

# ***Superficial Velocity Effects on HZ-PAN and AgZ-PAN for Kr/Xe Capture***

**Fuel Cycle Technology**

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U.S. Department of Energy  
Material Recovery and  
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Amy K Welty, Troy G. Garn  
and Mitchell Greenhalgh  
Idaho National Laboratory*

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## SUMMARY

Nearly all previous testing of HZ-PAN and AgZ-PAN was conducted at the same flow rate in order to maintain consistency among tests. This testing was sufficient for sorbent capacity determinations, but did not ensure that sorbents were capable of functioning under a range of flow regimes. For this reason, a series of tests were conducted on both HZ-PAN and AgZ-PAN at superficial velocities between 20 and 700 cm/min. For HZ-PAN, Kr capacity increased from 60 mmol/kg to 110 mmol/kg as superficial velocity increased from 21 to 679 cm/min. Results for AgZ-PAN were similar, with Xe capacity ranging from 72 to 124 mmol/kg over the same range of superficial velocities. These results are promising for scaling up to process flows, demonstrating flexibility to operate in a broad range of superficial velocities while maintaining sorbent capacity.

While preparing for superficial velocity testing it was also discovered that AgZ-PAN Xe capacity, previously observed to diminish over time, could be recovered with increased desorption temperature. Further, a substantial Xe capacity increase was observed. Previous room temperature capacities in the range of 22-25 mmol Xe/kg AgZ-PAN were increased to over 60 mmol Xe/kg AgZ-PAN. While this finding has not yet been fully explored to optimize activation and desorption temperatures, it is encouraging.

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## ACRONYMS

AgZ-PAN	Silver converted mordenite-polyacrylonitrile
D/d	Column diameter/particle diameter
GC-TCD	Gas Chromatograph with Thermal Conductivity Detector
HZ-PAN	Hydrogen mordenite-polyacrylonitrile
I.D.	Internal Diameter
INL	Idaho National Laboratory
K	Kelvin
L/d	Column length/particle diameter
PPMV	Part per million volume
SCCM	Standard Cubic Centimeters per Minute



# EFFECTS OF SUPERFICIAL VELOCITY ON HZ-PAN AND AGZ-PAN GAS CAPTURE CAPACITIES

## 1. Introduction

Previous testing of HZ-PAN and AgZ-PAN sorbents was conducted at a flow rate of 50 sccm and in a column 1.9 cm I.D. (internal diameter) and 22.9 cm length in order to maintain consistent residence times and flow patterns among all tests. Kr and Xe capacities were promising under those test conditions. It was desirable to test the sorbents under a variety of flow regimes for two main reasons. 1) The goal is to provide sorbents flexible enough to operate successfully in a variety of conditions to account for process variations and, more importantly, 2) Maintaining the slowest possible flow rate though adsorption beds provides the longest possible residence times for adsorption at the expense of excessive column diameter in full scale operations, along with a consequent increase in capital expenditure. In order to effectively size an adsorption column for pilot or full scale operation, test columns need to be operated at the expected scale up flow regime [1]. Sorbents that perform effectively over a range of flow rates ensure design flexibility for full scale operation.

## 2. Superficial Velocity Test Design

High pressure gas cylinders with a known gas composition were utilized to supply a feed gas to a sorbent test column via 0.46 cm internal diameter (I.D.) tubing. Feed gas flow was controlled via calibrated MKS mass flow controllers. After exiting the test column, the effluent gas flows to the GC-TCD for analysis. Tubing entering the GC is 0.06 cm I.D., which presents a flow restriction in the system. In order to maintain minimum system pressures and allow the highest possible flow rate through the system, helium was chosen as the carrier gas rather than air, due to its much lower dynamic viscosity. Even with helium gas, system flowrates were limited to 400 sccm for pressure considerations. When pressure drop due to fittings and the packed column are taken into account, the practical flow limit was closer to 325 sccm through the system. In order to allow the greatest range of flow conditions for testing, it was necessary to minimize sorbent column diameter. It was also desirable to use previously tested sorbent samples in order to maintain consistency. Average nominal particle sizes of the sorbents were in the 400-700 micron range.

A thorough investigation of the effects of column and sorbent size [1] was utilized when making test column decisions. Based on average nominal particle sizes of the sorbents in the 400-700 micron range, a column of 7.7 mm I.D. was chosen to allow a packed bed with a reasonable D/d (column diameter/particle diameter) ratio of 11 to 19. Ideally, to avoid channeling D/d should be greater than 20. At the same time, to avoid radial temperature gradients during desorption, where heat is applied through the walls of the column, D/d should be less than five or six. The chosen column diameter of 7.7 mm I.D. struck a balance between the two competing criteria. Column length of 25.4 cm was chosen to maximize sorbent mass while maintaining ease of installation within the confines of the Stirling cooler test apparatus. This length resulted in an L/d (column length/particle diameter) between 36.3 and 63.5, short of the ideal ratio of 100 that would minimize channeling due to wall effects. However, the non-ideality of the test represented a worst-case scenario for the purposes of scaling up to process flow rates.

Previous testing was conducted at 50 sccm through a 1.9 cm I.D., column, resulting in a superficial velocity of 21.3 cm/min. Therefore, one test for each sorbent was chosen to emulate the flow regime from previous testing. While superficial velocity provides a convenient measure for comparison, it does not fully define a flow regime in a packed bed. Packed-bed Reynolds number (Equation 1), which

incorporates superficial velocity, provides a better picture of flow regime [2]. The packed-bed Reynolds numbers for previous tests were calculated from this equation.

$$N_{Re,p} = \frac{\rho_f \bar{V}_0 D_p}{(1 - \varepsilon)\mu} \quad (1)$$

Where:  $N_{Re,p}$  = Reynolds number for a packed bed  
 $\rho_f$  = Fluid density  
 $\bar{V}_0$  = Superficial velocity  
 $D_p$  = Particle equivalent spherical diameter  
 $\varepsilon$  = packed bed void fraction  
 $\mu$  = Fluid dynamic viscosity

Under the test conditions and equipment configuration, this resulted in packed-bed Reynolds number of 2.0, a gas flow regime set firmly in the low laminar range (Table 1).

**Table 1. Reynolds number flow regimes.**

Flow Regime	Reynolds Number Range
Laminar	$N_{Re,p} < 10$
Transitional	$10 \leq N_{Re,p} \leq 2000$
Turbulent	$2000 < N_{Re,p}$

The first test flow rate was chosen to emulate the flow regime from previous testing. To duplicate a packed-bed Reynolds number of 2.0, the first test was conducted with a flow rate of 10 sccm. Subsequent tests were conducted over a range of flow rates in order to determine capacities of HZ-PAN and AgZ-PAN under higher flow rates which still remained in the laminar flow range, followed by flow rates defined as transitional flow regime. Five tests were conducted in a single column for each sorbent, with varying gas flow rates to achieve a wide range of superficial velocities and Reynolds numbers (Table 2).

**Table 2. Superficial Velocity Test Conditions and Flow Regimes**

Flow rate (sccm)	Superficial Velocity (cm/min)	HZ-PAN	AgZ-PAN
		$N_{Re,p}$	$N_{Re,p}$
10	21.2	1.5	1.9
20	42.4	3.0	3.7
80	169.7	12	12
160	339.4	24	24
320	678.9	65	60



## 2.1 HZ-PAN testing considerations

HZ-PAN capacity for Kr has been reported from previous testing at 191K, 220K, and 253K. Previous test results indicate that as temperature decreases, HZ-PAN capacity for Kr increases substantially. In order to keep testing time reasonable while still obtaining adequate data for accurate capacity calculations, it was decided to conduct all HZ-PAN tests at 220K.

## 2.2 AgZ-PAN testing considerations

Previous testing of AgZ-PAN has determined that adequate testing time and Xe capacities occur at ambient temperatures, so all superficial velocity tests for AgZ-PAN were conducted at 295K. Prior testing of AgZ-PAN over several years also revealed a tendency to lose about 65% of its capacity over the course of ten sequential thermal adsorption/desorption cycles (Figure 1).

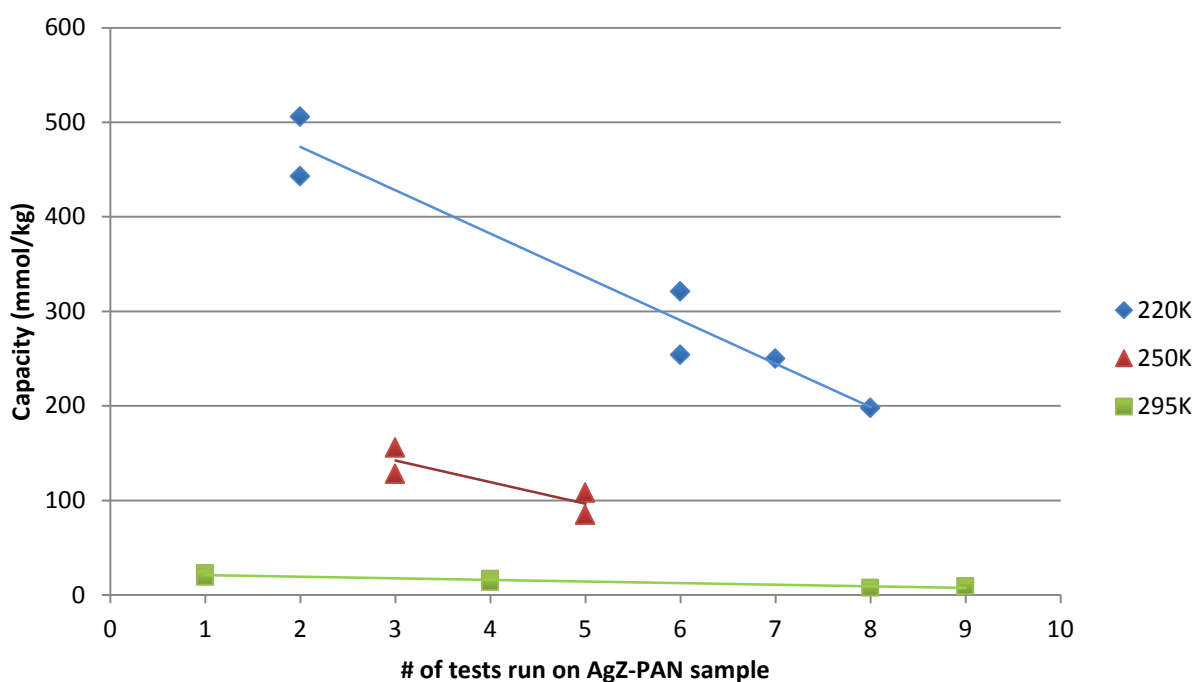


Figure 1. Xe capacity loss over adsorption/desorption cycles at 220K, 250K, and 295K for two different AgZ-PAN samples

The data in Figure 1 represents two different samples of AgZ-PAN. The same capacity trend was seen in each sample tested, regardless of test temperature. Data at 295K was broken out (Figure 2) for clarity.

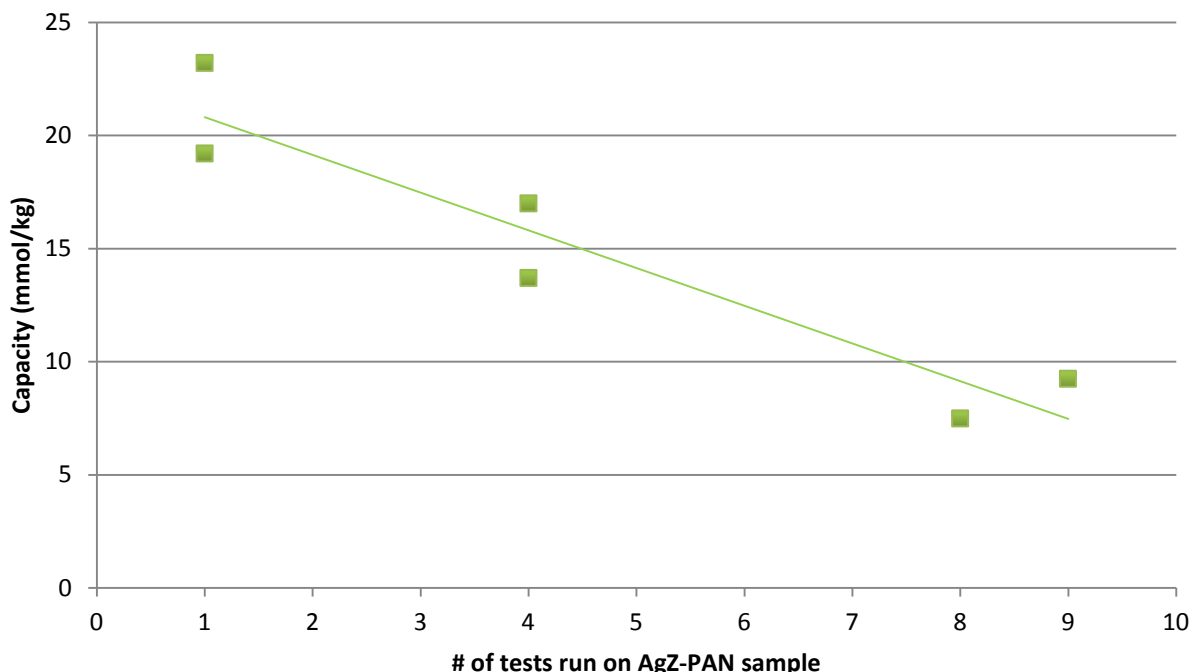


Figure 2. Xe capacity loss over adsorption/desorption cycles at 295K for two different AgZ-PAN samples

For previous desorption operations, the sorbent was desorbed at 370K with He flowing at 50sccm until no Xe remained as indicated by GC spectra. Review of data from all previous testing indicated the possibility of some adsorbed moisture remaining even after several hours of desorption at 370K. It was proposed that an increased desorption temperature had the potential to recover all or part of the original capacity of the sorbent. To test the theory, two different samples of AgZ-PAN that had lost significant capacity were desorbed at 420K for three hours with He flowing at 50 sccm. In both cases, full initial capacity was restored. This was a very encouraging result, as it was previously thought that once AgZ-PAN lost capacity it was not recoverable.

As superficial velocity testing progressed, initial results indicated a marked increase in capacity with increased superficial velocity. However, as tests were repeated, capacity continued to increase with each subsequent test, regardless of the velocity. Further investigation revealed that the desorption method, which simply involved starting the heat tape controller with a setpoint of 420K under Proportional-Integral-Derivative control, was resulting in significant temperature set point overshoot on the surface of the column and, therefore, on the sorbent closest to the column walls inside the column. This intense heat caused a change in the sorbent, resulting in capacities that were double that of previous AgZ-PAN tests. New baseline Xe capacity of AgZ-PAN after high-heat desorption was over 60 mmol/kg, compared to previous baseline capacities between 22 and 25 mmol/kg. The effects of desorption temperature on capacity of AgZ-PAN requires further study to determine optimum desorption conditions to maximize adsorption capacity and sorbent life cycle.

While the dramatic capacity increase was remarkable, it did present a challenge for superficial velocity testing that required subsequent tests. This was mitigated in two ways. Tests were conducted in random order to avoid a potential false trend and the desorption process was changed to avoid further intense heat on the column surface. The heat tape controller was programmed to slowly ramp up temperature to 420K over the course of one hour, followed by a two hour heat soak at 420K. The change provided consistent desorption results without any further altering of the sorbent over the

course of the superficial velocity series of tests. This modified desorption process was used throughout reported superficial velocity tests.

### 3. Effects of Superficial Velocity on HZ-PAN

As superficial velocity was increased by a factor of 32, Kr capacity of HZ-PAN increased by a factor of 1.6 (Figure 3). This is promising for scale-up potential for the sorbent as it indicates flexibility for operations over a variety of flow rates.

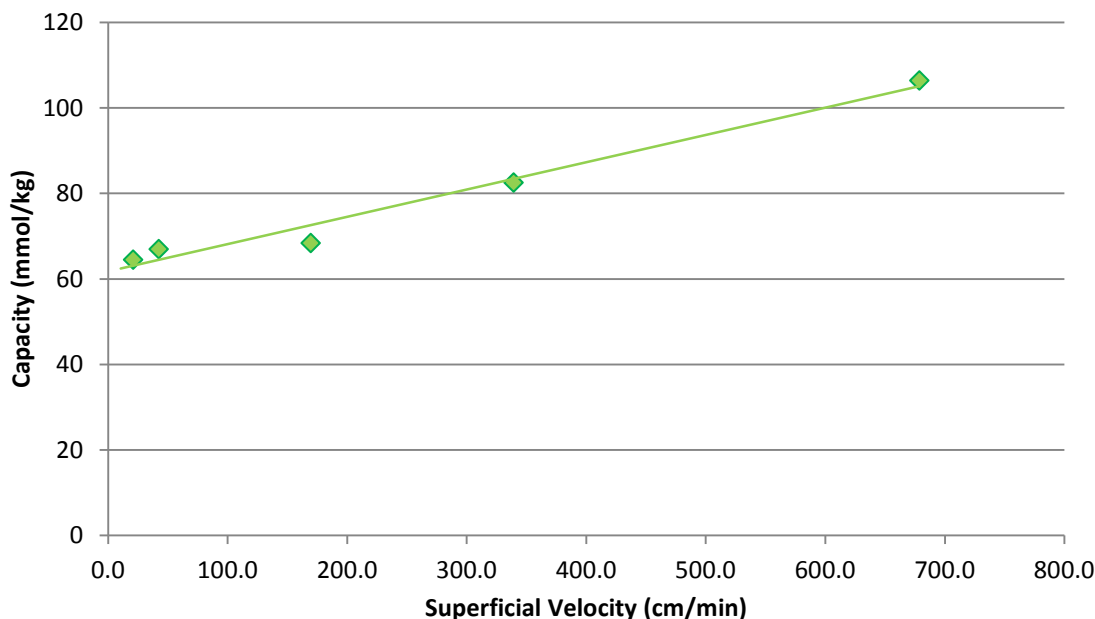


Figure 3. Superficial velocity effects on HZ-PAN Kr capacity, using 2544 ppm Kr in helium at 220K.

At the same time, as superficial velocity increased the amount of total feed gas volume at initial breakthrough of Kr appeared to increase slightly. However, the GC Kr analysis method has a seven minute lag between analyses, causing increasing uncertainty for initial breakthrough as flow rate increases. At the lowest superficial velocity 70 mL passed through the column between analyses, whereas at the highest superficial velocity 2240 mL passed through the column between analyses. Regardless, total volume of feed gas through the column at initial breakthrough was affected little, if at all, by increasing superficial velocity.

### 4. Effects of Superficial Velocity on AgZ-PAN

AgZ-PAN Xe capacity increase with increased superficial velocity was similar to that of Kr capacity on HZ-PAN. As superficial velocity increased by a factor of 32, Xe capacity increased by a factor of 1.7 (Figure 4).

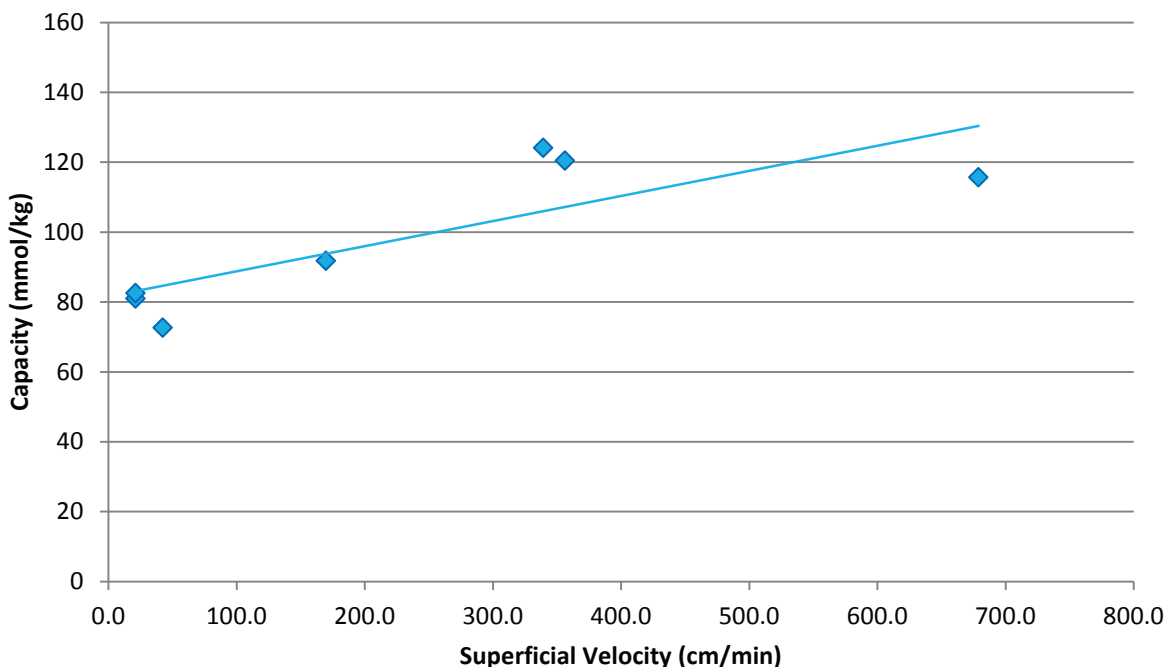


Figure 4. Effects of superficial velocity on AgZ-PAN Xe capacity using 1040 ppm Xe in helium at 295K.

Total feed gas volume through the column before initial breakthrough appeared to increase substantially. However, the GC Xe analysis method has a time lag of over 10 minutes between analyses. At the lowest superficial velocity 103 mL passed through the column between analyses, whereas at the highest superficial velocity 3280 mL passed through the column between analyses, causing sufficient uncertainty that this may not be a real effect. However, even assuming the worst case of initial breakthrough occurring ten minutes prior to the first observed initial breakthrough, it was apparent that increased superficial velocities in the range tested still had a slight positive effect on initial breakthrough volume.

## 5. Conclusions

For both HZ-PAN and AgZ-PAN, superficial velocity increases caused an increase in sorbent capacity for the sorbate of interest while at the same time causing little, if any, effect on the total feed gas volume prior to initial breakthrough of sorbates of interest. These results bode well for future scale-up to pilot and full-scale plant operating conditions, indicating that the sorbents will perform well over a variety of flow regimes. This will allow much more flexibility for equipment sizing and operations.

## 6. Recommendations

Further testing should be conducted to ensure both sorbents will behave as expected during scale up. Conditions for further testing should be based upon flow conditions expected in a full-scale facility to ensure proper column design.

Desorption modifications during preliminary superficial velocity testing resulted in capacities over twice as high as those previously seen on AgZ-PAN. A multi-pronged approach should be taken for

further exploration. Optimum activation conditions for AgZ-PAN need to be determined to maximize sorbent capacity while maintaining sorbent integrity. Desorption conditions for AgZ-PAN also need to be explored further to determine the optimum temperature and time to maintain maximum sorbent capacity while minimizing sorbent damage. Additionally, tests to determine expected AgZ-PAN life cycle should be conducted in order to evaluate operating costs.

## **7. References**

1. W. J. Thomas and B. Crittenden, Adsorption Technology & Design, Elsevier Science & Technology Books, 1998.
2. R. H. Perry, Perry's Chemical Engineers' Handbook, Sixth Edition, McGraw-Hill, 1984.