

RESIDUE CHARACTERIZATION AT THE ROCKY FLATS ENVIRONMENTAL TECHNOLOGY SITE

Karen A. Phillips, Safe Sites of Colorado, L.L.C.

ABSTRACT

A characterization program was developed at Rocky Flats to address possible safety risks associated with plutonium residue material generated during weapons production. The Residue Characterization Program at Rocky Flats was approved and implemented in December 1995. The purpose of the program is to obtain statistically significant information about the backlog residues stored at Rocky Flats, with a minimum amount of sampling, so that fact-based decisions can be made in addressing the final disposition of the materials. The preliminary characterization has provided information on how these materials are behaving in storage, RCRA, WIPP certifiability, and subsequent processing. All 99 residue item description codes (IDCs) (representing over 100 metric tons of material) have been characterized to an 80% confidence level; additionally, "higher" risk IDCs are being characterized to a 95% confidence level. To date, over 1000 residue containers, primarily in 55-gallon drums and vault cans, have been sampled and analyzed. The analysis has addressed safety hazards (pyrophoricity, flammability, shock sensitivity, reactive metals, dispersible fines), as well as parameters that affect the RCRA classification or final disposition path of the material (total metals, VOAs, SVOAs, moisture content, chemical composition). The residue materials are better understood, and less reactive than originally hypothesized. This translates to significant cost-savings to the taxpayer in that less handling (e.g., "processing") will be required for most of the materials, and most can be simply repackaged to meet off-site shipment requirements. In addition, the characterization program has gathered data regarding material packaging configuration, dose rates, and contamination of internal containers. This information has helped formulate operational aspects of the processing or repackaging plans. The Residue Characterization Program has been valuable in defining the future plans for residues.

BACKGROUND

In September 1993, Rocky Flats prepared a report addressing the safety risks associated with the storage of certain types of plutonium-bearing residues [Reference 1]. In a subsequent letter to Rocky Flats, the Department of Energy - Rocky Flats Field Office (DOE-RFFO) highlighted potential safety issues brought by the Defense Nuclear Facilities Safety Board (DNFSB) with regard to the storage and handling of residue drums. In response, Rocky Flats conducted a risk assessment, which concluded that the materials in question did not present immediate safety concerns to the public or the workers and reported those results to DOE. However, to confirm the results of the risk assessment, Rocky Flats committed to conduct additional investigatory actions to include the inspection, sampling, and analysis of the residue materials, their packaging, and their containers.

Originally, residues were characterized according to process knowledge [Reference 2]. This original characterization was followed by inspection and sampling of the residues to provide data to validate the process knowledge characterizations. The Project Plan for the Inspection, Sampling, and Characterization of Solid Residues [Reference 3] identified a prioritized/phased

approach for addressing all residues in the backlog based on potential safety, interim safe storage, Waste Isolation Pilot Plant/Waste Acceptance Criteria (WIPP/WAC), and RCRA considerations.

PURPOSE

The purpose of the Residue Characterization Program is to obtain statistically significant information about the backlog residues stored at Rocky Flats, with a minimum amount of sampling, so that fact-based decisions can be made in addressing the final disposition of the materials. The program was developed to 1) provide sampling data to substantiate whether or not the residues present immediate safety concerns for the general public or the workers at Rocky Flats; 2) determine the types and amounts of materials that may influence the potential for gas generation; 3) verify process knowledge in terms of material categories referred to as Item Description Codes (IDCs) and physical waste forms; 4) verify the absence of free liquids or establish the quantity of any free liquids; 5) evaluate any evidence of container corrosion; 6) determine the conditions of internal packaging materials; 7) assess compliance with Interim Storage Criteria; 8) establish the need and, if necessary, the type of repackaging, if changes are warranted; 9) provide a determination as to whether the residue requires stabilization, and if so, provide feedstock definition; 10) provide the bases for recommendations as to whether or not the residues should be regulated by RCRA; and 11) assess WIPP/WAC certifiability.

SCOPE

There are 99 residue IDCs (representing over 100 metric tons) at Rocky Flats. The residue materials are primarily stored in 55-gallon drums, 10-gallon drums, 8801/8802 Vollrath cans, Stacker/Retriever cans, 2-liter and 4-liter polyethylene bottles. The various drums/containers are currently located in several of the plutonium operations buildings at Rocky Flats. The residue backlog consists of 3943 55-gallon drums, and 3952 stand-alone cans.

Safety Considerations

The prioritization of residues for characterization was based primarily on hazard categorization. The hazards that were evaluated include: 1) flammable gas accumulation; 2) presence of shock sensitive materials; 3) presence of ignitable or flammable materials; 4) container pressure differential; 5) respirable radionuclides as a result of container failure due to corrosion; 6) presence of incompatible chemicals; 7) radiological exposure; and 8) toxicological exposure. The residues were ranked (1 through 5); with 1 being the highest risk potential.

The primary hazards associated with risk potential 1 residues were flammable gas accumulation and subsequent pressurization of unfiltered residue drums. As part of the residue characterization project in Fiscal Year (FY) 95, headspace gas sampling was performed on unfiltered, "high-risk" drums; the results of sampling confirmed the hazard assessment. Elevated levels of hydrogen, with depleted levels of oxygen, were detected in unfiltered residue drums. As a result of these findings, Rocky Flats embarked on a venting campaign to mitigate this hazard. The venting of the backlog residue drums resulted in a downgrading of the risk potential on some residue IDCs and specifically, the elimination of the Risk Potential 1 category.

Interim Safe Storage

In addition to safety considerations, characterization was performed to assess compliance to the Interim Safe Storage (ISS) criteria [Reference 4], which provide guidance for interim safe storage of plutonium-bearing solid materials for a period up to 20 years until final disposition.

Specifically, the material criteria address flammable gas buildup, pyrophoricity, decay heat, incompatible materials, explosive and shock-sensitive materials, moisture, and flammable materials. With the exception of decay heat, the Residue Characterization Program addressed all of the material criteria items. The program also assessed packaging configuration.

WIPP/WAC

To the extent possible, characterization was performed to assess the WIPP/WAC certifiability of the residues. With the exception of specific activity, all of the material criteria items listed in the waste form requirements matrix of the WIPP/WAC [Reference 5] were addressed by the program. The intent was not to certify the residues, but to provide a basis for a certification program.

In conjunction with the WAC, WIPP has provided guidance to the DOE sites on waste characterization. This guidance is contained in the "Transuranic Waste Characterization Quality Assurance Program Plan" [Reference 6]. The Quality Assurance Program Plan (QAPP) identifies the quality of data necessary, and techniques designed to attain and ensure the required quality, to meet the specific Data Quality Objectives (DQOs) associated with the DOE WIPP Transuranic Waste Characterization Program. The QAPP breaks down the waste types into four broad matrix parameter categories: homogeneous solids (summary category S3000); soil/gravel (summary category S4000), debris wastes (S5000); and special waste (X7000). For waste classified as debris waste and special waste, hazardous waste characteristics are determined using "acceptable knowledge." Homogeneous solids and soil/gravel, however, must be sampled and analyzed for total volatile organic analytes (VOAs), total semi-volatile organic analytes (SVOAs), and total metals, even if process knowledge indicates non-RCRA status. Most of the residues at Rocky Flats are classified as homogeneous solids.

RCRA Considerations

In addition to the above-mentioned considerations, characterization was performed to confirm or refute current RCRA designations. Based on process knowledge, RCRA codes have been assigned to the backlog residues. Characterization tests to address RCRA considerations [Reference 7] were performed in accordance with applicable standards [Reference 8].

STATISTICAL SAMPLING PLAN/SAMPLE SELECTION STRATEGY

Sampling of the residues is challenging due to the heterogeneity within a given residue container and the variability from container to container. Subject matter experts (SMEs) direct sampling efforts and have sufficient knowledge about the analyses that are performed on the samples to specify when a "representative" sample (for RCRA/QAPP/WIPP analyses) is appropriate and when a "worst-case" sample (for safety/interim safe storage analyses) is appropriate.

For a preliminary evaluation of the residues, the residue IDCs were divided into two primary subpopulations; drums and stand-alone cans. The initial sampling campaign consisted of

obtaining a statistical sampling of containers from each subpopulation. The number of containers required for sampling is based on a hypergeometric probability distribution. The prescribed sample size assumes an 80% confidence level for which the percentage of “hits” in the subpopulation does not exceed 15% (80%/15%). A “hit” is defined as a positive result (or confirmation of a characteristic) from the test used to analyze for the characteristic (e.g., shock sensitivity from the impact test). Based on the decisions that need to be made regarding stabilization of residues, additional sampling above the prescribed amount may be warranted. The logic flow diagram for residue characterization is represented in Figure 1.

If no “hits” are found during the initial characterization screen, a reassessment of the risk will be conducted. If the risks and consequences are acceptable, then the subpopulation meets the material criteria of the interim safe storage standard and no additional sampling will be conducted. If the risks and consequences associated with less than 15% of the subpopulation are not acceptable, then further characterization will be required. Similarly, if a few “hits” are found (20-30% of the containers sampled), the subpopulation will be evaluated for trends and additional characterization will be performed. For greater than 20-30% “hits,” the material will most likely require stabilization to mitigate the hazard associated with the “hit.”

Sampling of 765 containers (432 55-gallon drums and 333 stand-alone cans) was required for a preliminary evaluation of the residues. In order to obtain a representative sampling of containers within a subpopulation, the following items were considered for container selection: process history, gram Pu per gram net weight, and generation date.

Sampling and characterizing all of the solid residues was difficult to accomplish in FY96; therefore, a prioritized/phased approach was implemented. The approach concentrated on the residues that were currently risk category 2 and emphasized those IDCs that required key decisions to be made in FY96 to enable uninterrupted planning for FY97 and beyond years regarding processing and safe interim storage.

PROCESS KNOWLEDGE RESIDUE DESCRIPTIONS/HAZARDS

For characterization purposes, the 99 residue IDCs were grouped into material categories. A description of the materials [Reference 2] as well as the specific hazards (pre-sampling and analysis) associated with the materials is given below.

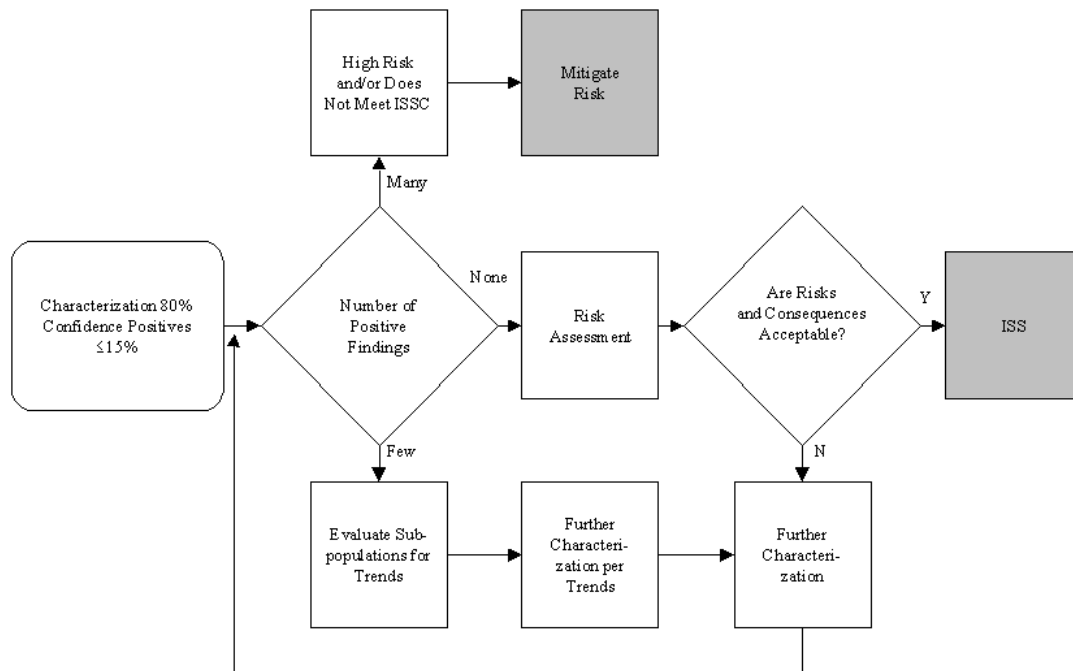


Fig. 1. Characterization Logic Diagram

Group 1: Salt

Pyrochemical salt residues were generated as by-products of Molten Salt Extraction (MSE), Electrorefining (ER), Direct Oxide Reduction (DOR), and nonproduction (R&D) processes at Rocky Flats. Safety concerns include the existence of sodium peroxide in those IDCs that may contain elemental sodium, and pyrophorics (e.g., plutonium hydride). The salt residues may contain elemental calcium (Ca), magnesium (Mg), aluminum (Al), sodium (Na), zinc (Zn), potassium (K), americium (Am), and plutonium (Pu), all of which are potentially reactive with water and pyrophoric, especially in finely divided form. These reactive metals can react with water to produce hydrogen. Some of the salt IDCs contain CaCl_2 , ZnCl_2 or MgCl_2 , which are hygroscopic, so these IDCs could contain absorbed water. Radiolysis of the water could be expected with time, resulting in the generation of H_2 . Possible trapped moisture may also cause this material to be corrosive, thus threatening containment if packaged in metal containers. Additionally, hydrogen accumulation and container pressurization is possible with salts packaged in sealed tin-plated, mild steel produce cans.

Group 2: Ash

The function of the residue recovery incinerator was to reduce volume and destroy volatile constituents prior to plutonium recovery operations for combustible wastes from production processes. The by-products of this process included ash, ash heel, soot, and soot heel. Ash IDCs consist of mixtures of oxides (SiO_2 , Al_2O_3 , CaO , Fe_2O_3 , Na_2O , BaO , CdO , Cr_2O_3 , PbO , and americium and plutonium oxides) and carbon, and may contain unburned, organic feed material. Incinerator ash may be considered mixed under the "Derived-From" rule. Volatile organic constituents are normally destroyed during the combustion process although trace quantities may have carried through with small particles of feed material that escape combustion. The volatile

organic constituent most likely to be detectable in trace quantities is carbon tetrachloride. Also, ash and soot heel materials were generated from acid dissolution processes and may contain free liquids. EPA codes D004-D011, F001, F002, F003, and F005 were assigned to the IDCs based on the characterization of incinerator feed materials. Alcohols, glycols, halogenated solvents, and metals may have been introduced into the incinerator. Because the specific sources of the incinerator feed cannot be determined at this time, it has been assumed that the process could have accepted any of the combustible, plastic, or filter waste currently contained in the inventory that were generated during the time the incinerator was operational. The F-listed solvents would have to be applied due to the "Derived-From" rule. The codes for the D-listed metals were applied because these metals would be concentrated during incineration.

Group 3: SS&C

Sand, slag, and crucible IDCs were generated from the reduction of plutonium tetrafluoride to plutonium metal using calcium as the reductant. Within the reduction vessel, magnesium oxide sand was used as an insulating material in the annulus between a magnesium oxide crucible and the reaction vessel wall. A slag was generated as a result of the molten reduction reaction and was subsequently separated from the plutonium metal button upon cooling of the vessel. The SS&C residues may contain pyrophoric materials. Also, sand, slag & crucible heel was generated from an acid dissolution process and may contain free liquids. The SS&C residues may also contain elemental calcium, which is reactive with water and may be pyrophoric, especially in finely divided form. Two of the SS&C IDCs have been characterized as hazardous due to presence of chromium (D007).

Group 4: Firebrick

Firebrick was generated during incinerator maintenance and strip-out operations. Alcohols, glycols, halogenated solvents, and metals may have been introduced into the incinerator. Because the specific sources of the incinerator feed cannot be determined at this time, it has been assumed that the process could have accepted any of the combustible, plastic, or filter waste currently contained in the inventory that were generated during the time the incinerator was operational. The F-listed solvents would have to be applied due to the "Derived-From" rule. The codes for the D-listed metals were applied because these metals would be concentrated during incineration. Also, firebrick heel was generated from an acid dissolution process and may contain free liquids. Unpulverized firebrick is considered a debris waste (S5000); although process knowledge is acceptable for the QAPP, total metals and total VOAs were determined for RCRA confirmation.

Group 5: Graphite

Graphite IDCs were generated during plutonium casting operations. There are no EPA codes assigned to the graphite IDCs because the associated process that generated the IDCs did not involve the use of regulated solvents or contact with RCRA metals. With the exception of graphite molds, a debris waste (S5000), total metals, total VOAs, and total SVOAs were assessed for WIPP/WAC certifiability. Graphite scarfings and fines were generated through mechanical

cleaning of graphite molds. This material is finely divided graphite contaminated with plutonium metal, which may be considered pyrophoric.

Group 6: Combustibles

Dry Combustibles were generated as a result of processing activities, routine cleanup, maintenance, and periodic inventories. The material includes paper, rags, cloth, Kimwipes, plastic, wood, surgical gloves, tape, paper coveralls, booties, personal protective equipment waste, packaging material, protective masks, V-belts, and other debris. This material may be either a mixed residue (F001, F002) or a non-mixed residue depending on the generating process or point of origin.

Ful-Flo Filters are in-line cartridge filters (cotton or polypropylene, and tinned steel or stainless steel) used throughout Rocky Flats to remove particulates from fluid streams. The filters may be contaminated with corrosive liquids (D002), and/or spent solvents (F001, F002) and are therefore characterized as hazardous. Ful-Flo Filters may contain free liquids.

Wet Combustibles consist of paper, rags, cloth, coveralls, plastic, rubber, and wood from glovebox cleanup operations. Depending on the building in which these residues were generated, corrosive liquids (e.g., HNO_3 , HCl , and caustics) or solvents (e.g., CCl_4) may be present; EPA codes D002, F001, F002, and F003 were therefore assigned. Also, since stainless steel piping and equipment, as well as leaded drybox gloves are subject to chemical attack by corrosive fluids, detectable levels of chromium (D007) and lead (D008) are expected to be present.

Plastics are polymeric materials (equipment and supplies) which may contain plutonium and which were used in various plutonium processes. The dominant components include Teflon, Kynar, polyvinyl chloride, polyethylene, polypropylene, plastic pipe, valving, Nalgene bottles, supplied-air suits, and gaskets. The material is characterized as nonhazardous.

Plastics and Wet-, as well as Dry-Combustibles may contain free liquids. Potentially explosive compounds may be produced by the reaction of nitric acid on various organic and inorganic materials. Conversely, if contaminated with solvents, the potential for plutonium organohalides exists, as does the potential for pyrophorics, if the material has been allowed to dry.

Resins were generated from the anion and cation exchange columns used in aqueous separation purification processes. Plutonium-contaminated materials were often dissolved in nitric acid and processed through ion exchange. The resin was periodically replaced when this process had depleted the efficiency of the resin. The ion exchange resins in use at Rocky Flats were generally small plastic (polystyrene) beads in which long-chain organic compounds with an activated group are imbedded (such as Dowex 1X2). The resins are categorized as nonhazardous, but may contain free liquids. Potentially explosive compounds may be produced by the reaction of nitric acid on these organic materials. (The Residue Stabilization Program has neutralized and repackaged all of the ion exchange resin; most of the material has been cemented or is awaiting encapsulation. Prior to this, characterization was performed on the material.) Since the resin

IDCs are the only combustible IDCs not classified as debris, total metals, total VOAs, and total SVOAs were determined in addition to safety analyses.

Group 7: Sludges

Sludges were generated as by-products from miscellaneous processes at Rocky Flats. The sludges are characterized as mixed residue because they could contain RCRA-listed constituents, metals (D004-D011) and listed solvents (D018, D019, D035, and D040) that are potentially leachable using TCLP. EPA codes D002, F001, F002, F003, and F005 are also assigned to specific subpopulations. Sludge IDCs may contain free liquids. Potentially explosive compounds may be produced by the reaction of nitric acid on various organic and inorganic materials. Conversely, if contaminated with solvents, the potential for plutonium organohalides exists, as does the potential for pyrophorics, if the material has been allowed to dry. Since the sludges are classified as homogeneous solids (S3000), total metals, total VOAs, and total SVOAs analyses were performed.

Group 8: HEPA Filters

High Efficiency Particulate Air (HEPA) filters have been and are currently used in all of the buildings which contain plutonium processing activities and are used on gloveboxes and in large filter plenums that filter room air. Two of the HEPA filter IDCs may contain free liquids. Because these IDCs may be contaminated with acids, the potential exists for explosive compounds from the reaction of nitric acid on various organic and inorganic materials. The HEPA-filter IDCs are classified as debris waste.

Group 9: Crucibles

Crucibles were generated during pyrochemical processes and may contain reactive metals, as well as pyrophoric materials. LECO crucibles were generated in the laboratories and are characterized as nonhazardous. Because these IDCs do not meet the definition of debris waste (<60mm), total metals, total VOAs, and total SVOAs analyses were performed.

Group 10: Glass

Glass IDCs consist of glass waste from analytical laboratories and recovery processes, standard light bulbs generated inside the Protected Area and Raschig Rings. Raschig ring IDCs may contain free liquids. Because glass IDCs do not meet the definition of debris waste (<60mm), total metals, total VOAs, and total SVOAs analyses were performed.

Group 11: Metal

With the exception of Ca Metal and Zn-Mg Alloy Metal, metal residues are characterized as debris waste. Heavy Non-SS Metal, Ca and Zn/Mg IDCs contain, and in some cases, are reactive metals. Heavy Non-SS Metal consists of materials used in various production processes at Rocky Flats and may contain pyrophoric materials. Prior to creation of the Lead IDC, the Heavy

Non-SS Metal IDC may have contained lead (D008). EPA code D008 has been assigned to Lead.

Group 12: Miscellaneous

With the exception of Grit, miscellaneous residues are debris wastes. Grit was generated by grit blasting operations. Since it is likely that lead shielding was the primary metal that was grit blasted, it is also likely that the grit waste is contaminated with lead (D008). Grit is characterized as a homogenous solid and was therefore subjected to total metals, total VOAs, and total SVOAs.

Group 13: Oxide

Duct Holdup Material may contain reactive metals, pyrophoric materials, and volatile organic compounds. Grease Oxide (Green Cake) is plutonium oxide which has been contaminated with grease. This material is a RCRA characteristic hazardous waste because it is believed to exceed the regulatory level for chromium (D007).

Group 14: Fluoride

Plutonium tetrafluoride was produced by fluorination of calcined plutonium peroxide (green cake) in the plutonium recovery process in Buildings 371 and 771 and includes PuF₄, Non-Spec Fluoride and Grease Fluoride. Fluoride heel is the solid material remaining after acid dissolution of plutonium tetrafluoride and may contain free liquids. With the exception of Sodium Fluoride Pellets, the fluoride IDCs are characterized as hazardous for chromium (D007). Fluoride IDCs are homogenous solids (S3000) and therefore require total metals, total VOAs, and total SVOAs.

Group 15: Classified

Classified shapes include graphite molds, obsolete tooling and parts generated during disassembly operations of site-return units or as rejected parts. The characterization requirements consisted of primarily a visual inspection. Once the shapes are sanitized, additional characterization may be required.

METHODOLOGY USED TO ASSESS MATERIAL CHARACTERISTICS

Using the process knowledge and characterization objectives as guidance, the analytical methodology was specified for each residue IDC.

Qualitative Inspection

The inspection includes the following: verification of IDC and container identification numbers and subsequent comparison to data on record; examination of drums and cans for signs of corrosion and/or pressurization; and inspection of gaskets and filters, and plastic packaging materials for signs of degradation. Containers and internal packages are visually inspected for the presence of free liquids. If free liquids are found during preliminary inspections, a quantity of the liquid is extracted from the container for analytical testing and a decision made on whether

the residues need to be repackaged or treated. A visual inspection of the residue materials is performed in conjunction with solid sampling operations.

Qualitative Analyses

Differential thermal analysis (DTA), using a Thermal Hazards Screening System, is conducted as a preliminary method for indicating thermal events. If reaction products are evident in combustible residues, DTA sample preparation involves cutting out affected areas or brushing the material into a sample vial. The presence of exotherms/endotherms on a DTA plot could indicate water desorption, thermal decomposition, or phase changes. Conversely, the absence of exotherms/endotherms would indicate that no thermal events have occurred. In addition to determining the possible existence of reactive compounds, DTA will provide a thermal map of each sample, thus providing a means to make a statement on the homogeneity from one container to another. DTA will be used only as a screen for pyrophoric materials. Any significant rates of temperature increase (dT/dt) are noted as well as exotherms with onset temperatures below 150°C.

Impact testing is performed in accordance with ASTM standard #E680-79 "Standard Test Method for Drop Weight Impact Sensitivity of Solid-Phase Hazardous Materials" [Reference 9] to assess the "shock sensitivity" of the select salt residues.

Dispersive Infrared (IR) is a qualitative test for determining the presence of nitrated organics/inorganics in combustible, sludge, and HEPA filter IDCs.

Real-time radiography (RTR) is used for 55-gallon drums of residue IDCs suspected of containing free liquids, pressurized containers, and/or degraded internal packaging.

Quantitative Analyses

To assess the physical characteristics of the residue, mass fractions, as applicable, are estimated prior to taking samples. Particle size distribution analysis is performed on the fines fraction to determine the amount of dispersible ($<10\text{ }\mu\text{m}$) fines. The amount is then extrapolated back to the whole container using the mass fraction value.

An analysis was desired for assessing reactive metals for select salt, crucible, metal, and oxide residues. One test available for testing for reactivity consists of exposing the residue material to water and monitoring the amount of hydrogen gas (H_2) given off. The Department of Transportation (DOT) test method 49 CFR 173.124 Appendix E [Reference 10] for detecting H_2 generation was adopted. A sample is placed in water and the amount of H_2 generated is measured. If the gas spontaneously ignites or the rate of H_2 generation exceeds 1 liter/kilogram material/hour in any one hour of the seven-hour test period, then the material is classified as reactive, per DOT. The information may be used to calculate potential concentrations of reactive metals.

X-ray diffraction (XRD) is performed to assess salt, ash, oxide, and fluoride residue constituents (crystallographic phases). XRD is an ancillary characterization tool that provides verification of process knowledge and IDC identification in some cases.

Surface contamination of individual drums, cans and packages is monitored with a Ludlum 12-1A air-proportional counter. If contamination suspension limits are approached, the operations being performed are stopped, and the drum is resealed.

Particle size distribution to assess fines dispersibility is performed on most of the residue IDCs, if appropriate, using the Quantimet 720 Analyzer and Reichert microscope. Samples are first screened using a set of 5 to 6 screens ranging between about 50 to 1000 microns. The smallest size fraction is then examined microscopically.

If free liquids are present in the residue containers, a quantity of liquid is extracted for radioassay (g/L Pu) using x-ray spectrometry, x-ray fluorescence, or ICP spectroscopy. Free liquids are also analyzed for RCRA-ignitability (D001) and corrosivity (D002) using EPA's *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition* [Reference 8], hereafter referred to as SW846. A modified SW846, Method 1020A, Setaflash Closed-Cup Method for Determining Ignitability, is used for ignitability analysis and Method 9040: pH Electrometric Measurement, for corrosivity analysis.

In addition to RCRA characterization (if applicable), homogenous solids (S3000) are analyzed for total metals per the WIPP QAPP; the targeted analytes and respective program required detection limits (PRDLs) are listed in Reference 6. If total metal concentrations exceed the program required detection limits, the Toxicity Characteristic Leaching Procedure (TCLP) is performed for RCRA closure. Samples of solid residue material are prepared for total metals analysis using SW846, Method 3050A: Acid Digestion of Sediments, Sludges, and Soils. Samples for TCLP analysis are prepared using SW846, Method 1311: Toxicity Characteristic Leaching Procedure. TCLP is designed to analyze only the leachable amount of analytes and total metals analysis yields the total constituent concentration of toxic characteristic (TC) metals. The procedure used to analyze the digestates is SW846, Method 6010A: Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-ES).

Moisture content is typically assessed on those residue IDCs that are considered "moderated" from a criticality safety standpoint. The material is heated to 105°C and then 210°C, and the weight loss is measured at each temperature. The higher temperature is required to capture water of hydration data for salt IDCs.

In addition to F-listed IDCs, samples of homogenous solids (S3000), with the exception of salts, are analyzed for total volatile organic analytes and total semi-volatile organic analytes. Sample preparation and extraction for the analysis of VOAs is performed as specified in SW846, Method 5030A: Volatile Organic Sample Preparation. Sample preparation and extraction for the analysis of SVOAs is performed as specified in SW846, Method 3540B: Soxhlet Extraction. Following the preparation of the sample, the sample is ready for further analysis. Total volatile organic analysis is performed by Gas Chromatography/Mass Spectrometry (GC/MS) using either SW846, Method 8240: Volatile Organics by GC/MS or Method 8260: Volatile Organic Compound by GC/MS; Capillary Column Technique. Total semi-volatile organic analysis is performed using either SW846, Method 8250A: Semi-volatile Organic Compounds by GC/MS or Method 8270B: Semi-volatile Organic Compounds by GC/MS; Capillary Column Technique. The targeted analytes and respective PRDLs for VOA and SVOA analysis are listed in Reference 12.

SAMPLING OPERATIONS

Residues are currently stored in various containers in several buildings on the site. Individual containers are sampled in a glovebox. If the containers are stored in a 10- or 55-gallon drum, the drum is opened in a contamination controlled area to remove the individual container. Sampling is conducted in three buildings. The drums, as well as the individual residue containers are inspected and the findings recorded. The entire contents of the container to be sampled are dumped into a sampling pan. After mass fractions are assessed, the prescribed number of samples is taken. The subject matter expert may direct the crew to take additional samples, if warranted. Once sampling and inspection activities are completed, the container contents are repackaged in the original container (if applicable) and returned back to the original storage location. If the original container is not suitable for storage of the residue material, the material is repacked into a more suitable container. The samples are packaged in metal cans and are shipped to the on-site laboratory for analysis.

CHARACTERIZATION SUMMARY

To date, over 1000 residue containers have been sampled and analyzed. An additional 115 containers have been attempted, but due to contamination, high radiation levels, or current operational constraints, have not yet been sampled. A summary of the visual inspection findings and analytical results of this effort is provided below. Additional sampling to achieve 95%/5% confidence was required for 14 “higher” risk IDCs (two ash, three combustible, and nine salt IDCs). The sampling scope included 498 containers above the 80%/15% requirements. To date, the sampling and analysis has shown that the two ash IDCs may be considered low risk. The results of this sampling effort have been incorporated into the summaries below.

Visual

1254 containers have been sampled or sampling has been attempted. The 115 containers, primarily 55-gallon drums, that could not be sampled provided useful characterization data points.

Packaging Configuration: In addition to 55-gallon drums, 10-gallon drums, 8801/8802 slip-lid Vollrath cans, Stacker/Retriever cans, 2-liter and 4-liter polyethylene bottles, the characterization effort revealed residue materials stored in 1-gallon paint cans, produce cans, lead capsules, Kraft tubes, 2030 pipes, Freezette containers, FiberPaks, clamshells, and PVC and polyethylene bags. In general, with the exception of Kraft tubes used to store ion-exchange resin and plastic bags around high-ameridium salt cans, the containers have withstood storage well. Kraft tubes were used to contain ion-exchange resin contaminated with nitric acid; the cardboard tubes were “reinforced” with yellow tape and showed significant degradation from residual nitric acid and radiolysis. The plastic bags between the primary can and secondary can of high-ameridium salts have shown significant degradation due to radiolysis and is evidenced with a black tar-like appearance. The number of packaging configurations encountered during the program as well as the package size variation was greater than expected. These findings resulted in improvements/modifications to criticality limits, and installation of larger bag-ports and chainveyor pendants.

Mislabeling: Of the 1254 containers sampled, 89 containers were found to be mislabeled. Generally, the mislabeling occurred within the same material category (e.g., the database indicated one salt IDC but the primary container label revealed a different salt IDC). Most of the salt mislabeling has been resolved with analytical (XRD) data; the process is ongoing with the other material categories. The XRD discovery of calcium chloride/calcium compounds in ER and MSE salts (NaCl/KCl-based) raised the concern that distinct subpopulations could exist within an IDC and prompted an investigation into the historical records of R&D ER and MSE salt processes. Ten percent of the mislabeling did not occur within the same material category. The results are tabulated in Table I.

Table I. Mislabeling Inconsistencies between Material Categories

Material Category As Indicated By Records	Material Category As Verified By Characterization
Graphite Fines	Filter Media
Ful-Flo Filters	Sludge
Drybox Filters	Ful-Flo Filters
Wet Combustibles	Crucibles
Wet Combustibles	Glass
Filter Media	Oxide
Filter Media	Graphite Fines
Filter Media	Graphite Fines
Pyrochemical Salt	Crucibles

Contamination/Not-Sampled: One hundred and fifteen containers could not be sampled due to contamination exceeding the contamination cell limits, high radiation levels exceeding the radiation work permits (RWPs), or packages too large to bag in (e.g., drum drop bags). Drums have also not been sampled due to noxious fumes. While sampling has not yet been completed on these drums, the conditions represent important characterization findings, and give a strong indication that special facilities (e.g., two-stage contamination control cells) will be required for the handling certain residue IDCs. Sixty-seven of the 115 drums have not yet been attempted due to high levels of contamination. The range of contamination in disintegrations per minute (DPM) is given below in Table II for the affected material categories.

Bulged Cans: Six cans, all pyrochemical salts, were notably bulged. Sampling has not yet been attempted on two of the cans (produce cans) due to operational concerns. Samples were taken on the remaining four (two produce cans, and two 8801 Vollrath cans). The material in the two 8801 cans appeared to have expanded, thus explaining the appearance of the cans. The two produce cans were in a nested produce can configuration, with a bag around the primary container. The proposed mechanism is the heat-sealed bag pressurized via radiolysis by-products thereby creating a bladder-effect and pressurizing the outer can. Both outer can ends gave way when pressed; indicating that the pressure had dissipated with time, so the sampling proceeded. The analytical results on the materials did not reveal anything out of the ordinary.

Table II. Contamination Levels

Material Category	# Drums Contaminated	Contamination Range, DPM
Combustibles	13	5,000-1,000,000
Graphite	7	2,000-16,000
Classified Shapes	7	8,000-15,000
Sludge	1	4,000
Metal	3	2,000-4,000
Firebrick	3	No levels specified
Filters	8	1,500-4,000
Glass	3	1,500-5,000
Salt	22	1,500-200,000

Pressurized Can: One pyrochemical salt produce can did not appear deformed or pressurized but when the can was punctured “material spewed out of the can.” The can had minimal headspace and the material appeared to be more like soot than salt. The standard analytical suite did not reveal anything out of the ordinary, but the material will be resampled for moisture content and VOAs.

The characterization effort has identified suspect residue IDCs/packaging configurations where gas generation/accumulation could be a problem. The safety hazard does warrant further characterization, and if necessary, mitigation. Special handling and safety measures will be required for the affected materials.

Free Liquids/Moisture: Free liquids/moisture was present in 34 containers; eight of the 34 contained free liquids. The breakdown by material category is provided below in Table III.

Table III. Free Liquids/Moisture “Hits” By Material Category

Material Category	# Containers With Free Liquids	# Additional Containers With Moisture
Combustible	5	20
Glass	0	3
Sludge	1	1
Ash	0	1
Salt	1	1*container also bulged
Metal	1	0

Since the quantity of free liquids is generally limited for shipment of materials to WIPP, the characterization information has shown which residue materials may have to be treated to remove liquids.

Loss of Primary Containment: Thirty containers failed the visual inspection in that primary containment was breached. Reasons for loss of primary containment included: 1) degraded polyethylene bag, 2) cracked polyethylene bottle, 3) disintegration of Kraft tube, 4) produce can crimp improperly applied, 5) lid of paint can not properly seated, 6) Freezette lid not secured, 7) polyethylene bottle lid “melted,” 8) Vollrath can lid not secured, and 9) paint can “lid” consisting of yellow tape which had degraded. The containers that failed the visual inspection were replaced/repackaged. Salt corrosivity toward metal containers was not as aggressive as initially expected; corrosion did not result in breach of primary containment.

RTR: RTR was used to complete the 80%/15% preliminary characterization of four IDCs; Graphite Molds (3 drums), Classified Shapes (9 drums), Scarfed Graphite Chunks (1 drum), and Processed Filter Media (6 drums). The statistical sampling of the IDCs could not be completed without RTR due to a high incidence of contamination encountered. In general, sampling is not required for these IDCs; a visual inspection is sufficient. The RTR resulted in many characterization findings, thus expanding the knowledge base of the IDCs. It also revealed why the incidence of contamination in the four IDCs is so high (e.g., sharp graphite edges and nails left in filter frames caused breach of primary containment, drum drop bags). A “drum-dump” facility will be required for dispositioning these materials in the future.

Contact Dose Rate: Ninety of the 697 containers measured failed the contact dose rate criterion of 200 mR/hr. Most of the failures were high-ameridium pyrochemical salt containers as shown in Table IV.

Table IV. Contact Dose Rate Failures

Contact Dose Rate, mR/hr	# Salt Container Failures	# Non-Salt Container Failures
≥200, <400	39	12
≥400, <1000	26	7
≥1000	6	0

The six salt containers that exceeded 1000 mR/hr ranged from 1 to 2.3 R/hr. In keeping with As-Low-As-Reasonably-Achievable (ALARA) principles, the salt operations project has responded to this information by installing radiation shields.

Analytical

Pyrophoricity: Differential thermal analysis (DTA), using a Thermal Hazards Screening System, was conducted on 852 samples; 598 (70.2% of the samples analyzed) passed the initial screen for pyrophoricity. The remaining 254 (29.8% of the samples analyzed) were flagged for exotherms below 150°C; 5 of the 254 yielded exotherms below 60°C, the ISS criterion for flammable materials. All exotherms below 150°C are individually assessed to determine if they show characteristic signs of ignition (sharp increase in temperature over a very short time period). Before an IDC may be declared “Low Risk,” the DTA review must be completed to assure that there is no hazard of pyrophoricity or flammability. The IDCs reviewed to date have

passed this assessment. The IDCs showing exotherms below 60°C are all planned for stabilization, which will eliminate any potential flammability issue.

Moisture: Moisture analysis was performed on 538 container samples at 105°C. Later in the program the analysis was conducted at 210°C to address/estimate waters of hydration in salts, and consequently, determine whether the salts should be moderated from a criticality standpoint. Two hundred and forty-eight of the 538 samples were salts, and of the 248, data at 210°C is available for 139. A summary of the moisture analysis for the salts is contained within Table V.

Table V. Moisture Summary of Pyrochemical Salts

Weight % Moisture	# @ 105°C	# @ 210°C
< 1%	217	37
≥1%, < 5%	30	101
≥5%, < 10%	0	1
≥10%	1	0

At the onset of the characterization program the definition of a “moderated” salt was more than 10% moisture. Mid-stream the definition was changed to an H to Pu ratio greater than three. While most of the salts sampled are less than 10% moisture, with the H:Pu>3 definition, it is difficult to prove any of the salts nonmoderated, in particular the low-plutonium salts. An evaluation of this criterion is on going and necessary for operational efficiency.

Dispersible Fines: Particle size distribution was performed on 756 samples. The weight % dispersible fines (< 10 µm) was estimated by multiplying the % dispersible measured in the fines fraction times the mass fraction of fines in the container. The materials that had more than 10 wt % dispersible fines (highest value was 14.70 wt %) consisted primarily of ash, sludge, SS&C, firebrick, and graphite fines. A summary of the analysis is provided in Table VI.

Table VI. Dispersible Fines Summary

Weight % Dispersible Fines	# Containers Analyzed	Percentage of Total Analyzed
<1%	602	79.6
≥1%, <5%	128	16.9
≥5%, <10%	18	2.4
≥10%	8	1.1

The data, in general, has been useful in pushing back on nuclear safety accident scenario assumptions. This translates to a higher material at risk (MAR) limit, and consequently, increased material handling efficiency for plutonium operations buildings.

Shock Sensitivity: Impact testing on 196 samples revealed no evidence of shock sensitive materials.

RCRA F: Total VOA and SVOA analyses were performed on 484 samples. Four combustible samples subsequently failed TCLP for the following VOAs: 1) Chloroform (26

ppm) and Carbon Tetrachloride (5.7 ppm), 2) Carbon Tetrachloride (14 ppm), 3) 1,2-Dichloroethane (1.1 ppm), and 4) Benzene (0.7 ppm). In addition to RCRA, total VOAs/SVOAs were performed to assess WIPP/QAPP requirements. For some materials that showed no detectable volatile organics (e.g., SS&C), the preliminary characterization will become “acceptable knowledge,” and may provide a basis for minimizing future WIPP/QAPP sampling and analysis.

RCRA D: Total metals analysis was conducted on 623 samples; 134 of the samples failed subsequent TCLP. The summary by material category is given below in Table VII.

Table VII. TCLP “Hits”

Material Category	Metals “Hit” On	# Containers That Failed TCLP	Percentage of Total Analyzed
Ash	Cd, Cr, Pb	33	58.9
Oxide	Cd, Cr, Pb	8	47.1
Sludge	Cd, Cr, Pb	19	55.9
Combustibles	Cd, Cr	2	8.3
Miscellaneous	Cd	1	100.0
Salt	Cd, Cr, Pb, Se, Ag	22	7.7
Firebrick	Cd, Pb	8	23.5
Fluoride	Cd, Cr, Se	26	56.5
Crucibles	Cr, Se	3	5.3
SS&C	Cr	1	1.1
Graphite	Cd, Cr, Pb, Se	5	6.5
Glass	Cr, Pb	2	11.1
Metal	Se	1	6.7
Filters	N/A	0	0

The analytical data may be used to confirm or refute the RCRA designation, which had been assigned, based on process knowledge. If the process knowledge was refuted, and only a certain percentage passed or failed, a statistical evaluation is required for RCRA determination. Several residue IDCs (those with only D-codes) will be removed from RCRA. One IDC, Duct Holdup Material, was not addressed by the process knowledge, and the resulting TCLP data indicated that it be considered a mixed waste; the material was subsequently put into RCRA.

Oxidizer/Fuel Mixtures: IR was conducted on 93 samples to determine in oxidizers were present. Although nitrates were confirmed in some cases, the IR analysis did not provide much more detail than that.

Water Reactivity: The water reactivity test was performed on 670 samples, 5 of which were unidentified metals from salt cans. All five of the special water reactivity samples generated greater than 20 liters of H₂/kg material in one or more hours of the test; the total amounts of hydrogen generated (7 hours) were: 282.50 (DOR salt), 281.75 (MSE salt), 142.52

(DOR salt), 116.80 (ER salt), and 99.59 (MSE salt). In general, the vault cans are more reactive than the 55-gallon drums. 38.7% of the 55-gallon drums generated more than 1 liter of H_2 /kg material in one or more hours of the test; the total amount of hydrogen generated (7 hours) ranged from 1.21 to 21.34 liters/kg material. One additional sample, calcium metal, yielded 166.44 liters in 7 hours. In comparison, 64.7% of the vault cans generated more than 1 liter/kg material in one or more hours of the test; the total amount of hydrogen generated (7 hours) ranged from 1.47 to 27.18 liters/kg material. The information from the water reactivity test was used to back-calculate potential concentrations of reactive metals.

Ignitability/Corrosivity: Of the eight containers that contained free liquids, three did not yield enough liquid for analysis. The D002 code (corrosivity) was confirmed on two combustible samples and refuted on one other.

CONCLUSION

The analysis of the residue materials has addressed safety hazards (pyrophoricity, flammability, shock sensitivity, reactive metals, dispersible fines), as well as parameters that affect the RCRA classification or final disposition path of the material (total metals, VOAs, SVOAs, moisture content, chemical composition). The residue materials are better understood, and less reactive than originally hypothesized. This translates to significant cost-savings to the taxpayer in that less handling (e.g., "processing") will be required for most of the materials, and most can be simply repackaged to meet off-site shipment requirements. In addition, the characterization program has gathered data regarding material packaging configuration, dose rates, and contamination of internal containers. This information has helped formulate operational aspects of the processing or repackaging plans.

REFERENCES

1. W. V. Conner, "Evaluation of Residue Drum Storage Safety Risks," RFP-4826, Rocky Flats Environmental Technology Site, Golden, Colorado, June 17, 1994.
2. Backlog Waste Reassessment Baseline Book
3. K. A. Phillips, "Project Plan for Inspection, Sampling, and Characterization of Solid Residues," Rocky Flats Environmental Technology Site, SRM-012-002, Revision E, February 25, 1998.
4. Criteria for Interim Safe Storage of Plutonium-Bearing Solid Materials, Addendum to The Department of Energy Implementation Plan for DNFSB Recommendation 94-1, November, 1995.
5. Waste Isolation Pilot Plant/Waste Acceptance Criteria (WIPP/WAC), WIPP-DOE-069, December 1991.
6. Transuranic Waste Characterization Quality Assurance Program Plan, CAO-94-1010, U.S. Department of Energy Carlsbad Area Office, April 30, 1995.

7. Code of Federal Regulations, 40 CFR Part 261, Identification and Listing of Hazardous Waste, Subpart C, Characteristics of Hazardous Waste.
8. EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW-846, Third Edition, Final Update I and Proposed Update II, Washington, D. C., Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency.
9. ASTM Standard E680-79, Standard Test Method for Drop Weight Impact Sensitivity of Solid-Phase Hazardous Materials. (ASTM Standards are available from ASTM, 1916 Race St., Philadelphia, PA 19103).
10. Code of Federal Regulations (Transportation), 49 CFR Ch. I (10-1-93 Edition), Appendix E to Part 173 - Guidelines for the Classification and Packing Group Assignment of Class 4 Materials, pp. 343-349.