Multi-lab Analytical Plan for Analysis of Legacy ^{85}Kr Samples

Fuel Cycle Research & Development

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SUMMARY

Legacy samples composed of ^{85}Kr encapsulated in solid zeolite 5A material and five small metal tubes containing a mixture of the zeolite combined with a glass matrix resulting from hot isostatic pressing have been preserved. The samples were a result of krypton R&D encapsulation efforts in the late 1970s performed at the Idaho Chemical Processing Plant.

These samples were shipped to Oak Ridge National Laboratory (ORNL) in mid-FY 2014. Upon receipt the outer shipping package was opened and the inner package removed and placed in a radiation hood. The individual capsules were double bagged as they were removed from the inner shipping pig and placed into individual glass sample bottles for further analysis.

The five capsules were then x-ray imaged. Capsules 1 and 4 appear to contain an amorphous mass within the capsules. Capsule 2 clearly shows the saw marks on the capsule and a quantity of loose pellet or bead-like material remaining in the capsule. Capsule 3 shows similar bead-like material within the intact capsule. Capsule 5 was previously opened. The end of this capsule appears to have been cut off and there are additional saw marks on the side of the capsule. X-ray tomography allowed the capsules to be viewed along the three axes. Of most interest was determining whether there was any residual material in the closed end of Capsule 5. The images confirmed the presence of residual material within this capsule. The material appears to be compacted but still retains some of the bead-like morphology.

A conference call was held on February 19, 2015, with participation from ORNL, Idaho National Laboratory, Sandia National Laboratories, and Pacific Northwest National Laboratory Sigma Team members. The nondestructive analysis (NDA) results were discussed, and a proposed path forward was formulated to advance this effort toward the original goals of understanding the effects of extended storage on the waste form and package. Based on the initial NDA and the fact that there are at least two breached samples it was proposed that exploratory tests be conducted with the breached specimens before opening the three intact capsules. Portions of these would be analyzed to determine the fraction of krypton/xenon remaining in the matrix and the amount of rubidium remaining in the matrix. The inner surface of the breached capsules would be examined for corrosion.

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FIGURES

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ACRONYMS

HFEF	Hot Fuels Examination Facility
HIP	hot isostatic press
ICP-MS	inductively coupled plasma mass spectrometry
ICPP	Idaho Chemical Processing Plant
INL	Idaho National Laboratory
NDA	nondestructive analysis
ORNL	Oak Ridge National Laboratory
SEM/EDX	scanning electron microscope/energy dispersive x-ray
TEM	transmission electron microscopy
XAS	x-ray absorption spectroscopy
XPS	x-ray photoelectron spectroscopy
XRD	x-ray diffraction

MATERIAL RECOVERY AND WASTE FORM DEVELOPMENT CAMPAIGN

MULTI-LAB ANALYTICAL PLAN FOR ANALYSIS OF LEGACY ^{85}KR SAMPLES

1. INTRODUCTION

Legacy samples composed of ^{85}Kr encapsulated in solid zeolite 5A material and five small metal tubes containing a mixture of the zeolite combined with a glass matrix resulting from hot isostatic pressing have been preserved. The samples are a result of krypton R&D encapsulation efforts in the late 1970s performed at the Idaho Chemical Processing Plant (ICPP). The samples were retrieved from archive storage and transported to the Hot Fuels Examination Facility (HFEF) within the Materials Fuels Complex at the Idaho National Laboratory (INL). Examination of such samples can lead to invaluable information on the long-term stability of ^{85}Kr waste forms. Numerous analytical options are available to investigate sample aging characteristics. These options include, but are not limited to, neutron radiography, scanning electron microscope/energy dispersive x-ray spectroscopy (SEM/EDX), transmission electron microscopy (TEM), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), and x-ray absorption spectroscopy (XAS).

2. BACKGROUND

The background regarding the origin of these samples is detailed by Garn et al.[1] and repeated here in an abbreviated form for completeness. In the late 1970s, an R&D effort to study ^{85}Kr encapsulation and leakage was performed at INL by Christensen, et al.[2–5] Off-gas resulting from fuel dissolution underwent treatment, with the fission products sent to the Rare Gas Plant at ICPP where the ^{85}Kr was removed via cryogenic distillation and collected in gas cylinders. A cylinder containing the ^{85}Kr was transferred to the Multi-Curie Cell where the encapsulation studies were completed.

The ^{85}Kr R&D encapsulation effort incorporated numerous materials, including sodalite, “thirsty” glass, and zeolite 5A, with zeolite 5A reportedly showing the best results. The R&D effort included evaluation of ^{85}Kr leakage, resulting in numerous samples of each material being cut apart to measure ^{85}Kr leakage via thermogravimetric analysis. Because the testing included numerous materials, there is a question as to the exact nature of the legacy samples. It is assumed that because the zeolite 5A material showed the most promise, these samples represent the zeolite material. Further support of this assumption was a recent verbal communication with one of the original researchers (retired), who stated that the samples included “loose” zeolite 5A encapsulating ^{85}Kr and zeolites hot isostatic pressed (HIPed) in a glass matrix contained in squashed metal tubes.[6] This statement was made from inspection of photographs of the samples transported to the HFEF. Photographs showing the loose zeolite and the squashed metal tubes are found in Figures 1–3.

Figure 1: Photo of the loose zeolite material in a Ziploc bag.

Figure 2: Photo of a metal tube, presumably containing potentially un-HIPed loose zeolites.

Figure 3: Photo of squashed metal tubes, presumably zeolite 5A HIPed in a glass matrix.

3. SCOPE/OBJECTIVE

The main objective of this document is to update the overall strategy developed in FY 2011[1] for the sampling and analysis of these valuable aged samples and to ensure that key information is not lost in the process of opening the capsules and collecting samples for analysis. This strategy includes development of an "unpackaging" and initial nondestructive analysis (NDA) characterization plan, a disassembly and subsampling plan, and individual subsample analysis plans dictating desired analyses and their respective results that can be disseminated from the analyses. Handling, disassembly, and analysis order is to be planned and documented to avoid compromising the data, beginning with radiation level measurements, detailed photographic analysis, gamma spectrometry, and radiography before the head-gas capture, disassembly, subsampling, and destructive analysis.

The general sequence of the work as originally planned was in three stages as shown in Figure 4. Stage one included NDA characterization of the samples (radiation levels, contamination levels, and gamma signature) and neutron imaging. Table 1 provides a list of the key analyses to be performed as a part of the stage one work. A hold point was established at the completion of the NDA characterization to review the results and develop the detailed plans for sampling the head-gas space and capsule opening. The efforts since FY 2011 have progressed to this hold point.

The initial characterization and imaging would support the selection of the handling facilities for unpackaging/disassembly and subsampling, the development of a disassembly plan, the development of shipping plans, and the initial identification of facilities for sample analysis. Stage two, shown in the shaded-dashed box following the initial hold point on Figure 4, was envisioned to include the unpackaging/gas sampling/disassembly/subsampling and packaging for shipment to the analysis sites. The final stage was the analysis of the subsamples at the appropriate laboratories.

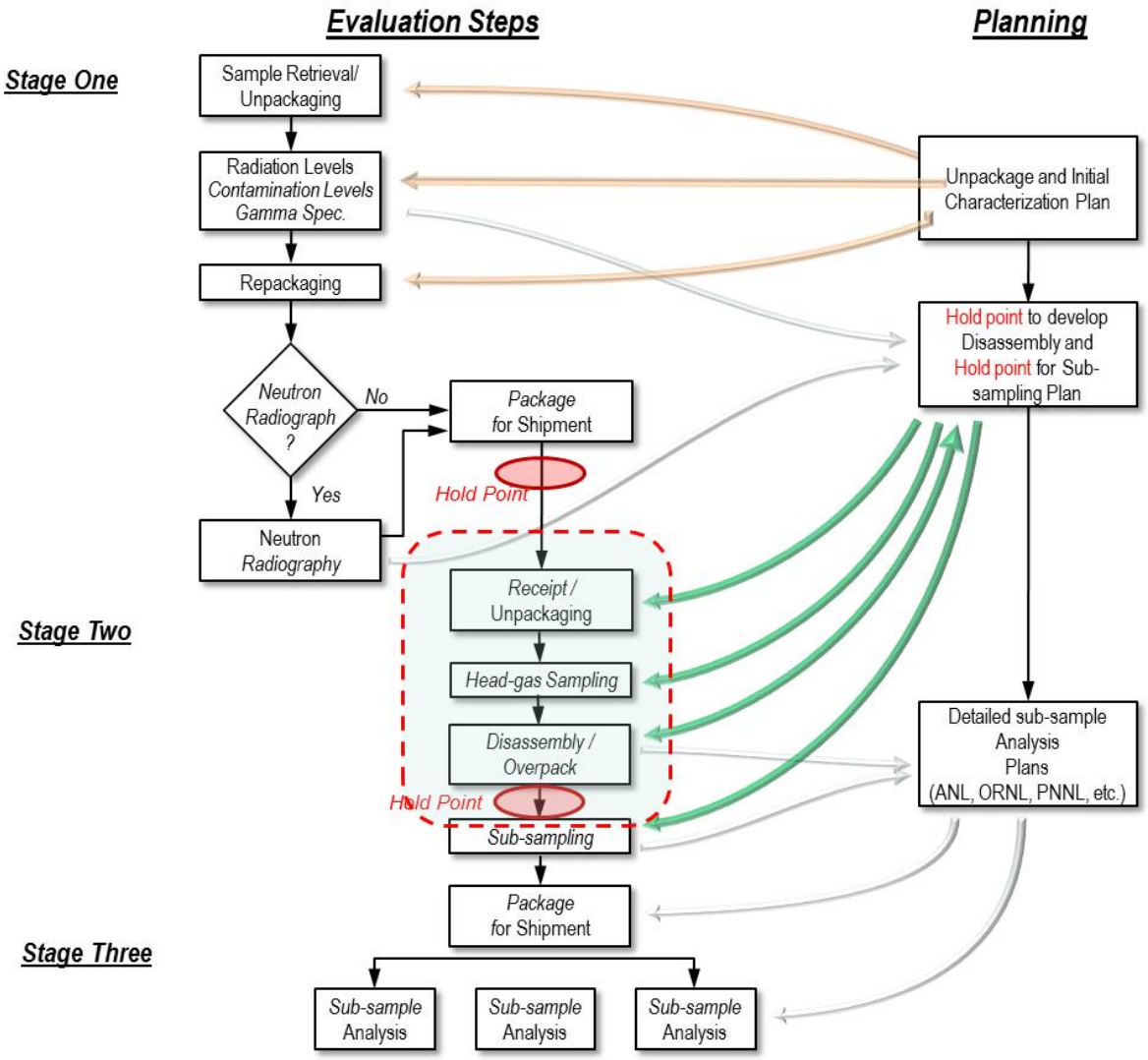

Figure 4: General sequence for the samples.

Table 1: Initial NDA analyses for the legacy samples

Analysis	**Data that will be obtained**
Photography/videography	Record of each step of analysis
Radiation/contamination levels	Radiation values for shipping and handling purposes
Gamma spectrometry	Gamma emitting radionuclides present
Neutron radiography	Sample form, HIPed container specifications
Helium leak detection	Sample capsule integrity

3.1 Initial NDA Characterization

These samples were shipped to Oak Ridge National Laboratory (ORNL) in mid-FY 2014. Figure 5 shows the shipping package as prepared at INL for transfer to ORNL. Upon receipt and completion of the required work-planning documents, the outer shipping package was opened and the inner package removed and placed in a radiation hood (Figure 6). Figure 7 shows the various individual packages contained in the inner package. These included the shielded pig containing the five ^{85}Kr capsules (Figure 8) and several packages of loose material. Figure 9 shows inside the pig after the lid was removed but before any of the capsules were removed.

Figure 5: Drum containing ^{85}Kr samples prepared for shipment to ORNL.

Figure 6: Inner shipping package in radiation hood.

Figure 7: Looking inside the inner pack after opening at ORNL.

Figure 8: Looking inside the inner pack after opening at ORNL.

Figure 9: Shielded pig containing wrapped ^{85}Kr samples.

At this point the unpackaging of samples was suspended due to unexpected radiological conditions. The expected removable contamination was on the order of 250,000 dpm, and the measured removable contamination was found to be almost 4,000,000 dpm. In addition, the dose rate was higher than

previously reported for this shipment. The measured value was 7 R/hr at contact. The gamma scan of the smears identified ^{85}Kr as the confirmed primary radionuclide. The ^{85}Kr contamination was assumed to be associated with ^{85}Kr bound in the zeolite matrix. As a result of these findings additional radiological precautions were established and revised work-planning documents were prepared and approved.

Table 2 provides radiological data and notes on each individual capsule. Figures 10–15 show the individual capsules as they were removed from the pig. They were then double bagged and placed into individual glass sample bottles. Figure 16 shows a representative repackaged capsule before it was placed in a sample jar.

Table 2: Radiological Data and Notes on ^{85}Kr capsules

Capsule	Figures	Rad dose	Notes
1	10	1.5 rad/hr @ contact 320 mrem/hr @ contact 60 mrem/hr @ 30 cm	Appeared crushed and intact
2	11, 12	>50 rad/hr @ contact 350 mrem/hr @ contact 70 mrem/hr @ 30 cm 580 rad/hr at contact of repackaged capsule (separated from initial loose material—additional material exited cut)	Did not appear to have been crushed. Cut mark on upper end of capsule near stem; loose material could/did fall out of cut

Table 2 (continued)

Capsule	Figures	Rad dose	Notes
3	13	2.3 rad/hr @ contact 900 mrem/hr @ contact 70 mrem/hr @ 30 cm	Appeared intact but not crushed
4	14	2.1 rad/hr @ contact 1,000 mrem/hr @ contact 90 mrem/hr @ 30 cm	Appeared crushed and intact
5	15	30 rad/hr @ contact 280 mrem/hr @ contact 34 mrem/hr @ 30 cm	Appeared crushed. Capsule was breached with much of the presumed contents removed

Figure 10: Capsule 1.

Figure 11: Capsule 2.

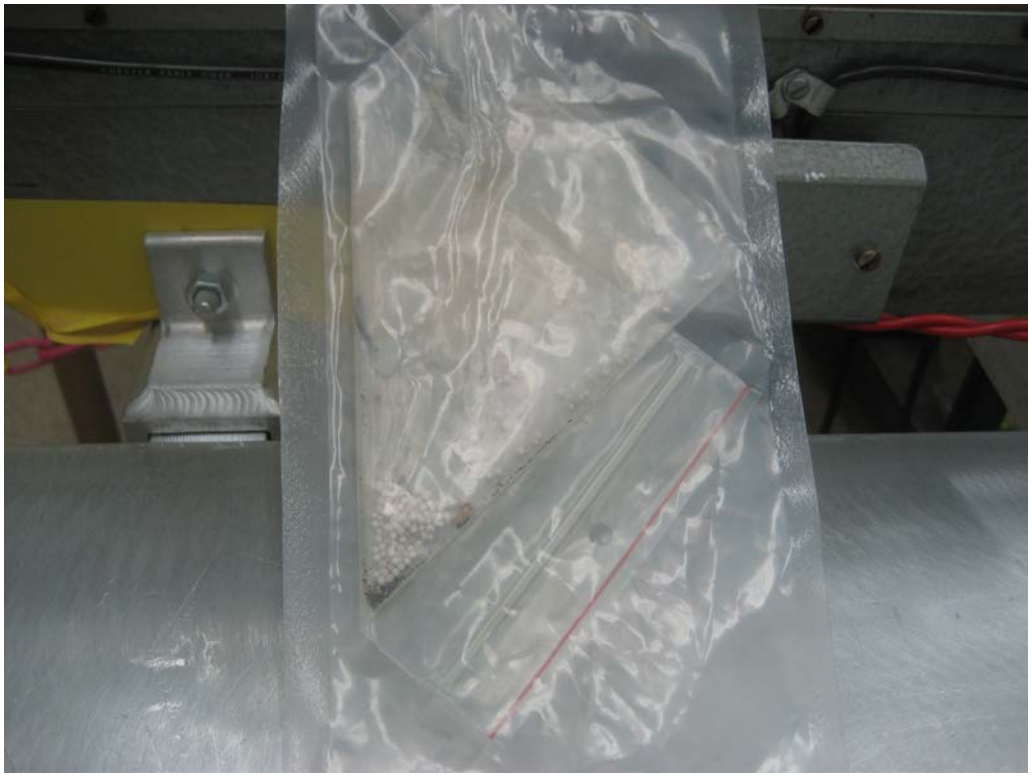

Figure 12: Loose material from Capsule 2.

Figure 13: Capsule 3.

Figure 14: Capsule 4.

Figure 15: Capsule 5.

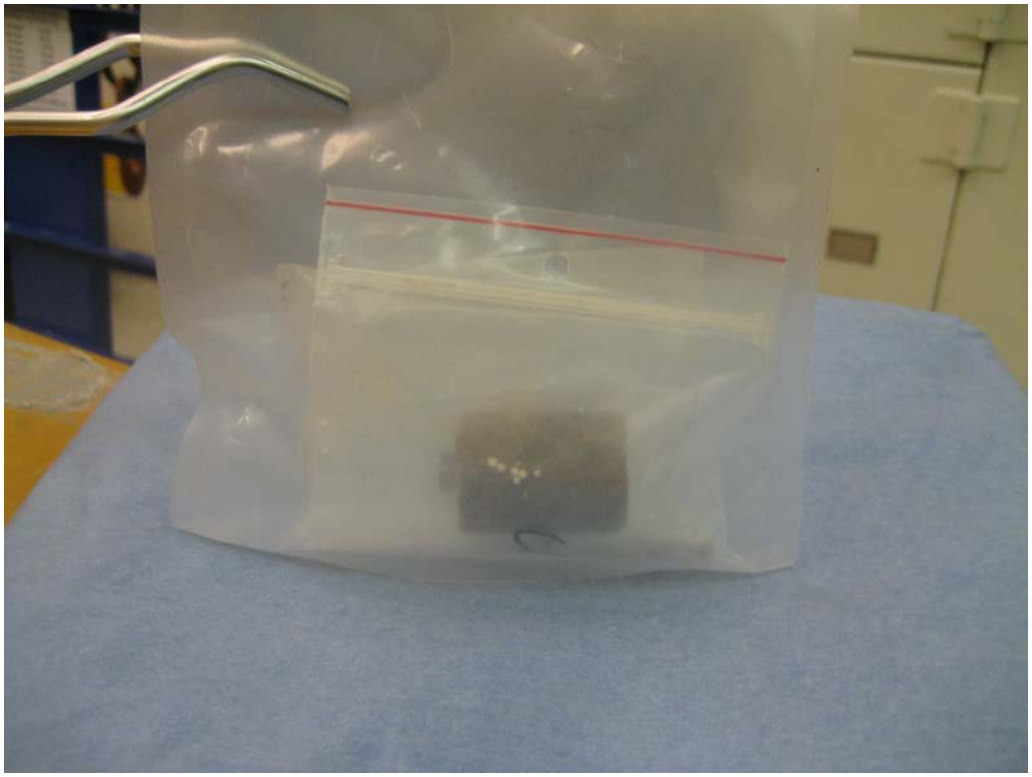

Figure 16: Capsule 2 after repackaging in an inner Ziploc bag and outer heat-sealed bag.

The capsules were then x-ray imaged to determine characteristics of the capsule and the material contained inside. The use of x-ray imaging in the place of neutron radiography avoided issues associated with the activation of the sample material. The objective of this step was to ascertain the container wall thickness and the state of the material inside (loose or a solid monolith).

4. X-RAY IMAGING RESULTS

Figures 17–21 are the x-ray images of Capsules 1–5 respectively. Figure 17 shows a monolithic mass within Capsule 1. Figure 18 clearly shows the saw marks on the capsule and a quantity of loose pellet or bead-like material remaining in Capsule 2. Figure 19 shows similar bead-like material within the intact Capsule 3. Figure 20 shows a monolithic mass within Capsule 4 similar to that of Capsule 1 (Figure 17). Figure 21 shows the opened Capsule 5. The end of this capsule appears to have been cut off, and there are additional saw marks on the side of the capsule. There appears to be a shadow of some sort at the closed end of the capsule that might indicate the presence of residual material.

X-ray tomography allowed the capsules to be viewed along the three axes. Determining whether there was any residual material in the closed end of Capsule 5 was of most interest. Figures 22–27 show slices taken along the x-axis of Capsule 5. As you progress from one image to the next you are passing through the capsule. The heavy light gray lines on either side of the capsule are the walls of the glass jar containing the capsule. The light curving lines are the metal walls of the capsule. These images confirm the presence of residual material within this capsule. The material appears to be compacted but still retains some of the bead-like morphology.

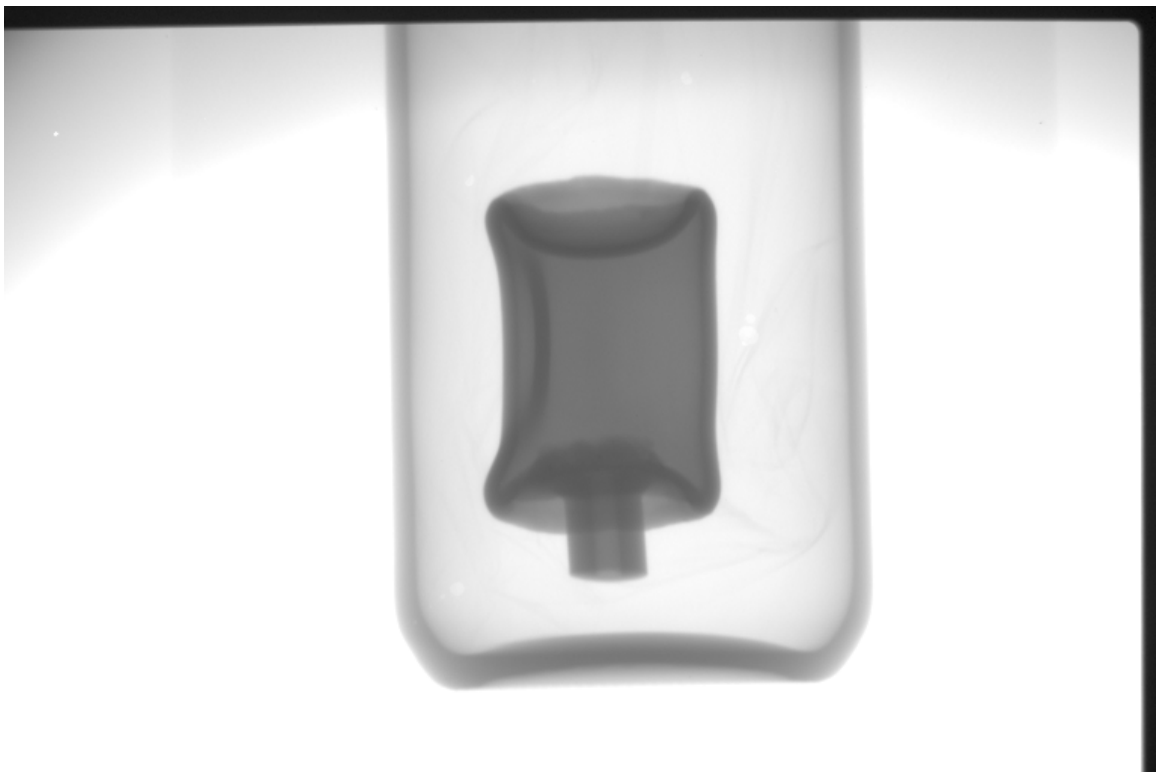

Figure 17: X-ray image of Capsule 1.

Figure 18: X-ray image of Capsule 2.

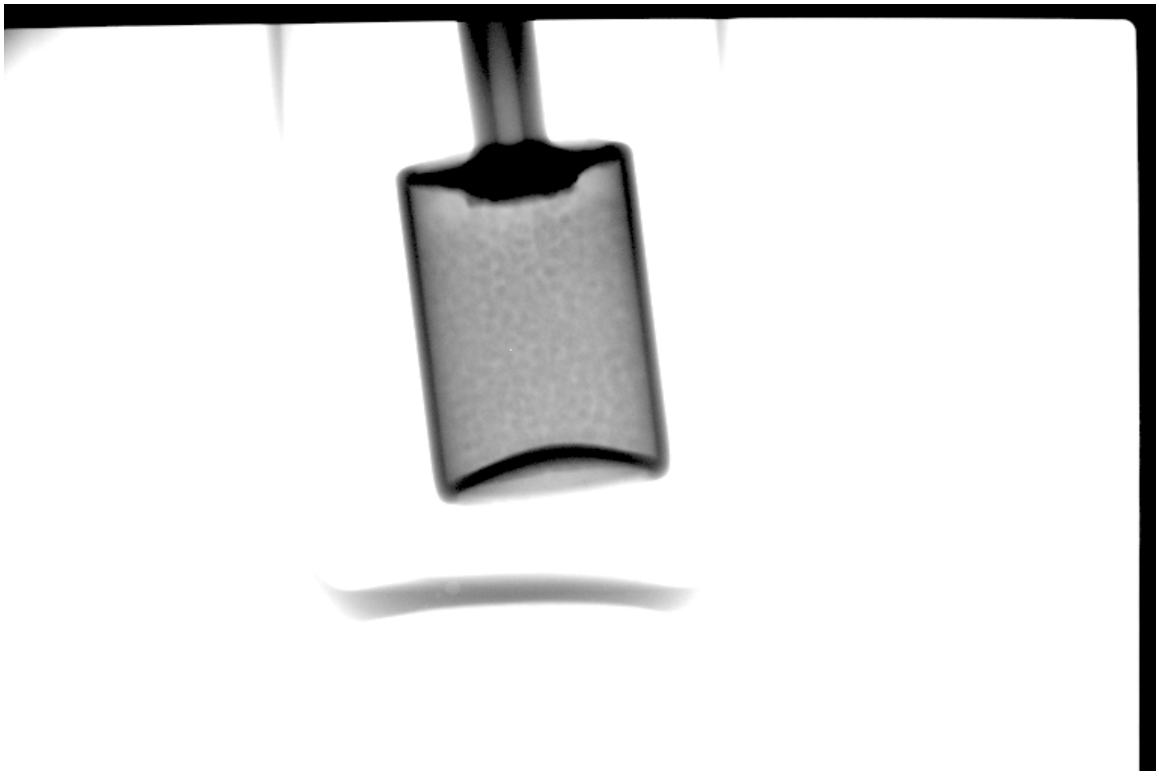

Figure 19: X-ray image of Capsule 3.

Figure 20: X-ray image of Capsule 4.

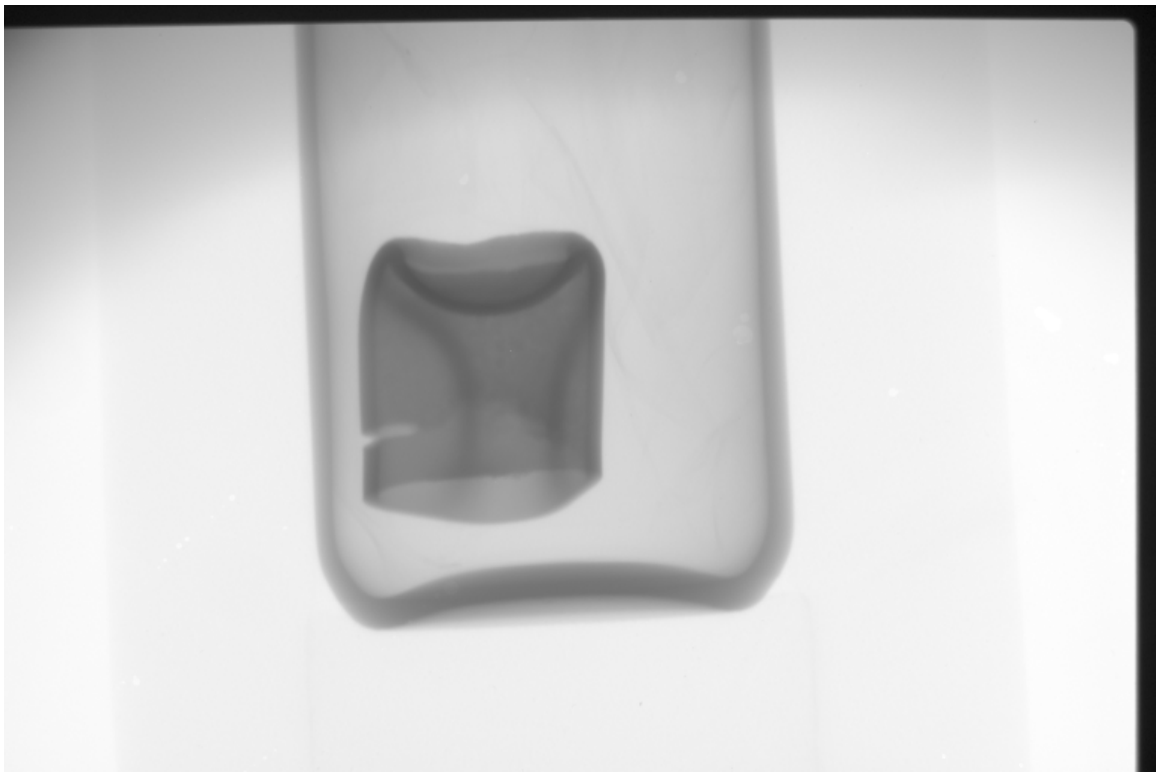

Figure 21: X-ray image of Capsule 5.

Figure 22: X-ray tomographic image of Capsule 5 cutting across the capsule in the vertical plane.

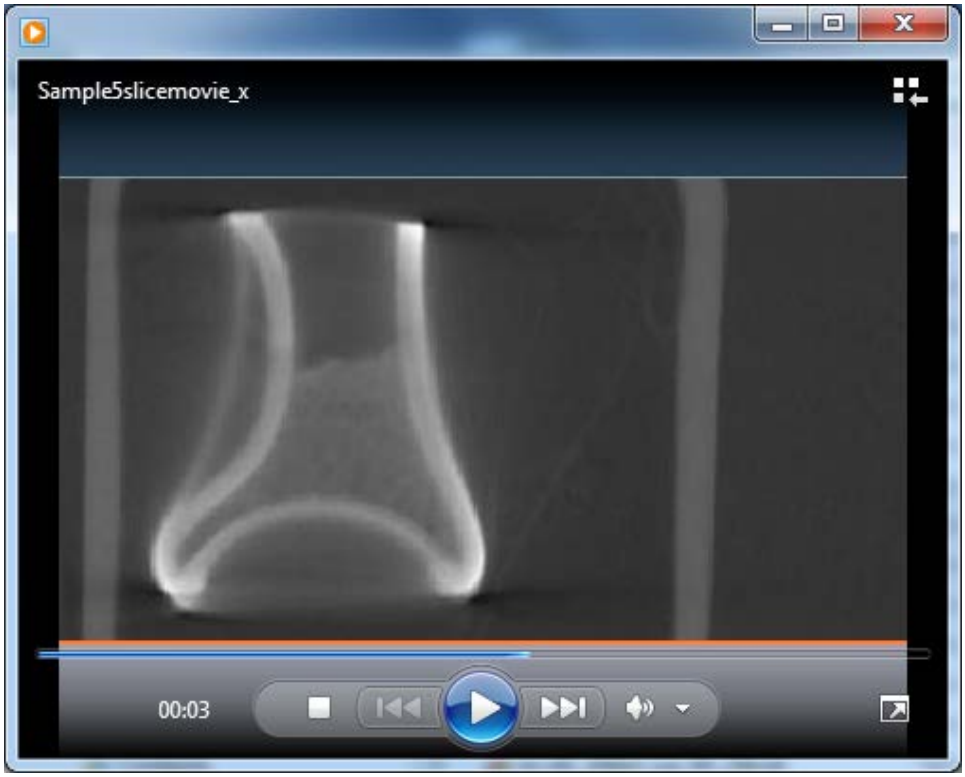

Figure 23: X-ray tomographic image of Capsule 5 cutting across the capsule in the vertical plane.

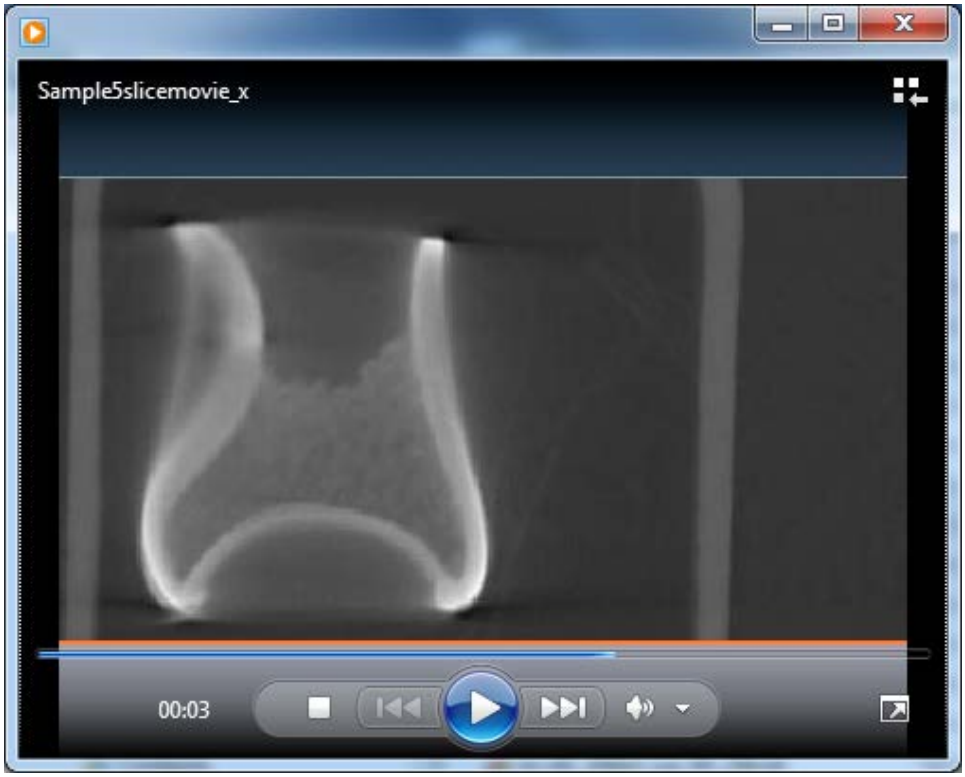

Figure 24: X-ray tomographic image of Capsule 5 cutting across the capsule in the vertical plane.

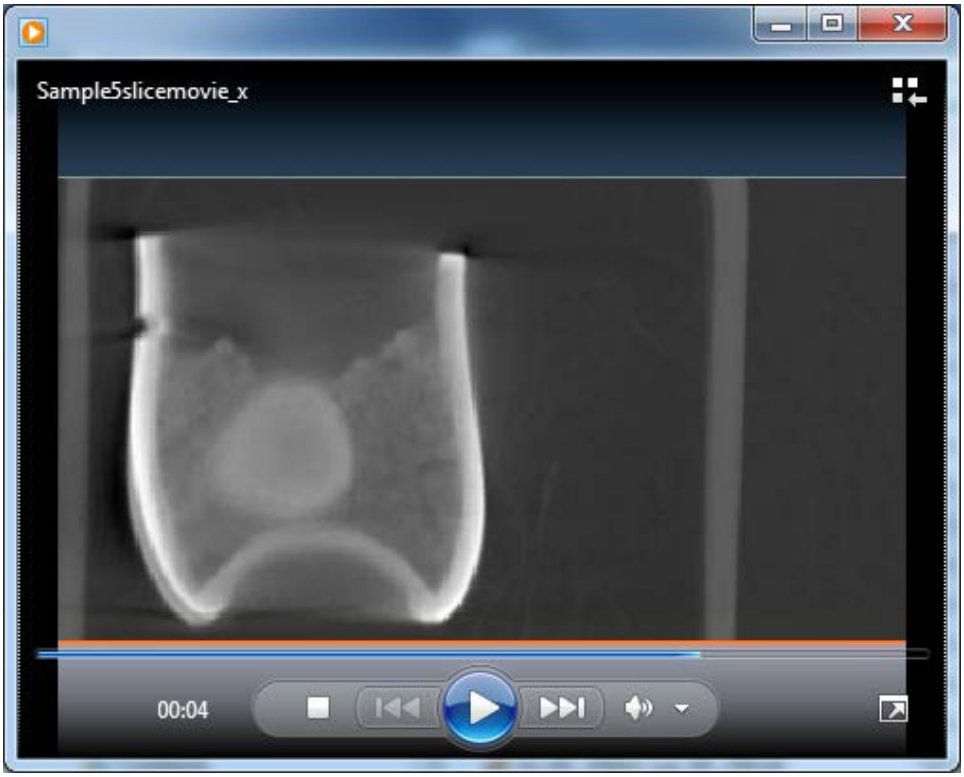

Figure 25: X-ray tomographic image of Capsule 5 cutting across the capsule in the vertical plane.

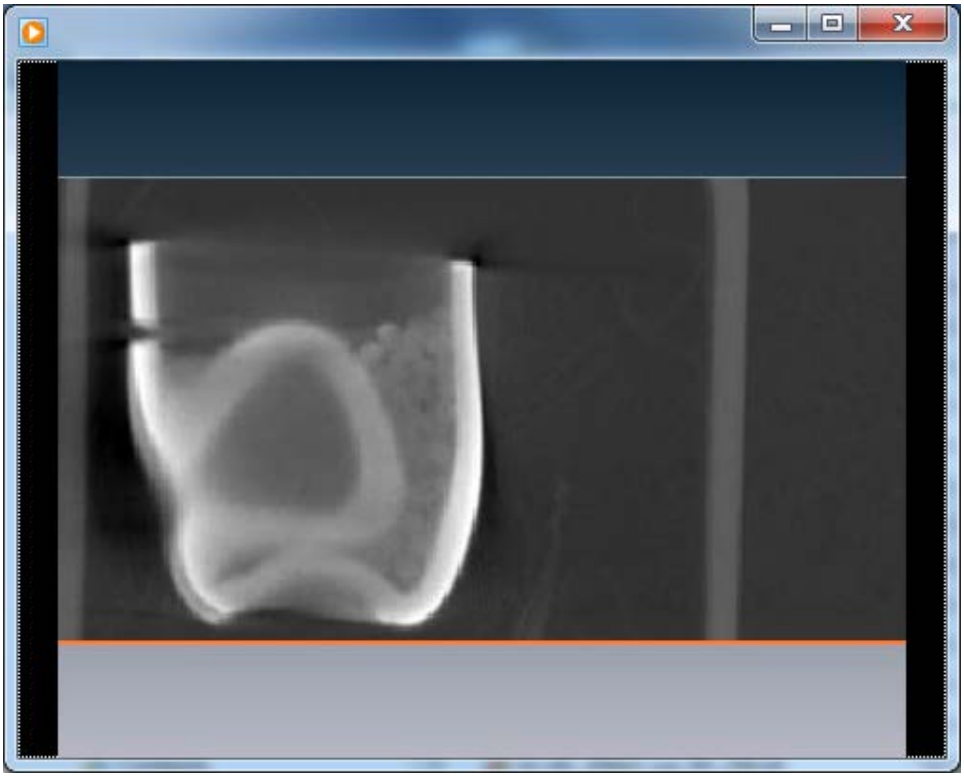

Figure 26: X-ray tomographic image of Capsule 5 cutting across the capsule in the vertical plane.

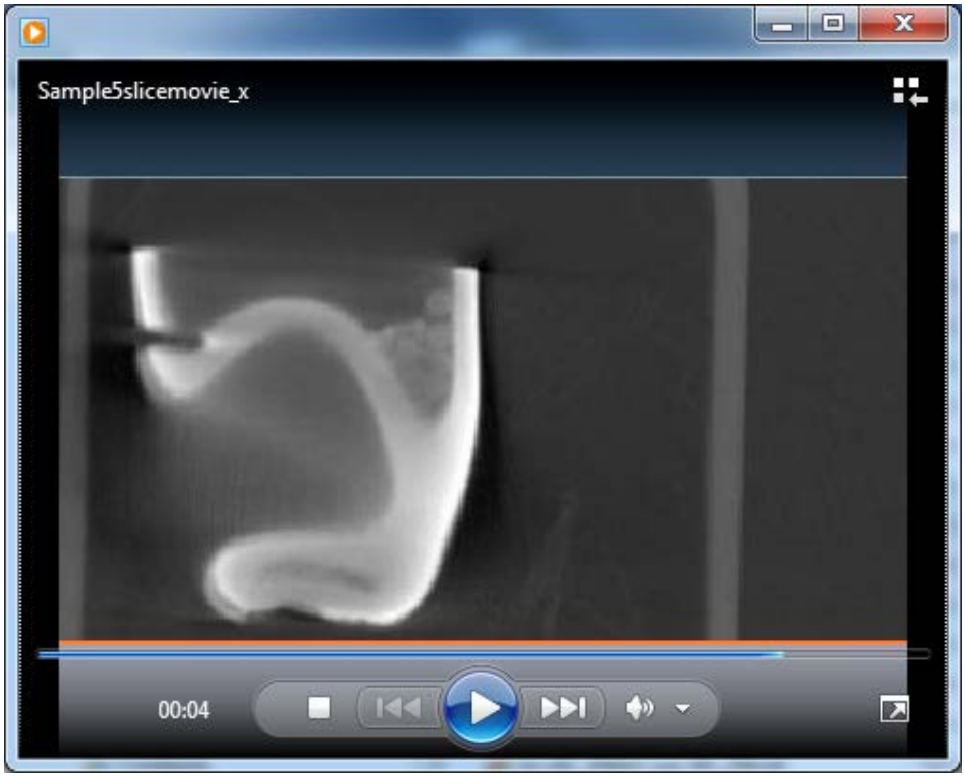

Figure 27: X-ray tomographic image of Capsule 5 cutting across the capsule in the vertical plane.

Figure 28 is a slice taken through the midsection of Capsule 3. By scaling to the diameter of the glass sample jar it is possible to determine the capsule wall thickness. This was determined to be ~1.7 mm. The overall capsule diameter was 29.5 mm. The particles appear to be about 1.7 mm in diameter.

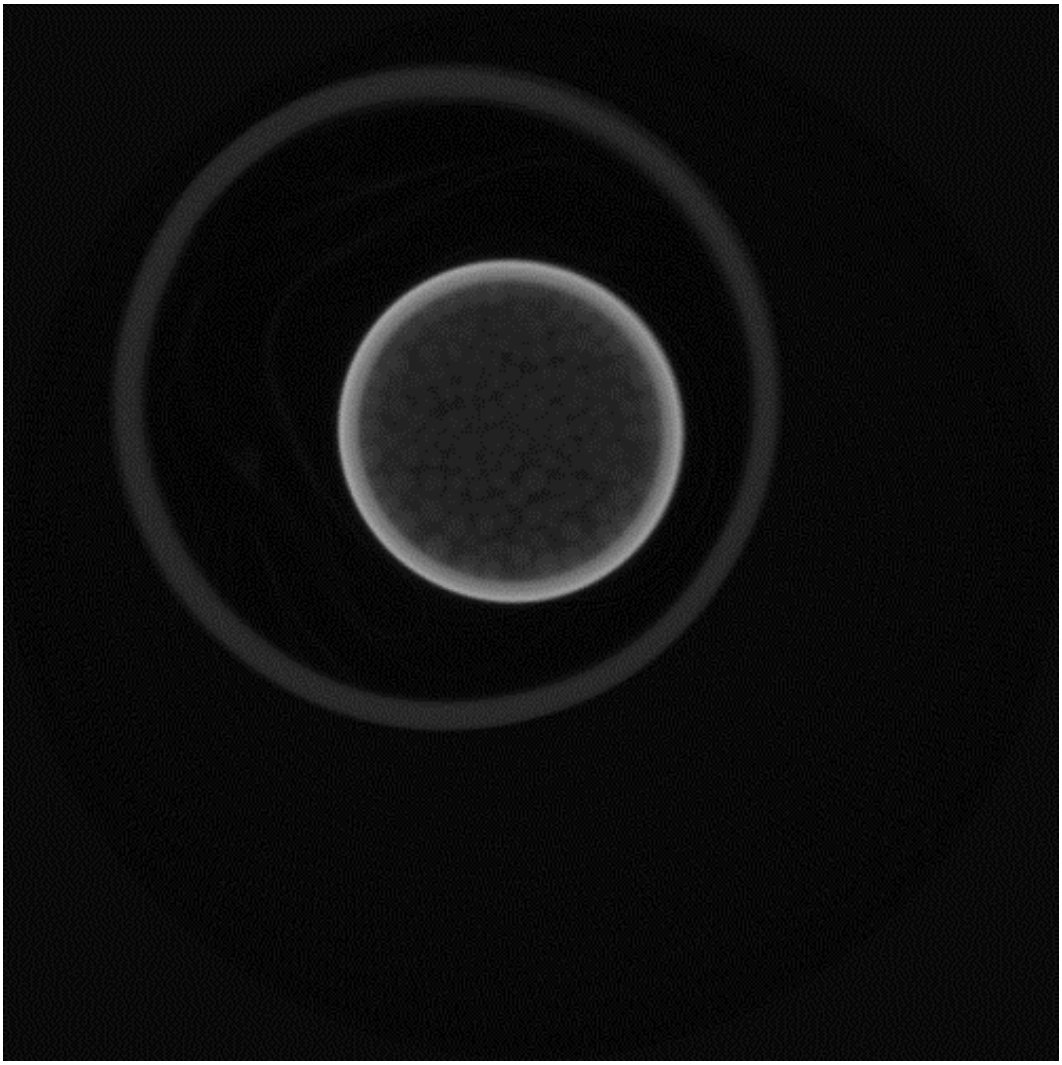

Figure 28: X-ray tomographic image of Capsule 3 cutting across the capsule in the horizontal plane.

5. DISCUSSION AND PATH FORWARD

A conference call was held on February 19, 2015, with participation from ORNL, INL, Sandia National Laboratories, and Pacific Northwest National Laboratory Sigma Team members. The NDA results were discussed and a proposed path forward was formulated to advance this effort toward the original goals. The analysis of these samples is expected to provide information on the following.

- Stability of the HIPed krypton-loaded zeolite-glass matrix
- Impact of the in-growth of the decay products on the zeolite-glass matrix
- Release fraction of the krypton from the waste matrix
- Integrity of the capsule, i.e., any penetration/leakage

- Corrosion inside of the capsule at both the zeolite-glass–capsule interface and at locations away from the waste matrix

A number of analytical techniques are available to ascertain crystal structure, chemical composition, material corrosion (rubidium in-growth), radiation damage to zeolite/glass, etc. A description of the various analysis techniques that could be performed to acquire material characterization for the samples is provided in Garn et al.[1] and summarized in Table 3.

Table 3: Potential analysis techniques for legacy samples

Analytic technique	Data that will be obtained
Photography/videography	Record of each step of analysis
Preparation of reference samples	Baseline matrix information. Validation of analysis techniques
Over gas analysis/rare gas analysis	Gaseous corrosion/reaction products/release rate from waste matrix
Container integrity	Chemical attack on container
Dissolution/gas sampling/chemical analysis/ICP-MS/rare gas analysis	Determination of fraction of krypton/xenon remaining in waste matrix; determination of rubidium remaining in matrix
SEM of capsule/waste matrix interface	Extent of corrosion, chemical attack on container
SEM/EDX	Chemical composition, morphology, and structure
TEM	Crystal orientation and electronic structure
XRD	Chemical composition, morphology, and structure
XAS	Radiation damage to zeolite matrix; fate of the decay product rubidium
XPS	Elemental composition and chemical state of the surface
µPIXE	Quantitative elemental composition

µPIXE = microbeam proton-induced x-ray emission.

Based on the initial NDA and the fact that there are at least two breached samples it was proposed that exploratory tests be conducted with the breached specimens before opening the three intact capsules.

5.1 Analysis of Loose Material

It was determined that several of the loose pellets/beads would be analyzed. SEM/EDX and XRD would be used to determine chemical composition, morphology, and structure. Several pellets would be dissolved and the effluent (liquid and gas) would be analyzed by inductively coupled plasma mass spectrometry (ICP-MS) and rare gas analysis to determine the fraction of krypton/xenon remaining in the un-HIPed zeolite matrix. The rubidium content in the matrix would also be determined.

5.2 Analysis of Capsule 2

Since Capsule 2 has already been breached, the capsule will be fully opened and the remaining loose material recovered. The inner surface of the capsule will be examined for corrosion. The results will be compared at a later date to those for the inner surfaces of the intact capsules.

5.3 Analysis of Capsule 5

This capsule will be cut lengthwise to reveal the residual compressed material and the sorbent-capsule interface. One half of this sample will be examined by SEM. Of particular interest will be an examination of the interface between the zeolite matrix and the metal capsule. Analysis of the inner surface of the metal capsule will also be performed to compare the surface in direct contact with the zeolite matrix with the noncontact surface.

Material will be recovered from the other half of the sample for powder XRD and chemical analysis. SEM/EDX and XRD will be used to determine chemical composition, morphology, and structure. A portion of the recovered material will be dissolved and the effluent (liquid and gas) will be analyzed by ICP-MS and rare gas analysis to determine the fraction of krypton/xenon remaining in the HIPed zeolite matrix. The rubidium content in the matrix will also be determined.

5.4 Head-Gas Analysis of Capsule 3

5.4.1 Helium Leak Determination.

Capsule 3 should be subjected to helium leak detection to determine the capsule integrity. Assuming that the capsule is intact, i.e., no pin hole leaks are detected, the head gas of the capsule will be sampled.

5.4.2 Head-Gas Sampling

Head-gas sampling of Capsule 3 could be conducted using similar equipment to that routinely used for the sampling and analysis of post-irradiation fuel pin/target samples. Procedures and equipment currently exist to conduct such sampling within building 3525 at ORNL. It is currently proposed that the samples be handled in an alpha free glove bag in one of the radiological laboratories. Figure 29 shows a schematic of the sampling system as configured for use with samples within the hot cell. For this application this would be the glove bag boundary. Figure 30 shows the existing valve table. The recovered gas would be analyzed for ^{85}Kr content. The punctured capsule would be repackaged and stored under an inert atmosphere for future analysis.

5.5 Reference Samples

To quantify the effects of radiation damage, etc., nonradioactive reference samples of zeolite 5A, HIPed and un-HIPed, should be prepared, but the existence of the two breached samples that are radioactive provides potentially better material for testing. These reference samples could have rubidium included in the matrices for comparison purposes. The same analyses performed on the legacy samples should be performed on these reference samples to provide baseline information. These reference samples could also be used to validate proposed destructive test methods to ensure that accurate, reliable data will be obtained when performing the analysis on the actual samples.

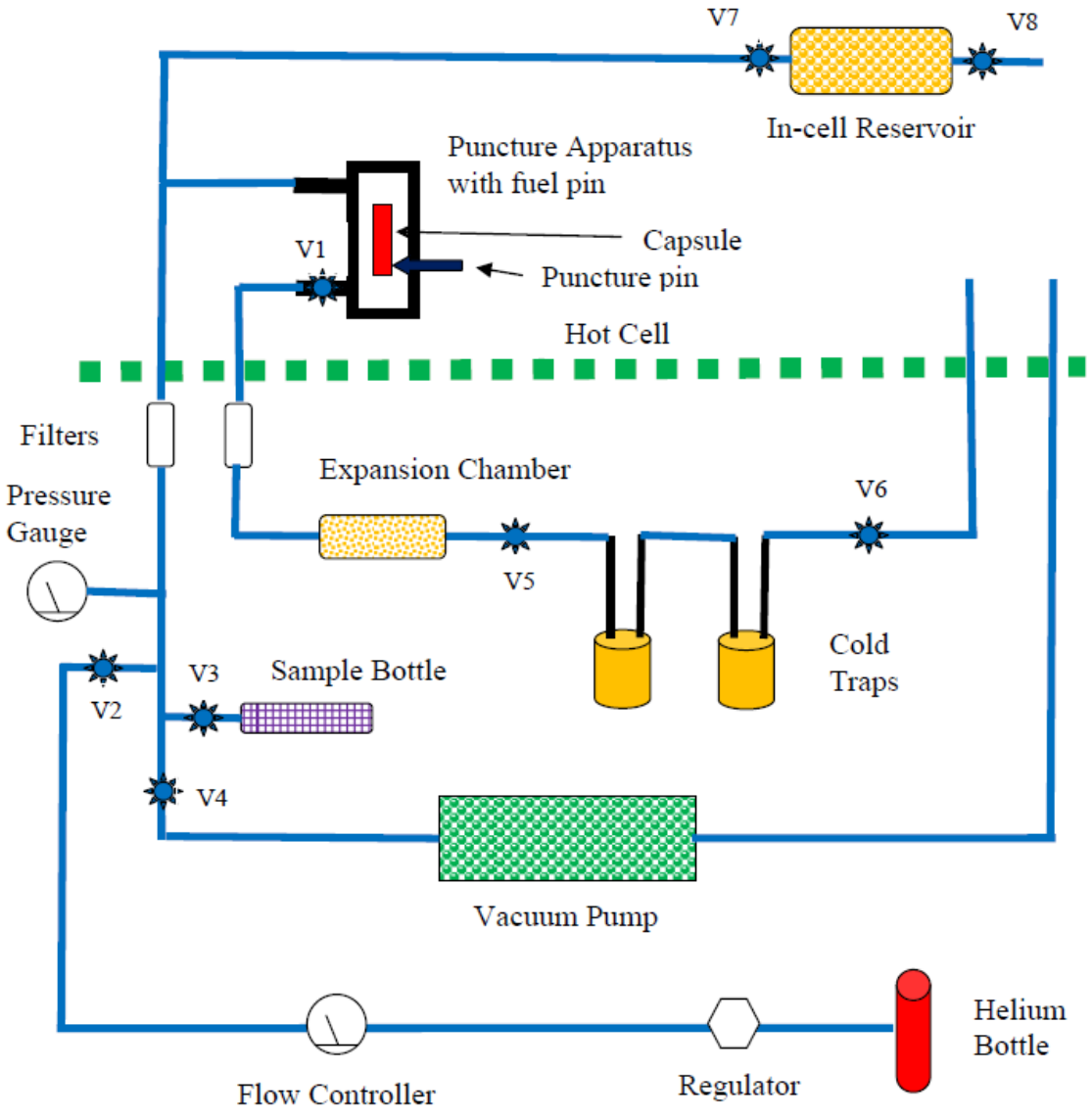

Figure 29: Schematic of the sampling system.

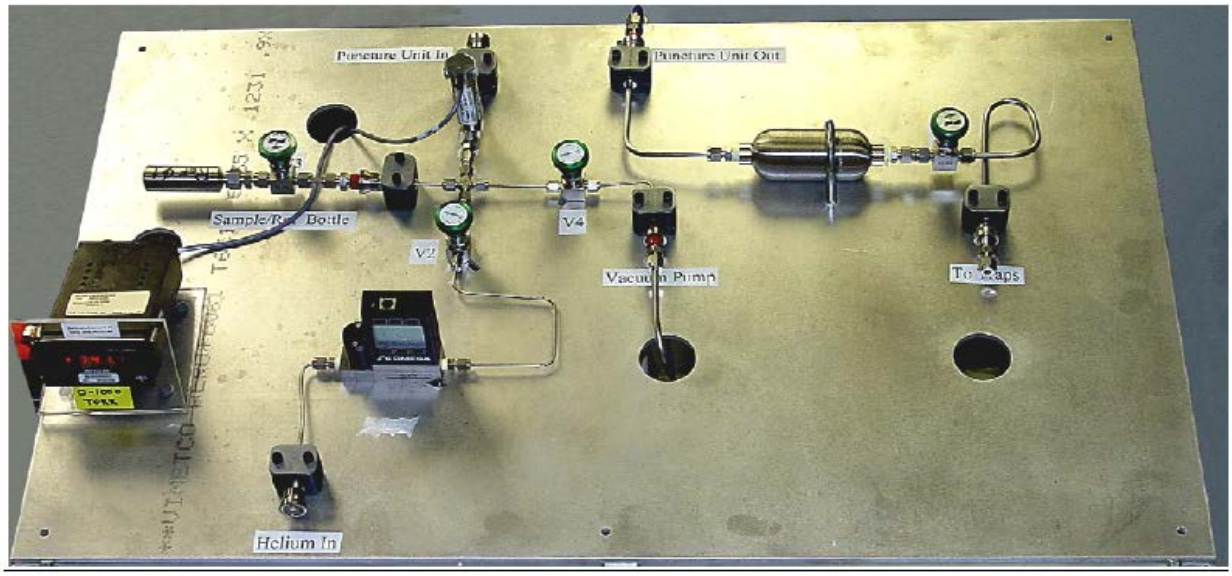

Figure 30: View of valve table showing the valve locations.

The opened capsules will be stored in an inert over-pack pending finalization of the subsampling and analytical plans. Preliminary analytical plans for the intact capsules will then be prepared based on the NDA results, analysis of the compromised samples, and possible surrogate material testing. It is recommended that only one capsule be processed at a time. Any cutting or destruction of the HIPed tubes will be performed in appropriate facilities to control the hazards associated with the sample or subsample.

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