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Pressure Swing and Thermal Swing Adsorption Capacity Comparisons for Kr and Xe using AgZ-PAN and HZ-PAN Sorbents

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SUMMARY

Pressure Swing Adsorption (PSA) tests were performed utilizing both the HZ-PAN and AgZ-PAN sorbents. The results were then compared with the previous Thermal Swing Adsorption (TSA) results for both Kr and Xe. The two different engineered form sorbents were evaluated for Kr and Xe capacities at ambient temperature and 20 psig pressure in PSA operations. The AgZ-PAN showed an increase of more than three times capacity for Xe when compared to TSA operations without pressure and a small Kr capacity increase was observed. The HZ-PAN sorbent had no capacity for either Kr or Xe at ambient temperature with TSA operations however; under 20 psig PSA operations, it obtained capacities of 27 mmol/kg and 2.9 mmol/kg for Xe and Kr respectively. The selectivities of Xe relative to Kr were also calculated for the sorbents. The results of these tests indicate that PSA operations can be utilized to increase the capacities of both Kr and Xe under ambient conditions with the sorbents tested.

CONTENTS

TABLES

ACRONYMS

AgZ-PAN	Silver engineered form sorbent
BET	Brunauer, Emmett, and Teller theory
GC-TCD	gas chromatograph with thermal conductivity detector
HZ-PAN	Hydrogen engineered form sorbent
INL	Idaho National Laboratory
K	Kelvin (°C + 273.15)
Kr	krypton
PSA	Pressure Swing Adsorption
psig	pounds per square inch gauge
TSA	Thermal Swing Adsorption
UNF	Used Nuclear Fuel
Xe	xenon

1. Pressure Swing and Thermal Swing Capacity Comparison for Kr and Xe using AgZ-PAN and HZ-PAN Sorbents

1.1 Introduction

The physical adsorption process has been selected for further evaluation for the capture of krypton and xenon from Used Nuclear Fuel (UNF) reprocessing off-gas streams. Physical adsorption processes can be operated in either thermal swing adsorption (TSA) or pressure swing adsorption (PSA) operations or a combination of both. A series of evaluations have previously been reported [1,2] utilizing TSA operations on two INL developed adsorbents with promising results under certain conditions.

In support of the DOE sponsored Off-Gas Sigma Team, PSA tests were performed utilizing both the HZ-PAN and AgZ-PAN sorbents. The results were then compared with previous TSA results for both Kr and Xe capacities. The delivery of this report satisfies milestone M3FT-13IN0312024.

1.2 Purpose and Scope

The purpose of these investigations was to perform PSA operations to determine the capacities for Kr and Xe utilizing the same sorbents that have previously been evaluated with TSA operations and compare the results. The results will provide information that will be used to determine if one operation provides any advantages over the other for the capture of Kr and Xe.

AgZ-PAN and HZ-PAN were both evaluated under PSA conditions and the results were then compared with the TSA results. These two sorbents were previously evaluated with TSA operations and their preparation was described in previous reports.[1,2] This report does not include any evaluations with metal-organic framework materials due to time constraints. All evaluations were performed at ambient temperature and 20 psig pressure.

1.3 AgZ-PAN Kr and Xe Evaluations

The AgZ-PAN sorbent material was prepared as previously described[1] and 4.75 grams of the activated material was loaded into the cryostat cold column. This material was activated again at 100°C for 6 hours with He gas flowing at 50 sccm. A test was performed with a feed gas of 150 ppm Kr, 1000 ppm Xe with the balance being air and a flowrate of 36 sccm. The cryostat was maintained at a temperature of 295 K and the pressure inside the system was held at 20 psig throughout the test. The column effluent was monitored via a gas chromatograph with a thermal conductivity detector (GC-TCD). The GC data was utilized to make a breakthrough curve for each Kr and Xe. The breakthrough curves were then evaluated to find the area under the curve and determine the capacity for each species. An additional test was performed under the same conditions, adjusting only the feed gas flowrate to 50 sccm. Two evaluations were also performed on the same sorbent at atmospheric pressure and ambient temperature for comparison at a feed gas flowrate of 50 sccm.

Table 1: Comparison of PSA and TSA Kr and Xe adsorption on AgZ-PAN at 20 psig and 295K

Test and pressure (psig)	Temperature (K)	Flowrate (sccm)	Xe Capacity (mmol/kg)	Kr Capacity (mmol/kg)	Selectivity (Xe relative to Kr)
1 (0 psig)	295	50	6.32	none	none
2 (0 psig)	295	50	10.2	none	none
3 (20 psig)	295	36	38.7	2.70	2.19
4 (20 psig)	295	50	34.6	2.72	1.94

The results of these tests along with the test conditions are shown in Table 1. It can be seen from the table that the PSA operation at ambient temperature increases the Xe capacity more than three times than at ambient pressure and a small Kr capacity was also observed at 20 psig. The selectivity of Xe relative to Kr was also calculated for tests where both Xe and Kr capacities were obtained using Equation 1:

$$Sel_{Xe,Kr} = \frac{X_{Xe}/Y_{Xe}}{X_{Kr}/Y_{Kr}} \qquad (1)$$

Where X_{Xe} and X_{Kr} are mol fractions of Xe and Kr in the adsorbed phase, and Y_{Xe} and Y_{Kr} are mol fractions of Xe and Kr in the bulk phase.

1.4 HZ-PAN Kr and Xe Evaluations

The HZ-PAN sorbent material was prepared as previously described[2] and 4.61 grams of the activated material was loaded into the cryostat cold column. This material was activated again at 85°C for 18 hours with He gas flowing at 50 sccm. Two tests were performed with a feed gas of 150 ppm Kr, 1000 ppm Xe with the balance being air at a flowrate of 50 sccm. The cryostat was maintained at a temperature of 295 K and the pressure inside the system was held at 20 psig throughout the tests. The sorbent capacities for each test were obtained in the same manner as described previously.

Table 2 contains the results of the PSA evaluations of the HZ-PAN sorbent along with the results of the previously obtained TSA results from the same sorbent under similar conditions. The results show that at ambient temperature and pressure, capacities for Xe and Kr were not observed. At 20 psig pressure however, the sorbent had a Xe capacity of 27 mmol/kg and Kr capacity of 2.9 mmol/kg. The selectivity of Xe relative to Kr was also calculated for tests where both Xe and Kr capacities were obtained using Equation 1 and are included in the table.

Table 2: Comparison of PSA and TSA Kr and Xe adsorption on HZ-PAN at 20 psig and 295K

Test and pressure (psig)	Temperature (K)	Flowrate (sccm)	Xe Capacity (mmol/kg)	Kr Capacity (mmol/kg)	Selectivity (Xe relative to Kr)
1 (0 psig)	295	50	none	none	none
2 (20 psig)	295	50	27.9	2.91	1.47
3 (20 psig)	295	50	26.3	2.92	1.38

1.5 Conclusions

Two different engineered form sorbents HZ-PAN and AgZ-PAN were evaluated for Kr and Xe capacities at ambient temperature and 20 psig pressure in PSA operations. The AgZ-PAN showed an increase of more than three times capacity for Xe when compared to similar TSA operations without pressure and a small Kr capacity was observed. The HZ-PAN sorbent had no capacity for either Kr or Xe in TSA operations however, under 20 psig PSA operations, capacities of 27 mmol/kg and 2.9 mmol/kg for Xe and Kr respectively were obtained. The results of these tests indicate that PSA operations can be utilized to increase the capacities of both Kr and Xe with the sorbents tested. The capacities and selectivities were similar for the two sorbents indicating a very small advantage of AgZ-PAN over the HZ-PAN for Xe capacity. Additional evaluations with a combination of PSA and TSA operations are needed to investigate the capacity and selectivity advantages of combining the two operations in the future.

1.6 References

1. TROY GARN, MITCHELL GREENHALGH, JACK LAW, “FY-12 INL Krypton Capture Activities Supporting the Off-Gas Sigma Team,” FCRD-SWF-2012-000252, August 2012.
2. MITCHELL GREENHALGH, TROY GARN, KRISTI CHRISTENSEN, VERONICA RUTLEDGE, JACK LAW, “Summary of FY-11 Krypton Capture Activities at the Idaho National Laboratory,” FCRD-SWF-2011-000312, August 2011.