Summary of FY-11 Krypton Capture Activities at the Idaho National Laboratory

Mitchell Greenhalgh
Troy G. Garn
Kristi Christensen
Veronica Rutledge
Jack D. Law

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Idaho National Laboratory
Fuel Cycle Research & Development
Idaho Falls, Idaho 83415

http://www.inl.gov

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ABSTRACT

Dissolution and voloxidation steps performed in the nuclear fuel reprocessing cycle result in the production of radioactive fission products in their respective off-gas streams. Various isotopes of Kr and Xe are included in the composition of the off-gas radioactive constituents. Depending on the fuel cooling times, Kr-85, with a half-life of 10.7 years may need to be captured per EPA regulations for radioactive emissions. This report includes the results of the ongoing investigations into the solid phase adsorption of Kr, specifically using thermal swing operation, as part of the Off-Gas Sigma Team effort. Experimental results produced from sorbent capacity evaluations have been included. Additionally, Kr adsorption isotherms were produced at two test temperatures to assist with modeling efforts. A final task was to define a strategy for legacy samples obtained from historical Kr immobilization experiments performed in the late '70's at the INL. The results reported herein will be included in a compiled final report describing the work completed by the Off-Gas Sigma team members in FY-11.

ACRONYMS

Å	Angstroms
ANL	Argonne National Laboratory
BET	Brunauer, Emmet and Teller
DFT	Density Functional Theory
FY	Fiscal Year
GC	Gas Chromatograph
HIPed	Hot Isostatically Pressed
ICPP	Idaho Chemical Processing Plant
INL	Idaho National Laboratory
MFC	Mass Flow Controller
MOF	Metal Organic Framework
NDA	Non Destructive Analysis
NEAMS	Nuclear Energy Advanced Modeling and Simulation
ORNL	Oakridge National Laboratory
PI	Pressure Indicating
SafeSeps	Safeguards and Separations
sccm	Standard cubic centimeter per minute
SNL	Sandia National Laboratory
TCD	Thermal Conductivity Detector
UHP	Ultra High Purity

SEPARATIONS AND WASTE FORMS
SUMMARY OF FY-11 KRYPTON CAPTURE ACTIVITIES AT THE IDAHO NATIONAL LABORATORY

1.   INTRODUCTION

This report summarizes the Kr capture activities completed in FY-11 at the INL. This work is a continuation of the previous activities from FY-09 and FY-10 in support of the Off-Gas Sigma Team objectives. The main goal of this activity is to evaluate selected solid sorbents for their feasible use for effective ^{85}Kr capture from used nuclear fuel reprocessing off-gas streams, most specifically fuel dissolution and voloxidation processing steps.

In FY-10, a custom built cryostat system was procured and installed at the INL to enable sorbents to be evaluated at temperatures from 150 to 500K with sorbent bed sizes ranging from 2 to 600 grams. Sorbents were evaluated with various gases containing Kr, Xe, N_2 and He at 190K. The initial sorbents evaluated were commercially available sorbents IONEX Ag-900 and Ag-mordenite "light phase" obtained from ORNL. A newly synthesized sorbent developed at the INL was also tested, herein referred to as FY-10 sorbent. Initial results were promising with the FY-10 sorbent, therefore most of the adsorption evaluations were performed with it.

Primarily using the FY-10 sorbent, evaluations were designed to elucidate the capacity for Kr in the presence of both Xe and N_2. Four additional feed gases were acquired and utilized for the testing containing various compositions of Kr, Xe and N_2 with a He balance. The sorbent was activated under vacuum at 150° C for 18 hours to remove any residual water from the micropores prior to being placed in the cryostat. All evaluations were performed in the cryostat system where the column effluent was analyzed with a gas chromatograph (GC) for Kr, Xe and N_2 concentrations. Kr capacities were calculated from breakthrough curves generated from GC data. Kr adsorption isotherms on the FY-10 sorbent were also obtained to supply the NEAMS SafeSeps program with initial Kr adsorption data to support modeling development.

As a secondary project goal, a ^{85}Kr Legacy Sample Analysis Strategy was prepared to define a logical analysis plan for the legacy samples acquired in FY-10. These samples were prepared in the late 70's while testing Kr immobilization using zeolite 5A material. The Kr was separated from the aluminum fuel dissolution process off-gas via the cryogenic distillation process at the Idaho Chemical Processing Plant (ICPP) at the INL. The separated Kr gas product was stored in pressurized cylinders and was used for the immobilization tests. Some of the Kr adsorbed 5A material was Hot Isostatically Pressed (HIPed) in a glass matrix. Small samples of loose zeolite material and HIPed zeolite material are now archived at the INL and have experienced more than three 10.7 year ^{85}Kr half-lives of decay. The analysis strategy was developed to ensure that the invaluable waste form information these samples could provide would be maximized while performing sequential analysis steps.

2.   KRYPTON SORBENT EVALUATIONS

2.1   Equipment/Gases/Materials

The adsorption test equipment consists of the following; a feed gas mass flow controller (MFC) calibrated for a 0-100 sccm/minute flow rate, the custom cryostat column and a GC utilizing a Supelco carboxen 1010 plot fused silica capillary column with a thermal conductivity detector (TCD) to monitor the column effluent. A system flow diagram is shown in Figure 1. This equipment was employed for all adsorption evaluations performed in FY-11.
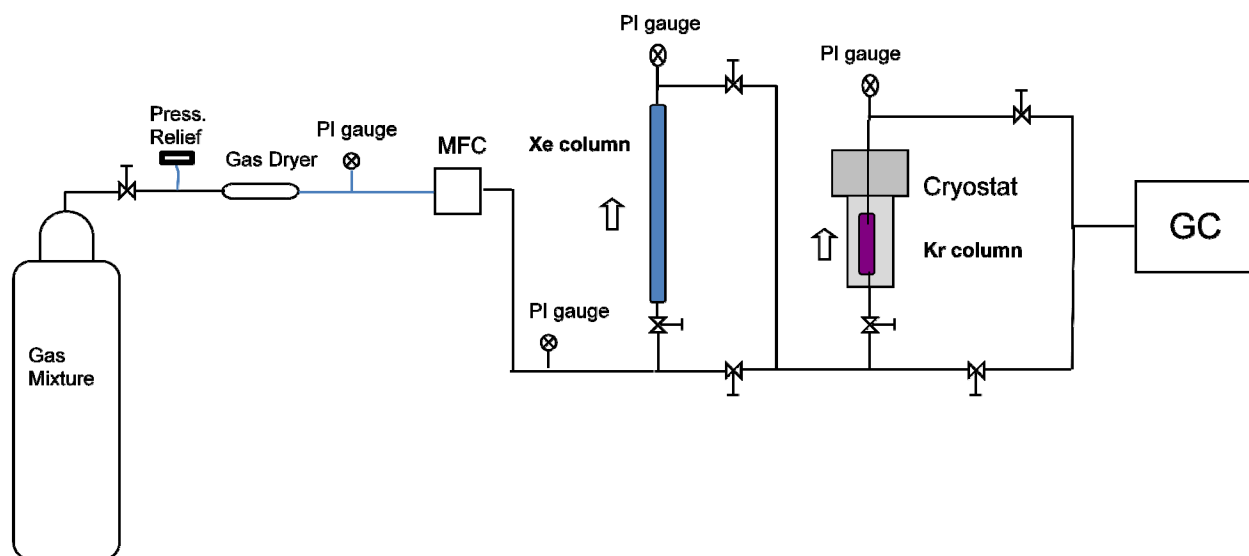
Figure 1. System flow diagram

To investigate the effects of competition/selectivity with N_2 and Xe on Kr capacity, a total of seven different gas mixtures were available with varying compositions of Kr, Xe, N_2 and He, these gases were utilized for selectivity and isotherm testing. Concentrations of the respective individual components are 150 ppm Kr, 1000 ppm Xe and 79% N_2 with the balance made up with He. These concentrations were chosen to represent fission product off-gas concentrations in a fuel reprocessing facility. Concentration calibrations for all test gases were performed using the GC prior to use.

Three sorbent materials were tested during the year. FY-10 sorbent and FY-11 sorbent, both synthesized at the INL, and NC-77 material developed at Sandia National Laboratory (SNL). Prior to testing, each material was analyzed for surface area and porosity using a Micrometrics ASAP 2020 surface area analyzer.

Initial adsorption tests were performed at ambient temperature to evaluate the efficacy for either Kr or Xe capture using test gases with or without N_2. Ambient temperature tests with the NC-77 material indicated no measurable capacity for either Kr or Xe, so its evaluation was discontinued. The FY-11 sorbent was synthesized mainly to evaluate Xe capacity, as such its use was primarily to act as a guard column for Xe removal. Minimal testing was completed at ambient temperature with the sorbent for evaluation as guard column material, however, more testing is warranted as initial tests were inconclusive. Initial ambient test results using the FY-10 sorbent indicated there was a measurable capacity for Kr and Xe, thus the bulk of testing throughout the year focused on evaluating this sorbent. The following experimental section includes a description of the testing performed using the FY-10 sorbent.

2.2   Experimental

The FY-10 sorbent was prepared and sieved to a particle size range of 355-850 μm. Analysis of the surface area and porosity was performed to confirm material preparation did not affect the porosity of the sorbent. The sorbent was activated by heating to 150° C for 18 hrs under 20 inches of Hg vacuum. This activation was performed to ensure all of the residual water was removed from the micropores prior to use. A mass of 5.02 grams of the activated sorbent was placed into the cryostat cold column which was

then installed in the cryostat apparatus. All tests performed during the year were performed on the same sorbent while the gas compositions and temperatures were varied. Periodically during the testing, the sorbent Kr capacity was measured using a "baseline" parameter test with 150 ppm Kr in He feed gas at 190K to monitor the effects of adsorption/desorption thermal cycling on sorbent performance.

The experimental procedure was performed in the same manner for each test. The cryostat was cooled to the desired temperature with Ultra High Purity (UHP) He flow at ~ 70 sccm/min. Once the system had reached the selected temperature set point, the He was turned off and the desired feed gas was introduced into the cryostat column with a cross-sectional area of 0.713 cm^2 at flowrates ranging from 50 - 72 sccm/min. The column effluent was monitored with the GC until a minimum of ~ 90% breakthrough was attained as indicated by GC peak areas. This would complete the adsorption phase of the experiment. At breakthrough, the feed gas was stopped, the He flow was started and the cryostat was heated to 316K for desorption. This phase was continued until there was no detectable Kr, N_2 or Xe on the GC chromatogram. The detection limit of the GC for Kr, Xe and N_2 was ~ 10 ppm. The experiments were designed for two different purposes; the first was to evaluate the impacts of Xe and N_2 on the Kr capacity at 190K, and the second was to obtain the necessary data to create Kr adsorption isotherms at 190 and 222K. The isotherm data was supplied to NEAMS SafeSeps program in support of their modeling efforts. Table 1 summarizes the variety of tests performed throughout the year

To determine the correct capacity of each sorbent by accounting for gas dilution by volume, tests were performed at room temperature with selected gases.   The time required for the gas concentration at the effluent of the cryostat to match the calibrated concentration of the feed gas was measured. This information was used to determine correction factors to account for the effects of dilution in the system. These correction factors were included in the final Kr/Xe capacities reported in Tables 3 and 4.

Table 1. Summary of Kr adsorption test on FY-10 sorbent, sorbent mass 5.02g

Adsorption Temperature (K)	Feed Gas Composition
190	150 ppm Kr in He
190	150 ppm Kr 79% N2 in He
190	150 ppm Kr, 1020 ppm Xe in He
190	150 ppm Kr, 999 ppm Xe, 79.1% N2 in He
190	84.5 ppm Kr in He
190	111 ppm Kr in He
190	333 ppm Kr in He
190	889 ppm Kr in He
190	1675 ppm Kr in He
190	2544 ppm Kr in He
222	150 ppm Kr in He
222	861 ppm Kr in He
222	1707 ppm Kr in He
222	2544 ppm Kr in He

Breakthrough curves are generated by plotting the concentration of the constituent of interest (C) in the column effluent as a function of the volume (*v*) of gas processed. The collected breakthrough curves are used to calculate the sorbent capacity (SC) for each constituent in the feed gas. The sorbent capacities are calculated from the following equation:

$$SC = \int_0^V \frac{(C_0 - C)}{M} dv \qquad (1)$$

Where:

V = total volume processed at breakthrough, liters

C_0 = concentration in feed, mol/L

C = concentration in effluent at *v*, mol/L

M = sorbent mass, grams

Because C_o and M are constant, Equation 1 can be rewritten as:

$$SC = \frac{1}{M}\left(C_oV - \int_0^V Cdv\right) \qquad (2)$$

The statistical software TableCurve®, from Jandel Scientific, was used to find the best-fit for equations representing the breakthrough curves. The software was used to define the area below the breakthrough curve to obtain the value for the last term in Equation 2. This result was then subtracted from the total area C_oV to give the amount of Kr and Xe adsorbed on the material. The adsorbed amount was then divided by the sorbent bed mass to give a final sorbent capacity in mol Kr or Xe/grams sorbent. An example breakthrough curve using GC generated data for Kr, Xe and N_2 can be seen in Figure 2. From this curve it is apparent that the nitrogen breaks through first followed by the Kr and finally Xe for the sorbent tested. The results of the fiscal year's testing are presented in the following section.
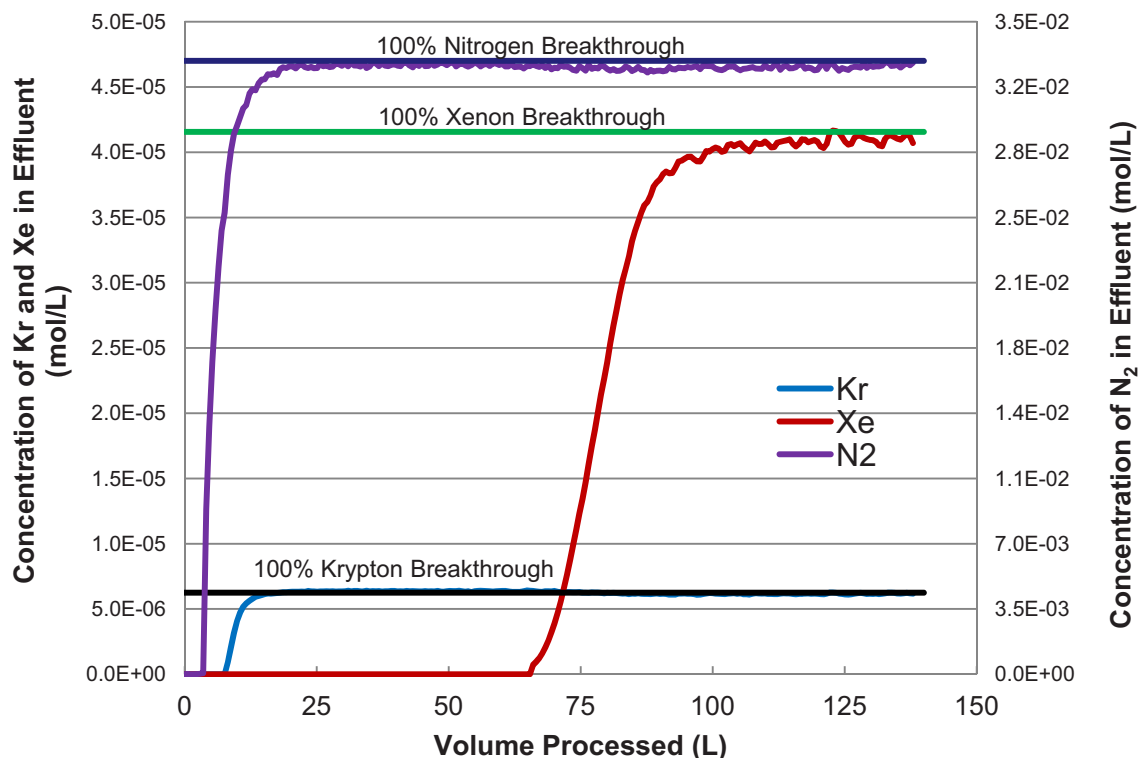

Figure 2. Example breakthrough curves

2.3   Results and Discussion

2.3.1   Surface Area and Porosity Results

Measurements of the surface area and microporosity were performed on all of the available sorbents with a Micromeritics ASAP 2020 utilizing N_2 adsorption. Using Brunauer, Emmet, and Teller (BET) and Langmuir theories, surface areas were calculated while micropore area and volume in the range of 4-10 angstroms (Å) were determined from the Density Functional Theory (DFT). The 4-10 Å range is reported because the relative diameters of Kr, Xe and N_2 are within this range. The results indicate both Ag-mordenite sorbents have lower surface area, micropore surface area and micropore volumes than the INL sorbents. The reduced surface area and micropore volumes are likely due to the pelletization process used for Ag-mordenite production. Although the NC-77 has a high surface area, its micropore area and volume are quite low in the 4-10 Å range. The results of the surface area and porosity analyses are located in Table 2 for all of the sorbents.

Table 2. Surface area and porosity results

Sorbent	BET surface area (m^2/g)	Langmuir surface area (m^2/g)	DFT micropore area (m^2/g)	DFT micropore volume (cm^3/g)
IONEX Ag900	14	N/A	2.4	0.001
Ag-mord-LP	59	N/A	40	0.01
NC-77	298	398	39	0.01
FY-10	336	440	427	0.1
FY-11	80	104	128	0.03

2.3.2   FY-10 Sorbent Capacity Results

To test the effects of Xe and N_2 on Kr adsorption, the FY-10 sorbent was evaluated with four feed gases at 190K. The reported Kr (and Xe if present) sorbent capacities were calculated using breakthrough curves generated from the GC data using the previously described technique. The MFC utilized for these tests was factory calibrated for a 79% N_2 and 21% He mixture. It was set to 50 sccm/min for each test. For gases without N_2, the flowrate was calculated using the appropriate gas correction factors supplied by the manufacturer. This adjustment resulted in an actual flowrate of 69 sccm/min for these gases. This change in actual flow results in a larger total volume being processed and hence, a slight increase in the capacities in comparison to those previously reported. The results are reported in Table 3 and indicate as expected that both Xe and N_2 affect the Kr capacity. The sorbent demonstrated a reasonable capacity for Kr in the absence of N_2 and Xe, however, the presence of N_2 decreased the Kr capacity by nearly three orders of magnitude while Xe lowered it by only one order of magnitude. This suggests that the Kr capacity of the sorbent is impacted more by the presence of high concentration N_2 than by Xe. It is interesting to note that in the presence of both Xe and N_2, the Kr capacity was reduced by only two orders of magnitude. More evaluations are needed to better understand this phenomenon and to investigate the potential of removing the N_2 from the gas stream to increase Kr capture. The FY-10 sorbent Kr capacities reported below for a Kr/He gas mixture are speculatively higher than those reported in previous literature. The speculation arises from not enough information being included in previous literature as to the actual

physical characteristics of the sorbent tested i.e. powder form, engineered form, etc. The FY-10 sorbent is in an engineered form desirable for use in actual process applications.

Table 3. FY-10 sorbent capacity results, sorbent mass 5.02g

Feed gas mixture	Kr Capacity (mol/g)	Xe Capacity (mol/g)
Kr/He	1.04e-4	N/A
Kr/N$_2$/He	5.83e-7	N/A
Kr/Xe/He	1.13e-5	1.10e-3
Kr/Xe/N$_2$/He	7.67e-6	6.36e-4

2.3.3   Adsorption/Desorption Effects

The same 5.02 gram mass of FY-10 sorbent was utilized for all evaluations during the year. Intermittently, baseline tests using the Kr/He feed gas, at 150 ppm Kr and 190K, were performed on the sorbent. These tests were intended to ensure that the adsorption/desorption thermal cycles were not impacting the sorbent capacities. If the Kr breakthrough curve and calculated capacity remains relatively unchanged after undergoing multiple thermal cycles, the sorbent's thermal stability and cycling assets are validated. Figure 3 is a compilation of the "baseline" breakthrough curves from these tests. It can be seen from the graph that the sorbent's breakthrough curve remained the same over the course of the testing. Table 4 lists the calculated capacities of Kr for each test and indicates that they are in excellent agreement with each other.
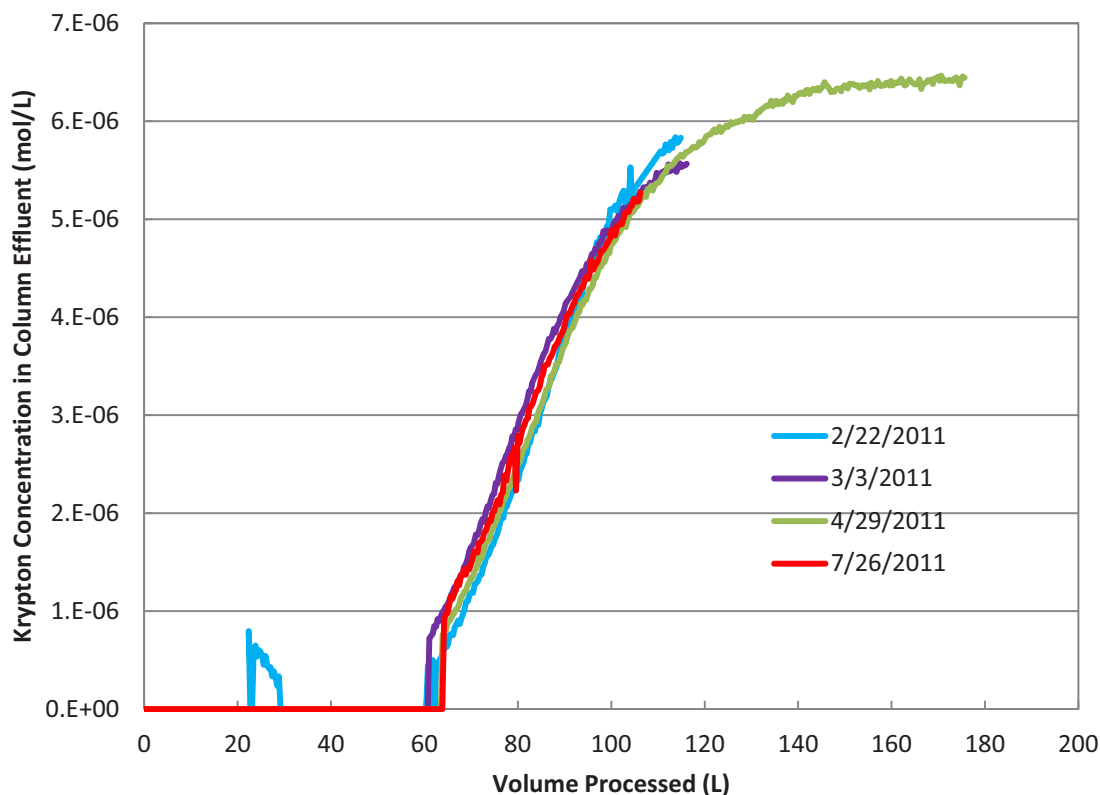
Figure 3. Baseline feed gas breakthrough curves

Table 4. Kr capacities of sorbent baseline tests, 150 ppm Kr at 190K

Test Date	Kr capacity (moles/g sorbent)	Breakthrough (%)
02/22/2011	1.02e-4	93.8
03/03/2011	1.00e-4	89.5
04/29/2011	1.12e-4	100
07/26/2011	1.00e-4	84.7

At the conclusion of all the testing, the FY-10 sorbent was removed from the cryostat cold column. The sorbent visually appeared to be in the same condition as when it was first placed in the system. A mass measurement indicated all 5.02 grams were recovered. The relatively unchanged physical structure together with no mass lost reveals that the sorbent held up well to the thermal cycling and is quite robust for operating conditions tested. A final surface area and porosity analysis was completed on this cycled sorbent with results indicating negligible change when compared with the initial analysis. Figure 4 is a picture of the sorbent upon removal from the cryostat. The slight yellowish discoloration was noted prior to use, resulting from the initial activation sequence.
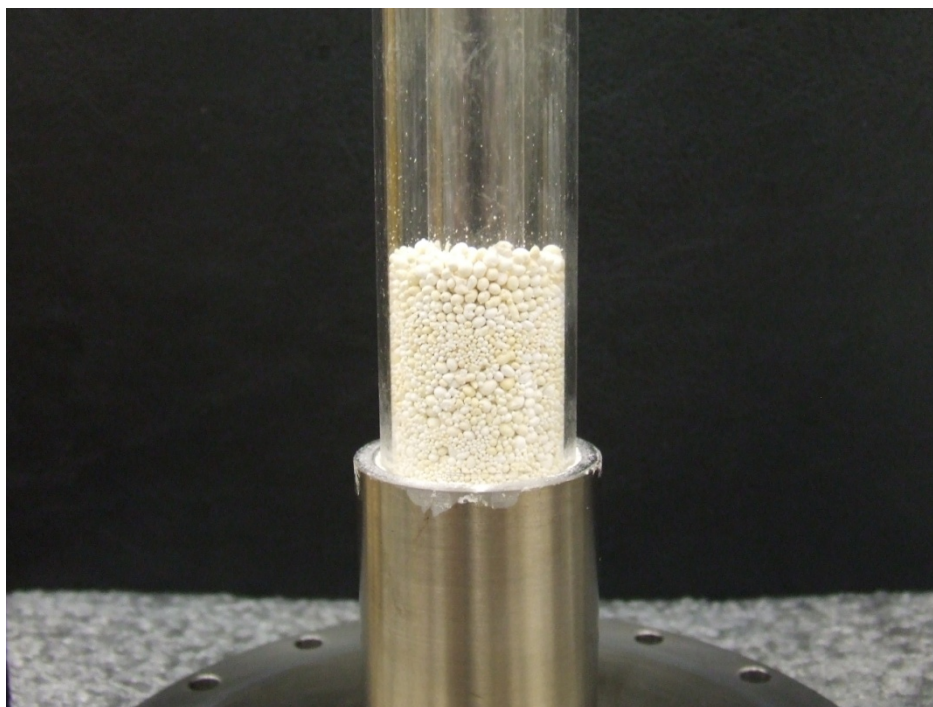
Figure 4. Photo of the sorbent removed from the cryostat after multiple cycles

2.3.4   Kr Adsorption Isotherms

In support of the NEAMS SafeSeps modeling effort, two Kr adsorption isotherms were generated. Isotherm data was collected at temperatures of 190K and 220K, with feed concentrations ranging from 75 ppm to 2544 ppm Kr in helium. Kr feed concentration was varied by adding a second MFC to the system shown in Figure 1, and diluting the 2544 ppm Kr feed gas using helium to the desired concentration.

The purpose of the isotherms is to provide experimentally measured values for equilibrium parameters to be used as input data for modeling. It was determined that the Langmuir equilibrium isotherm was the best fit for the data set. The Langmuir equilibrium model is written as:

$$q = \frac{q_{max}K_{eq}C}{1+K_{eq}C} \tag{3}$$

Where q is the sorbent capacity at equilibrium with feed concentration (C), q_{max} is maximum capacity of the sorbent at the specified temperature, and K_{eq} is the equilibrium constant. The values for q_{max} and K_{eq} at 190K and 220K are reported in Table 5. The isotherm data and corresponding Langmuir fits are shown in Figure 5.

Table 5. Equilibrium parameters

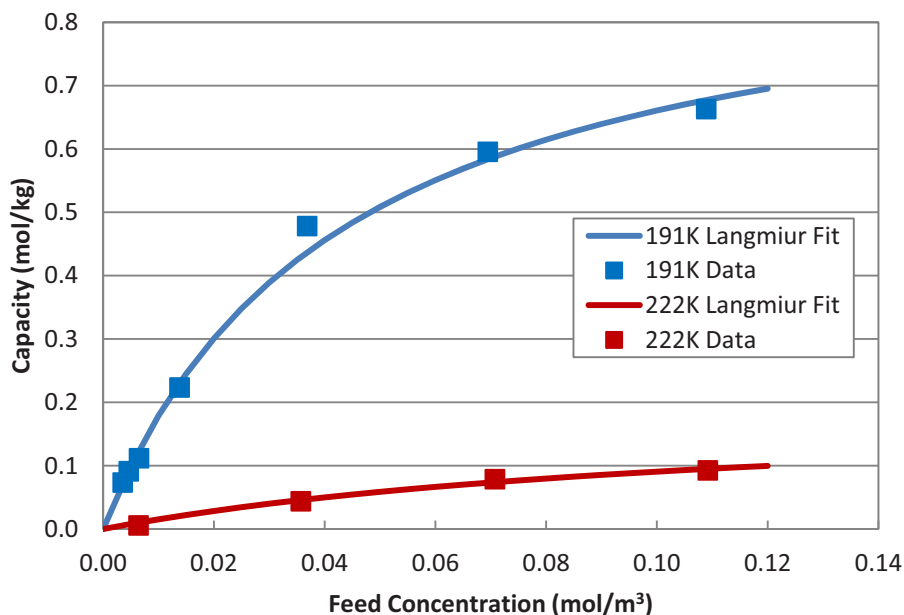| Temperature	q_{max} (mol/kg)	K_{eq} (m^3/mol)
191K	0.94	23.4
220K	0.20	8.4

Figure 5. Equilibrium isotherms

3.   [85]Kr LEGACY SAMPLE ANALYSIS

A [85]Kr Legacy Sample Analyses Strategy was prepared during the FY-11 activities. This plan is intended to ensure a logical analysis sequence is followed so that the invaluable waste form information will not be jeopardized over the course of the performed analyses. The general sequence of the work will be in three stages as shown in Figure 6. Stage one will include non destruction analysis (NDA) characterization of the samples (radiation levels, contamination levels and gamma signature) and neutron imaging. The initial characterization and imaging will support the selection of the handling facilities for un-packaging/disassembly and sub-sampling, the development of a disassembly plan, the development of shipping plans and the initial identification of facilities for sample analysis. Stage two is the un-packaging/gas sampling/disassembly/sub-sampling and packaging for shipment to the analysis sites. The final stage is the analysis of the subsamples at the appropriate laboratories. Analyses of these legacy samples is expected to give valuable information as to the state of the samples, corrosion of the containers and the potential radiation damage to the crystal structure of the zeolite material.
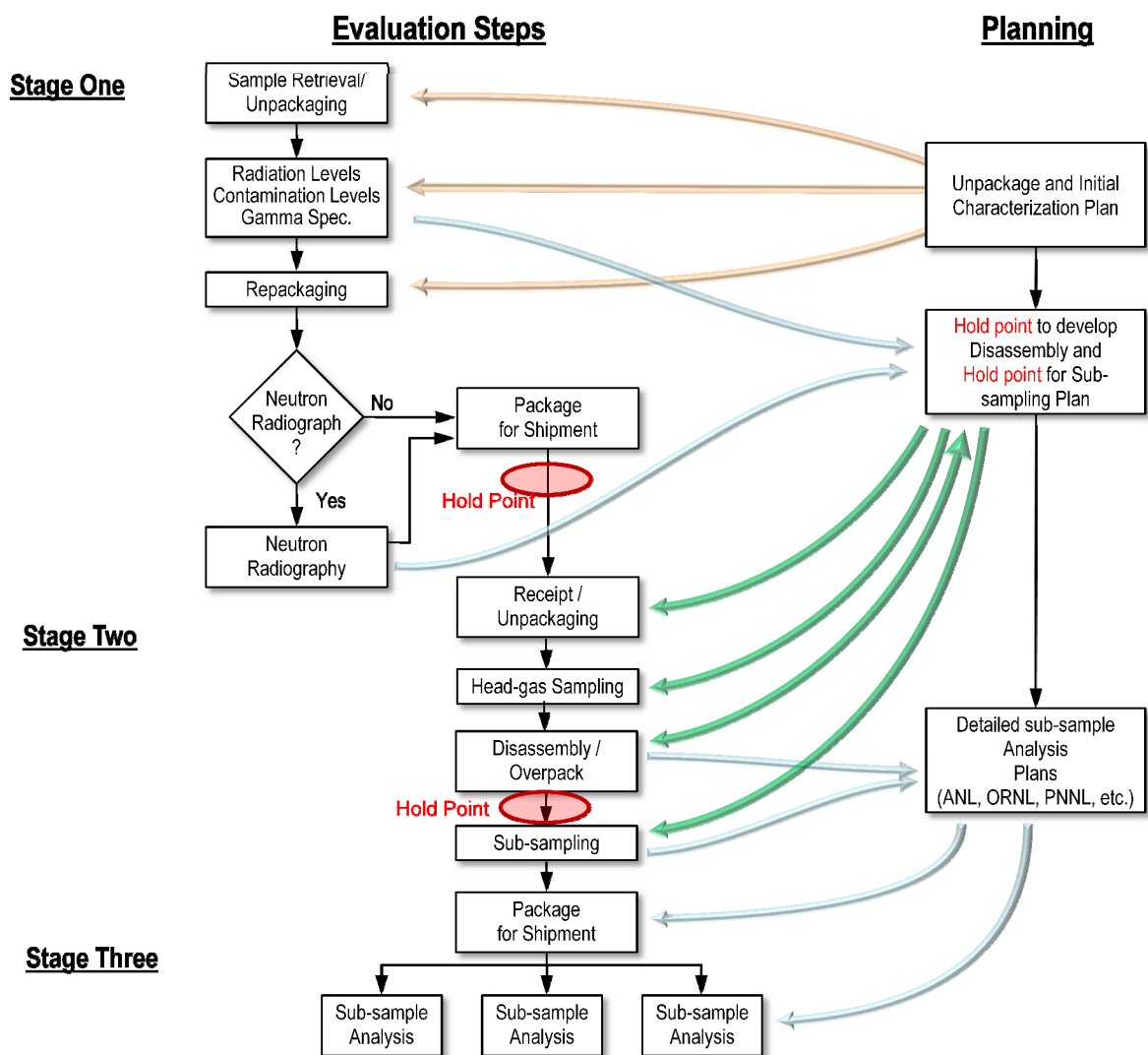
Figure 6. Sample analysis strategy flowchart

4.   PLANNED FY-12 TESTING

The research will continue to investigate FY-10 sorbent utilizing thermal and potentially pressure swing operations, evaluate O_2 impacts to capacities, and collect necessary data for adsorption isotherm development. Ultimately, the data can be used to perform equipment scale-up calculations supporting process feasibility determinations.

More FY-11 sorbent will need to be prepared so evaluations at ambient temperatures can be completed to investigate its use as a Xe guard column. FY-11 sorbent may also be tested at reduced temperatures to compare Kr/Xe capacities with FY-10 sorbent.

MOFs and other sorbents will be evaluated in the cryostat as they become available and new sorbents such as titanosilicates or inorganic nano-materials may be investigated as time permits.

Stage one of the legacy sample analysis strategy will be undertaken. Results of the completion for stage one will be used to implement stage two of the strategy.