Multi-Column Experimental Test Bed for Xe/Kr Separation

Fuel Cycle Technology

SUMMARY

Previous research studies have shown that INL-developed engineered form sorbents are capable of capturing both xenon and krypton from various composite gas streams. The existing experimental test bed provided the capability of single column testing for capacity evaluations over a broad temperature range. To advance research capabilities, the employment of an additional column to study selective capture of target species to provide a defined final gas composition for waste storage was warranted. The second column addition also allows for compositional analyses of the final gas products to provide for final storage determinations.

The INL krypton capture system was modified by adding an additional adsorption column to create a multi-column test bed. The purpose of this modification was to allow for the investigation of the separation of xenon from krypton supplied as a mixed gas feed. An extra (upstream) column was placed in a Stirling Ultra-low Temperature Cooler, capable of controlling temperatures between 190 and 253K and the column was filled with AgZ-PAN sorbent to capture the xenon from the feed gas. The effluent from this column would then be routed to the column in the cryostat filled with HZ-PAN to capture the krypton. Additional piping and valves were incorporated into the system to allow for a variety of flow path configurations.

A limited scope of testing was performed to evaluate the performance of this updated test bed and to determine xenon and krypton separation, adsorption selectivity, desorption, and final concentrations in the desorbed gas streams. Sampling and analysis methods used in these tests included on-line GC-TCD analysis of the AgZ-PAN column outlet gas for xenon and krypton, as has been used in prior tests, and the addition of GC-MS evaluation of evacuated sample bombs. The sample bombs were analyzed after each test completion to measure xenon and krypton desorption from the columns as they were heated to above room temperature, with no purge gas flow.

Two separation tests were performed utilizing a feed gas consisting of 1000 ppmv xenon and 150 ppmv krypton with the balance made up of air. The AgZ-PAN column temperature was held at 295 or 253K while the HZ-PAN column was held at 191K for both tests. The effluent from the AgZ-PAN column was monitored for xenon and krypton via GC-TCD during the tests. No xenon was detected exiting the AgZ-PAN column 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. No purge gas flowed during the sample bomb collection; the sample collection relied only on the evacuated bombs that drew gas from the sorbent beds when the connecting valve was opened.

Results of these evaluations verified that the system operated as designed and demonstrated that AgZ-PAN exhibits excellent selectivity for xenon over krypton in air at or near room temperature, and that krypton with only small amounts of xenon was captured in the HZ-PAN column at 191K. The ability to separate xenon from krypton from a mixed gas feed was demonstrated utilizing the new multi-column system.

The sample bomb gas collection and analysis procedure provided inconsistent results, although it does indicate that effective xenon and krypton desorption from the sorbents requires not only temperature or pressure-swing operation but also a flow of purge gas, which is to be expected based on adsorption isotherm theory. 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 initial 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.

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FIGURES

TABLES

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
$SEL_{Xe/Kr}$	Selectivity of Xe over Kr

MULTI-COLUMN EXPERIMENTAL TEST BED FOR XE/KR SEPARATION

1.   Introduction

Research activities performed at INL supporting the Off-Gas Sigma Team have demonstrated that a hydrogen mordenite-polyacrylonitrile (HZ-PAN) engineered form sorbent can be used to effectively capture Kr at reduced temperatures (~ 190K) and a silver converted mordenite-polyacrylonitrile (AgZ-PAN) engineered form sorbent has shown a high selectivity for Xe over Kr at or near room temperature (295 to 220K)[1]. Building upon this information, a second cooler and column were added to the existing test setup establishing a multi-column test bed to allow for concurrent testing of the two engineered forms, as well as other sorbents developed by the sigma team, at varying temperatures. This new system was used to verify the ability to selectively separate Xe from Kr and ultimately capture the effluent Kr for final composition determination in the final Kr product stream.

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

The first challenge driving design modification decisions was the need to control the Xe column (AgZ-PAN) temperature for adsorption (i.e., cooling) and desorption (i.e., heating). This challenge was met by adding a cooling apparatus capable of housing a column and tightly controlling the temperature down to a minimum of 220K in conjunction with the addition of heat tape around the column for heating the column enough to desorb the captured constituents.[2] Specifications of the new cooling apparatus are 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 ± 0.75°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

The Xe column was sized to contain enough sorbent to run for a sufficient amount of time to provide measurable Kr concentrations to the Kr column (HZ-PAN) but small enough to fit inside the cooling apparatus. The column sizing design utilized Xe breakthrough data with AgZ-PAN from previous testing at room temperature (i.e., lowest capacities measured).[1] The final dimensions of the stainless steel Xe

column were 1.65 cm I.D. x 22.9 cm long. This ~50 cm^3 volume holds roughly 20 grams of the AgZ-PAN material with a bulk density of ~0.4 g/cm^3. Three thermowells were welded into the column to allow for thermocouple insertion to monitor internal sorbent temperature. The as-built Xe column wrapped with heat tape and inserted thermocouples can be seen in Figure 1.
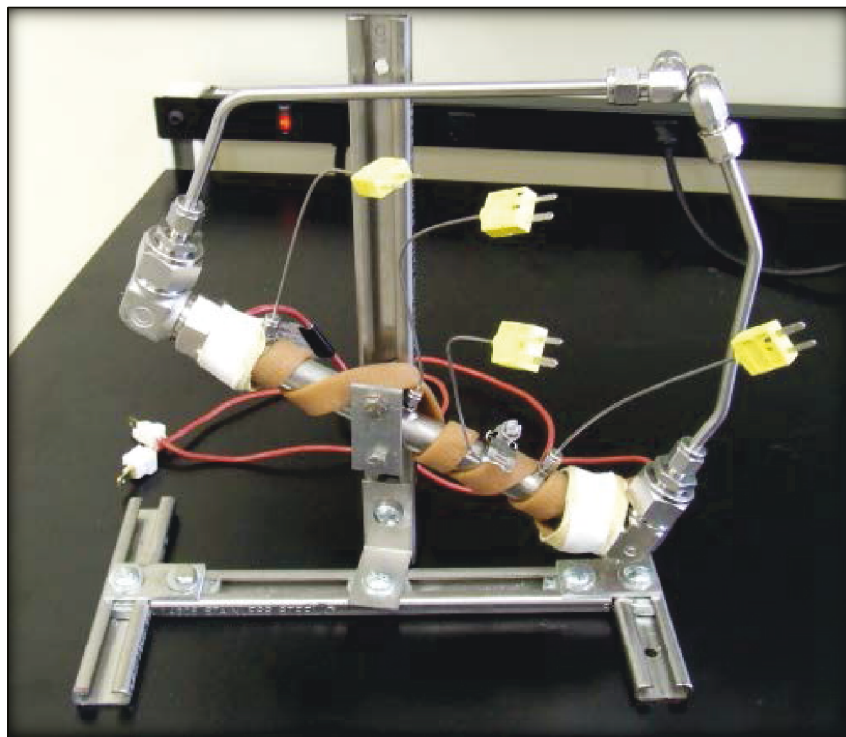
Figure 1. The newly constructed Xe column.

In order to determine product stream compositions, sample ports were added to the modified system to allow the connection of evacuated gas sample bombs. A Shimadzu GC-MS 2010 gas analyzer was utilized to determine the Kr and Xe concentrations for each sample. A schematic of the multi-column experimental test setup 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.
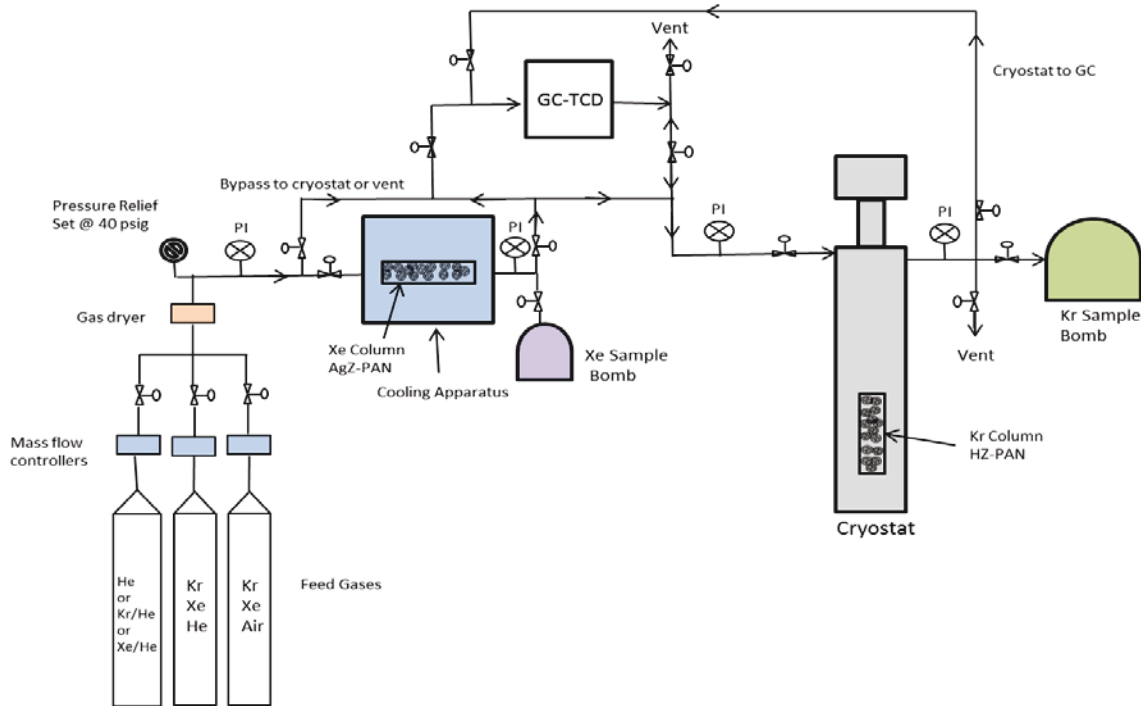
Figure 2. Schematic of the multi-column experimental setup.

3.   Selectivity Testing

Testing of the Xe column in the new Stirling cooler was performed with the 1000 ppmv Xe, 150 ppmv Kr in He balance test gas. Test flowrates were set to 50 sccm resulting in a superficial velocity of 23 cm/min and were not changed throughout the entire test regime. Three tests were performed at 295, 250 and 220K temperatures. 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.[1] This procedure was repeated using the 1000 ppmv Xe, 150 ppmv Kr in air balance feed gas. After each test, desorption of the sorbent was performed at 370K with He only flow at 50 sccm until no Xe or Kr was present as determined by GC analysis.

Using the calculated Xe and Kr capacities and feed gas concentrations, the Xe/Kr selectivity of the AgZ-PAN sorbent for all test conditions was determined by equation (1).

$$\text{Sel}_{\text{Xe,Kr}} = \frac{X_{\text{Xe}}/Y_{\text{Xe}}}{X_{Kr}/Y_{Kr}} \qquad (1)$$

Where X_{Xe} and X_{Kr} are mole fractions of Xe and Kr in the adsorbed phase (capacities), and Y_{Xe} and Y_{Kr} are mole fractions of Xe and Kr in the bulk phase (feed gas concentrations). The selectivity of Xe over Kr for both feed gas compositions at 295, 250 and 220K are reported in Table 2.[3]

Table 2. Selectivity of Xe over Kr for AgZ-PAN

Gas Composition	Temperature (K)	Xe capacity (mmol/kg)	Kr capacity (mmol/kg)	Selectivity (Xe/Kr)
1000 ppmv Xe, 150 ppmv Kr in He balance	295	19.2	0.04	72
	250	128	0.56	34
	220	443	3.04	22
1000 ppmv Xe, 150 ppmv Kr in air balance	295	13.7	0.06	35
	250	84.9	0.43	30
	220	254	1.36	29

Overall, the selectivity for Xe over Kr using test conditions from 220 to 295K is 22-35. The high selectivity (72) at 295K with the He gas balance is simply an artifact of a low Kr capacity calculated which was used in the selectivity equation.

These selectivities and capacity measurements were utilized to determine the operating conditions that would be used for the multi-column testing to demonstrate the separation of Xe from Kr and to obtain the optimum Kr composition captured on the HZ-PAN. A graph depicting breakthrough curves generated from selectivity testing is shown below in Figure 3 to provide an example of actual Kr and Xe breakthrough times for use in determining multi-column test run times.
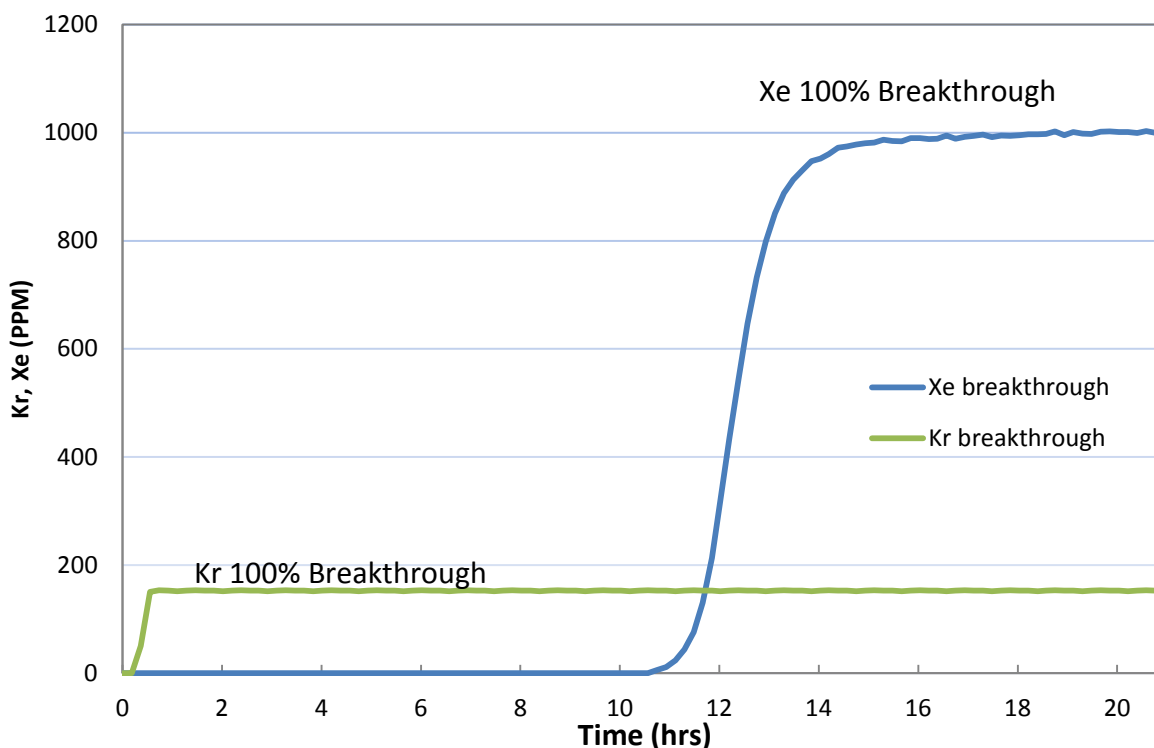

Figure 3. Breakthrough Curves for Kr and Xe at 253K

In the case of selectivity testing at 253K, the two column test could run for nearly 11 hrs before Xe begins to break through the Xe column and contaminating the Kr rich stream being fed to the Kr column. This rational for selecting test runtimes was used for the 295 and 253K testing performed.

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 1000 ppmv Xe, 150 ppmv Kr with a balance of air flowing at 50 sccm. The Xe column contained 18.3 grams of AgZ-PAN and its adsorption temperature was maintained at either 295 or 253K. The gas exiting this column was analyzed for Xe and Kr using the GC-TCD and subsequently flowed to the Kr column in the cryostat for Kr capture. The cryostat contained 4.45 grams of HZ-PAN sorbent 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 vented to atmosphere and was not analyzed for these tests. 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 4.

Figure 4. 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. Previous selectivity tests at 295K showed that Xe does not start to break through the AgZ-PAN until 1.8 hours of feed gas flow but the Kr breaks through in less than 15 minutes under these conditions. Based on this information, a conservative test time of 55 minutes was chosen to minimize the amount of Xe that would end up on the Kr column. After 55 minutes of operation, both columns were isolated and heated to 320K. Pressure on the Xe column increased from 0 psig to 1.5 psig and the pressure in the Kr column increased from 0 psig to 12.5 psig.

A 125 mL sample bomb evacuated to 22 inches of Hg was connected to the Xe column and the valve was opened. The vacuum on the sample bomb decreased to 17 inches of Hg during this time. 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 320K. 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 2 liter sample bomb evacuated to 27 inches of Hg was connected to the Kr column and the sample valve was opened. The vacuum on the sample bomb decreased to 10 inches of Hg during this time. 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	52.0	70.3
Kr Column	1.1	50

These results demonstrate the separation of Xe from Kr can be achieved; however, they also show a small amount of Xe was detected in the Kr column sample indicating some of the Xe from the Xe column was not adsorbed under these conditions. Approximately 70% of the Kr introduced into the system was accounted for in the Kr column sample. The low Xe concentration for the Xe column sample confirmed that removal of Xe from the AgZ-PAN was ineffective without helium flow, even at 320K 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. Previous selectivity tests at 253K showed that Xe does not start to break through the AgZ-PAN until approximately 10 hours of feed gas flow. Kr at 191K with this feed gas and sorbent mass will begin to breakthrough at 2 hours of feed gas flow. Based on this information, a conservative test time of 105 minutes was chosen to minimize the amount of Kr that would be lost from the Kr column. At 105 minutes into the test, both columns were isolated and heated to 320K.

A 125 mL sample bomb evacuated to 12 inches of Hg was connected to the Xe column and opened immediately as the column began to heat. Once this column's temperature reached 320K, the pressure on the sample bomb indicated 0 psig and the sample valve was closed. After taking the Xe column sample, the column was desorbed by flowing He at 50 sccm while maintaining the column temperature at 320K. On-line GC-TCD analysis of this desorption process indicated that all of the Xe remained on the sorbent during the sampling phase.

A 250 mL sample bomb evacuated to 26 inches of Hg was connected to the Kr column but the valve was not opened immediately. The valve on this sample was not opened until the column reached a temperature of 320K and the pressure had stabilized to 12.5 psig in the Kr column. At this point, the sample valve was opened and remained open until the pressure equalized to 7.5 psig on the sample bomb. The valve was then closed on the sample bomb and it 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	BDL	91.0
Kr Column	BDL	273

These results demonstrate the separation of Xe from Kr was achieved and there was no detectable Xe in the Kr column sample. Approximately 84% of the Kr introduced into the system was accounted for in the Kr column sample. The non-detectable Xe concentration for the Xe column sample along with the desorption data, again revealed that removal of Xe from the AgZ-PAN was ineffective without He flow, even at 320K.

5.   Conclusions

A second cooling apparatus was installed in the existing experimental test setup to provide an avenue for multi-column testing including the ability for independent column temperature control. The performance of selectivity testing provided the additional opportunity to test the operability of the cooler. The cooler operated with tight temperature control and provided for thermal desorption operations with no unintended consequences.

Selectivity experiments were performed at test temperatures of 295, 250 and 220K with two feed gas compositions of 1000 ppmv Xe, 150 ppmv Kr in a balance of He or air. The AgZ-PAN sorbent selectivity was calculated using Xe and Kr capacity determinations and feed gas concentrations. Results of this testing were used to determine the operating parameters for the multi-column testing.

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. Results demonstrate, however, the choice of operational parameters will affect the purity of the Kr product. Additional testing of the multi-column system will help elucidate the optimal parameters for this separation for sorbent masses tested. The 320K desorption of captured Xe from the AgZ-PAN sorbent was ineffective in the absence of He flow. Heat and vacuum alone did not provide adequate motivation to "push" the Xe off the sorbent.

The sample bomb gas collection and analysis procedure provided inconsistent results, although it does indicate that effective xenon and krypton desorption from the sorbents requires not only temperature or pressure-swing operation but also a flow of purge gas, which is to be expected based on adsorption isotherm theory. The sample bomb procedure should be refined and made consistent from sample to sample if it is to be used in future tests.

6.   References

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3. Garn, T.G., Greenhalgh, M., Watson, T., "Xe/Kr Selectivity Measurements using AgZ-PAN at Various Temperatures", FCRD-MRWFD-2015-000586, May 15, 2015.