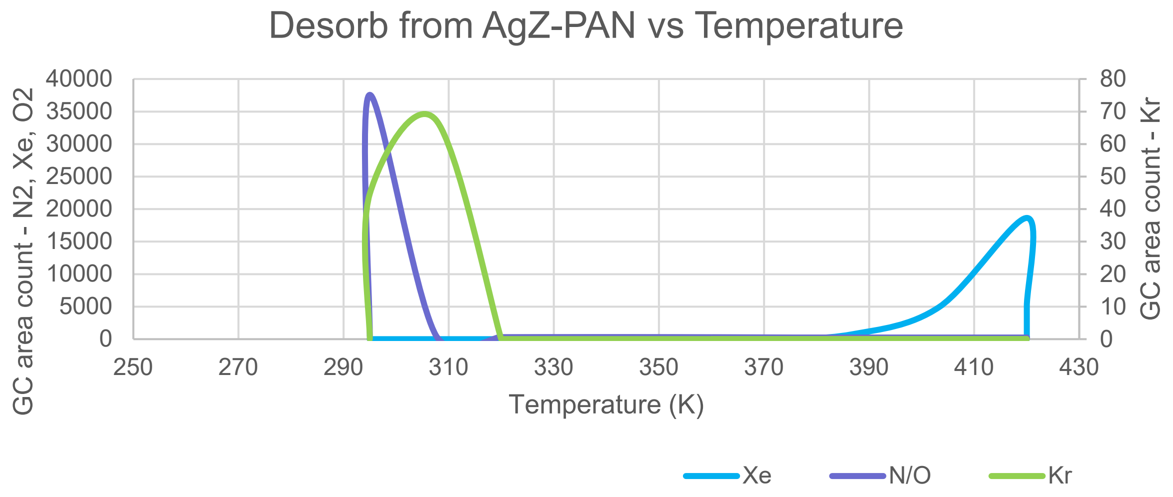
AgZ-PAN and HZ-PAN cycle testing

- Cycling tests
  - Evaluate sorbent efficacy over numerous thermal cycles
  - Flow gas through columns at proposed adsorption/desorption temperatures
  - Air and He evaluated as desorption gases
  - Measure sorbent capacity intermittently to ensure sorbent doesn't lose performance
- AgZ-PAN
  - Temperature range of 293 to 420 K
  - Results, 100 cycles without decrease in capacity measurements
  - An increase in capacity over time has been observed
- HZ-PAN
  - Temperature range 191 to 420 K
  - 24 cycles and counting, no decrease in capacity observed to date

FY-18 Desorption Studies

- AgZ-PAN
  - Xe/Kr separation
  - Ambient temperature adsorption
  - Adsorbed phase contains Xe, Kr and air
  - Desorption requires purge gas (He)
  - Ramp temperature slowly over 12 hours
  - Step temperature and soak 6 hours
  - 99-100% Xe separation





Outside Interest from Research

PNNL

GAIN voucher with Flibe Energy

Noble gas management using MOFs with Liquid Fluoride Thorium Reactor

Praxair

Interested in MOF technology to separate Xe from oxygen rich stream at room temperature /Kr separation

Involved in discussions with several companies including

DTRA Fundamental science

Awarded a grant to understand the role of surface chemistry and pore size on noble gas adsorption

DOE NP Isotope program

Involved in discussion with various labs who are working on isotope program to selectively trap noble gases

INL

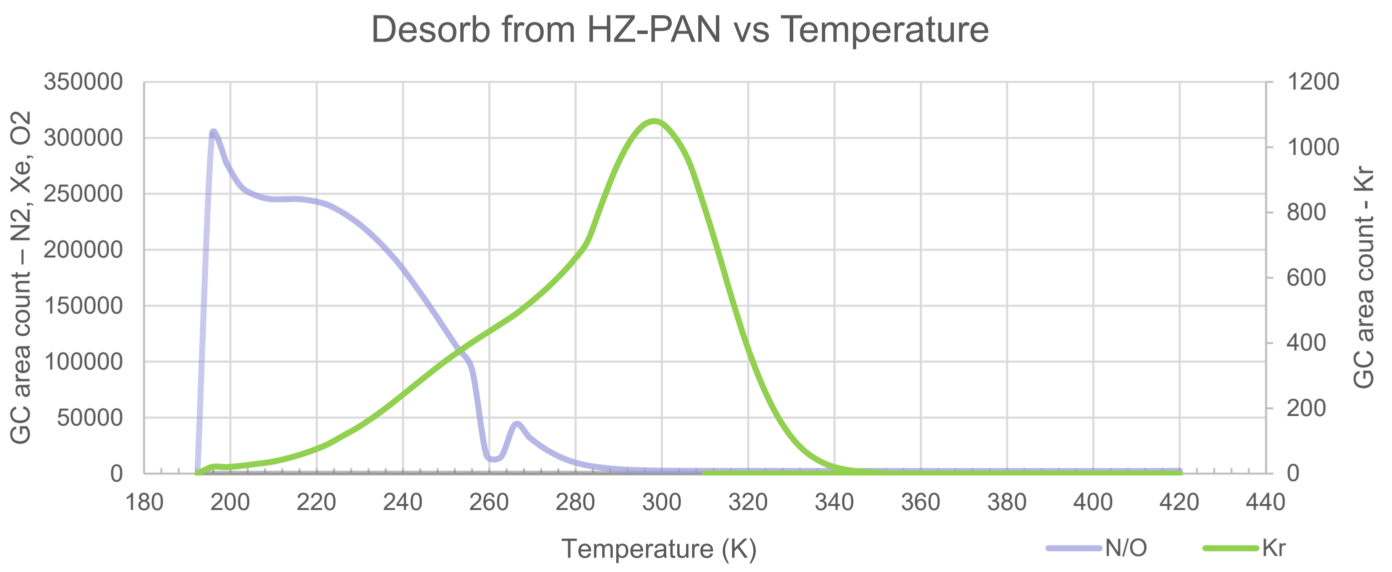
- **GAIN voucher with GE-Hitachi**
  - Enabling System Technologies to Improve the Economics and Performance of Existing LWRs and Advanced BWR Plants: Improving Off-gas System Performance
  - Recommendation made to improve monitoring and performance of off-gas system.
- **Phase II SBIR with TDA Research Inc. from NASA**
  - Testing of sorbents for Nuclear Thermal Propulsion (ground testing)
  - Testing Complete
- **Licensed patent with Global Phosphate Solutions**
  - “Phosphate Sponge”
  - Received R&D100 Special Recognition Green Tech Award

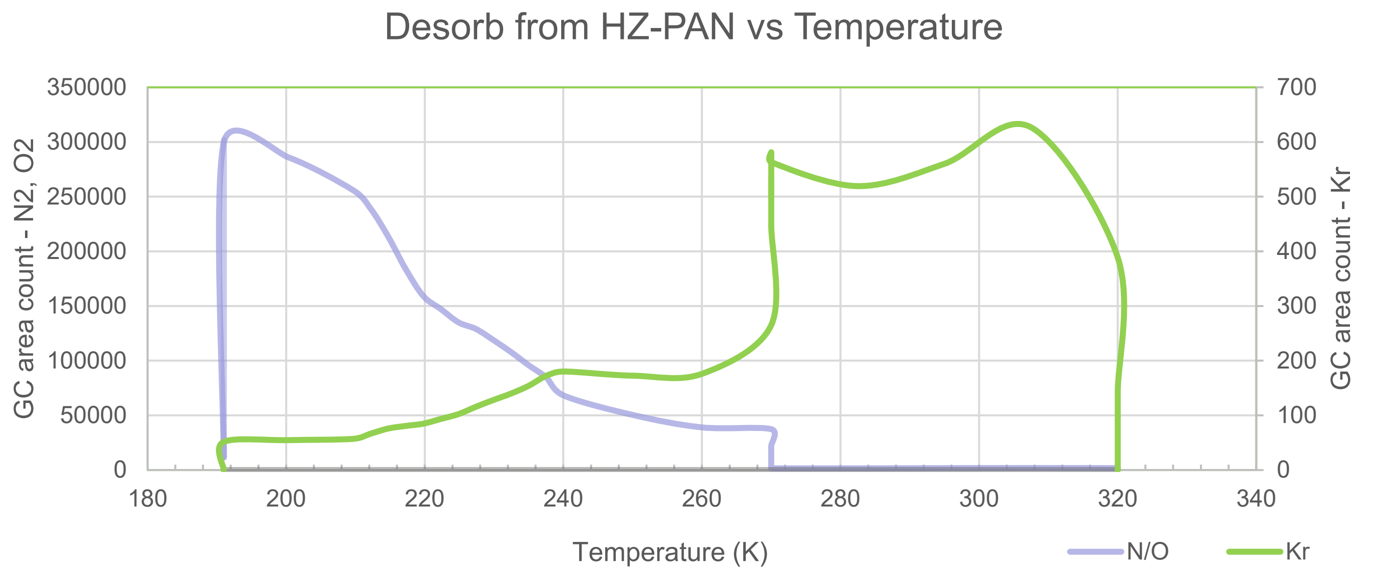
Current/Future Research

- Continued MOF development with thin-bed testing
- Continued deep-bed testing of promising sorbents
- Focus on applied testing and optimization
- Advanced reactor off-gas treatment sorbents
- Alternate reprocessing (e.g. pyroprocessing) off-gas treatment sorbents

Backup Slides

FY-18 Desorption Studies

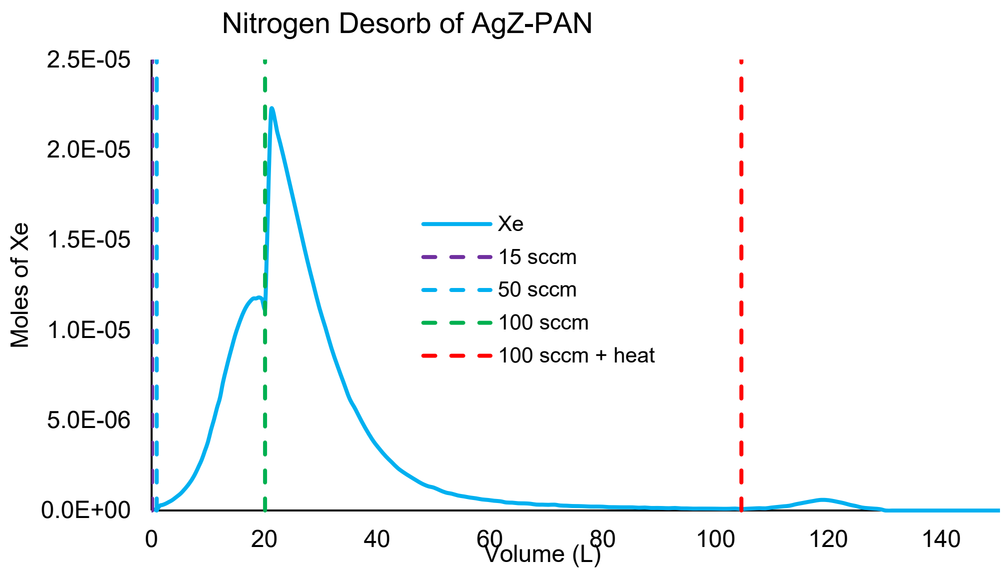




- **HZ-PAN**
  - Kr capture
  - 191 K adsorption
  - Adsorbed phase contains Kr and air
  - Desorption requires purge gas (He)
  - Ramp temperature slowly over 12 hours
  - Step temperature and soak 9 hours
  - ~80% Kr separation
  - 3.5 to 5 times Kr concentration

FY-19 and 20 Desorption

- **Desorption of HZ-PAN and AgZ-PAN**
  - AgZ-PAN Xe Desorb
  - Investigated flow rate and temperature
  - Viability of alternative sweep gas
    - Air
    - Argon
    - Nitrogen



  - HZ-PAN Kr Desorb
    - Low flow Argon
    - Removal at near ambient temps