Analysis of Legacy ^{85}Kr Waste Form Samples – 16319*

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ABSTRACT

In the late 1970s, the Idaho Chemical Processing Plant conducted an R&D program on krypton encapsulation. Legacy samples composed of ^{85}Kr incorporated 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. These samples were shipped to Oak Ridge National Laboratory (ORNL) in mid-FY 2014. After receipt and repackaging, the samples were examined by x-ray imaging and x-ray tomography.

Two of the capsules appear to contain an amorphous mass within the capsules. An image of one capsule clearly shows the saw marks on the capsule and a quantity of loose pellet or bead-like material remaining in the capsule. An image of another capsule shows similar bead-like material within the intact capsule. One of the capsules 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 this capsule. 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.

Based on the initial nondestructive assay (NDA) and the fact that there are two obviously breached samples, a plan was developed for exploratory tests that would be conducted with the breached specimens before opening the three intact capsules. Preparations are being made to determine the fraction of krypton/xenon remaining in the waste form matrix and the amount of rubidium remaining in the waste form matrix. The inner surface of the breached capsules will be examined for corrosion.

INTRODUCTION

In the late 1970s, an R&D effort to study ^{85}Kr encapsulation and leakage was performed at Idaho National Laboratory (INL) by Christensen, et al.[1-4] Off-gas resulting from fuel dissolution underwent treatment, with the fission products sent

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to the Rare Gas Recovery Facility at the Idaho Chemical Processing Plant (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 research and development (R&D) encapsulation effort incorporated ^{85}Kr in 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.[5] This statement was made from inspection of photographs of the samples transported to the Hot Fuel Examination Facility (HFEF). Photographs showing the loose zeolite and the squashed metal tubes are provided in Figures 1–3.

Figure 1: Photo of the loose zeolite material in a Ziploc bag[6].

Figure 2: Photo of a metal tube, presumably containing potentially un-HIPed loose zeolites[6].

Figure 3: Photo of squashed metal tubes, presumably zeolite 5A HIPed in a glass matrix[6].

ANALYSIS PLAN

The analysis plan was developed in FY 2011[6] and detailed the overall strategy for the sampling and analysis of these valuable samples. This strategy included development of an “unpackaging” and initial nondestructive analysis (NDA) characterization plan, a disassembly and subsampling plan, and individual subsample analysis plans defining desired analyses and their respective results that can be disseminated from the analyses. The sequence of handling, disassembly, and analysis 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 I provides a list of the key analyses to be performed as 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-space gas and capsule opening. Work has now progressed to this hold point[7].

The initial characterization and imaging is guiding 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, is envisioned to include the unpackaging, gas sampling, disassembly, subsampling and repackaging for shipment to the analysis sites. The final stage is the analysis of the subsamples at the appropriate laboratories.

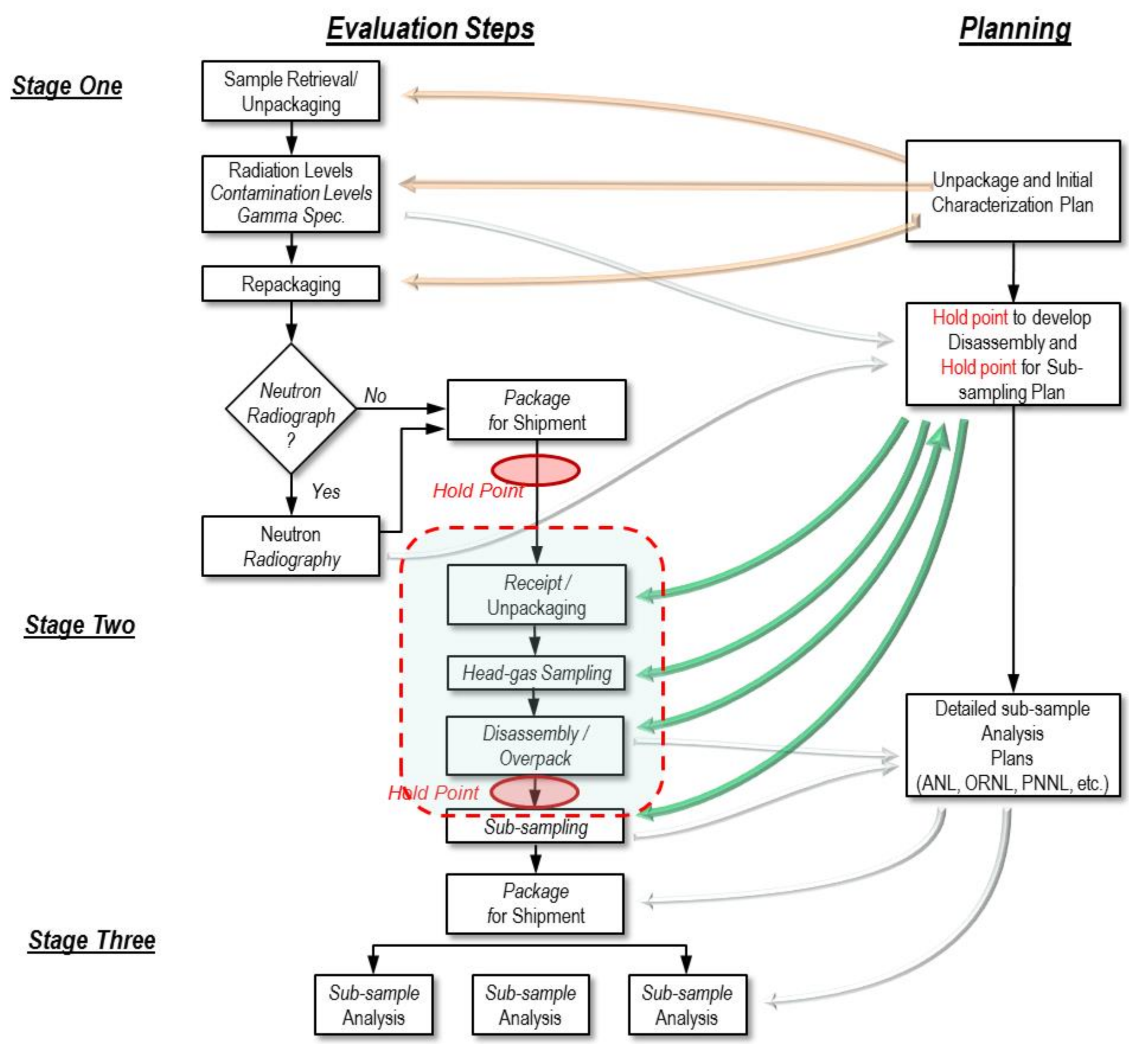

Figure 4: General sequence for the samples.

TABLE I: 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

INITIAL NDA CHARACTERIZATION

The ^{85}Kr samples which had been stored at INL 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 radiological work hood. Figure 6 shows the various individual packages contained in the inner package. These included the shielded pig containing the five ^{85}Kr capsules and several packages of loose material. Figure 7 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.

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 rad/h 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 II provides radiological data and notes on each individual capsule. Figures 8–11 show several of the individual capsules as they were removed from the pig. They were then double bagged and placed into individual glass sample bottles.

Figure 6: Looking inside the inner pack after opening at ORNL.

Figure 7: Shielded pig containing wrapped ^{85}Kr samples.

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

Capsule	Figures	Rad dose	Notes
1	8	1.5 rad/h @ contact 320 mrem/h @ contact 60 mrem/h @ 30 cm	Appeared crushed and intact.
2	9	>50 rad/h @ contact 350 mrem/h @ contact 70 mrem/h @ 30 cm 580 rad/h 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.
3	10	2.3 rad/h @ contact 900 mrem/h @ contact 70 mrem/h @ 30 cm	Appeared intact but not crushed.
4	Not shown	2.1 rad/h @ contact 1,000 mrem/h @ contact 90 mrem/h @ 30 cm	Appeared crushed and intact.
5	11	30 rad/h @ contact 280 mrem/h @ contact 34 mrem/h @ 30 cm	Appeared crushed. Capsule was breached with much of the presumed contents removed.

Figure 8: Capsule 1.

Figure 9: Capsule 2.

Figure 10: Capsule 3.

Figure 11: Capsule 5.

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).

X-RAY IMAGING RESULTS

Figures 12–21 are the x-ray images of Capsules 1–5, respectively. Figure 12 shows a monolithic mass within Capsule 1. Figure 13 clearly shows the saw marks on the capsule and a quantity of loose pellet or bead-like material remaining in Capsule 2. Figure 14 shows similar bead-like material within the intact Capsule 3. Figure 15 shows a monolithic mass within Capsule 4 similar to that of Capsule 1 (Figure 12). Figure 16 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 17–19 show slices taken along the z-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.

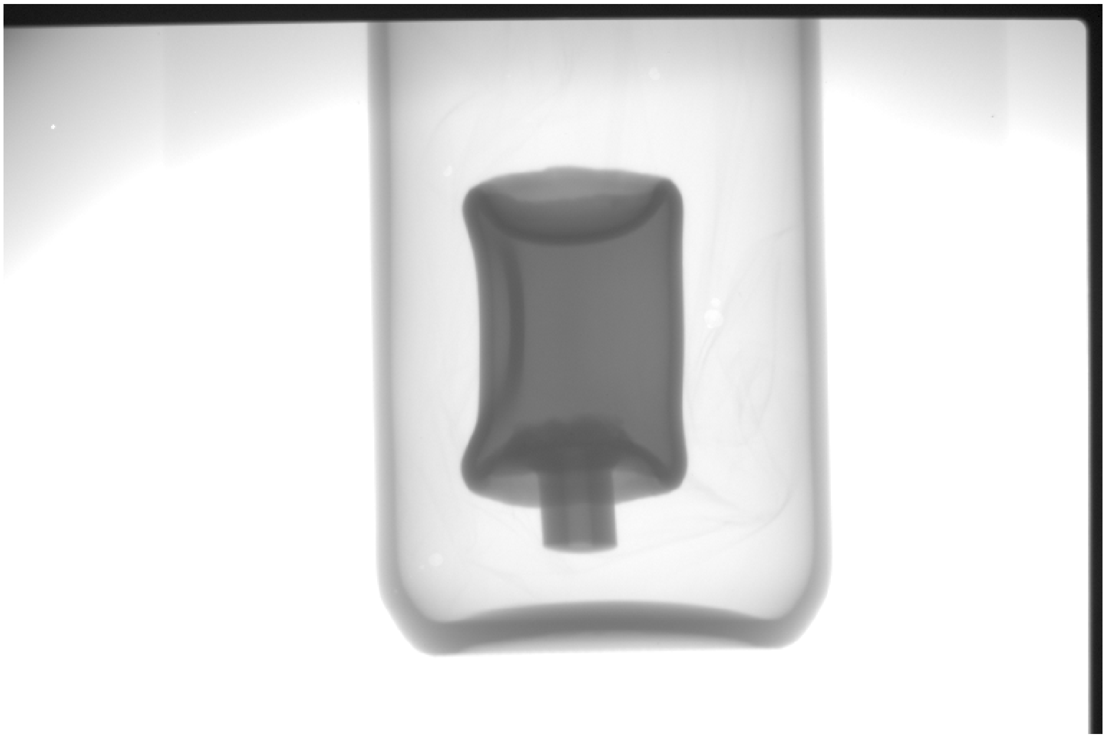

Figure 12: X-ray image of Capsule 1.

Figure 13: X-ray image of Capsule 2.

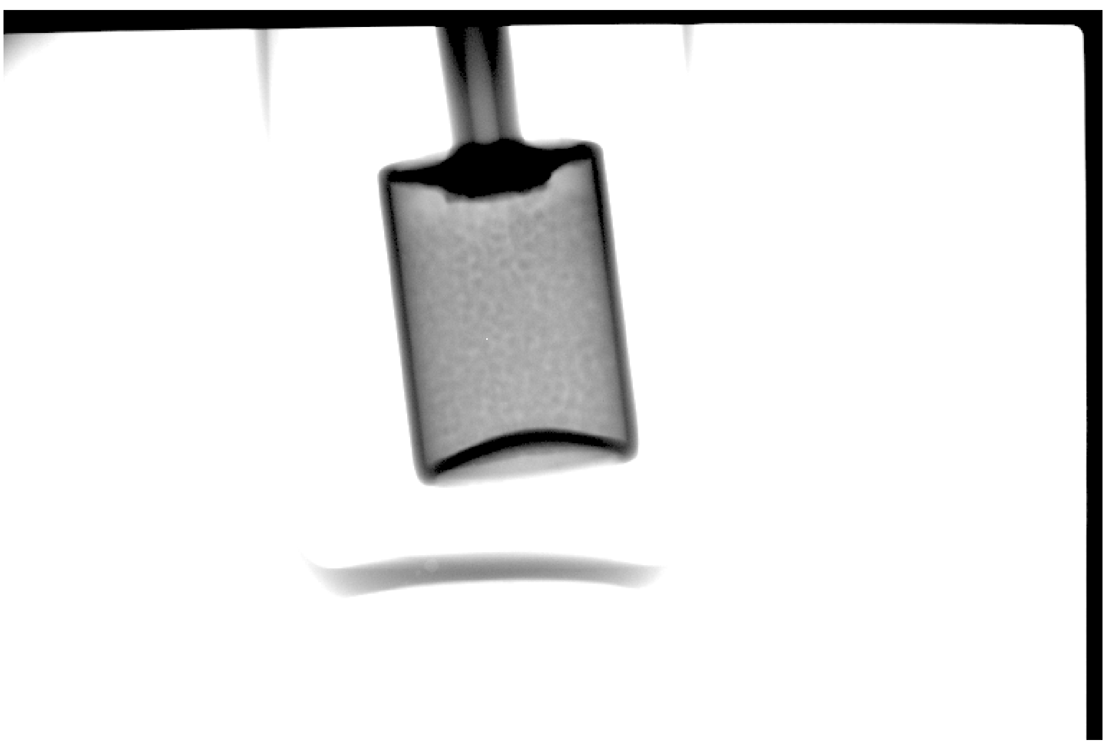

Figure 14: X-ray image of Capsule 3.

Figure 15: X-ray image of Capsule 4.

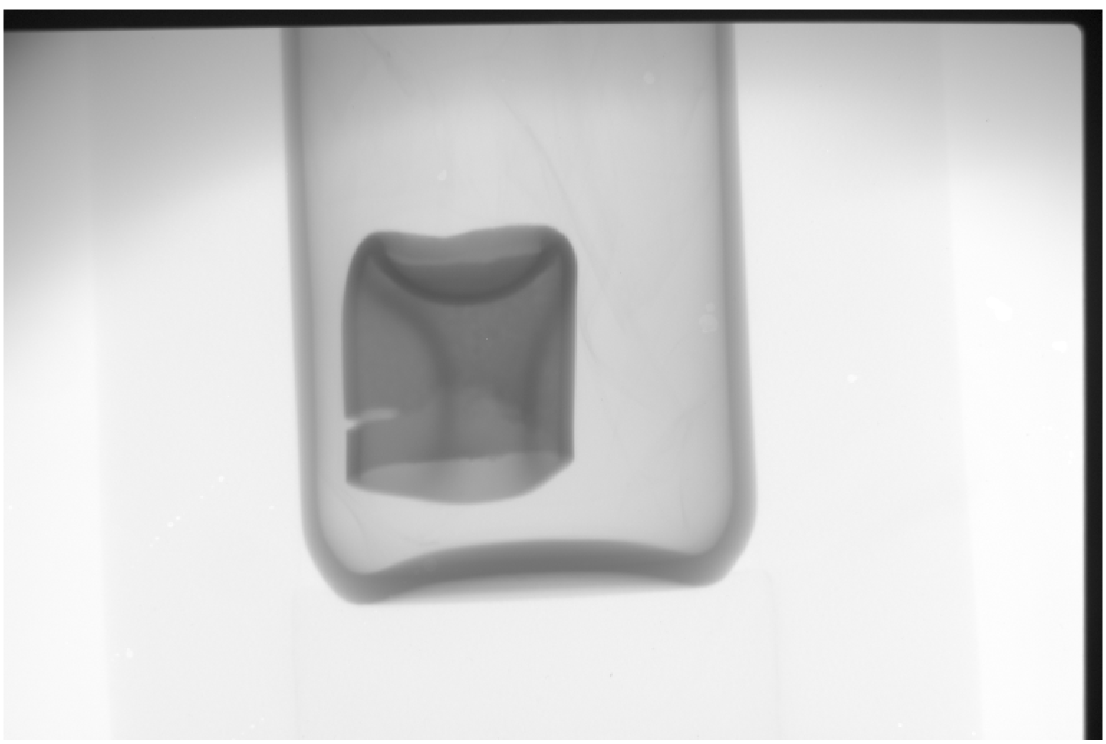

Figure 16: X-ray image of Capsule 5

Figure 17: X-ray tomographic image of Capsule 5 cutting across the capsule in the vertical plane.

Figure 18: X-ray tomographic image of Capsule 5 cutting across the capsule in the vertical plane.

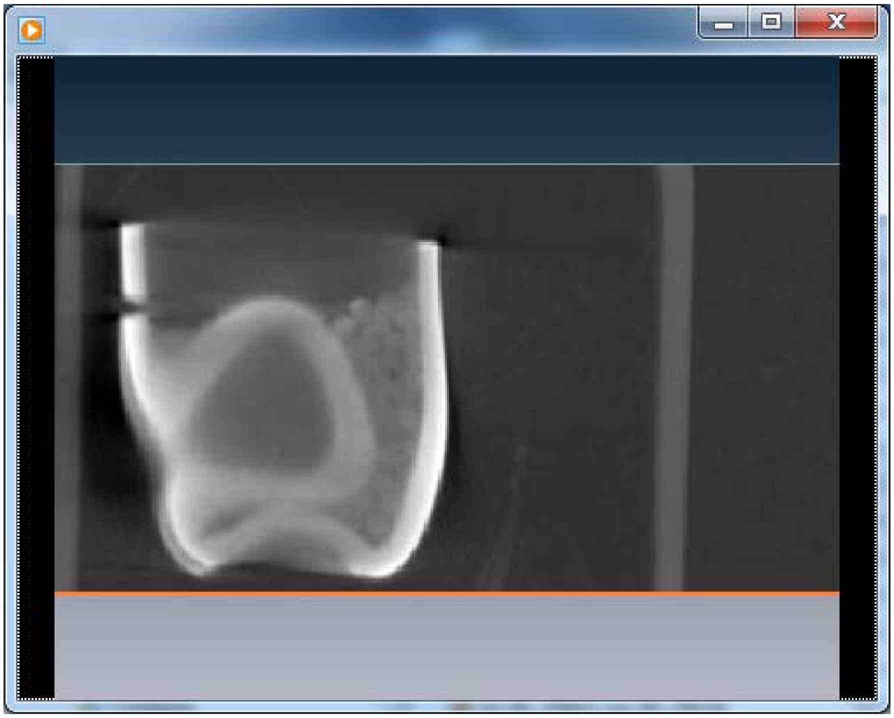

Figure 19: X-ray tomographic image of Capsule 5 cutting across the capsule in the vertical plane.

Figure 20 is a slice taken through the radial plane 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.

DISCUSSION AND PATH FORWARD

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.

Analysis of Loose Material

It was determined that several of the loose pellets/beads will be analyzed. Scanning electron microscopy/energy dispersive x-ray spectroscopy (SEM/EDX) and x-ray diffraction (XRD) will be used to determine chemical composition, morphology, and structure. Several pellets will be dissolved, and the effluent (liquid and gas) will 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 will also be determined.

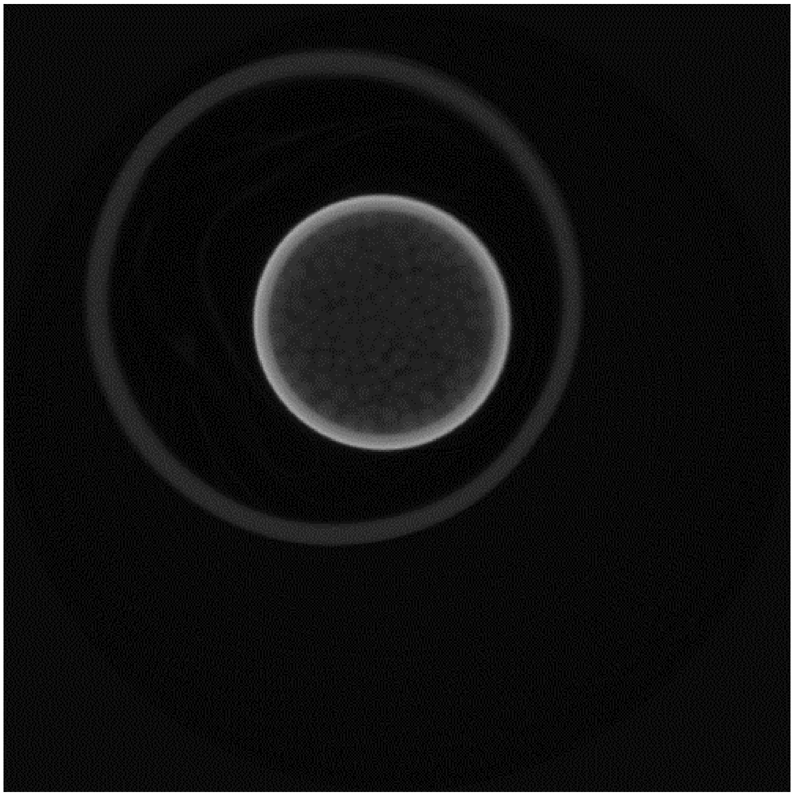

Figure 20: X-ray tomographic image of Capsule 3 cutting across the capsule in the radial plane.

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.

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.

The analysis of these samples and then of the unbreached 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

REFERENCES

1) A. B. CHRISTENSEN, J. A. DEL DEBBIO, D.A KNECHT, J. E. TANNER, Immobilization and Leakage of Krypton Encapsulated in Zeolite or Glass. Materials Research Society Symposia Proceedings, v 6, p 525-532, 1982.
2) A. B. CHRISTENSEN, J. A. DEL DEBBIO, D.A KNECHT, J. E. TANNER, S. C. COSSEL, Immobilization of Krypton-85 In Zeolite 5A, Proceedings of the DOE Nuclear Air Cleaning Conference, v 1, p 333-356, 1983.
3) A. B. CHRISTENSEN, J. A. DEL DEBBIO, D.A KNECHT, J. E. TANNER, Loading and Leakage of Krypton Immobilized in Zeolites and Glass, Scientific Basis for Nuclear Waste Management, v 3, p 251-258, 1981.
4) R. W. BENEDICT, A. B. CHRISTENSEN, J. A. DEL DEBBIO, J. H. KELLER, D. A KNECHT, Technical and Economic Feasibility of Zeolite Encapsulation for Krypton-85 Storage (Exxon Nuclear Idaho Co., Inc., Idaho Falls.), Sponsor: U.S. Department of Energy., 96p, Sep 1979.
5) Personal Communications, Deiter Knecht. Oct, 2010.
6) T. GARN, M. GREENHALGH, and J. LAW, *Strategy for Analysis of Legacy Kr-85 Samples*, FCRD-SEPA-2011-000027, INL/MIS-10-20449, Dec 23, 2010.
7) R. T. JUBIN, Multi-lab Analytical Plan for Analysis of Legacy ^{85}Kr Samples, FCRD-MRWRD-2015-000624, ORNL/SPR-2015/188, Apr 10, 2015.

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