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Troy G. Garn
Mitchell Greenhalgh
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Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

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Fuel Cycle Technology

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U.S. Department of Energy
Material Recovery and Waste Form Development

Troy G. Garn, Mitchell Greenhalgh and Tony Watson
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SUMMARY

In preparation for planned FY-15 Xe/Kr multi-column testing, a series of experiments were performed to determine the selectivity of Xe over Kr using the silver converted mordenite-polyacrylonitrile (AgZ-PAN) sorbent. Results from these experiments will be used for parameter selection guidelines to define test conditions for Kr gas capture purity evaluations later this year.

The currently configured experimental test bed was modified by installing a new cooling apparatus to permit future multi-column testing with independent column temperature control. The modified test bed will allow for multi-column testing to facilitate a Xe separation followed by a Kr separation using engineered form sorbents.

Selectivity experiments were run at temperatures of 295, 250 and 220 K. Two feed gas compositions of 1000 ppmv Xe, 150 ppmv Kr in either a He or an air balance were used. AgZ-PAN sorbent selectivity was calculated using Xe and Kr capacity determinations.

AgZ-PAN sorbent selectivities for Xe over Kr of 72 were calculated at room temperature (295 K) using the feed gas with a He balance and 34 using the feed gas with an air balance. As the test temperatures were decreased the selectivity of Xe over Kr also decreased due to an increase in both Xe and Kr capacities. At 220 K, the sorbent selectivities for Xe over Kr were 22 using the feed gas with a He balance and 28 using the feed gas with an air balance. The selectivity results indicate that AgZ-PAN used in the first column of a multi-column configuration will provide adequate partitioning of Xe from Kr in the tested temperature range to produce a more pure Kr end product for collection.

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ACRONYMS

AgZ-PAN	Silver converted mordenite-polyacrylonitrile
HZ-PAN	Hydrogen mordenite-polycrylonitrile
He	Helium
HF	Hydrofluoric acid
HNO_3	Nitric acid
ICP-MS	Inductively Coupled Plasma with Mass Spectrometer
I.D.	Inside diameter
INL	Idaho National Laboratory
K	Kelvin
P/P_0	Relative pressure range
PPMV	Part per million by volume
PTFE	Polytetrafluoroethylene
$SEL_{Xe/Kr}$	Selectivity of Xe over Kr
UNF	Used Nuclear Fuel
Wt.%	Weight percent

XE/KR SELECTIVITY USING AGZ-PAN AT VARIOUS TEST TEMPERATURES

1. INTRODUCTION

The ability to separate Kr from other volatile components present in used nuclear fuel (UNF) reprocessing off-gas streams is necessary to meet the current radioactive emissions limits and would also reduce the final volume of a Kr waste form. By utilizing simplified physisorption techniques, Xe can be separated from Kr resulting in a “Xe free” Kr final product for waste treatment.

A patented procedure developed at Idaho National Laboratory (INL) has resulted in the ability to prepare engineered form sorbents consisting of bound mordenite powders in a macroporous polymer.(1) Previous testing has indicated that a hydrogen mordenite-polyacrylonitrile (HZ-PAN) engineered form sorbent can be used to effectively capture Kr at reduced temperatures (~ 190 K).(2) A silver converted mordenite-polyacrylonitrile (AgZ-PAN) engineered form sorbent is expected to exhibit selectivity for Xe over Kr up to and including room temperature based on reported capacity results at ambient temperature.(3)

In support of a FY-15 level 2 milestone to evaluate the potential for capturing a purified Kr gas product using physisorption techniques, modifications to the existing test setup incorporating a multi-column test bed have been completed.(4) The multi-column configuration will allow for testing of the two INL engineered forms, as well as other sorbents developed by the Off-Gas Sigma Team, at varying temperatures to determine the ability to separate Xe from Kr and ultimately determine the Kr purity of the final collected product stream.

The purpose of this document is to determine Xe/Kr selectivities for AgZ-PAN using two feed gas compositions consisting of 1000 ppmv Xe and 150 ppmv Kr in either a He or air balance at three test temperatures of 295, 250 and 220 K. The results of selectivity testing will be used as guidance for parameter selection to perform multi-column testing for initial Kr captured product purity investigations.

2. Experimental Equipment

A Stirling Ultra Low temperature cooling apparatus capable of tightly controlling temperatures from 295K down to 193 K was installed in the existing experimental test setup. Specifications for the cooling apparatus are found in Table 1. A photo of the cooling apparatus is shown in Figure 1.

Table 1. Cooling apparatus specifications

Make/model	Stirling Ultra Low temperature freezer/ShuttleC ULT:25N
Cooling temperature range	-86 °C to 20 °C @ 32 °C (90 °F) ambient, uniformity ± 0.75 °C
Interior dimensions	13.1” L x 8.7” W x 13.4” D (332 x 221 x 340 mm)
Misc. Specifications	Cooldown time = 2.2 hrs from ambient to -80 °C Ambient operating temperature +5 °C to +35 °C (41 °F to 95 °F) Refrigerant, R-508B non-flammable CFC/HCFC-Free Electrical Power 120V AC or 12V DC from mobile source

Figure 1. Stirling cooler

A stainless steel column was designed to fit inside the cooling chamber and to contain the sorbent. The column dimensions are 1.65 cm I.D. x 23 cm long equating to a volume of ~50 cm^3 so it can accommodate ~ 20 grams of AgZ-PAN (density = 0.4 g/cm^3) sorbent . Thermowells were welded into the wall of the column to measure the temperature of the sorbent bed at three locations. This allows for triplicate bed temperature monitoring and secondary validation of interior cooler temperatures. Heat tape was wound around the column to heat the sorbent bed for desorption. The heat tape temperature is controlled by a thermocouple communicating with an independent temperature controller. A photo of the column prior to being installed in the cooling chamber is shown in Figure 2.

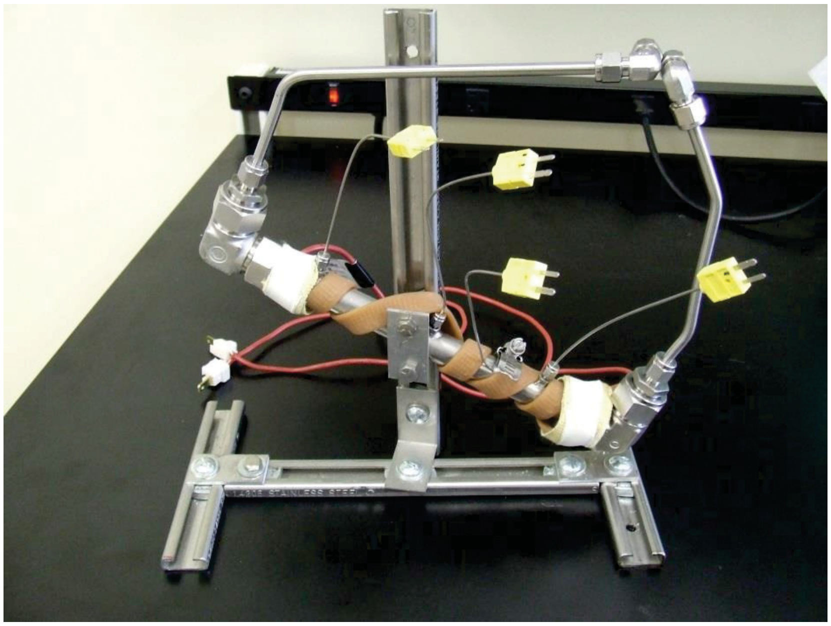

Figure 2. Sorbent column with heat tape and TC's installed

3. Sorbent Preparation

A 25 gram mass of AgZ-PAN was prepared for use in this testing. The makeup procedure started with a sodium mordenite-polyacrylonitrile (NaZ-PAN) pre-preparation followed by a Na/Ag conversion using a 0.1 M $AgNO_3$ solution. The Brunauer- Emmett - Teller (BET) surface area was measured on a Micromeritics ASAP 2020 surface area analyzer which resulted in a surface area of 263 m^2/g in the 0.05-0.1 relative pressure range (P/P_0). The Ag wt.% was also determined by dissolving a known mass of the sorbent in a HNO_3/HF acid solution, filtering the resulting solution through a 0.2 µm PTFE filter, and analyzing the filtrate Ag content with a Perkin Elmer ICP-MS. The sorbent Ag composition was calculated to be 9.86 wt.%. Both the surface area and Ag wt.% determinations were in excellent agreement with previous AgZ-PAN preparations and indicate that the preparatory procedure results in repeatable sorbent compositions.(3)

This AgZ-PAN sorbent was activated at 150 °C under 20 inches Hg vacuum for 18 hours prior to putting in the test column. A mass of 18.3 grams of the activated material was loaded into the test column. All gas lines and connections were leak checked prior to start of selectivity testing.

4. Selectivity Testing

Testing was initiated 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 220 K 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 by the total moles of sorbate processed.(2,3) This procedure was repeated using the 1000 ppmv Xe, 150 ppmv Kr in air balance feed gas. After each test, a desorption was performed at 370 K with He only flow at 50 sccm until no Xe or Kr was present in the column effluent as determined by GC analyses.

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).

$$\mathrm{Sel}_{\mathrm{Xe/Kr}} = \frac{\boldsymbol{X}_{\mathrm{Xe}}/\boldsymbol{Y}_{\mathrm{Xe}}}{\boldsymbol{X}_{Kr}/\boldsymbol{Y}_{Kr}} \tag{1}$$

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).

5. Results and Discussion

Selectivity of Xe over Kr for two feed gas compositions at 295, 250 and 220 K were determined for AgZ-PAN with results reported in Table 2.

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	34
	250	84.9	0.43	30
	220	254	1.36	28

The AgZ-PAN sorbent exhibits selectivity for Xe over Kr that increases with increasing temperature. In the case of the feed gas in He balance, this is primarily attributed to a 70 fold reduction in Kr capacity compared to a 23 fold reduction in Xe capacity when increasing the temperature from 220 K to 295 K.

Both Xe and Kr capacities are reduced by a factor of approximately 2 using the feed gas in air balance compared to those with a feed gas in a He balance. Although Xe and Kr capacities decrease with increasing temperature for both test gases, selectivity of Xe over Kr for the feed gas in air (28) is actually higher at 220 K when compared to Xe over Kr selectivity for the feed gas in He (22) at the same temperature. The Kr capacities at 250 and 295 K for both feed gases, although measurable, are nearing the point where the method for capacity determinations include sufficient error to consider the AgZ-PAN has relatively little or no Kr capacity at those temperatures. These selectivity data strongly support the affirmation that the use of AgZ-PAN would provide effective partitioning of Xe from Kr in both He or air streams, particularly at temperatures closer to and including room temperature (295 K). The use of larger columns would likely be needed if higher temperatures are designated depending on total number and rate of Xe and Kr moles released during UNF reprocessing.

A graph depicting the amount of time from when Kr broke through to when the Xe began to breakthrough for AgZ-PAN at 250 K is presented in Figure 3. The graph indicates a Kr/air stream containing no measurable Xe passing through the AgZ-PAN sorbent for 10 hours offering a “Xe free” gas stream available for Kr capture on a second sorbent column consisting of HZ-PAN at reduced temperature.

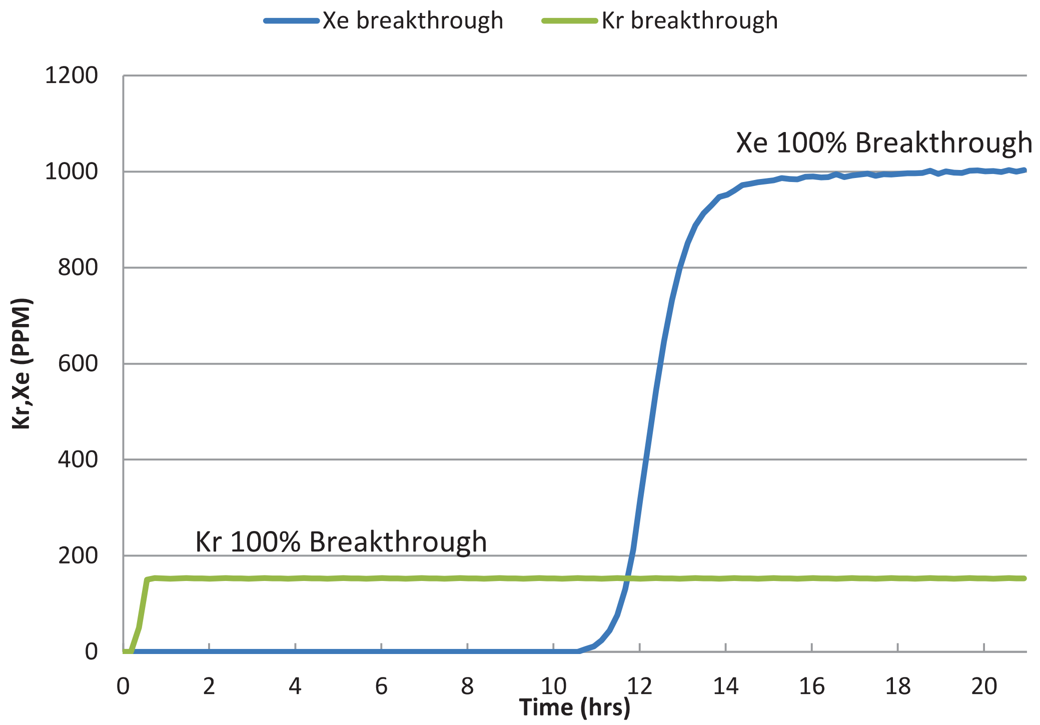

Figure 3. Kr and Xe breakthrough curves for AgZ-PAN at 250 K with a feed gas balance of air

6. Conclusions

A second cooling apparatus was installed in the 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 220 K. Two feed gas compositions of 1000 ppmv Xe, 150 ppmv Kr in a He or air balance were used. The AgZ-PAN sorbent selectivity was calculated using Xe and Kr capacity determinations and feed gas concentrations.

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The Xe over Kr selectivity of the AgZ-PAN sorbent was demonstrated and tested conditions provide good starting points for future tests to partition Xe from Kr to determine Kr purity of a final captured volume. Future tests can be performed to provide data to support Kr waste stream volume reductions.

7. References

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