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Concentration of Kr from Simulated Dissolver Off-gas Streams Utilizing a Solid Sorbent, HZ-PAN

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Idaho National Laboratory has developed and tested engineered sorbents to separate and capture volatile fission products such as iodine (I), xenon (Xe), and krypton (Kr) from off-gas streams. A study was conducted using a solid sorbent, HZ-PAN, to concentrate Kr from a simulated dissolver off-gas stream. The study demonstrates that four adsorption-desorption cycles can transform a 150 ppmv Kr stream into a 37.5% Kr stream, an overall concentration factor of 2497.

Keywords: off-gas, krypton, engineered sorbents, concentrate, adsorption, desorption, capture, HZ-PAN, separation, volatile fission products, hydrogen mordenite polyacrylonitrile

Introduction

Over the past decade, Idaho National Laboratory (INL) developed and tested engineered sorbents to separate and capture volatile fission products such as iodine (I), xenon (Xe), and krypton (Kr) from off-gas streams. Historically, cryogenic distillation has been used to execute the separation. However, performing this separation from bulk air streams is expensive and can pose significant hazards. INL has successfully developed two different sorbents for Xe and Kr capture, silver mordenite polyacrylonitrile and hydrogen mordenite polyacrylonitrile (HZ-PAN). This presentation focuses on concentrating Kr while utilizing HZ-PAN as the concentrating media.

INL conducted extensive studies to understand how the Kr capacity of HZ-PAN changes under various conditions including flowrate, temperature, concentration, carrier gas, and irradiation. While these studies were performed to prove the Kr can be completely desorbed from the column, concentration of Kr was not studied. Concentrating Kr during desorption would be ideal for two scenarios: (1) to produce Kr for commercial and research applications or (2) to minimize the volume of the radioactive gaseous waste stream for disposal. This presentation details the Kr concentrating potential of HZ-PAN by performing adsorption and desorption tests at varying Kr concentrations.

Experimental

These experiments used a ¾" x 20" stainless-steel column packed with 27.8 grams of HZ-PAN. A mixture of Kr and air or Kr, He, and air was used as the feed gas to load the column. Before adsorption, the column was conditioned using a heat cycle with He flow to remove any moisture and impurities from the HZ-PAN. During conditioning and testing, a slipstream of the effluent was directed to an Agilent 7890B dual gas chromatograph with thermal conductivity detectors (GC-TCD). For the higher concentration tests, a flow meter with a totalizer was installed on the vent to quantify the volume of the desorbed stream. A moisture probe in the effluent stream was used to monitor moisture content and temperature. A Stirling cooler was used to cool and maintain the HZ-PAN column at 191 K.

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For the adsorption test, the column was cooled to 191 K, and then isolated. The test gas was then directed to the GC, bypassing the column, at 100 sccm to obtain a baseline GC spectrum area for Kr. Once the test gas baseline was consistent through multiple GC injections, the test gas was redirected through the cooled HZ-PAN column. The test gas was run through the column until the column was completely saturated with Kr, which was defined as when the Kr concentration of the effluent from the HZ-PAN column reached the concentration of the uninhibited feed gas concentration matching the baseline spectrum area. The column was then isolated and held for desorption. For the desorption test, the column was isolated, the test gas was stopped, and the lines were swept with a 50 sccm He flow until no Kr was observed on the GC. The He flow was then reduced to 5 sccm and the zero Kr state of the lines was confirmed. He flow was then directed through the HZ-PAN column, the cooler was shut off, and a heat cycle was started. The column temperature was ramped up to 420 K over one hour and held there until no Kr peak was seen on the GC spectrum. Subsequent test parameters were dictated by the Kr concentration from previous desorption profiles. This set of experiments used the target Kr concentrations and respective test gas parameters in **Table 1**.

Table 1 Target Kr concentrations in feed and test gas flow parameters

Target Kr Feed Gas Concentration (ppmv)	Test Gas Parameters	
150	6 sccm 2544 ppmv Kr in He	94 sccm air
1,800	70 sccm 2544 ppmv Kr in He	30 sccm air
32,300	32.3 sccm 10% Kr in Air	67.7 sccm air
135,000	13.5 sccm 100% Kr	86.5 sccm air

Results and Discussion

The Kr feed gas concentrations and respective concentration factors, based on the desorption analysis, are in **Table 2**. The concentration factor was calculated by dividing the average Kr concentration of the column effluent during desorption by the Kr concentration of the test gas used during adsorption for each test. At low feed gas concentrations, concentration factors were high, at 12 and 18. After the Kr concentration in the feed gas increased to 32,300 ppmv and higher, the concentration factor stabilized to around 3-5 times the Kr feed gas concentration. This provides evidence that the Kr fed to the column could be adsorbed and concentrated significantly. However, the Kr concentration factor begins to plateau with a higher average Kr concentration in the desorbed stream.

Table 2 Concentration factors achieved from starting Kr feed gas concentration

Kr Feed Gas Concentration (ppmv)	Concentration Factor Based on Desorption
150	12
1,800	18
32,300	4.7, 4.8, 5.1
135,000	3.4

The rate at which Kr was desorbed off the column and its concentration in the effluent stream was dependent on the Kr concentration in the feed gas. The Kr concentration seen during desorption from each test is displayed in **Figure 1**. As can be seen from the figure, the tests with a higher Kr concentration in the feed gas, desorbed the fastest. This data does not show the entire run time for the experiments but focused on the time at which a majority of the Kr was desorbed from the column and where the peak Kr concentration was seen. In addition, **Figure 1** shows that the tests

that had a higher Kr concentration in the feed gas had a higher concentration of Kr in the effluent stream during desorption. This demonstrates rapid sequential concentration of Kr.

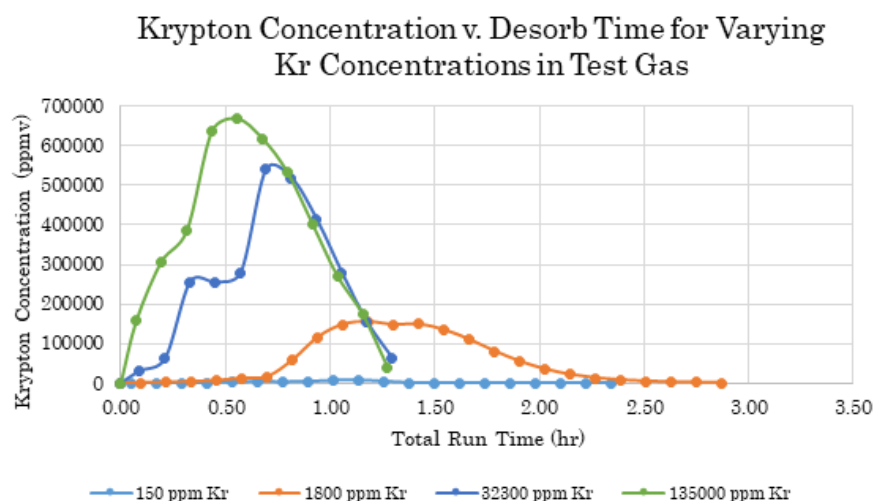


Figure 1. Kr desorption curves for HZ-PAN using varying Kr concentrations in He/Air at 100 sccm.

Table 3 shows the average Kr concentration from the desorption tests run with varying Kr feed gas concentrations. Throughout the study, when the Kr feed gas concentration was increased the average Kr concentration during desorption increased. The final test had a Kr feed gas concentration of 135000 ppmv or 13.5% Kr and the average Kr concentration analyzed during desorption was 3.745×10^5 ppmv.

Table 3. Kr feed gas concentrations and their respective average Kr concentration during desorption

Kr Feed Gas Concentration (ppmv)	Average Kr Concentration during Desorption (ppmv)
150	1.187×10^3
1800	2.592×10^4
32300	1.347×10^5
135000	3.745×10^5

Table 4 shows when the peak Kr concentration was seen in the effluent stream during desorption and the concentration calculated from the curve. As can be seen in **Table 4**, the desorption time at which the Kr concentration peaks were observed decreased as the Kr feed gas concentration increased. In addition, the Kr peak concentration increased as the Kr feed gas concentration increased. There was a large increase in Kr peak concentration when the Kr feed gas concentration was increased from 150 to 1,800 ppmv. Whereas, when the Kr feed gas concentration increased from 1,800 to 32,300 to 135,000, there was a smaller increase in Kr peak concentration. This indicates a limit of Kr concentration via HZ-PAN, with the point of diminishing returns yet to be determined. **Table 4** also highlights that with each sequential test and higher Kr peak concentrations being seen, the time of the Kr peak became shorter. This shows that the majority of Kr desorbed from a saturated HZ-PAN column could be collected in smaller volumes of more concentrated Kr. For example, the last test loaded from a 135,000 ppmv Kr stream yielded a peak concentration of nearly 67% Kr during desorption.

Table 4. Peak Kr concentrations and 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

Conclusion

HZ-PAN can be used to significantly concentrate Kr by performing adsorption-desorption cycles in series. Higher concentration factors were observed when feed gas concentrations were lower, 12 and 18x. At higher feed concentrations there still were concentration factors between 3-5x. However, additional testing is needed to determine the concentration limit. Regardless, this experiment found that with four short cycles, a 150 ppmv Kr in air feed gas could be transformed into at least a 37.5% Kr stream, an overall concentration factor of 2497. Each concentration step results in successively smaller volumes desorbed, reducing the volume by a factor of approximately 40,000. From previous HZ-PAN desorption studies, many different gases can effectively remove Kr from the column. If adsorption and desorption cycles are performed in series, the carrier gas of the desorbed stream, and thus the next feed gas stream, changes depending on the gas used to desorb the column. Thus, this method could be used to both concentrate Kr and replace its carrier gas stream with an inert gas from which Kr is more easily separated, such as He.

This study was designed to collect the majority of Kr desorbed from a saturated HZ-PAN column to prevent Kr loss. Operations could easily be altered to collect smaller volumes of more concentrated Kr. For example, the last test loaded from a 135,000 ppmv Kr stream yielded a peak concentration of nearly 67% Kr during desorption. This demonstration should be considered proof-of-concept. Further refinement is required to gather sufficient data to develop optimum operating schemes to integrate into used nuclear fuel off-gas treatment.

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