This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

WSRC-TR-2005-00332
Rev. 0

Plutonium Surveillance Destructive Examination Requirements at Savannah River National Laboratory for K-Area Interim Surveillance (U)

T.M. Stefek

Savannah River National Laboratory

Publication Date: September 2005

Contributors:

K.A. Dunn – 3013 Surveillance Program, SRS Program Lead
G.T. Chandler – Pu Surveillance DE Manager
F.A Cheek, D.Z. Nelson – Metallurgical Analysis
R.R Livingston, J.M. Duffey, D.C. Witt – Gas Analysis and Oxide Characterization
A.R. Jurgensen – Chemical Analysis
J.W. McClard – MIS Representative

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

This document was prepared in connection with work done under Contract No. DE-AC09-89SR18035 with the U. S. Department of Energy

DISCLAIMER

Plutonium Surveillance Destructive Examination Requirements at Savannah River National Laboratory for K-Area Interim Surveillance (U)

APPROVALS:

T.M. Stefek Date: 9/29/05
T.M. Stefek, Pu Surveillance DE Coordinator

Kerry A. Dunn Date: 10/3/05
K.A. Dunn, 3013 Surveillance Program, SRS Program Lead

Greg T. Chandler Date: 10/3/05
G.T. Chandler, Pu Surveillance DE Manager

Alice M. Murray Date: October 6, 2005
A.M. Murray, Actinide Technology Section Manager

L. M. Chandler Date: 10-11-05
L. M. Chandler, Analytical Development Section Manager

Natraj Iyer Date: 10-17-05
N.C. Iyer, Materials Technology Section Manager

Cindy G. Head Date: 10-20-05
C.G. Head, SRNL Radiological Controls Manager

S.D. Burke Date: 10/26/05
S.D. Burke, NMM Engineering Manager

J.W. McClard Date: 11/3/05
J.W. McClard, MIS Representative

L.E. Traver Date: 10/26/05
L.E. Traver, NMM Engineering

Revision Log

Document No. WSRC-TR-2005-00332 **Rev. No.** 0

Document Title Plutonium Surveillance Destructive Examination Requirements at Savannah River National Laboratory for K-Area Interim Surveillance

Rev. #	Page #	Description of Revision	Date
0	all	Original document	9/29/2005

Table of Contents

1. INTRODUCTION

The DOE 3013 storage standard requires nested, welded 300 series stainless steel containers to store plutonium-bearing materials for up to 50 years.[1] Packaged contents include stabilized plutonium-bearing residues that contain chloride salts and a low (< 0.5 weight %) water content. The DOE 3013 STD requires surveillance of the packages over the 50 year lifetime. These surveillance requirements have been further defined by the Integrated Surveillance Program[2] to include both non-destructive examination (NDE) and destructive examination (DE) of the 3013 container. The DE portion of surveillance involves examining the 3013 nested containers, analyzing the head space gas, and evaluating the plutonium oxide chemistry. At SRS, the stored 3013 containers will undergo preparation for the DE surveillance activities in facilities located in K-Area. The actual DE surveillance will be performed in SRNL.

This report provides preliminary functional requirements for the destructive examination (DE) of plutonium-bearing oxide materials and containers in support of K-Area Interim Surveillance (KIS). The KIS project will install interim facilities to prepare the samples for analysis in SRNL. This document covers the requirements for the interim period beginning in 2007, and lasting until the Container Storage and Surveillance Capability (CSSC) project provides the permanent facilities in K-Area to perform sampling and repackaging operations associated with the 3013 container storage and surveillance program. Initial requirements for the CSSC project have been previously defined in WSRC-TR-2004-00584 “Plutonium Surveillance Destructive Examination Requirements at Savannah River National Laboratory”. As part of the Plutonium Surveillance Program of 3013 Containers at the Savannah River Site (SRS), the Savannah River National Laboratory (SRNL) will receive the emptied 3013 container components, plutonium oxide samples and headspace gas samples from K-Area. The DE program scope includes chemical and metallurgical analyses for a maximum of 25 DE sets a year to provide essential data in support of the SRS Plutonium Surveillance Program. The normal operation is expected to be approximately 15 DE sets a year.

2. ASSUMPTIONS

The requirements outlined in this document are based on the following assumptions:

2.1 K-Area Operations will package and ship the set of 3013 container components and samples required for the DE examination to SRNL in a DSF-6 package, or approved equivalent.

2.2 Each DE set will include three empty 3013 containers (i.e. outer container, inner container and convenience can) for metallurgical evaluation, up to three headspace gas samples, and up to three plutonium oxide samples.

2.3 SRNL will have the capacity to perform one DE every two weeks and can complete up to 25 DE's per year. However, the normal operation is expected to be approximately 15 DE sets a year.

2.4 Only routine metallographic and chemical measurements described in this document are included in the SRNL baseline DE scope and schedule. Identification of conditions outside the expected range for the 3013 container or contents require additional review based on observed anomalous conditions to determine what additional analyses are necessary.

2.5 Plutonium oxide sample residues including both liquids and powders will be consolidated and sent to HB-Line. Characterization or additional processing of materials to HB-Line receipt criteria is new scope and will be defined in subsequent documents.

2.6 The metal waste from 3013 containers (e.g., surface contaminated stainless steel samples) will be disposed of by SRNL.

2.7 Metallurgical samples will be archived in SRNL facilities.

2.8 Pu-oxide samples will be archived in either SRNL facilities or in the K-Area Complex.

3. OPERATIONAL CONCEPTS

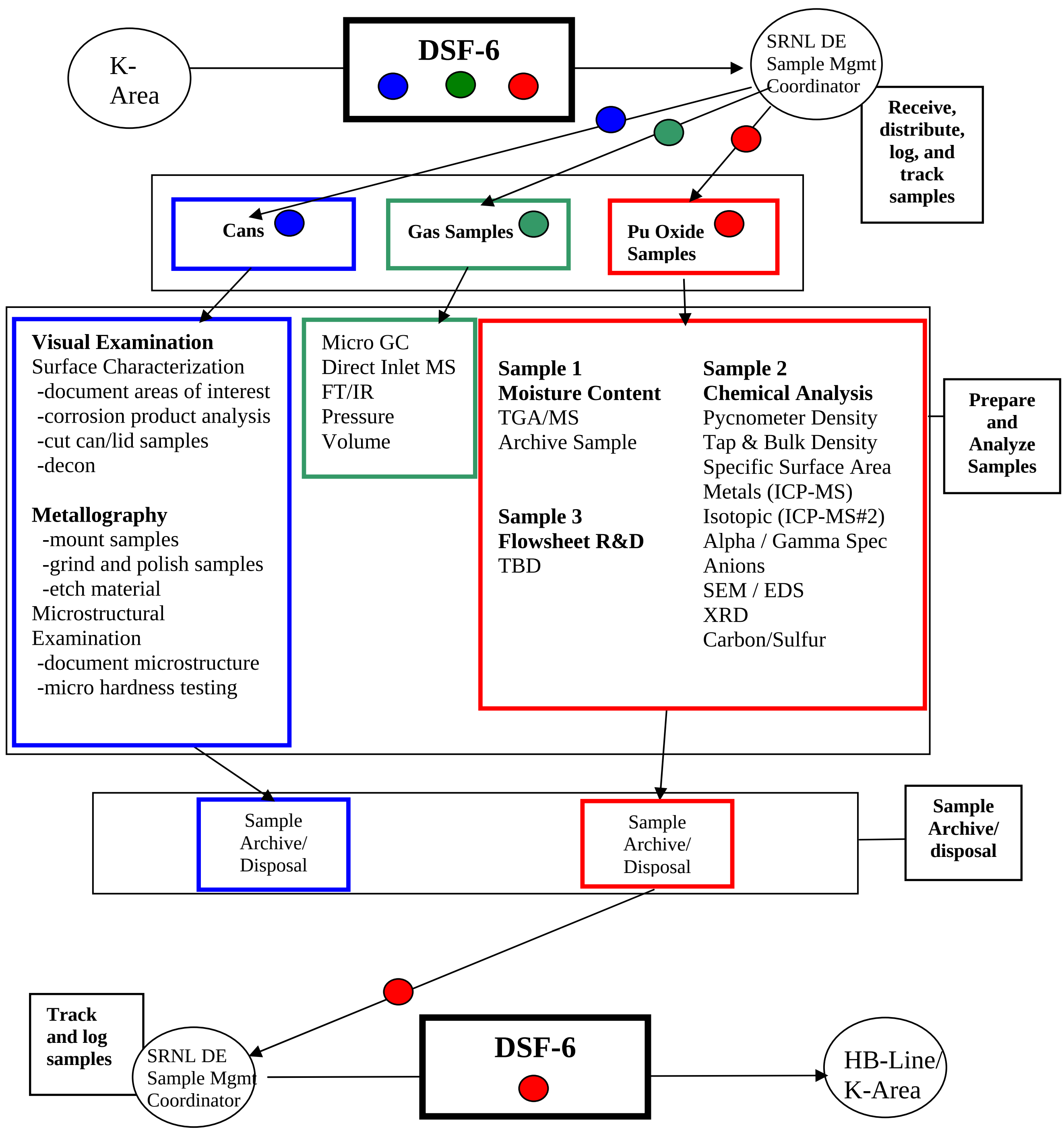
The following operational concepts give narrative descriptions of the expected process for the metallurgical evaluation of the 3013 containers, gas analysis, and plutonium oxide analysis. These concepts provide the rationale for the system design requirements that are presented in the next section. Materials Science and Technology (MST) in SRNL will coordinate activities for the DE program. Other SRNL organizations which are contributors to the success of the DE program include the Actinide Technology Section (ATS), Analytical Development Section (ADS) and Laboratory Services Department (LSD). The current division of responsibilities for DE testing is identified in Table 1.

Table 1. SRNL Section Responsibilities for DE Components.

DE Components	**Section**
Program Coordination	MST
Sample Management / Shipping	MST / ATS
Visual Examination	MST
Metallography	MST
Gas Analysis	ATS
Moisture Content	ATS / ADS
Flowsheet R&D	ATS
Chemical Analysis	ATS / ADS
Infrastructure Support	LSD

3.1 The following figure provides a process flow logic for samples received by SRNL.

Figure 1 Process Flow Sheet for DE of 3013 Container Metal Components, Headspace Gas, and Pu-Oxide Content



3.2 Normal Operation of Process

K-Area Operations personnel will cut the lids off the outer and inner cans, and open the convenience can. All cuts should be made at least 1/2 inch away from any closure weld, fabrication weld, and any heat affected zone (HAZ). K-Area Operations will perform light decontamination of containers to remove any residual plutonium-bearing oxide material. Light decontamination includes such things as tapping the container or brushing the container with a soft bristled brush. Light decontamination does not include wiping the containers with a cloth or using chemical agents to aid in removing residual material from the container. In fact, such activities are prohibited. The convenience can along with the inner and outer 3013 container components will be sent to SRNL for metallurgical evaluation. The initial evaluation will be conducted in a glove box and will consist of a visual examination, surface characterization, and documentation of areas of interest. Corrosion product and pitting may be analyzed; one technique available is Scanning Electron Microscopy (SEM) /Energy Dispersive System (EDS). The samples for routine analysis will be cut, decontaminated, and mounted prior to removal from the glove box. Samples will be metallographically prepared by grinding, polishing, and etching the samples for microstructural examination. A hardness test will be performed on a representative number of samples. The metallographic samples will be archived for a duration to be determined. Remnant container material will be discarded via the SRNL waste system.

K-Area Operations will be responsible for capturing a gas sample from between the outer and inner can, from between the inner and convenience can, and if possible from within the convenience can, by utilizing the can puncture device. Some convenience can designs are expected to allow gas to move between convenience can and the inner 3013 container. However, an attempt to collect a gas sample from each space may still provide additional information on the movement of various gases. Gas samples will be analyzed using a contained Micro Gas Chromatograph (GC), Direct Inlet Mass Spectrometer (MS), and Fourier Transform - Infrared Spectrophotometer (FTIR). The pressure and volume of the sample will be measured by SRNL in order to back calculate moles of gas generated. The sample containers will be monitored by SRNL prior to use to assure cleanliness and proper evacuation. The protocol for sample container preparation and implementation with the can puncture device will be incorporated in K-Area procedures, as required.

Three separate and representative samples of plutonium oxide, two containing approximately 20 grams, and one containing approximately 30 grams, will be packaged in K-area for transfer to SRNL for analysis. The first sample consists of an 8 mL stainless steel B-vial with o-ring seal filled approximately 80% full with a powder sample. This sample will be analyzed in a glove box using Thermo-Gravimetric Analyzer (TGA) MS to determine loss on ignition (LOI) and moisture content. The stainless steel vials will be pre-weighed to the nearest 0.1 gram before sampling to allow determination of the sample mass after sealing and tracking any changes in sample due to adsorption or desorption of moisture after sealing. The mass of this sample is expected to be somewhere around 20grams of bulk, depending on sample density. This sample is packaged separately to ensure the moisture content is preserved during handling. The size of this sample allows for duplicate TGA measurements when required and the remaining unused sample and stainless steel vial will be used for the archive sample.

The second sample of Pu-bearing oxide (20 grams) will be split into four parts and prepared, as required, for various analytical measurements. The first part will be analyzed using the pycnometer to determine the sample's crystal density. The second part will be used for bulk and tap density measurements then subsequently evaluated for specific surface area using the Brunauer Emmet Teller (BET) method. The second part will be characterized using the SEM/EDS and X-Ray Diffraction (XRD) to determine powder morphology, elemental analysis by x-ray fluorescence (XRF) and composition of the crystaline oxides by XRD. The third part will be dissolved and submitted to ADS for Inductively Coupled Plasma Emission Spectroscopy (ICP/ES), ICP-MS, Radchem, and Ion Chromatography. This analysis may require multiple dissolution techniques to gain somewhat complete digestion of the sample and allow for compatibility with the analytical methods recommended. The fourth part will be used for carbon sulfur analysis by ignition of the sample in LECO analyzer and quantitative infrared measurement of a carrier gas for CO_2 and SO_2 composition. Excess plutonium materials, both solid and liquid, will be packaged and sent to HB-Line recovery. It is assumed that this activity will require minimal preparation of the materials prior to shipping and the existing safety basis for the DSF-6 is sufficient for this activity.

The third sample of material (approximately 30 grams) will be used for flowsheet analysis. This scope is new for the SRNL DE program and additional details are required to be worked out separately between SRNL and H-Area to determine flowsheet test requirements and to more precisely define sample size. Key information includes baseline flowsheet conditions, analytical requirements, and identification of adequate glove box capability in SRNL. The dissolution of larger quantities of potentially high chloride-bearing oxides may present some new challenges for the SRNL facility infrastructure.

SRNL operating procedures will be used to conduct the DE, as prescribed by the surveillance program. The data collected will be entered in a DE Field Surveillance Module (FSM) for the ISP (Integrated Surveillance Program) Database. SRNL will have the capacity to perform one DE every two weeks and can complete up to 25 DE's per year. However the normal operation is expected to be approximately 15 DE sets a year.

The cut 3013 containers, gas samples, and plutonium oxide samples will be individually packaged for transportation to SRNL in a DSF-6 package, or an approved equivalent. These items constitute one DE set. Transportation of the DE set will be coordinated between K-Area and the SRNL DE Sample Management Coordinator (SMC). The DE set will be received, logged, distributed and tracked by the SMC.

3.3 Handling Anomalous Conditions

Anomalous conditions identified during the evaluation (e.g., unexpected gas composition or extensive corrosion of a containment layer) will be reviewed on a case by case basis. If it is determined that the conditions warrant further evaluation, additional analytical and metallographic measurements may be performed to provide insight into the observed conditions. These measurements and subsequent evaluation are beyond the established baseline for this program.

4. FUNCTIONAL REQUIREMENTS

This section provides the requirements for the test analyses, equipment needs, nuclear material accountability, safety and environmental concerns, and facility interface requirements. These requirements are grouped into major functional categories and split into sections for each type of analysis: 1) container metallurgy 2) headspace gas composition, and 3) Pu-bearing oxide properties. Detailed information will be presented in other documents to support these functional requirements.

4.1 Analysis Requirements

This table displays the analysis requirements for the DE of the 3013 containers, gas analyses and plutonium-bearing oxide analyses. SRNL and Materials Identification and Surveillance (MIS) representatives developed these requirements based on the ISP and the Surveillance and Monitoring (S&M) Plan. Equipment expected to be used for these analyses is listed in section 4.2.

Table 2 Analysis Requirements

EVALUATION	**ISP EXAMPLES [ref.1]**	**S&M PLAN [ref.2]**	**TECHNICAL REQUIREMENTS**
Pressure	Pressure measurement in puncture device	Pressure measurement in puncture device	Pressure instrument calibrated to measure 0 – 700 psig
Gas Analysis	MS or Raman	GC and MS	Identify species causing pressure buildup and possible corrosive species. At a minimum, measurement of H_2, O_2, N_2, H_2O, He, HCl, HF, CO, CO_2, NO_x, SO_x, CH_x
Moisture Content of Material	Approved method	Unspecified	TGA-MS
Chemical Composition of Material	Actinide assay, ICP/ES, ICP/MS, XRF, LIBS, Cl, S, F, etc.	Unspecified	Impurity analyses to interpret gas and corrosion analyses. At a minimum, measurement of metal impurities, Cl, F, S, C. Also ability to identify corrosion/gas generating compounds
Physical Characteristics of Material	Visual, image documentation, density, particle size, surface area	Visual, image documentation, density, particle size, surface area	General characterization to interpret other results
Container/Content Interaction	Visual, image documentation, metallography, SEM/EDS	Visual, metallography, SEM, EDS	Evaluate for indications of corrosion/ degradation of containers.

4.1.1 Metallurgical Evaluation

A metallurgical evaluation of the 3013 container is required to identify whether any degradation of the container, such as pitting corrosion or stress corrosion cracking, is occurring. This metallurgical evaluation will examine the interaction between the plutonium contents and the containers. The outer can, inner can, and convenience can from each 3013 package chosen for destructive surveillance activities will be provided to SRNL for metallurgical analyses. Each container will be visually examined. When present in sufficient quantity, the corrosion product(s) will be analyzed to assist in determining the corrosive species and mechanism. Approximately eight metallographic samples will be sectioned from each container, with a focus on high stress regions and areas with corrosion product or degradation.

4.1.2 Gas Analysis

The 3013 package selected for DE as part of the plutonium surveillance program will be punctured in order to capture the gases present within each void volume. The outer can will be punctured first and a gas sample will be captured. A gas sample will be taken from between the inner can and the convenience can, and possibly from within the convenience can. The pressure of each void volume will be measured and each gas sample will be transferred to SRNL. The gas samples will be analyzed to identify the different species present and measure the major components. Sample container volume and associated pressure limits will be established with K-area Operations in a future document to support implementation of SRNL flammable gas limits for glove box operations. Techniques capable of detecting and measuring trace quantities of the following headspace gas species have been selected: H_2, O_2, N_2, H_2O, He, HCl, HF, CO, CO_2, NO_x, SO_x, CH_x.

4.1.3 Pu-bearing Oxide Analysis

Representative samples of the Pu-bearing oxide material will be taken from the 3013 container chosen for DE and will be subjected to moisture analysis, chemical analyses and physical property measurements, and flowsheet analysis. The accepted methods for moisture analysis within the DOE complex are TGA/MS and TGA/ IR.

Physical characteristics of the Pu-bearing oxide, such as density, particle size, and surface area must be obtained and documented along with a visual inspection of the material. These measurements will support a comparison of material characteristics with other samples.

A chemical composition analysis of the Pu-bearing oxide shall be performed to identify the impurities within the material in order to aid in the interpretation of the gas and corrosion analyses results. At a minimum, a measurement of elemental impurities such as Cl, F, S, and C is required. The identification of corrosion/gas generating compounds is expected to provide important data for surveillance program management.

4.2 Equipment Requirements

The following section consists of tables describing the expected equipment needs for the DE of the 3013 containers, gas analyses and plutonium-bearing oxide analyses. The equipment needs were developed based on the analysis requirements presented in the previous section. The locations listed in Table 3 – 5 are currently the preferred locations for equipment and analyses. Details regarding cost estimates and scheduling of modifications to the labs and equipment will be provided in a separate document.

4.2.1 Metallurgical Evaluation Equipment Requirements

Table 3. Metallurgical Evaluation Equipment Requirements

Location	Equipment	Purpose	Purchase/ Exists
SRNL, C-059	Microscope	Visual characterization of containers	Order Placed
SRNL, C-059	Saw	Cut container specimens	Order Placed
SRNL, C-059	Camera	Documentation of visual characterization	Purchase
SRNL, C-059	Ultrasonic Cleaner	Metallography – sample preparation	Exists
SRNL, C-059	Mounting Equipment	Metallography – sample preparation	Exists
SRNL, C-126	Automatic Grinder/Polisher	Metallography – sample preparation	Exists
SRNL, C-126	Etcher/Power Supply	Metallography – sample preparation	Exists
SRNL, C-126	Metallograph	Microstructural evaluation/documentation	Order Placed
SRNL, C-126	Microhardness Tester	Microstructural evaluation	Exists

4.2.2 Gas Analysis Equipment Requirements

Table 4. Gas Analysis Equipment Requirements

Location	Equipment	Purpose	Purchase/ Exists
SRNL, B-135/139	Micro Gas Chromatograph	H_2, N_2, O_2, CO, CO_2, CH_4	Exists
SRNL, B-135/139	Direct Inlet Mass Spec	CH_x, CH_xO, CH_xN	Exists
SRNL, B-135/139	FT/IR	HF, HCl, NO_x, SO_x	Purchase

4.2.3 Pu-bearing Oxide Analysis Equipment Requirements

Table 5. Plutonium Oxide Analysis Equipment Requirements

Location	Equipment	Purpose	Purchase/ Exists
SRNL, B-135/139	Camera	Pu Oxide characterization (homogeneity)	Purchase
SRNL, B-135/139	Balance	Pu Oxide sample prep and dissolution	Purchase
SRNL, B-135/139	Furnace/Hot Plate	Dissolution for chemical analysis	Purchase
SRNL, C-154/158	TGA/MS	Moisture content, adsorbed species, validate stabilization	Exists
SRNL, C-154/158	BET	Specific Surface Area	Exists
SRNL, C-154/158	Pycnometer	Crystal Density (needed to calculate free volume in 3013)	Purchase
SRNL, C-154/158	Bulk/Tap Density	Pu Oxide characterization (validate 3013 assumptions)	Purchase
SRNL, B-147 B-067	ICP/MS and ICP/ES	Isotopic measurements, Impurities analysis	Exists
SRNL, B-142	Rad chem	Specific heat calculation, Rad material composition	Exists
SRNL, B-134	Ion Chromatograph	Anion quantitation (e.g. Cl, SO_4)	Exists
SRNL, B-135/139	Carbon/ Sulfur Analyzer	Carbon / Sulfur Analysis	Purchase
SRNL, C-134	SEM/EDS	Particle size, elemental analysis, sample morphology	Exists
SRNL, C-119	XRD	Identification of major components (e.g. PuO_2, U_xO_y, $PuCl_3$, MgO, $KMgCl_3$ etc)	Exists

4.3 Material Accountability Requirements

A cross-divisional task team has been established and is working to ensure that material accountability requirements are properly dispositioned. Material transfers, movement from K-Area to SRNL, within SRNL, and returns to HB-Line and K-Area are being addressed. An accountability system will be used to track accountable nuclear material throughout the process. DE shipments to SRNL and sample returns to HB-Line and/or K-Area will be coordinated by the SRNL DE SMC. Detailed information will be presented in future documents to define the material accountability requirements.

4.4 Safety and Environmental Requirements

The process for the DE of the 3013 containers shall include operating practices and/or administrative controls designed to ensure effective radiological control practices in accordance with the appropriate site and regulatory requirements.

A detailed safety evaluation addressing the hazards associated with SRNL activities required for 3013 DE will be presented in the Conduct of Research and Development Hazard Assessment document, which will include the controls required for handling beryllium. This document will serve as the umbrella for the safety evaluation of DE activities and will include consideration of the following: Job Hazards Analysis (JHA), Radiological Safety, Unreviewed Safety Question (USQ) Determination, Fire Protection, Industrial Hygiene and Chemical Hazards, Environmental Conditions and Compliance, and Waste Management.

5. COLD TESTING AND DEMONSTRATION

A task and quality assurance plan will be developed to detail how SRNL will perform non-radioactive testing. This task plan will use simulated containers and contents to support a demonstration of the SRNL facility and equipment capabilities for routine examination of 3013 containers, gas and Pu-bearing oxide samples.

6. REFERENCES

[1] Surveillance and Monitoring Plan for DOE-STD-3013 Materials (U), SR-NMPD-03-001, Rev 0.
[2] Integrated Surveillance Program in Support of Long-Term Storage of Plutonium-Bearing Materials, LA-UR-00-3246 Rev. 1, Los Alamos National Laboratory
[3] WSRC-TR-2004-00584, Plutonium Surveillance Destructive Examination Requirements at Savannah River National Laboratory, November 2004

7. ABBREVIATIONS AND ACRONYMS

ADS	Analytical Development Section
ATS	Actinide Technology Section
BET	Brunauer Emmet Teller analysis
CSSC	Container Storage and Surveillance Capability
DE	Destructive examination
FSM	Field Surveillance Module
FT/IR	Fourier Transform – Infrared Spectrophotometer
GC	Gas Chromatograph
HAZ	Heat Affected Zone
ICP/ES	Inductively Coupled Plasma Emission Spectroscopy
ISP	Integrated Surveillance Program
KAMS	K-Area Material Storage
KIS	K-Area Interim Surveillance
LIBS	Laser-Induced Breakdown Spectrometer
LOI	Loss on Ignition
MS	Mass Spectrometer
MIS	Materials Identification and Surveillance
MTD	Measurement Technology Department
MST	Materials Science and Technology
NMM	Nuclear Materials Management
R & D	Research and Development
RCO	Radiological Control Operations
S&M	Surveillance and Monitoring
SEM/EDS	Scanning Electron Microscope/Energy Dispersive System
SMC	Sample Management Coordinator
SMTD	Strategic Materials & Technology Department
SRNL	Savannah River National Laboratory
TGA	Thermo-Gravimetric Analyzer
TRU Waste	Transuranic Waste
XRD	X-Ray Diffraction System
XRF	X-Ray Fluorescence

CC:

D.M. Barnes, 705-K
S.D. Burke, 705-K
G.T. Chandler, 773-A
L.M. Chandler, 773-A
F.A. Cheek, 773-A
K.A. Dunn, 773-41A
K.J. Durrwachter, 705-K
C.G. Head, 773-A
N.C. Iyer, 773-41A
A.R. Jurgensen, 773-A
R.R. Livingston, 773-A
J.W. McClard, 703-H
D.Z. Nelson, 773-A
R.J. Martini, 704-9K
A.M. Murray, 773-A
J.B. Schaade, 704-2H
B.R. Seward, 705-K
F.D. Sinclair, 707-C
R.M. Sprague, 705-K
T.M. Stefek, 773-41A
L.E. Traver, 705-K
D.C. Witt, 773-A
Records Management