INL/CON-22-70242-Revision-0

Kr/Xe Separation and Capture: Sorbent Development and Testing

November 2022

Changing the World's Energy Future

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

Idaho National Laboratory

INL/CON-22-70242-Revision-0

Kr/Xe Separation and Capture: Sorbent Development and Testing

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

November 2022

Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

November 28, 2022

Amy Keil Welty
Chemical Engineer

Kr/Xe Separation and Capture

Sorbent Development and Testing

Acknowledgements

- Funding: US Department of Energy – Office of Nuclear Energy

- Researchers
  - Mitchell Greenhalgh
  - Meghan Fujimoto
  - Troy Garn
  - Emma MacLaughlin

Drivers

^{85}Kr

$T_{1/2}$ = 10.8 yr

^{x}Xe

$T_{1/2}$ = days

^{3}H

$T_{1/2}$ = 12.3 yr

Used nuclear fuel reprocessing off gas

Regulations 40 CFR 190

^{129}I

$T_{1/2}$ = 16M yr

^{14}C

$T_{1/2}$ = 5730 yr

Solutions

- Cryogenic Distillation
  - Utilized to separate Xe from Kr and produce a purified Kr stream
  - Operated at INL
  - Difficult to control
  - Issues with ozone accumulation
  - Very expensive
- Solid-phase adsorption (physisorption)
  - Activated carbon is well-known as a highly selective material for capturing Kr and Xe at reduced temperatures.
    - Most commercial reactors use it to delay Xe and Kr to meet regulatory release requirements
  - Fire hazards associated with activated charcoal sorbents have been reported
  - Zeolite-based sorbents have shown adsorption characteristics comparable to activated charcoal
  - New metal organic framework (MOF) materials have shown high porosity and gas adsorption properties

Research Focus: Krypton and Xenon Capture

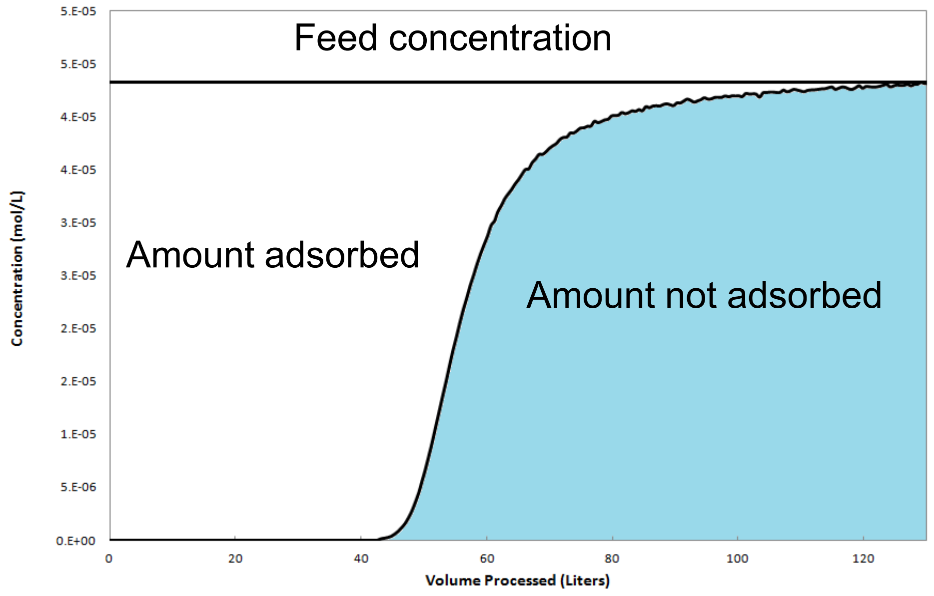
- Investigate Xe/Kr capture on existing and emerging solid phase sorbents as an alternative to cryogenic distillation
  - Develop sorbents with high porosity and affinity for target species
  - Prepare sorbents into a functional engineered form
  - Construct testing apparatuses and methodology for performance assessments
  - Characterize sorbents' performance under expected conditions
  - Evaluate temperature, radiological and cycling effects on sorbents
  - Determine appropriate sorbent desorption parameters
    - Temperature swing effects
    - Pressure swing effects
    - Desorption gas composition effects
- Use the data to inform design and operation of UNF reprocessing plant

Sorbent Development

- Design and develop new sorbents
- Evaluate newly developed sorbents
  - As they become available
- Perform engineering studies for system design and economics
  - Determine value/market volume of Xe
  - Cost comparisons of current sorbents (i.e., mordenites vs. MOFs)
  - Economic evaluation of solid phase capture vs. cryogenic distillation
- Apply techniques to other processing avenues
  - Pyroprocessing
  - Advanced reactors
  - Others

Sorbent Development

- Sorbent Characteristics
  - Surface area analysis
    - Micromeritics ASAP Surface area analyzer
    - Nitrogen BET
  - Scanning electron microscope analysis
  - Calculated from breakthrough curve
    - Capacity of analyte(s)
    - Selectivity of one analyte for another
- Xe and Kr adsorption
  - Various feed-gas compositions
  - Multiple feed gas flowrates (i.e., superficial velocities)
  - Multiple sorbent temperatures
  - Multiple sorbent materials (HZ, AgZ and MOFs)
  - Breakthrough curves generated from GC data
  - Jandel Scientific's TableCurve utilized for determining the area under the curve



$$Sel_{Xe,Kr} = \frac{X_{Xe}/Y_{Xe}}{X_{Kr}/Y_{Kr}}$$

Sorbent Development

Active Species

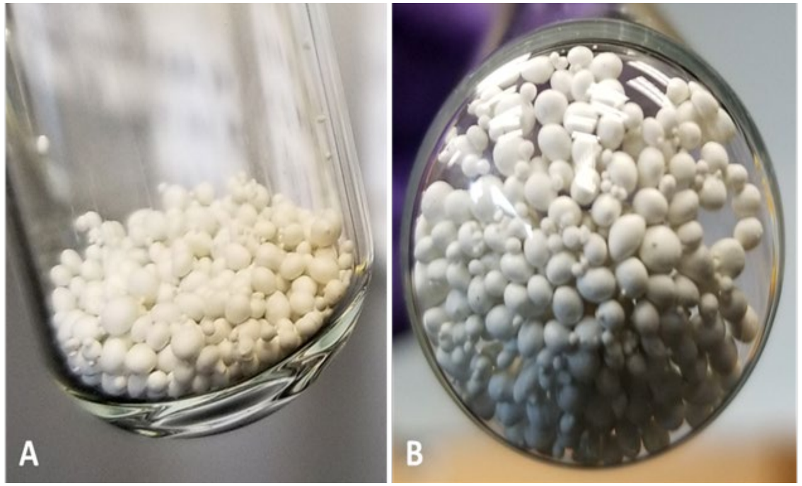
- Hydrogen form (HZ)
- Silver form (AgZ)

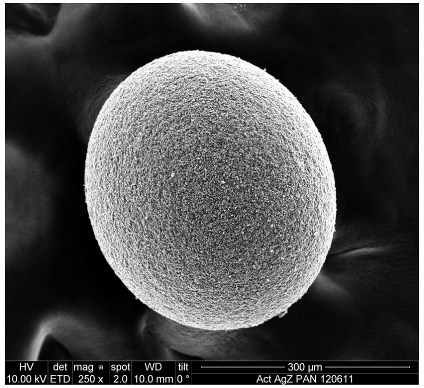
Strength and Stability

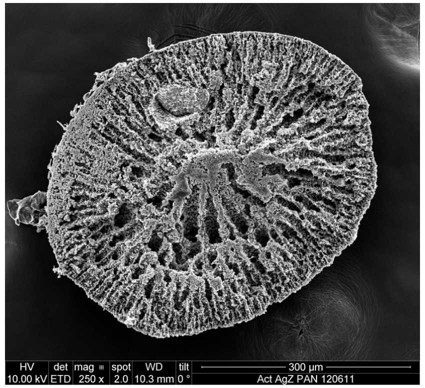
- Incorporated into polyacrylonitrile (PAN)

Engineered Form Sorbents

- HZ-PAN for Xe/Kr capture
- AgZ-PAN for Xe capture

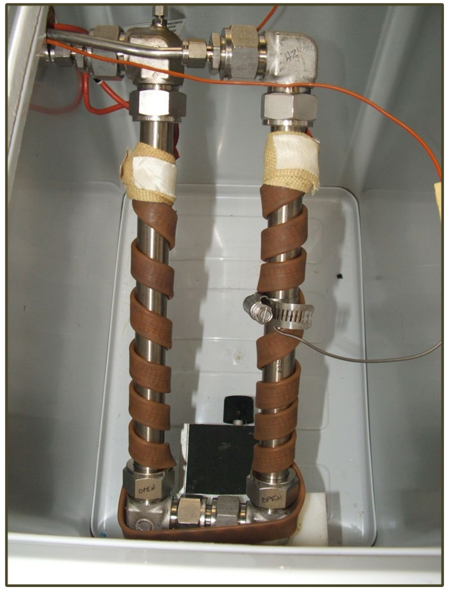




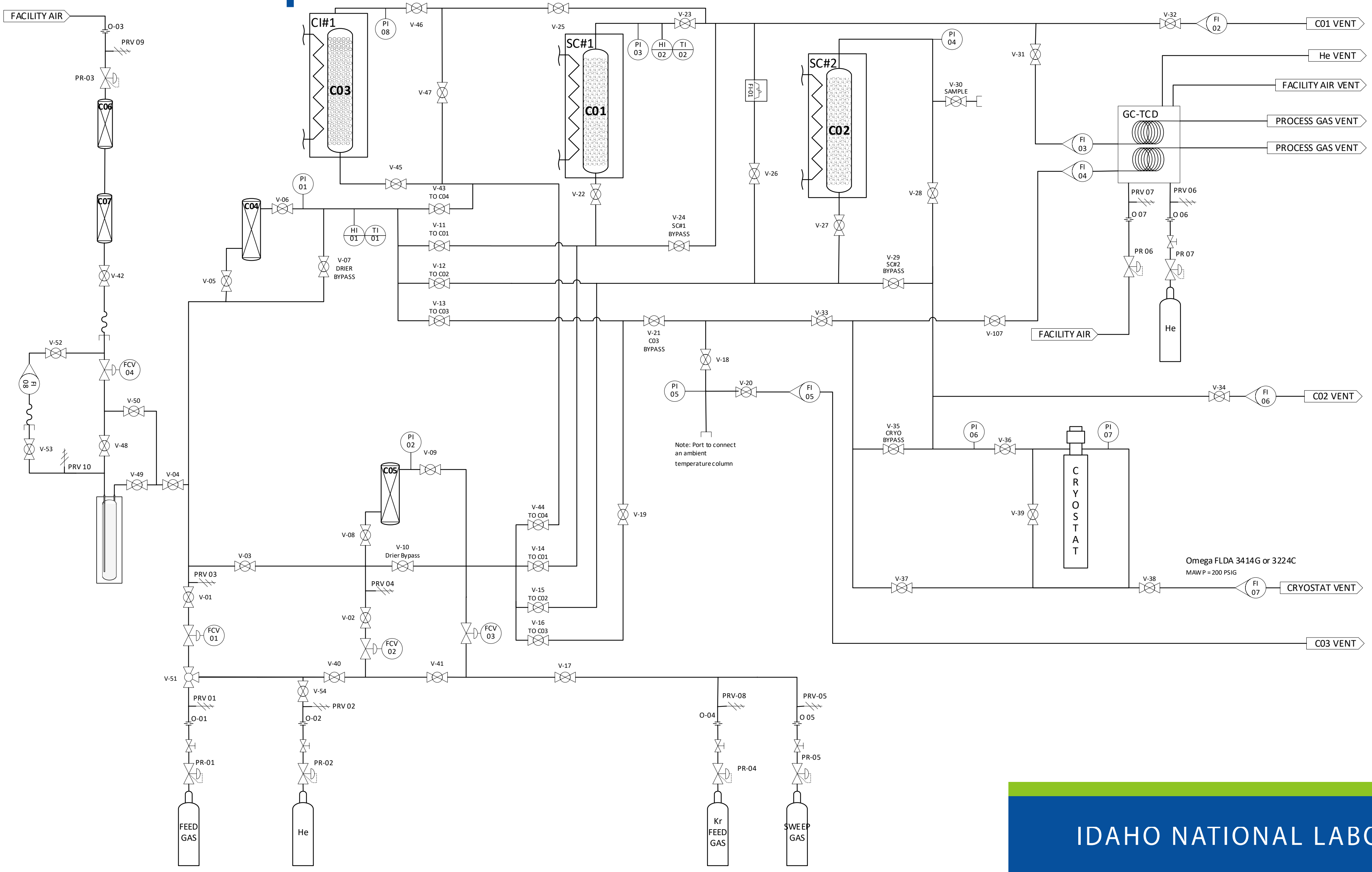


INL Testing Apparatus

- Two Stirling coolers
  - Temperatures from ambient to -82°C
  - Connected in series/parallel
- Dual GC-TCD
  - Monitor effluents of both columns
- Gas delivery system
  - Mass flow controllers for accurate delivery of desired feed gases
- Multiple columns
  - Temperature controlled
  - Variable sizes
  - AgZ-PAN or HZ-PAN packed

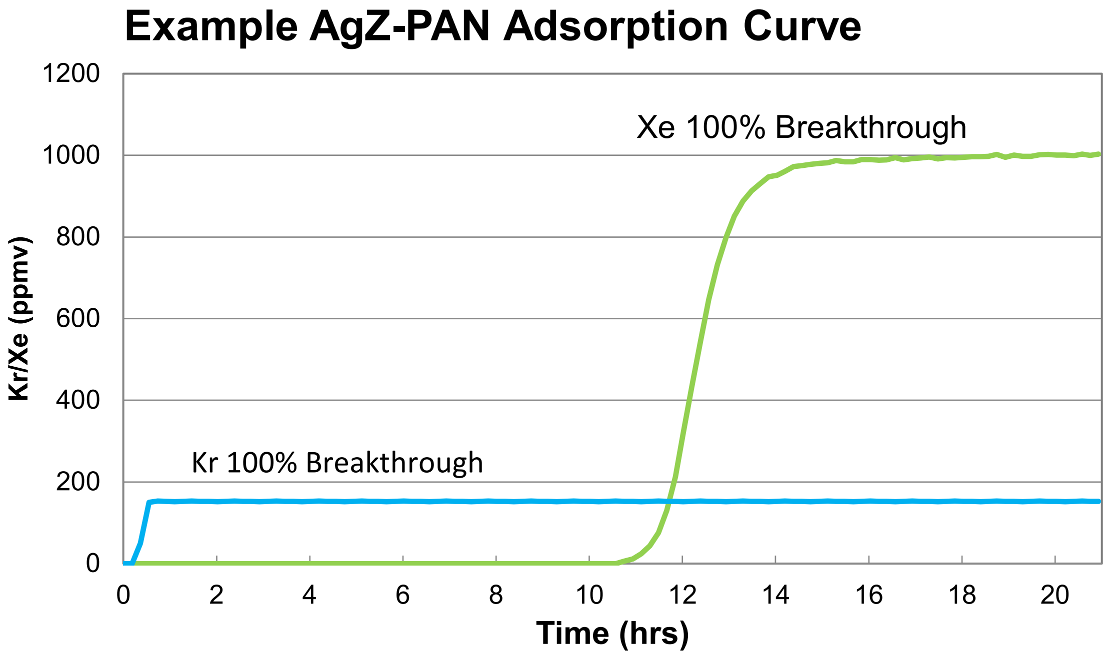


INL Testbed Capabilities



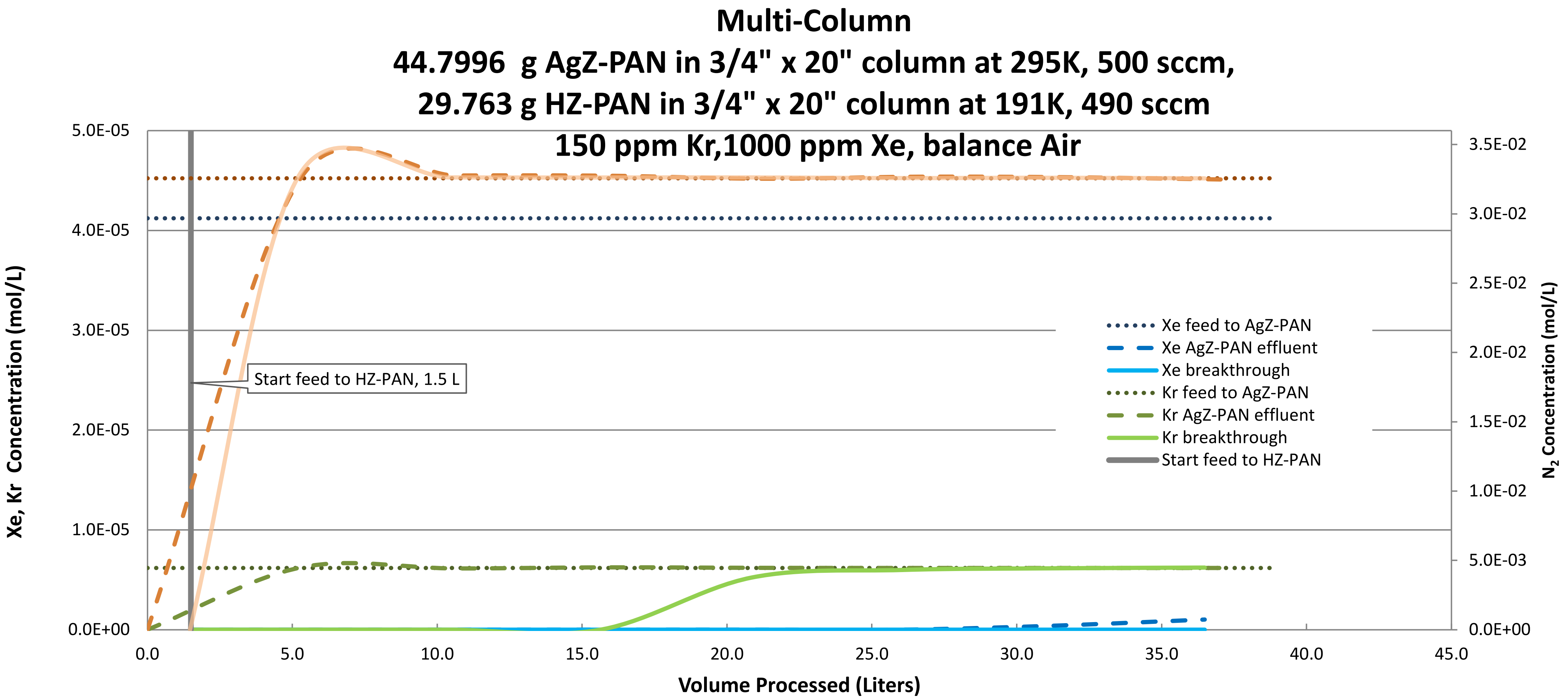
Testing

- 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

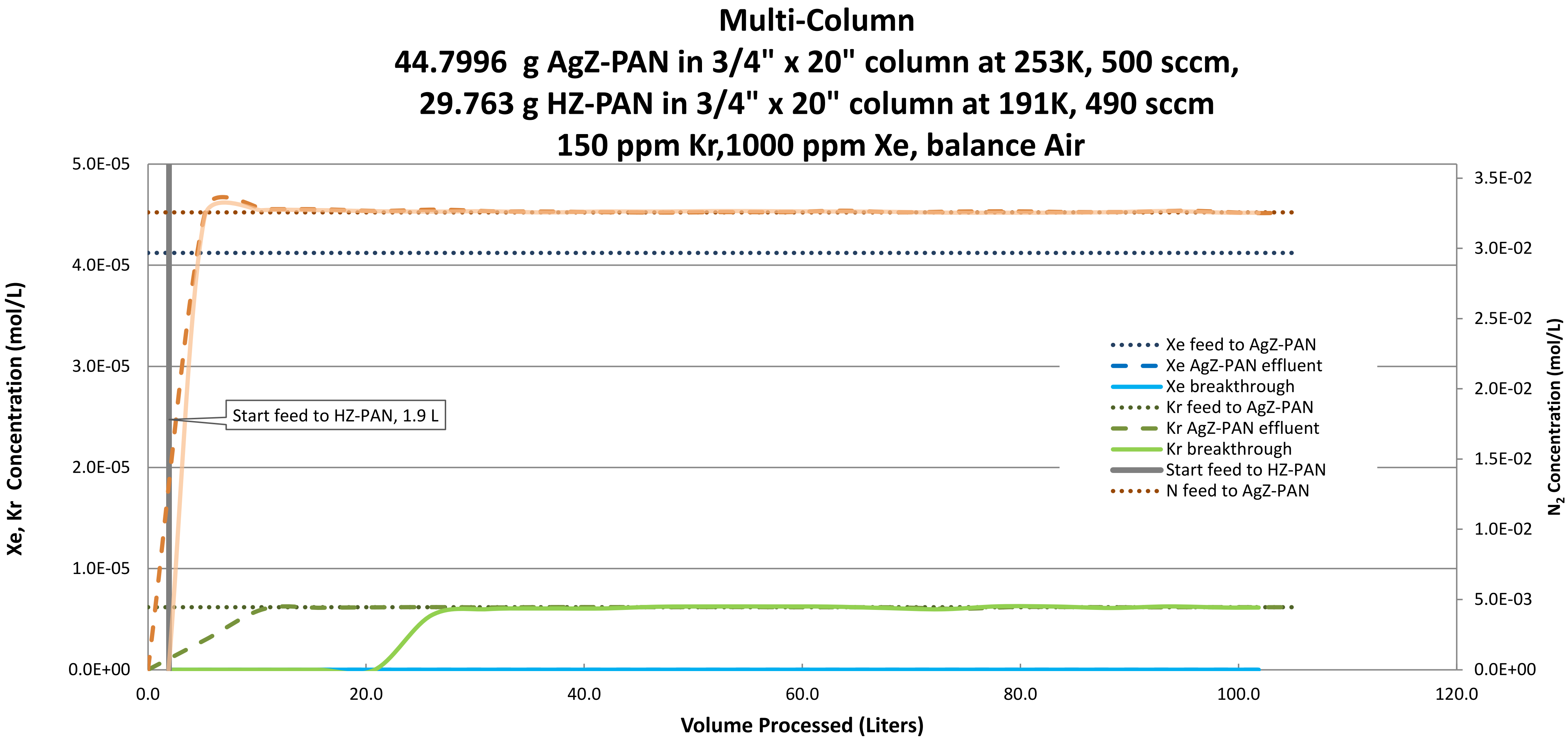


- Demonstrate feasibility of Xe removal with solid phase sorbents
- Produce pure Kr waste stream
- Determine adsorbed phase composition of both columns

Separation Results – Ambient Xe Capture



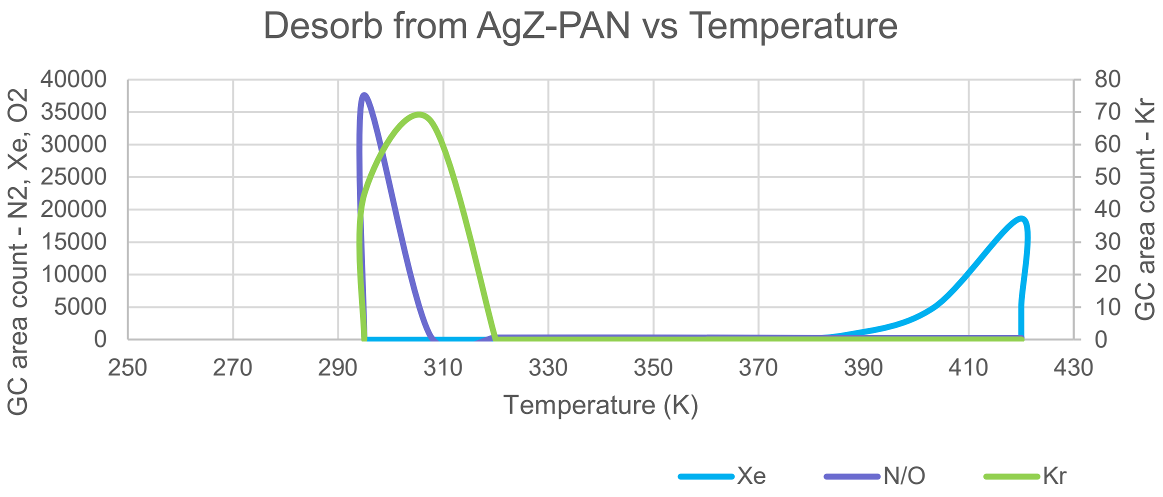
Separation Results – Sub-zero Xe Capture



Desorption Studies

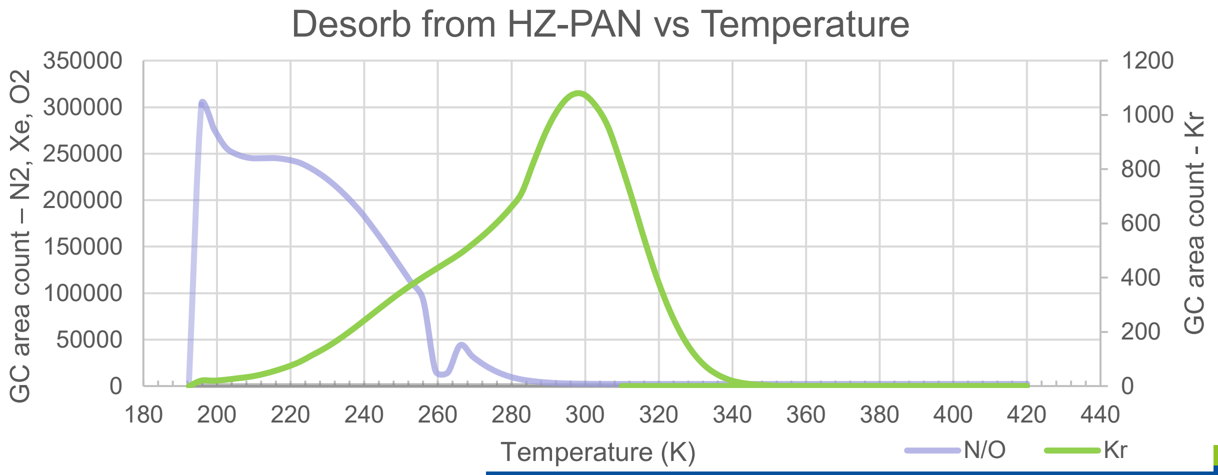
AgZ-PAN

- Adsorbed phase contains Xe, Kr and air
- Desorption requires purge gas (He)
- 99-100% Xe separation



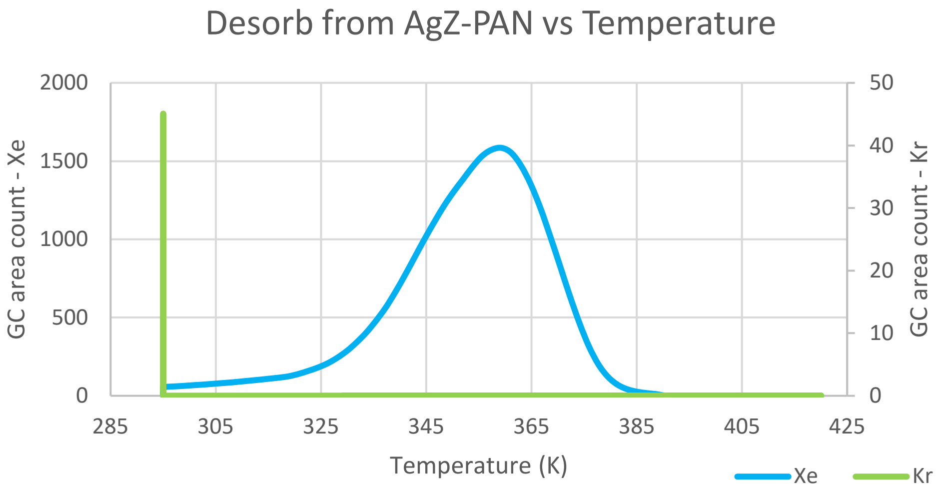
HZ-PAN

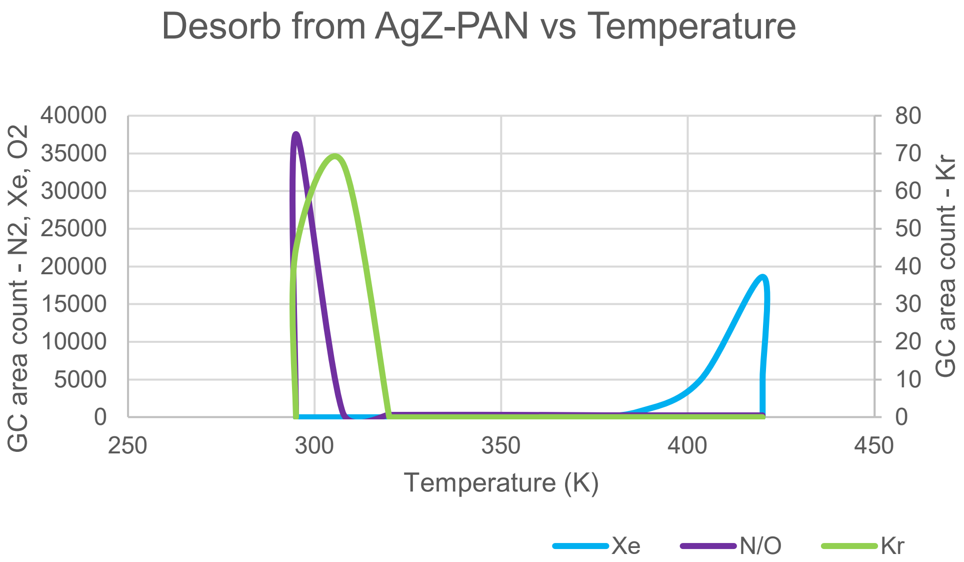
- Adsorbed phase contains Kr and air
- Desorption requires purge gas (He)
- ~80% Kr separation
- 3.5 to 5 times Kr concentration



AgZ-PAN Desorption

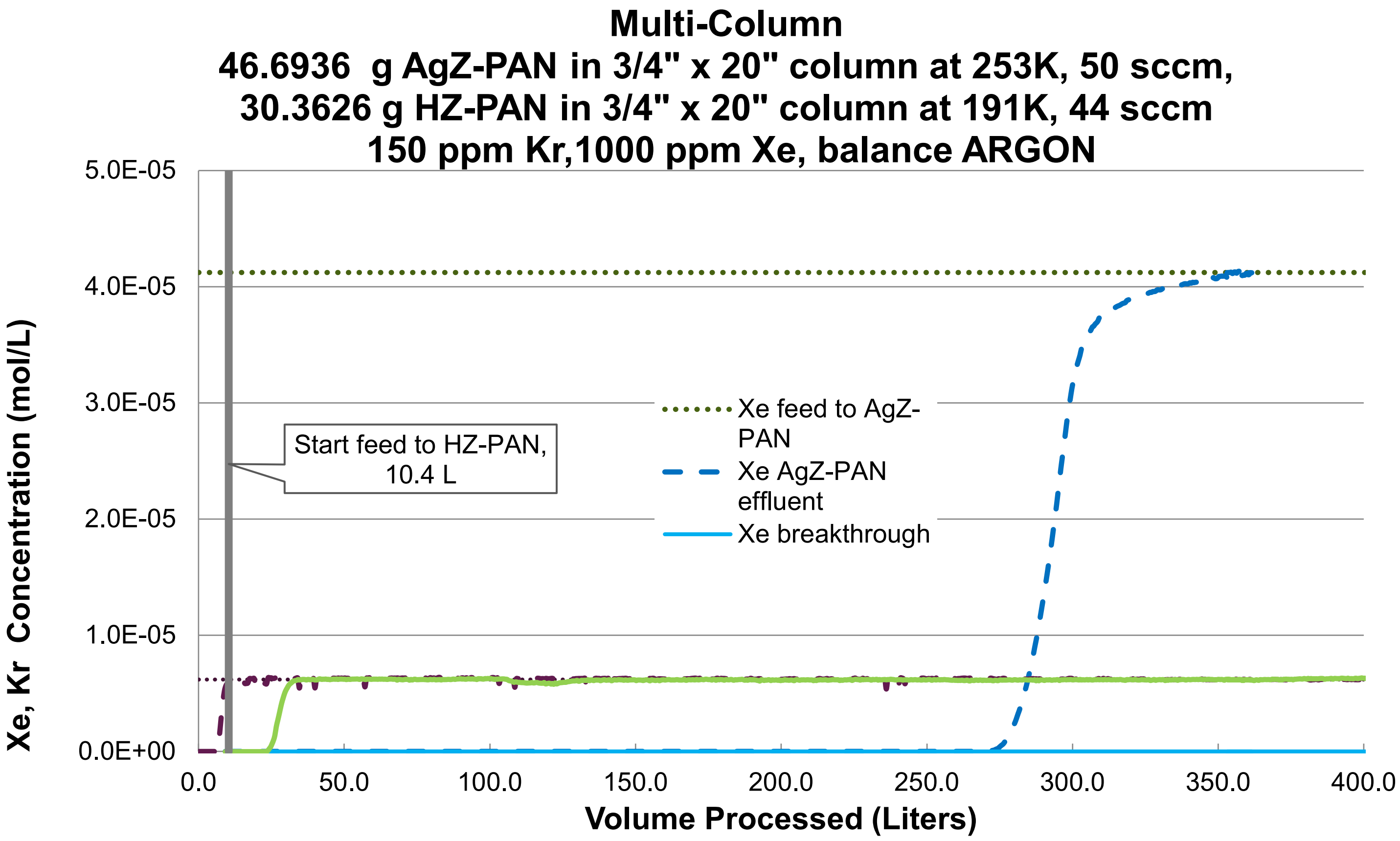
- Xe/Kr separation
- Ambient temperature adsorption
- Adsorbed phase contains Xe, Kr, and air
- Desorption requires purge gas (air, N_2, Ar, or He)
- Slowly ramp to temperature over 12 hours
- Step temperature and soak 6 hours at max temp.
- 99–100% Xe separation





Xe/Kr Separation and Capture from Argon

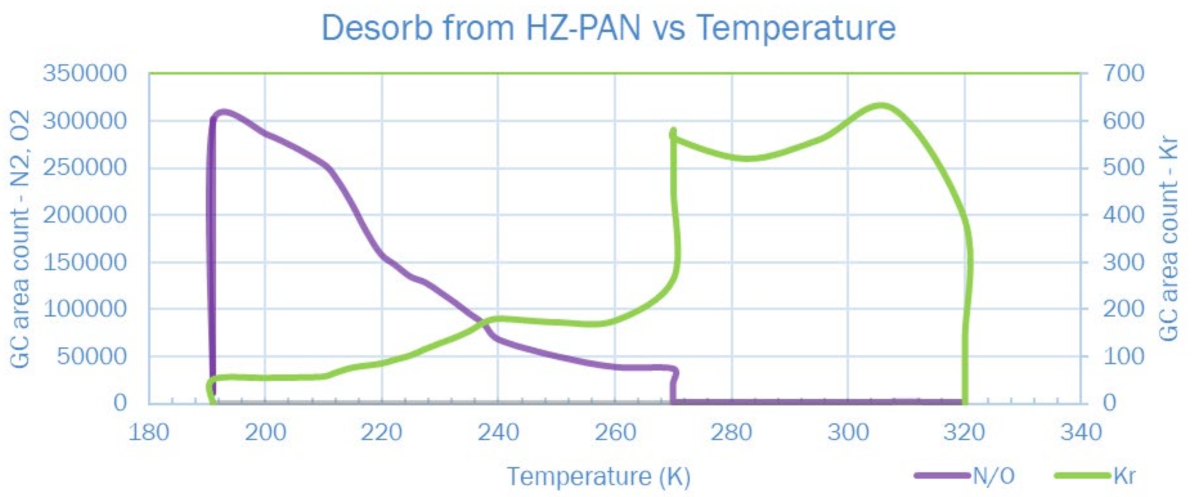
- **Applications**
  - **Advanced molten salt reactors**
  - **Pyroprocessing**



- **1st Argon Study Results**
  - **264 mmol Xe/Kg AgZ**
  - **6L processed/g AgZ to Xe breakthrough**

HZ-PAN Preliminary Concentration Study

- Kr concentration with HZ-PAN
  - Goal to increase purity of Kr product
    - Investigate multiple cycles of adsorption/desorption
    - Increasing Kr feed concentration each cycle
    - Determine maximum purity achievable with HZ-PAN
  - Testing conditions
    - Adsorption temperature -82°C
    - 27 grams HZ-PAN
    - 50 cm column length
    - Various concentrations of Kr in air
    - Feed flow 100 sccm

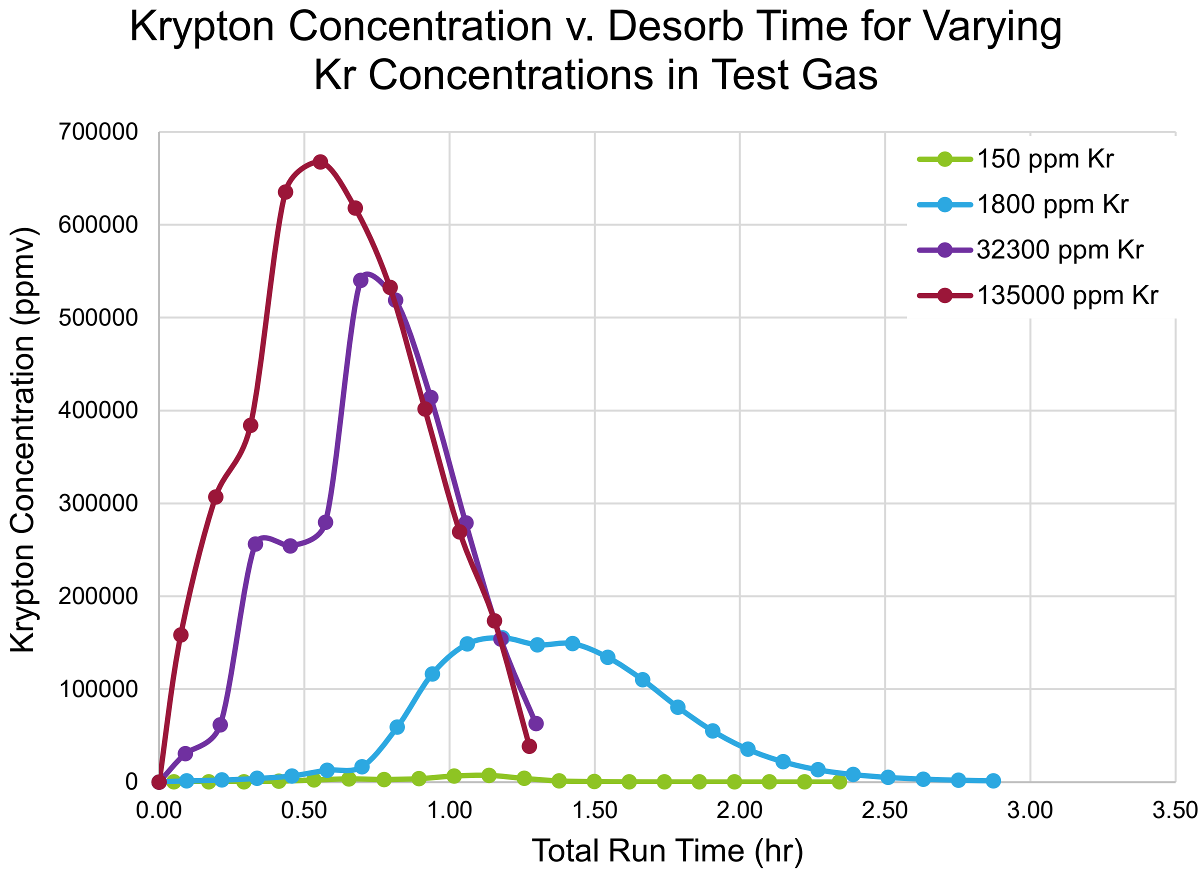


Kr Concentration Study Results

Concentration factors achieved from starting Kr feed gas concentration

Kr Feed Gas Concentration (ppmv)	Average Kr Concentration during Desorption (ppmv)	Stage Concentration	Total Concentration
150	1.187×10^{3}	8	8
1,800	2.592×10^{4}	14	173
32,300	1.347×10^{5}	4.1	898
135,000	3.745×10^{5}	2.8	2497

Kr Concentration Study



Peak Kr concentrations and their respective times for varying Kr feed gas concentration

Kr Feed Gas Concentration (ppmv)	Time of Kr Peak (hours)	Kr Peak Concentration (ppmv)
150	1.14	7.12×10^3
1800	1.18	1.55×10^5
32300	0.69	5.40×10^5
135000	0.55	6.68×10^5

Work for Others

- **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.
- **TDA Research Inc. (for NASA)**
  - Testing of sorbents for Nuclear Thermal Propulsion (ground testing)
- **Licensed patent with Global Phosphate Solutions**
  - “Phosphate Sponge”
  - Received R&D100 Special Recognition Green Tech Award
- Mainstream Engineerning (for Arpa·e)
  - Applied MOF testing for Kr/Xe separation and capture

Continued Research

- Xe concentration studies
- Kr concentration verification
- Cost analysis
- Pilot studies

Idaho National Laboratory

Battelle Energy Alliance manages INL for the U.S. Department of Energy's Office of Nuclear Energy. INL is the nation's center for nuclear energy research and development, and also performs research in each of DOE's strategic goal areas: energy, national security, science and the environment.