

HZ-PAN and AgZ-PAN Desorption Characterization

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SUMMARY

While previous research focused on adsorption of Kr and Xe on HZ-PAN and AgZ-PAN, recent focus has shifted to desorption. Preliminary testing was completed last year, providing valuable information to guide further research.

Previous isotherm studies indicated that thermal swing operations, along with a sweep gas, are required for effective desorption of captured species from both AgZ-PAN and HZ-PAN. This series of tests focused on characterizing the bulk gases removed from each sorbent and relative separation of Kr and Xe from each other and from the bulk air. Stepwise thermal desorption resulted in 99-100% separation of Xe from Kr, and 77-83% separation of Kr from air while concentrating Xe seven to tenfold and Kr three to fivefold from initial feed stream compositions. Previous isothermal studies of both sorbents have shown that sorbent capacity is proportional to feed gas concentration. Therefore, it is anticipated that additional HZ-PAN columns operated in series will further concentrate and purify the final Kr stream with higher efficiency. It is expected that Xe will be released to atmosphere after desorption. However, it could also be purified further with more AgZ-PAN columns in series. Further testing should be done to determine maximum purity achievable for both Kr and Xe. Additionally, renewed focus on increasing Xe capacity on AgZ-PAN and Kr capacity on HZ-PAN is recommended.

CONTENTS

SUMMARY	iii
ACRONYMS	vii
1. Introduction	1
2. Experimental setup	1
3. AgZ-PAN Desorption.....	1
4. HZ-PAN Desorption.....	3
5. Conclusions and Recommendations	6
6. References	6

FIGURES

Figure 1. Desorption from AgZ-PAN while slowly heating from 295K to 420K over 12 hours.	2
Figure 2. AgZ-PAN desorbed with stepwise temperature control and 45 sccm He flow over 2.9 hours.	2
Figure 3. Desorption from HZ-PAN while slowly heating from 191K to 420K over 12 hours	4
Figure 4. HZ-PAN desorption with temperature ramped from 191K to 420K over 12 hours	4
Figure 5. HZ-PAN Desorbed with stepwise temperature control	5

TABLES

Table 1. Summary of AgZ-PAN Desorption Results	3
Table 2. Summary of HZ-PAN Desorption Results	5

ACRONYMS

AgZ-PAN	Engineered form silver-exchanged mordenite in polyacrylonitrile matrix
HZ-PAN	Engineered form hydrogen mordenite in polyacrylonitrile matrix
He	Helium
INL	Idaho National Laboratory
Kr	Krypton
Xe	Xenon

HZ-PAN AND AGZ-PAN DESORPTION CHARACTERIZATION

1. Introduction

Reprocessing of used nuclear fuel releases several volatile radionuclides into the off gas stream. United States emissions regulations will require them to be removed from the bulk gas stream prior to release to atmosphere. INL has developed and tested the composite sorbents, AgZ-PAN and HZ-PAN, to remove Xe and Kr from the bulk gas stream. Recent engineering studies (Jubin, et al., 2016) (Jubin, et al., 2017) indicated a need for desorption data in order to advance the technological readiness for development of integrated off-gas treatment systems. To that end, preliminary desorption studies were carried out last year to guide further desorption research (Welty, Greenhalgh, & Garn, 2017). This series of tests is a continuation of those studies to further characterize desorbed gases.

2. Experimental setup

Desorption tests were conducted using a multi-column configuration, where feed gas consisting of 150 ppm Kr and 1000 ppm Xe in a balance of air was first passed through AgZ-PAN for Xe adsorption, followed by HZ-PAN for Kr adsorption. Both columns were 1.9 cm nominal diameter stainless steel tubing, 51 cm in length. Each column was installed in a Stirling Ultracold portable freezer for sub-zero temperature control, and wrapped with heat tape controlled by a Digi-Sense temperature controller for consistent external heating during desorption. Flow was controlled by Teledyne Hastings 300 VUE thermal mass flow controllers.

In all cases, AgZ-PAN adsorption temperature was ambient, ~295K. HZ-PAN adsorption temperature was controlled at 191K. Tests were timed to minimize the amount of Xe allowed to the HZ-PAN column. Desorption was accomplished by stepwise heating of the columns, along with He sweep gas. Analyses of the effluent from each column, during both adsorption and desorption, were performed via an Agilent 7890 gas chromatograph with auto sampling every 10.5 minutes.

3. AgZ-PAN Desorption

Previous desorption tests focused on removing Kr and Xe gases in bulk, as quickly and thoroughly as possible. The ability to remove adsorbed species efficiently has been demonstrated repeatedly and consistently. Previous studies suggested that reducing the rate of temperature increase during desorption may provide an opportunity for further separation of Xe from Kr and air adsorbed on the AgZ-PAN (Welty, Greenhalgh, & Garn, 2017). With careful temperature control during desorption, nearly complete separation of Kr from Xe was achieved (Figure 1).

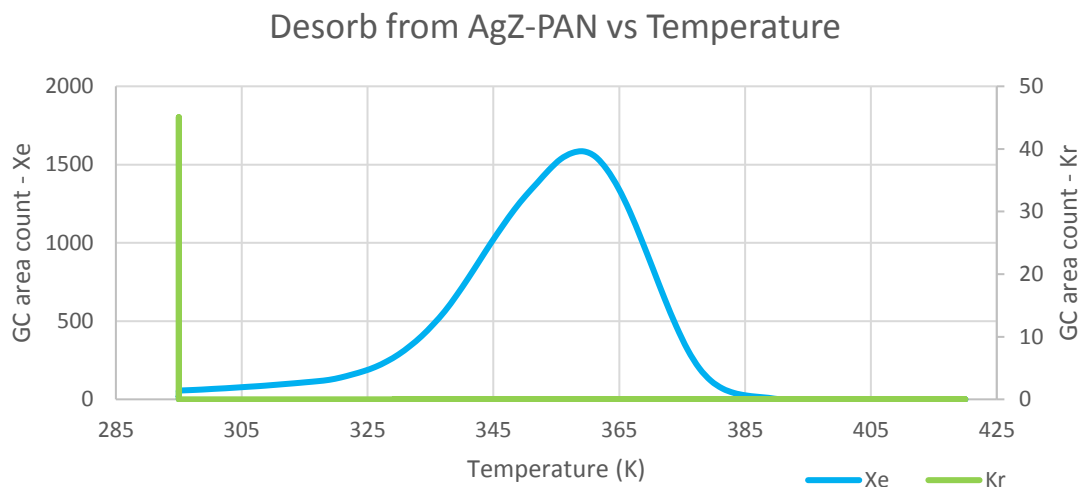


Figure 1. Desorption from AgZ-PAN while slowly heating from 295K to 420K over 12 hours.

The observed temperature gap was explored further to determine if the same separation was achievable with better time efficiency. Rather than the very slow temperature ramp employed during preliminary studies, stepwise temperature increases were used. Based on the graph in Figure 1, 320K was chosen as the first temperature step. Heating tape was used as the heat source, controlled by a DigiSense temperature controller, to raise the temperature from 295K to 320K over 20 minutes. The first temperature step was held for 40 minutes, at which point all of the Kr and air were desorbed, leaving only Xe on the sorbent. Temperature was then ramped to 420K over one hour and held for four hours, desorbing all of the Xe. Separation of Xe from Kr and air was successful in all cases, widening the gap observed during preliminary studies (Figure 2). There was little, if any, further separation of Kr from air during desorption. However, at full scale, that early portion of the desorb gas would need to be sent through HZ-PAN regardless, to ensure complete capture of the Kr.

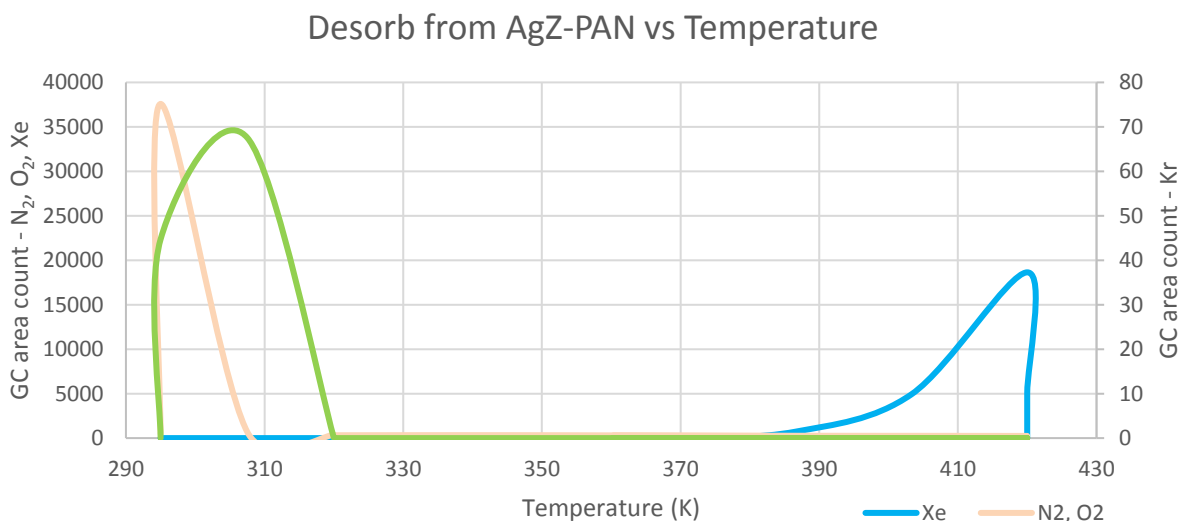


Figure 2. AgZ-PAN desorbed with stepwise temperature control and 45 sccm He flow over 2.9 hours.

Four tests were run using this temperature control scheme during desorption. He flow through the column during desorption was 45 sccm for two tests and reduced to 15 sccm for the other two. Lower He flow during desorption resulted in higher concentrations of Xe in the bulk desorbed gas, at the expense of more time required for complete desorption and higher concentrations of air remaining in the desorbed gas, as seen in Table 1.

Table 1. Summary of AgZ-PAN Desorption Results

Test #	Flow (sccm)	Xe (ppm)	Kr (ppm)	Air (ppm)	Xe Separation
1	45	5,799	35	10,064	100%
2	45	804	5	4,607	100%
3	15	7,725	49	92,055	100%
4	15	10,864	78	190,693	99%

Concentrations in Table 1 were calculated by integration of the GC analyses data from each test over the sweep gas volume. Separation percentages were calculated from volume of Xe without any air or Kr contamination versus total Xe desorbed. Note that in test #2, above, Xe concentration in the desorbed gas was lower than the feed gas concentration of 1000 ppm. This test was conducted differently from the others. Rather than run as long as possible through both columns, three separate, very short runs were made through the AgZ-PAN column, with desorption of only the AgZ-PAN after each run. The effluent from the AgZ-PAN column was then routed through the HZ-PAN column for each run. This was designed to ensure absolutely no Xe could enter the HZ-PAN column, while at the same time operating the HZ-PAN column to Kr saturation. Those very short runs resulted in very little Xe adsorbed on the AgZ-PAN during each run, and a longer over-all desorption time due to the time required for heating the column each time. AgZ-PAN efficiency was sacrificed in order achieve HZ-PAN Kr saturation.

If there is interest in recovering and purifying Xe for sale, additional columns operated in series will likely be necessary. More testing will be required to determine maximum Xe purity achievable. However, it will be more cost effective to simply release the Xe to atmosphere, along with the remaining air. This should allow further cost savings by using air as the sweep gas to desorb adsorbed species from the AgZ-PAN, followed by using minimal He as a final step to remove the air from the column prior to the next adsorption cycle. Kr and Xe adsorbed onto AgZ-PAN have been successfully desorbed with He, He with Kr and Xe, air, and feed gas. Although sweep gas was required, within the limited gases tested so far, Ag-PAN desorption was independent of sweep gas composition. A final sweep of He was used to remove the air while the column was still heated; all adsorbed Kr, Xe, and air were successfully desorbed.

4. HZ-PAN Desorption

As with AgZ-PAN, previous HZ-PAN testing was concerned primarily with adsorption, using desorption analyses purely as a means to check the material balances. However, last year's preliminary desorption studies indicated some potential for further separation of Kr from Xe during desorption (Figure 3).

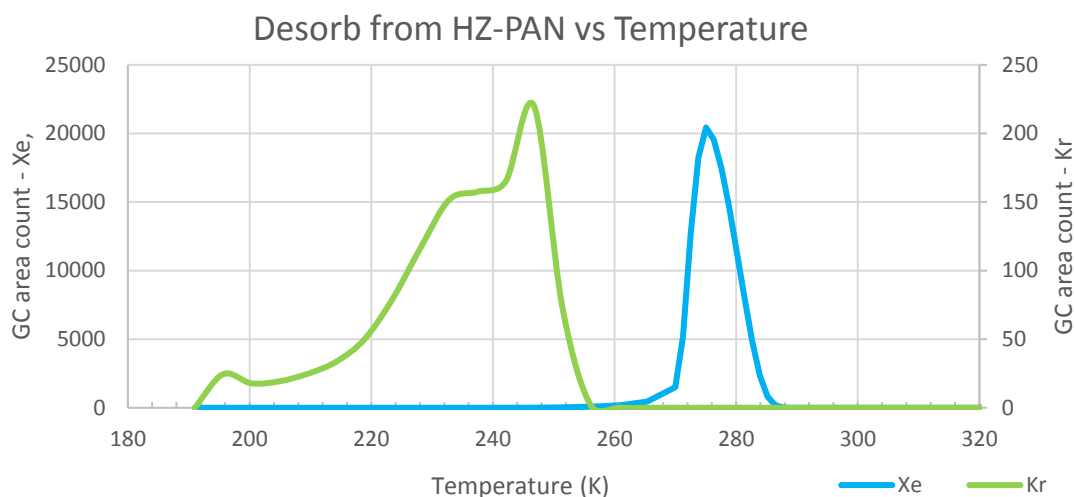


Figure 3. Desorption from HZ-PAN while slowly heating from 191K to 420K over 12 hours

As seen in the figure above, when compared to AgZ-PAN in Figure 1, there is a much smaller thermal separation between species during desorption from HZ-PAN. This behavior was not unexpected, as HZ-PAN requires lower temperatures to adsorb noble gases, and tends to hold Kr and Xe more loosely due to weak Van der Waals forces. While pressure swing operations showed some promise during preliminary studies (Welty, Greenhalgh, & Garn, 2017), the added expense is likely not justifiable so the focus of these tests was on developing more effective thermal swing desorption.

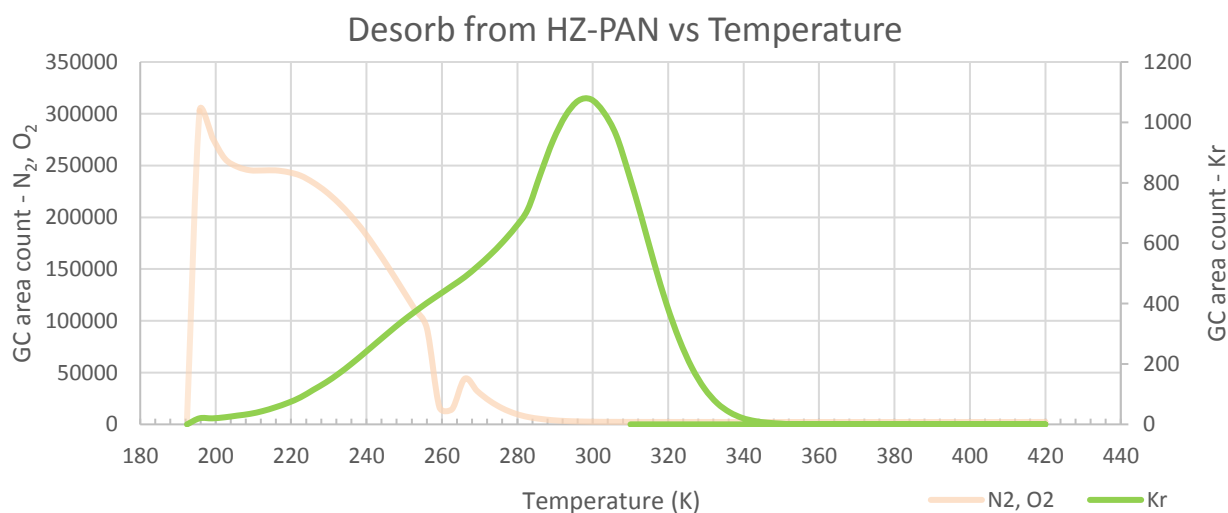


Figure 4. HZ-PAN desorption with temperature ramped from 191K to 420K over 12 hours

An initial test of HZ-PAN desorption with only air and Kr adsorbed indicated air desorption occurs at very low temperatures (Figure 4). In an attempt to separate Kr from air as much as possible, temperature steps of 210 K, 270 K, and 370 K were chosen. The temperature controller was programmed to ramp the temperature from 191 K to 210 K over 20 minutes and hold for two hours, ramp to 270 K over 30 minutes and hold for one hour, then ramp to 370 K over one hour and hold for four hours. The temperature scheme was partially successful. Better separation of Kr from air was achieved (Figure 5), however, when

the Stirling Ultracold freezer was turned off for desorption, the column warmed more rapidly than desired. The result was the initial ramp rising to 260 K over the first 2.5 hours due to heat transfer from the lab space. This is a limitation of the temperature control system, as employed, that will need to be remedied for finer control in future.

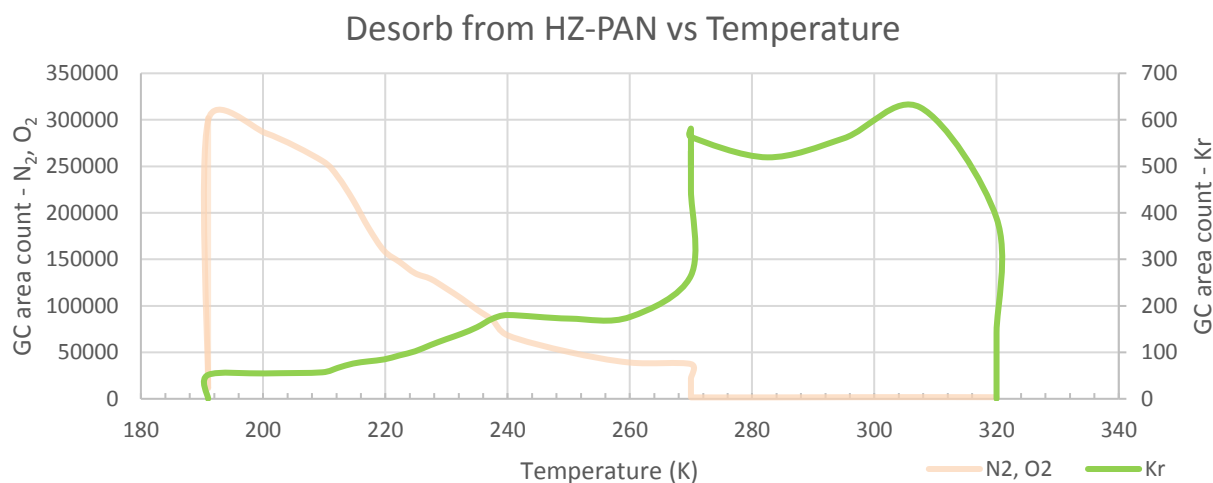


Figure 5. HZ-PAN Desorbed with stepwise temperature control over 5.8 hours.

While the resulting separation of Kr from air was not as clean as was desired, separation between 77 and 83% was accomplished over all tests (Table 2). Better temperature control may result in a more desirable separation.

Table 2. Summary of HZ-PAN Desorption Results

Test #	Xe (ppm)	Kr (ppm)	Air (ppm)	Kr Separation
1	0	762	72,606	83%
2	0	528	53,190	78%
3	36,903	322	104,430	77%
4	338	374	155,140	77%

Concentrations in Table 2 were calculated by integration of the GC analysis data from each test over the sweep gas volume. Separation percentages were calculated from volume of Kr without any air or versus total Kr desorbed. During tests one and two, the adsorption cycle was kept short enough to ensure no Xe entered the HZ-PAN column. Kr was concentrated in these cases by a factor of 3.5 – 5. In tests three and four, Xe was allowed to break through the AgZ-PAN and enter the HZ-PAN column. At low temperatures, HZ-PAN readily adsorbs Xe. While this does not seem to affect the sorbent's capacity for Kr, it does result in lower overall Kr concentration in the desorbed gas because more time and sweep gas is required to remove the Xe. Kr separation from the bulk gas was not as high as Xe separation in the

AgZ-PAN, and Kr was only concentrated by a factor of two. However, feed gas concentration of Kr is over six times lower than that of Xe. Given that sorbent capacity for these gases is highly dependent upon feed gas concentration, the observed separation is quite good, given the low Kr concentration in the feed gas. Additional HZ-PAN stages should be both smaller and progressively more effective at concentrating Kr.

5. Conclusions and Recommendations

With careful temperature control, greater than 99% separation of Xe from Kr and air can be achieved during desorption. Once desorbed from HZ-PAN, Kr concentrations can be increased five to seven times. It is anticipated that further adsorption/desorption stages will further increase Kr concentrations. A series of successively smaller columns could be employed to further purify and concentrate the Kr stream. It is recommended that further studies be conducted to determine the maximum practical purity of Kr and Xe achievable utilizing gas adsorption.

As continuous improvement should remain a priority, it is also recommended AgZ-PAN and HZ-PAN research renew focus on increasing capacities for Kr and Xe.

Additionally, it is recommended that Kr and Xe adsorption be integrated with upstream off gas treatment systems, such as iodine adsorption in order to advance technical readiness for potential used nuclear fuel reprocessing.

In order to further advance the technological readiness of gas adsorption for the separation and concentration of Kr and Xe, it will eventually be necessary to scale up columns and adsorption/desorption techniques to process sizing. Applied research on the pilot scale will need to be employed, along with carefully planning and economic analyses, to determine how best to apply techniques developed at laboratory scale in an industrial setting.

6. References

- Jubin, R. T., Bruffey, S. H., Jordan, J. A., Spencer, B. B., Soelberg, N. R., Welty, A. K., & Greenhalgh, M. R. (2017). *Data Requirements and Test System Needs for Development of an Integrated Off-Gas Treatment System*. ORNL.
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