



Xe Concentration Activity

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Changing the World's Energy Future

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To: Amy K. Welty

From: Meghan S. Fujimoto and Emma R. MacLaughlin

Re: M4FT-24INL0301040214 - Xe Concentration using AgZ-PAN

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Introduction:

Over the past decade, researchers at 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. As noble gases, Xe and Kr can be difficult to capture and separate. Historically, cryogenic distillation has been used to execute the separation, but this method can pose significant hazards. INL has successfully developed and tested two different sorbents for Xe and Kr capture – silver mordenite polyacrylonitrile (AgZ-PAN) and hydrogen mordenite polyacrylonitrile (HZ-PAN).

INL conducted extensive studies to understand how the Xe capacity of AgZ-PAN changes under various conditions including flowrate, temperature, analyte concentration, and carrier gas. Therefore, it is well understood that AgZ-PAN can capture Xe under a wide variety of conditions. Additional studies were performed to characterize Xe desorption from AgZ-PAN, including temperature, purge gas, and flowrate. However, the ability to concentrate Xe during desorption was not studied. Concentrating Xe during desorption would be ideal to produce Xe that can be used for commercial and research applications. This memo investigates the Xe concentrating potential of AgZ-PAN by simulating operation of columns with sequentially increasing feed concentrations.

Experimental:

Adsorption and Desorption Test Set-up

To evaluate the extent Xe could be concentrated by an AgZ-PAN packed column, adsorption and desorption tests were performed at sequentially increasing Xe concentrations. A 1.9 cm ID x 50.8 cm stainless-steel column packed with 44.8 grams of AgZ-PAN was used for these experiments. Before adsorption, the column was conditioned using a heat cycle with helium (He) flow to remove any moisture and impurities from the AgZ-PAN, as they negatively affect the overall Xe column capacity. Mixtures of Xe, air, and He were used as the feed gas to load the column.

During conditioning and testing, the effluent of the column was monitored by feeding a slipstream of the effluent to an Agilent 7890B dual gas chromatograph with thermal conductivity detectors (GC-TCD). Additionally, a Vaisala HMP7 humidity and temperature probe installed in the effluent stream was used to monitor real-time moisture content and temperature. The test gas, a mixture of Xe and air or Xe, He, and air, was then directed through the system at 100 sccm. A baseline GC spectrum was obtained for Xe, as the feed gas flowed directly to the GC and bypassed the column. Once the test gas baseline was consistent for multiple consecutive GC injections, the AgZ-PAN column, at ambient temperature, was

opened to the test gas flow. The test gas was run through the column until it was completely saturated with Xe. Saturation was defined as when the Xe concentration of the effluent from the AgZ-PAN column reached the concentration of the unabated feed gas concentration, also referred to as the baseline spectrum area. The column was then isolated and held for desorption.

With the column isolated, the test gas was stopped, and the lines were purged with 50 sccm He flow until no Xe was observed on the GC spectrum. For desorption, the He flow was reduced to 5 sccm. The He flow was then directed through the AgZ-PAN column and a heat cycle was started. The heat cycle consisted of ramping up to 420 K over one hour and holding at 420 K until no Xe peak was seen on the GC spectrum. It is important for the volume of the effluent stream to be accurately quantified. Therefore, a flow meter with a totalizer was installed on the column effluent vent to quantify the total volume of the desorbed stream. The flow rate of the effluent stream directed through the totalizer was recorded and combined with the flow rate of the GC slip stream for analysis.

Determination of Xe Feed Gas Concentration

For this set of experiments, sequentially increasing concentrations of Xe in the test gas were based on the average Xe concentration of the desorbed stream in the previous test. This was done to determine the maximum practical Xe concentration during desorption. To achieve the desired Xe concentrations, existing Xe containing test gases were volumetrically down blended with air and/or He. The target Xe concentrations and the respective test gas parameters can be seen in Table 1. A slip stream of the column effluent was directly fed to a GC-TCD for Xe analysis and quantification. Samples were automatically taken approximately every 11 minutes. A calibration curve was used to transfigure Xe area peaks from individual GC spectra to Xe concentration in ppmv.

Table 1. Target Xe concentrations in feed and test gas flow parameters.

Target Xe Feed Gas Concentration (ppmv)	Test Gas Parameters	
1,000	100 sccm 1000 ppmv Xe, 150 ppmv Kr in Air	
10,000	1 sccm 100% Xe	95 sccm He/5 sccm air
40,000	4 sccm 100% Xe	96 sccm He
300,000	30 sccm 100% Xe	70 sccm He

The initial test had a target Xe feed gas concentration of 1000 ppmv. The target feed Xe concentration for the subsequent tests were based on the average Xe concentration analyzed in the column effluent during the desorption of the previous run. Concentration factors were calculated by comparing the average Xe concentration from the desorption of a saturated AgZ-PAN column and the Xe concentration of the test gas used to load the column.

Xe Calibration Curve

A calibration curve was created to ensure the GC was able to analyze the large Xe peaks seen during desorption with accuracy and consistency. The calibration curve was based on gas injections, taken in triplicate, that had a concentration of Xe ranging from 1 to 100% in air. To make the curve, the area count for Xe from the GC was plotted against the Xe concentration in ppmv from the injection. This can be seen in Figure 1. This calibration curve equation was used to convert the Xe peak area from the GC to a Xe concentration in ppmv for further analysis of the adsorption and desorption data.

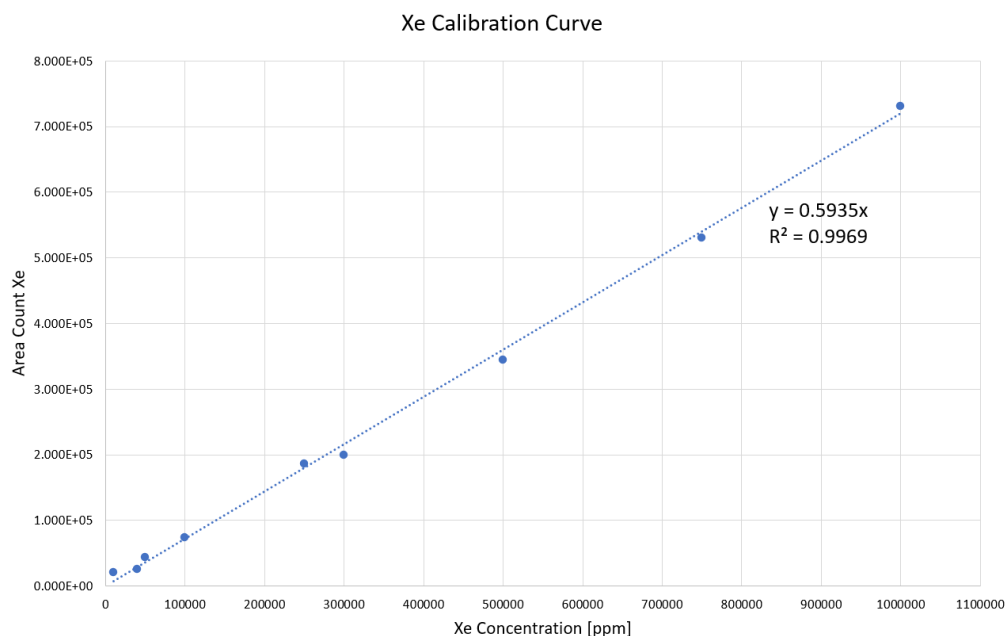


Figure 1. Calibration curve for xenon concentration analyzed by gas chromatograph.

Results:

Adsorption and Desorption Testing

The rate at which Xe was desorbed off the column and its concentration in the effluent stream was dependent on the concentration of Xe in the feed gas. Xe concentration desorption curves from each test are displayed in Figure 2. The figure shows that with higher Xe concentrations in the feed stream there were higher concentrations of Xe in the effluent stream during desorption. This confirms that the column was able to adsorb a large amount of Xe from the test gas feed and was able to concentrate the Xe during desorption.

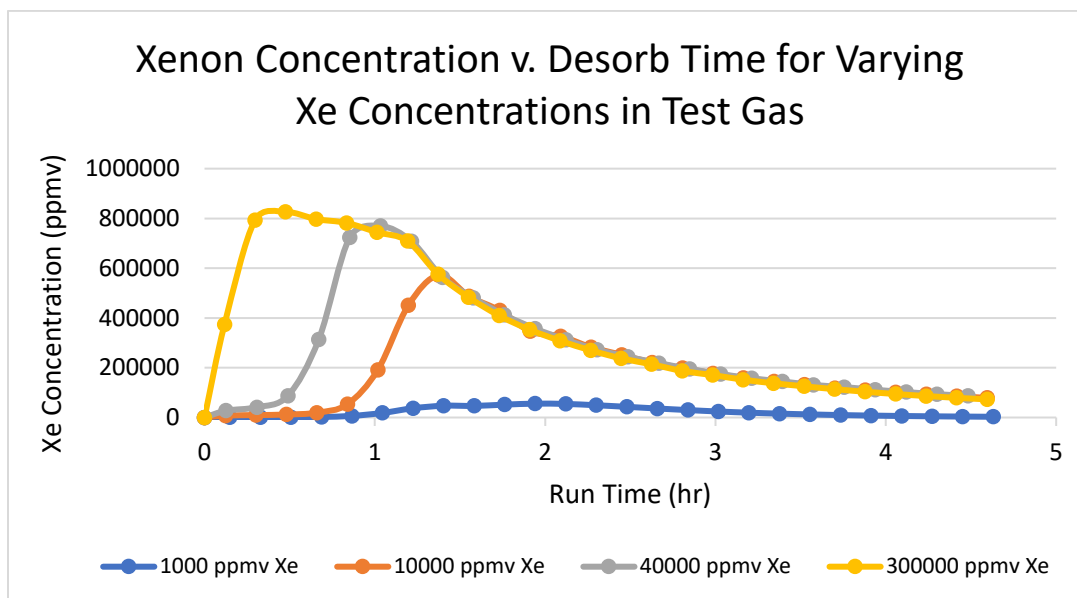


Figure 2. Xe desorption curve for AgZ-PAN using varying Xe concentrations in He/Air at 100 sccm.

Figure 2 does not show the entire run time for the experiments but focuses on when a majority of the Xe was desorbed from the column and when the peak Xe concentration was observed. As can be seen from the figure, the higher the Xe concentration was in the feed gas, the faster the peak Xe concentration was desorbed. Table 2 shows the time and concentration of maximum Xe peaks in the effluent stream during desorption. The desorption time at which the Xe concentration peaks were observed decreased as the Xe feed gas concentration increased. In addition, the Xe peak concentration increased as the Xe feed gas concentration increased. There was a large increase in Xe peak concentration when the Xe feed gas concentration was increased from 1,000 to 10,000 ppmv and from 10,000 to 40,000 ppmv. Whereas, when the Xe feed gas concentration increased from 40,000 to 300,000 there was a smaller increase in peak concentration. This indicates that the concentration of Xe during desorption will likely reach a stabilizing point regardless of the Xe feed gas concentration.

Table 2. Peak Xe Concentrations and their respective times for varying Xe feed gas concentration

Xe Feed Gas Concentration (ppmv)	Time of Xe Peak (hours)	Xe Peak Concentration (ppmv)
1,000	1.94	5.57×10^4
10,000	1.38	5.72×10^5
40,000	1.03	7.69×10^5
300,000	0.48	8.26×10^5

The main purpose of this study was to determine how much the Xe stream could be concentrated during desorption cycles from the AgZ-PAN column. Table 3 shows the average Xe concentration from the entire desorption and from only collecting about 90% of the Xe during desorption. The volume from each desorption cycle is tabulated as well. The initial test was 1000 ppmv Xe balanced in air. By selectively collecting 90% of the Xe during the desorption, the average air content in the desorb stream can be reduced from 5% to 0.1%, creating a purer xenon stream. This means the initial carrier gas can effectively be replaced by a more desirable carrier gas in one adsorption/desorption cycle, while also concentrating the Xe. This can be beneficial for downstream processing as Xe capacity can be higher in different carrier gases. Table 3 also shows that as the xenon feed gas concentration increases, the average Xe concentration during desorption increases and the total volume of the effluent stream increases. Yet, by only collecting 90% of the xenon stream, the average concentrations continued to increase through the testing, while the stream effluent volumes decreased. Two major points can be taken away from this study, (1) when the Xe feed gas concentration was increased the average Xe concentration during desorption also increased, supporting the claim that AgZ-PAN can concentrate Xe during desorption and (2) the Xe concentration can be purified and collected in smaller volumes.

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

Xe Feed Gas Concentration (ppmv)	Based on Collection of the Entire Xenon Stream during Desorption		Based on Collection of ~90% of the Xenon Stream during Desorption	
	Average Xe Concentration (ppmv)	Total Volume of Effluent Stream (L)	Average Xe Concentration (ppmv)	Total Volume of Effluent Stream (L)
1,000	1.01×10^4	3.63	1.13×10^4	3.16
10,000	4.01×10^4	11.1	1.26×10^5	3.39
40,000	5.56×10^4	22.74	3.01×10^5	1.88
300,000	1.02×10^5	23.06	6.31×10^5	1.68

Concentration Factors

The Xe feed gas concentration and its respective concentration factor, based on the desorption analysis, is seen in Table 4. The concentration factor was calculated by dividing the average Xe concentration of the column effluent during desorption by the Xe concentration of the test gas used during adsorption for each test. As the Xe concentration in the feed gas increased for each test the concentration factor decreased. Although the concentration factor continued to decrease through the testing, the final test produced a 63% pure Xe stream. The values provide evidence that the Xe fed to the column can be adsorbed and concentrated significantly beyond what was being fed into the system. Additional testing is needed to determine what the limitations are, whether it is the sorbent or test system, for a concentrated Xe stream.

Table 4. Concentration factors achieved from starting Xe feed gas concentration.

Xe Feed Gas Concentration (ppmv)	Concentration Factor Based on Desorption	Concentration Factor Based on Collection of ~90% of Xe Desorption Peak
1000	10.1	11.3
10000	4.0	12.5
40000	1.4	7.5
300000	0.3	2.1

Conclusion

AgZ-PAN can be used to significantly concentrate Xe by performing adsorption-desorption cycles in series. This series of tests indicate there may be practical limitation to the achievable Xe concentration using AgZ-PAN. Additional testing is needed to determine whether the limitation is sorbent or system dependent. Regardless, from this experiment it was found that with four short cycles, a 1000 ppmv Xe in air feed gas could be transformed into a 63% Xe in He stream. From previous AgZ-PAN desorption studies, many different gases have been proven to effectively remove Xe from the column. If adsorption/desorption cycles are performed in series, the carrier gas of the desorbed stream, and thus, the next feed gas stream, may change depending on the gas used to desorb the column. This method could therefore be used to both concentrate Xe and replace its carrier gas stream with an inert gas from which Xe is more easily separated, such as He. While cost of He is prohibitive in large quantities, successive concentration cycles rapidly decrease in size and volume, making He a potentially viable choice.

This study was designed to collect the majority of Xe desorbed from a saturated AgZ-PAN column to prevent loss of Xe. Operations could easily be altered to collect smaller volumes of more concentrated Xe. For example, the last test loaded from a 300,000 ppmv Xe stream yielded a peak concentration of nearly 63% Xe during desorption. This should be considered a proof-of-concept demonstration. Further refinement is required to gather sufficient data to develop optimum operating schemes to integrate into UNF off-gas treatment.

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