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3013 Surveillance Program Interim Summary Report (FY16- FY21)

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3013 Surveillance Program Interim Summary Report

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I. EXECUTIVE SUMMARY

The K-Area Documented Safety Analysis (DSA) requires the facility participate in the SRS Site Surveillance Program as a part of Shipping Package Qualification and Storage Surveillance Program [Ref. 1]. The Site Surveillance Program outlines activities for field surveillance and laboratory tests that demonstrate the 3013 containers meet the functional performance requirements described in the DSA. The SRS Surveillance Program also supports the complex-wide Integrated Surveillance Program (ISP) [Ref. 2] for 3013 containers in accordance with DOE-STD-3013 [Ref. 3]. The purpose of this report is to provide a summary of the SRS portion of the surveillance program activities from FY16 through FY21 and formally communicate the interpretation of these results by the Surveillance Program Authority (SPA).

In FY16 thru FY21 a total of 33 destructive examinations (DE) of 3013s were performed. To date, 134 DE's has been completed of which 94 are Random and 40 are engineering Judgment (EF) selections. Of the 134 DE's there were 122 from the Pressure and Corrosion (P&C) bin, 11 from the Pressure bin, and 1 from the Innocuous bin. All but one was performed at KAC (the other was done at Los Alamos National Lab (LANL). This container exceeded the 3013 Standard moisture limit and therefore was not authorized to be received and stored in KAC. The maximum pressurization seen to date in the DE's performed in KIS is 22.9 psia (the container opened at LANL was estimated to be pressurized to 43.4 psia). The MIS working group has concluded that pressure is an unlikely failure mechanism for 3013 containers.

However, pitting corrosion has been observed on some convenience containers and inside several inner containers, particularly at the inner can closure weld region (ICCWR). Stress corrosion cracking (SCC) of the inner container by a mechanism involving gas phase transport of corrosive species, whereby failure of the inner container allows for corrosive species to damage or even fail the outer 3013 container, is the only credible failure mechanism for the outer 3013 container in the existing 3013 population. A revised ISP was approved in May of 2015 [Ref. 2] to focus on SCC in the ICCWR. This Program specified a stratified approach to high moisture 3013 containers (≥0.08 wt.%) in the Pressure and Corrosion bin to better focus on containers where corrosion has been observed. The same statistical criterion (99.9%/5%) will continue to be used for determining random samples for 3013 surveillances.

To date the inner and outer 3013 container gas analysis has verified no through wall pitting or cracking has occurred. Although the limited extent of corrosion and small cracks and crack like features observed to date has not jeopardized the integrity of the inner 3013 containers, it does highlight the importance of continuing to perform DE and the Shelf Life program to assure that stress corrosion cracking has not or will not occur in the packaged inventory during the 50 year storage requirement. The current ISP allows completion of the random sample selection based on completion of five 3013 DEs per year from the random sample through FY25.

Since 3013 containers are stored inside 9975 shipping packages, surveillances of 9975 shipping packages are performed in conjunction with 3013 container surveillances. Lastly, the Surveillance

Program technical basis document was revised in July 2021 with updated field surveillance results and SRNL studies [Ref. 1].

II. BACKGROUND

The 3013 surveillance sampling approach was originally defined in the Surveillance and Monitoring Plan (S&MP) [Ref. 4]. The approach combines statistical and EJ sampling to provide a powerful, cost-effective method for ensuring the safe storage of 3013 containers. To select the statistical sample, the population of containers is organized into three bins based on a container's contents and potential degradation mechanism. Using pressure and corrosion as the two potential degradation mechanisms, the three bins are defined as: Pressure & Corrosion, Pressure, and Innocuous. The requirement of 99.9% probability of observing at least one of the worst 5% (in terms of potential degradation) is used to guide the statistical sampling process for the Pressure & Corrosion and Pressure bins [Ref. 4]. The sample size for the Innocuous bin is based on evaluating the assumption that these containers will show no degradation; therefore, these containers will have almost no variability in the surveillance results. The EJ sampling uses engineering judgment and results of the shelf-life studies to augment the statistical sample with additional containers that are judged to have the greatest potential for degradation.

In May of 2015 a revised Integrated Surveillance Program was approved by DOE [Ref. 2]. This document superseded the previous ISP [Ref. 5] and the Surveillance and Monitoring Plan [Ref. 4]. The new ISP modified the program based on results from Field Surveillance and Shelf-life testing. The program concluded that it is highly unlikely for pressurization to cause failure of a 3013 container during its 50 year life. Additional surveillance for pressure buildup is not necessary unless a new material is packaged that is not included in the current program. However, pitting corrosion has been observed in both Shelf Life tests and in convenience and inner containers during Field Surveillance. Stress corrosion cracking (SCC) has been observed under a variety of conditions in the Shelf Life Testing. For this reason, the surveillance plan was revised by the Materials Identification and Surveillance (MIS) Working Group to better focus on corrosion of 3013 containers in the P&C bin and to better align with the corrosion test program [Ref. 6]. As a part of that focus, there is recognition that the strongest correlation to corrosion inside the 3013 is moisture. Therefore, a stratified approach has been taken with the remaining random containers in the P&C bin [Ref. 2].

All but one of the 32 DE containers, which underwent DE through FY14, with observed corrosion of the convenience can or inner container had a moisture content of 0.08 wt.% or greater. All the 3013 containers with observed corrosion of the inner containers are in the high moisture stratum. Over 60% of the random containers in the P&C bin are in the lower moisture stratum. Concentrating the random sampling on the higher moisture stratum will allow DEs to be better focused on corrosion and will result in a smaller random sample while still maintaining the same (99.9%/5%) statistical criterion. The random samples were regenerated in support of the revised Program with a forecasted completion of the random selections by 2025 based on a minimum rate of 7 DEs per year. Previous DE protocols have not had the ability to thoroughly examine the ICCWR for pitting or SCC. New protocols are being developed for the ICCWR examination.

All the NDE surveillance examinations for the Innocuous bin and the Pressure bin have been completed, and there is no indication of corrosion or significant pressurization. Table 1 shows a breakdown of the number of each surveillance type for each bin. Table 2 shows the number of NDE and DE surveillances performed at SRS in each fiscal year.

III. DISCUSSION:

The SRS Site Surveillance Program [Ref. 1] requires a combination of field inspections and laboratory tests to validate the technical assumption regarding package performance and life expectancy. This report will provide information and data analyses to date for the surveillances performed through FY21. Destructive Examination of Pressure & Corrosion bin containers is currently scheduled to continue through FY25.

1. 3013 DE Surveillance Activities

The 3013 surveillance program completed all field surveillance activities through FY21 which includes completion of all planned 3013 Non-Destructive Examinations (NDE) and 134 Destructive Examinations (DE). Tables 1 through 6 provide a summary of results to date.

1.1 3013 DE Surveillance in KIS

The 3013 DE surveillance is performed in the K-Area Interim Surveillance (KIS) glove box. Through FY19 a can puncture device was used to safely puncture and collect gas samples from both the outer and inner 3013 containers during each DE. After FY19 the KIS glove box was upgraded to support plutonium oxide optimized down blending for final disposition at the Waste Isolation Pilot Plant (WIPP). No major findings that challenge the integrity of the 3013 containers were noted. A summary is provided below for each process.

i. Can Puncture

Gas pressures and compositions of each inner 3013 container for FY16 – FY19 are provided in Table 4. Pressures are calculated using a software model to determine the pressure inside the 3013 prior to puncture [Ref. 7]. The highest observed pressure was 18.7 psia for FY17 DE4. In nearly all cases the pressure is less than the KIS glove box ambient. The highest hydrogen concentration measured was 46.6 vol. % (FY17 DE4) while most containers had hydrogen concentrations less than 4 vol. In all containers the oxygen concentration is less than 0.1 vol. %.

ii. Can Cutter

KIS utilizes a conventional pipe cutter to open the welded 3013 cans. The pipe cutter parts the metal with a rolling blade. Various collets are used to hold the different sized inner cans. In all cases the inner most convenience can is opened manually without needing to use the can cutter.

iii. Oxide Inspection

Once the convenience can is removed from the 3013, a scoop sample of the oxide is taken from the top of the powder as soon as the convenience can is opened to determine the as-found moisture level in the 3013. A special lid is installed on the convenience can that allows temperature and humidity to be recorded for at least 6 hours (See Table 6). Next the oxide is poured out in a pan for examination and additional sampling. Beginning in FY20 oxide samples were taken for shipment to LANL to be used for Cl gas generation determination and corrosion coupon testing. A composite sample is taken from four quadrants of the pan for analysis at SRNL. No items of interest were collected during DEs performed from FY16-FY21.

iv. Visual Can Inspection

After removing the oxide, the outer and inner cans are visually inspected for any corrosion or evidence of degradation caused by the storage of Pu oxide. In the majority of the cases, the cans appeared in excellent shape. It is not uncommon for the convenience container to have a coating either in the region of the oxide or more commonly in the head space region (see Figures 1 and 2). Some staining or coating of the containers was seen during the FY16-FY21 field surveillances performed in KAC, however, no significant degradation that would compromise integrity of the 3013 container was observed. In addition, starting in FY22 visual inspections of all 3013 containers opened for down blending will be visually inspected. Specifically, convenience and inner containers with corrosion worse the that shown in Figures 3 and 4 (ring of corrosion on inner container lid and corrosion pits/spots on convenience container wall) will result in the 3013 SPA being notified.

Figure 1. Corrosion on FY18 DE #5 (H003523) Convenience Can Lid

Figure 2. Corrosion on FY18 DE #5 (H003523) Convenience Can Body

Figure 3. Inner Container Lid from FY09 DE2 (H004111)

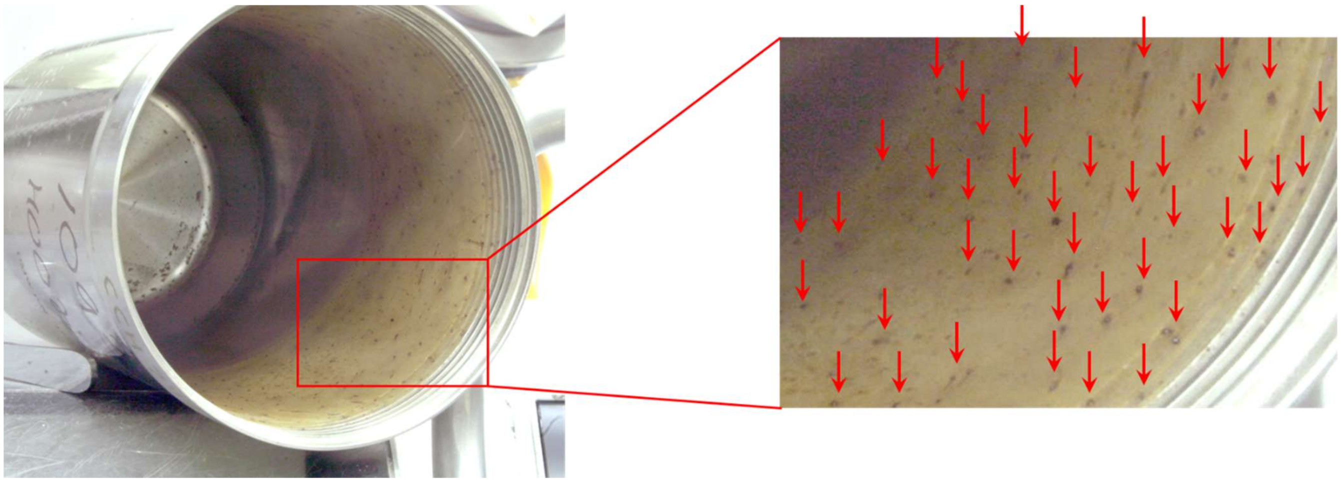

Figure 4: Convenience Container From FY16 DE2 (H002556)

v. Packaging of Materials for SRNL

All of the samples taken during the DE process are sent to SRNL for additional examination. The convenience can, the inner and outer cut can pieces, and through FY19 the gas samples were shipped to SRNL. Starting in FY20 the inner container lids are leak tested at SRNL to demonstrate that the lids did not suffer a through wall crack [Ref. 8,9].

1.2 3013 DE Surveillance Activities in SRNL

SRNL receives the empty 3013 containers (outer, inner and convenience), Pu oxide samples from the bulk material, and through FY19 gas samples from the outer/inner volume and the inner/convenience volume [Ref. 9].

i. Gas Analysis

During destructive examination, headspace gas samples are obtained from the 3013 inner container and the annulus between the outer and inner containers. To characterize gas species, the samples are analyzed in SRNL by gas chromatography (GC), and either direct-inlet mass spectrometry (DIMS)or Fourier-transform infrared spectroscopy (FTIR). GC results, as well as other parameters, are utilized as input into the gas evaluation software tool (GEST) program for computation of pre-puncture gas compositions and pressures. Gas composition and container pressure results obtained provide important data on the gas generation characteristics of plutonium-bearing material from actual 3013 storage inventory.

Several of the nineteen containers evaluated at SRS in FY16-19 contained appreciable H_2 content (some greater than 30 mol %), yet only trace or no oxygen was detected in any of the cans, including those exhibiting high H_2 concentrations. The maximum observed pressure was found in FY17 DE04 with a value of 4.0 psig (18.7 psia). This is below the highest observed in KIS which was found in FY14 DE02 with a value of 8.2 psig (22.9 psia) [Ref. 10]. Table 4 provides the pressures determined through DE for the FY16-19 containers. No impact to the structural integrity of the 3013 containers was observed.

Initially, the GEST tool has only been applied to the Inner 3013 container. With the observations of pitting found on the inner container, the MIS working group proposed comparing the inner gas composition and pressure to the outer gas composition and pressure. The GEST model was revised to Version 2.3, and beginning with FY14DE03 GEST was used to calculate the outer container gas pressure and compositions prior to puncture. A comparison of the GEST gas composition and pressure results for the outer and inner 3013 DE containers, together with observations of corrosion on DE containers indicate it is unlikely that a corrosion induced breach of the inner container occurred prior to DE for any of the containers examined during fiscal year 2016 through 2019. However, starting in FY20 no gas samples are collected. The Surveillance Program Authority (SPA) and the MIS Working Group have concluded that the inner and outer gas sampling can be replaced by a leak test on the ICCWR at SRNL prior to metallurgical examination [Ref. 8,9]. The leak test is at least as good as, or better than, the gas sampling method used for the task of inner container leak determination.

ii. He Leak Testing

SRNL developed and evaluated a He leak testing system using a configuration very similar, but not identical to, the configuration installed in the glove box [Ref. 8]. A total of sixty-five leak rate measurements were made on 10 containers. The data analysis shows that the leak detection system can identify leaks in the lid, including the weld and heat affected zone of 3013 inner containers, during destructive examination. The measurements taken support that a 3013 inner container lid with a leak rate value greater than 2.0×10^{-7} atm cc/sec helium will be identified using the leak test system.

After the system was installed in the glove box, functional testing of the 3013 inner container lid leak detection system was performed in FY20 to provide additional data to ensure acceptable performance and to verify that the variability of the data was similar to the data for the testing performed in the clean laboratory [Ref. 8]. Thirty-three leak rate measurements were made on seventeen container lids from the DE backlog and from FY20 DEs. Table 5 shows the container IDs, the testing dates, the background levels (atm cc/sec helium) and the leak rates at stabilization (atm cc/sec helium). Replicate measurements were obtained for the three containers with the largest differences between the leak rate and background (FY18DE06, FY15DE04, and FY16DE03). In all three cases the repeat measurements had leak rates that did not differ significantly from background. These tests demonstrate the acceptable functioning of the 3013 inner container lid leak detection system in the glove box environment.

iii. Can Inspections

The 3013 container system consists of nested welded 300 series stainless steel containers with the outer container credited to stay leak tight throughout a 50 year period of storage. In FY16 thru FY21 thirty containers packaged at Rocky Flats Environmental Test Site (RFETS), Hanford, SRS, Los Alamos National Laboratory (LANL), and Lawrence Livermore National Laboratory (LLNL) were examined destructively. During destructive examination analyses in SRNL, a variety of analyses are performed on the Pu oxide samples, through FY19 the gas samples were analyzed for pressure and composition and starting in FY20 the inner container lids are leak tested. Also, the empty containers are metallurgically examined for damage and a laser confocal microscope (LCM) is used to perform close visual examination of the surface of the ICCWR.

Previously, the presence of pitting corrosion in the headspace region of certain 3013 inner containers as well as the presence of a dusting or coating on convenience and inner cans was observed during destructive examination. The postulated pitting mechanism requires the presence of a radiation source (alpha radiation from the plutonium material) to dissociate and ionize the gases present and form a more volatile vapor or gas containing chlorine. The chloride rich vapor or gas provided a mechanism to transport chloride to stainless steel surfaces exposed only to the headspace region and make that region susceptible to corrosion.

The degradation observed during destructive examination of convenience and inner containers could be correlated with the chemistry of the plutonium bearing materials stored in the convenience containers and the environmental conditions during packaging. The majority of indications of incipient corrosion occurred in the headspace gas region of containers that stored plutonium bearing materials with high chloride and moisture contents. Little to no damage was observed in the plutonium oxide contact region of the convenience container. Conversely, stress corrosion cracking has been observed in some of the inner containers examined to date. However, gas analysis and statistical evaluation of the gas compositions and pressures via GEST analyses suggest that leakage between the Outer-Inner (OI) and Inner-Convenience (IC) volumes was unlikely.

One container, known as the Hanford High Moisture Can (HHMC) appeared to have been packaged with moisture in excess of 0.5 wt.% which is the limit in DOE-STD-3013. Since this container did not meet DOE-STD-3013, it could not be received and stored at SRS in K-Area due to safety basis limitations. The container was sent to LANL where it was destructively examined. The examination of HHMC revealed the greatest general corrosion found during a DE. Because of material found on the inner can lid, a decision was made to section the inner container lid because the gap between the lid and side wall cannot be visually inspected. After observing corrosion in this gap, it was decided to examine other archived DE containers because a through wall crack in this region would provide a path for corrosive gasses to contact the interior surfaces of the outer container and potentially jeopardize the primary barrier.

It is recognized that the area near the inner container closure weld is a region of increased corrosion susceptibility because the area has higher residual stresses, an altered microstructure (heat affected zone) and less corrosion resistant weld oxides as a result of the welding process. As a result, a protocol for the examination of the Inner Can Closure Weld Region (ICCWR) was established in 2014, which includes chemical analysis, stereo microscopes imaging, serial metallography as needed, Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS), and a laser confocal microscope to perform a surface visual examination. These examination techniques characterize not only the corrosion mechanism(s), but also the extent of the corrosion (percentage of area and depth of attack) and the variables impacting this corrosion (chloride concentration and metallurgical condition). The observations are currently rolled up into a corrosion categorization scheme that covers all of the DEs (See Table 6). Revisions to the protocol include the introduction of the Wide Area 3D Measurement System (WAMS) used as a method for faster inspection of the ICCWR while the LCM can be utilized to obtain higher resolution images of those areas identified by the WAMS [Ref. 11]. However, additional revisions to the protocol are being developed to improve the ability to identify cracks and to establish how much of the ICCWR needs to be examined for each DE.

DE containers from FY13 through FY16 were evaluated to select three candidates for a full circumference evaluation (FCE) of the ICCWR [Ref. 12, 13]. During the FCE, FY16 DE05 and FY15 DE07 showed suspect major corrosion events. FY16 DE05 Section C2 shows two crack-like features, identified as Denebola and Draco. Both features are located at the boundary of Zone 2 and Zone 3. Consequently, Section C2 of FY16 DE05 was selected for examination by serial metallography at Savannah River National Laboratory (SRNL). For FY15 DE07 the suspect corrosion events were observed on Sections C1 and C2. Section C1 shows one crack-like feature, identified as Acrux. Section C2 shows three crack-like features, identified as Bellatrix, Cursa Minor and Cursa Major. Unlike Acrux and Bellatrix, which are located at the boundary of Zone 2 and Zone 3, Cursa Minor and Cursa Major are located in Zone 2. Sections C1 and C2 of FY15 DE07 were sent to Los Alamos National Laboratory (LANL) for characterization by X-Ray Tomography (XRT).

The corrosion observations at the ICCWR emphasizes the importance of continued surveillances of the stored containers. The surveillance program will continue to evaluate containers to gain sufficient data to validate the 50 year container integrity criteria, as specified in the DOE-STD-3013. Gaseous transport of chloride and characterization of the extent of stress corrosion cracking are a strong focus of the evaluations.

iv Oxide Analysis

The packaging sites used several different techniques to demonstrate that the moisture content of the packaged material was less than the allowed limit of 0.5 wt.%. Many of the containers were analyzed by either Loss-On-Ignition (LOI), Thermogravimetric Analysis (TGA), or Thermogravimetric Analysis with Mass Spectroscopy (TGA-MS). LOI and TGA techniques are conservative in that they report all weight loss as water; other adsorbed species such as CO_2 and NO will also contribute to the weight loss in addition to water. TGA-MS is less conservative, as the water signal can be directly measured without interference from other adsorbed species.

The low moisture content specification creates oxides that are relatively dry compared to typical ambient conditions; these oxides can readily pick up moisture from atmospheres of 20% relative humidity. To best estimate the moisture content of the sample at the time of DE, it is necessary to minimize the amount of water picked up due to handling. Immediately after opening the container, a non-representative “initial moisture” (IM) sample is scooped from the top of the oxide and packaged expeditiously. The IM sample after DE is analyzed by TGA-MS, which can quantify the actual amount of water that is present in the sample.

Table 7 lists the moisture value reported by the packaging site and the IM value obtained during DE. There is little correlation between the best moisture at packaging and the measured moisture at the time of DE. This is due to a variety of factors; for a more detailed explanation of most of these factors, see SRNL-STI-2017-00419 [Ref 18].

Immediately after the moisture sample has been obtained, a special lid equipped with a humidity sensor and thermocouples is installed on selected convenience cans. Temperature and humidity data are collected (See Table 7) to assist in understanding the impact of humidity on corrosion. A graph showing the correlation of the head space temperature and oxide centerline temperature vs. heat load is found in Figures 5 and 6. The humidity data has proven invaluable for developing an understanding of the behavior of chloride bearing plutonium materials. Future DE containers will require temperature and humidity measurements to provide additional data for understanding corrosion results.

After the humidity measurement of the convenience can, oxide is poured into a pan. Before FY20, if large clumps were present, they were ground to ensure a composite, representative sample could be obtained. In FY20 however, the process changed to where all the oxide is ground regardless if large clumps are observed. The sample is then shipped to SRNL for analysis. The bulk material properties (bulk density, tap density, particle density using gas pycnometry) were obtained using the entire sample, and specific surface area was obtained using a large subsample. As of FY15, bulk density, tap density, and specific surface area are no longer performed. Before FY20, particle density was used by the GEST model to calculate the pressure in the container prior to puncturing, however this is no longer required, as no gas samples are now collected. However, the particle density measurement is still performed.

After the bulk properties are determined, the sample is then split into several smaller sub samples for further analysis. A portion of the material is leached in hot water to determine the soluble material content (mostly chlorides). The soluble species are analyzed by Inductively Coupled Plasma Emission Spectrometry (ICP-ES) and Ion Chromatography (IC)-anions. Another portion of the sample is dissolved in strong acid to determine the chemical (elemental) makeup of the material. After dissolution, the solution is analyzed by ICP-ES to determine the elemental makeup of the solute. Other analyses are performed as required. These include

- Ion Coupled Plasma Mass Spectrometry (ICP-MS) and Gamma peak height analysis of the dissolved solution
- Powder X-Ray Diffraction (XRD) of the original solids
- Scanning Electron Microscopy (SEM) of the original solids
- XRD and X-Ray Fluorescence (XRF) of any undissolved material from the dissolution
- XRD of the leached solids.

As each suite of analyses is completed, the properties of, and any changes in, the Pu-bearing materials are used to interpret any package interactions (corrosion) that may have occurred during storage. These analyses can then be used to deduce the chemical interactions that led to speciation of the headspace gas samples.

A flowchart of typical solids sample flow within SRNL is in Figure 7.

2. 3013 Corrosion Program

The integrated corrosion program consists of shelf-life program experiments, both small-scale and full-scale performed at LANL and SRNL that provide an early response to any gas generation or corrosion concerns that might be observed in the field. These tests also help guide the selection of engineering judgment surveillance. Since the shelf-life program tests focus on bounding conditions, they can produce effects such as gas generation or corrosion that are more severe and more rapid than would occur in packaged 3013 containers. As expected, field surveillance destructive examinations (DE) and non-destructive examinations (NDE) to date have shown that the pressure and corrosion inside the 3013 containers are significantly less severe than observed in the shelf-life tests. Stress corrosion cracking (SCC) was observed during small-scale 3013 corrosion tests in FY08. The SCC was observed in replicate stainless steel 304L test specimens for a room temperature plutonium oxide-salt composition with bounding (0.5 wt. %) water content. These results have raised a concern because they show that SCC can occur under conditions allowed by DOE-STD-3013. Based on these results, the MIS Working Group could not ensure that SCC events were absent in 3013 packages. The integrated corrosion test plan was developed under the direction of the MIS Working Group and addresses the requirements defined in the letter from the MIS Corrosion Working Group titled “Impact of stress corrosion cracking observed in shelf-life specimens for 3013 containers”. The test plan was developed to address the conditions under which SCC occurs with respect to the parameters that were controlled during stabilization and packaging of 3013 containers. The major activities included:

- Determine the influence of temperature, salt composition, and moisture uptake during packaging on the resulting Relative Humidity (RH) in the packaged container
- Determine the threshold RH of various plutonium oxide-salt mixtures for SCC to occur in direct contact and headspace exposure
- Establish the residual stress or weld chemistry conditions for SCC
- Evaluate the reduction of the RH over time within a sealed 3013 package including water consumption mechanisms and redistribution of the moisture within the material.

The goal of the integrated corrosion program is to resolve the stress corrosion cracking issues within 3013 storage containers. Results from tests identified in this plan will define the conditions under which stress corrosion cracking occurs with respect to the parameters that were controlled during stabilization and packaging of plutonium-bearing materials for storage in 3013 containers. The identified conditions of concern will be used to evaluate the 3013 storage inventory in conjunction with the Integrated Surveillance Program (ISP) Database to provide refined groupings of the pressure & corrosion bin. In the event that conditions are present for SCC, a more rigorous approach for the ISP would be adopted for a subset of the inventory that warrants closer scrutiny.

One of the main focus areas of the 3013 Surveillance Program is a thorough evaluation of the inner container closure weld region (ICCWR) opened for destructive examination (DE). This included revamping the ICCWR examination protocol and the use of extensive image data collection and analysis.

In FY16, the examination protocol was updated to include a thorough cleaning procedure for removing surface oxides, corrosion products or other materials from the surface of the ICCWR samples. This allowed a better analysis of the surface using laser imaging, surface profilometry and pit depth measurements. The FY11 Hanford High Moisture Container (HHMC), which has been previously analyzed by SEM/EDS [Ref. 14], was selected to validate the cleaning protocol by re-analyzing it by LCM. Analysis from the LCM confirmed the ICCWR corrosion categorization and yielded similar results as reported in [Ref. 15].

In FY17, the LCM parameters were investigated to identify the appropriate values for data acquisition and identification of regions of interest within the ICCWR with detection of cracks of, at least, 1 μm. Analysis of samples showed that the corrosion can be extended as far as 6 mm in Zone 3. Also, DE containers from FY13 through FY16 were evaluated to select candidates for a full circumference analysis of the ICCWR. The selected DE containers were prioritized in the following order: FY15 DE07, FY16 DE05, and FY15 DE08 [Ref. 16]. The intent of this analysis is to provide information about the distribution of the corrosion features of interest and help support a determination of how much of an ICCWR needs to be examined to make the assertion of whether cracking has occurred and develop an ICCWR sampling plan for analysis of subsequent containers.

In FY18 the selected DE containers for full circumference analysis were processed according to the ICCWR protocol. LCM data collection of high magnification images, height, and laser intensity data for the full circumference of the ICCWR was a time intensive task due to the large number of images and amount of data. It required approximately 4 months to complete the full circumference, including overnight time. The LCM data collection was completed for FY15 DE07 in FY18 [Ref 12]. In FY19 the LCM data collection of the full circumference for FY16 DE05 and FY15 DE08 were completed [Ref. 13].

In FY20, the Wide Area 3D Measurement System (WAMS) was introduced and tested as a method for faster inspection of the ICCWR. Optimization of the WAMS parameters for data collection was carried out using a generic tear-drop type sample containing large and fine Stress Corrosion Cracking (SCC) fractures and high-resolution images were compared to the image obtained with the LCM. The advantage of collecting data for the full circumference using the WAMS is that it can take about a week to complete, which represents 1/16 of the time needed with the LCM. Nonetheless, both systems offer capabilities that combined can be utilized to expedite the examination of the ICCWR. The WAMS can be utilized to obtain images for faster screening or identification of corrosion features on the surface while the LCM can be utilized to obtain higher resolution images of those areas identified by the WAMS. The ICCWR full circumference data collection for FY17 DE04 and FY18 DE03 were completed using the WAMS. [Ref. 11]

The use of the WAMS also represented an opportunity to improve the ICCWR examination protocol. This consisted in eliminating the use of the stereo microscope from the examination protocol for performing a panoramic assembly of the ICCWR and executing the SEM of the archive sample and the dye penetrant of the surfaces of the samples on an as-needed basis. In FY21, a document for the ICCWR examination protocol was drafted in collaboration with LANL. In addition, and in collaboration with LANL, analyses of the ICCWR data collected by LCM and WAMS on previous DE inner containers, including DEs from the backlog, has been the focus in FY21 to determine the best method for collecting and analyzing the data.

Another major focus since FY18 is the development of automated computer analysis for processing large amount of image data. One of these efforts is the development of algorithms for machine learning by SRNL in collaboration with the University of South Carolina (USC). SRNL and USC have developed methods to extract data from large binary files and to convert the data to physical attributes that can then be analyzed. A Matlab-based Graphical User Interface (GUI) was created to integrate the data input with the software developed for processing and evaluation [Ref. 17].

3. ISP Database

Surveillance data from both NDE and DE activities in KAC have been input to the 3013 Field Surveillance Module (FSM) through FY21. SRS continues to manage the ISP database and has implemented a configuration control program in compliance with site requirements. Site organizations evaluating disposition of materials also routinely use the database to evaluate the disposition paths of the currently packaged 3013 containers.

IV. CONCLUSION

A summary of the 3013 surveillance activities from FY16-FY21 have been presented. A total of 33 DE's were performed in FY16-FY21 and 134 total DE's have been performed to date. From FY07 through FY19 the inner and outer 3013 container gas analysis has verified no through wall pitting or cracking has occurred, and the maximum pressurization seen to date in the DE's performed in KIS is 22.9 psia. Starting in FY20 the 3013 containers were cut directly without using the Can Puncture Device which resulted in elimination of gas sampling, and the cut inner container lids were leak tested at SRNL to verify through wall pitting or cracking has not occurred. Inner containers lids continue to be examined for corrosion and potential cracks using multiple techniques. Specifically, the ICCWR region is examined using stereo microscope imaging, serial metallography, SEM, EDS, WAMS, and LCM. The WAMS and other methods are used to identify potential regions and features of interest for further detailed investigation using the very high resolution LCM. This approach was used to identify and examine multiple cracks in the ICCWR on several inner container lids. Thus far none of the cracks appear to be very deep, which is consistent with previously performed inner and outer container gas analyses for these containers. Nevertheless, investigations using additional techniques geared towards examining sub surface cracks are ongoing to better estimate the crack depth. Finally, Tables 1 through 7 provide an overview of data collected and status of the DE program. The random sampling program is expected to be completed in FY25.

V. REFERENCES

1. WSRC-TR-2001-00286, Revision 10, The Savannah River Site Surveillance Program for the Storage of 9975/3013 Plutonium Packages in KAC, July 2021
2. AMNMS-15-0014, Integrated Surveillance And Monitoring Program For Materials Packaged To Meet DOE-STD-3013, May 2015
3. DOE-STD-3013-2018, DOE Standard: Stabilization, Packaging, and Storage of Plutonium-Bearing Materials, Washington, D.C.: U.S. Department of Energy, 2018
4. SR-NMPD-03-001, Rev. 0, Surveillance and Monitoring Plan for DOE-STD-3013 Materials
5. LA-UR-00-3246, Integrated Surveillance Program In Support Of Long-Term Storage Of Plutonium Bearing Materials, Rev. 1, March 2001
6. LA-UR-14-20785, Test Plan for Assessing Potential for Stress Corrosion Cracking in the 3013 Inner Container Closure Weld Region (FY14), Aug 2014
7. WSRC-TR-2007-00218, Version 2.0 of the 3013 Gas Evaluation Software Tool (GEST), June 2007
8. SRNL-STI-2019-00392, Rev. 1, 3013 Inner Can Lid Leak Test System Development, September 2020
9. SRNL-L5400-2019-00010, Elimination of Gas Analysis From Required 3013 Destructive Examination Analyses, July 2019
10. U-TRT-K-00012, 3013 Surveillance Program Interim Summary Report, October 2016
11. SRNL-STI-2020-00418, Wide Area 3D Measurement System for Analysis of 3013 Inner Container Closure Weld Region, September 2020
12. SRNL-L4400-2018-00017, Status of the Full Circumference Examination of the Inner Container Closure Weld Region for Selected 3013 DE Containers, July 2018
13. SRNL-L5400-2019-00011, FY19 Status of the Full Circumference Examination of the Inner Container Closure Weld Region for Selected 3013 DE Containers, July 2019
14. SRNL-STI-2013-00527, 3013 DE Inner Container Closure Weld Corrosion Evaluation, September 2013
15. SRNL-L4400-2016-00021, Status of the Inner Container Closure Weld Region for Selected 3013 DE Containers, September 2016
16. SRNL-STI-2017-00589, Laser Confocal Microscope for Analysis of 3013 Inner Container Closure Weld Region, October 2017
17. SRNL-STI-2021-00680, FY21 Progress Report: SRNL Analysis of ICCWR LCM and WAMS Data for Corrosion and Cracking, September 2021
18. SRNL-STI-2017-00419, Factors Influencing Moisture Analysis in the 3013 Destructive Examination Surveillance Program, 2017

VI. Tables and Additional Figures

Table 1: 3013 Statistical Sample Sizes

Bin	Random NDE Only		Random DE		EJ DE
	Planned	Complete*	Planned	Complete*	Complete*
Innocuous	10	10	0	1	0
Pressure	130	130	7	7	4
P and C	0	0	106	86	36

*Completed through FY21

Table 2: 3013 Surveillances Performed To Date By Fiscal Year

Fiscal Year	Innocuous	Random Pressure		Random Pressure and Corrosion	Engineering Judgment
	NDE	NDE	NDE/DE	NDE/DE	NDE/DE
2005	3 (1)[a]	11 (14)[a]	0	5 (5) – NDE Only	8 (5) – NDE Only
2006	0 (1)[a]	14 (13)[a]	0	3 (5) – NDE Only	3 (6) – NDE Only
2007	2 (1)[a]	12 (13)[a]	2	2	2
2008	1	24	3	12	2
2009	2	24	2	10	7
2010	2[b]	8[b]	0	13 NDE/DE 6 NDE Only[b]	5
2011	0	0	0	7	6[c]
2012	0	0	0	5	4
2013	0	0	0	0	1
2014	0	0	0	6	2
2015	0	0	0	7	2
2016	0	0	0	5	1
2017	0	0	0	5	1
2018	0	0	0	5	1
2019	0	0	0	0	1
2020	0	0	0	3	4
2021	0	0	0	6	1

[a] Numbers in parentheses indicate additional surveillances performed at Hanford and/or LLNL
[b] NDEs performed to inspect for foreign material
[c] One container was opened at LANL

Table 3: Categorization Levels for 3013 DE Containers

Category	Description
0	Nothing or wipeable coating
0*	Corrosion observed in RFETS convenience can threads or lids
1	Adherent coating on convenience can
2	Pitting < 50 µm on convenience can
3A	Suspect pitting > 50 µm on convenience can – pit covered with corrosion product
3B	3B Confirmed pitting > 50 µm on convenience – generally confirmed with SEM
4	Adherent coating on inner can
5	Pitting < 50 µm on inner can
6	Pitting > 50 µm on inner can
7	SCC on inner can

Table 4: FY16-FY19 Gas Results

RUN	3013 ID	Surv. ID (SRNS-SRV-)	Surveillance BIN	Gases (%)									GEST 3013 P (psia)
				CH_4	CO_2	N_2O	He	H_2	O_2	N_2	CO	Ar	
FY16 DE-1	H001191	2015-003	Pressure	ND	Trace	Trace	59.3	5.5	ND	35.2	ND	ND	13.0±0.4
DE-2	H002556	2015-004	P & C	ND	<0.1	Trace	63.3	0.2	ND	36.5	ND	ND	10.5±0.4
DE-3	H004173	2015-005	P & C	ND	<0.1	Trace	80.7	0.7	ND	18.5	ND	ND	10.4±0.4
DE-4	H004247	2015-006	P & C	ND	ND	Trace	55.7	Trace	ND	44.3	ND	ND	12.0±0.4
DE-5	H003775	2015-007	P & C	Trace	ND	Trace	60.8	<0.1	ND	39.2	ND	ND	10.4±0.4
DE-6	H004024	2015-011	P & C	ND	Trace	Trace	59.6	<0.1	ND	40.4	ND	ND	11.1±0.4
FY17 DE-1	H001304	2016-002	P & C	ND	ND	Trace	47.0	2.9	ND	50.1	ND	ND	12.3±0.4
DE-2	H002575	2016-003	P & C	ND	Trace	Trace	45.2	22.0	ND	32.8	ND	ND	13.7±0.4
DE-3	H003352	2016-004	P & C	ND	Trace	Trace	75.3	2.5	ND	22.1	ND	ND	8.4±0.4
DE-4	H003695	2016-005	P & C	<0.1	<0.1	ND	35.2	46.6	ND	18.1	ND	ND	18.7±0.4
DE-5	H002508	2016-006	P & C	Trace	<0.1	Trace	43.8	30.7	ND	25.5	ND	ND	15.1±0.4
DE-6	R600793	2016-001	P & C	ND	ND	Trace	90.0	Trace	ND	10.0	ND	ND	13.1±0.4
FY18 DE-1	H003345	2017-002	P & C	ND	<0.1	ND	58.2	16.0	ND	25.8	ND	ND	11.4±0.4
DE-2	H003626	2017-003	P & C	ND	ND	<0.1	62.6	0.5	ND	36.9	ND	ND	10.1±0.4
DE-3	H003645	2017-004	P & C	ND	ND	ND	60.1	16.4	ND	23.5	ND	ND	10.5±0.4
DE-4	H002524	2017-006	P & C	ND	Trace	Trace	71.1	0.9	ND	28.0	ND	ND	9.6±0.4
DE-5	H003523	2017-005	P & C	ND	ND	Trace	68.7	0.1	ND	31.2	ND	ND	10.4±0.4
DE-6	H004153	2017-007	P & C	ND	<0.1	Trace	76.3	1.1	ND	22.5	ND	ND	8.6±0.4
FY19 DE-1	A000632	2018-001	P & C	ND	Trace	ND	99.4	Trace	<0.1	0.6	<0.1	ND	10.5±0.4

Table 5: Inner Container Lid Leak Test Data for Backlog and DEs Tested in FY20§

Sample	Date	Background Level (atm cc/sec Helium)	Leak Rate @Stabilization (atm cc/sec Helium)
FY14DE08	6/25/2020	1.3e-8	1.3e-8
FY15DE04	7/7/2020	1.3E-8	1.4E-7
	7/22/2020	1.3E-8	1.4E-8
	7/22/2020	2.9E-8	2.5E-8
FY15DE05	6/25/2020	1.9e-8	2.0e-8
FY15DE06	4/20/2020	2.4e-8	2.5e-8
	4/20/2020	0e-8	0e-8
	4/20/2020	1.7e-8	1.6e-8
FY16DE02	4/20/2020	1.4e-8	1.3e-8
	4/20/2020	3.0e-8	3.0e-8
	4/21/2020	2.5e-8	2.2e-8
FY16DE03	6/25/2020	0.2e-8	1.0e-7
	8/5/2020	0.0E-8	0.1E-8
	8/5/2020	1.3E-8	1.4E-8
FY17DE02	4/21/2020	0.2e-8	8.0e-8
	4/21/2020	0.6e-8	8.5e-8
	4/21/2020	0.5e-8	7.3e-8
FY17DE03	6/25/2020	0.2e-8	0.2e-8
FY17DE04	4/20/2020	4.1e-8	4.0e-8
	4/21/2020	0.1e-8	0.1e-8
	4/21/2020	0.3e-8	0.2e-8
FY17DE05	7/7/2020	0.6E-8	0.6E-8
FY18DE02	6/25/2020	0.2e-8	6.8e-8
FY18DE03	4/16/2020	0.2e-8	0.2e-8
	4/16/2020	0.5e-8	0.5e-8
	4/16/2020	0.8e-8	0.6e-8
FY18DE04	7/7/2020	0.5E-8	5.2E-8
FY18DE05	7/7/2020	0.4E-8	5.8E-8
FY18DE06	7/7/2020	2.0E-8	1.6E-7
	7/22/2020	0.0E-8	0.0E-8
	7/22/2020	1.5E-8	1.3E-8
FY20DE01	8/24/2020	0.2E-8	0.2E-8
FY20DE02	8/24/2020	0.3E-8	0.3E-8

§ Table from G. Rawls, L. Ward, E. Kelly, and D. Kirk Veirs, 3013 Inner Can Lid Leak Test System Development, SRNL-STI-2019-00392, Rev 1, 2020.

Table 6: Summary of Categorizations for DE 3013 Containers from FY07-FY19

Cat.	FY07	FY08	FY09	FY10	FY11	FY12	FY13	FY14	FY15	FY16	FY17	FY18	FY19	Total
0	5	13	14	11	6	5		3	3				1	61
0*	2	1							1		1			5
1			3			1								4
2		1												1
3A		1	1	3	4	3		4	1	3				20
3B				2	3									5
4				1				1			1			3
5				1					3		2	2		8
6		1	1				1		1	3	2	4		13
7														
Total	7	17	19	18	13	9	1	8	9	6	6	6	1	120

Note: Corrosion categorization for FY20 and FY21 DE’s have not been finalized

Table 7: Temperature and Humidity Collected

DE Number	3013	Heat Load (W)	Final Humidity (%RH)	Headspace Temp (F)	Oxide Temp Center (F)
FY16 DE-1	H001191	1.84	1.20	83.3	83.9
DE-2	H002556	4.50	4.50	84.0	117.1
DE-3	H004173	4.39	1.40	82.7	119.8
DE-4	H004247	4.04	0.80	86.6	117.6
DE-5	H003775	5.32	0.97	83.0	131.2
DE-6	H004024	4.36	0.95	84.4	117.5
FY17 DE-1	H001304	1.17	4.49	75.6	80.6
DE-2	H002575	4.58	6.99	80.5	125.0
DE-3	H003352	4.54	3.94	84.0	115.0
DE-4	H003695	4.4	2.59	86.3	121.2
DE-5	H002508	4.18	2.81	80.4	110.1
DE-6	R600793	9.88	1.09	96.5	177.9
FY18 DE-1	H003345	3.67	3.52	83.6	115.0
DE-2	H003626	4.66	2.16	85.1	125.0
DE-3	H003645	4.49	5.68	78.0	123.0
DE-4	H002524	4.35	1.06	84.6	121.0
DE-5	H003523	4.32	0.52	78.3	120.0
DE-6	H004153	3.49	1.38	88.4	116.1
FY19 DE-1	A000632	11.36	0.65	97.9	135.6
FY20 DE-1	H003308	3.68	3.33	87.8	107.5
DE-2	H003311	3.90	N/A	84.0	104.2
DE-3	H003676	4.58	N/A	86.4	116.8
DE-4	H004005	4.77	1.95	83.9	118.4
DE-5	H004226	2.97	N/A	85.0	96.0
DE-6	H002531	4.16	2.91	80.2	104.8
DE-7	H003271	4.62	N/A	86.3	117.2
FY21 DE-1	H004216	4.30	4.14	81.3	108.6
DE-2	H003731	4.55	1.05	83.7	112.0
DE-3	S002151	10.14	0.61	119.8	152.4
DE-4	R610910	4.53	No Value	No value	No value
DE-5	S002219	9.65	0.23	100.1	164.1
DE-6	H001746	2.06	0.87	81.4	94.2
DE-7	H003564	4.57	2.73	81.9	109.4

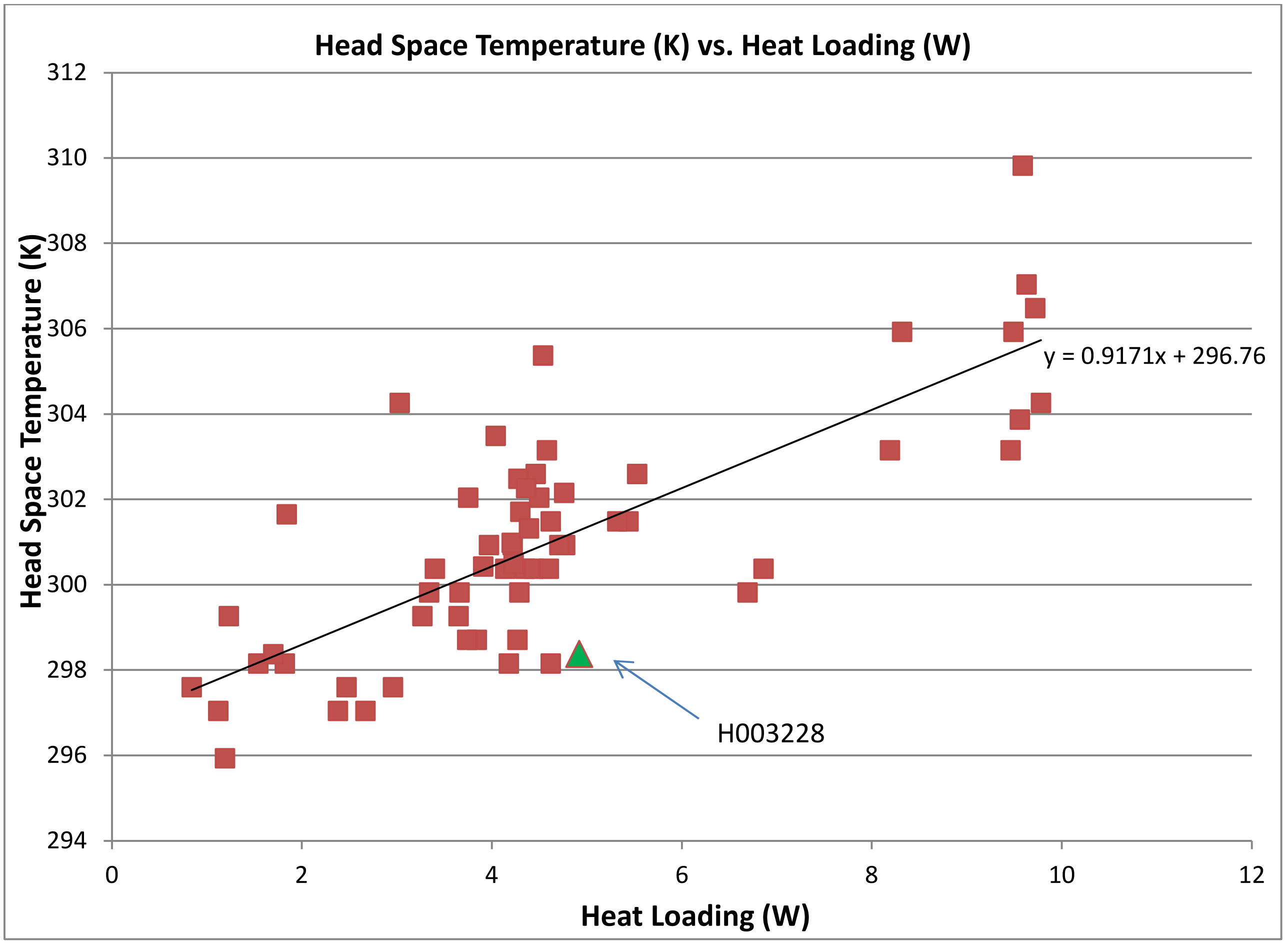

Figure 5: Convenience Container Head Space Temperature vs. Heat Loading

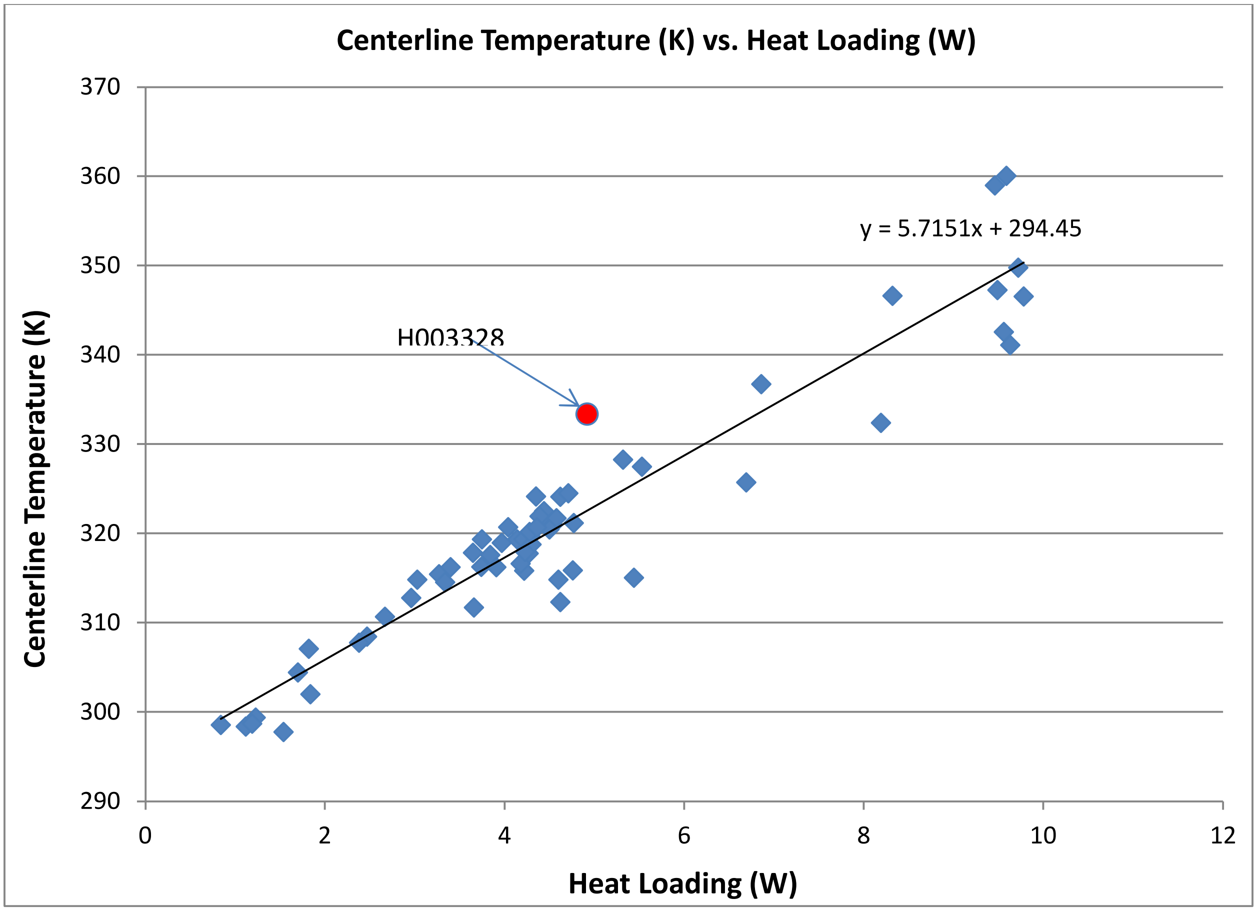

Figure 6: Oxide Centerline Temperature vs. Heat Loading

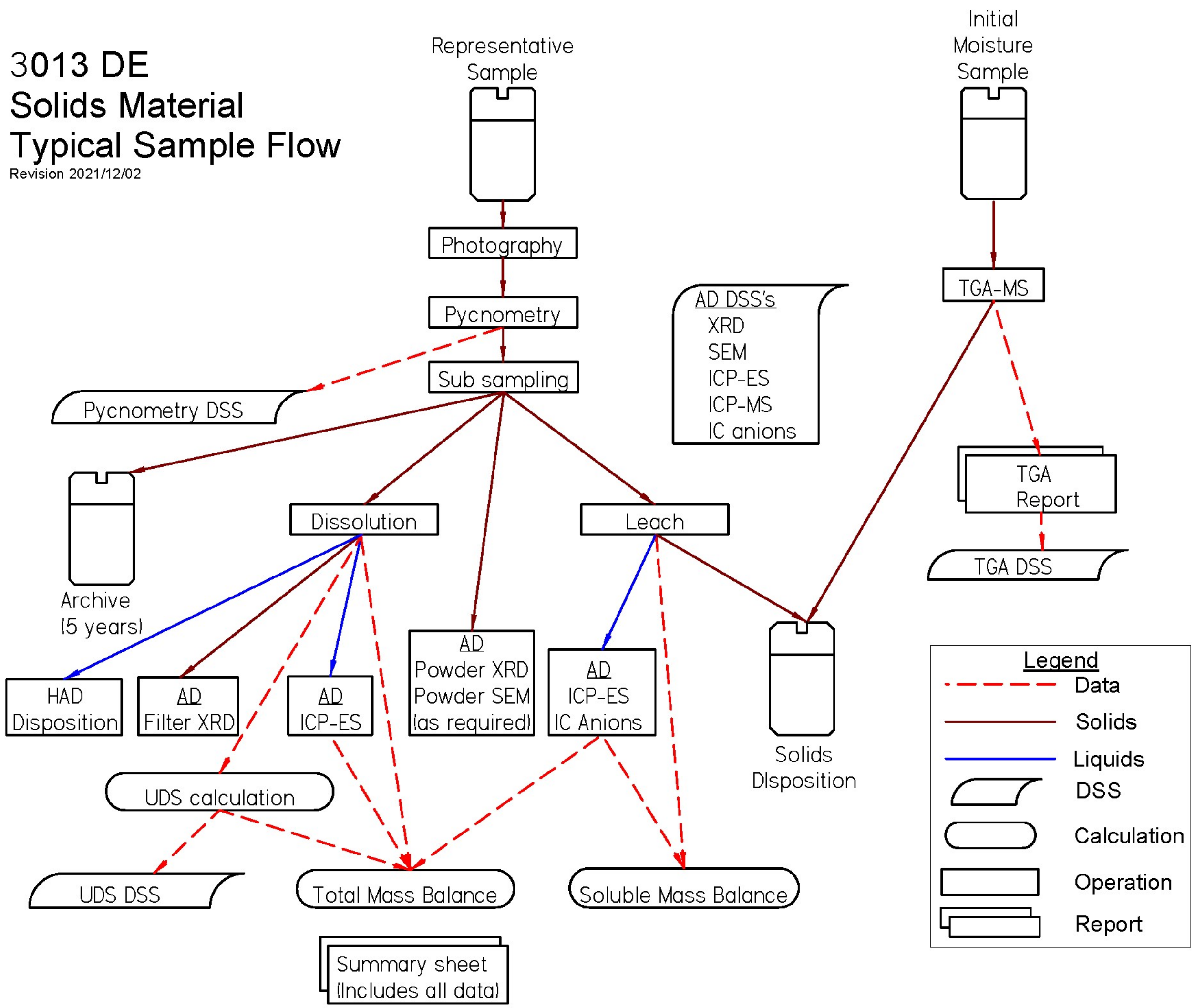

Figure 7 SRNL Oxide Flow