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December 16, 2010

To: Terry Todd

From: Robert T. Jubin

Subject: Completion of the ORNL Fuel Cycle Research and Development (FCR&D) Level 4 Milestone – Off-Gas Sigma Team - FTOR11SW0309, MS# M41SW030910, "Test Plan for Kr Loaded Zeolite Samples," due 12/31/2010

This letter documents the completion of the FCR&D Level 4 milestone for the Off-Gas Sigma Team - ORNL work package (FTOR11SW0309), "Test Plan for Kr Loaded Zeolite Samples" (M41SW030910), due 31 December 2010. The test plan drafted by staff at Idaho National Laboratory was reviewed by ORNL Off-Gas Sigma Team members and other staff. Based on that review, suggestions and additional test requirements were provided by e-mail from R. T. Jubin to Mitchell Greenhalgh on 10 December. That email and attachments are attached to this memo. This milestone was completed early.

If you have any questions, please contact me at (865) 574-4934.

cc: C. V. Bates (INL)
E. D. Collins
L. K. Felker
D. K. Jensen (INL)
B. D. Patton
D. W. Ramey
B. B. Spencer

Jubin, Robert Thomas

From: Jubin, Robert Thomas
Sent: Friday, December 10, 2010 3:21 PM
To: Mitchell Greenhalgh
Cc: Jack D Law; Jubin, Robert Thomas; Patton, Bradley D.
Subject: RE: Draft Kr Legacy Sample Test plan
Attachments: 2010-12-02_Evaluation_Stages.pptx; Kr-85_draft_test_plan-Patton_Jubin comments[1].docx

Mitch, Jack,

Attached are comments from ORNL. We have some ball park costs shown in the table below but these really should be considered preliminary until be better understand the condition of the samples. I would recommend leaving out individual cost in this document as I suspect that the basis of these will differ from site to site and we certainly need to understand the full cost of this as we propose to conduct this analysis. Also we should factor some cold test costs into the total be for this is finalized.

Analysis	Data that can be obtained	Location of analysis	Estimated cost ($)
Photography / videography	Record of each step of analysis	INL/ORNL	1000-5000
Radiation Levels	Radiation values for shipping purposes	INL	1000
Gamma Spectrometry	Gamma emitting radionuclides present	INL	??
Neutron Radiography	Sample form, HIPed container specifications	INL	7000
Over gas analysis / Rare Gas Analysis	Gaseous corrosion/reaction products/release rate from waste matrix	ORNL	Design/fab equipment $125K Receive material/subsample ship 50K Gas sampling and loadout 50K
Container Integrity	Chemical attack on container	ORNL	3525 SEM $30K
Dissolution/gas sampling/chemical analysis/ICPMS/Rare Gas Analysis	Determination of fraction of Kr/Xe remaining in waste matrix – determination of Rb remaining in matrix	ORNL	4501 $150K
SEM of capsule/waste matrix interface	Extent of corrosion, chemical attack on container	ORNL	Sample prep 3525 $50K SEM at K25 $30K
SEM/EDX	Chemical composition, morphology and structure	PNNL??	???
TEM	Crystal orientation and	PNNL??	???

	electronic structure		
XRD	Chemical composition, morphology and structure	ANL??	???
XAS	Radiation damage to zeolite matrix, fate of the decay product Rb	ANL	45,000
XPS	Elemental composition and chemical state of the surface	???	???

If I / we come up with more ideas we will send these as soon as possible. Please call if you have any questions.

Bob

From: Mitchell Greenhalgh [Mitchell.Greenhalgh@inl.gov]
Sent: Monday, November 29, 2010 6:20 PM
To: Jubin, Robert Thomas
Cc: Jack D Law
Subject: Draft Kr Legacy Sample Test plan

Bob,

Attached is the draft test plan for the Kr-85 legacy samples. Will you please distribute the document to the other Sigma Team members for their review. I would like to have comments back by Dec. 10, to allow time for incorporation into the final document by Dec. 24.

Thanks

Mitchell Greenhalgh
Aqueous Separations & Radiochemistry
Idaho National Laboratory
Phone: (208) 526-0913
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StrategyTest Plan for Analysis of Legacy Kr-85 Samples

Introduction

Legacy samples composed of Kr-85 encapsulated on solid zeolite 5A material and small metal tubes containing a mixture of the zeolite combined with a glass matrix resulting from Hot Isostatic Pressing (HIP) processing have been preserved. The samples are a result of R&D Kr encapsulation efforts in the late 1970's performed at the Idaho Chemical Processing Plant (ICPP). The samples were recently retrieved from archive storage in the soon to be D&D CPP-602 facility and transported to the Hot Fuels Examination Facility (HFEF) within the Materials Fuels Complex (MFC) at the Idaho National Laboratory (INL). The preservation of the samples can lead to determinations of aging data providing invaluable information to ongoing Sigma Team off-gas treatment and waste form R&D efforts. 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).

~~The radiation levels of the samples and the metal storage cylinder containing the samples will also need to be acquired. The radiation levels are important as they will guide decisions as to where the analytical efforts may occur and the appropriate shipping requirements are met.~~

Background

In the late 1970's, an R&D effort to study Kr-85 encapsulation and leakage was performed at the INL by Christensen, et al.[1-4] Off-gas resulting from fuel dissolution underwent treatment with the fission products sent to the Rare Gas Plant (RGP) at ICPP where the Kr-85 was removed via cryogenic distillation and collected in gas cylinders. A cylinder containing the Kr-85 was transferred to the Multi-Curie Cell (MCC) where the encapsulation studies were completed.

The R&D Kr-85 encapsulation effort incorporated numerous materials including sodalite, "thirsty" glass and zeolite 5A, with zeolite 5A reportedly showing the best results. However, included in the R&D effort was the evaluation of Kr-85 leakage resulting in numerous samples of each material being cut apart to measure Kr-85 leakage via thermogravimetric analysis (TGA). With the testing including numerous materials, there is a question as to exactly what the BEA owned samples truly represent. It is assumed that since 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 researchers (retired) stating that the samples include "loose" zeolite 5A encapsulating Kr-85 and zeolites 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 HFEF. Photographs showing the "loose" zeolite and the squashed metal tubes are found in Figures 1, 2 and 3.

Upon completion of this study, samples were archived and stored in the CPP-602 analytical process support facility. With the decision to D&D this facility in 2010, the fate of these samples to either be disposed in sub-surface burial or transferred to a new storage location under new ownership, the latter was optioned. In June 2010 Battelle Energy Alliance became the owner of these samples. The samples were transported from CPP to the HFEF facility within the MFC complex.

Figure 1. Photo of the "loose" zeolite material in a Ziplok bag.

Figure 2. Photo of a metal tube presumably containing potentially unHIPed "loose" zeolites.

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

Scope/Objectives

The main objective of this document is to establish the overall strategy for the sampling and analysis of this valuable aged sampled and to ensure that key information is not lost in the process of opening the capsules and collecting samples for analysis.

The scope of this task is to ascertain the research benefits of performing various types of sample analyses using resources available throughout the DOE complex or alternatively at other academic laboratories. This ~~may~~ includes the development of ~~-~~an unpackaging and ~~intial~~initial NDA characterization plan, a disassembly and subsampling plan and individual subsample ~~anaylis~~analysis plans~~a sample plan~~ dictating desired analyses and their respective results that can be disseminated from the analyses. Handling, disassembly and a~~A~~nalysis order will~~should~~ be planned and documented to avoid compromising the data~~on an as needed basis~~, beginning with radiation level measurements, detailed photographic analysis, gamma spectrometry and neutron radiography ~~and radiation level measurements~~ prior to the head-gas capture, disassembly, subsampling and destructive analysis that are driven by safety precautions and mitigations. A hold point will be established at the completion of the NDA characterization to review the results and to develop the detailed plans for sampling the head-gas space, capsule opening. The opened capsule will be stored in an inert over-pack pending finalization of the sub-sampling and analytical plans. Preliminary analytical plans will be prepared based on the NDA results and possible surrogate material testing. These preliminary analytical plans will be revised and finalized based on the results from the head-gas analysis and observations during the capsule opening. It is recommended that only one capsule be processed at a time. Any cutting or destruction of the HIPed tubes will be performed in ~~a~~ appropriate facilities to control the hazards associated sample or subsamples~~hielded cell, mitigating the release of any radioactive material.~~

The general sequence of the work will ~~as~~ be in three stages as shown in Figure 1.~~.~~ Stage one will be to initially characterization of the samples (radiation levels, contamination levels and gamma signature) and neutron imaging. The initially characterization and imaging will allow the handling facilities for unpackaging/dissembly and subsampling to be selected, a disassemble plan to be developed, shipping plans to be developed and facilitities for analysis to be proposed. Stage two is the unpackaging/gas sampling/disassembly/~~.~~subsampling and packaging fo~~-~~r shipment to the analysis sites. The final stage is the analysis of the subsamples a~~t~~and the appropriate laboratories.

Data mining to collect as much data on the construction of the samples containers and the specific conditions under which they were loaded should be given a high priority. ~~The main objective of this document task is~~will be to advertise the existence of the samples to prospective interests.

The numerous analytical techniques that can be used to acquire sample information will need to be identified along with the respective laboratories with those analytical capabilities. DHS Forensics Exercises involving sealed sources can provide significant insight into sampling sequences and protocols and should be mined for lessons learned. An example of a proposal for analysis plan is provided in Appendix A. ~~Due to the radioactive nature of the samples, the prospective laboratories must be able to perform analyses in a shielded environment.~~

After identifying prospective laboratories, cost estimates associated with analyses and shipping of the samples will be required. ~~Costs will include sample handling on the INL side in the HFEF.~~

Potential Data Information

Analysis of the legacy samples will give valuable information of the state of the samples, corrosion of the containers and the zeolite material and radiation damage. Analysis of these aged samples is expected to provide information on:

- Stability of the HIPed Kr loaded zeolite/glass matrix
- Impact of the in-growth of the decay products on the zeolite/glass matrix
- Release fraction of the Kr 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.

In order to quantify the effects of ~~corrosion,~~ radiation damage, etc., non-radioactive reference samples of zeolite 5A HIPed and unHIPed could be prepared. These reference samples could have Rb included in the matrix for comparison purposes. The same analyses performed on the legacy samples could be performed on these reference samples to provide baseline information from which to compare. These "reference" samples should also be used to validate proposed destructive test methods to ensure that accurate/reliable data will be obtained when performing the analysis of the actual samples

The radiation levels~~-~~ and contamination levels of the samples and the metal storage cylinder containing the samples will be the first characterization step.~~will also need to be acquired~~. Gamma spectrometry will be conducted on the samples to provide some indication of the gamma emitters present in the samples. These radiological properties ~~e radiation levels~~ are important as they will guide decisions as to where the analytical efforts may occur and the appropriate shipping requirements are met.

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Prior to shipping samples to interested parties, neutron radiography analysis should be performed on the metal tubes. This analysis would determine characteristics on the material in the tubes and of the containers themselves. The ultimate purpose would be to ascertain the container wall thickness and if the state of the material inside is in a "loose" or a solid monolith form. It should be noted that the neutron radiography analysis will activate the stainless steel containers adding to the overall radioactivity of the containers. Coinciding with the neutron radiography would be the acquisition of radiation readings for the container and if feasible, the samples within. Radiation levels will be used to ensure shipping regulations are met should portions of the samples be shipped to off-site laboratories. Following the initial neutron radiography analysis, a number of techniques are available to ascertain crystal structure, chemical composition, material corrosion (Rb in-growth), radiation damage to zeolites/glass, etc.

The following paragraphs include a brief description of arbitrary analysis techniques that could be performed to acquire material characterization for the samples:

The SEM/EDX method is used to determine the chemical composition of a specimen including its morphology and structure. This method provides higher resolution via better spatial resolution than X-ray fluorescence (XRF) or optical spectroscopy. [6] An analysis location has yet to be determined for this technique.

TEM is a microscopy technique transmitting a beam of electrons to image a specimen thus allowing for magnification and focus by an imaging device. This method would provide information as to crystal orientation and electronic structure of a specimen. [6] An analysis location has yet to be determined for this technique.

XRD is used to determine the arrangement of atoms in minerals such as aluminosilicates. Chemical composition, crystal structure and physical properties can also be obtained from this analysis technique. [6] An analysis location has yet to be determined for this technique.

XAS is used to study the chemical speciation of atoms in various materials. In particular, synchrotron x-ray spectroscopy can be utilized to explore oxidation states and near-neighbor coordination environments by x-ray absorption near edge spectroscopy (XANES) and by extended x-ray absorption fine structure (EXAFS) methods, respectively[7] (see Appendix A).

XPS is used to measure the elemental surface composition typically at 1-10 nm depths. This technique is also routinely utilized to determine the chemical or electronic state of each element in the surface. [6] An analysis location has yet to be determined for this technique.

The availability and location of analytical instruments is key in determining where the analyses can or will be performed. Radiation levels of the samples will also drive where additional analyses can be performed. Table 1 describes the types of analysis, the data that can be obtained, the location where the analysis could be performed and an estimated cost of the analysis including shipping.

Table 1. Potential analyses for the legacy samples

Analysis	Data that can be obtained	Location of analysis	Estimated cost ($)
Photography / videography	Record of each step of analysis	INL/ORNL	1000-5000
Radiation Levels	Radiation values for shipping purposes	INL	1000
Gamma Spectrometry	Gamma emitting radionuclides present	INL	??
Neutron Radiography	Sample form, HIPed container specifications	INL	7000
~~Radiation Levels~~	~~Radiation values for shipping purposes~~	~~INL~~	~~1000~~
Over gas analysis / Rare Gas Analysis	Gaseous corrosion/reaction products/release rate from waste matrix	ORNL	
Container Integrity~~Corrison~~	Chemical attack on container	ORNL	
Dissolution/gas sampling/chemical analysis/ICPMS/Rare Gas Analysis	Determination of fraction of Kr/Xe remaining in waste matrix – determination of Rb remaining in matrix	ORNL	
SEM of capsule/waste matrix interface	Extent of corrosion, chemical attack on container	ORNL	
SEM/EDX	Chemical composition, morphology and structure	PNNL??	???
TEM	Crystal orientation and electronic structure	PNNL??	???
XRD	Chemical composition, morphology and structure	ANL??	???
XAS	Radiation damage to zeolite matrix, fate of the decay product Rb	ANL	45,000
XPS	Elemental composition and chemical state of the surface	???	???

References

1. IMMOBILIZATION AND LEAKAGE OF KRYPTON ENCAPSULATED IN ZEOLITE OR GLASS. Christensen, A.B.; Del Debbio, J.A.; Knecht, D.A.; Tanner, J.E. Source: Materials Research Society Symposia Proceedings, v 6, p 525-532, 1982

2. IMMOBILIZATION OF KRYPTON-85 IN ZEOLITE 5A. Christensen, A.B.; Del Debbio, J.A.; Knecht, Dieter; Tanner, J.E.; Cossel, S.C. Source: Proceedings of the DOE Nuclear Air Cleaning Conference, v 1, p 333-356, 1983

3. LOADING AND LEAKAGE OF KRYPTON IMMOBILIZED IN ZEOLITES AND GLASS. Christensen, A.B.; Del Debbio, J.A.; Knecht, D.A.; Tanner, J.E. Source: Scientific Basis for Nuclear Waste Management, v 3, p 251-258, 1981

4. TECHNICAL AND ECONOMIC FEASIBILITY OF ZEOLITE ENCAPSULATION FOR KRYPTON-85 STORAGE. Benedict, R. W.; Christensen, A. B.; Del Debbio, J. A.; Keller, J. H.; Knecht, D. A. (Exxon Nuclear Idaho Co., Inc., Idaho Falls.) Sponsor: Department of Energy., 96p, Sep 1979

5. Personal Communications Deiter Knecht. Oct, 2010.

6. Brief descriptions of analyses were obtained from the en.wikipedia.org website

7. Proposal to Perform synchrotron X-ray spectroscopic analysis of legacy ^{85}Kr zeolites with significant radioparagenic ^{85}Rb. Fortner, J. A.; Kropf, J.; Argonne National Laboratory

Appendix A

Title of Project: Proposal to Perform synchrotron X-ray spectroscopic analysis of legacy ^{85}Kr zeolites with significant radioparagenic ^{85}Rb

Principal investigators and institution: Jeffrey A. Fortner and A. Jeremy Kropf, Argonne National Laboratory

Background and scope

Most radioactive decay results in the transmutation of one element into another (radioparagenesis), a process that may affect the physical and chemical properties of the material in which the transmutation occurs. In natural uranium minerals and in actinide-containing waste forms, the concentration of the decaying isotope is usually low and the isotope decays to a daughter element with multiple valences, one of which is the same as the parent isotope. For the fission product ^{85}Kr, this is not the case. The ^{85}Kr starts as an element with rigid valence requirements as a noble gas and decays to rubidium, an alkali metal. For the waste forms under consideration to capture and contain off-gas from recycle of used nuclear fuel, ^{85}Kr concentrations can be relatively high. Thus, decay transmutation of ^{85}Kr to ^{85}Rb can have a major impact on the chemical and physical properties of the waste form, especially those of concern for the long-term storage and performance assessment of these waste forms in a repository. A particular concern is that radioparagenic rubidium, if present as free metal or in an unstable compound, can be highly corrosive to many types of metal that would be preferred for use as containment of the sorbents, including stainless steels.

Specimens of aluminosilicate sorbents that had been loaded with krypton gas during used nuclear fuel dissolution have become available to the DOE FCR&D Program. These specimens are several decades old, and most of the fission-product ^{85}Kr has since decayed to stable ^{85}Rb. Only about 4.5% of the total krypton in used fuel, however, is radioactive, so the current specimens will have more than 20x as much krypton as radioparagenic rubidium, complicating chemical analysis. We propose to use x-ray absorption spectroscopy (XAS) to study the chemical speciation of the rubidium and krypton within these materials. This technique has been applied successfully to a similar, and even more technically challenging system, aged pollucite ($CsAlSi_2O_6$) that had undergone significant radioparagenesis of ^{137}Cs to ^{137}Ba [1,2].

By analyzing XAS data from a particular absorption edge, we can determine the local environment of a specific atomic species, including distances to near neighbors, types and

numbers of neighboring atoms, and details of the radial distribution function. The energy of the absorption threshold and near-edge absorption features also can be used to obtain information about the charge state of the central atom and the site symmetry. Typically, one measures absorption as a function of incident x-ray energy by monitoring the fluorescence yield in an energy window that includes an emission line of the element of interest. A fundamental difficulty in detecting and measuring the hard x-ray absorption spectra of small quantities of rubidium in the presence of a larger quantity of krypton is the small energy separation of the fluorescent x-ray spectral lines—about 874 eV between the Kα lines of Kr and Rb. In order to obtain high-fidelity spectra from low levels of Rb in the presence of abundant Kr, we will employ a narrow bandwidth analyzer based on diffractive optics. One such diffractive geometry is the Laue configuration, where x-rays are transmitted through the crystal, rather than reflected from the crystal. We have developed the bent Laue technique for XANES/EXAFS to study corroded oxide used nuclear fuels and neptunium-containing uranyl compounds [3-8].

We will use synchrotron x-ray spectroscopy to explore oxidation states and near-neighbor coordination environments by x-ray absorption near edge spectroscopy (XANES) and by extended x-ray absorption fine structure (EXAFS) methods, respectively. The measurements will be made on the insertion device beamline of the Materials Research Collaborative Access Team (MRCAT) at Argonne's Advanced Photon Source (APS) synchrotron.

Deliverables

The deliverable will consist of a final report that details the XAS findings and uses them, along with other available information, to develop an assessment of the damage caused by the decay transmutation from Kr to Rb on the structure of the aluminosilicate matrix and the fate of the decay-generated Rb.

Funding

XAS study: We are requesting a budget of $45,000 to cover the costs of sample transfer, specimen preparation, safety documentation and review, APS beam time, data acquisition and analysis, and report preparation.

References

1. J. A. Fortner, S. B. Aase, and D. T. Reed, "Radiogenic Transmutation Effects in Crystalline Aluminosilicate Ceramic: A TEM Study." *Mat. Res. Soc. Symp. Proc. Vol.* **713** (2002).

Appendix A

2. J. Fortner, J. Kropf, and M. Kaminski, “Annual Report on Characterization of Aged Radioactive Pollucite.” Prepared for U.S. Department of Energy Waste Form Campaign, September 15, 2008.

3. A. J. Kropf, J. A. Fortner, R. J. Finch, J. C. Cunnane and C. Karanfil, “A Bent Silicon Crystal in the Laue Geometry to Resolve X-ray Fluorescence for X-ray Absorption Spectroscopy,” *Physica Scripta* Vol. **T115**, 998–1000, (2005).

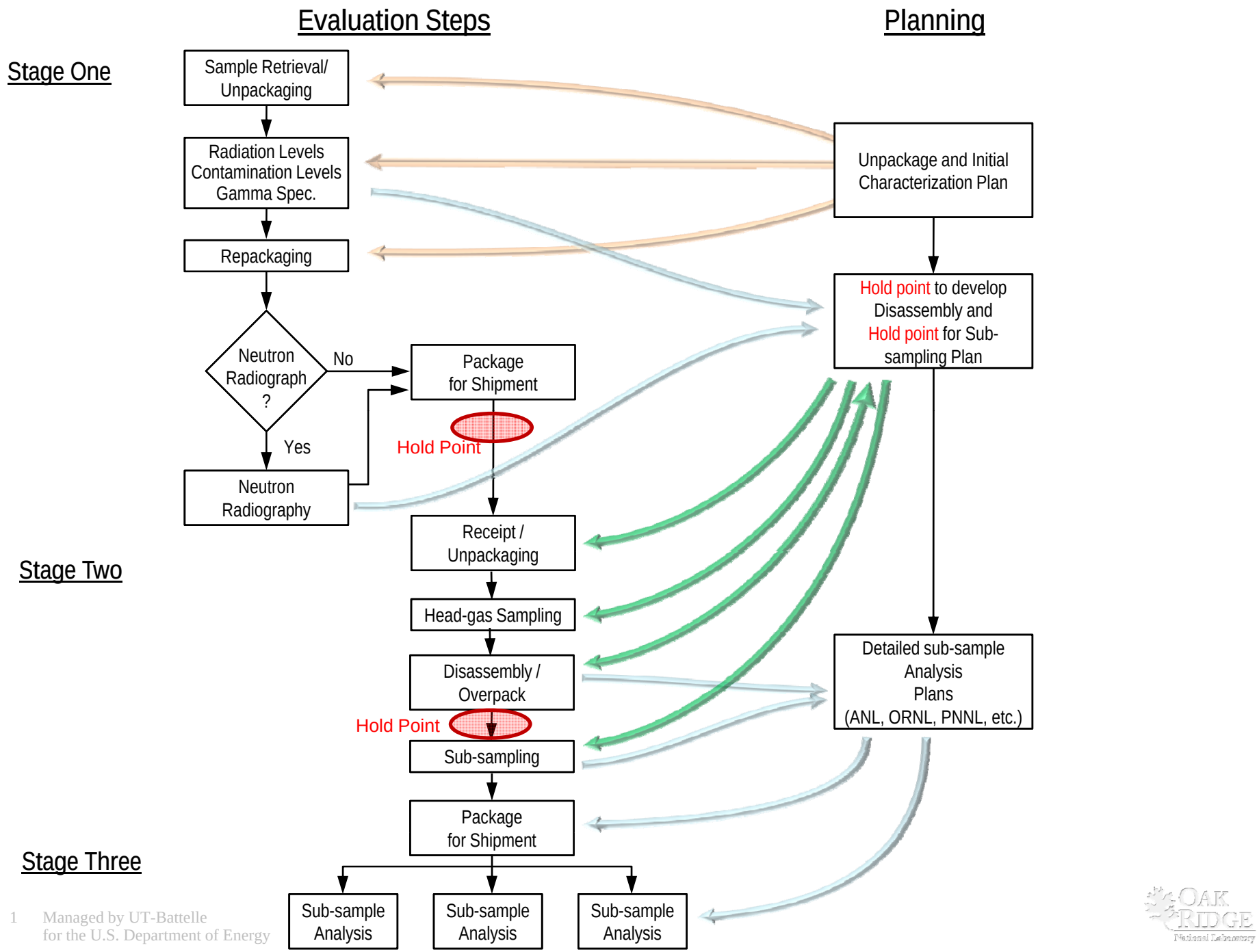
4. J. A. Fortner, A. J. Kropf, R. J. Finch, and J. C. Cunnane, “Technetium and Molybdenum in Oxide Spent Nuclear Fuel: Impact on Release Estimates,” in *Scientific Basis for Nuclear Waste Management XXVIII*, edited by John M. Hanchar, Simcha Stroes-Gascoyne, and Lauren Browning (Mater. Res. Soc. Symp. Proc. **824**, Warrendale, PA , 2004), paper number CC2.11.

5. J. A. Fortner, R. J. Finch, A. J. Kropf, and J. C. Cunnane, “Re-evaluating Neptunium in Uranyl Alteration Phases from Corroded Spent Fuel,” *Nuclear Technology* **148** (2) 174-180 (November 2004).

6. A. J. Kropf, R. J. Finch, J. A. Fortner, S. Aase, C. Karanfil, C. U. Segre, J. Terry, G. Bunker, and L. D. Chapman, “On a Bent Silicon Crystal in the Laue Geometry to Resolve X-ray Fluorescence for X-ray Absorption Spectroscopy.” *Rev. Sci. Inst.*, **74**, 4696-4702 (2003).

7. A. J. Kropf, C. Karanfil, C. U. Segre, R. J. Finch, J. A. Fortner, S. Aase, J. Terry, G. Bunker, L. D. Chapman, “On a Bent Silicon Crystal in the Laue Geometry to Resolve X-ray Fluorescence for X-ray Absorption Spectroscopy,” *Rev. Sci. Instrum*. **74**, 4696-4702 (2003).

8. J. A. Fortner, A. J. Kropf, J. L. Jerden, and J. C. Cunnane, “Chemical Effects at the Reaction Front in Corroding Spent Nuclear Fuel,” in *Scientific Basis for Nuclear Waste Management XXX*, edited by D.S. Dunn, C. Poinssot, B. Begg (Mater. Res. Soc. Symp. Proc. **985**, Warrendale, PA, 2007), paper number NN01-03.


Evaluation Steps
Planning
Stage One
Sample Retrieval/ Unpackaging
Radiation Levels Contamination Levels Gamma Spec.
Repackaging
Neutron Radiograph ?
No
Yes
Package for Shipment
Hold Point
Neutron Radiography
Unpackage and Initial Characterization Plan
Hold point to develop Disassembly and Hold point for Sub-sampling Plan
Stage Two
Receipt / Unpackaging
Head-gas Sampling
Disassembly / Overpack
Hold Point
Sub-sampling
Package for Shipment
Detailed sub-sample Analysis Plans (ANL, ORNL, PNNL, etc.)
Stage Three
Sub-sample Analysis
Sub-sample Analysis
Sub-sample Analysis