

# ***Multi-Column Xe/Kr Separation with AgZ- PAN and HZ-PAN***

**Fuel Cycle Technology**

*Prepared for  
U.S. Department of Energy  
Material Recovery and Waste Form  
Development  
Mitchell Greenhalgh, Troy G. Garn,  
Amy K. Welty and Tony Watson  
Idaho National Laboratory  
August 19, 2016  
FCRD-MRWFD-2016-000046  
INL/EXT-16-39618*





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## SUMMARY

Previous multi-column xenon/krypton separation tests demonstrated the capability of separating xenon from krypton in a mixed gas feed stream. The results of this initial testing with AgZ-PAN and HZ-PAN indicated that an excellent separation of xenon from krypton could be achieved. Building upon these initial results, a series of additional multi-column tests were performed in FY-16. The purpose of this testing was to scale up the sorbent beds, test a different composition of feed gas and attempt to improve the accuracy of the analysis of the individual capture columns' compositions.

Two Stirling coolers were installed in series to perform this testing. The use of the coolers instead of the cryostat provided two desired improvements, 1) removal of the large dilution due to the internal volume of the cryostat adsorption chamber, and 2) ability to increase the sorbent bed size for scale-up. The AgZ-PAN sorbent, due to its xenon selectivity, was loaded in the first column to capture the xenon while allowing the krypton to flow through and be routed to a second column containing the HZ-PAN for capture and analysis. The gases captured on both columns were sampled with evacuated sample bombs and subsequently analyzed via GC-MS for both krypton and xenon.

Preliminary adsorption tests were performed on both sorbents with the feed gas of 400 ppmv Xe and 40 ppmv Kr in a balance of air at the desired temperature and flow rates. Analyses of the results indicated that the krypton column filled with HZ-PAN was the limiting factor for all conditions and the test time could only be 5 hours to avoid any loss of krypton.

Two separation tests were performed utilizing the same feed gas as in the preliminary tests. The AgZ-PAN (Xe column) temperature was held at 295 or 253K while the HZ-PAN (Kr column) was held at 191K for both tests. The effluent from the columns was monitored for xenon and krypton via GC-TCD during the tests. No xenon or krypton was detected exiting the columns during the adsorption phase of either test.

During the desorption phase of each test, gas samples from each column were taken via evacuated sample bombs and were analyzed by GC-MS analysis. Helium purge gas was allowed to flow during the sample bomb collection until the sample bomb reached a desired pressure. Results of these evaluations demonstrated that xenon can be selectively removed from krypton in air at or near room temperature, and that a "xenon free" krypton product can be obtained.

The sample bomb gas collection and analysis procedure again provided inconsistent results even with a flow of purge gas. Analysis was not indicative of relative concentrations of adsorbed gases due to differences in the tenacity with which the sorbents retain xenon versus krypton, once captured. The sample bomb procedure should be refined and made consistent from sample to sample if it is to be used in future tests.

The results of these tests can be used to develop the scope of future testing and analysis using this test bed for demonstrating the capture and separation of xenon and krypton using sorbents, for demonstrating desorption and regeneration of the sorbents, and for determining compositions of the desorbed gases. They indicate a need for future desorption studies in order to better quantify co-adsorbed species and final krypton purity.

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## ACRONYMS

AgZ-PAN	Silver converted mordenite-polyacrylonitrile
HZ-PAN	Hydrogen mordenite-polyacrylonitrile
GC-MS	Gas Chromatograph with Mass Spectrometer
GC-TCD	Gas Chromatograph with Thermal Conductivity Detector
I.D.	Inside diameter
INL	Idaho National Laboratory
K	Kelvin
PPMV	Part per million volume
SCCM	Standard Cubic Centimeters per Minute







# XE/KR SEPARATION WITH AGZ-PAN AND HZ-PAN

## 1. Introduction

In FY-15 a series of multi-column Xe/Kr separation tests were performed to demonstrate the possibility of separating Xe from Kr in a mixed gas feed stream. The results of initial testing of the two column system with AgZ-PAN and HZ-PAN indicate that an excellent separation of Xe from Kr could be attained using the newly installed multi-column system. [1] Building upon these initial results, a series of additional multi-column testing was planned to be performed in FY-16. The purpose of this testing was to scale up the sorbent beds, test a different composition of feed gas and attempt to improve the accuracy of the analysis of the individual capture columns' compositions.

The AgZ-PAN sorbent, due to its Xe selectivity, was loaded in the first column to capture the Xe while allowing the Kr to flow through and be routed to a second column containing the HZ-PAN for capture and analysis. The gases captured on both columns were sampled with evacuated sample bombs and subsequently analyzed via GC-MS for both Kr and Xe. The results indicated that an excellent separation of Xe from Kr could be attained using the newly installed multi-column system.

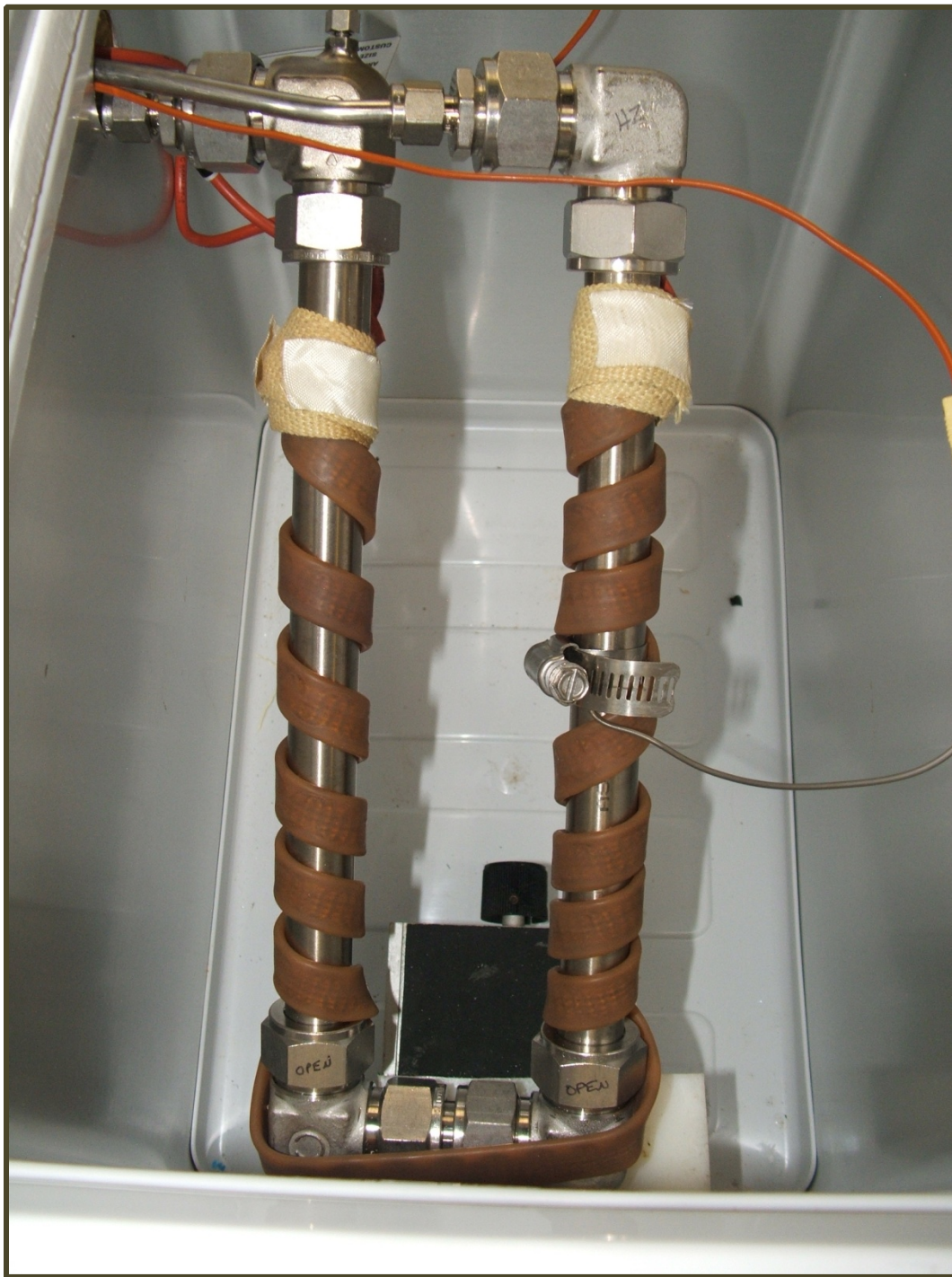
## 2. Two Column Test Bed Design

Two Stirling coolers (SC#1 and SC#2) installed in series were utilized to perform this testing. The use of the coolers instead of the cryostat provided two desired improvements, 1) removal of the large dilution due to the internal volume of the cryostat adsorption chamber, and 2) ability to increase the sorbent bed size for scale-up. The specifications of both coolers can be found in Table 1.

**Table 1. Cooling apparatus specifications.**

Make/model	Stirling Ultra Low Temperature Cooler/ShuttleC ULT:25N
Cooling temperature range	-86°C to 20°C @ 32°C (90°F) ambient, uniformity $\pm 0.75^\circ\text{C}$
Specifications	Ambient operating temperature +5°C to +35°C (41°F to 95°F)
	Chamber dimensions: 33 cm x 23 cm x 28 cm
	Refrigerant, R-508B non-flammable CFC/HCFC-Free
	Cooling engine- Humm helium charge free-piston Stirling engine with continuous modulation
	Electrical Power 120V AC or 12V DC from mobile source

Sorbent columns for both Xe and Kr beds were made of two interconnected 1.65 cm I.D. x 25.4 cm long sections of stainless steel tubing. Each of the columns had a thermocouple inserted into the center of the column to monitor internal bed temperature. The as-built columns for each bed were identical and a picture of the Kr column wrapped with heat tape and inserted thermocouples can be seen in Figure 1.



**Figure 1. The newly constructed Kr column.**

A schematic of the multi-column experimental test setup using the two Stirling coolers is shown in Figure 2. This design allows gas flow initiated from the feed gas cylinders to be routed through both columns, through either column or to bypass both columns and flow directly to the GC-TCD. All flow can be routed through the GC-TCD in any valve lineup configuration. Locations for sample bomb connections are also shown in Figure 2.

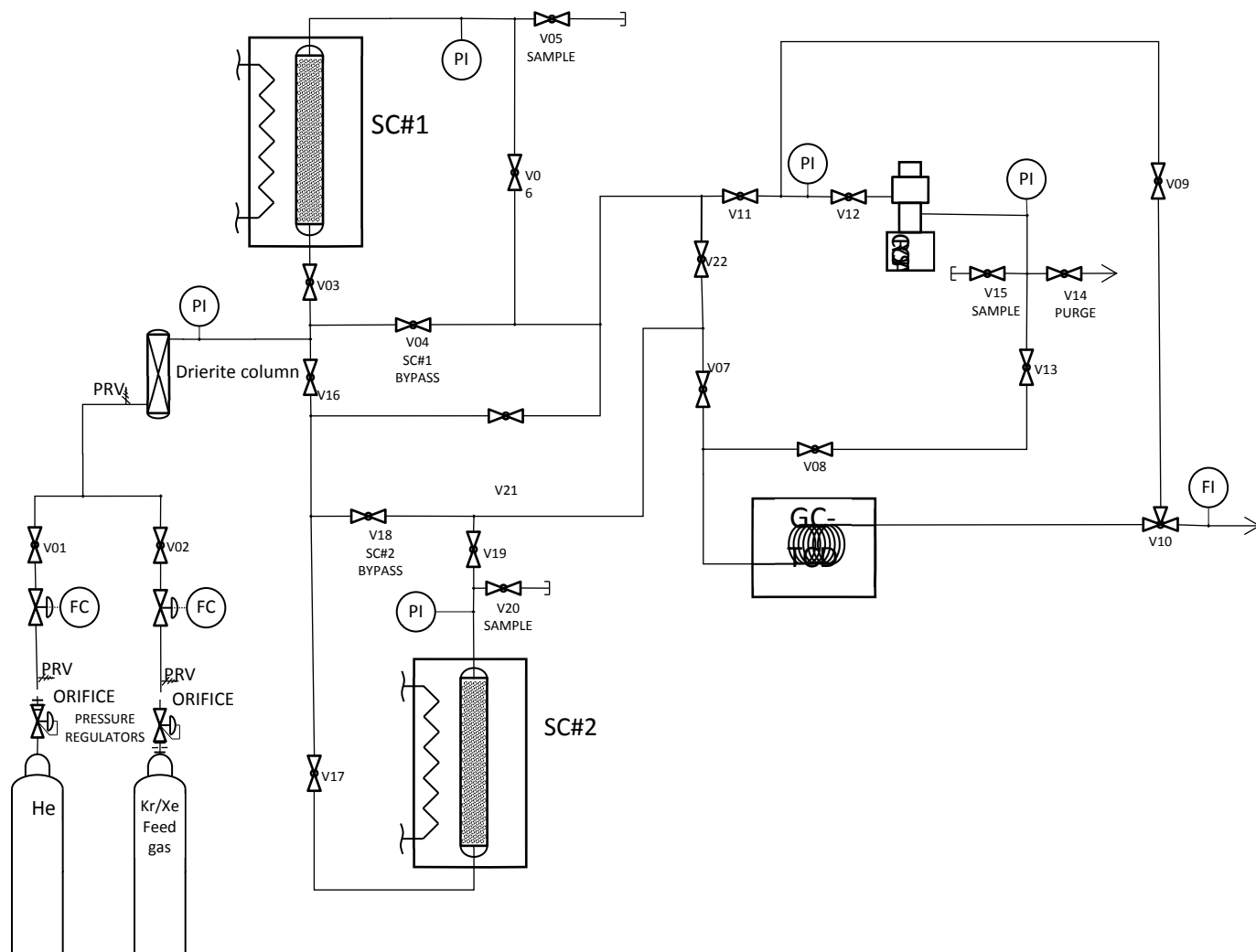


Figure 2. Schematic of the multi-column experimental setup.

### 3. Testing Parameters Determinations

Testing of the columns was performed with the 400 ppmv Xe, 40 ppmv Kr in air balance test gas. Test flowrates were set to 20 sccm resulting in a superficial velocity of 23 cm/min and were not changed throughout the entire testing regime. Xe and Kr capacities of AgZ-PAN and HZ-PAN are well established at higher feed gas concentrations from previous testing. It was expected that the relationship between feed gas concentration and capacities would be approximately linear. To test this assumption and establish capacities at low concentrations, three tests were conducted. All three were conducted in columns 0.77 cm I.D. x 25.4 cm long, wrapped with heat tape and installed in a Stirling Cooler. Results are tabulated in Table 2.

**Table 2: Sorbent Capacity Tests with 400 ppm Xe, 40 ppm Kr in air**

	AgZ-PAN tests		HZ-PAN test
Sorbent (g)	5.215	5.215	3.5563
Temperature (K)	295	295	220
Xe capacity mmol/kg	27.9	33.2	120.3
Kr capacity mmol/kg	0.07	0.13	0.64

Capacities were determined, as reported previously, by plotting breakthrough curve data over time and using TableCurve software to select best fit equations for determination of area under the curve then subtracting this value from the total moles of sorbate processed[2]. After each test, desorption of the sorbent was performed at 420K with He flow at 20 sccm until no Xe or Kr was present as determined by GC-TCD analysis.

These capacity measurements and breakthrough times were utilized to determine the operating conditions that would be used for the multi-column testing. In all cases, while Xe capacities were about half that previously observed in more concentrated feed gas (1000 ppmv Xe, 150 ppmv Kr in air), Kr capacities were lower by a factor of five. This may have partially been an issue with instrument sensitivity at such low Kr concentrations. Regardless, Kr was the limiting factor for the multi-column testing.

One additional test was performed to determine precisely the available test time before initial Kr breakthrough. The large columns constructed for the multi-column test were prepared for testing, with the Xe-capture columns filled with 44.8 g AgZ-PAN and the Kr-capture column filled with 29.8 g HZ-PAN. With the Xe-capture column at ambient temperature (~296K) and the Kr-capture column at 191K, the test feed gas was fed at 50 sccm through the Xe-capture column followed by the Kr-capture column and allowed to run for 24 hours. Initial Kr breakthrough occurred after five hours, with full breakthrough at ten hours. No Xe breakthrough occurred during the test period. To ensure maximum testing time with minimal Kr loss, five hours was chosen for test time for multi-column testing.

## 4. Xe/Kr Separation

In order to demonstrate the separation of Xe from Kr utilizing the newly installed multi-column test system, two adsorption tests were performed using a feed gas of 400 ppmv Xe, 40 ppmv Kr with a balance of air flowing at 50 sccm. The Xe column placed in SC#1 contained 44.8 grams of AgZ-PAN (2.4 times more than previously tested) and its adsorption temperature was maintained at either 295 or 253K. The gas exiting this column flowed to the Kr column in SC#2 for Kr capture. The Kr column contained 29.8 grams of HZ-PAN sorbent (6.7 times more than previously tested) and its adsorption temperature was maintained at 192K to capture all of the Kr passing through the first column. The gas exiting the Kr column was subsequently analyzed for Xe and Kr via GC-TCD and then vented to atmosphere. Samples of each column were taken utilizing evacuated sample bombs and were analyzed for Xe and Kr via GC-MS. A picture of the sample bombs utilized in this testing can be seen in Figure 3.





Figure 3. Sample bombs used in testing.

#### 4.1 Xe Column 295K Test

A separation test was performed with the multi-column system by maintaining the Xe column at 295K and the Kr column at 192K. After 310 minutes of operation, both columns were isolated and heated to 420K and allowed to soak at this temperature for 2 hours. Pressure on the Xe column increased from 0 psig to 5.0 psig. Pressure on the Kr column increased from 0 psig to 2.5 psig. A plot of both columns' effluents monitored by GC-TCD during the test can be seen in Figure 4. The dashed lines represent the concentration at 100% breakthrough and the solid lines are the actual concentrations. It can be seen that neither Xe for the Xe-column, nor Kr for the Kr-column was detected in the column effluent during the course of the test.

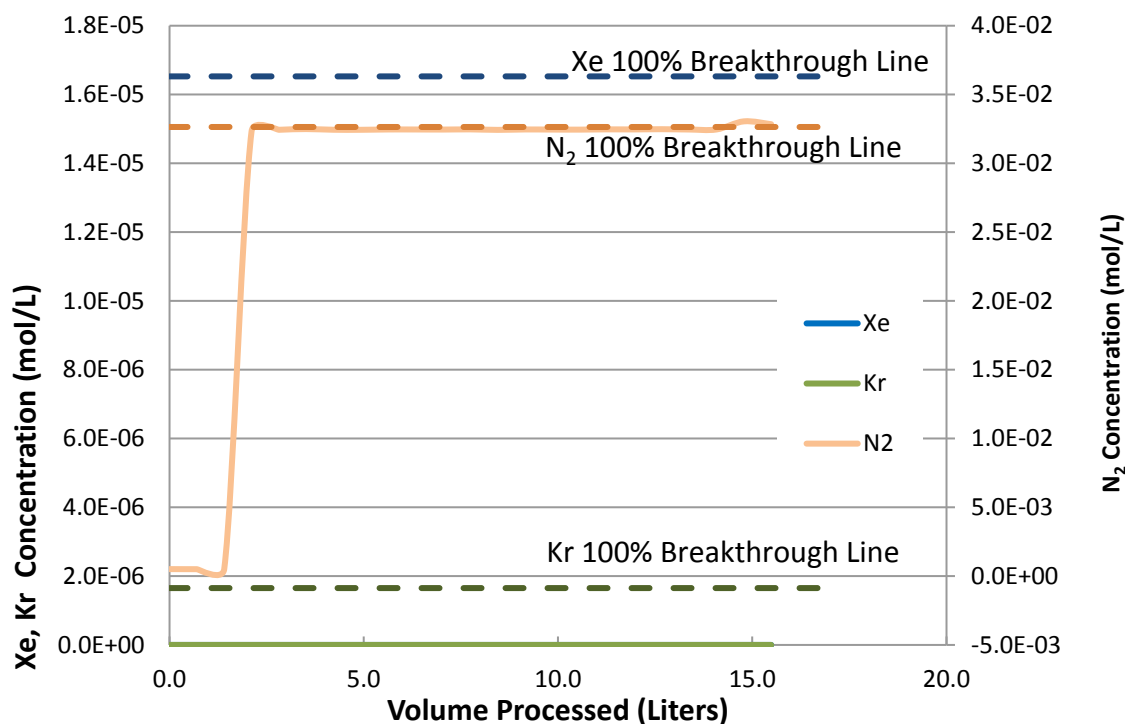


Figure 4. Plot of column effluent during the 298K test

A 46 mL sample bomb evacuated to 25 inches of Hg was connected to the Xe column in SC#1. The valve was opened and He was allowed to flow until the pressure on the sample bomb reached 7.0 psig. The sample valve was closed and the sample bomb was removed from the system. After taking the Xe column sample, the column was desorbed by flowing He at 50 sccm while maintaining the column temperature at 420K. On-line GC-TCD analysis of this desorption process indicated that nearly all of the Xe remained on the sorbent during the sampling phase.

A 44 mL sample bomb evacuated to 24 inches of Hg was connected to the Kr column in SC#2. The sample valve was opened and He was allowed to flow until the pressure on the sample bomb reached 5.5 psig. The sample valve was closed and the sample bomb was removed from the system. Analyses for both Xe and Kr were performed with the GC-MS for both the Xe column and the Kr column samples and the results are reported in Table 3.

Table 3. GC-MS Kr and Xe multi-column results at 295K.

Column Sample	Xe (ppm)	Kr (ppm)
Xe Column	41.3	81.2
Kr Column	BDL*	367

\*Below Detection Limits

These results demonstrate the separation of Xe from Kr was achieved and no Xe was detected in the Kr column sample. From a material balance perspective, only about 4% of the Kr introduced into the system was accounted for in the Kr column sample. This was largely due to the small size of the sample bomb used, compared to the relatively large columns. The remainder of the Kr fed to the columns during the adsorption phase of this test was accounted for after the sample bomb was removed from the system and



the columns were regenerated with He flow along with GC-TCD analysis. The low Xe concentration for the Xe column sample again confirmed that removal of Xe from the AgZ-PAN was ineffective even with helium flow at 420K using the sample bomb technique.

## 4.2 Xe Column 253K Test

Another separation test was performed with the multi-column system by maintaining the Xe column at 253K and the Kr column at 192K. After 296 minutes of operation, both columns were isolated and heated to 420K and allowed to soak at this temperature for 2 hours. Pressure on the Xe column increased from 0 psig to 2.0 psig. Pressure on the Kr column increased from 0 psig to 1.0 psig. A plot of both columns' effluents monitored by GC-TCD during the test can be seen in Figure 5. The dashed lines represent the concentration at 100% breakthrough and the solid lines are the actual concentrations. It can be seen that neither Xe for the Xe-column, nor Kr for the Kr-column was detected in the column effluent during the course of the test.

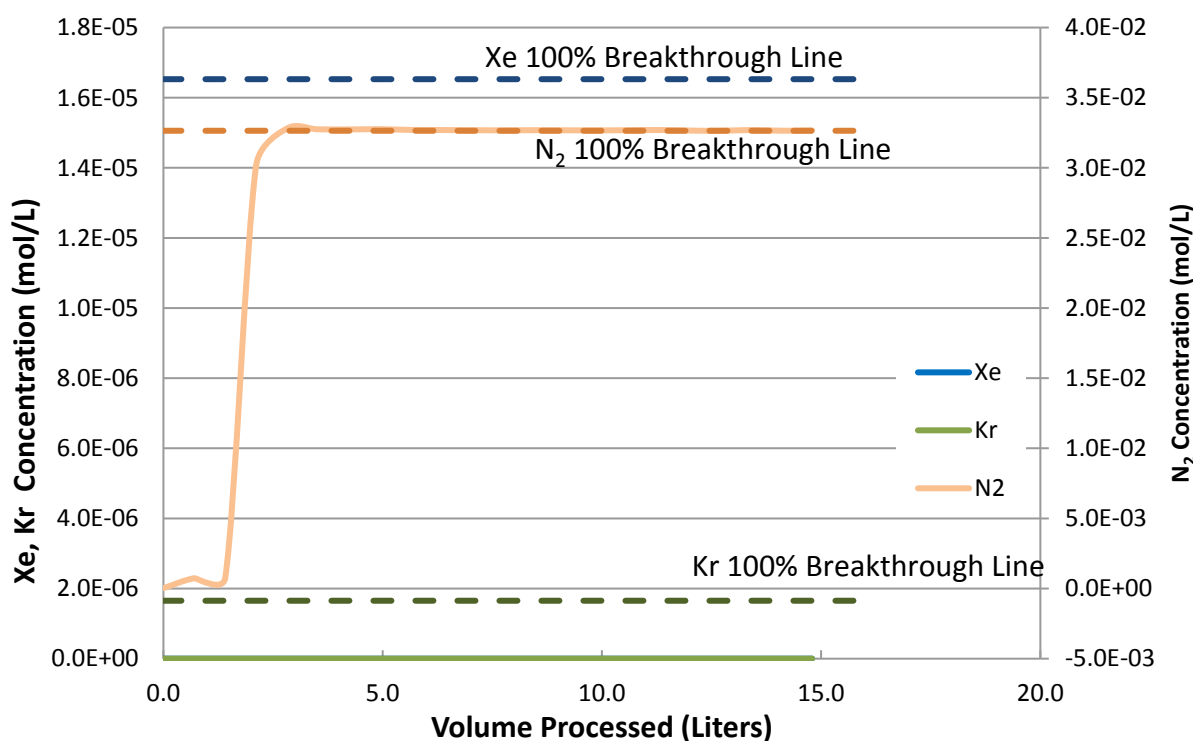


Figure 5. Plot of column effluent during the 253K test

A 250 mL sample bomb evacuated to 22 inches of Hg was connected to the Xe column in SC#1. The valve was opened and He was allowed to flow until the pressure on the sample bomb reached 7.0 psig. The sample valve was closed and the sample bomb was removed from the system. After taking the Xe column sample, the column was desorbed by flowing He at 50 sccm while maintaining the column

temperature at 420K. On-line GC-TCD analysis of this desorption process indicated that nearly all of the Xe remained on the sorbent during the sampling phase.

A 250 mL sample bomb evacuated to 24 inches of Hg was connected to the Kr column in SC#2. The sample valve was opened and He was allowed to flow until the pressure on the sample bomb reached 5.4 psig. The sample valve was closed and the sample bomb was removed from the system. Analyses for both Xe and Kr were performed on the GC-MS analyzer for both the Xe column and the Kr column samples. The GC-MS results from this test are presented in Table 4.

**Table 4. GC-MS Kr and Xe multi-column results at 253K.**

Column Sample	Average Xe (ppm)	Average Kr (ppm)
Xe Column	25.6	179
Kr Column	BDL*	586

\*Below Detection Limits

These results demonstrate the separation of Xe from Kr was achieved and there was no detectable Xe in the Kr column sample. A larger sample bomb was used for this test, resulting in a larger portion of the total Kr accounted for in the sample bomb. Approximately 41% of the Kr introduced into the system was accounted for in the Kr column sample bomb, with much of the remaining Kr accounted for with GC-TCD analysis during column desorption after sampling. Overall, 82% of the Kr was accounted for. The discrepancy between the Kr fed and the Kr recovered is likely due to the timing of the first GC sample. Again, the low Xe concentration for the Xe column sample along with the desorption data, revealed that removal of Xe from the AgZ-PAN was ineffective even with He flow at 420K.

## 5. Conclusions

A second Stirling cooling apparatus was added to the existing experimental test setup in order to remove the large dilution due to the internal volume of the cryostat adsorption chamber and increase the sorbent bed size for scale-up.

Preliminary adsorption tests were performed on both sorbents with a feed gas of 400 ppmv Xe and 40 ppmv Kr in a balance of air at the desired temperature and flow rates. These tests were only run to initial breakthrough in order to determine the testing times to ensure an acceptable xenon/krypton separation.

Multi-column Xe/Kr separation tests were performed to demonstrate the separation of Xe from Kr in a mixed gas feed stream. The results of the testing indicated that an excellent separation of Xe from Kr was achieved. There was no detectable xenon found in the Kr column samples. Additional testing of the multi-column system will help elucidate the optimal parameters for this separation for sorbent masses tested. The 420K desorption of captured Xe from the AgZ-PAN sorbent was ineffective even in the presence of He flow. Heat, He flow and vacuum alone did not provide adequate motivation to “push” the Xe off the sorbent.

The sample bomb gas collection and analysis procedure again provided inconsistent results even with a flow of He purge gas. The sample bomb procedure should be refined and made consistent from sample to sample if it is to be used in future tests. Fortunately, periodic sampling with GC-TCD continues to be a reliable method for determining overall material balance in the system and is expected to provide good data for ongoing testing.

## 6. Future Work

The adsorption cycle for capture of Xe and Kr has been proven effective. However, a data gap exists in regard to the desorption cycle. In order to move toward operability and optimization of a Xe/Kr capture and separation system, desorption of Kr and Xe, along with co-absorbed species needs to be quantified to determine purity of the final Kr stream and attempt to optimize the entire process. Ongoing testing of sorbents should include desorption studies to determine temperature at which the cleanest separation between Kr and co-adsorbed species occurs, as well as the maximum purity of the final Kr product stream.

## 7. References

1. Greenhalgh, M., Garn, T.G., Welty, A.K., Lyon, K., Watson, T., “Multi-Column Experimental Test Bed for Xe/Kr Separation”, FCRD-MRWFD-2015-000047, August 31, 2015.
2. Garn, T.G., Greenhalgh, M., Law, J.D., “FY-12 INL Krypton Capture Activities Supporting the Off-Gas Sigma Team”, FCR&D-SWF-2012-000252, August 30, 2012.