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Recommendations on Stabilization of Plutonium Material Shipped to Hanford from Rocky Flats

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Abstract

This report responds to a request from the Plateau Transition Division of the Department of Energy's (DOE's) Richland Operations Office. It summarizes the results of evaluations by a technical team (the authors) assembled in response to the request, and it provides the technical basis for demonstrating equivalency of 750°C stabilization of certain chloride-bearing plutonium (Pu) oxides with the requirements of DOE standard DOE-STD-3013-2000. The Pu oxides evaluated were received at the Hanford Plutonium Finishing Plant from the Rocky Flats Environmental Technology Site.

Stabilization at 750°C and confirmation of moisture content at 1000°C will comply with the stated objectives of stabilization for chloride-bearing oxides identified by prompt gamma-ray analysis. As documented by evaluation of data on moisture content and other material chemical characteristics, 750°C stabilization will meet the objectives of the standard to stabilize material for long-term storage.

The technical team concludes that changing the baseline from water washing to lower-temperature stabilization will result in stabilization equivalent to compliance with DOE-STD-3013-2000 for material with >50 wt % Pu and in reduced cost, dose, and possibly time to stabilize these materials without discernable effect on risk. Material below this Pu level should be processed through the washing system. Items below 30 wt % Pu have already been prepared for shipment to the Waste Isolation Pilot Plant. The team further concludes that no additional risk is likely for these chloride-bearing oxides and that future surveillance will ensure adequate validation of this judgment.

Acronyms and Abbreviations

Acronym or Abbreviation	Definition
94-1	DNFSB Recommendation 94-1, issued in January 1994 (DNFSB 1994)
94-1 R&D	Research and development program supporting the stabilization, packaging, and storage of 94-1 plutonium-bearing materials
ALP	Actinide Laboratory Program
ARF	DOE RIS (see below) code for Rocky Flats
D&D	decontamination and decommissioning
DNFSB	Defense Nuclear Facility Safety Board
DOE	Department of Energy
DOE-HQ	DOE Headquarters
DOR	direct oxide reduction
ER	electrorefining
ER oxide	material from Pu ER furnaces
ESO	Environmental Stewardship Office
eU	enriched uranium
FTIR	Fourier transform infrared spectroscopy
IAEA	International Atomic Energy Agency
IDC	item description code
IPRP	Implementation Plan for the Recovery of Plutonium
IR	infrared spectroscopy
ISP	Integrated Surveillance Program
LANL	Los Alamos National Laboratory
LOI	loss on ignition
MBA	material balance area
MIS	Materials Identification and Surveillance
MMEC	Materials Management Executive Committee
MS	mass spectrometry
MSE	molten salt extraction
NDA	nondestructive assay
NWC	nuclear weapons complex
PFP	Plutonium Finishing Plant
PGA	prompt gamma-ray analysis

PNNL	Pacific Northwest National Laboratory
PPSL	Plutonium Process Support Laboratory
PTFE	polytetrafluoroethylene
Pu	plutonium
PUREX	Plutonium Uranium Extraction Plant
PuSPS	Plutonium Stabilization and Packaging System
PVDF	polyvinylidene
R&D	research and development
RCT	radiological control technician
rem	roentgen equivalent man
RFETS	Rocky Flats Environmental Technology Site
Rocky Flats	Rocky Flats Environmental Technology Site or Rocky Flats Plant
RH	relative humidity
RIS	reporting identification symbol
RMC	Remote Mechanical C
SPE	Stabilization and Packaging Equipment
TGA	thermogravimetric analysis
TRU	transuranic
WIPP	Waste Isolation Pilot Plant
WR	war reserve
wt %	weight percent
XRD	x-ray diffraction

Executive Summary

This report is a deliverable in response to a request from the Plateau Transition Division of the Department of Energy's (DOE's) Richland Operations Office (see Appendix A). It summarizes the results of evaluations by a technical team (the authors) assembled in response to the request, and it provides the technical basis for demonstrating equivalency of 750°C stabilization of certain chloride-bearing plutonium (Pu) oxides with the requirements of DOE standard DOE-STD-3013-2000 (DOE 2000). The Pu oxides evaluated were received at the Hanford Plutonium Finishing Plant (PFP) from the Rocky Flats Environmental Technology Site (Rocky Flats, previously known as the Rocky Flats Plant or RFP).

On January 10, 2003, the Plateau Transition Division of the DOE's Richland Operations Office requested technical assistance from the Office of Science and Technology (EM-50) to do the following:

> "Advance a case to lower the thermal stabilization temperature to less than 800°C and lower the maximum moisture evolution measurement temperature of the thermally stabilized product to <1000°C for chloride-bearing Pu oxides at the Hanford Plutonium Finishing Plant (PFP) that were received from Rocky Flats, while maintaining technical equivalency with the goals of the standard DOE-STD-3013-2000."
>
> "Document the technical case as a basis for its use to obtain approval of the alternative stabilization and moisture measurement practices for chloride-containing Pu oxides at the Hanford PFP." (Appendix A)

The request also calls for the technical assistance team to do the following:

1. Determine the characteristics of the Chloride-bearing oxides at PFP that are represented by the electrorefining oxides defined in LA-UR-02-6054 (Boak et al. 2002);
2. Recommend characterization techniques to identify additional chloride-bearing oxide categories at PFP that might benefit from lower stabilization temperature;
3. Develop an implementation strategy for lower temperature processing to:
   - obtain valid moisture measurement data using TGA-inert at lower temperatures to avoid counting weight loss due to salt evaporation,
   - minimize moisture re-adsorption in stabilized materials, and
   - ensure that only Chloride-bearing material is stabilized at lower temperature;
4. Compare the efficacies of lower temperature stabilization with chloride salt washing followed by 950°C stabilization to select the better means to mitigate the deleterious effects of chloride; identify potential roles for chloride salt washing; and

5. Develop technical arguments to show that moisture evolution during moisture verification measurements is complete at temperatures well below 1000°C.

Hanford requested this technical assistance to enable the site to change its stabilization process to minimize the operational impacts of salt washing, salt volatilization, and corrosion, while still ensuring the technical objectives of DOE-STD-3013-2000 are met. Hanford considered it likely that a reduction in thermal stabilization and moisture measurement temperatures would have the following results:

1. Improve the efficiency of PFP operations.
2. Reduce or eliminate the complex and dose-intensive washing operation.
3. Decrease the liquid waste generated by the water wash steps.
4. Avoid excessive failure impacts of process and moisture measurement (hardware and installation costs, process downtime) at an incremental daily savings of $120,000 (from process downtime alone).
5. Avoid worker exposure associated with equipment repair due to corrosion.
6. Free personnel for other stabilization and decontamination and decommissioning activities.

This document represents the work of a technical team assembled by EM-50, and summarizes the data supporting its conclusions and recommendations. The recommendations of the technical team follow:

- *Task 1:* The available data from Rocky Flats and PFP are adequate to characterize with reasonable certainty the material shipped from Rocky Flats to Hanford. The item description codes (IDCs) that cover all the items shipped to Hanford are sufficiently well understood to support identification of chloride-bearing Pu oxide, and to justify their stabilization at 750°C.

- *Task 2:* The technical team recommends the use of prompt gamma-ray analysis (PGA) to identify chloride-bearing material that may be stabilized at lower temperature. The PGA can be used in conjunction with available assay data to define items that might potentially corrode or plug critical subsystems in the stabilization furnaces.

  Rapid screening for Na, K, and Cl to identify candidates for lower-temperature stabilization will be sufficient to distinguish items that pose a risk to stabilization equipment. This will include material from IDCs related to the ones described in Boak et al. (2002), but also identifies other IDCs shipped from Rocky Flats that have characteristics sufficiently similar to the Rocky Flats electrorefining (ER) oxide to be screened by PGA for lower-temperature

stabilization. Analysis of the full PGA spectrum after stabilization may be used to identify containers for enhanced monitoring by the Integrated Surveillance Program (ISP), which has already identified chloride-bearing Pu oxide as requiring higher levels of surveillance.

The technical team recommends that the ISP, in cooperation with Rocky Flats and PFP, expedite preparation of a document that lays out the technical basis for PGA and describes the instruments now being used at LANL, Rocky Flats, and Hanford.

The technical team has not reviewed any material at PFP other than the items shipped from Rocky Flats. The conclusions of this report apply only to the Rocky Flats material.

- *Task 3:* The discussions in Section 4 and Appendix G of this document provide the rationale for using mass loss by thermogravimetric analysis (TGA) in inert atmosphere (TGA-Inert) to 750°C, divided by a correction factor of 0.9 to provide a conservative estimate of the total moisture content of the stabilized item. However, the technical team recommends that PFP continue to measure moisture by TGA-Inert to 1000°C, and restabilize items that fail the moisture content criterion.

  The technical team recommends that the alternative moisture content measure described above be submitted for peer review to validate the technical conclusion of this team that it constitutes an equivalent measure of the total moisture content with respect to compliance with DOE-STD-3013-2000.

  Following the procedures identified in Section 4, many of which are already in place for all Pu oxides, will minimize re-adsorption. Prestabilization PGA screening will adequately identify items that warrant 750°C stabilization and will ensure that only Chloride-bearing material is stabilized at lower temperature.

- *Task 4*: The evaluation in this report indicates that stabilization of chloride-bearing material at 750°C reduces cost, dose, and schedule risk over washing and 950°C stabilization.

- *Task 5*: The report discusses the evidence that >85 wt % of moisture is evolved below 600°C, and that >90 wt % is evolved below 750°C in a very wide range of material stabilized to date, including chloride-bearing Pu oxide. Recent data on Rocky Flats material relevant to this evaluation is summarized and supports this conclusion.

  Although the technical team concludes that bias-corrected mass losses at these lower temperatures constitute conservative (and therefore equivalent) measures of the total moisture content released by 1000°C, the technical team recommends restabilizing any material that fails at 1000°C unless a significant fraction of the items

fail the 0.5 wt % criterion on this basis. The technical team recommends an external peer review of the above conclusion regarding equivalency to ensure its robustness and to support any subsequent need to review the moisture measurement procedure.

The technical team recommends that PFP reserve the right to request a change to the procedure for moisture measurement if a significant fraction of items fails the moisture content criterion, or if the TGA equipment shows rapid failure when run to 1000°C.

Thus, this document concludes that chloride-bearing Pu-oxides shipped to Hanford from Rocky Flats, identified by PGA and stabilized at 750°C, with a moisture content confirmed by weight loss up to 1000°C, will be in full compliance with the intent of DOE-STD-3013-2000. As documented by the evaluation of data on moisture content and other material chemical characteristics, lower-temperature stabilization will meet the objectives of the standard to stabilize material for long-term storage.

The technical team concludes that changing the baseline from water washing with 950°C stabilization to 750°C stabilization without washing will result in stabilization equivalent to compliance with DOE-STD-3013-2000 for material with >50 wt % Pu and will result in reduced cost, dose, waste volume, and possibly time to stabilize these materials, without discernable effect on risk. Material below this Pu level should be processed through the washing system. Items below 30 wt % Pu have already been prepared for shipment to the Waste Isolation Pilot Plant. The team further concludes that no additional risk is likely for these chloride-bearing oxides and that future surveillance will ensure adequate validation of this judgment.

Recommendations on Stabilization of Plutonium Material Shipped to Hanford from Rocky Flats

1 Introduction

1.1 Purpose

The purpose of this report is to present the case that a large fraction of the plutonium (Pu) oxides at the Hanford Plutonium Finishing Plant (PFP) that were received from Rocky Flats Environmental Technology Site (hereafter referred to as Rocky Flats) in the mid-1980s may be stabilized and tested for moisture content at lower temperatures while maintaining technical equivalency with the goals of the standard DOE-STD-3013-2000 (DOE 2000). The report builds on the technical basis defined in LA-UR-02-6054 (Boak et al. 2002) for lower-temperature stabilization equivalency for chloride-bearing Pu oxides from electrorefining (ER) at Rocky Flats.

This report also discusses the potential benefits of the lower-temperature stabilization in comparison to the baseline method for the Rocky Flats chloride-bearing Pu oxide. The baseline method involves subjecting most of the chloride-bearing material to a water wash to remove the Cl (chloride) salts. Benefits from the reduction of operator exposure and simplification of operation are expected with the lower-temperature stabilization versus the water wash.

1.2 Hanford request for technical assistance

The Plateau Transition Division of the Department of Energy's (DOE's) Richland Operations Office requested technical assistance from the Office of Science and Technology (EM-50) to do the following:

> "Advance a case to lower the thermal stabilization temperature to less than 800°C and lower the maximum moisture evolution measurement temperature of the thermally stabilized product to <1000°C for chloride-bearing Pu oxides at the Hanford Plutonium Finishing Plant (PFP) that were received from Rocky Flats, while maintaining technical equivalency with the goals of the standard DOE-STD-3013-2000. Review and modify the approved technical basis (LA-UR-02-6054) for chloride-contaminated Pu oxides at Rocky Flats as a template to apply to Hanford's chloride-contaminated Pu oxides.
>
> Document the technical case as a basis for its use to obtain approval of the alternative stabilization and moisture measurement practices for chloride-containing Pu oxides at the Hanford PFP." (Appendix A)

The request also calls for the technical assistance team to do the following:

1. Determine the characteristics of the Chloride-bearing oxides at PFP that are represented by the electrorefining oxides defined in LA-UR-02-6054.

2. Recommend characterization techniques to identify additional chloride-bearing oxide categories at PFP that might benefit from lower stabilization temperature.
3. Develop an implementation strategy for lower temperature processing to
   - obtain valid moisture measurement data using TGA-inert at lower temperatures to avoid counting weight loss due to salt evaporation,
   - minimize moisture re-adsorption in stabilized materials, and
   - ensure that only Chloride-bearing material is stabilized at lower temperature.
4. Compare the efficacies of direct lower temperature (for example, 750°C) stabilization with chloride salt washing followed by 950°C stabilization to select the better means to mitigate the deleterious effects of chloride; identify potential roles for chloride salt washing.
5. Develop technical arguments to show that moisture evolution during moisture verification measurements is complete at temperatures well below 1000°C (for example, ~600°C as observed for other pure and impure materials tested to-date).

1.3 Consequences of high-temperature stabilization and moisture measurement of chloride-bearing Pu oxide

1.3.1 Current baseline stabilization technology

PFP has ~1,100 kg of impure Pu oxide that contain variable amounts of Cl salt from Rocky Flats pyrochemical operations. This oxide must be stabilized in accordance with DOE-STD-3013-2000. The present process plan calls for water washing to remove chloride to <1 weight percent (wt %) total salt (to mitigate moisture reabsorption as well as plugging and corrosion problems) before thermal stabilization in furnaces in PFP's Remote Mechanical C (RMC) line.

1.3.2 Current moisture measurement technology

The current baseline technology for measurement of moisture content of stabilized material is thermogravimetric analysis (TGA) in inert atmosphere (TGA-Inert) as a substitute for loss-on-ignition (LOI) measurement. This method measures weight loss as a function of temperature. The TGA-Inert measurement integrates weight loss from room temperature to 1000°C. A backup method is the combination of TGA with mass spectrometry (TGA/MS), which can measure water (as mass 18) specifically.

1.3.3 Potential risks of baseline technology

Furnace tests with simulated chloride-bearing oxide discussed later in this document show that even 1 wt % Cl salt evaporates from process boats at 950°C to deposit on cooler, downstream off-gas surfaces, plug off-gas filters, and cause localized furnace equipment corrosion.

Due to the volatilization of the Cl salt and other salts at temperatures above ~800°C, stabilization of these materials in accordance with DOE-STD-3013-2000 at >950°C has the potential to cause significant process downtime and increased worker exposure due to the following:

- restabilization operations (because of failure to pass TGA-Inert),
- replacement of corroded stabilization furnace and moisture measurement equipment components,
- clearing of obstructions in process off-gas equipment due to plugging by condensed salts, and
- difficulty in handling fused materials after high-temperature stabilization.

Of particular concern, should processing occur in the PFP's Stabilization and Packaging Equipment (SPE) line, is the fact that the furnace wall in the PFP SPE line constitutes a primary glove box containment barrier such that undue corrosion penetration would cause escape of Pu particles into the manned process areas.

Each day of downtime or unnecessary operation extends the PFP processing campaign one day at a cost of ~$120,000. Extension of the PFP campaign will also delay reassignment of PFP personnel to decontamination and decommissioning (D&D) activities for the PFP and ancillary support rooms.

1.3.4 Potential risks of moisture measurement baseline technology

Measurement of moisture concentration for thermally stabilized chloride-bearing materials by weight loss will overstate the actual moisture concentration, and this overestimation may result in unwarranted batch failure and subsequent recycling through thermal stabilization. Moisture measurement by the backup TGA/MS method may be used to quantify water (and other constituents, as needed). However, this method is time-consuming, susceptible to equipment failure (chloride deposition plugs and corrodes the small-diameter gas lines), and limits the availability of the TGA/MS to other process support activities.

1.3.5 Improvement over the baseline technology

Reduction in the thermal stabilization and moisture measurement temperatures will minimize the operational impacts from volatilization of the salt and related plugging and corrosion. However, the technical objectives of the DOE-STD-3013-2000 for stabilization of materials (described in the next section) must be met even with the lower temperature for stabilization and moisture measurement. Reduction of these temperatures would have the following results:

1. Improve the efficiency of PFP operations.
2. Decrease (perhaps eliminate) the complex and dose-intensive washing operation.
3. Decrease liquid-waste generation from the water wash steps.

4. Avoid impacts of failure of process and moisture measurement equipment (hardware and installation costs, process downtime).
5. Avoid worker exposure associated with equipment repair due to corrosion.
6. Free personnel for other stabilization and D&D activities.

As noted above, avoiding slip in PFP stabilization provides an incremental daily savings of $120,000. Further discussion of the relative merits of alternative stabilization paths is provided in Section 5.

1.3.6 Potential disadvantages of lower-temperature processing

The purpose of this introduction is to identify the concerns about the baseline technology that led the PFP to request the evaluations conducted in this report. However, it is important also to note some concerns that have been raised about the lower temperature for stabilization and moisture measurement, which will be evaluated in the subsequent sections of the report.

One benefit of the chloride-washing process that would be sacrificed if the lower-temperature processes are used is the reduction in mass of material due to removal of the salt. If all of the material in an item that is not Pu oxide consisted of salt, and if all of that salt were removed by washing, the total mass of impure oxides would be reduced by 245 kg, or 21.7%. However, the Materials Identification and Surveillance (MIS) data indicate that other oxides are commonly present in the impure oxides, and the salt washing is not expected to be completely effective. The overall benefit in mass reduction might be in the range of 10% to 20%, probably closer to the lower end.

The possibility that hygroscopic Cl salts ($MgCl_2$ and $CaCl_2$) are present raises concerns about the re-adsorption of moisture after stabilization and before packaging is complete. This issue was addressed in Boak et al. (2002), although the analysis was primarily concerned with $MgCl_2$ and intermediate composition salts. The probability is low that many items contain these salts, and the PFP has procedures in place to ensure that re-adsorption is not an issue.

A concern was also raised that melting of the salt in chloride-bearing oxide will produce brick-like masses in the stabilization furnace trays. Additional operator effort (and therefore dose) may be required to remove these items from the trays. This problem has not occurred during stabilization of chloride-bearing oxide at 750°C at Rocky Flats.

A final concern is that items stabilized at 750°C—and measured for moisture (and presumably other volatile constituents) at similarly low temperatures—might contain material that escaped destruction and detection, but would later compromise storage containers. This concern must be addressed in designing and evaluating the Integrated Surveillance

Program (ISP) for all material governed by DOE-STD-3013-2000. The program has identified chloride-bearing material as a primary focus.

None of these potential threats to long-term stability can be ruled out unequivocally. Each must be addressed from the perspective of relative risk. Ultimately, it is a management choice whether to accept that risk or to mitigate it.

1.4 Definition of equivalency to DOE-STD-3013-2002

Appendix A (*Technical Basis*) to DOE-STD-3013-2000 (DOE 2000) states in Section A.6.1.2, p. 21, that:

> "The stabilization requirements of this Standard are intended to accomplish the following objectives:
>
> - Eliminate reactive materials such as finely divided metal or substoichiometric plutonium oxides;
> - Eliminate organic materials;
> - Reduce the water content to <0.5 weight percent (wt %) and similarly reduce equivalent quantities of species such as hydrates and hydroxides that might produce water;
> - Minimize potential for re-adsorption of water above the 0.5 wt % threshold; and
> - Stabilize any other potential gas-producing constituents."

The ultimate objective of stabilization is to ensure safe long-term (50-year) storage of stabilized nuclear material in a specified, sealed, stainless steel container. The major risks to this objective come from corrosion and pressurization of the container (DOE 2000). Equivalency for the purpose of this document means that the modified stabilization process proposed herein meets the same objectives as the process in the standard, for the purpose of ensuring long-term stability in storage.

It is important to note that in asserting equivalency for a process that does not follow the *letter* of the standard, the Rocky Flats technical basis document and this one do not seek to relax the standard. The purpose of Boak et al. (2002) was to demonstrate that the proposed alternative process meets the *intent* of the standard with respect to stabilization. This document follows the same approach.

DOE will provide assurance of adequate stabilization by defining quality assurance and surveillance measures including moisture measurement. This program is already embodied in the ISP, which will be updated as needed. Material containing Cl salts has already been identified as presenting the highest potential risk during storage, and therefore has already been identified as requiring the highest level of surveillance.

1.5 Applicability of prior demonstration of equivalency

A previous technical assistance task for Rocky Flats developed the technical basis for equivalency of lower-temperature stabilization to the requirements of DOE-STD-3013-2000 for Rocky Flats ER oxide (Boak et al. 2002). The material that Rocky Flats is now stabilizing at 750°C came from two item description codes (IDCs) that were both associated with scrape out of tilt-pour furnaces used for ER.

Knowledge of the process and available chemical data from this material permitted the technical assistance team to argue strongly that the composition of the material was limited to mixtures of sodium (Na)-potassium (K)-magnesium (Mg) chloride salt with Pu oxide, and very small amounts of metallic oxide impurities.

Boak et al. (2002) identified the primary concern in high-temperature processing of chloride-bearing Pu oxide material as the potential for corrosion and plugging of furnace system components by Cl salt species volatile at the 950°C stabilization temperature. Available data on the vapor pressure of various relevant Cl salts are shown in Figure 1. The figure shows that a 200°C decrease in temperature leads to an approximately 20-fold decrease in the vapor pressure of these salts. Experimental data summarized in this report demonstrate that processing temperature strongly influences the amount of Cl salt removed from samples during

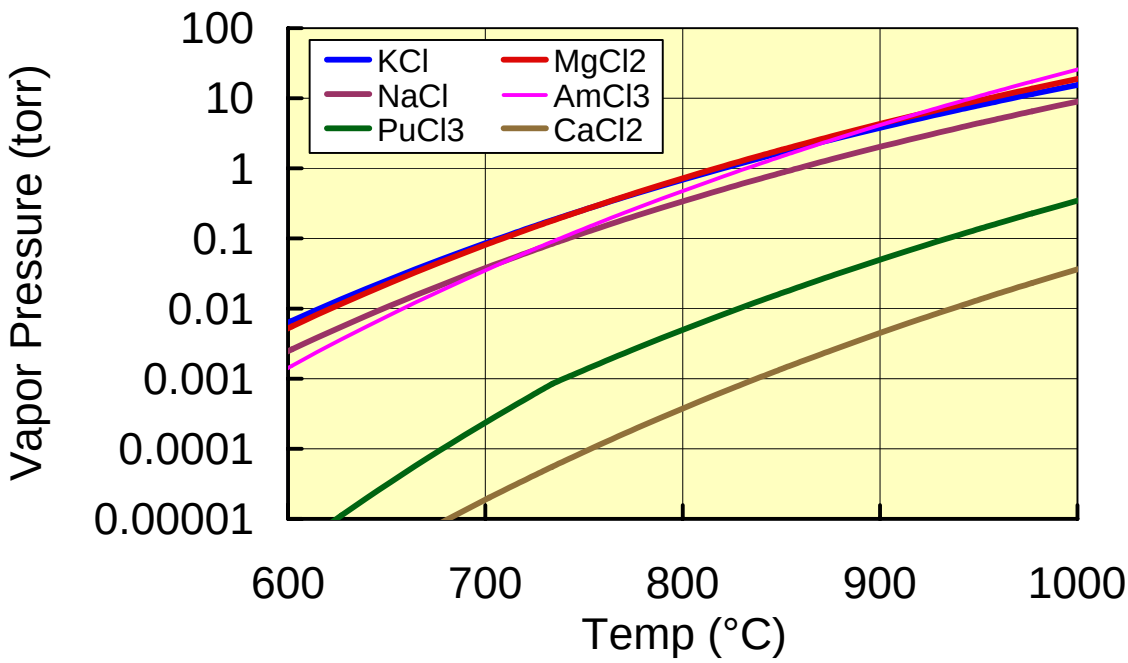

Figure 1: Vapor pressure curves of Cl salts relevant to stabilization of chloride-bearing Pu oxide material.

stabilization. This result supports the central role of vapor pressure in controlling the Cl salt release.

With respect to the five purposes of stabilization listed above, the Rocky Flats technical basis document (Boak et al. 2002) presented the following technical case for each purpose:

- *Elimination of Reactive Materials*: Rocky Flats ER oxide had already been calcined twice at 450°C or above. Therefore, the feed material to processing already has a low risk of pyrophoricity. There will be no significant difference in pyrophoricity between material stabilized at 750°C and at 950°C. Thus, reactive material, such as finely divided metal or substoichiometric Pu oxide, is unlikely to pose a threat after lower-temperature stabilization.
- *Elimination of Organic Material*: Process knowledge strongly suggests that there is no organic material in Rocky Flats ER-derived oxide materials. Carbon concentration of the ER oxide is typically <500 ppm, and is not present as organic compounds. Stabilization at 750°C will destroy virtually any trace organic compounds as effectively as stabilization at 950°C.
- *Reduction of Moisture Content*: Moisture measurement will verify that <0.5 wt % moisture remains in stabilized ER oxide. Any sample failing this criterion will be stabilized again. Stabilization at 750°C will drive off virtually all water and hydroxides in chloride material. The small quantity of moisture that is removed at temperatures above 600°C returns to the surface of these materials at relative humidity (RH) above 1%. TGA with Fourier transform infrared moisture measurements should continue to be integrated to 1000°C.
- *Prevention of Moisture Re-adsorption*: As noted above, moisture measurement will verify that <0.5 wt % moisture remains in stabilized ER oxide. Any sample failing this criterion will be stabilized again. Moisture measurement, process controls, and an integrated surveillance program will confirm the lack of reabsorbed moisture. There is no significant difference in specific surface area (or other properties affecting moisture re-adsorption) between chloride-bearing material stabilized at 950°C and 750°C. Thus, moisture content in stabilized items below the threshold defined in DOE-STD-3013-2000 is unlikely to result in undetected failure of containers.
- *Stabilization of Other Gas-Producing Constituents*: Other than trace amounts of re-adsorbed moisture (as hydroxide) and atmospheric CO_2, potential gas-producing constituents are highly unlikely to be present in IDC 067 and IDC 086. The threat to container integrity is negligible for either gross gas generation or stress corrosion cracking induced by these oxyanions in Rocky Flats ER oxide materials.

Two additional questions arose during the development of the Rocky Flats technical basis and resulted in a recommendation for further evaluation. One aspect not recognized in the earlier technical basis document (Boak et al. 2002) is the destruction of fluorine-containing plastics such as Teflon™ and Kynar™. Destruction of these plastics is discussed in Appendix B, which concludes that they will be destroyed during stabilization at 750°C.

The second issue raised concerned the stability of carbonate compounds during stabilization and in subsequent storage environments. Examination of this issue must include review of the potential for radiolysis to pressurize containers by generating CO_2, or to corrode containers through formation of acidic species.

1.6 Potential for gas generation or corrosion of residual carbonate compounds

The Rocky Flats technical basis document (Boak et al. 2002) recommendations included the following:

> "The technical team recommends a survey of the literature on radiolysis of carbonate compounds be completed to ensure that trace carbonates will not adversely impact storage containers."

A recent survey of the literature and of the data from the MIS program (Berg et al. 2003) concludes that currently available information does not indicate a risk of problematic pressurization of a 3013 storage container by CO_2.

According to Berg et al. (2003) the available evidence suggests that TGA observations of CO_2 evolved from stabilized material are best explained by the incomplete destruction of some carbonate compounds in the stabilization process. That is, CO_2 released at 600°C and higher results from the continuing breakdown of carbonates that were not completely broken down during stabilization.

These carbonate compounds are likely to be thermally and radiolytically stable under storage conditions that will not rise above 300°C; they are unlikely to release significant CO_2 into the 3013 container. CO_2 observed within containers of Pu-bearing oxide materials is not likely to have been caused by decomposition of carbonate compounds.

Berg et al. further conclude that the principal uncertainties in these conclusions stem from the heterogeneous nature and the diversity of materials to be packaged. Their conclusions are based on the large amount of scientific literature on the behavior of pure compounds and on more limited observations on impure Pu material. Shelf-life studies and surveillance activities are important to assure that any unanticipated effects are identified and addressed.

2 Characteristics of the Material

2.1 Background

The "Implementation Plan for the Recovery of Plutonium (IPRP) from Nonspecification Plutonium Inventories" (Hahn 1983) was developed in 1983 to facilitate the processing of Pu residues within the DOE nuclear weapons complex (NWC). The goal of the IPRP was to maximize metal receipt at the RFP foundry while minimizing residue process time by distributing RFP residues to other NWC sites for processing. RFP was unable to process all of its residues, and its Pu recovery was focused on high-Pu-content residues that could be readily processed, for example, foundry oxide that met specifications.

Hanford was one of the NWC sites that supported the IPRP. The negotiations between Hanford and RFP resulted in Hanford agreeing to accept RFP incinerator ash and Pu oxide. The authorization for the processing of RFP incinerator ash at Hanford was given in December 1983, and 22 cans of incinerator ash were received at Hanford in September 1984.

In April 1984, similar negotiations were held between Hanford and RFP regarding nonspecification Pu oxide with Pu concentrations ≤70%. The agreed maximum Pu content of the impure oxide sent to Hanford was increased to ≤80% Pu during the campaign (Ball 1985). The authorization for Hanford to receive RFP Pu oxide in Fiscal Years 1984 and 1985 was given in August 1984. The first shipment of RFP Pu oxide was received at Hanford in September 1984. That shipment consisted of 50 cans. Material was calcined at >450°C, measured for LOI, and recalcined if it failed. Shipments of RFP Pu oxide to Hanford continued until August 1986.

2.2 Compositional characteristics

The Pu content of Rocky Flats items currently stored at Hanford is summarized in Figure 2. The total mass is approximately 1,130 kg. It is evident that a significant fraction (~58%) of the material contains >70 wt % Pu, indicating the change from the initial cutoff value during the campaign of shipments to Hanford mentioned above.

Less than 1% of the total (10 kg) of the material contains <30 wt % Pu and does not meet the requirements of DOE-STD-3013-2000. This material has been prepared for shipment to the Waste Isolation Pilot Plant (WIPP). An additional 60 kg (5%) consists of material between 30 and 50 wt % Pu. Only 3% of the total mass (34 kg) consists of >80 wt % Pu material. It may be that these higher assay values resulted from material that was initially lower than 80%, but, through mass loss on stabilization, increased in Pu concentration. Thus, the bulk of the material shipped to Hanford

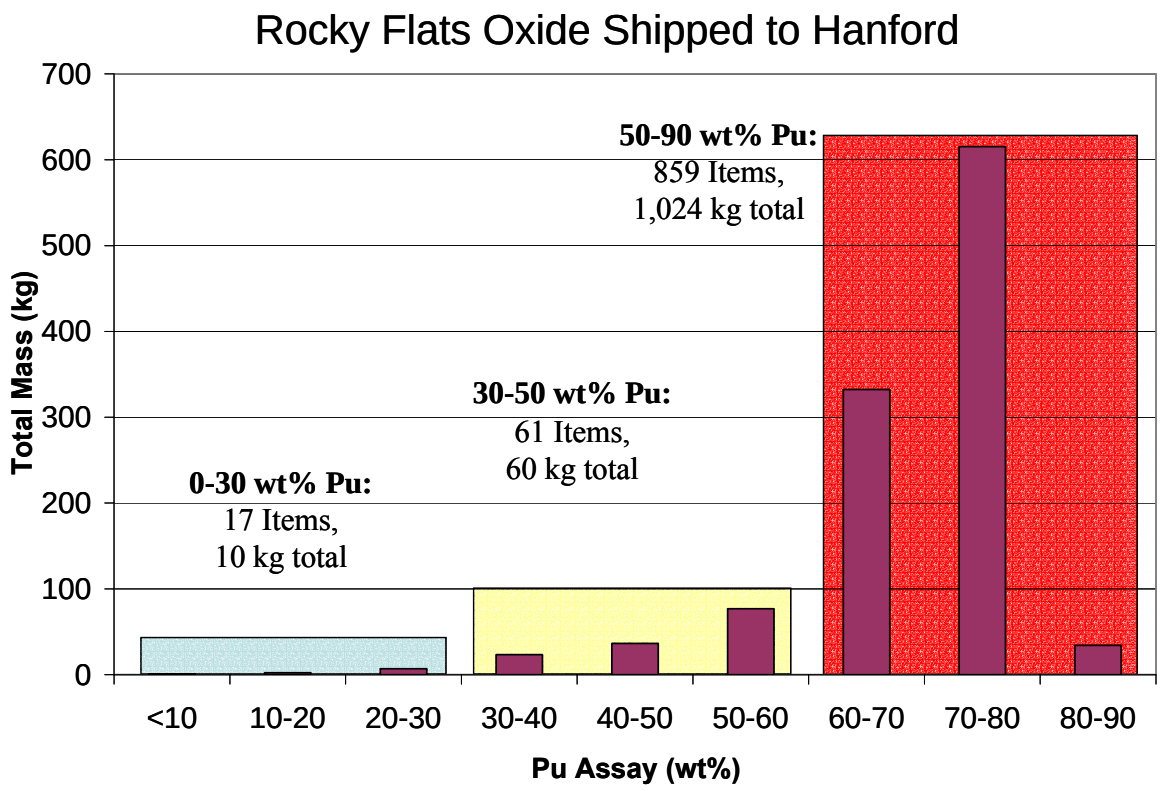

Figure 2: Total mass versus Pu assay for remaining Rocky Flats oxide transferred to Hanford (data from Fluor Hanford).

(1,024 kg, 90%) consisted of impure oxide with Pu content in the range 50–80 wt %. This distribution of Pu assay values is similar to those of the Rocky Flats material described in Boak et al. (2002), although generally lower in Pu content.

2.3 Review of material control and accountability records

Material control and accountability requirements call for accountable quantities of Pu to be tracked by item numbers throughout the life of the material until safeguards are terminated on the material. The usual process has been to give an item number and, at RFP, an IDC indicating the process responsible for creating that item. When an item was processed, the original item (the feed material to the process) was "killed" and a new item (the product material) was "created" so that the special nuclear material was tracked.

Davies (2003) conducted an analysis of the inventory records for all items "killed" at RFP during the same time periods as the items shipped to Hanford were "created." The kill/create comparison was initially across all buildings and material balance areas (MBAs) at RFP during the shipping periods and identified 1,183 items.

The records show that there were 15 discrete campaign periods between August 1984 and August 1986 during which oxides were stabilized and packaged for shipment to Hanford. The "created" oxide items destined for Hanford were designated with an "ORHOxxx" item number. Unfortunately, because the data on "killed" items encompassed all items from all buildings and MBAs at RFP, a one-to-one correlation between "killed" items and the ORHO items "created" is not possible.

Davies's initial review was later refined with the technical assistance team to identify the MBA that an item was "killed" from, to determine whether any items could be eliminated based on the MBA location. By looking at the relevant MBAs, we narrowed down the list of items potentially shipped from RFP to Hanford. The second review identified items "killed" in Building 371 MBAs that had a clear functional relation to the MBAs where packaging for shipment occurred. This second review also included those items that did not have any MBA specified. This inclusion does not imply that all of these "killed" items without specific MBA data were ultimately shipped to Hanford, but only that the data are not available to clearly eliminate them from consideration. That second review produced a list of 1,138 items.

During the fifteen campaigns to ship material to Hanford, 1,509 items were "created." The larger number of "created" items appears to reflect the fact that Hanford had lower limits than Rocky Flats on the amount of Pu that could be stored in a single container. Of the 1,509 items received at Hanford, 939 remain. The other 570 items were processed for recovery at Hanford. The relationship between "killed" and "created" items is shown in Figure 3, which indicates that nearly all of the items "killed" at Rocky Flats during the time of the 15 shipping campaigns were indeed repackaged and shipped to Hanford.

All items received at Hanford were assigned item numbers beginning in the letters "ARF," which is the DOE reporting identification symbol code for Rocky Flats in the nuclear materials inventory system. In addition, all oxide items received the PFP material category code 102 for Weapons Grade Oxide for Recovery. A two-number code element was added for the year in which the item was received. Thus, all items being discussed in this report have item codes of the form ARF-102-8x-xxx.

Two IDCs dominate the list of 1,138 items that were apparently shipped to Hanford. There were 495 IDC 067 items (Chlorinated Oxide), and 401 IDC 061 items (Non-spec. Oxide), accounting for 79% of the items. Of the remainder, there were 176 items accounting for 15% of the total from eight IDCs, primarily from the same processes that generated these two dominant IDCs. The remaining 66 items came from 21 other IDC categories and include eight items that do not have an identified IDC. A table identifying the IDCs and the number of items in each IDC on the Rocky Flats "kill" list is included in Appendix D.

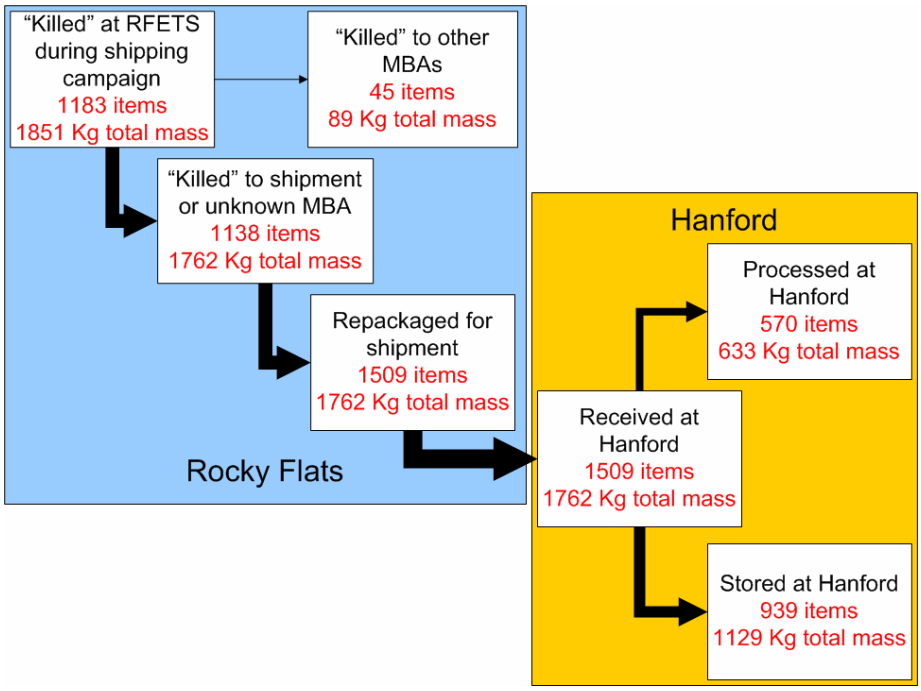

Figure 3: Items shipped from Rocky Flats to Hanford.

The items designated as "killed" can be separated into three groups of material. One group consists of Pu metal and oxide items, many with high levels of chloride, which were either feeds to, or byproducts of, the Building 371 tilt-pour ER process. The second group consists of byproducts of the Building 371 foundry. The third group consists of only 40 items that cannot be readily categorized into either the first or second group. A detailed discussion of the properties, IDCs, and number of items in each category is included in Appendix D, with special focus on the two categories that are not directly related to the ER oxide. The characteristics of these three groups are discussed in the next sections.

2.4 Categories of material

2.4.1 Electrorefining feed and byproduct oxides

Of the items that were "killed" during the period when items were shipped to Hanford, approximately 55% (628 items) consisted either of IDC 067 (Chlorinated Oxide), or of other IDCs directly associated with the tilt-pour furnace ER process (see Figure 4). All of these items could be expected to contain Cl salt at levels from trace amounts to 70 wt %. As noted above, material with <30 wt % Pu does not meet the requirements of DOE-STD-3013-2000.

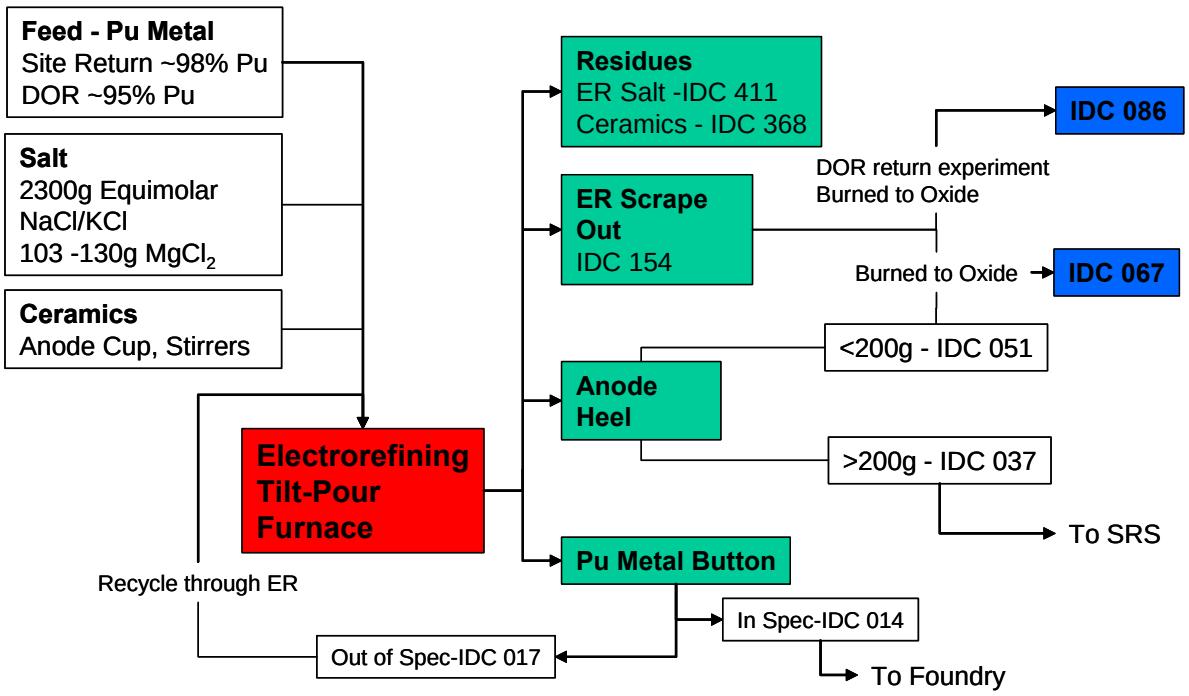

Figure 4: Electrorefining process flow diagram, showing IDCs associated with the process.

Similarities among the items consisting of Pu oxide with Cl salts include the following:

a) The materials were feeds to or were generated from the tilt-pour ER process in Building 371. Items of other IDCs in this group were generated from similar pyroprocessing products.

b) All materials are expected to have some amount of Cl salt from the salt matrix used in the ER process (equimolar NaCl/KCl with 5% $MgCl_2$).

c) The materials for shipment to Hanford were calcined at least once, and generally twice at ~450°C; thus, metal materials would have been converted to oxide.

ER oxide items that were shipped to Hanford are similar to, if not exactly like, the materials considered in Boak et al. (2002). Those materials are IDC 067 and 086 items that are currently either stabilized or in storage at Rocky Flats awaiting stabilization to meet DOE-STD-3013-2000 requirements. The technical team concludes that the stabilization equivalency established for the Rocky Flats materials to meet DOE-STD-3013-2000 requirements would apply to the Hanford materials for this group of IDCs. Appendix C lists compositional data on items from Rocky Flats that are part of the MIS program at Los Alamos National Laboratory (LANL).

2.4.2 Foundry byproduct oxides

Of the items "killed" at Rocky Flats for shipment to Hanford, approximately 41% (470 items) came from IDC 061 (Non-Spec Oxide—foundry oxide not meeting specifications) or from similar IDCs. The foundry oxide items consist of impure Pu oxides generated from nonaqueous processes (see Figure 5). Specifically, these oxides were generated from the calcination of foundry residues. As a result, no nitrates or sulfates are present in foundry oxide.

The water content of the foundry oxide should be substantially lower than the water content of oxides produced from aqueous processes, such as green cake (IDC 082—oxide derived from peroxide precipitation) because the foundry oxide was not produced via an aqueous process. A report by Steinmeyer, Hobbs, and Oetting (Rocky Flats Plant, July 1986) provided a detailed description of the generation of foundry oxide. That information is summarized in Appendix D.

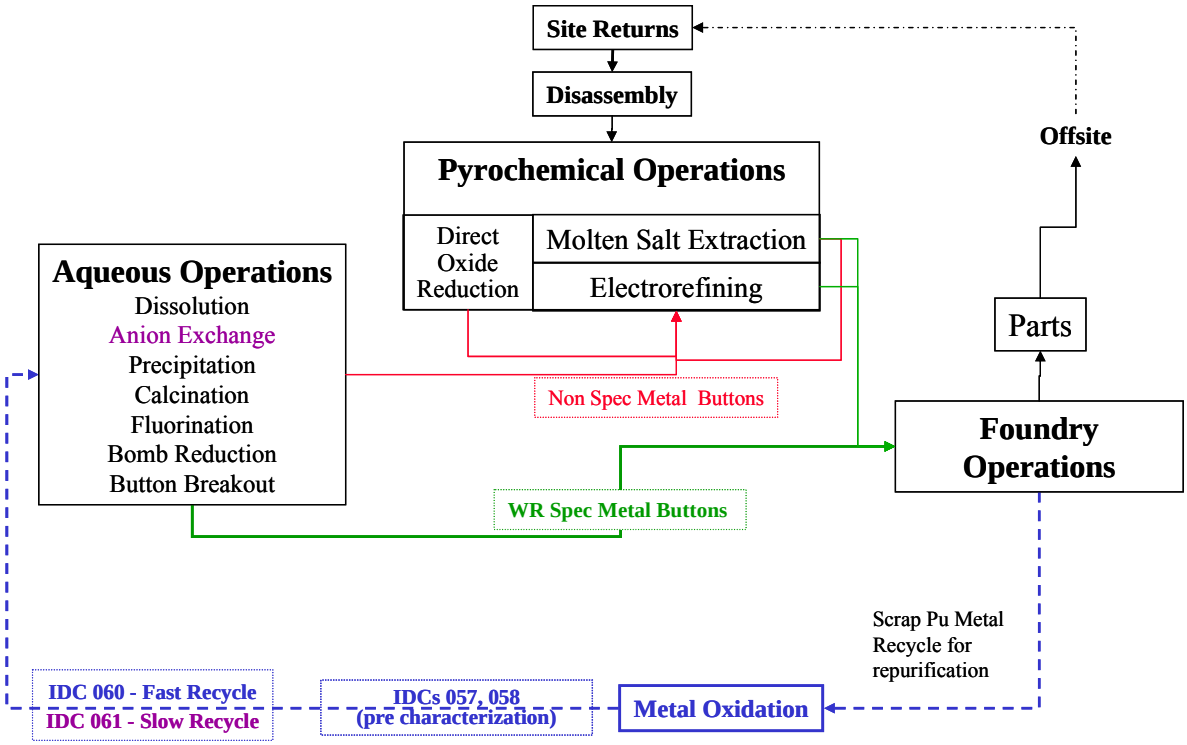

Figure 5: Foundry process flow diagram, showing IDCs associated with the process.

The majority of the impurities in the foundry oxide consist of other metal oxides. However, because some of the foundry oxides were prepared from metal produced by pyroprocessing, there is some likelihood that Cl salt from those processes would be included in this material. Additionally, the foundry oxide material could include some items that contain significant graphite from molds and calcium fluoride (CaF_2) used to coat molds. Delegard and Bouse (1985a) observed very small quantities of Pu metal as spherules in an ARF item in PFP lab tests. Plutonium oxide (PuO_2) was the only Pu phase identified by x-ray diffractometry in this and related characterization of ARF items (Delegard and Bouse 1985b, and Mason et al. 1999).

Bubbles observed to form in water-wash lab testing of ARF items conducted during process-development testing at PFP also give evidence of the presence of an active metal (Jones 2002). The bubbling is most readily explained as the reaction of plutonium with chloride-bearing water to form hydrogen gas (H_2). The reaction of plutonium with Cl salt solutions to form H_2 is based on observations of H_2 produced by the reaction of Pu (in an IDC 411 ER salt that had not been stabilized) with room-temperature water to form Pu hydroxide (Haschke and Phillips 2000, and Appendix B of Boak et al. 2002). The presence of very small quantities of metal is not considered to be a significant problem with respect to pyrophoricity, as discussed in Boak et al. (2002).

Appendix C tabulates the chemistry of nine items derived from foundry oxides from Rocky Flats (IDC 061 and IDC 060, the latter consisting of oxide that met the specification for fast recycle). These constitute the data for items as received in the MIS program at LANL. The table includes all elements that occur at >1 wt %, and the remainder of the analytical data is summarized in the line for Trace Metal. Oxygen values are calculated assuming that all actinides (U, Pu, Am), as well as Al, Si, Ga, Fe, Ni, and Cr, are present as standard oxides. Appendix D describes the compositional characteristics of foundry oxide constituents in greater detail.

For the foundry oxides, the mass balance is remarkably good. Samples with >60 wt % Pu show totals above 92 wt %, and those over 69 wt % show totals >96 wt %. Thus, it is reasonable to conclude that foundry oxide items consist primarily of Pu oxide from nonaqueous processes. These items consist mainly of actinide oxides (U, Pu, Am), mixed with oxides of various metals (Al, Si, Ga, Fe, Ni, Cr) and salt constituents (Na, K, Mg, Ca, F, Cl). Both groups of nonactinide constituents are traceable to processing of the material. Appendix C also shows that carbon and sulfur are present only in trace amounts.

This chemical trend is shown in Figure 6, which plots the sum of oxide constituents against the sum of salt constituents. A similar argument was presented with respect to the ER oxide in Boak et al. (2002), and data for ER oxide from both the MIS data and the earlier data of Guadagnoli and Esquibel (1986) for Rocky Flats ER oxide are shown on the plot. The two ARF items from the MIS database that show the lowest oxide contents are unusually heterogeneous. One contained significant graphite, and the other consisted of powder and "chunks" that were chemically distinct.

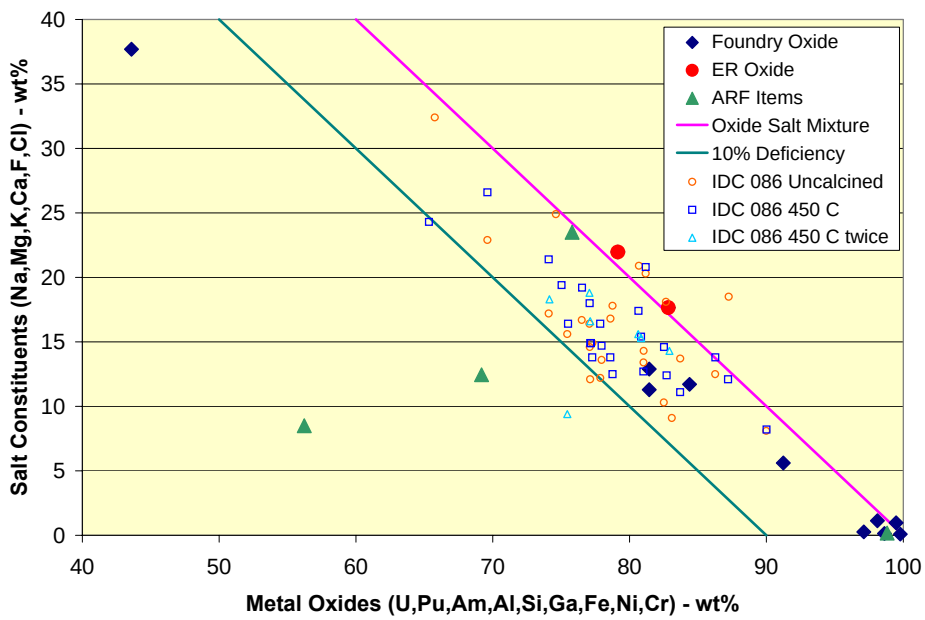

Figure 6: Metal oxide vs. salt constituents of MIS items from IDC 061 (foundry oxide), IDC 067/086 (ER oxide), and the ARF items. Mass balance is good for most items, especially above 50 wt % Pu (~60 wt oxides). Data from Guadagnoli and Esquibel (1986) for IDC 086 are also shown.

2.4.3 Miscellaneous oxides

From the revised list of "killed" items, there are 40 items that are grouped as miscellaneous. Those 40 items represent about 3% of the 1090 items that were "killed." They are derived from a wide range of IDCs, for many of which only a single item was "killed" at Rocky Flats.

These 40 items fall into three groups. The first group consists of 15 items from IDCs that indicate they are very unlikely to contain Cl salts, including bomb-reduction byproduct, direct oxide reduction (DOR) feeds, incinerator byproduct, and Pu/U site returns.

The second category consists of ten items derived from the pyroprocessing and foundry processes described in the previous two subsections and designated specifically for off-site shipment. These are likely to have Cl salt present, but, as described above, are unlikely to have other impurities of concern, and therefore may be screened for Cl salt content to determine an appropriate stabilization pathway.

The third category consists of fifteen items for which the history is less certain. Eight of these have no IDC listed. However, review of the item numbers indicates that most of these are items that failed the LOI measurement and were restabilized. They are therefore likely to be drawn from among the other IDCs discussed above. The other items are likely to consist either of oxide with no Cl salt or potentially chloride-bearing oxide with no other impurities except metal oxides.

These items would have all been screened and calcined at >450°C at least once before shipment. The technical team considers it unlikely that any of these items that contain Cl salts in quantities above 1 wt % also contained a constituent that would:

1. survive 750°C stabilization as well as previous high-temperature stabilizations, but
2. would not survive 950°C stabilization, and
3. would subsequently generate significant volatile and/or corrosive species at <300°C.

All three categories of miscellaneous oxides are discussed at greater length in Appendix D, where each IDC is listed and the items described.

2.4.4 Summary

In summary, the 1,138 items “killed” at Rocky Flats that might have been sent to Hanford fall into three categories. The first, comprising 55% of the “killed” items, consists of oxide from ER directly comparable to the ER oxides described in Boak et al. (2002). The second, consisting of foundry byproduct oxides and comprising 41% of the items, has properties similar to the material in the first category, in that salt and metal oxides constitute the sole significant impurities.

The third category, only 3% of the items possibly sent to Hanford, comprises a variety of subcategories. Twenty-five of forty can be established, on the basis of available process history, to be either unlikely to contain sufficient Cl salt to be selected for low-temperature stabilization, or unlikely to cause problems after low-temperature stabilization.

The technical team considers the likelihood low that the remaining <1% of the material poses sufficient threat to the program to challenge the equivalency of the screening and stabilization process proposed in the next section.

3 Thermal Stabilization Options

3.1 Choice of the RMC processing line for stabilization of ARF material

According to present PFP operations personnel, thermal stabilization of Pu oxide to satisfy the criteria for long-term storage (DOE 2000) can occur in two locations—in two glove boxes located in the RMC line of the 234-5Z facility and in the SPE (special process equipment) glove box located in the 2736-ZB facility.

Thermal stabilization in the RMC line takes place in five muffle furnaces located in glove boxes HC-21C and HA-21I. The glove box air is obtained from the Dry Air System (which no longer supplies dry air) through the adjacent conveyor glove boxes. The glove box air has RH ranging from about 20% in the winter to 60% in the summer, when evaporative cooling is used in the plant. Pu material destined for 3013 packaging is not thermally stabilized in the RMC when ambient humidity is higher than 60% RH. This engineering control has been imposed to minimize undue moisture re-adsorption after stabilization.

Thermal stabilization and packaging of Pu oxide to meet DOE-STD-3013-2000 can also occur in the 2736-ZB facility's SPE glove box. The SPE furnaces are swept with dry nitrogen at temperatures <200°C and with dry air after the temperature is >200°C to satisfy the requirement for oxidizing atmosphere stated in the standard. Other spaces in the SPE glove box are swept with dry nitrogen controlled to ≤250 ppm moisture. The low humidity of the dry nitrogen limits moisture re-adsorption of the thermally stabilized material prior to packaging.

The furnaces in 2736-ZB are built around retorts bolted to, and projecting laterally from, the glove box wall. The furnace heaters are exterior to the glove box and transfer heat through the retort wall to the furnace interior. The retort thus constitutes an integral part of the glove box confinement system. To achieve adequate heat transfer and reach target calcination bed temperatures of >950°C, the retort wall must be heated to about 1100°C maximum. The retort is made of the high-nickel alloy RA602CA (see Table 3).

In this design, failure of the attachment bolts, or retort breach due to corrosion or any other cause would threaten release of contamination to the manned process areas. Subsequent recovery actions would cause a long delay in operations. The following statement was made in the document describing the selection of the material of construction for the retort (Jeppson and Larkin 2001):

Table 3: 2736-ZB Retort Metal RA602CA* Composition

Element	Concentration (wt %)
Fe	9.5
Cr	25
Al	2.1
C	0.2
Ti	0.15
Y	0.08
Mn	<0.15
Si	<0.5
Cu	<0.1
Ni	Balance
UNS Specification N06025	

* RA602CA™ is a trademark of Rolled Alloys, Inc., Temperance, Michigan; http://www.rolledalloys.com

> "For processing plutonium oxide with chlorides present with a retort temperature of 1200°C, it is recommended that a platinum, rhodium, and a diffusion inhibitor coating be applied to Haynes alloy 230 or RA602CA alloy to inhibit corrosion."

The aggressiveness of hot chloride vapors on most metals, the lack of specific performance data for the RA602CA alloy in hot chloride environments, and the serious consequences of glove box containment failure by corrosion call into question the safety and practicality of processing chloride-bearing Pu oxide in the SPE glove box, notwithstanding use of a resistant liner material.

Experimental data from the Hanford site that bear on the risks of stabilizing chloride-bearing materials are discussed in Appendix E. Because of the above concerns, combined with evidence of risk from these experiments, thermal processing of chloride-bearing oxide in the SPE, even at lower thermal stabilization temperatures, is not currently acceptable in the SPE design basis. Thermal processing of the ARF items must occur in the RMC line furnaces.

3.1.1 Baseline and low-temperature alternative process plans for the ARF items

Plans have been developed and equipment modifications are underway to process the 939 ARF items to deal with their contained volatile and corrosive Cl salts. The baseline approach is to use prompt gamma-ray analysis (PGA) screening to identify items containing Cl salts and water washing to remove Cl salts, prior to 950°C thermal stabilization. An alternative approach is to stabilize chloride-bearing items from Rocky Flats that contain >50 wt % Pu at 750°C to eliminate the washing step.

This section describes processing scenarios under the baseline and low-temperature alternative processing plans. The section also describes moisture measurement methods applying to products from the stabilization process.

3.1.2 Baseline processing plan

The baseline plan to process the ARF items is shown in Figure 7. According to this plan, items containing <30 wt % Pu have been packaged for disposal at the WIPP. PGA screening would be used to sort the remaining >30 wt % Pu items to identify those containing chlorine. Items found to contain no or low levels of Cl (threshold levels to be determined) would be sent directly to the RMC line furnaces for thermal stabilization (two hours of heating at 950°C). Items containing greater than threshold levels of chlorine would be water-washed to <1 wt % residual Cl salt (see Appendix F for a description of the wash system). The washed solids would be dried on hot plates and then stabilized in the RMC furnaces (two hours of heating at 950°C).

The residual moisture content for all stabilized material would be measured by TGA-Inert methods (measuring the weight loss occurring when a sample is heated to 1000°C). According to current practice, the material is recycled through thermal stabilization if the sample yields >0.4 wt % loss and is packaged if it passes (that is, yields a ≤0.4 wt % loss). Alternatively, should the sample exceed the 0.4 wt % loss threshold by TGA-Inert, it may be remeasured using TGA/MS techniques, which are specific for water, with the same outcomes for passage or failure but based specifically on water mass loss, not total mass loss.

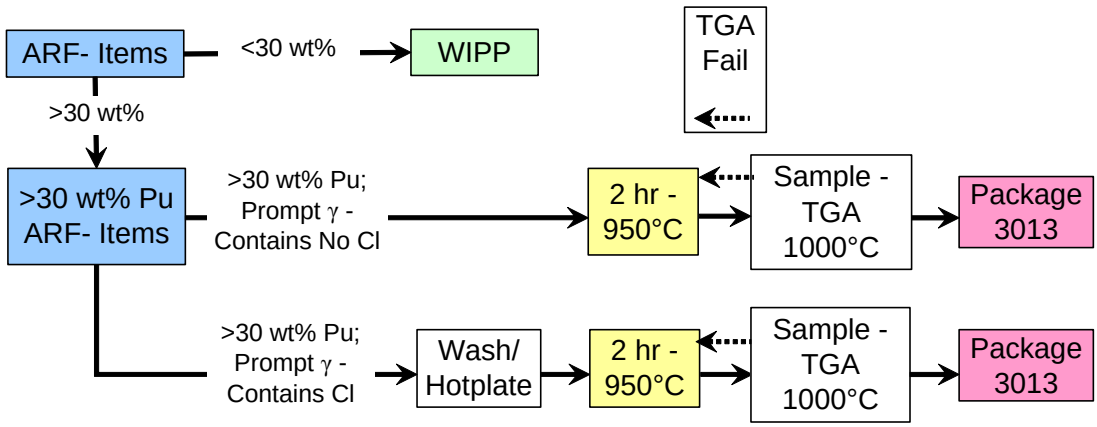

Figure 7. Baseline plan for processing ARF materials.

3.1.3 Low-temperature processing plan

The alternative plan for ARF processing, including lower-temperature thermal stabilization for items containing NaCl/KCl and >50 wt % Pu, is illustrated in Figure 8. Processing of those items containing <50 wt % Pu would proceed according to a scheme unchanged from the baseline plan described in Figure 7. Thus, the ARF items containing <30 wt % Pu have been packaged for WIPP disposal.

Items containing from 30 to 50 wt % Pu would be screened by PGA to detect Cl salt. The screening would use the same PGA technique as described in the baseline approach for all items containing >30 wt % Pu. As in the baseline approach, items containing no or low levels of Cl salt would go directly to the RMC line furnaces for 2 hours of 950°C thermal stabilization.

Items with 30–50 wt % Pu containing greater than threshold levels of chlorine would be water-washed to <1 wt % residual Cl salt, with the washed solids dried on hot plates and then stabilized in the RMC furnaces (2 hours at 950°C). Moisture analyses by TGA-Inert and TGA/MS would occur as described for the baseline approach.

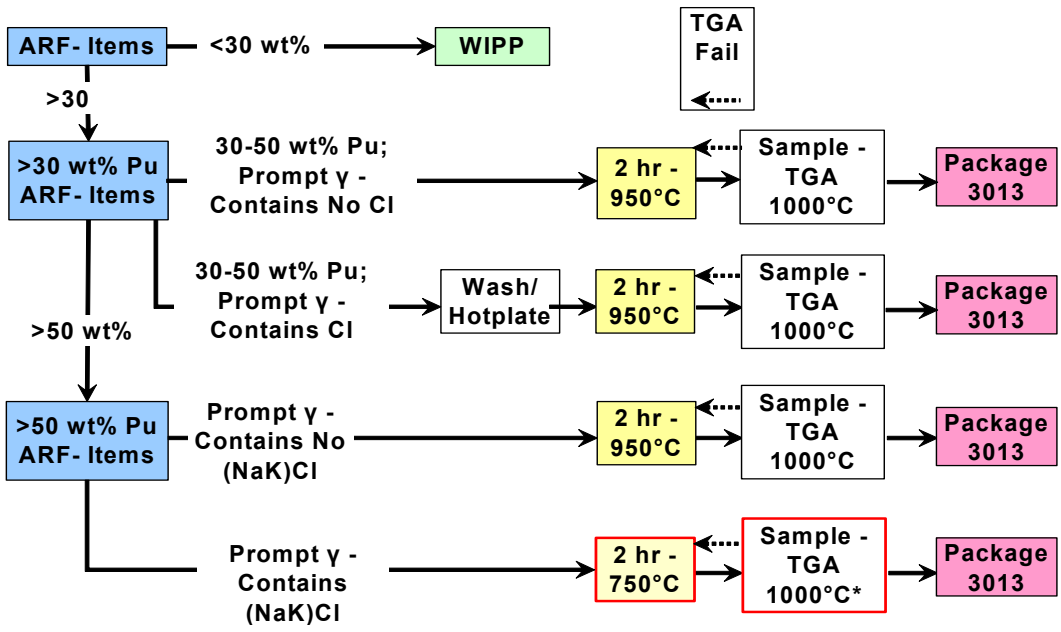

Figure 8: Alternative low-temperature plan for processing ARF material. * indicates that moisture measurement determination may be modified by calculating 750°C mass loss with bias correction if a sample fails at 1000°C, as described in text.

Under the alternative low-temperature stabilization, items containing >50 wt % Pu would undergo additional PGA screening to detect those alkali-salt elements present in volatile Cl salts, that is, sodium, chlorine, and potassium. The logic diagram used to identify the volatile-salt-bearing items is shown in Figure 9. If the item is judged not to contain such salt, it would undergo the prescribed 2-hour, 950°C thermal stabilization. Verification of moisture content would be performed using TGA-Inert techniques, supported, as necessary, by TGA/MS with the same 0.4 wt % threshold.

For >50 wt % Pu items found to contain NaCl/KCl salt, however, the alternative low-temperature stabilization would call for 2 hours at 750°C to be used for thermal stabilization instead of 2 hours at 950°C. Verification of moisture content would be performed using TGA-Inert techniques with heating up to 1000°C (see Section 4 and Appendix G).

Concern about damage to the TGA/MS in analyzing any samples containing Cl salts practically precludes its routine use to measure water evolved from ARF items containing the volatile Cl salts (that is, NaCl, KCl) present in many ARF items, which may produce corrosive hydrogen chloride (HCl). The rationale for using TGA-Inert and TGA/MS for moisture measurement is described in Section 4 and Appendix G.

3.2 Categorization of material by PGA

As discussed previously in Section 2, the oxides shipped from Rocky Flats to Hanford can be grouped generally into three major categories, although a clear one-to-one correlation between the “killed” and the shipped items cannot be attained. However, items likely to contain Cl salt can be identified nondestructively before stabilization.

As described above, the PFP proposes to use PGA to screen the Rocky Flats items for Cl salt constituents. PGA has been developed by the 94-1 ISP as a means of identifying stabilized material requiring enhanced surveillance due to constituents that may pressurize or corrode storage containers. It is considered to be a valuable qualitative and semiquantitative screening tool that can identify a suite of elements of potential concern.

Three elements are important to identify in determining which materials may contain significant quantities of the salts of concern—sodium (Na), potassium (K), and chlorine (Cl). The estimated detection limits for counts of 60 minutes, using an instrument designed at LANL and deployed also at Rocky Flats, are shown in Table 4 (Narlesky, personal communication). The instrument and procedure to be used at PFP is described in Appendix H.

Mg can also be detected by PGA, but does not provide sufficient discrimination of chloride-bearing versus non-chloride-bearing oxides. Mg is very common in many different oxides because MgO ceramics were

Table 4: Detection Limits for PGA for Elements of Concern

Element	Primary Gamma-Ray Peak (keV)	Approximate Detection Limit (wt %)
Na	1808	0.04
Cl	2168	0.75
K	1524	1.40

used in a variety of the processes at Rocky Flats. MgO sand was used to extinguish Pu metal pyrophoric reactions and was usually present in glove boxes that processed Pu metal. The Mg detection limit is very low, so that it is likely to be detected in many oxides, even those with very little Cl salt. In addition, possible interferences with the main peak make it preferable to evaluate prompt gamma rays of two different energies. Evaluation of two peaks commonly requires expert review, so that rapid screening is more difficult.

The decision tree in Figure 9 shows the logic that would be used to screen items for the lower-temperature stabilization process. In this diagram, the arrows connecting decision boxes are proportional in size to the estimated

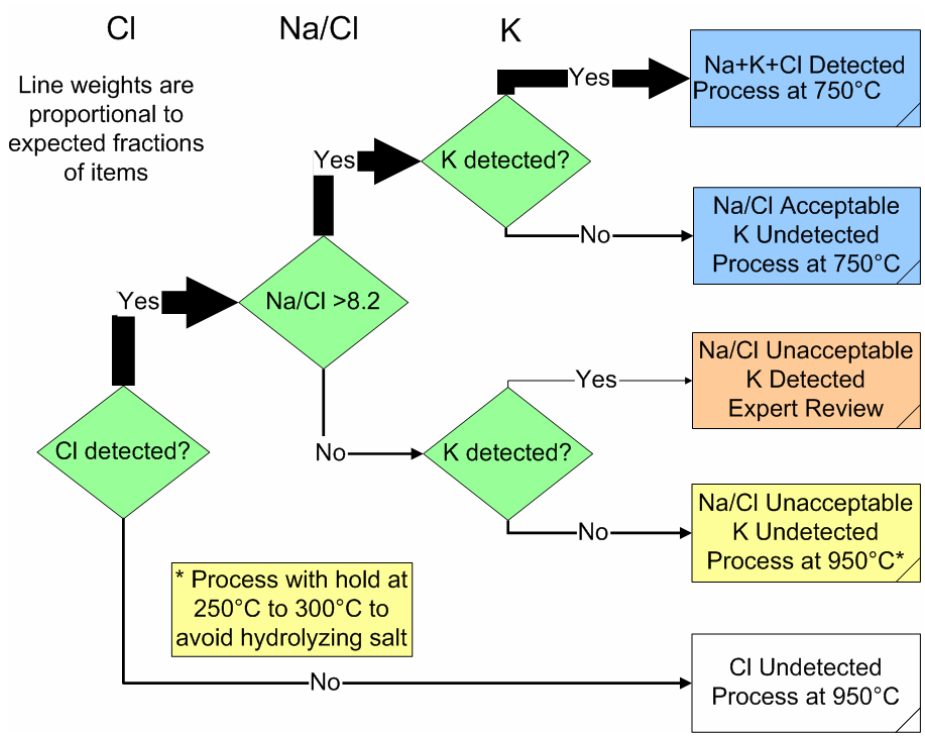

Figure 9: Logic of screening process for PGA of Rocky Flats oxide shipped to Hanford.

fraction of items expected to follow the given path. The vast majority of samples (from the two predominant IDCs) are expected to follow paths consistent with the clear-cut presence or absence of the primary salt constituents—Na, K, and Cl. This expectation is based upon the relatively small amount of material with very high Pu content (as indicated in Figure 2), and the relatively low detection levels estimated for the PGA method.

Chlorine as Cl salt is expected to be detected in nearly all ER feed and byproduct items, as well as many foundry byproduct items. Thus, the majority of items will follow the upper branch. If Cl salt is not detected, the item should be stabilized at 950°C, in accordance with the standard. The highest assay items might be expected to follow this path, as well as lower assay items not associated with pyrochemical processes.

The possibility exists that the lack of detection of Cl salt may be due to inadequate mixing of Cl salt present with the Pu responsible for generating the prompt gamma-ray signal. This could be tested by checking for the presence or absence of a Na peak. However, the primary remedy for this problem would be to heat the sample to melting and measure again. The technical team recommends that any such item be processed at 950°C, as any likely (Na,K)Cl salt-bearing item should have been melted at least once during its process history.

The detection limit for K is the highest of the three critical elements, probably >1% for the PFP systems. Because of the potential for interference with the F peak, K may not be detected unless the total (Na,K)Cl salt level exceeds 3–4 wt %. The second screening criterion will therefore examine the ratio of the peak area counts for Na to those for Cl, as described in Appendix H. This criterion examines the ratio to determine whether it is within the range of values seen in the ER oxides processed to date at Rocky Flats.

Although the peak areas are generally larger in the PFP system due to its higher efficiency and the longer counts proposed for the ARF items, the technical team considers the PFP system a valid screening tool. If the Na/Cl peak-area ratio is greater than the cutoff defined by Rocky Flats ER oxide PGA spectra (8.2), the material will be processed at 750°C, whether K is detected or not. This will allow sending all likely (Na,K)Cl salt-bearing material, down to the ~1 wt % total salt limit that would be equivalent to washing, to be stabilized at the lower temperature.

The detection of K serves as an additional check on the presence of ER salt, where sufficient salt is present to exceed the K detection limit. In items with Na/Cl ratios above the limit, the presence of K confirms the character of the salt present. If K is detected in an item with Na/Cl below the limit discussed above, the item should be held for expert review. This result is considered highly unlikely, as the detection limit for K is so much higher than that for Na. Only at the highest Pu assay levels would Na be

expected to go undetected, and these items can reasonably be processed at 950°C.

A sample with an assay value below 80 wt % that shows none of the three elements should be considered as a candidate for review of the full spectrum of the PGA, to see if any signal is present at all. The absence of a signal in such low assay material indicates a lack of adequate contact between the Pu and impurity elements. Any such material will have to be handled case by case. Unless some evidence exists for preferential removal of Na from the salt, such an item would probably have to be processed at 950°C. Appendix H discusses a potential case where expert review might lead to stabilization at 750°C.

Should K be absent in a chloride-bearing item, and the Na/Cl ratio be below the threshold, the material would be interpreted to contain some other Cl salt. Certain processes (primarily DOR) used $CaCl_2$ salt, which would be expected to give a strong Cl salt signal. Na might be present in such items at levels detectable by PGA, but the Na/Cl ratio would likely be low. DOR processing was primarily an experimental approach at Rocky Flats, and the percentage of items showing such a pattern is expected to be <10%.

Material with $CaCl_2$ alone does not pose the same threat of volatilization, as the vapor pressure is significantly lower than that for the alkali Cl salts at any temperature. However, there is potential for hydrolyzing the $CaCl_2$, producing HCl, a corrosive gas. The recommended stabilization path for such material would consist of drying the material at 250°C to 300°C for several hours, followed by immediate processing at 950°C. There may be sufficient concern about pyrohydrolysis to dry all chloride-bearing material in this manner.

Because the preprocessing PGA measurement is intended solely to screen material to identify those items containing sufficient quantities of (Na,K)Cl salt to pose potential corrosion and plugging threats, it is not necessary to specify a minimum count time. Counting may be cut off as soon as the error in the background corrected peak height for K (the element with the highest detection limit) is reduced to an adequate level to provide assurance of detection of the element. A maximum count time of 180 minutes should provide assurance that salt is detected at a low enough level to be adequately protective.

PGA cannot by itself provide an unambiguous identification of the original IDC of an ARF item. However, the main purpose for using the PGA is to identify those items that contain volatile Cl salts that can potentially threaten the stabilization furnace systems. It is therefore important to ensure that, for virtually all materials that potentially were shipped to Hanford from Rocky Flats, items that contain NaCl and KCl can reasonably be stabilized at 750°C and still meet the objectives of stabilization laid out in DOE-STD-3013-2000. The following sections

discuss the three groups of material defined in Chapter 2, and the reasons it is appropriate to stabilize chloride-bearing items in each group at the lower temperature.

3.2.1 Electrorefining oxide

Based upon the analysis of Rocky Flats "killed" items in Chapter 2, approximately 55% of the items that could have been shipped to Hanford from Rocky Flats consisted of material directly associated with the ER tilt-pour furnace process. Most of these items are likely to have belonged to IDC 067, the primary IDC addressed in Boak et al. (2002).

The other IDCs of this type include predecessor IDCs to the chloride-bearing oxide that constitutes IDC 067, such as anode heels, buttons from cell cleanout, the unburned ER scrape out material, and ER oxide. All of these items would have been calcined on a hot plate at ≥450°C (at least once) to minimize moisture, as confirmed by LOI measurement, before shipment to Hanford.

Items in the Hanford inventory from these IDCs with very high Pu content would still not show sufficient Cl salt, and would be stabilized at 950°C. Only 3% of the Hanford inventory has assay values above 80 wt % Pu, so this category is likely to be small. Items with assays in the range ~50% to 85% should show Cl salt by PGA and should be stabilized at 750°C.

The technical team recommends that items with assay values between 30 and 50 wt % Pu should be washed and stabilized at 950°C. The available data suggest that such items consist primarily of oxide and salt, but are not conclusive (Figure 6 and Appendix C). Rocky Flats chose to stabilize the very small quantity of material in this range at 950°C. Only 5% (60 kg) of the total mass of ARF items falls into the range between 30 and 50 wt % Pu. Alternatively, these items might be further characterized to ensure that only Cl salt and metal (including actinide) oxides are present.

Items with <30 wt % Pu have already been packaged for shipment as transuranic (TRU) waste to the WIPP, as they do not meet the criterion for stabilization under DOE-STD-3013-2000.

Experience with PGA on IDC 067 and IDC 086 chloride-bearing oxide items from Rocky Flats is described in Appendix I. Evaluation of those items supports the above recommendations.

3.2.2 Foundry oxide

Approximately 41% of the "killed" items from the relevant time period at Rocky Flats fall into the foundry oxide group. This group is likely to include some items with graphite as well as Cl salt (such as ARF-102-85-355). However, the graphite is expected to fully react at 750°C (as indeed was the case, for example, for ARF-102-85-355 even at 600°C). The foundry oxides are expected to consist of actinide oxides and other metal

oxides as described in Chapter 2. In addition, based upon the MIS data from IDC 061 in Appendix C, significant quantities of Cl salt are expected in many ARF items that originated as foundry oxide.

No other significant impurities are expected in this material, however, and the logic developed for ER oxide is reasonably extended to this material. Material containing detectable Cl salt should be stabilized at 750°C. Material without Cl salt or with $CaCl_2$ (indicated by the presence of Cl but with a Na/Cl peak-area ratio below the threshold defined by Rocky Flats ER oxide) should be processed at 950°C, and is unlikely to induce furnace corrosion.

3.2.3 Other material types

Only 3% of the items that could have been shipped to Hanford do not fall directly into one of the above categories. Of those, slightly over half can be eliminated as sources of concern, either because they have characteristics that are sufficiently similar to one of the other major categories that the same arguments apply, or because they are likely to show very low Cl salt content when screened by the PGA system.

Of the forty items that fall into this category,

- fifteen items are from IDCs that are highly unlikely to have contained any Cl salts. At least one of these showed an 8% assay value, and was likely packaged at Hanford for shipment to WIPP.
- nine items are from IDCs that indicate that they were designated for off-site shipment and originally belonged to one of the two main categories of ER feed and byproduct oxide or foundry byproduct oxide. One other consists of pyroprocessing oxide similar to other ER feed and byproduct oxides.
- seven miscellaneous oxides are from uncertain IDCs that are likely to have been material derived from either ER feed and byproduct oxide or foundry byproduct oxide. Seven of eight items without an IDC are likely to have been reworked items from ER feed and byproduct oxide or foundry byproduct oxide, based upon MBA of origin or item number.

These items are unlikely to simultaneously

- have been shipped to Hanford,
- contain Cl salt >1 wt %,
- contain some other constituent that would require 950°C stabilization, and
- escape detection through subsequent surveillance.

The technical team considers the residual risk for storage minimal.

3.3 Summary of stabilization temperature options

3.3.1 Stabilization at 750°C

Items that PGA shows contain NaCl/KCl mixtures in detectable amounts, and with Pu assay >50 wt % should be stabilized at 750°C to avoid corrosion and plugging and the related operational delays, costs, and doses. The technical team has not identified any constituents likely present in items that contain Cl salt at levels >1 wt % that will survive stabilization at 750°C but would be destroyed at 950°C that also pose a threat to DOE-STD-3013-2000-compliant containers.

3.3.2 Stabilization at 950°C

Material that is not contaminated with Cl salt should be stabilized at 950°C. The ~1 wt % Cl salt level detectable with PGA is considered to be a reasonable threshold for minimizing the threat to furnace elements, glove box systems, and moisture-measurement system components. This category would include the dried product of Cl salt washing. It would also include items that show the presence of Cl salt but show very low levels of Na and no detectable K, as these probably constitute oxide mixed with $CaCl_2$.

4 Integrated Risk Management

A variety of measures will ensure that DOE-STD-3013-2000 material will be stabilized, packaged, and stored in compliance with the requirements of the standard. All of these measures offer assurance that the ARF items at the PFP will be properly stabilized, and that the potential for risks higher than those for other Pu material will be identified and mitigated. These measures include the process controls and quality assurance program at PFP, the ISP for the 94-1 material (including the represented materials database and shelf-life programs), and the surveillance program at the storage site or sites (Savannah River Site or Hanford site).

The process controls include controls to ensure that

- the appropriate stabilization process is applied so that only chloride-bearing items will be stabilized at lower temperature,
- verification measurements of the moisture content at the end of stabilization demonstrate compliance with the 0.5 wt % moisture content criterion of the standard, and
- procedures are followed to minimize and to monitor for re-adsorption of moisture after stabilization but before welding of the container to ensure levels are in compliance with the limit in the standard.

In addition, after stabilization, PGA measurements will be made to ensure that only chloride-bearing material was stabilized at 750°C. These steps are discussed in the next sections. Programmatic controls such as the ISP and the site surveillance program at Savannah River are described in Section 4.4.

4.1 Controls on lower-temperature stabilization process

The following controls will be established to ensure that low-temperature stabilization is applied only where justified and necessary:

- The furnaces that are used will have a separate furnace program developed to allow the reduced temperature. The low-temperature program will be identified on the furnace operating data sheets, allowing verification that the low-temperature program was used for only the allowed materials. Surrogate testing at Pacific Northwest National Laboratory (PNNL) and Plutonium Process Support Laboratory (PPSL) has shown that, with the RMC furnace, a furnace temperature of 750ºC will ensure the material exceeds 750ºC (Appendix E, Schmidt 2003).
- Only Rocky Flats source material feed items (with a PFP source code ARF) that are greater than 50 wt % Pu will be evaluated for

lowered furnace temperature using the enhanced PGA screen proposed in this document. In addition, only material meeting the "pass criteria" logic shown in Figure 9 will be selected for low-temperature stabilization. The results of the PGA screen will be output and placed into the 3013 data packages to allow subsequent third-party verification.

- If it is found during the data package review that material was stabilized at 750ºC that did not meet the logic criterion proposed in Figure 9, the 3013 container will be opened and the material will be restabilized at 950ºC.
- The existing controls on sample representativeness and the monitoring of postsampling weight gain will be retained (Risenmay 2003).

4.2 Verification of moisture content

Moisture analysis is required for the contents of each 3013 can. This will be performed using TGA-Inert measurement (that is, total weight loss observed as the sample is heated under inert gas flow at 20°C/minute from room temperature to 1000°C) as currently practiced at the PFP. All weight loss will be assumed to be water. This 100% sampling frequency requirement will remain in place throughout the life of the project. The existing acceptance criterion of <0.4 wt % will be retained. If the TGA/MS is used for water analysis, the presence of HCl will be measured as a function of temperature. HCl evolution at low temperatures could be an indication of decomposition of hydrated salts, such as $MgCl_2 \cdot 6H_2O$.

The proposed means to measure moisture in thermally stabilized chloride-bearing oxide is to use the plant-installed TGA instruments to measure the amount of weight lost from verification samples heated to 1000°C under an inert atmosphere. If the item fails to meet the <0.4 wt % criterion, it would be restabilized. Otherwise, it would be packaged and stored.

The technical team evaluated several alternative approaches to determining that the moisture content did not exceed the 0.5 wt % required by the standard. They concluded that one alternative could reasonably substitute for this procedure from a technical standpoint. If PFP encountered a high rate of failure of ARF items on moisture measurement, and review of the TGA record indicated that the failure was largely due to mass loss above 750°C, it would be likely that failure was due to volatilization of (NaK)Cl salt, not due to moisture.

In this case, PFP would be technically justified in analyzing the TGA record to determine the weight loss at 750°C. The weight lost would be divided by a factor of 0.9 to provide a conservative measure of the total moisture content. If the item failed again to meet the <0.4 wt % criterion

using the bias-corrected 750°C weight-loss value, it would then be restabilized. Otherwise, it would be packaged and stored.

The justification for this approach is built on the following observations:

- Water evolution from Cl salts (NaCl, KCl, $MgCl_2$, mixtures of $CaCl_2$ with NaCl and KCl, and their hydrates and hydroxides) in the absence of PuO_2 is complete by 600°C. This temperature is below the observed onset of rapid NaCl, KCl, and $MgCl_2$ evaporation seen above about 700°C.
- Water lost from the Cl salts but evolved as hydrogen chloride (HCl) by pyrohydrolysis reactions is gravimetrically conservative (that is, weighs more than the equivalent amount of water).
- TGA/MS measurements of a large variety of pure and impure Pu oxide at PFP and of chloride-bearing MIS items from Rocky Flats at LANL show that water evolved by 750°C is nearly always >90% of the total amount observed by heating to 1000°C. The only exceptions identified to date are samples with very low total water content, for which the most strongly bound moisture is a significant fraction of the total. These items are not near violation of the limit.
- Total weight loss to 750°C is necessarily equal to, or more than, the weight loss due to water alone.

Thermogravimetric measurement of weight loss to 750°C, divided by a factor of 0.9, thus provides a conservative estimate of the concentration of moisture in a sample when compared with the amount that would have been observed by TGA/MS measurement to 1000°C, had such measurements been practicable. The technical bases of the observations that underpin the proposed use of TGA weight loss to 750°C are presented in Appendix G.

This approach would represent a change from the recommendation of the technical team for the Rocky Flats chloride-bearing oxides. The data summarized in Appendix G had not been evaluated as thoroughly at the time of the Rocky Flats evaluation. The Rocky Flats technical team considered recommending lower temperature for the moisture-measurement threshold. However, this document presents a technical case for the lower-temperature measurement that the team feels is robust enough to warrant consideration where concern exists about the potential threat to measurement instruments.

The technical team has evaluated issues related to the acceptability of its assertion that the data support moisture measurement at temperatures lower than the 1000°C. First, experience at Rocky Flats suggests that chloride-bearing oxides stabilized at 750°C contain very small quantities of water, and that salt volatilization by TGA-Inert results in very low failure rates for these oxides. Only one of twenty runs required evaluation of the FTIR analysis, and that was due to irregularities at low

temperatures, not due to failure of the mass-loss criterion. Thus, it is possible that the high projected failure rate due to salt volatilization that led PFP to request evaluation of lower-temperature moisture measurement will not be realized.

Second, the technical team is aware that the conclusions put forward in Appendix G, although comprehensive and, in the view of the team, conclusive, have not been widely reviewed by the relevant peer community. Therefore, the team recommends moisture measurement in compliance with the standard (to 1000°C). Items that fail should be restabilized. However, it is also the recommendation of the team that PFP should reserve the right to change the approach to the alternative described above, should the failure rate be greater than at Rocky Flats.

In the introduction to this report, the team pointed out that the maximum decrease in number of containers as a result of washing would be in the range of 10% to 20%. Somewhere in this range would be a reasonable failure rate (increase in stabilization runs) to drive reconsideration of the moisture-measurement protocol. However, the team recognizes that this is strictly a management choice.

4.3 Prevention of moisture re-adsorption

Because humidity in the RMC line is not actively controlled, it is close to the in-plant humidity, ranging from about 20% to 30% RH in the winter to ~40% RH or higher in the summer, when evaporative cooling is used. Under these conditions, moisture re-adsorption on material destined for storage under the 3013 standard can occur after the thermal treatment step, but before the material is hermetically sealed.

Recognizing the potential for re-adsorption in the RMC line, PFP implements specific measurements and controls to ensure samples are representative and to detect and quantify any significant re-adsorption that could occur after stabilization and sampling, but before the stabilized material is packaged. These controls have been documented, are enforced by procedure (Risenmay 2003), and have been accepted by the Savannah River Site (SRS), which is slated to store this material. These controls have been reviewed and are believed to be adequate for the chloride-bearing oxide addressed in this report. In summary these controls include the following:

- Glove box humidity is <60% RH during stabilization and packaging. Glove box humidity is continuously monitored, and canning and sampling operations are curtailed when the humidity exceeds 60% RH.
- The thermally stabilized product is sieved, and a representative sample is gathered by collection from three separate locations in the receiver pan into a sample vial.

- The thermally stabilized product is transferred into a vented convenience can and the lid placed on the can.
- The sample vial for the moisture analysis sample is sealed after the lid is placed on the filled and vented convenience can.
- The vented convenience can is monitored for weight gain in the time after sampling until the convenience can is to be sealed into the inner 3013 can. All weight gained in this interval is assumed to be water and added to the analysis result.
- Moisture in the representative sample is measured by an authorized moisture-measurement method.
- The TGA instruments used to analyze samples from the RMC line are in glove boxes supplied by the same air system, and the ambient humidity is approximately the same. This ensures that the sample does not desorb moisture before the analysis is run.
- The total quantity of moisture, including that from sample analysis plus the weight gain in the convenience can, must be <0.4 wt % for the material to be packaged.

The control methods, coupled with timely packaging, have proved effective in detecting and controlling re-adsorption in material shown to be hygroscopic, that is, oxides from precipitation of filtrate and miscellaneous solutions.

For the chloride-bearing Pu oxide, the main constituents of the salt fraction are NaCl and KCl. Neither of these salts is highly hygroscopic, and thus is not expected to reabsorb significant amounts of moisture, even in the RMC line. Indeed, these salts take up little water until they reach deliquescence at >70% RH, as described by Smith et al. (2000) and Veirs et al. (2002). Table 5 summarizes RH at deliquescence (the critical RH) for a variety of relevant salt constituents.

Table 5: Critical Relative Humidity for Various Salts

Compound	Critical Relative Humidity
$CaCl_2 \cdot 6H_2O$	29%
$MgCl_2 \cdot 6H_2O$	33%
NaCl	75%
KCl	84%
Equimolar NaCl/KCl	72%

The $CaCl_2$ and $MgCl_2$ salts can form hydrates at very low RH. In fact, Veirs concludes, "At room temperature, reducing the RH to a level where hydration of $MgCl_2$ salts will not form is not practical." However these waters of hydration are easily removed. Again Veirs states: "Calcination of $CaCl_2 \cdot 6H_2O$ results in loss of the six waters of hydration by 200°C" and, "$MgCl_2 \cdot 6H_2O$ loses four waters of hydration by 200°C, and then decomposes by releasing HCl at higher temperatures." Therefore, if the magnesium and calcium salts are present, any re-adsorbed water would be easily detected in the TGA analysis. If re-adsorption occurs on the bulk material after sampling, it will be detected by the weight-gain monitoring performed on the item after sampling.

Because significant re-adsorption is not expected to occur and, if it did, it is readily detectable, the "risk" of failing an item containing salt is therefore entirely under the control and detection of the PFP operations. The technical team strongly recommends the following actions to minimize, as much as is practicable, the potential for re-adsorption of moisture before can welding:

- Minimize the time between stabilization and packaging to limit the time material is at risk. This is the current practice and has proved effective on other materials packaged in RMC line.
- Limit moisture re-adsorption by covering the filtered vent on the convenience can while the can is in glove box storage.

If, in practice, items fail due to excessive reported moisture on the sample analysis or excessive weight gains on the bulk material after sampling, the following recommendations are given:

- If packaging capability is unavailable, consider holding material in the furnace at elevated temperatures, such as 400°C, to prevent bulk water adsorption.
- Cover the boats between the end of thermal stabilization and sampling/packaging operations to limit the access of atmospheric moisture to the material.

4.4 Poststabilization PGA

A PGA measurement will be made of each of the ARF items after stabilization. The ISP will review the prompt gamma results to verify, where possible, the determination that all material stabilized at lower temperature was chloride-bearing oxide.

4.5 Integrated Surveillance Program

There are five ARF samples in the MIS program. The samples will be used as part of the shelf-life program to evaluate DOE-STD-3013-2000 material and containers. The behavior of the Rocky Flats material

stabilized at low temperature can be considered also in determining overall storage performance.

The MIS program already has samples of IDC 067 (CLLANL025) and IDC 086 (C00695). These items are part of the shelf-life study to evaluate the behavior of DOE-STD-3013-2000 material. The object of this study is to refine technical understanding of the behavior of this material. That understanding can then ensure that current projections of the potential for this material to corrode or pressurize 3013 containers are accurate enough to make reasonable management decisions regarding continued storage.

Because the two MIS items mentioned above are in the mid-range of Cl salt concentration for these IDCs, currently there is no representative sample of the higher range of Cl salt concentrations for ER oxide. There are other Cl-rich items in the MIS database that may adequately represent this range. LANL should evaluate whether other items adequately represent the Cl-rich range before the end of the stabilization campaign for IDC 067 and IDC 086.

The draft ISP (Dworzak et al. 2002) identifies four categories of risk for DOE-STD-3013-2000 material. The highest risk category consists of those items that pose potential threats of corrosion and pressurization of the 3013 container. The bulk of the surveillance program will be focused on this category, which includes all of the pyrochemical salt material. A planned number will be removed and shipped to LANL for destructive evaluation. The Rocky Flats ER oxide will be represented in these analyses. The ARF chloride-bearing Pu oxides stabilized at low temperature will also be included in this category. It is significant to note that even if the material were washed, sufficient Cl salt would remain to keep the item in this high-risk category.

All of these measures taken together are expected to ensure that, if there is additional risk in the behavior of these materials, it will be appropriately acted upon.

5 Comparison of Alternative Stabilization Methods

Options for processing the high-Cl-salt items were evaluated by the PNNL (Silvers 2000b) and included the following:

1. Stabilize the material in the Stabilization and Packaging Equipment (SPE) furnaces using a protective shroud and quench system.
2. Stabilize the material in the RMC line furnaces using additives to reduce Cl salt volatilization and moisture absorption.
3. Use the existing precipitation equipment in room 230C to wash out the Cl salts.
4. Use a ball mill wash system to remove the Cl salts.
5. Use the Russian "salt washer" centrifuge currently in use at Lawrence Livermore National Laboratory (LLNL) to wash out the Cl salts.

The PNNL evaluation concluded that washing the items in the Room 230C glove boxes using the precipitation columns was the best option of those considered. The LLNL salt-washing system was not selected, because to meet PFP throughput requirements, 3–5 salt-washing machines would be required. At present, no citable report is available on the LLNL experience. Discussions with site personnel suggested that a 0.8-liter-solution capacity would require 8–11 wash cycles per batch on operations. The high cost and high schedule impact of the LLNL system lead to an unfavorable ranking in the evaluation. Water washing of the chloride-bearing Pu oxide items therefore became the baseline process for addressing the problems attendant to the presence of Cl salt.

The current baseline plan (described in Section 3 and Appendix F) involves water washing to remove Cl salts, followed by thermal stabilization of the washed product at 950°C. However, even washing to reduce the Cl salt content to the target levels of <1% will not eliminate furnace and off-gas operability issues. Developmental testing has shown that frequent maintenance will still be required.

For comparison, the amount of salt expected to be vaporized at 750°C, even in unwashed feed, is expected to be at least 10-times less than that expected to be vaporized in materials washed to <1% Cl salt and stabilized at 950°C. The cumulative extent of corrosion and salt deposition within the off-gas lines during the four tests conducted with 20 wt % Cl salts at 750ºC was less than that experienced in a single test with 1 wt % Cl salts at 1000ºC (see Appendix E).

The major elements of work for both stabilization options are described in detail in Appendix F. Based on these work elements, differences in approximate cost and worker exposure have been estimated.

The low-temperature stabilization option offers significant benefits over the current plan to wash and stabilize at 950°C. These benefits include the following:

- Elimination of a significant volume of liquid waste, estimated at 5,200 liters, and attendant long-term storage and disposal costs.
- Significant reduction in operator exposure by elimination of the highly dose-intensive "hands-on" wash process, estimated at 10–15 person-rem extremity and 1–2 person-rem whole body.
- Cost savings from elimination of washing, filtrate collection, and waste disposal estimated at $1,500,000.
- Reduction of schedule risk by freeing resources currently assigned to the wash process to other stabilization and deactivation activities.
- Reduction of technical and schedule risk for completion of stabilization by greatly simplifying the overall operation.

However, the low-temperature stabilization option offers some potentially negative aspects over the current plan to wash and stabilize at 950°C. These include the following:

- Some risk of additional exposure from the step to remove agglomerated material from the stabilization boat and reduce particle size to allow sampling. The problem of "brick" formation due to melting of salt constituents is seen in some surrogate studies, but has not been a problem in stabilization of actual materials at Rocky Flats.

- Some potential for additional 3013 cans to be generated based on the additional bulk volume of Cl salt solids that would not be removed. It is not clear that this will indeed be the case. The total reduction in mass (the main constraint on can filling) by washing would almost certainly be <20%. Operational considerations, such as the batch size for washing, would likely result in the reduction in number of cans stabilized. The numbers of additional cans would most likely be no more than 10% of the total, or 45 cans.

On balance, the technical team concludes that the expected benefits of lower-temperature stabilization outweigh these potential costs.

6 Conclusions and Recommendations

In the end, it is a management decision to weigh the risks and benefits of a technically complex issue of the type discussed here and to make a cost- and risk-based decision on the path forward. The request for technical assistance from Hanford asked that the Technical Assistance Team

> "Advance a case to lower the thermal stabilization temperature to less than 800°C and lower the maximum moisture evolution measurement temperature of the thermally stabilized product to <1000°C for chloride-bearing Pu oxides at the Hanford Plutonium Finishing Plant (PFP) that were received from Rocky Flats, while maintaining technical equivalency with the goals of the standard DOE-STD-3013-2000. Review and modify the approved technical basis (LA-UR-02-6054) for chloride-contaminated Pu oxides at Rocky Flats as a template to apply to Hanford's chloride-contaminated Pu oxides.
>
> Document the technical case as a basis for its use to obtain approval of the alternative stabilization and moisture measurement practices for chloride-containing Pu oxides at the Hanford PFP. Thermal stabilization of chloride-bearing materials shipped from Rocky Flats to Hanford at 750°C will be equivalent to compliance."

To do this, the request asked that the team complete five tasks. The technical team provides the following results and recommendations in respect to each of these tasks:

1. Determine the characteristics of the Cl-bearing oxides at PFP that are represented by the electrorefining oxides defined in LA-UR-02-6054.

The characteristics of materials shipped to Hanford are described in Section 2 of this report. It identifies the likely Cl salt constituents in the range of materials potentially shipped, and the other expected impurities that might be expected to be present with the Cl salts and actinide oxides.

2. Recommend characterization techniques to identify additional chloride-bearing oxide categories at PFP that might benefit from lower stabilization temperature.

The technical team recommends the use of PGA to identify chloride-bearing material that may be stabilized at lower temperature. The PGA can be used in conjunction with available assay data to define items that might potentially corrode or plug critical subsystems in the stabilization furnaces.

Rapid screening for Na, K, and Cl to identify candidates for lower-temperature stabilization will be sufficient to distinguish items that pose a risk to stabilization equipment. This will include material from IDCs related to the ones described in Boak et al. (2002), but also identifies

other IDCs shipped from Rocky Flats that have characteristics sufficiently similar to the Rocky Flats ER oxide to be screened by PGA for lower-temperature stabilization. Analysis of the full PGA spectrum after stabilization may be used to identify containers for enhanced monitoring by the ISP, which has already identified chloride-bearing Pu oxide as requiring higher levels of surveillance.

The technical team recommends that the ISP, in cooperation with Rocky Flats and PFP, expedite preparation of a document that lays out the technical basis for PGA and describes the instruments now being used at LANL, Rocky Flats, and Hanford.

The technical team has not reviewed any material at PFP other than the ARF items shipped from Rocky Flats. The conclusions of this report apply only to the Rocky Flats material.

3. Develop an implementation strategy for lower-temperature processing to:
   - obtain valid moisture measurement data using TGA-inert at lower temperatures to avoid counting weight loss due to salt evaporation,
   - minimize moisture re-adsorption in stabilized materials, and
   - ensure that only Chloride-bearing material is stabilized at lower temperature.

The discussions in Section 4 and Appendix G of this document provide the rationale for using mass loss by TGA-Inert to 750°C, divided by a correction factor of 0.9 to provide a conservative estimate of the total moisture content of the stabilized item. However, the technical team recommends that PFP continue to measure moisture by TGA-Inert to 1000°C, and restabilize items that fail the moisture content criterion.

The technical team recommends that the alternative moisture content measure described above be submitted for peer review to validate the technical conclusion of this team that it constitutes an equivalent measure of the total moisture content with respect to compliance with DOE-STD-3013-2000.

Re-adsorption will be minimized by following the procedures identified in Section 4, many of which are already in place for all Pu oxides. Prestabilization PGA screening will adequately identify items that warrant 750°C stabilization and will ensure that only chloride-bearing material is stabilized at lower temperature.

4. Compare the efficacies of direct lower temperature (*e.g.*, 750°C) stabilization, and chloride salt washing followed by 950°C stabilization to select the better means to mitigate the deleterious effects of chloride; identify potential roles for chloride salt washing.

The evaluation in Appendix F indicates that stabilization of chloride-bearing material at 750°C reduces cost, dose, and schedule risk over washing and 950°C stabilization.

5. Develop technical arguments to show that moisture evolution during moisture verification measurements is complete at temperatures well below 1000°C (*e.g.*, ~600°C as observed for other pure and impure materials tested to-date).

The report discusses the evidence that >85 wt % of moisture is evolved below 600°C, and that >90 wt % is evolved below 750°C in a very wide range of material stabilized to date, including chloride-bearing Pu oxide. Recent data on Rocky Flats material relevant to this evaluation are summarized in support of this conclusion.

Although the technical team concludes that bias-corrected mass losses at these lower temperatures constitute conservative (and therefore equivalent) measures of the total moisture content released by 1000°C, the technical team recommends restabilizing any material that fails at 1000°C, unless a significant fraction of the items fail the 0.5 wt % criterion on this basis. The technical team recommends an external peer review of the above conclusion regarding equivalency to ensure its robustness, and to support any subsequent need to review the moisture measurement procedure.

The technical team recommends that PFP reserve the right to request a change to the procedure for moisture measurement if a significant fraction of items fails the moisture-content criterion, or if the TGA equipment shows rapid failure when run to 1000°C. If the failure fraction for items is large, the TGA results can be recalculated at 750°C and bias-corrected to provide a more accurate measure of moisture content. If the TGA fails, measurement could be truncated at 750°C

Thus, this document concludes that chloride-bearing Pu-oxides shipped to Hanford from Rocky Flats, identified by PGA and stabilized at 750°C, with a moisture content confirmed by weight loss up to 1000°C, will be in full compliance with the intent of DOE-STD-3013-2000. As documented by evaluation of data on moisture content and other material chemical characteristics, lower-temperature stabilization will meet the objectives of the standard to stabilize material for long-term storage.

The technical team concludes that changing the baseline from water washing to lower-temperature stabilization will result in stabilization equivalent to compliance with DOE-STD-3013-2000 for material with >50 wt % Pu. Material below this Pu level should be processed through the washing system. Items below 30 wt % Pu have already been prepared for shipment to the WIPP. The team further concludes that no additional risk is likely for these chloride-bearing oxides and that future surveillance will ensure adequate validation of this judgment.

7 Acknowledgements

The authors acknowledge the assistance of the members of the Materials Identification and Surveillance Working Group: Jerry Stakebake, Richard Szempruch, James McClard, and Karen Dodson, all of whom contributed to defining the issues and positions taken in this document, and provided much of the data supporting equivalency.

The 94-1 R&D team at LANL also provided data, technical support, and invaluable review comments. We acknowledge Richard Mason, Kirk Veirs, Laura Worl, Luis Morales, and Mark Paffett. All contributed materially to the document as it now stands. Gary Eller provided review and critique of the technical content and structure of the arguments presented here that was essential to integrating the many threads that make up this document. Scott Barney of Fluor-Hanford and Andrew Schmidt of Pacific Northwest National Laboratory provided critical input to the document. Don Thorp provided invaluable knowledge of events and processes at Rocky Flats during the time the ARF items were being shipped from Rocky Flats to Hanford.

The document was reviewed by the 94-1 Technical Review Board (Jerry Stakebake at Rocky Flats, Allen Gunter at Savannah River, and Leonard Gray of Lawrence Livermore National Laboratory). In addition, Charles O'Dell and Stanley Wolf (DOE-HQ) and Suzanne Clarke (DOE-RL) also reviewed the technical content and management implications of this document.

Appendix A: Hanford Technical Assistance Request

TECHNICAL ASSISTANCE REQUEST

Tracking Number:	
Request Title:	Extend RFETS Technical Equivalency for Lower Temperature Stabilization of Chloride-Contaminated Pu Oxides To Chloride-Bearing Pu Oxides at the Hanford Plutonium Finishing Plant
Contact Individual:	Ted Venetz-FH, Marcus Glasper -RL, Suzanne Clarke—RL/AMCP
Requesting Organization:	Richland Operations Office—Plateau Transition Division
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Phone Number:	509-376-9669 (Venetz) 509-373-9075 (Glasper) 509-373-4931 (Clarke)
Fax Number:	509-376-5454 (Venetz) 509-376-0306 (Glasper) 509-376-0695 (Clarke)

Scope of Work:

Technical Assistance

Description

Technical assistance is requested to:

Advance a case to lower the thermal stabilization temperature to less than 800°C and lower the maximum moisture evolution measurement temperature of the thermally stabilized product to <1000°C for chloride-bearing Pu oxides at the Hanford Plutonium Finishing Plant (PFP) that were received from Rocky Flats while maintaining technical equivalency with the goals of the standard DOE-STD-3013-2000. Review and modify the approved technical basis (LA-UR-02-6054) for chloride-contaminated Pu oxides at Rocky Flats as a template to apply to Hanford's chloride-contaminated Pu oxides.

Document the technical case as a basis for its use to obtain approval of the alternative stabilization and moisture measurement practices for chloride-containing Pu oxides at the Hanford PFP.

Approach:

1. Review existing composition data (e.g., prompt gamma, chemical analysis, additional RFETS historical information, etc.) to determine the characteristics of the Chloride-bearing oxides population at PFP that already are represented by the electrorefining oxides defined in LA-UR-02-6054.
2. Recommend characterization techniques that may be used to identify additional chloride-bearing oxide categories, beyond those identified in (1) above, within the Chloride-bearing and other scrap oxide population at PFP that might benefit from lower stabilization temperature.
3. Develop an implementation strategy for the lower temperature processing with goals such as
   - obtaining valid moisture measurement data using TGA-inert at lower temperatures to avoid unduly ascribing weight loss due to salt evaporation to moisture
   - proposing process practices to minimize moisture re-adsorption of thermally stabilized materials
   - developing controls to ensure that only the Chloride-bearing material is stabilized at lower temperature.

4. Compare the efficacies of
   - direct lower temperature (e.g., 750°C) stabilization, and
   - the reference approach of chloride salt washing followed by 950°C stabilization

   to select the better means to mitigate the deleterious effects of chloride; identify potential roles for chloride salt washing.
5. Develop technical arguments to show that moisture evolution during moisture verification measurements is complete at temperatures well below 1000°C (e.g., ~600°C as observed for all other pure and impure materials tested to-date).

Baseline Technology

Description

Hanford's Plutonium Finishing Plant (PFP) has 1100 kgs of scrap Pu oxide that are potentially contaminated with chloride from Rocky Flats pyrochemical operations. This scrap must be stabilized per DOE-STD-3013-2000. The present process plan calls for water-washing to remove chloride to <1 wt % total salt (to mitigate moisture re-absorption and corrosion problems) before thermal stabilization in furnaces in PFP's RMC line. Furnace tests with simulated chloride-bearing scrap show that even 1 wt % chloride salt evaporates from process boats at current 950°C flowsheet conditions to deposit on cooler downstream offgas surfaces, plug offgas filters, and cause localized furnace equipment corrosion. A further inventory of ~250 Hanford-origin items is projected to fail "TGA Inert as LOI" testing due to salt volatilization and decomposition unrelated to water loss even after their planned thermal stabilization in the PFP's SPE line.

It is expected that measurement of moisture concentration for thermally stabilized chloride-bearing materials by weight loss ("TGA Inert as LOI") will overstate the actual moisture concentration, resulting in unwarranted batch failure and subsequent recycling through thermal stabilization. Moisture measurement by the backup TGA/MS method, which is specific for water, is time consuming, susceptible to equipment failure by plugging and corrosion of small diameter gas lines caused by chloride deposition, and limits the availability of the TGA/MS to other valuable process support activities.

Due to the volatilization of the chloride and other salts at temperatures above ~800°C, stabilization of these materials per 3013 at >950°C has the potential to cause significant process downtime and increased worker exposure due to re-stabilization operations (because of failure to pass "TGA Inert as LOI"), replacement of corroded stabilization furnace and moisture measurement equipment components, and obstruction of process offgas equipment due to plugging by condensed salts. Of particular concern, should processing occur in the PFP's SPE line, is the fact that the furnace wall in the PFP SPE line constitutes a primary glovebox containment barrier such that undue corrosion penetration would cause escape of Pu particles into the manned process areas.

Each day of downtime or unnecessary operation extends the PFP processing campaign on a day-for-day basis at a daily cost of ~$120 k. Extension of the PFP campaign will also delay reassignment of PFP personnel to D&D activities for the PFP and ancillary support rooms.

Improvement Over the Baseline Technology

Description

Reduction in the thermal stabilization and the subsequent moisture measurement temperatures to temperatures that minimize the salt volatilization/corrosion operational impacts and yet ensure that the technical objectives of the DOE-STD-3013-2000 are met (i.e., moisture content <0.5 wt % is attained) would:

1. Improve the efficiency of PFP operations
2. Decrease and perhaps eliminate the complex and dose-intensive washing operation
3. Decrease the attendant liquid waste generation from the water wash steps
4. Avoid excessive process and moisture measurement equipment failure impacts (hardware and installation costs, process downtime) at an incremental daily savings of $120k
5. Avoid added worker exposure associated with equipment repair
6. Free personnel resources for other stabilization and D&D activities.

Support:

What resource(s) have been selected?

Principal Investigator and Other Key Participants

The recommended team members are:

GD Roberson	DOE/AL	505 845-5805
JD Boak	LANL	505 667-0835
PG Eller	LANL	505 667-7111
AM Murray	SRTC	803 725-0440
EA Conrad	RFETS	303 966-2641
CH Delegard	PNNL	509 376-0548

Schedule

Milestones or Major Tasks / Activities

1/10/2003:	Initiate Technical Assistance Program.
1/23/2003:	Conduct kickoff meeting at Hanford.
2/10/2003:	Complete data collection on chloride-bearing inventory materials.
2/18/2003:	Complete evaluation of data and prepare draft technical basis document.
3/3/2003:	Submit draft technical basis document and recommendations for peer review.
3/17/2003:	Submit completed technical basis document and recommendations to the DOE Preparing Authority for the DOE-STD-3013-2000 and the Technical Review Board.

What resources were offered, but not selected?

N/A

Requested Start Date: 01/20/03

Requested Completion Date: TBD

Estimated Cost:

Labor:	$125k
Mat'ls:	$0k
Supplies:	$5k
Travel costs:	$15
Total:	$145k

Submitted By: Marcus J. Glasper_____

Appendix B: Thermal Stability of Fluorine-Containing Thermoplastics

Residual plastics or plastic chars (remaining from prior thermal processing and stabilization steps) may be present in the items shipped from Rocky Flats to Hanford as debris or particles from engineered items (for example, containers, process vessels, gaskets, bags, and glove box structures) used in RFP operations. Satisfaction of the terms of DOE-STD-3013-2000 (DOE 2000) requires destruction of organic materials, such as plastics, during thermal stabilization prior to packaging.

Technical arguments advanced in paragraph A.6.1.2.1.2 of the standard conclude that plastics are destroyed by 2 hours of oxidative heating at 950°C. The discussion goes on to assert that

> "all plastics less than about one inch in diameter and any other organic materials likely to accompany unstabilized Pu materials are completely oxidized by air in less than five minutes at 800°C."

By the Arrhenius equation, the rate of organic material oxidation at 750°C would be only about 5% slower than at 800°C, such that ready decomposition of plastics by 2 hours of oxidation at 750°C would be expected.

Evaluation in the prior technical equivalency document (Boak et al. 2002) concluded that the fluorine-containing thermoplastics are the organic materials most stable to combustion. At Rocky Flats, the most frequently used fluorine-containing plastics were polytetrafluoroethylene (PTFE, $[CF_2CF_2]_n$, commonly known as Teflon™) and polyvinylidene difluoride (PVDF, $[CF_2CH_2]_n$, generally marketed as Kynar™). Therefore, the technical literature was reexamined to assess the thermal stabilities of PTFE and PVDF. According to data found in the technical literature, 2 hours of oxidative heating to 750°C is more than sufficient to destroy both PTFE and PVDF by depolymerization, decomposition, and by oxidation to produce volatile species.

A review of fluorocarbon stability in a monograph on heat-resistant polymers (Critchley et al. 1983) shows that under oxidizing conditions to comparable end states, the thermal decomposition of PVDF occurs at about 100°C lower temperatures than for PTFE. Therefore, as might be expected, PVDF is less thermally stable than PTFE. The technical data also show that PTFE thermally decomposes to the same extent under either oxidizing or oxygen-free conditions, while PVDF decomposes at about 40°C lower temperatures under oxygenated conditions than it does in the absence of oxygen.

In particular, weight loss under oxidative heating increases steeply around 370°C for PVDF and ~500°C for PTFE to reach ~70 % weight loss after 2 hours of heating at the named temperature for each plastic. Thermal decomposition of PTFE produces volatile carbonyl fluoride (COF_2) below 650°C; above 650°C, the COF_2 disproportionates to produce CO_2 and CF_4. With sufficient air-flow, PTFE will auto-ignite (at about 575°C) to produce COF_2, CO_2, and saturated fluorocarbons (for example, CF_4, C_2F_6). As noted previously, thermal analyses of PTFE membranes show that thermal decomposition in air commences at about 350°C, with no further weight loss occurring above 750°C (Fleszar 2000).

In comparison, hydrofluoro-polymers such as PVDF decompose by hydrogen fluoride (HF) elimination followed by chain scission. For PVDF, HF elimination begins at about 214°C in air. Pyrolysis (heating in the absence of air or oxygen) of PVDF to 450°C to 500°C produces volatile constituents including HF, low-molecular-weight polymers, and trifluorobenzene ($C_6H_3F_3$), presumably by ring closure of the dehydrofluorinated trimer (Bock 1972). Decomposition of PVDF in air occurs in the range 400°C to 475°C (Thompson 1972).

Together, research into the thermal stabilities of PTFE and PVDF shows that 2 hours of oxidative 750°C-heating is sufficient to completely destroy these fluorocarbon polymers to produce volatile products.

To assure complete thermal degradation of organic material possibly present in Pu oxide residues, a minimum 750°C material stabilization temperature should be maintained for 2 hours in an air atmosphere. Additionally, large pieces of plastic material should be removed before stabilization, as required by DOE-STD-3013-2000. These conditions will result in a minimal residual risk of the presence of organic material, including the fluorocarbon polymers, in Pu oxide material following stabilization.

Appendix C: Composition of Relevant Rocky Flats Items in the MIS Database

Item	ORF52-011608 (P1608)	ORF59-011589A (F1589)	ORF52-TS707013 (M7013)	ORF52-07221730 (U1730)	ORF52-5501579 (B1579)	ORF59-TS707001 (E7001)	CAN 92	ORF59-C00024A (V0024)	ORF52-520610020 (N0020)
IDC	*60*	*60*	*60*	*61*	*61*	*61*	*61*	*61*	*61*
Pu	85.62	77	67.34	87.53	86.43	86.30	81.58	69.47	30.95
U	0.00	0.01	0.09	not meas.	not meas.	0.37	2.61	not meas.	0.05
Am	0.18	0.23	0.30	0.13	0.11	0.00	0.26	0.31	1.63
Na	0.20	0.37	1.02	<0.0040	<0.003	<0.0100	<0.008	2.19	1.35
K	0.13	0.70	1.51	<0.0050	0.03	<0.0100	0.02	2.62	1.75
Mg	0.07	2.27	1.26	0.35	<0.0008	0.01	<0.0004	1.15	6.62
Ca	0.26	0.39	0.18	0.36	0.003	0.01	0.0007	0.02	11.07
Cl	0.20	1.63	8.90	0.10	0.06	0.01	0.25	5.68	16.90
F	0.27	0.26	0.022	0.16	not meas.	0.11	not meas.	0.05	<0.03
Al	not meas.	0.47	0.29	<0.0081	<0.0025	0.01	<0.0030	0.05	1.11
Si	<0.0008	0.79	0.08	not meas.	0.05	0.06	<0.0050	<0.10	0.19
Ga	0.54	0.35	0.39	0.01	1.00	0.07	0.36	2.40	0.06
Fe	0.06	0.37	1.48	0.04	0.20	0.02	0.40	0.72	0.95
Ni	0.01	0.02	0.26	0.01	0.05	0.02	0.06	0.05	1.47
Cr	<0.0005	0.04	0.50	0.01	0.01	0.02	0.07	0.45	0.44
C	0.42	0.74	0.06	0.03	0.02	0.07	0.02	0.02	0.18
S	<0.004	0.020	0.006	0.005	<0.005	not meas.	0.0036	0.0306	0.055
Trace Metals*	0.16	0.24	0.20	0.01	0.11	0.02	0.68	0.31	0.14
Oxygen**	11.70	11.97	10.71	11.76	12.04	11.75	12.18	10.94	6.75
Total	**99.81**	**97.84**	**94.59**	**100.49**	**100.02**	**98.85**	**98.09**	**96.45**	**81.66**

Not meas.—not measured

* Trace metals include Be, B, Cu, Pb, Mo, Ta, W, and Zn

** Oxygen calculated assuming Pu, U, Am, Al, Si, Ga, Fe, Ni, Cr are present as oxides

Item	ORF59-CLLANL025 (HLO25)	ORF52-C00695 (T0695)	ORF59-C06032A ("I" 6032)	ARF-102-85-114-1	ARF-102-85-223	ARF-102-85-365	ARF-102-85-355	ARF-102-85-295A (Powder)
IDC	*67*	*86*	*159*					
Pu	71.29	69.17	51.78	86.40	66.36	60.46	48.48	26.59
U	not meas.	not meas.	0.01	not meas.	not meas.	not meas.	not meas.	not meas.
Am	0.25	0.15	0.35	0.23	0.21	0.21	0.36	0.27
Na	1.96	7.43	2.25	0.09	4.78	4.43	0.10	3.65
K	5.12	3.47	4.14	0.05	6.62	5.77	0.08	5.44
Mg	0.55	2.00	2.23	0.01	0.86	1.09	<0.008	6.75
Ca	0.0061	0.04	0.03	0.02	0.02	0.01	0.07	0.12
Cl	10.00	9.00	16.20	0.01	11.20	1.13	6.10	20.40
F	0.021	0.03	0.09	0.003	0.02	0.02	2.15	not meas.
Al	0.34	0.02	0.01	<0.0008	0.01	<0.003	0.02	0.20
Si	0.38	<0.16	0.45	<0.16	<0.16	0.05	<0.087	0.29
Ga	0.036	0.01	0.17	0.41	0.01	0.10	0.03	0.40
Fe	0.04	0.08	0.03	0.03	0.03	0.04	0.32	2.49
Ni	0.09	0.27	0.06	0.005	0.15	0.05	0.03	2.03
Cr	0.02	0.02	0.02	0.003	0.03	0.02	0.15	0.35
C	0.02	0.01	0.044	0.032	0.07	0.43	>67?	0.36
S	<0.008	0.077	not meas.	<0.0056	0.01	0.0199	<0.008	0.0223
Trace Metals*	0.08	0.03	0.10	0.22	0.04	0.35	0.10	0.4093
Oxygen**	10.38	9.42	7.60	11.75	9.00	8.25	6.84	6.17
Total	**100.59**	**101.23**	**85.55**	**99.26**	**99.41**	**82.44**	**?**	**75.93**

Not meas.—not measured
* Trace metals include Be, B, Cu, Pb, Mo, Ta, W, and Zn
** Oxygen calculated assuming Pu, U, Am, Al, Si, Ga, Fe, Ni, Cr are present as oxides

Appendix D: Characteristics of Rocky Flats Oxides Shipped to Hanford

Categories of Material Shipped

As discussed in Section 2.3, the 1,138 items "killed" at Rocky Flats during the fifteen Hanford shipping campaigns during 1984 to 1986 fall into three categories. This section provides additional detailed description of the three categories, including IDC number and title, as well as the number of items in each. In addition, the section provides additional detail for the Foundry Byproduct category and discussion of the characteristics of the items included in the Miscellaneous Oxide category. Table D-1 lists each IDC on the Rocky Flats "kill" list, as well as the IDC description and the number of items "killed." It is sorted by the three categories identified in Section 2.

Electrorefining Feed and Byproduct Oxide

Of the items that were "killed" during the period when items were shipped to Hanford, approximately 55% (628 items) consisted either of IDC 067 (Chlorinated Oxide), or of other IDCs directly associated with the tilt-pour furnace ER process. These other IDCs included a variety of feed and byproduct IDCs, which appear in Figure 4 in the main text of this document, as well as in Table D-1. All of these items could be expected to contain Cl salt at levels from trace amounts to 70 wt %. Material with <30 wt % Pu does not meet the requirements of DOE-STD-3013-2000.

Similarities among the items consisting of Pu oxide with chlorides include the following:

a) The materials were generated from the tilt-pour ER process in Building 371. Ball (1985) indicates that ≥90% of the IDC 067 items originated in the ER process. The remaining material in IDC 067 was oxide from other Building 371 processes. Items for shipment to Hanford were initially selected from the IDC 067 inventory based on having <80 wt % Pu content (Ball 1985). Items of other IDCs in this group were generated from similar pyroprocessing products.

b) All materials are expected to have some amount of Cl salt from the salt matrix used in the ER process (equimolar NaCl/ KCl with 5% $MgCl_2$).

   In tests at RFP, three batches of anode heels were converted to oxide (using a hydride/dehydride process). The Cl salt levels in those batches indicated a Cl salt content of 0.3–1.0 wt % (Davies 2003).

Table D-1: Categories of Items "Killed" at Rocky Flats

IDC	Description	Items
	Electrorefining Feed and Byproducts	*628, 55.2%*
017	Nonroutine ER Metal Unacceptable Purity	3
031	Anode Feed for ER, Non-Spec.	10
037	Anode Heel >200 gms Pu	52
038	039 (Metal) Prepared for ER	1
039	ER Button from Cell Cleanout	23
051	Anode Heel	25
052	Oxide Pyro RF	1
067	*Chlorinated Oxide*	*495*
154	ER Scrapeout Material	10
237	Anode Heel for Offsite Shipment	2
368	MgO Ceramic Crucible - Not LECO	1
411	Electrorefining Salt	5
	Impure Foundry Oxide	*470, 41.3%*
057	Oxide Awaiting Spec. Analysis	10
058	Oxide Awaiting Product Categorization	10
060	Oxide	22
061	*Non-Spec. Oxide*	*401*
151	Free Metal Fines, Non-Spec.	26
310	Graphite Scarfing & Fines	1
	Miscellaneous Oxides	*40, 3.2%*
022	IDC Unknown, Likely Metal	2
042	Oxide for Special Sampling, Bldg 371	2
043	Oxide Special Sampling Waiting Lab Results	3
046	Oxide <0.80 g/g Pu Selected for MMEC	2
053	Oxide for Calcining	1
054	Oxide >0.85 g/g Pu Selected for MMEC	3
056	Oxide 0.80–0.85 g/g Pu Selected for MMEC	1
059	Oxide 0.80–0.85 g/g Pu Packaged for SRP	1
082	Green Cake in Small Inner Can, Bldg 371	2
083	High-Fired Oxide DOR	8
146	Oxide–LOI Reject	1
391	Unpulverized Sand, Slag, and Crucible	2
398	Pulverized Sand, Slag, and Crucible	1
406	Molten Salt, Unknown % Pulverized	1
420	Pulverized Incinerator Ash	1
U61	Pu/eU Oxide, <10,000 ppm eU	1
N/A	No IDC Available	8
	Total	**1,138**

In tests at RFP, a small subset of IDC 067 (eventually categorized as IDC 086 [Oxide ER Scrape Out]) was tested for potential use as feed in the DOR process (Guadagnoli and Esquibel 1986). As part of that testing, those items were characterized and the Cl salt content was found to range from 5–32 wt %, with most of the 26 items having about 10–11 wt % Cl salt. Those same items had Pu contents ranging from 13–85 wt %, based on calorimetry/gamma-ray scanning assays. The item with the lowest Pu content (13 wt %) had the highest Cl salt content (32 wt %).

c) The materials for shipment to Hanford were calcined at least once, and generally two times at ~450°C; thus metal, if present, would have been converted to oxide.

The ER oxide items that were shipped to Hanford are similar to, if not exactly like, the materials considered in Boak et al. (2002). Those materials are IDC 067 and 086 items that are currently either stabilized or in storage at Rocky Flats awaiting stabilization to meet DOE-STD-3013-2000 requirements. The technical team concludes that the stabilization equivalency established for the Rocky Flats materials to meet DOE-STD-3013-2000 requirements would apply to the Hanford materials for this group of IDCs.

Foundry Byproduct Oxide

Of the items “killed” at Rocky Flats for shipment to Hanford, approximately 41% (470 items) came from IDC 061 (Non-Spec. Oxide—foundry oxide not meeting specifications) or from similar IDCs shown in Table D-1.

The foundry oxide items consist of impure Pu oxides generated from nonaqueous processes. Specifically, these oxides were generated from the stabilization of foundry residues. As a result, nitrates or sulfates are highly unlikely to be present in foundry oxide. The water content of the foundry oxide should be substantially lower than the water content of aqueous process oxides, such as green cake (IDC 082—oxide derived from peroxide precipitation), because the foundry oxide was not produced via an aqueous process. A detailed description of the generation of foundry oxide was given in a report by Steinmeyer, Hobbs, and Oetting (1986).

The foundry oxide may be contaminated with Cl salts. The Cl salts originated on the surface of, or as occlusions in, Pu metal buttons produced via pyrochemical processes. Steinmeyer et al (1986) noted that the wire brushing of molten salt extraction (MSE) Pu metal buttons removed much of the Cl salt residue. However, the irregular surface of buttons still retained a significant amount of various volatile species.

Those species include the $NaCl/KCl/MgCl_2$ salt matrix and magnesium that formed a skin on the Pu metal button. Mg metal was a byproduct of the MSE process. The presence of those volatile components caused splatter during feed ingot casting. Pu metal was carried along with the volatile impurities to a splatter shield on which the Pu was captured.

The amount of $MgCl_2$ is expected to be variable because different amounts were used in MSE and ER. During the casting process, the salts may have volatilized. Boak et al. (2002) discuss extensively the Mg-bearing phases that might be present in stabilized chloride-bearing oxide.

The magnesium and calcium skins associated with MSE and DOR buttons, respectively, would also have been expected to volatilize. The magnesium and calcium might be present in the calcined foundry oxides as oxide. However, the high-Cl salt content of some of the foundry oxides listed in Appendix C suggests that Mg and/or Ca chlorides may be present.

Operational experience suggests that the amount of Mg-bearing Cl salt will be small due to the multiple stages of processing the material has seen, all of which tend to consume the $MgCl_2$ constituent (by reduction to metal, by hydrolysis or other oxidative reactions, and by crystallization of binary alkali-magnesium salts). $MgCl_2$ as a separate phase is unlikely to be present in any of these materials, as the original Cl salt mixture has been melted and would be expected to crystallize as a mixed salt ($KMgCl_3$ or Na_2MgCl_4), as described in Boak et al. (2002).

For the purposes of this evaluation, the primary salt constituents, Na, Mg, K, Ca, F, and Cl are presumed to be present in typical processing salts, such as NaCl, KCl, $MgCl_2$, $CaCl_2$, and the CaF_2 used to coat molds. Mass balance calculations generally show some excess of the cations over the anions. These excesses likely represent the presence of some of the cations as oxides (especially MgO, used in stirrers and other refractory items), which would add to the oxygen calculated.

The Pu metal feed to the casting furnaces was produced from bomb reduction and from pyrochemical processes (ER, MSE, DOR). The metal was produced from SRS, Hanford, LANL, and RFP. The metal feed was combined into briquetted machine turnings, scrap, and metal from sorted skull to make a feed ingot casting. The feed ingots then were analyzed, blended appropriately, mixed with gallium, and cast to make war reserve (WR) ingots. Tantalum crucibles were used in the casting process.

The casting process was done in a vacuum furnace. A skull residue was always generated; however, the amount and impurities depended on the feed. The ingots were cast into two types of molds: feed ingots in metallic molds coated with erbium oxide and WR ingots in graphite molds.

After sorting, the skull from several castings was recast. The skull from that casting was considered unusable. That unusable skull was subjected to two burnings on a hot plate to convert it to oxide and sampled. The analytical results determined how the oxide was processed to recover the Pu. If the impurity levels met specification (Table D-2), the foundry oxide was categorized as IDC 060 and processed through the fast aqueous recycle process: dissolution followed directly by peroxide precipitation (no ion exchange). Foundry oxide that did not meet specifications was categorized as IDC 061 and processed through the slow aqueous recycle process: dissolution followed by ion exchange followed by peroxide precipitation.

Table D-2. Maximum Allowable Impurity Concentration for Oxide Dissolution

Element	Limit for Fast Recovery Process (ppm)	Element	Limit for Fast Recovery Process (ppm)
Iron + Nickel	10,000	Silicon	10,000
Beryllium	19	Carbon	5,000
Chromium	5,000	Zirconium	300
Copper	3,000	Uranium	5,000
Gallium	15,000	Neptunium	20

Several impurities were of concern. For example, iron (Fe) and nickel (Ni) above certain levels could lead to safety concerns in the aqueous Pu recycle processes. Specifically, excess levels of Fe and Ni in the precipitator feed vessel could lead to the autocatalytic degradation of hydrogen peroxide added to precipitate Pu peroxide. Therefore, foundry oxide with excessive amounts of Fe+Ni was categorized as IDC 061 and sent through the slow recycle process. The Fe and Ni impurities were removed from the Pu stream during ion exchange.

An example of how the impurities in the foundry oxide were tracked during the sieving, sorting, and reburning of casting skull is given in Figure D-1. This specific example involved the tracking of carbon (C) and tantalum (Ta) impurities. The classification of the foundry oxides based on the C and Ta impurity level is given in Table D-3.

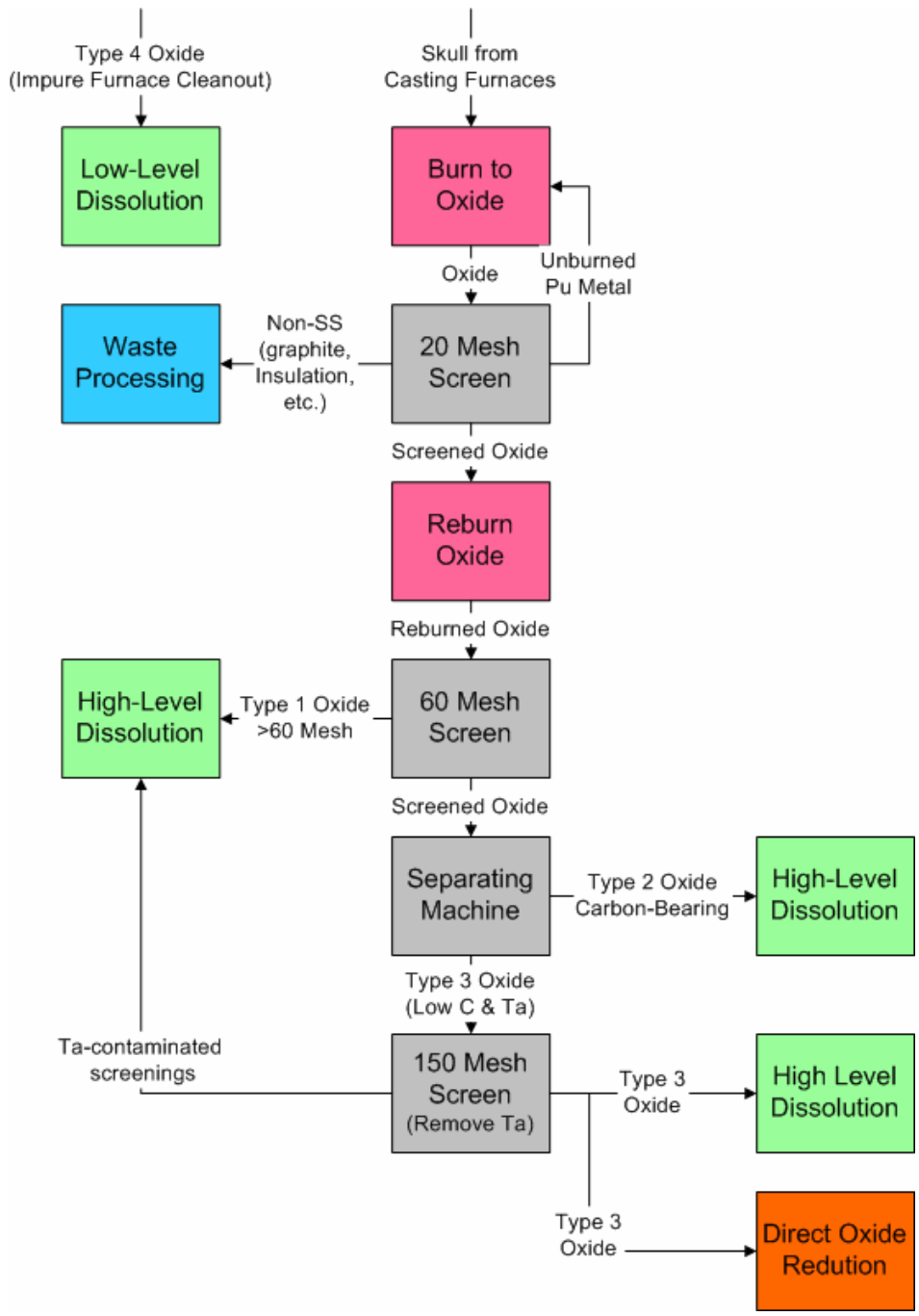

Figure D-1: Foundry oxide process flow.

Table D-3: Characteristics of Foundry Oxide Typs

Type of Foundry Oxide	Carbon (Average ppm)	Tantalum (Average ppm)	Weight % of Each Type
Type 1	3500	3000	10
Type 2	2500	2500	65
Type 3	1500	1000	20
Type 4	5000	3000	5

If the oxide contained high levels of carbon and tantalum (5000 ppm carbon and 3000 ppm tantalum), it was set aside for recovery via the slow recycle process in Building 771 (that is, ion exchange was used for purification prior to precipitation). Oxide with lower levels of carbon and tantalum (1500 ppm carbon and 1000 ppm tantalum) was either dissolved in the fast recycle process in Building 771 (no ion exchange) or used as feed for the DOR process in Building 776.

The DOR process converted high-fired Pu oxide to Pu metal using calcium metal as the reductant in the presence of a $CaCl_2$ molten salt bath. Typical operation temperatures were 800°C to 850°C. Oxide with intermediate levels of carbon and tantalum was sent to the fast recycle process in Building 771 if the other impurities met specifications.

Another source of foundry oxide is the material that accumulates in the casting crucible. The casting furnaces were either tilt-pour furnaces or bottom-pour furnaces. The transfer of molten Pu to the mold using tilt-pour furnaces was not complete, due to the Pu wetting of the crucible and funnel. At a certain point, the accumulated Pu was converted to the oxide using a hot plate. That material was analyzed and, based on the results, was sent to Building 771 or 776 for appropriate processing.

As noted in Figure D-1, there are several screening steps. The material that did pass through the screens was considered “dirty oxide” and contained large amounts of graphite and insulation. Typically, that dirty oxide was sent to waste processing.

To support the storage of Rocky Flats foundry oxide at the SRS K-Area Modified Storage facility, a study was done in 1999 to characterize that material (Murray 1999). That characterization was based on historical analytical data of foundry oxide that was used in a demonstration of the DOR process in Building 776 in 1983. Those analytical data for the foundry oxide coincide in time with the shipments of RFP impure oxide to Hanford: 1984 into 1986. Thus, these data should be representative of the purer IDC 061 and 060 material that were sent to Hanford. These results

also provide an indication of the types of impurities that should be expected in the less pure IDC 061 oxides.

The DOR process was run in the Building 776 pyrochemical production facility during the 1980s. In 1983 there was a DOR production campaign in which foundry oxide was used as the Pu oxide feed. Typically, that foundry oxide was calcined for 6–8 hours at 850°C to prepare it for the DOR process.

Analytical data for foundry oxide from 50 of the first 60 DOR production runs were obtained. Samples were analyzed for the material before and after calcination. Before calcination the Pu oxide was designated as IDC 061 or IDC 060, and after calcination the Pu oxide was designated as IDC 083.

Table D-4 contains the three highest values for the metal species. Those three values for each element demonstrate the diverse nature of the impurities in the foundry oxide. The high values for carbon, magnesium and tantalum are not unexpected, based on the processing equipment and metal feed to the casting operation.

The high value of silver is anomalous and is probably due to a cross-contamination of the analytical standards. Such cross-contamination of silver was occasionally observed. The tables in this appendix contain the analytical data for 44 Pu oxide items used in the first production DOR runs.

Calcination was successful in reducing the carbon levels in the foundry oxide. Figure D-2 shows the carbon analytical data for the Pu oxide before and after calcination. It shows that calcination generally reduced the carbon content between 50% and 98%.

Miscellaneous Oxides

From the revised list of “killed” items, there are 40 items that are grouped as miscellaneous oxide. Those 40 items represent about 3% of the 1,138 items that were “killed.” They are derived from a wide range of IDCs, for many of which only a single item was “killed” at Rocky Flats.

These 40 items fall into three groups. The first group consists of 15 items from IDCs that indicate they are very unlikely to contain Cl salts, including bomb reduction byproduct, DOR feeds, incinerator byproduct, and Pu/U site returns. The IDCs from which these items are derived include 082, 083, 391, 398, 420, and U61. (See Table D-1 for the number of items in each category.)

Table D-4. Maximum Values of Impurities in Foundry Pu Oxide Used in 1983 DOR Production.

	Before Calcination			After Calcination		
Element	Maximum Value	Second Highest Value	Third Highest Value	Maximum Value	Second Highest Value	Third Highest Value
Ag	>1000	500	25	1000	25	<20
Al	1000	144	77	134	98	97
As	<10	<10	<10	<10	<10	<10
B	<10	<10	<10	10	<10	<10
Ba	5	5	5	5	5	<5
Be	5	2.5	2.5	2.5	2.5	2.5
Bi	<5	<5	<5	<5	<5	<5
C	18005	15808	10661	9419	5592	2849
Ca	>1000	>1000	1000	1500	>1000	1000
Cd	<100	<100	<100	<100	<100	<100
Cr	106	100	50	270	207	109
Cu	>1000	1000	500	1000	1000	1000
Fe	2350	700	600	9378	6016	1020
Ge	5	5	2	<2	<2	<2
In	<5	<5	<5	<5	<5	<5
K	>1000	1000	1000	>1000	>1000	1000
Mg	2500	2500	2500	10000	2500	2500
Mn	50	25	10	50	50	25
Mo	100	50	50	>250	250	50
Nb	<100	<100	<100	<100	<100	<100
Ni	500	412	224	9757	9611	1020
P	<100	<100	<100	<100	<100	<100
Pb	>1000	250	250	500	250	250
Pd	<5	<5	<5	15	10	<5
Sb	<2	<2	<2	10	<2	<2
Si	264	153	120	670	243	202
Sn	25	25	10	50	25	10
Sr	<5	<5	<5	<5	<5	<5
Ta	4000	4000	4000	5000	4000	4000
Ti	100	50	10	50	50	25
Tl	<50	<50	<50	<50	<50	<50
V	<5	<5	<5	25	<5	<5
W	1000	100	100	50	50	20
Zn	100	50	50	100	50	50
Zr	10	10	<10	<10	<10	<10

Impurity amounts in ppm. 50 analyses were reviewed. Samples were analyzed for material before and after calcination. Fe analyses for uncalcined Pu oxide by atomic absorption. C analyses by chemistry laboratory. Ta, W, and Zr analyses by emission spectroscopy. Remaining analyses by photoelectric emission spectroscopy.

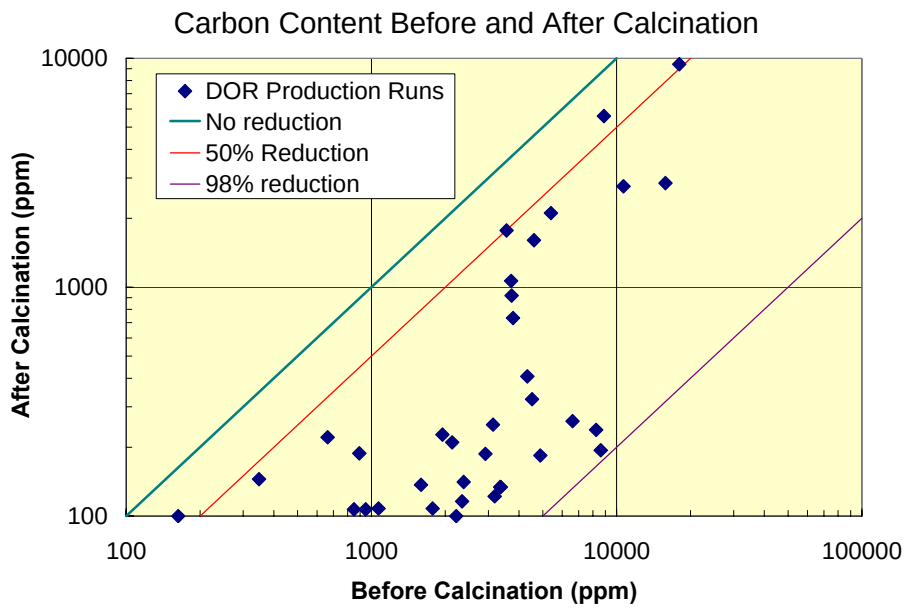

Figure D-2: Carbon content of Rocky Flats foundry oxides before and after calcination.

The IDC 082 item is a product of aqueous processing and is unlikely to have been contaminated with Cl salt. The items from IDC 083 (High-Fired Oxide DOR) consist of pure oxide feed to the DOR process, and would have been free of $CaCl_2$ until it actually entered the process.

The items from IDCs 391 and 398 consist of MgO sand, slag, and crucible fragments and are highly unlikely to have been contaminated with Cl salt. The Pulverized Incinerator Ash (IDC 420) was unlikely to have been contaminated with salts. The U61 site return Pu/enriched Uranium (eU) item, in addition to being recorded as having a very low assay (8 wt % Pu), was unlikely to have been contaminated with Cl salt.

The second category consists of ten items derived from the pyroprocessing and foundry processes described in the previous two subsections and designated specifically for off-site shipment. These are likely to have Cl salt present, but, as described above, are unlikely to have other impurities of concern and therefore may be screened for Cl salt content to determine an appropriate stabilization pathway.

IDCs 046, 053, 054, 056, 059, were material from the other two main categories specifically designated for shipment to Hanford under the Materials Management Executive Committee (MMEC). IDC 146 (LOI Reject) would have been restabilized before shipment until it met the LOI criterion, but was otherwise most likely a foundry oxide or

chlorinated oxide. The IDC 406 (Molten Salt, Unknown % Pulverized) would be comparable to the IDC 067 (Chlorinated Oxide), although probably initially richer in Mg. It would likely be a mixture of actinide and other metal oxides with various Cl salt constituents, but little else.

The third category consists of fifteen items for which the history is less certain. Eight of these have no IDC listed. However, review of the item numbers indicates that most of these are items that failed the LOI measurement and were restabilized (see Table D-3). The likely origin of these materials is given based on review of the originating MBA or item ID. Seven of these items are most likely similar materials to those already discussed.

The other seven items in this category are likely to consist either of oxide with no Cl salt or potentially chloride-bearing oxide with no other impurities except metal oxides. IDC 022 is most likely a metal IDC, and these two items are likely to have been relatively pure material. The five items with IDC 042 and 043 are likely to have been relatively pure experimental items. No processing source for this material has been identified. It could have been generated from foundry operations or from aqueous processing.

Table D-5: Items "Killed" at Rocky Flats With IDC Not Specified

Kill Item	MBA	Comments/Likely Origin
C00407	1375-10 pyro ops	Likely ER-related material, based on MBA of origin
C00142	1375-10 pyro ops	
007221514C01291	1375-80 repack	Probably IDC 061, based on identical item with different stacker can number
CRHO111	Not specified	Appears to be a recycle of "ORHO" items created for shipment, likely to be 061 or 067 oxides, based on makeup of whole lot
CRHO116	Not specified	
CRHO71	Not specified	
008355C04365	Not specified	IDC 061 or 060 based on Item ID
9896C05609	Not specified	

Once the items described above as unlikely to cause a problem during PGA screening and subsequent stabilization are removed from the list of "killed" items of miscellaneous origin, there are only five items (one unknown IDC and four from IDCs of uncertain description) of uncertain origin that might possibly have been sent to be packaged for shipment to Hanford. These five items would have all been screened and calcined at >400°C at least once before shipment.

The technical team considers it unlikely that any of these items contained Cl salts in quantities above 1 wt % and also contained a constituent that would

1. survive 750°C stabilization as well as previous high-temperature stabilizations, but
2. would not survive 950°C stabilization, and
3. would subsequently generate significant volatile and/or corrosive species at <300°C.

Appendix E: Stabilization of Chloride-Bearing Oxide at PFP

Introduction

This appendix summarizes two suites of experiments performed at the Hanford site to examine the potential risk of processing chloride-bearing Pu oxides at PFP. The first suite consisted of experiments on chloride-bearing surrogate material that were conducted at PNNL (Schmidt 2003). The second suite was conducted at the PPSL, and also consisted of experiments on surrogate material. Both series of tests were conducted using cold mockups using the same model muffle furnace, controller, boat, and similar off-gas system as used in the RMC line. Operating parameters such as ramp rate, airflow, charge size, and so forth, were the same as RMC operation. Before testing was performed at stabilization temperatures lower than nominal 950°C to 1000°C, engineering calculations were performed to assess the potential magnitude of decreased salt evaporation.

The results of the engineering calculations demonstrate that almost a 25-fold decrease in salt evaporation is obtained by lowering the stabilization temperature 200°C. The mass of salt removed from the furnace also should decrease if sweep gas throughput rates are decreased. The results of the laboratory testing at PNNL confirm the relative magnitude of the calculated salt evaporation decrease and show the additional benefits in materials performance and decreased formation of corrosive hydrogen chloride (HCl) gas caused by the pyrohydrolytic reaction of water vapor from humid air with the hot Cl salts. Findings from the testing at the PPSL, although more qualitative in nature, are consistent with the PNNL results and further demonstrate corrosion difficulties encountered due to HCl.

Engineering Calculation of Salt Evaporation

Washing operations to remove soluble salts are time- and dose-intensive and may produce wash waters requiring subsequent treatment to remove dissolved Pu. Furthermore, even with multiple water washes, the quantity of residual salt volatilized in 950°C thermal processing still may exceed the quantity of salt volatilized by 750°C processing without washing. Accordingly, engineering calculations were made to estimate salt quantities that might be expected to evaporate during thermal stabilization operations, based on nominal operations with target 1000°C and 800°C oxide bed temperatures. This section presents the technical bases, and calculation results for engineering calculations are based on salt vapor pressures, some assumptions about salt melt behavior, and nominal process flow sheet conditions.

Salt vapor pressures

The Cl salts used at RFP in various pyrochemical processes (and present in impure oxide shipped to the PFP) are primarily NaCl and KCl, with some potential for $MgCl_2$ and $CaCl_2$. All four salts have melting points between about 710°C and 800°C. The first three salts have similar vapor pressures, with $CaCl_2$ being much less volatile (Stull 1947, Stull and Prophet 1971, and Novikov and Gavryuchenkov 1964). The salt vapor pressure and melting-point data are depicted in Figure E-1, as are equations describing the salt vapor pressures as functions of the temperature.

Rocky Flats used minor amounts of $MgCl_2$ in ER and larger amounts in MSE processes to purify Pu metal. The ER salt is nominally an equimolar mixture of NaCl and KCl with ~4–5 wt % $MgCl_2$ added (Boak et al. 2002). The $MgCl_2$ was added to oxidize a portion of the impure Pu metal at the anode to Pu^{+3} for its transport through the molten salt and electrodeposition as purified metal at the cathode. The ER processing and subsequent thermal stabilization operations of the ER oxide cause the $MgCl_2$ to convert first to metal (Mg) and then be air oxidized to form MgO. Similar reactions produced MgO from the $MgCl_2$ in MSE oxide. Therefore, little $MgCl_2$ is expected in the ARF items. The $CaCl_2$, used primarily as a flux in direct oxide reduction, has low vapor pressure and thus should not evaporate to cause salt deposition problems during PFP thermal stabilization processing. The strongly hygroscopic character of

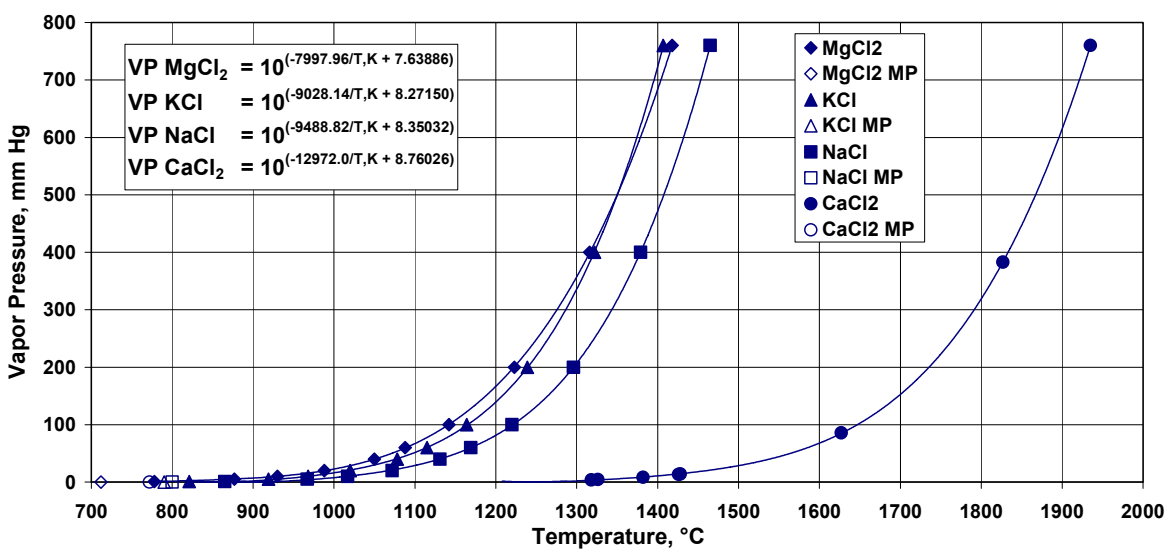

Figure E-1: Cl salt vapor pressures as a function of temperature. See also Figure 1 in the main document.

$CaCl_2$ and its reaction with water during thermal stabilization to produce corrosive HCl gas still pose significant processing challenges. However, the salt volatilization and downstream deposition problems attendant to thermal stabilization of ARF Pu oxide items at the PFP would largely be due to NaCl and KCl.

Data on the vapor pressures of the individual NaCl and KCl salts in NaCl/KCl mixtures were not found in the technical literature. However, assuming that molten NaCl/KCl forms an ideal solution, the vapor pressures of the individual NaCl and KCl salts (P_{NaCl} and P_{KCl}, respectively) in a mixture of the two salts would be proportional to each salt's mole fraction (x_{NaCl} and x_{KCl}, respectively) according to Raoult's Law, that is:

$$P_{NaCl} = P_{NaCl}^{0}\, x_{NaCl}$$

$$P_{KCl} = P_{KCl}^{0}\, x_{KCl}$$

where P_{NaCl}^{0} and P_{KCl}^{0} are the vapor pressures of the pure salts. For the equimolar NaCl/KCl mixtures used in the ER and MSE processes, the vapor pressures of the individual salts, therefore, would be half those of the respective pure salts.

PFP process operations

During thermal stabilization processing in muffle furnaces at the PFP's RMC line, air flow rates of 1 standard cubic foot per minute (scfm) are used to guarantee the oxidizing conditions demanded by the 3013 standard. In practice, air-flow rates as low as 0.25 scfm could be used, according to plant practice. The air flow is achieved by drawing air through a pipe in the back wall of the furnace, with fresh air entering around the front-facing furnace door.

The following thermal stabilization furnace heating program is used at PFP's RMC line:

1. heat from room temperature to 500°C at 300°C/hour,
2. heat from 500°C to 700°C at 200°C/hour,
3. heat from 700°C to 900°C at 125°C/hour,
4. heat from 900°C to 1000°C at 75°C/hour,
5. hold at 1000°C for 2 hours (PFP uses 1000°C to guarantee meeting the 3013 standard's 950°C requirement), then
6. shut off heat and cool by continued air flow at 1 scfm.

A similar heat-up profile would be expected if a lower thermal stabilization temperature were adopted with a similar 2-hour hold at the target temperature. The furnace cooling profile to 600°C may be gathered using observations from recent furnace testing conducted at PNNL (Fischer et al. 2002).

Engineering calculations

The maximum quantity of salt evaporated during the thermal stabilization processing was estimated based on the following assumptions:

- one-scfm air-flow rates are maintained,
- air becomes saturated with the respective NaCl and KCl salts according to the individual pure salt vapor pressures and their 0.5/0.5 mole fractions according to Raoult's Law, and
- the salt composition remains at 0.5 NaCl/0.5 KCl (that is, evaporation does not alter the molten salt composition—effectively, an "infinite" source of salt).

Note that a 1-scfm flow rate is equivalent to ~4.3 cubic feet per minute at 1000°C.

Based on these assumptions, the mass-loss rates of NaCl and KCl as a function of temperature were calculated. Results (Figure E-2) show that significant evaporation occurs only above ~750°C. This behavior is consistent with observations made in thermogravimetric testing of genuine ARF items (Delegard and Bouse 1985, Morales et al. 2002). The mass-loss-rate data also show that KCl evaporates about two times faster than NaCl. Therefore, the residual salt would become enriched in NaCl as thermal processing proceeds. Though not shown in the figure, the salt evaporation rates would decrease in proportion to the throughput air sweep gas rate.

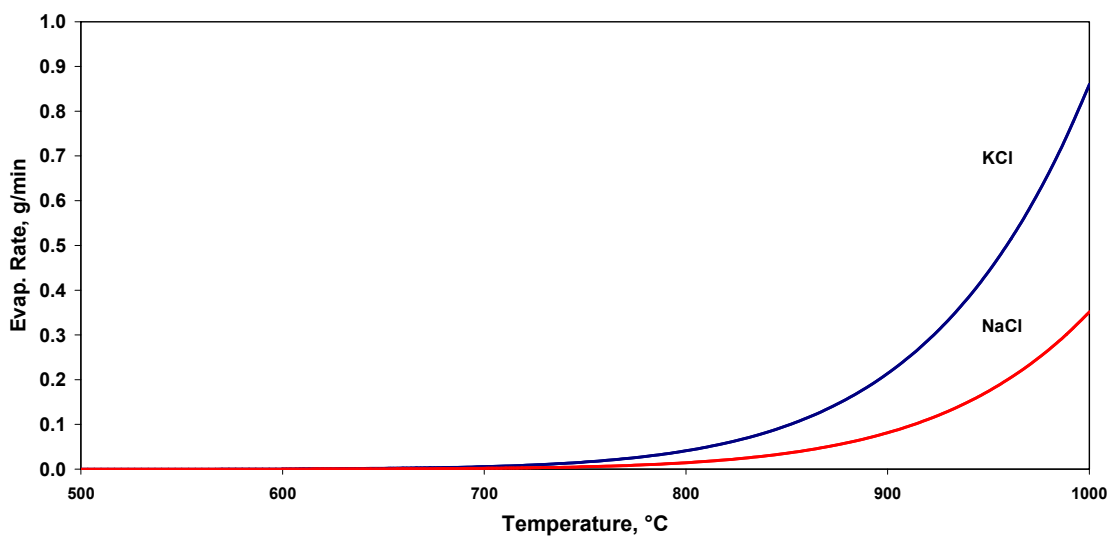

Figure E-2: Salt evaporation rates as a function of temperature at 1 scfm.

The total quantities of salt evaporating according to thermal stabilization programs run with target 2-hour dwells at 1000°C and 800°C are predicted, as shown in Figure E-3. According to these predictions, unlimited by salt availability in the stabilization boat or salt diffusion from the oxide bed, about 160 g of KCl and 64 g of NaCl would evaporate during a 1000°C thermal stabilization cycle. In comparison, thermal stabilization to 800°C would evaporate a predicted 6.6 g of KCl and 2.3 g of NaCl, about a factor of 25 lower than predicted in the 1000°C processing.

Assuming that salt evaporation is not limited by diffusion from the bed, but only by availability and vapor pressure in the sweep gas, salt quantities in water-washed feed stabilized at 1000°C would have to be lower than 6.6 g KCl and 2.3 g NaCl to be an improvement over 800°C processing of unwashed oxide. For a 2 kg oxide charge in the boat, this salt loading is equivalent to 0.44 wt % salt or ~0.23 wt % chloride. The thermal stabilization cycle also would be 174 minutes (about 3 hours) shorter at 800°C than at 1000°C, with 128 minutes saved on the heating and 46 minutes on the cooling segments.

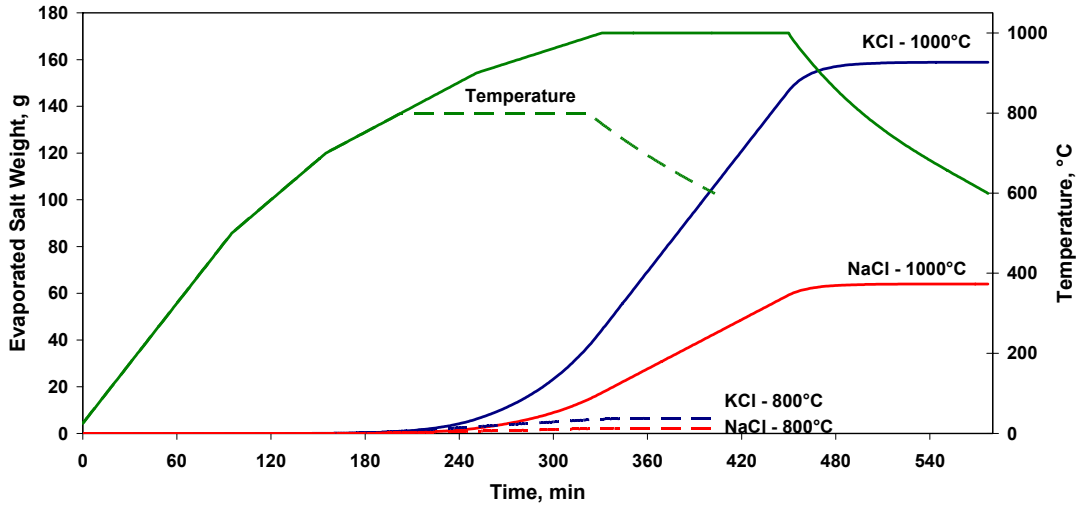

Figure E-3: Predicted salt evaporation for 800°C and 1000°C process profiles.

Surrogate Material Furnace Experiments

The present plan for processing chloride-bearing Pu oxides includes water-washing to remove Cl salt to <1 wt % total salt before thermal stabilization to mitigate corrosion problems and lessen concerns about moisture reabsorption in the RMC line furnaces at PFP. Fifty cycles of furnace tests with simulated chloride-bearing Pu oxides, at 1 wt % total salt, were conducted at the PNNL to examine system vulnerabilities in the RMC furnaces under baseline thermal stabilization conditions (2 hr at 1000°C) and to develop and validate system improvements (Fischer et al. 2002). The methods of preparation of the surrogates varied slightly. For the high-temperature tests on washed stimulant, the salts were sprayed on, mixed thoroughly and dried slowly at low temperature to represent what is expected from washed material.

The tests by Fischer and colleagues showed that, at a 1 wt % Cl salt loading, most of the Cl salts were removed during thermal processing, and consequently resulted in corrosion to off-gas lines and deposition/plugging in cooler downstream off-gas lines, as well as off-gas filters. Even with the improvements to the process equipment, the system had to be shut down for line cleaning and filter replacement every three to five cycles.

Four subsequent furnace tests were conducted at 750°C to develop material balance and system operability data to support the evaluation of lower-temperature thermal stabilization. For each test, a process boat was loaded with simulant (CeO_2 for PuO_2) that represented a 2000-g chloride-bearing Pu oxide charge containing 20 wt % Cl salt (that is, 1600 g PuO_2 + 400 g Cl salt).

The unwashed simulants used in these lower-temperature tests were not prestabilized like the actual materials, which would have mostly been stabilized at least once at ~450°C. For experiments involving only the NaCl/KCl mixtures, no difference would be expected, as the 450°C prestabilization step would not affect that mixture. For experiments involving the NaCl/KCl/$MgCl_2$, the prestabilization step would be expected to result in some decomposition of the $MgCl_2$ component. The surrogate experiments on these mixtures might be expected to represent worst-case, as the majority of salt volatilization, corrosion, and plugging is likely a result of this $MgCl_2$ decomposition.

The loaded boat was placed in an RMC line prototypical furnace system, and the charged furnace was ramped to and held at 750°C for 2 hours. Air flow through the furnace (room air at 20% to 40% RH) was maintained at 1 scfm. Results from the 750°C testing were compared with previous results from furnace testing using the same test apparatus but conducted at 1000°C with simulant that contained 16–20 g of chloride salt per charge

(that is, simulant represented washed chloride-bearing Pu oxide items containing 1 wt % residual Cl salts).

The Cl salts present in the chloride-bearing Pu oxide items pose considerable challenges to stabilization, because volatile Cl salts and decomposition products (that is, HCl) can corrode furnace heating elements and downstream ventilation components. In the cooler zones of the ventilation system, the Cl salts can condense and blind filters or plug the off-gas lines. As shown in the engineering calculations (previous section), Cl salt vapor pressures are about 25 times higher at 1000°C than at 800°C, and pyrohydrolysis reactions (reaction of water vapor with Cl salt to produce HCl) occur more readily at higher temperature. Therefore, processing at lower temperatures can potentially decrease the deleterious effects of the Cl salts.

The complete test findings are summarized in a separate report (Schmidt et al. 2003). The following conclusions, derived by comparing results from the 750°C/20 wt % salt (unwashed) and 1000°C/1 wt % salt (washed) tests, show the operational benefits in the lower-temperature processing without washing:

- Less than 0.9 g (0.5 wt %) of the Cl salt was volatilized into process equipment by 750°C processing of a simulant containing 400 g of NaCl and KCl. In contrast, 6.9 to 8.5 g (65% to 99%) of the Cl salt were volatilized in 1000°C processing of a nominal washed simulant containing 16 to 20 g of NaCl and KCl. Table E-1 summarizes the comparisons between the two series of tests.
- For the same experiments, 0.39–0.72 g of HCl (generated by pyrohydrolysis of the NaCl/KCl by the humid purge air) were produced from 400 g of salt at 750°C, less than the 0.82 g of HCl produced from only 16–20 g of salt at 1000°C. This comparison is based on analysis of the scrubber water and chloride balance calculations.
- Less corrosion and salt deposition in off-gas lines occurred in the four tests with 20 wt % Cl salt at 750°C (that is, 1600 g of Cl salt in the four tests) than in a single test with 1 wt % Cl salt at 1000°C (that is, 16–20 g of Cl salt).

Table E-1. PNNL Test Results

Cycle No.	Furnace Hold Temp., °C	Chloride Salt in Simulant		Mass of Chloride and Chloride Salt Lost from Simulant in Boat		% of Chloride Removed from Boat	
		Mass in Charge, g	Mole ratio, $NaCl:KCl:MgCl_2$	Grams per Charge [(a)]	As % of Chloride Salt in Charge[(b)]	Chloride Chemical Analysis[(c)]	Based on Chloride Recovered[(d)]
51	750	395.2	50:50:0	1.22	0.309	[Note e]	0.34
52	750	395.3	50:50:0	1.36	0.344		0.42
53	750	396.7	45:45:10	14.62	3.69	13.2	6.97
54	750	396.3	45:45:10	15.40	3.89		7.25
2-7	1000	16	45:45:10	15.6*	No data	97.5	No data
9 (front)	1000	16	45:45:10	15.7*	No data	98.4	No data
9 (back)	1000	16	45:45:10	15.6*	No data	97.6	No data
34	1000	20	45:45:10	16.6	83	No data	No data
35	1000	20.1	45:45:10	16.5	82	66.3	No data
36	1000	20.1	45:45:10	20.0	99.7	72.4	No data

(a) Values from Cycles 51 through 54 taken from Table 1. Values marked with * were determined based on chloride analyses and by assuming chloride and chloride salt losses are proportional.
(b) = 100% x *Mass of Chloride and Chloride Salt Lost from Simulant in Boat (g/charge)* divided by *Chloride Salt in Simulant*.
(c) Values based on measured chloride (ISE) content in feed simulant and calcined simulant.
(d) Values based on recovery of chloride from materials collected in the filter, filter housing, scrubber water, and condensate (see Table 1).
(e) Due to analytical uncertainty introduced in sample preparation and ISE analyses, and the very small difference between the feed and calcined sample, no measurable difference in chloride content was found between the feed and calcined material.

- At 750°C, severe corrosion was confined to the materials in direct contact with the high-salt-content simulant (boat, metal coupon, and thermocouples); at 1000°C, severe corrosion was noted in off-gas lines as well.

In summary, the low-Cl salt removal and subsequent reduced corrosion to the off-gas lines at 750°C can largely be attributed to the significantly lower vapor pressure of the Cl salts and the reduced rate of pyrohydrolysis reactions at 750°C vs. 1000°C.

Specific key findings from the furnace testing at 750°C are summarized below, with respect to material balance, operability, and moisture uptake.

Material balance

- Less than 0.5 wt % of the Cl salt and <0.1 wt % of the initial simulant mass (~1.4 g) was removed while processing the NaCl/KCl simulant at 750°C. Of the Cl salt recovered in the off-gas system, about 75% to 80% was captured in the wet scrubber and the condenser, both located downstream of a 5-µm filter. Approximately 80% of the Cl salt in the wet scrubber was derived from HCl generated from the simulant in the furnace, presumably due to a reaction (pyrohydrolysis) between the alkali Cl salts and the moisture in the furnace sweep gas. This estimate is derived from analysis of the scrubber water and Cl salt balance calculations.
- About 7% to 13% of the Cl salt in the charge was removed while processing the NaCl/KCl/$MgCl_2$ simulant at 750°C. Most of the Cl salt removal was from the decomposition of $MgCl_2$ in moist air, resulting in the release of HCl. Based on mass balance data, approximately 40% of the $MgCl_2$ in the feed simulant decomposed to produce HCl, which was removed from the simulant in the boat, and MgO, which was retained in the boat. $MgCl_2$ decomposition continued during furnace cooling. About one-third of the HCl in the scrubber was captured while the furnace cooled from 750ºC to 400ºC. Results from x-ray diffraction (XRD) analyses support the conclusion that some $MgCl_2$ remained in the simulant after processing at 750ºC. This result is unusual in that fully molten salt of this composition should not have crystallized $MgCl_2$, but either $KMgCl_3$ or Na_2MgCl_4, as noted by Boak et al. (2002).
- The effects of the presence of $CaCl_2$ in chloride-bearing Pu oxides were not evaluated as part of the current furnace testing. However, previous work included limited furnace testing with a simulant containing 34.5 wt % $CaCl_2$ in CeO_2 that was calcined at 750°C for 2 hours before using the material in washing tests (Silvers 2002). Based on chemical analyses and evaluation of the data, it was estimated that between 2 and 6 wt % of the $CaCl_2$ was pyrohydrolyzed to CaO and HCl during the stabilization at 750°C for 2 hours. This finding suggests that the extent of pyrohydrolysis of $CaCl_2$ will be between that of NaCl/KCl and $MgCl_2$.
- XRD analysis of the calcined material identified significant quantities of binary sodium/potassium Cl salts.
- In the tests with the NaCl/KCl/$MgCl_2$ simulant, significant quantities (5 to 10 g per test) of hydrated iron and nickel chloride compounds accumulated in the filter housing and on the filter. As there was no evidence of corrosion to the filter housing or filter, the iron chloride

compounds most likely originated in the furnace (generated from reactions between simulant, moisture, and boat/metal coupons) and were transported to the filter as vapor. In these tests, very little iron was collected in the wet scrubber.

- The mass of material removed from the boat while processing 20 wt % $NaCl/KCl/MgCl_2$ simulant at 750ºC was comparable to the mass lost when processing 1 wt % chloride salt at 1000ºC under otherwise similar conditions.

Operability

- During the 2-hour hold time, the temperature of the material in the boat was 50ºC to 120ºC higher than the furnace control thermocouple (750ºC). Thus, little incentive or justification exists to control the furnace at a temperature higher than 750ºC.
- While processing 20 wt % NaCl/KCl simulant at 750°C, corrosion and plugging of off-gas lines were minimal, and very little material was collected on the filter. It is estimated that more than 10 batches of such material could be charged to the furnace before shutdown is required to clean or replace off-gas lines or filters. The extent of corrosion to the Hastelloy X boat was similar to that experienced while processing 1 wt % Cl salt at 1000°C.
- The Hastelloy X boat and the metal coupons (RA602CA and Inconel 690) experienced severe weight loss due to corrosion while processing the 20 wt % $NaCl/KCl/MgCl_2$ simulant at 750°C. However, the severe corrosive attack was confined to materials in direct contact with the simulant (that is, boat, thermocouples, and metal coupons). Significant quantities of material (alkali chlorides and hydrated nickel and iron chlorides) did accumulate in the filter element. It is estimated that three to five batches of composition like the $NaCl/KCl/MgCl_2$ simulant could be completed before blinding the filter element.
- The cumulative extent of corrosion and salt deposition within the off-gas lines during the four tests conducted with 20 wt % Cl salt at 750ºC was less than that experienced in a single test with 1 wt % Cl salt at 1000ºC.
- The high-salt loading resulted in the creation of brick-like calcined products. A hammer and a screwdriver were needed to chip the calcined material out of the boat after processing the NaCl/KCl simulant. The thermally-processed $NaCl/KCl/MgCl_2$ simulant was more friable and was removed by inverting the boat, then dropping the boat down several inches onto a hard surface.

- In the test system used, HCl was largely removed from the off-gas stream in the wet scrubber and chilled condenser. Post-test rinsing of off-gas lines downstream of the scrubber was performed to remove any HCl. At the PFP, engineering and operational controls will likely be required to minimize the potential for HCl condensation and subsequent Cl salt-induced pitting and stress corrosion cracking in the off-gas line components.
- Intake air flow (at ambient humidity in the RMC) should be maintained at the minimum rate to guarantee oxidizing conditions required by the 3013 standard, while minimizing water vapor and the resulting pyrohydrolysis reactions that form HCl.

Postcalcination moisture uptake testing

- Moisture uptake testing was conducted by reheating (to 250°C and 500°C) the feed and calcined samples from the 750°C furnace tests and then placing the samples in a controlled humidity chamber (51% RH).

In general, samples from the NaCl/KCl simulant only gained about 0.1 wt % after 24 hours in the controlled humidity chamber. Samples from the NaCl/KCl/$MgCl_2$ simulant that were crushed and screened to <1/4 in. (6.35 mm), the current PFP process specification, gained ~0.5 wt % after 8 to 10 hours, whereas a sample that was screened to <16 mesh (1 mm) gained ~0.5 wt % after only 2 hours. The CeO_2 used in the simulants exhibited a very low moisture uptake capacity. Moisture uptake rates for actual chloride-bearing Pu oxide items (containing the same Cl salts) would likely be slightly higher, given the moisture uptake behavior of PuO_2 calcined at 750°C.

Summary of Salt Vaporization Testing in PPSL

Five experimental tests were performed at the PPSL of the PFP to determine the effects of changing the thermal stabilization temperature from 1000ºC to 750ºC for chloride-bearing Pu oxide. Tests were performed using ceria (CeO_2) as a PuO_2 simulant and containing 50:50 (mole basis) NaCl:KCl salt. The first three runs had 1 wt % Cl salt and 750ºC stabilization temperature. The fourth run had 20 wt % salt at 750ºC. The fifth run used 20 wt % salt at 1000ºC. All tests used Hastelloy X furnace boats that had been oxidized previously at 1000ºC.

The thermal stabilization furnace, the pleated Rosemount off-gas filter, and the ribbed 1-inch flexible stainless steel tubing section used in the tests were of the same design as those in the RMC thermal stabilization line. In this arrangement, glove box air (at 1.0-scfm gas-flow rate) is drawn into the furnace around the furnace door, to the off-gas filter, and

then to a flex line section. In the RMC line, the gases are vented to the exhaust plenum. The test system, however, had a process water-cooled heat exchanger downstream of the flex line that the production furnaces do not have. A rotameter downstream of the heat exchanger was used in the test apparatus to monitor the gas-flow rate. The inlet air was normal PFP room air, which runs about 20% RH this time of year.

These initial tests revealed a weakness in the current design involving the newly installed corrugated stainless steel flue hose. The relatively thin-walled section was found to have failed due to pinhole corrosion after the first three runs. A replacement flex line used only in Run 4 was found to leak after the run, even though it successfully held air at 80 psi before installation. A second replacement flex line, used for Run 5, is expected to have numerous small holes based on gas-flow control observations. The current and continuing effort has focused on the use of a chemical adsorbent to scrub the off-gas by removing the volatile Cl salt to extend the service life of the flex line.

The off-gas lines and filter did not plug during any of the runs. After the first four runs, the filter and lines had only thin powder coatings, the filter medium was not visibly corroded, nor was any evidence of corrosion found at the outlet end of the filter. The filter used in Run 5 showed significant deposition of material when opened and inspected.

Small amounts of green liquid were observed when the off-gas lines were opened after three runs. The fourth run left no liquid deposit anywhere, despite having a much higher salt content in the powder bed. Run 5 resulted in significant liquid deposition in the off-gas system, with a greenish liquid clearly visible in the off-gas rotameter. The humidity of the intake air was insufficient to cause condensation in the system, even downstream of the water-cooled heat exchanger. The liquid is believed to have been formed by the deliquescence of hygroscopic reaction products resulting from reaction of the boat metals and the salt mixture, such as iron, nickel or chromium chloride. As such, the rate of formation of these reaction products would be greater at the higher temperature.

The Cl salt quantities vaporized in these runs cannot be determined with absolute certainty due to error introduced by the other mechanisms for weight loss, such as driving off chemically bound moisture, by powder spills while moving the boat in and out of the furnace, or by inserting and removing thermocouples from the powder bed. The boat could gain weight by oxidation of the boat or the test thermocouples. Nonetheless, runs 1–4 had total weight losses of <0.2% of the starting powder weight. Run 5 lost 2.0% of the powder's starting net weight.

Powder bed temperatures exceeded the control temperature at the thermocouple in the furnace air space in all cases.

Conclusions that may be drawn from the studies to date include the following:

- Lower stabilization temperatures will reduce the amount of Cl salts vaporized during stabilization.
- Lower stabilization will lessen the amount of off-gas deposition, plugging, and corrosion.
- Powder temperatures exceed the furnace temperature at 750°C and 1000°C.
- The new flex line sections represent the weak spot in the off-gas system and justify the efforts to employ an absorber/scrubber to protect this component from failure and protect downstream components.

Appendix F: Alternative Stabilization Methods

Introduction

There are 939 items bearing the "ARF" item designation remaining in the PFP inventory. These items were received from Rocky Flats in the period 1984–1986. The RFP used pyrochemical processes involving molten Cl salts (NaCl, KCl, $MgCl_2$, and $CaCl_2$). Based on prior analyses of similar materials, it is estimated that one half to two thirds—and potentially more—of the 939 items contain >1 wt % Cl salt.

At these concentrations, the Cl salts, if not removed prior to 950°C stabilization or thermally stabilized at lower temperature, will vaporize and condense in the off-gas line and are likely to cause corrosion in the furnace and off-gas line and plugging of the off-gas line and filter. In addition, certain Cl salts in the stabilized Pu oxide are hygroscopic and, even if thermally stabilized, may challenge the DOE-STD-3013-2000 moisture criterion if processed in the ambient humidity conditions of the PFP RMC line.

Options for processing the high-Cl salt items were evaluated by the PNNL (Silvers 2000b) and included the following:

- stabilize the material in the SPE furnaces using a protective shroud and quench system,
- stabilize the material in the RMC line furnaces using additives to reduce Cl salt volatilization and moisture absorption,
- use the existing precipitation equipment in room 230C to wash out the Cl salts,
- use a ball mill wash system to remove the Cl salts, and
- use the Russian "salt washer" centrifuge to wash out the Cl salts.

The PNNL study was prepared prior to the acceptance of the technical equivalency arguments made for Rocky Flats (Boak et al. 2002), and thus did not consider the option of using lower stabilization temperature. The PNNL evaluation concluded that washing the items in the Room 230C glove boxes using the precipitation columns was the best option. Water washing of the high-Cl salt items therefore became the baseline process for addressing the problems attendant to the presence of Cl salt.

Preparations and facility modifications have been made to implement the Cl salt wash process in glove boxes HC-230C-3 and HC-230C-4 in room 230C of the 234-5 building at the PFP. Certain modifications to the thermal stabilization furnaces in glove boxes HC-21A and HA-21I also will be made to allow stabilization of the high-Cl salt items at 950°C after washing or at lower temperature without washing. The Cl salt wash project interfaces with the thermal stabilization furnaces, the 241-Z waste tanks, the E4 ventilation system, plant water, plant air, and plant electrical

power. The design and features of the washing system being installed in the PFP to process the chloride-bearing Pu oxide items are described in this section.

Process Description

The Cl salt wash process will use the $Mg(OH)_2$/oxalic acid precipitation equipment located in room 230C of the 234-5Z building at PFP. The equipment includes three criticality-safe glass columns, a pan filter, drying hot plates, a phase separator, polishing filters, a vacuum system, and filtrate tanks. The Cl salt washing will be done in the three glass columns that were previously used for precipitation.

The inventory items in slip lid cans will be transferred into glove box HC-230C-3 via the conveyor system. The column to be charged will be filled with approximately 10 L of fresh wash water. Each can will then be opened and the contents poured into the top of the column. The contents of up to two additional items will be added to the column in the same way.

The column will be sparged for about 20 minutes with pressurized air introduced at two points in the column bottom cone to mix the column contents and dissolve the Cl salts. The columns may be sparged with the lids removed, since the vacuum system is not designed to handle the total volume of air sparge if more than one column is sparged at one time.

After the sparging is completed, the solids will be allowed to settle and the supernatant wash water will be decanted to the pan filter. The initial Cl salt concentrations of the feed materials are unknown. Based on prior analyses and wash testing with surrogate materials, from 1 to 4 wash cycles will be required to reduce the Cl salt content to a level that will allow the material to be stabilized in a furnace.

To determine the number of wash cycles required for any particular item, the Cl salt concentrations in the wash solution will be monitored by conductivity sensors lowered into the columns. The sensors will send a signal to a transmitter/indicator that can be read by the operators and converted to percent Cl salt in the washed solids. If the sensors indicate high residual Cl salt, additional fresh water will be added to the column and the sparge/decant/conductivity cycle repeated. All washes will be performed using fresh water.

Once the Cl salt concentration reaches satisfactorily low levels, the water from the last wash will be partially decanted, leaving sufficient water to provide a slurry consistency that is easily drained from the bottom sparge line in the column bottom to the filter pan. A pressurized air sparge at the second sparge line will suspend the solids while draining to keep the slurry fluid. The water that drains to the pan filter with the solids will be vacuum

transferred to the phase separator (TK-004). The cake collected on the pan filter is expected to contain 55 to 60 wt % solution when it is transferred to the furnace boat for drying on the hot plates.

The filtered solids will be manually transferred to the filter boats and dried on the hot plates in a manner similar to the way it was done for the $Mg(OH)_2$/oxalic acid precipitation process. The solids will be raked and stirred to accelerate drying. Once the solids are dry, the boats with dried solids will be transferred by the conveyor system to the muffle furnaces in glove boxes HC-21C and HA-21I for thermal stabilization.

There is not a precise determination of moisture content after the hot plate step; duration is set by procedure. Solids temperatures up to about 200°C are attainable. Residual moisture is estimated to be about 20% to 30%, based on measurements made before and after drying on washed items processed to date. A low-temperature soak is used in the washed product furnace cycle to allow the moisture to be released before the onset of salt evaporation. The completeness of water removal during the hot plate drying step is not known.

The filtrate from the pan filter will be pumped through bag filters to the filtrate tanks in glove box HC-230C-4. The filtrate will be sampled for analysis of Pu, Am, and Cl concentrations as a minimum. The solution then will be drained to TK-D8 in the 241-Z facility for ultimate disposal to the Hanford underground waste storage tank system or into drums filled with absorbent for disposal as solid waste.

The criticality limit for each column will need to be raised to 2500 g Pu prior to the start of Cl salt washing to allow two to three items to be added to each column. The amount of Pu allowed in the HC-230C-3 and HC-230C-5 glove boxes will be increased to 24 kg to accommodate the increased processing rate. The Pu oxide charged to the columns will remain as Pu oxide during the washing process. However, there may be some small Pu metal particles in a few of the items. Some Pu metal may react with the water to form $Pu(OH)_4$ and hydrogen gas, which will be diluted to less than the flammability limit by the sparge air.

Processing of the high-Cl salt inventory is scheduled to start in April 2003 and be completed December 31, 2004. At completion, all the Pu oxide will be packaged into bagless transfer can containers to meet DOE-STD-3013-2000 packaging requirements (DOE 2000). Each of the five thermal stabilization furnaces in the 234-5 building must stabilize one furnace boat of Pu oxide per day to meet the schedule for completing Pu stabilization at PFP. The Cl salt wash equipment must process at a rate of nine items per day to supply five boats (each containing ~2000 g Pu) per day for thermal stabilization.

Comparison of Processing Methods

The current baseline plan (described in Section 3 and this appendix) involves water washing to remove Cl salts, followed by thermal stabilization of the washed product at 950°C. Stabilization at 950°C without washing to remove the Cl salt component may result in frequent furnace and equipment failure resulting in excessive operator exposure, unacceptable delays to the stabilization schedule, and unnecessary exposure to operations and maintenance personnel. This certainty of equipment failure from stabilization of the Cl salt materials at 950°C is well documented in tests done by PFP, PNNL, LANL, and limited processing at Rocky Flats (Schmidt et al. 2002, Compton 2000, Boak et al. 2002; Appendix I of this document) and has led to the decision to use the wash process to reduce Cl salt levels before stabilization.

However, even washing to reduce the Cl salt content to the target levels of <1%, will not certainly eliminate furnace and off-gas operability issues. Developmental testing has shown that frequent maintenance will still be required. Furnace off-gas filters were plugged and off-gas piping was corroded after about five runs (Fischer et al. 2002). Design changes made as a result of this are expected to extend maintenance intervals (filter change out, off-gas piping change) to about every 15 charges. Modifications have been made to the existing furnaces to allow rapid component change out. By comparison, the amount of salt expected to be vaporized at 750°C, even in unwashed feed is expected to be at least 10 times less than that expected to be vaporized in materials washed to <1% chloride and stabilized at 950°C.

The major work elements for both options are described in Table F-1. Based on these work elements, differences in approximate cost (Table F-2) and worker exposure (Table F-3) are estimated. As wash equipment will still be installed and used on some materials, at least those <50 wt % Pu, no equipment/engineering cost saving can be realized if the wash process is eliminated. However, elimination of operating expense for the wash process can be realized. The resultant benefits are greater if a larger fraction of the material is chloride-bearing.

Table F-1: Comparison of Work Elements

Element	Wash/Calcine at 950°C	Calcine at 750°C
Prompt gamma screen	Each feed item (900 total)	Each feed item (900 total)
Wash batches	225 batches (one half of total, two feed items/batch)	None
Filtrate collection and sample	520 filtrate batches and sample analysis (5,200 L total and 10 L/filtrate tank)	None
D-8/D-7 batches, sample, transfer to tank farms	One waste tank batch, sample and transfer to tank farms	None
Hot plate cycles	225 hot plate cycles (2 feed items/cycle)	None
Furnace charges	225 furnace cycles (2 feed items/ cycle)—slightly longer cycle time to ensure all entrained wash water is removed.	225 furnace charges (2 feed items/cycle)—slightly shorter cycle time from shortened ramp time to 750°C
Filter changes and off-gas line replacement	15 total (every 15 furnace cycles)	2–3 total (every 100 furnace cycles) (10 times less salt lost to vapor phase)
Boat unloading/stabilized product size reduction	All material is screened prior to packaging after removal from boat	Some fraction of boats may be difficult to unload and require additional effort for size reduction of stabilized product—assume 20% or 45 boats
Moisture measurement	TGA-Inert as LOI—225 samples	TGA-Inert as LOI—225 samples
Packaging	400 3013s expected, some potential for reduced number of 3013 cans by removing Cl salt, reduction may be 10%	400 3013s expected
Surveillance	No difference; both retain sufficient Cl salt to be in potential for corrosion category	

Table F-2: Resulting Cost Comparison (Based on Work Elements)

Element	Wash/Stabilize at 950°C	Stabilize at 750°C
Prompt gamma screen	No difference; all items screened in both options	
Washing	Direct labor~$500,000 (6 FTE * 8 months * 10,000/man month); (4 NCOs, 1 supervisor, 1 HPT)	None
Filtrate collection and sample	~$260,000 for filtrate sample analysis (520 analysis * $500/analysis)	None
D-8/D-7 batches, sample, transfer to tank farms	Liquid waste disposal cost ~$500,000 (5,200 L * $100/L disposal cost—requires storage in tank farms and treatment in waste treatment plant	None
Hot plate cycles	None; equipment existing and labor included in washing above	None
Furnace charges	No difference	
Filter changes and off-gas line replacement	~$250,000 (50 change outs * $5,000/ change out)	25,000 (5 change outs * $5,000/change out)
Boat unloading/ stabilized product size reduction	Some size reduction, screening, grinding still likely (need not totally eliminated)	Size reduction will use existing equipment but require additional effort
Moisture measurement	No difference	
Packaging	No difference	
Surveillance	No difference, both retain sufficient Cl salt to be in potential for corrosion category	
Total cost difference	~$1,500,000 additional cost for wash option	

Table F-3: Personal Exposure Comparison Based on Work Elements

Element	Wash/Stabilize at 950°C	Stabilize at 750°C
PGA screen	No difference	
Wash batches	450 touches to charge feed items to vessel, 450 touches to wash (2 washes per batch), 225 touches to drain/filter	None
Filtrate collection and sample	520 touches to sample, 170 seal outs for samples (3 samples per seal outs), plus additional exposure to lab techs for sample analysis. 520 touches to discharge filtrate	None
D-8/D-7 batches, sample, transfer to tank farms	No significant exposure in waste sampling, and only one sample seal out and one waste batch	None
Hot plate cycles	225 touches to hot plate material, 225 touches to transfer to furnace	None
Furnace charges	No difference	
Filter changes and off-gas line replacement	Five times exposure to maintenance personnel during filter/piping change outs, based on numbers of expected changes	
Boat unloading/stabilized product size reduction	Some screening/grinding normally expected	45 * 2 additional touches required for size reduction for "problem" boats—grind/rescreen
Moisture measurement	No Difference	
Packaging	No Difference	
Surveillance	No difference	
Summary personnel exposure differences	~2600 additional hands-on activities for the operator (significant extremity dose), total whole body similar to solutions plus additional exposure to lab techs from filtrate analysis and maintenance personnel from more frequent equipment maintenance. Total estimated additional dose—10–15 rem extremity; 1–2 man rem whole body	

Schedule and Schedule Risk

As additional personnel are being used to staff the wash process separately, and it will be operated independently, there is no significant reduction in the stabilization schedule if the wash process is eliminated. The 750°C furnace calcination cycle would shorten the overall heat up and cool down by about 3 hours, but this savings does not permit an additional furnace run during a daily shift.

There is benefit in that the resources freed from washing can be reapplied to legacy holdup removal and other activities. There is also a significant reduction in the schedule risk. The wash process is inherently more complex, and any problems in either the wash step, waste disposal, or the subsequent furnace operation step have the potential to delay the overall stabilization schedule and require continued use of RMC beyond that currently planned.

Any delays in 234-5Z deactivation would also involve significant cost risk, as the current cost of maintaining thermal stabilization/packaging capability in RMC is $120,000 per day.

Potential Disadvantages of Lower-Temperature Processing

Several potential disadvantages to low-temperature stabilization are discussed in this section.

Greater mass of material to package

One benefit of the Cl salt washing process that would be sacrificed if the lower-temperature processes are used is the reduction in mass of material due to removal of the salt. If all of the material that is not Pu oxide consisted of salt, and if all were removed by washing, this would amount to 245 kg, 21.7% of the total mass. However, the MIS data indicate that other oxides are commonly present in the impure oxides, and the salt washing is not expected to be completely effective. A more reasonable estimate would be based on the following:

- consider only the candidate material for low-temperature stabilization—that greater than 50 wt % Pu;
- consider that only a fraction has Cl salt—assume two-thirds of the total based in the kill/create list, general descriptions of the material, and available analysis;
- recognize that the washing process may leave as much as 1% Cl salt in the product; and
- acknowledge that other insoluble metal oxide impurities are known to exist in the material—assume 5% of the total mass.

Using these assumptions, the estimated mass reduction is ~104 kg of salt, or <10% of the total mass. This reduction in the mass of material could reduce the number of 3013 cans by 40. In practice this savings may not be realized, as these materials will be volume-limited in a 3013 can and the effect of washing on volume change is not known. In addition, the need for timely packaging and feed sequencing to meet the wash vessel and boat charge size limits may in fact not allow this potential savings to be realized.

Hygroscopic nature of product

The possibility that hygroscopic Cl salts that would have otherwise been removed by washing ($MgCl_2$ and $CaCl_2$) are present raises concerns about the re-adsorption of moisture after stabilization and before packaging is complete. This issue was addressed in Boak et al. (2002), although the analysis was primarily concerned with $MgCl_2$ and intermediate composition salts. The probability is low that many items contain these salts, and the PFP has procedures in place to ensure that if re-adsorption occurs it is detected and accounted for in the overall moisture determination and is therefore not an issue.

Formation of agglomerated mass from salt melting

It is possible that the salt in chloride-bearing oxide will melt and produce brick-like masses in the stabilization furnace trays. Although some effort is usually required for impure material, additional operator effort (and therefore dose) may be required to remove these items from the trays. This effect was seen in some of the surrogate tests described earlier in this appendix. The salt loading was high, 20–28 wt %, but not outside the range expected for ARF items. No problems in this regard have been reported by Rocky Flats in the low-temperature stabilization of actual materials ranging from 50–85 wt % Pu.

Unknown, quasi stable impurities

A final concern is that items stabilized at lower temperature and measured for moisture (and presumably other volatile constituents) at similarly low temperatures, might contain material that escaped destruction and detection, but would later compromise storage containers. The sources of feed materials provided some assurance that nothing exists in these materials that would not be stabilized adequately at the lower temperature. This concern must be addressed in designing and evaluating the ISP for all material governed by DOE-STD-3013. The program has identified chloride-bearing material as a primary focus.

Summary

The low-temperature stabilization option offers significant benefits over the current plan to wash and stabilize at 950°C. These benefits include the following:

- elimination of a significant volume of liquid waste and attendant long-term storage and disposal costs;
- significant reduction in operator exposure by elimination of the highly dose-intensive “hands-on” wash process;
- reduction of cost from elimination of washing, filtrate collection, and waste disposal activities;

- reduction of schedule risk by freeing resources currently assigned to the wash process to other stabilization and deactivation activities; and
- reduction of technical and schedule risk for completion of stabilization by simplification of the overall operation.

Appendix G: Moisture Measurement by TGA for Chloride-Bearing Oxide

Introduction

Plutonium oxide (PuO_2)-bearing materials originating from the PFP inventory are being processed and packaged to meet the DOE-STD-3013-2000 standard (DOE 2000) for packaging and storage. Some of the materials have come from solution stabilization operations. In this case, the solutions were first treated with magnesium hydroxide [$Mg(OH)_2$], oxalic acid [$H_2C_2O_4$], or sometimes both reagents to precipitate the Pu in a solid form. The solids then were filtered (to remove associated solution), dried, and calcined. Solid Pu oxide also is being subjected to thermal stabilization processing prior to packaging to meet the 3013 standard.

The solutions campaign was completed in July 2002. Completion of stabilization and packaging of the solid oxide inventory is forecast for May 2004. PFP is considering efforts to reach earlier completion dates.

The calcined PuO_2 solids were packaged hermetically in stainless steel cans according to DOE-STD-3013-2000 (DOE 2000). However, prior to packaging, each can's contents must have the moisture content measured to verify that it meets the <0.5 wt % moisture criterion required by the standard. The measurement is made by measuring weight lost by heating to 1000°C.

A variety of measurement techniques have been used at the PFP to measure the moisture concentrations in the stabilized PuO_2 material (Risenmay et al. 2003). For pure PuO_2, moisture concentrations after thermal stabilization are low (~0.15 wt %), even in atmospheres up to 70% RH. Measurement of weight loss upon heating to 1000°C (LOI) is conservative for this material, if provision is made for the bias of 0.15 wt % induced by moisture re-adsorption.

In 2001, the PFP supplanted the LOI method with more accurate and robust TGA techniques as the means to measure weight lost during ignition to 1000°C. Because the TGA technique allows weight loss at temperature to be measured, it precludes uncertainty due to moisture re-adsorption that occurs upon cooling.

In certain impure PuO_2 materials, constituents besides water also can be released in heating. For example, carbon dioxide (CO_2) is found to be adsorbed even on pure PuO_2, and is produced by decomposition of carbonate compounds. Thermal analyses show that CO_2 is released at various temperatures depending on the particular material. For example, surface-adsorbed CO_2 and $NaHCO_3$ decomposition both release CO_2 at 100°C to 200°C, whereas decomposition of most carbonate salts releases CO_2 at higher temperatures. $CaCO_3$ decomposes to give CaO and CO_2 at

~600°C to to 800°C (Duval 1963). Carbon dioxide surface adsorbed onto PuO_2 generally is released at moderate temperatures.

As shown in Appendix E, vapors of Cl salts (for example, NaCl and KCl) are released at higher temperatures (for example, at 1000°C, the vapor pressures of NaCl and KCl are 7.9 and 15.1 Torr, respectively). These salts were used in pyrochemical Pu processes at Rocky Flats and may also be present as process chemical impurities. At high concentrations of these constituents, weight losses from their evaporation can exceed 0.5 wt %, and thus cause failure to meet the DOE-STD-3013-2000 criterion because the measurement process cannot distinguish among the different species causing the weight loss.

Results of a TGA measurement of a ~3-g sample of NaCl/KCl equimolar are compared with results predicted under the same measurement conditions, with the assumption that the cover gas becomes instantly saturated in the NaCl and KCl vapors. The salt evaporation calculation was performed in a manner similar to that described in Appendix E for salt evaporation during thermal processing.

The TGA measurement was made in the PFP's RMC line using the same instrumentation (Netzsch STA 409 PC Luxx) and analysis routine as is used in moisture measurement of thermally stabilized materials destined for packaging under the 3013 standard in the RMC line. As shown in Figure G-1, the measured weight-loss curve has the same shape as the predicted curve, but has a value (~0.33 wt %) about 63% lower than predicted (~0.9 wt %). Nevertheless, the weight loss solely due to salt

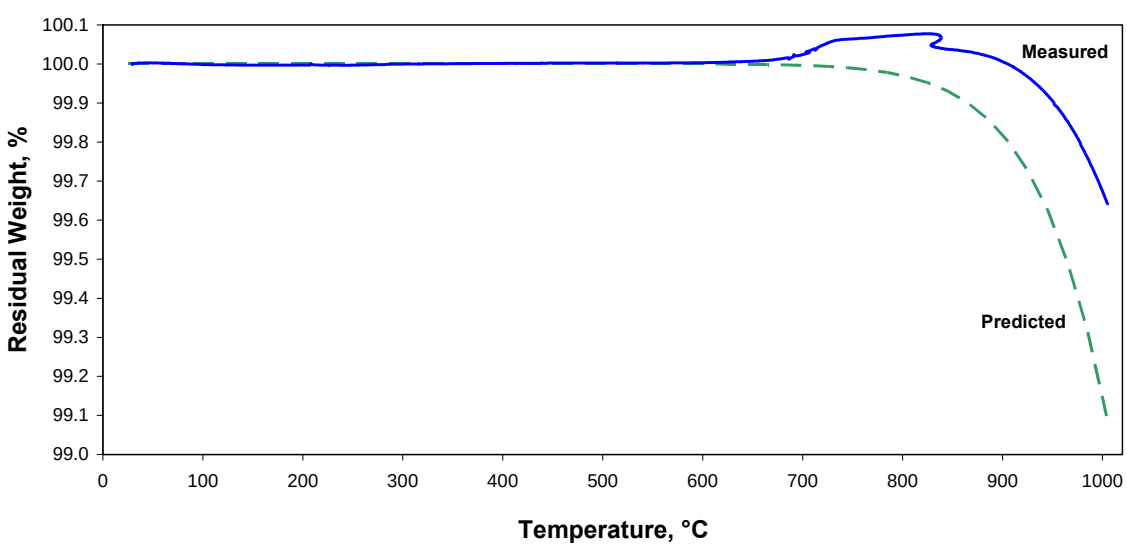

Figure G-1: Predicted and observed TGA of equimolar NaCl:KCl.

evaporation is sufficiently large in itself to threaten failure to meet the PFP weight-loss threshold of <0.4 wt %.

A similar experiment, but with 20 wt % equimolar NaCl:KCl (that is, 11.22 wt % KCl and 8.78 wt % NaCl) in CeO_2, was performed to test the effects of gas-flow rate. The results (Figure G-2) show the characteristic salt evaporation onset above ~800°C. The tests also show that decreasing the purge gas-flow rate in the thermal analyzer from the nominal 100 mL/min, specified in the PFP TGA-Inert procedure, to 50 mL/min had only a small (~0.02 wt % decrease) effect on salt evaporation. Weight losses were 0.16 wt % for the test run at nominal 100 mL/min purge rates and 0.14 wt % at the 50 mL/min rate. These weight losses are small relative to the 0.4 wt % administrative TGA weight loss limit and suggest that TGA-Inert measurements will not fail too frequently due to salt evaporation from chloride-bearing Pu oxide.

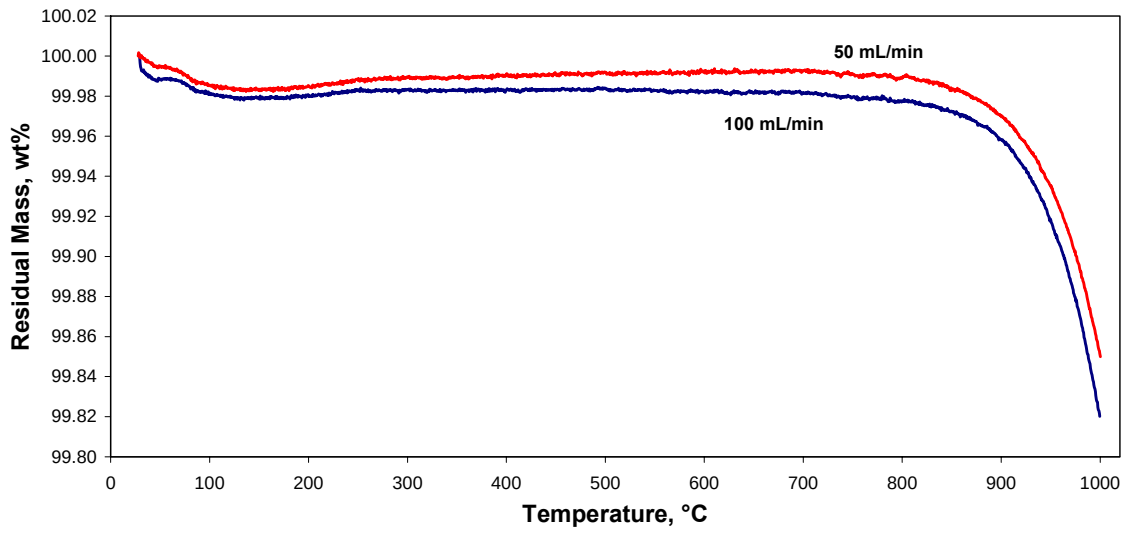

Figure G-2: TGA of 20 wt % equimolar NaCl:KCl in 80 wt % CeO_2 at nominal 100 mL/min and 50 mL/min purge gas-flow rates.

Products from 950°C thermal stabilization of relatively low-Cl-salt-content ARF items have been analyzed by TGA-Inert. Chlorine concentrations for all feed items were estimated to be ~3 wt %, based on PGA techniques. Each of the six items (one was a duplicate) easily passed the administratively set <0.4% weight-loss criterion (Figure G-3). However, the increasing weight loss above ~800°C, characteristic of NaCl/KCl evaporation, is seen in all curves.

TGA/MS can be used at the PFP to identify specifically the water present in the gases released during heating. This method can thus segregate water from other evaporating or thermally decomposing constituents, such as when high weight loss is due to salt decomposition or evaporation. The H_2O is identified in the mass spectrum by its characteristic molecular mass of 18 and CO_2 by its mass of 44.

However, operational difficulties are anticipated in determining the moisture concentrations of Cl-salt-bearing items using the TGA/MS. The anticipated problems arise from the following two sources:

- deposition of Cl salts onto the 2-m-long, 0.15 mm inner diameter capillary connecting the top of the thermal analyzer and the mass spectrometer (causing plugging of the capillary); and
- attack of the stainless steel capillary and other metal components in the TGA/MS by HCL vapors emitted from the salt-bearing samples.

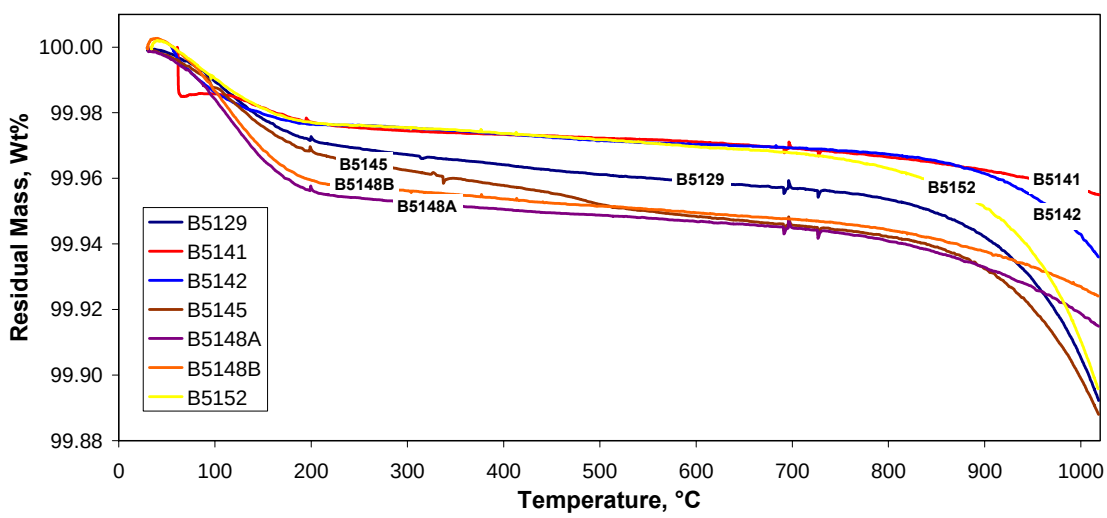

Figure G-3: TGA of 1000°C thermally stabilized low-Cl-salt ARF material.

These phenomena would cause costly and time-consuming breakdown of the TGA/MS instrument, precluding its use to measure other materials.

PFP personnel estimate that at least 225 3013 containers with salt-rich stabilized ARF items will be created. If each container required TGA/MS analysis (possible for high-salt items), more than 225 duplicate measurements would be required. Moisture analysis by TGA/MS, even without equipment breakdown, requires at least one working day per item. Measurement of this number of items would require more than one year, and would unduly extend PFP operations on a day-for-day basis and delay its D&D. Such a delay would result in very large increases in costs. An alternative means to measure moisture in chloride-bearing Pu oxide items is clearly required for those instances when the contribution to weight loss above ~800°C (that is, the weight loss attributable to salt evaporation) causes total weight loss to exceed the 0.4 wt % criterion.

The baseline means to measure moisture in thermally stabilized chloride-bearing oxide is to use the plant-installed TGA instruments to measure the amount of weight lost from verification samples by heating to 1000°C. A potential alternative would be to measure the weight loss to 750°C and use this value, divided by a factor of 0.9, as a conservative measure of the total moisture content. Exercise of this option would occur for only those instances meeting the following tests:

1. the TGA-Inert weight loss measured to 1000°C exceeded the 0.4 wt % criterion,
2. the weight loss below 750°C was less than the 0.4 wt % criterion, and
3. the material originated from ARF items shown by PGA to contain ER salt according to the logic diagram given in Figure 9 of the main section of this document.

The justification for this approach is built on the following observations:

1. Water evolution from Cl salts (NaCl, KCl, $MgCl_2$, mixtures of $CaCl_2$ with NaCl and KCl, and their hydrates and hydroxides) is complete by 600°C. This temperature is below the observed onset of rapid NaCl, KCl, and $MgCl_2$ evaporation seen above about 750°C (see Figure G-1 for equimolar NaCl:KCl).
2. Water lost from the Cl salts but evolved as HCl by pyrohydrolysis reactions is gravimetrically conservative (that is, weighs more than the equivalent amount of water).
3. Water evolution observed by TGA/MS measurements to 600°C of a large variety of pure and impure Pu oxide at PFP, and in LANL measurements of chloride-bearing MIS items from Rocky Flats is >85% (for the most part, >90%) of the total amount observed by

heating to 1000°C; the amount evolved by 750°C is >90% of the total amount observed.

4. Total weight loss to 750°C is necessarily equal to, or more than, the weight loss due to water alone.

Together, these observations indicate that thermogravimetric measurement of weight loss to 750°C, divided by a factor of 0.9, provides a conservative estimate of the concentration of moisture in a sample when compared with the amount that would have been observed by TGA/MS measurement to 1000°C, had such measurements been practicable.

The data and technical bases supporting the four key observations are presented in the following sections.

Thermolysis of Magnesium, Calcium, Sodium, and Potassium Chloride Salts and the Role of HCl

The pyrochemical salts used in Rocky Flats processing include NaCl, KCl, $MgCl_2$, and $CaCl_2$. The alkaline earth chlorides, $MgCl_2$ and $CaCl_2$, are hygroscopic and can form the respective mono-, di-, tetra-, and hexahydrate salts, whereas the alkali chlorides, NaCl and KCl, only adsorb moisture on surfaces at relatively high humidity (Smith et al. 2000).

Water evolved during the heating of materials containing Cl salts can react, at elevated temperatures, to form hydrogen chloride gas, HCl. This reaction is called pyrohydrolysis. For example, pyrohydrolysis reactions, undertaken by passing humidified air over Pu-oxide powders heated to 1000°C, are used to drive Cl salt and fluoride impurities from the powders as HCl and hydrogen fluoride (HF). The HCl and HF are captured in downstream scrubbers for analysis (ASTM 1997).

As shown in Figure 9 in the main text of this document, inventory items found to contain chlorine but not sodium or potassium (calcium being undetectable by PGA) are presumed to arise from DOR processes, and thus contain $CaCl_2$. Aside from pyrohydrolytic reactions to produce HCl, such items can be safely processed at 950°C because $CaCl_2$ is relatively nonvolatile (vapor pressure at 1000°C is ~0.052 Torr). Thus, weight loss by salt evaporation will be low, and water concentration in the thermally stabilized product may be analyzed by existing TGA-Inert methods to 1000°C. Because the DOR oxide would be thermally processed (at 950°C) and analyzed (TGA-Inert to 1000°C) in the usual manner, it is not subject to the technical equivalency arguments.

If, however, NaCl and KCl (from ER processes) are present with $CaCl_2$ (from DOR) in an inventory item, TGA-Inert measurement of the thermally stabilized product at 1000°C could yield weight losses near or above 0.4 wt % due to NaCl/KCl salt evaporation. Such items would be

identified for lower-temperature stabilization by their prompt gamma signatures for sodium and chlorine (see Appendix H). The complete dehydration of pure $CaCl_2$ is slow below ~750°C (Smith et al. 2000, Lawrence and Bu 2000). However, the presence of a few percent NaCl and KCl, separately or in combination, lowers the temperature of $CaCl_2$ dehydration to ~300 °C (Arbanas et al. 1989). Based on the weight-loss curves, the water is lost as H_2O and not as HCl.

Magnesium chloride hydrate salt dehydration occurs more readily than that of pure $CaCl_2$ hydrates. For example, $MgCl_2 \cdot 6H_2O$ decomposes on heating at 100°C to lose two hydrate waters (that is, to form $MgCl_2 \cdot 4H_2O$) and with further heating to 110°C, produces some HCl (Merck 1976). In the presence of excess water, magnesium chloride will convert to MgO at temperatures above 505°C, but the conversion may be incomplete, depending on the specific conditions (Smith et al. 2000).

For example, the thermal analysis of $MgCl_2 \cdot 5.5H_2O$ reaches a steady weight corresponding to MgO above 615°C, according to Duval (1963). In contrast, a review of various studies showed that the initial product of thermolysis of $MgCl_2 \cdot 6H_2O$ is the tetra-, di-, and monohydrates. This stage is followed by separate decompositions of the monohydrate to give $MgCl_2$ and MgO. The final product is a nonstoichiometric oxychloride $Mg_{1-0.5x}OCl_x$ (Berg 1970). Transformation to the oxychloride is complete at 400°C (Shoval and Yariv 1985). These observations may be summarized in the following chemical reaction:

$$MgCl_2 \cdot 6H_2O \rightarrow (5+0.5x)\ H_2O + (2-x)\ HCl + MgO_{1-0.5x}Cl_x$$

The pyrochemical salts containing $MgCl_2$ used at Rocky Flats also contain NaCl and KCl at concentrations higher than that of $MgCl_2$. Thermolysis of $MgCl_2 \cdot 6H_2O$ in the presence of NaCl or KCl leaves no magnesium oxychloride (as is observed in thermolysis of pure $MgCl_2 \cdot 6H_2O$) and instead forms MgO as the final product above 400°C or 450°C, respectively (Shoval and Yariv 1985, Shoval et al. 1986).

For the ER products, the chemical reduction of $MgCl_2$ to Mg metal in the process, the subsequent ~450°C thermal stabilization at Rocky Flats of material destined for shipment to Hanford, and the observations and cited thermal analytical studies by Shoval and colleagues, it may be concluded that the magnesium in the ER material is primarily present as MgO. Neither NaCl nor KCl form hydrates. Removal of the surface-adsorbed water from NaCl and KCl occurs at relatively low temperatures.

The technical literature therefore shows that, with the exception of pure $CaCl_2$ and its hydrates, heating of the alkali and alkaline earth Cl salts and their hydrates and hydroxides to ~600°C removes essentially all of the

contained water. The water is released as H_2O with varying amounts of HCl.

Note that the hydrogen equivalent weight of H_2O (the mass lost per mole of hydrogen atoms) is 9 g (18 g water per 2 moles of H atoms) and the hydrogen equivalent weight of HCl is 36.5 g. Therefore, weight lost by the release of HCl resulting from pyrohydrolysis in the TGA measurement is a conservative measure (that is, overstated by a factor of 36.5/9 = ~4) of the quantity of H_2O from which it arose in the heating of the Cl salts.

TGA/MS Measurements of Pu Oxide Items at PFP and LANL

Thermogravimetric and mass spectrometric measurements were made of PFP-stabilized PuO_2 product materials in the PPSL with a Netzsch model thermogravimetric mass analyzer with quadrupole mass spectrometer (TGA/MS). A similar, but not identical, Netzsch TGA/MS has been used at LANL to characterize materials received in the MIS program (Morales et al. 2002). The origin and properties of the material types measured by the TGA/MS at PFP and at LANL are summarized in Tables G-1 and G-2.

Table G-1: Origins and Properties of PFP PuO_2 Stabilization Product Materials.

Originated from Solutions		
Material Type	**Description**	**Precipitation Agent**
$Mg(OH)_2$	~200–350 g/L Pu nitrate, product quality	$Mg(OH)_2$
CML	Critical Mass Lab; ~45 g Pu/L, 100 g U/L	Oxalic acid
Filtrates	Single- and double-pass filtrate concentrates from prior oxalic acid precipitation of Pu; ~40 g Pu/L with likely Na, K, Al, Fe, Cr, Ni	Oxalic acid
Cats & Dogs	Concentrated solutions from analytical lab; PRF flush solutions	Oxalic acid; some with $Mg(OH)_2$
Originated from Solids		
Material Type	**Description**	
Alloy Oxide	Oxides produced from burned metal alloys	
GEO Oxide	Aged fuels-grade oxide	
Polycube Oxide	Fuels-grade oxide prepared by pyrolysis of Pu-oxide-bearing polystyrene cubes used in criticality studies	
PRF Floor	Oxides derived from materials scraped from the floor of the solvent extraction canyon	
QA Verification	Varied materials sampled for QA verification	

Table G-2. Origins and Properties of LANL $Pu0_2$ Stabilization Product Material (After 950°C Stabilization).

Item ID	IDC*	WT % Cl*	Wt % H_20
ARF-102-85-295	??	7.70	0.27
5501407 (C1407)	Y61	0.16	0.76
Can 92	061	0.09	0.068
053038 (03038)	Y61	4.45	0.020
C00695 (T0695)	086	0.26	0.026
07242201 (J2201)	289	0.47	0.022
07242141 (K2141)	159	??	0.015

*IDC and wt % Cl from MIS database

Experimental Conditions

The TGA/MS is calibrated periodically using sodium bicarbonate ($NaHCO_3$), which thermally decomposes at 125-210 °C to form solid sodium carbonate (Na_2CO_3) and water (H_2O) and carbon dioxide (CO_2) gases:

$$2\ NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2.$$

The LANL instrument is calibrated in a similar manner using gypsum ($CaSO_4 \cdot 2H_2O$) standards.

Samples are prepared by adding ~3-g aliquots of the powder materials into tare-weighed and prefired alumina (Al_2O_3) crucibles. The samples are weighed in a glove box and capped tightly to prevent exposure to the uncontrolled humidity of the glove box air.

Air density decreases with increasing temperature, and thus changes the apparent mass measured by the TGA balance. To counter this effect, buoyancy corrections were made for each TGA measurement. Buoyancy corrections were based on the apparent weight gain observed in heating ~3-g masses of granular Al_2O_3 under the same temperature program. The samples in their alumina crucibles were heated in flowing 99.999% argon cover gas. For some samples, simple exposure to the dry argon gas caused perceptible water loss even before the onset of heating.

The temperature ramp rate used in all measurements was 20°C/min and ceased at 1000°C. Water evolution, observed as the mass 18 peak in the mass spectrometer, was observed as a function of temperature. A water evolution curve for a thermally stabilized chloride-bearing Pu oxide from the PFP is shown in Figure G-4.

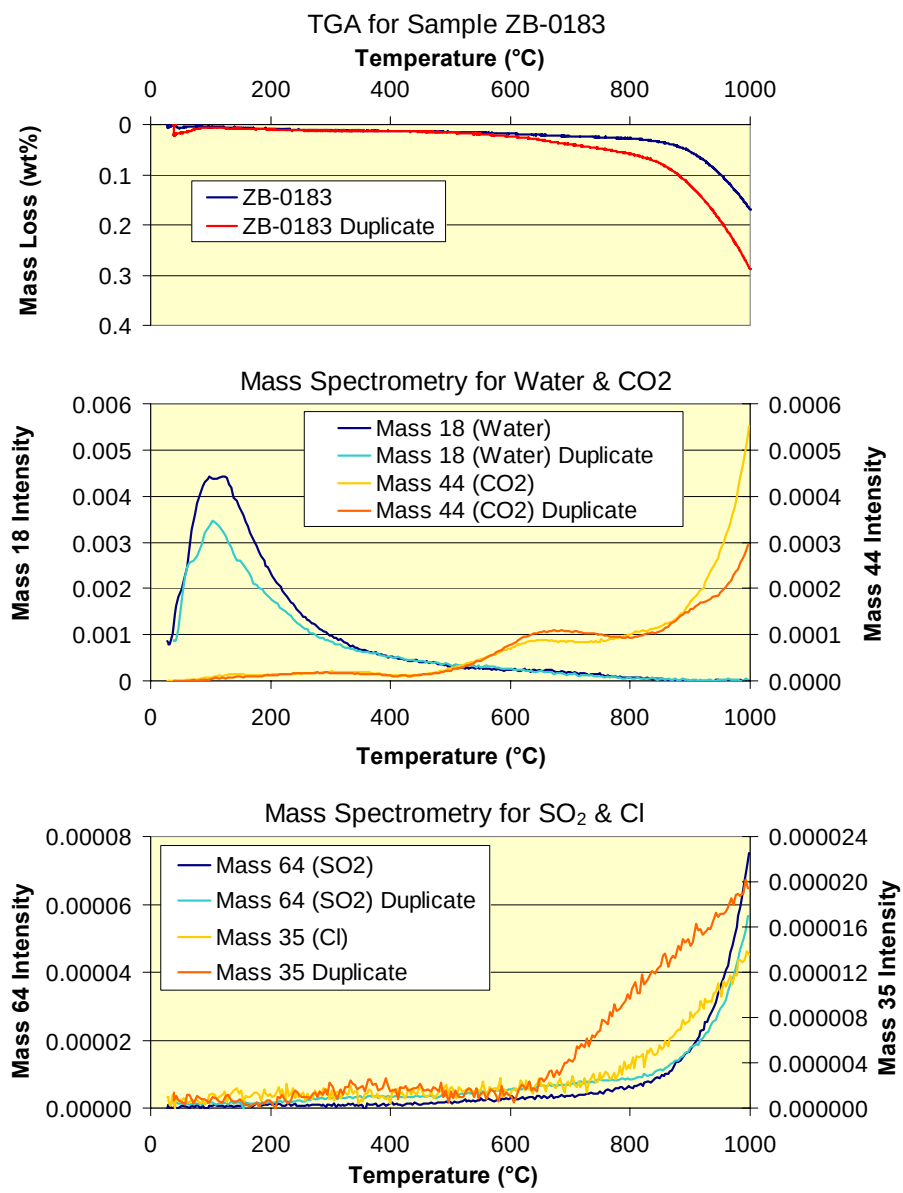

Figure G-4: TGA/MS scan of PFP Pu oxide item ZB0183 for water, CO_2, Cl, and SO_4. Note that mass 44 scale is 1/10 that of mass 18.

The water evolution is shown to peak at about 120°C and tail off at higher temperatures such that little water is observed above about 600°C. Some carbonate salt decomposition evidently is occurring above about 500°C. This decomposition accelerates at higher temperatures and is still not complete even at 1000°C. The mass spectrometer also detects chlorine atoms (mass 35), though not HCl (mass 36), above that of the background argon sweep gas contribution (^{36}Ar constitutes 0.337 mole% of natural argon). Sulfur dioxide (SO_2) also is observed.

The water evolution curves were evaluated from both the PPSL and LANL instruments for the Pu oxide material described, respectively, in Tables G-1 and G-2. The curves were integrated up to cut-off temperatures of 500°C, 600°C, 750°C, and 900°C and compared with the total water observed at 1000°C. The data at these cut-off temperatures for the PFP materials (Figures G-5 through G-8, respectively) show that water evolution is >90% complete by 750°C for all materials studied (except for the four "QA verification" items, which had been stored in a food pack can for three years after 1000°C stabilization). In the other cases (that is, material recently stabilized), heating above 750°C removed little additional water but only drove off or decomposed salts for certain impure items.

Significantly, similar observations are made for the Rocky Flats-origin items in the MIS inventory analyzed at LANL (Figure G-9, for 750°C). In this case, water evolution is >92% complete by 750°C for all items, irrespective of their thermal-stabilization history (that is, whether or not the items had been first stabilized to 950°C).

The PFP observations for a variety of pure and impure Pu oxides, and the LANL observations for Rocky Flats materials, both chloride-bearing and largely chloride-free, show that >85% of the water released by heating to 1000°C is released by 600°C, and >90% of the water is released by 750°C.

Water loss versus total weight loss in TGA/MS

It is evident that total weight loss by heating to 600°C is necessarily equal to, or greater than, the weight loss due to water alone. Based on TGA/MS measurements at PFP, this is largely because CO_2 loss from surface-adsorbed CO_2 or decomposition of carbonate salts and desorption of other surface-adsorbed gases (such as nitric oxide, NO) occur below 600°C.

The conservatism of estimating water concentration at 600°C by the total weight loss at 600°C for the PFP Pu oxide materials is shown in Figure G-7. The observed total weight losses are rarely lower (and only at small values), as measured by TGA, than the weight losses due to water, as observed by TGA/MS. The TGA weight-loss measurement to 600°C, therefore, provides a conservative measure of the water concentration found by TGA/MS to 600°C. These arguments hold equally well for measurements made at 750°C.

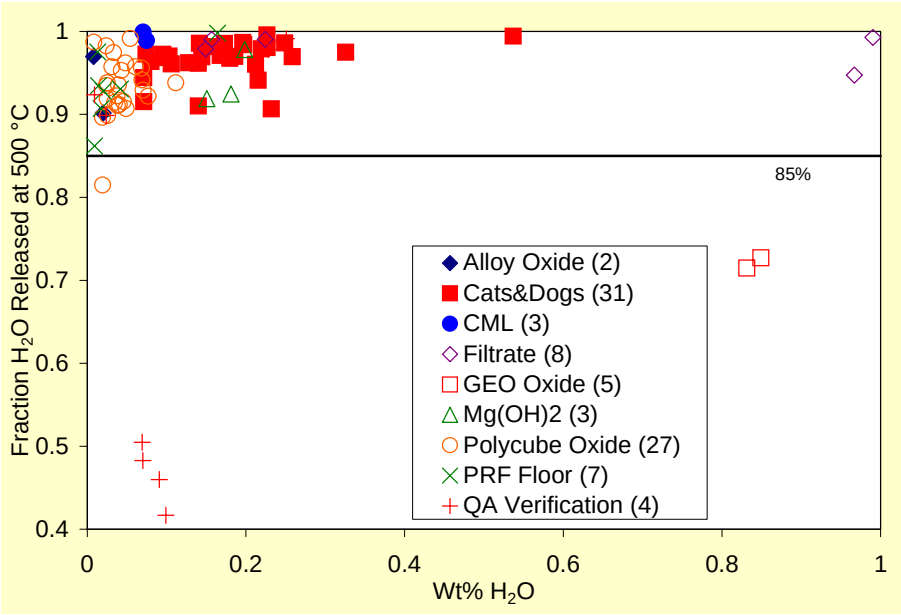

Figure G-5: Fraction of water evolved at 500°C as a function of total water evolved at 1000°C by TGA/MS measurements at PFP.

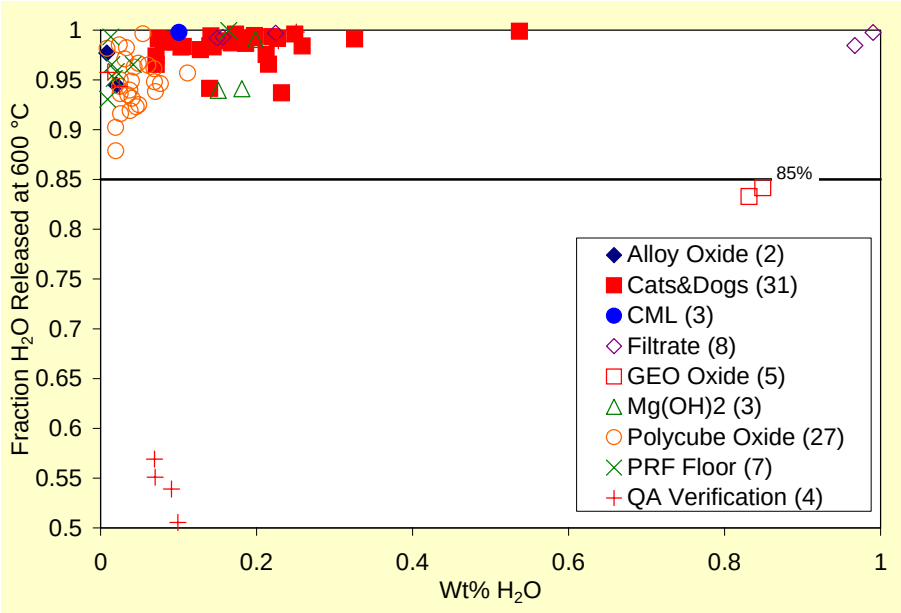

Figure G-6: Fraction of water evolved at 600°C as a function of total water evolved at 1000°C by TGA/MS measurements at PFP.

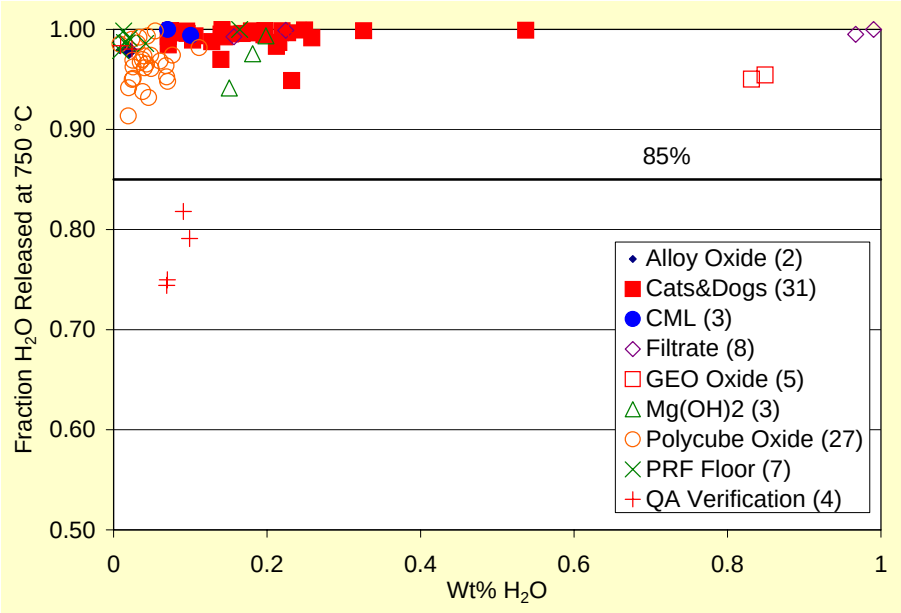

Figure G-7: Fraction of water evolved at 750°C as a function of total water evolved at 1000 °C by TGA/MS measurements at PFP.

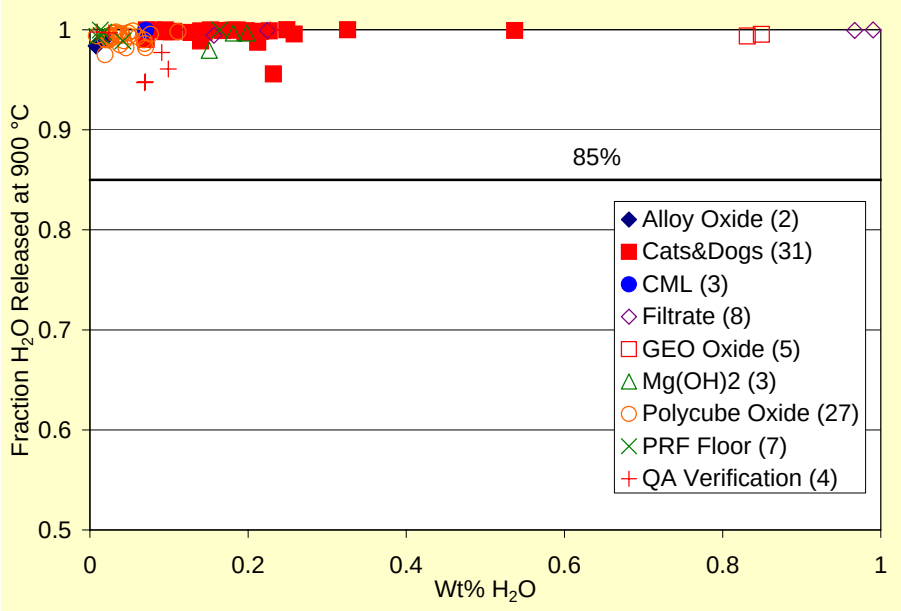

Figure G-8: Fraction of water evolved at 900°C as a function of total water evolved at 1000°C by TGA/MS measurements at PFP.

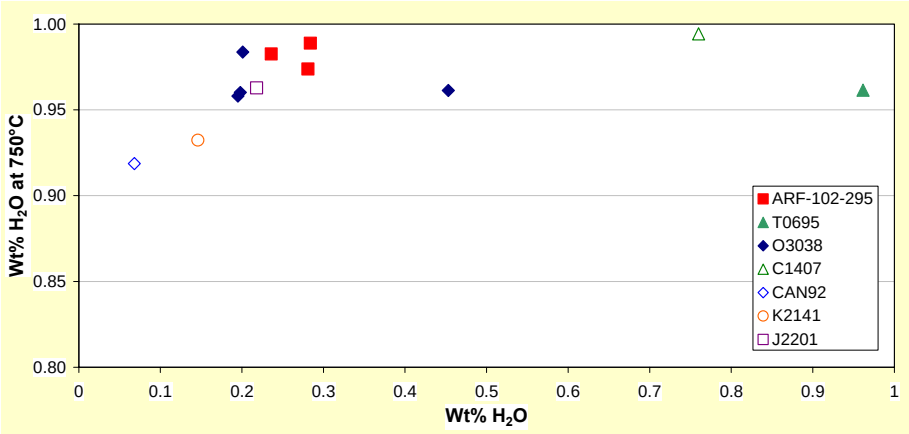

Figure G-9: Fraction of water evolved at 600°C as a function of total water evolved at 1000 °C by TGA/MS measurements at LANL.

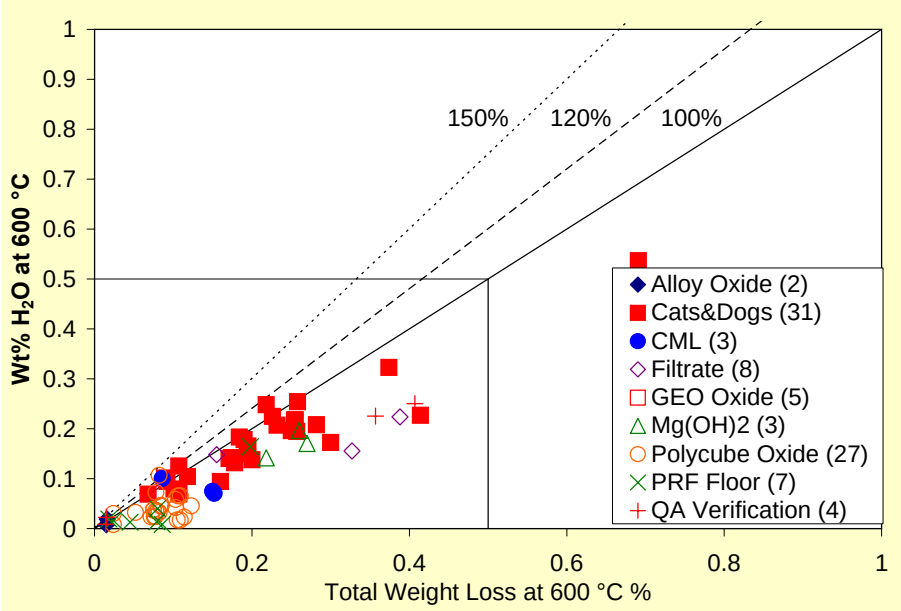

Figure G-10: Water loss at 600°C versus total weight loss at 600 °C.

Conclusions

The proposed means to measure moisture in thermally-stabilized chloride-bearing oxide by using the plant-installed TGA instruments to measure the amount of weight lost from verification samples heated to 750°C and dividing this value by a factor of 0.9 provides a conservative measure of the total moisture. Exercise of this option would occur only for those instances meeting the following tests:

- the TGA-Inert weight loss measured to 1000°C exceeded the 0.4 wt % criterion,
- the weight loss below 750°C was less than the 0.4 wt % criterion, and
- the material originated from ARF items shown by PGA to contain ER salt according to the logic diagram given in Figure 9 in the main section of this document.

The justification for this approach is built on the following observations:

- Water evolution from Cl salts (NaCl, KCl, $MgCl_2$, mixtures of $CaCl_2$ with NaCl and KCl, and their hydrates and hydroxides) is complete by 600°C. This temperature is below the observed onset of rapid NaCl, KCl, and $MgCl_2$ evaporation seen above about 800°C.
- Water lost from the Cl salts but evolved as HCl by pyrohydrolysis reactions is gravimetrically conservative (that is, weighs more than the equivalent amount of water).
- Water evolution observed by TGA/MS measurements to 750°C of a large variety of pure and impure Pu oxide at PFP and in LANL measurements of chloride-bearing MIS items from Rocky Flats is >90% of the total amount observed by heating to 1000°C.
- Total weight loss to 750°C is necessarily equal to, or more than, the weight loss due to water alone.

TGA of weight loss to 750°C, divided by a factor of 0.9, provides a conservative estimate of the concentration of moisture in a sample when compared with the amount that would have been observed by TGA/MS measurement to 1000°C, had such measurements been practicable.

Appendix H: PGA as Applied at the PFP

The PGA measurement method is based on the identification of gamma rays induced by alpha particles interacting with nuclei of other elements. As the Pu and Am in the Pu oxide decay by alpha emission, some fraction of these alpha particles will interact with the impurities in the oxide, particularly low-atomic-number elements, to undergo (α,nγ) and (α,pγ) nuclear reactions. These reactions excite the product nucleus; subsequent decay produces gamma rays with energies characteristic of the product element.

These characteristic gamma rays give a fingerprint of some of the impurities contained in the Pu oxide matrix. Methods to use analysis of prompt gamma spectra to characterize alpha particle-emitting materials have been presented in the technical literature (McKibben 1967, Martin 1975, Ovechkin et al. 1976, Giles and Peisach 1979, Ovechkin 1980, and Shumakov et al. 1994). Elements that can be readily identified by PGA include beryllium, fluorine, sodium, magnesium and chlorine (Giles and Peisach 1979 and Martin 1975). All of these impurities have been identified in oxide materials from the MIS program. Other elements produce characteristic gamma rays and may also be identified, but a few notable exceptions, such as carbon, calcium, and gallium, produce no significant gamma yield and cannot be identified by PGA.

Because alpha particles deposit their energy in a very short interval, the PGA method depends upon intimate admixture of the Pu and the elements of concern (at approximately the 10-μ scale). This dependency of the signature leads to some possibility of a false negative (no detection when the element is actually present). Such false negatives may be of concern, as they might direct material to higher-temperature stabilization that could cause corrosion and plugging in the system. False negatives do not pose a threat of stabilizing material that does not contain Cl salts at lower temperatures.

PGA demonstrated the effects of intimate mixing of PuO_2 powder blended with 5 wt % particulate CaF_2 and a 5-wt % 1:1 mole ratio NaCl:KCl mixture (Foster et al. 2002). The characteristic 1274, 1528, and 2081 keV emissions from the $^{19}F(\alpha,p\gamma)$ reaction could be discerned after the powders had been simply mechanically blended. The 1809 keV peak characteristic of the $^{23}Na(\alpha,p\gamma)$ reaction and the 2168 keV peak of the $^{35}Cl(\alpha,p\gamma)$ reaction were observable but not as prominent as the 2081 keV peak for fluorine. However, when the mixtures were heated to 800°C, above the melting point of the NaCl:KCl eutectic, the 1809 and 2168 keV peaks characteristic of sodium and chlorine, respectively, strengthened about an order of magnitude. Further heating to 950°C did not change the spectrum from that observed in the 800°C product. It is expected, however, that

heating above the 1403°C melting point of CaF_2 would have improved the fluorine signal. It is important to note that because the NaCl:KCl was molten in ER processing, intimate mixing of the salt with the plutonium/americium alpha emitters is reasonably assured for materials containing ER salt.

The PFP has brought online several PGA systems to characterize the stabilized products packaged in their 3013 containers as part of the ISP. The new systems are also being used to estimate the chlorine content in ARF items destined for thermal stabilization and packaging. A 45% efficient, coaxial, high-purity germanium detector is used to gather the prompt gamma spectra at the PFP. A 1-in.-thick Pb (lead) filter is interposed between the sample and detector to minimize x-ray pulses from Pu (mostly multiplets around 100 keV) and americium-241 (~60 keV) to decrease the detector dead time. Some attenuation of 331 to 450 and 600 to 660 keV energy peaks from Pu also occurs. Two software programs are used to interpret the gamma energy spectra. Both peak analysis software routines can operate on the same spectral data set.

The first program, developed by PFP personnel, is used to measure chlorine quantities in ARF inventory items. The quantification is based on PGA of selected ARF items having known chlorine and Pu quantities. The selected ARF items are reserved for periodic checks of system performance. The Pu quantities for each reference item were determined by the accepted Pu assay techniques combining gamma spectrometric isotopic analysis and calorimetry. The chlorine concentrations were determined by water leaching of samples of the materials and analysis of the leachates by chloride-ion-selective electrode.

The background-subtracted specific count rates [that is, the count rate per gram of chlorine and per gram of Pu or counts/(second·g Cl·g Pu)] for the $^{35}Cl(\alpha, p)$ reaction at 2168 keV are determined for each standard in a fixed geometry for each of the four detector systems. The specific count rates at fixed geometries and for a given system are constants. The program analyzes spectra collected with an ORTEC digital spectrometer and stored in their “integer” (.CHN) format.

Because the software was developed to screen feed items for wash processing to remove Cl salts, the spectra are gathered with counting times set to attain a given precision in the chlorine prompt gamma signal at 2168 keV, or 3 hours, whichever comes first. The program produces a report at the end of the counting time. The system calibration and sample analysis routines are formalized in PFP operating procedures (PFP 2003a and 2003b).

The second program, developed by LANL personnel, is designed to identify the presence of prompt gamma rays from ~100 through 5000 keV. The LANL program also provides a background-corrected measurement of the area of each analytical peak. A custom data file can be created to analyze a specific data set. In this case, prompt gamma rays associated with aluminum, beryllium, chlorine, chromium, copper, fluorine, iron, magnesium, potassium, sodium, silicon, and tantalum are analyzed, and the presence of each of these elements is flagged based on the sample spectrum.

Because overlap occurs for prompt gamma peaks from several of these elements (for example, aluminum and magnesium at 1014 keV, fluorine and magnesium at 1274 keV), analysis routines are used to separate the peaks. The potassium and fluorine peaks near 1528 keV present a special case, as the fluorine peak is prominent and can easily overwhelm the neighboring weak potassium peak. The software also uses results from secondary gamma peaks to help the operator determine the relative contributions of the elements producing the overlapping peaks. Unfortunately, potassium does not have a useful secondary peak, so that the presence of significant fluorine in a sample can obscure the potassium prompt gamma signature.

Because interpretation of the more complicated peak-analysis results requires the knowledge and judgment of a trained scientist or specialist, reports from the LANL software are not automatic. Therefore, to accelerate the processing of material, PFP has implemented the simpler software, with the option for expert review using the more complicated software as needed.

An example of a prompt gamma spectrum for an ARF item is given in Figure H-1. This item, ARF-102-85-295, has been characterized at LANL and found to contain PuO_2 and 19 wt % chlorine in the form of NaCl and KCl. The spectrum, gathered using a LANL counting system, shows the many Pu peaks in two regions around 331 to 450 and 600 to 660 keV. Peaks associated with sodium, potassium, chlorine, fluorine, and magnesium are identified as present, as noted in the figure, according to the LANL software.

A prompt gamma spectrum of an ARF inventory item from the PFP is given in Figure H-2. The item is one used in the calibration of the PFP PGA program to measure chlorine quantities in inventory items. As shown in the figure, this item contains 20 wt % chlorine. The inset in the spectrum magnifies the interval near 1528 keV and illustrates the overlap of the potassium (K-39) and fluorine (F-19) peaks.

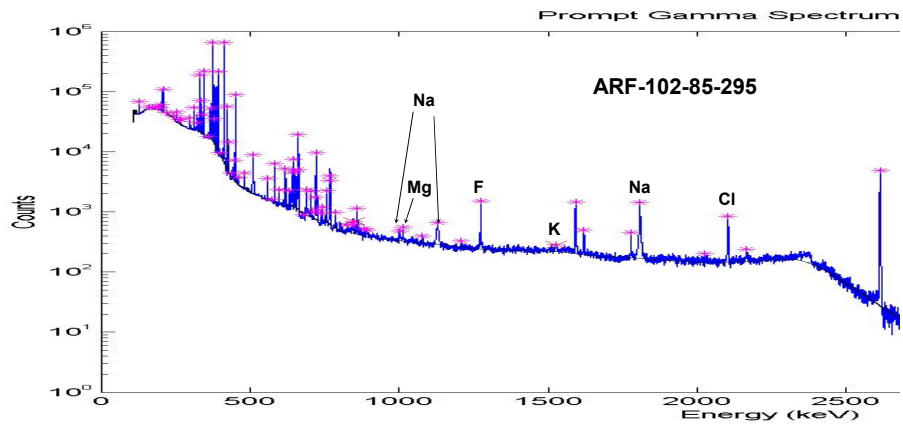

Figure H-1: Prompt gamma spectrum of MIS item ARF-102-85-295.

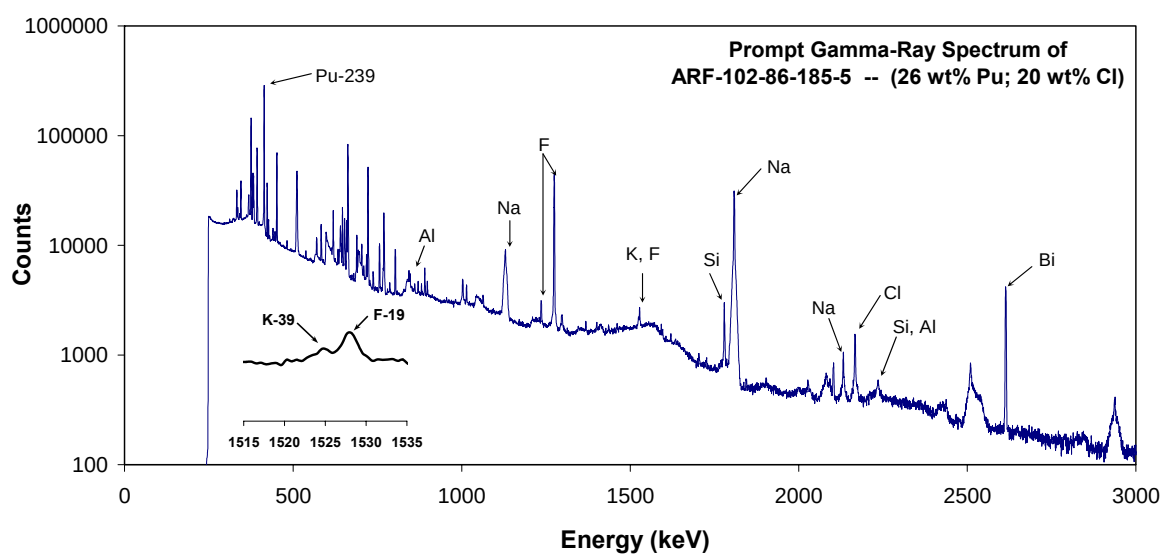

Figure H-2. Prompt gamma spectrum of PFP item ARF-102-86-185-5. (Inset shows overlap of ^{39}K and ^{19}F peaks)

According to the baseline process (shown in Figure 7 of the main section of this document), items found to contain >1 wt % Cl salt (that is, >0.53 wt % chlorine for an equimolar NaCl:KCl salt) would undergo washing. In the same way, according to the alternative low-temperature stabilization plan (Figure 8 of the main section of this document), items having between 30 and 50 wt % Pu, and also containing >1 wt % Cl salt, would undergo washing as they would have under the baseline plan. However, items having >50 wt % Pu, >1 wt % Cl salt (>0.53 wt % chlorine), and which could be demonstrated to contain ER salt according to the logic diagram shown in Figure 8 would be candidates to undergo stabilization at 750°C.

In particular, the LANL spectral software would be used to identify the presence of potassium. The counting times would be optimized to <3.5% error for chlorine detection or 3 hours, whichever comes first. This sensitivity for chlorine would yield an error for the potassium peak of <7% for items containing ER salt impurity. The error estimate arises given the ~2-fold lower sensitivity for potassium (see Table 3 in the main text) and the fact that ER salt (equimolar NaCl/KCl) contains about twice as much chlorine as potassium.

The identification of the presence of ER salt in ARF items is based on the relative peak intensities of $^{23}Na(\alpha,p\gamma)$ at 1808 keV and $^{35}Cl(\alpha,p\gamma)$ at 2167 keV. PGA spectra were taken at Rocky Flats of 20 Rocky Flats IDC 067 and 086 feed items and of the 10 product 3013 items created from thermal stabilization of the 20 items (see Appendix I), and the spectra were analyzed by the PFP software. Three of the feed and one of the 3013 product items did not emit sufficient signal from chlorine to produce a discernable peak for the PFP software. The integrated 1808 (Na) and 2167 (Cl) keV peak areas for the remaining 26 containers, plotted in Figure H-3, show good correlation, such that the average net background-subtracted Na peak is about 12-times as high as the net Cl peak.

PFP measurements of the Na and Cl prompt gamma peak areas for 59 ARF items, several in duplicate, are also plotted in Figure H-3. Although the individual peak areas generally are larger (probably because of the greater sensitivity of the PFP detector system), the relative areas of the Na and Cl integrated peaks are similar to those observed for the Rocky Flats ER salt items. All but a few of the Na/Cl peak ratios lie between the $\pm 2\sigma$ limits of the linear regression of the Na/Cl peak area ratio observed for the Rocky Flats items that would be expected if the items contained only ER salt. Though the sodium signal is prominent in all of the ARF items measured by PGA, the observation of Na/Cl peaks ratios lower than 8 might be evidence of the presence of additional Cl salt from DOR salt ($CaCl_2$) with a significant ER component.

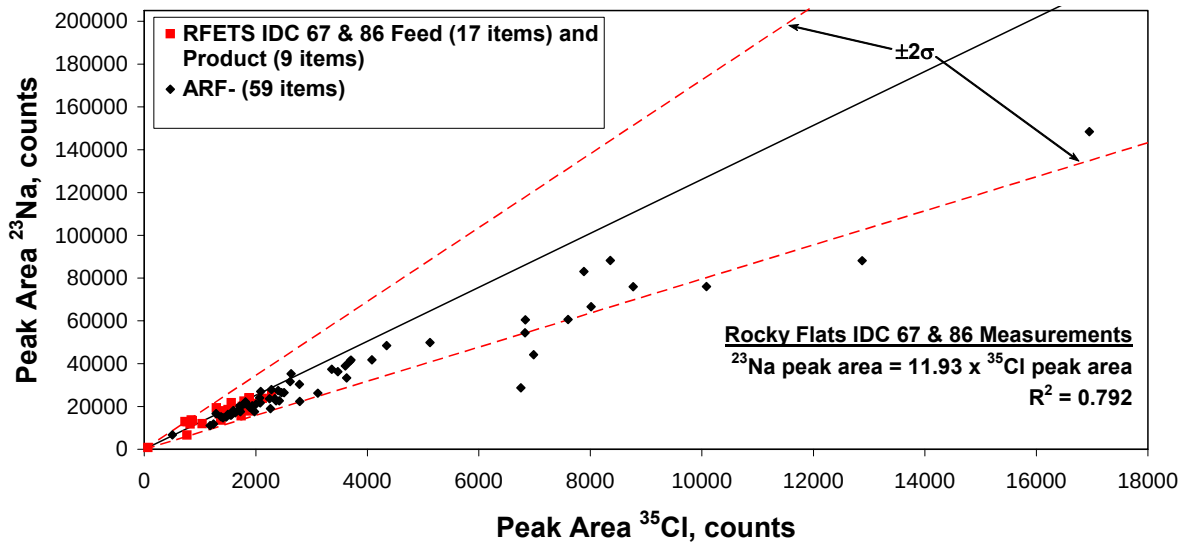

Figure H-3. Prompt gamma peak areas for ^{23}Na at 1808 keV as a function of peak areas for ^{35}Cl at 2167 keV for items containing ER salt at RFETS and for ARF items at PFP.

The Rocky Flats' and PFP's ARF data are replotted as the Na/Cl peak area ratio against ^{35}Cl peak area in Figure H-4. The ER materials from Rocky Flats have an average ratio of Na/Cl peak areas of 12.6±4.6 (at ±2σ) or 8.0–17.2. Also plotted in Figure H-4 are the analogous data obtained from Foster and colleagues (2002) for their tests of PuO_2 blended with equimolar NaCl/KCl and CaF_2 and heated past NaCl/KCl melting to 800°C or 950°C. These spectra were interpreted using the PFP software.

The Na/Cl peak-area ratios observed for the simulated pyrochemical salt PuO_2/NaCl/KCl/CaF_2 blends are about 13.6 to 15.8, consistent with ratios observed for Rocky Flats materials containing ER salts. Results from duplicate LANL prompt gamma measurements of MIS item ARF-85-102-295, also given in Figure H-4 and interpreted by the PFP software, show Na/Cl peak-area ratios around 13.9, again consistent with ER salt, as would be expected based on the LANL chemical analysis of this item.

One feature of the data plotted in Figures H-3 and H-4 is that some of the points for ARF items that plot below the lower limit for Na/Cl ratio clearly have significant quantities of sodium. This may be due to slight differences in the peak-area ratio for the Hanford instrument. Detection of K in some of these items might be an indicator that, although the Na/Cl peak-area ratio was low, the dominant Cl salts were still (NaK)Cl. Only expert review of the spectrum can distinguish material that would be likely to contain mainly other Cl salts from ER oxide with an anomalously high K/Na ratio.

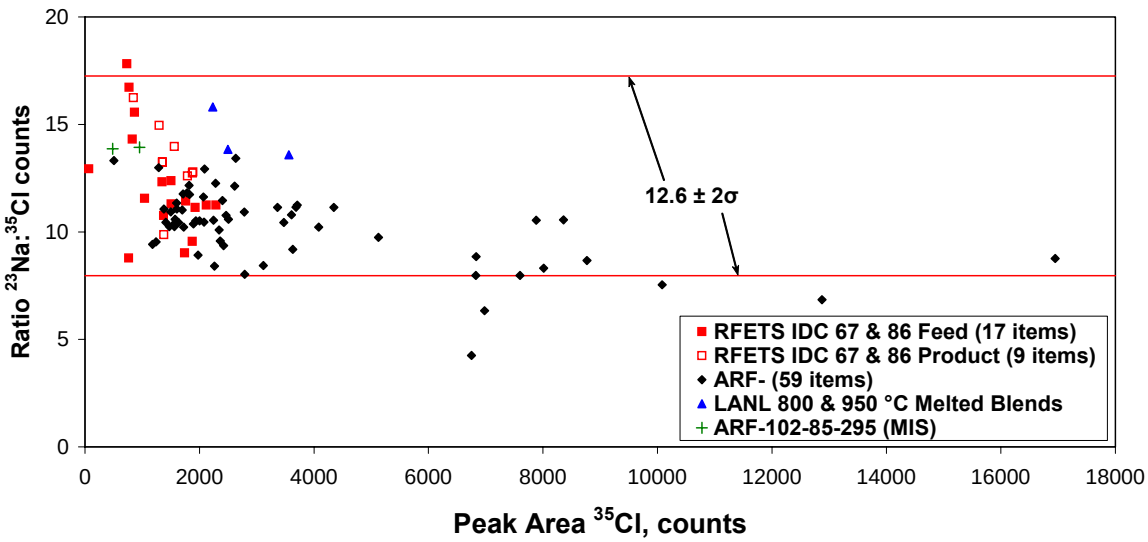

Figure H-4: Ratio of prompt gamma peak areas for ^{23}Na at 1808 keV to ^{35}Cl at 2167 keV as a function of ^{35}Cl peak area for items containing ER salt at RFETS and for ARF items at PFP.

Thus, a further means to identify ER salt is to search for the presence of potassium, as indicated by its peak at 1525 keV, using the PFP software. To detect potassium reliably, the counting times mandated by the PFP counting routine would be optimized to <3.5% error for chlorine detection or 3 hours, whichever comes first. This sensitivity for chlorine would yield an error for the potassium peak of <7% for items containing ER salt impurity. The error estimate arises given the ~2-fold lower sensitivity for potassium (see Table 3 in the main text) and the fact that ER salt (equimolar NaCl/KCl) contains about twice as much chlorine as potassium. Note, however, that the potassium peak could be obscured if enough fluorine (with peak at 1528 keV) is present. Therefore, expert review of the spectral evidence also is needed to judge the presence of ER salt by assessment of the potassium peak.

In summary, PGA made at Rocky Flats of materials certifiably originating from ER processes shows relative constancy of their 1808 keV ^{23}Na and 2167 keV ^{35}Cl peak-area ratios. Therefore, evaluation of the Na/Cl peak-area ratio for ARF items, and comparison of the measured ratio with those observed for Rocky Flats ER material, provides a simple means for PFP operations to sort for the presence of ER salt. Further assessment of the prompt gamma spectrum to find evidence for the presence of potassium also could be performed, but with possible compromise if significant fluorine were present.

Appendix I: Stabilization Experience for Relevant Oxides at Rocky Flats

Rocky Flats started processing chloride-bearing Pu oxide at 750°C on February 20, 2003, with stabilization of the 10th Cl salt batch completed on March 12, 2003. The distribution of the first 10 batches was targeted to cover the Pu concentration range of both the Rocky Flats chloride-bearing oxide and the oxides that were shipped from Rocky Flats to Hanford in the mid-1980s. The distribution of the Rocky Flats oxide that is eligible for the 750°C stabilization temperature is shown below in Figure I-1. The numbered diamonds provide the batch number, the feed source IDCs, and the approximate assay of the batch (that is, the vertical axis of the diamond labeled as #1 is aligned at ~69%).

In addition to the standard moisture analysis and PGA measurement on the output 3013 cans, PGA measurements were performed on the feed items at the request of the technical team working on demonstrating the equivalence of a lower stabilization temperature for the oxides shipped from Rocky Flats to Hanford. Additionally, photos of material and furnace condition were requested as part of this effort. Unfortunately, a good

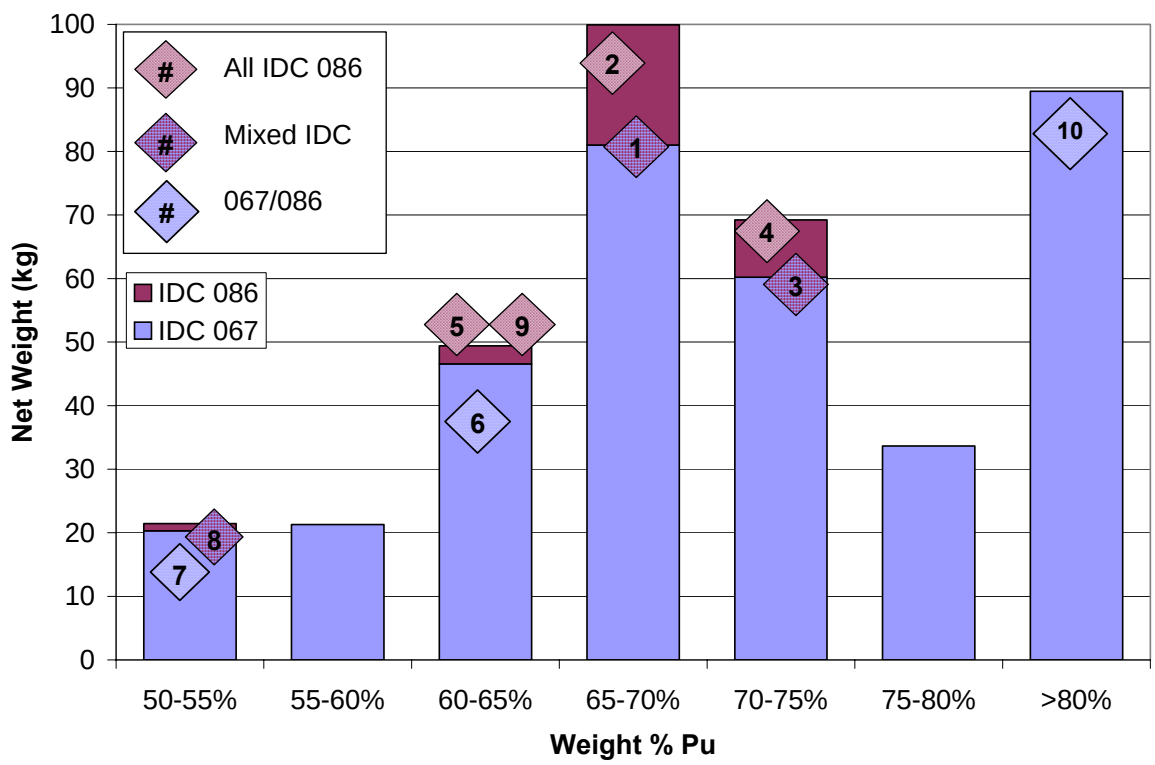

Figure I-1: Rocky Flats chloride-bearing oxide distribution, with first 10 batches shown.

baseline set of furnace photos was not taken just prior to stabilization of the first batch, although a set had been taken one week before the Cl salt batch processing began. Photos of the first six feed items from both IDCs were taken, as required by the Rocky Flats Plutonium Stabilization and Packaging System (PuSPS) Campaign Plan.

The first batch stabilized was representative of the average Pu assay of the Rocky Flats material, or approximately 69 wt % Pu. Figure I-2 below shows the material as it was screened in the feed preparation glove box. The material did require a moderate amount of effort to break up enough to fit through the 3/16-in. screen in the volume limiter.

Initial observations of the first batch after stabilization indicated that the furnace stand may have corroded, but earlier photos of Furnace 5 showed that corrosion was well underway before this batch was processed (Figure I-3). The stand was changed out after the first chloride-bearing batch was stabilized. The furnace tray also showed signs of corrosion in one corner, although no appreciable weight loss was noted in the tray tare weight after this batch was stabilized.

Figure I-2: Oxide from first Cl salt stabilization batch. Note crucible pieces in the right photo.

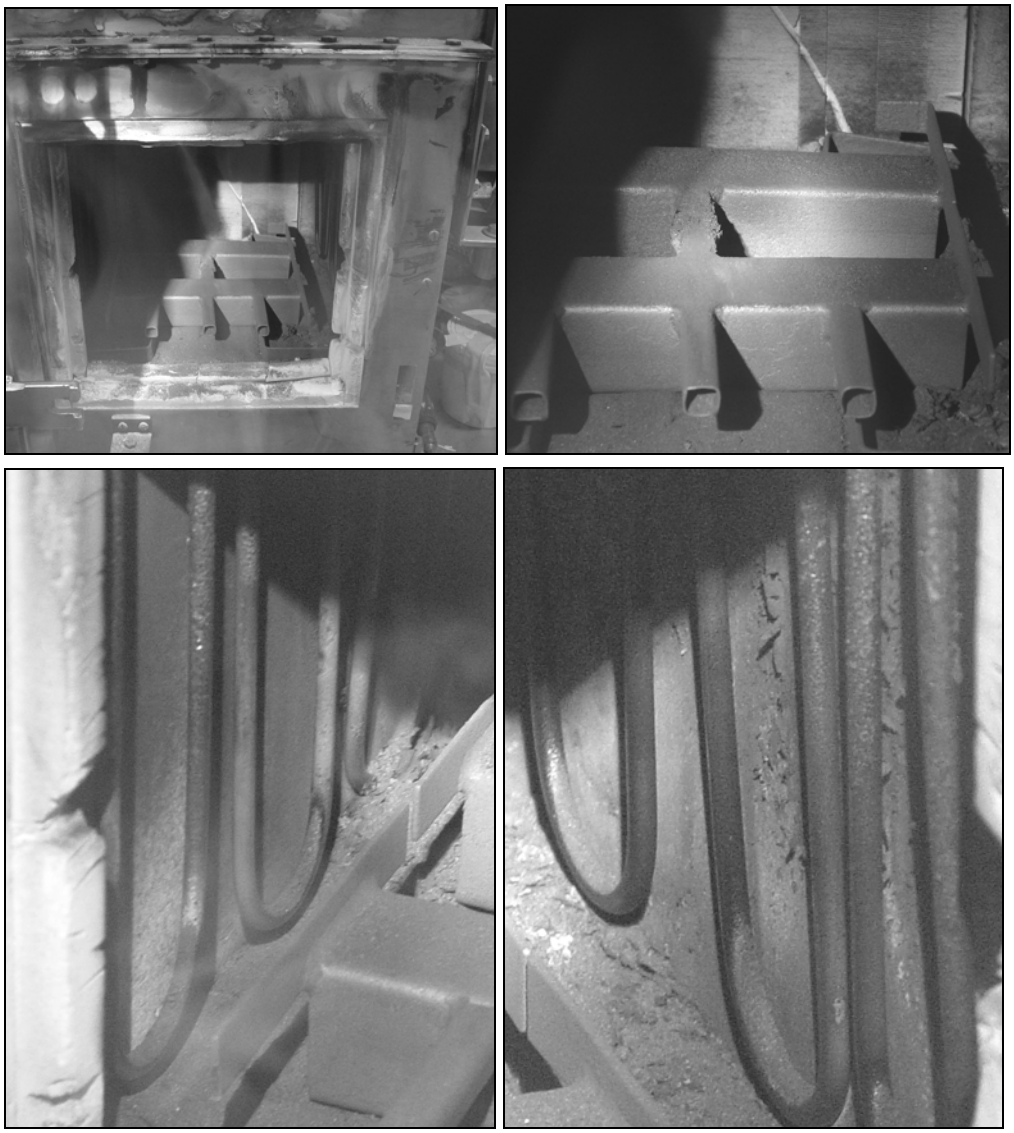

Figure I-3: Furnace 5 on February 13, 2003 (about a week before the start of Cl salt processing). Note that the stand is showing signs of corrosion on the center cross member. The center member had corroded through by February 21, 2003, after the first Cl salt batch was stabilized, and it was replaced. However, failure cannot be attributed to the Cl salt batch, given the condition shown in the upper right photo.

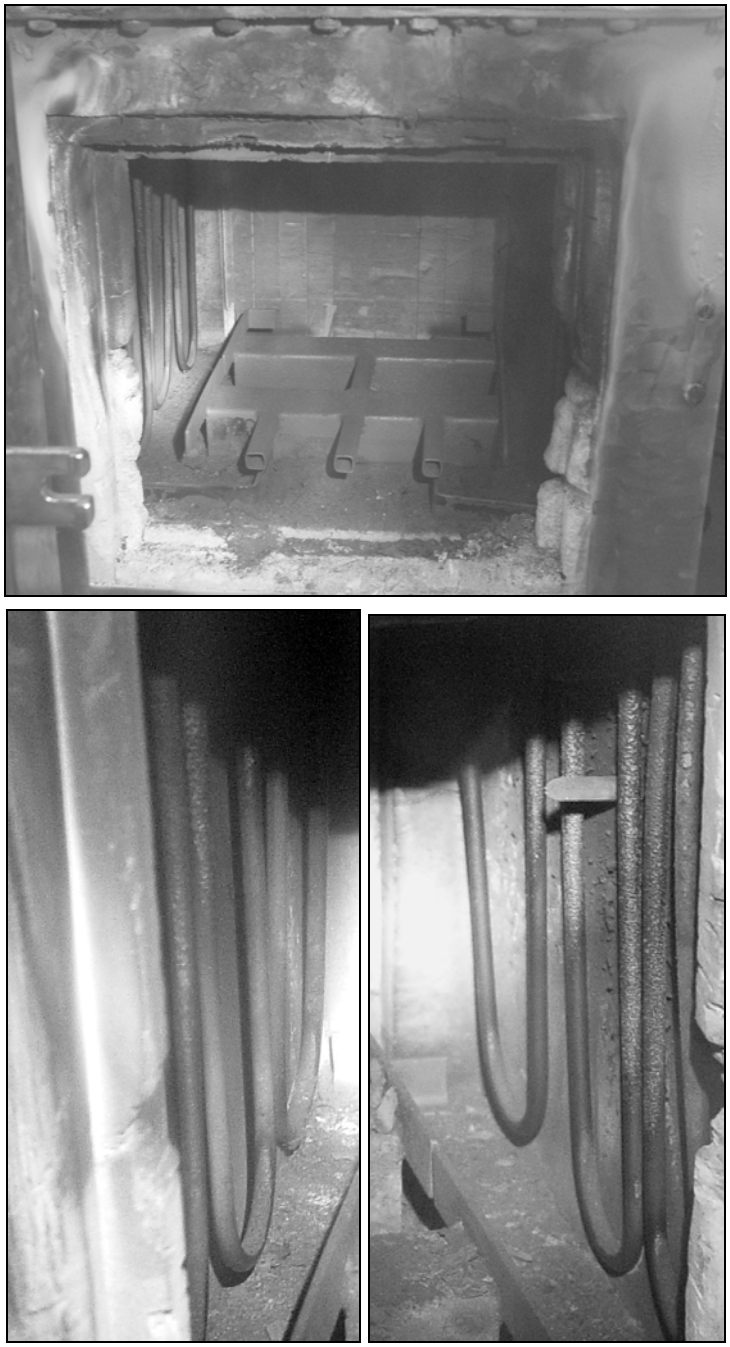

Figure I-4: Furnace 5 on March 13, 2003, after the 10th Cl salt batch was processed. More material is deposited on the furnace face than noted in the February 13th photos, but any change in the condition of the furnace elements is difficult to discern from the photos.

Prompt Gamma Measurements

PGA was performed on the feed items to demonstrate the use of this technique to discriminate Hanford's chloride- and non-chloride-bearing oxides, in addition to the standard measurement on the 3013 containers after stabilization. The count time for the PGA measurements is 30 minutes; thus, the detection capability is somewhat limited compared with the 1-hour count data from LANL and the more efficient detector system used at Hanford. No data were obtained for feed item CLLANL060C015131 (blank electronic file), and the feed item had already been processed before the lack of data was discovered. The PGA data are summarized for the feed items and 3013s in Table I-1

Chlorine was detected on all but one 1 of the 19 feed items analyzed and in 9 of the 10 output 3013 containers. The lack of detection of Cl for the one feed item and the output 3013 container that it was batched into is not surprising, given the high Pu assay of the feed and final 3013 and the short duration of the PGA measurement. The expected Cl-salt level for this batch would be in the 1% to 2% range.

The frequency of detection for Mg, K, and Na was 17 of 19, 11 of 19, and 19 of 19 feed items, respectively. In most cases, the output 3013 PGA measurements mirrored the feed item measurements, showing the same Mg, K, and Na hits if these elements showed up in at least one of the feed items, with two exceptions.

Magnesium was detected in the poststabilization measurement for 3013 container R610269, although Mg was not seen in either of the two feed items. 3013 container R610391 also showed Mg, when the one feed item analyzed did not; unfortunately, no conclusion regarding the Mg hit can be made due to the missing data on the other feed item.

Surprisingly, small F peaks were seen in seven of the feed items, and F was also seen in three out of the four resulting output 3013 containers. Note, however, that the magnitude of the F peaks was very small compared with PGA measurements of F on Rocky Flats foundry oxide. F would be expected as a contaminant in foundry oxide due the CaF_2 coating on the graphite molds. Also the lower detection limit for F is 0.1 wt % (for a 15-minute measurement) and 0.03 wt % (for a 60-minute measurement); the instrument is thus much more sensitive to F than to Cl.

Finally, weak Be and Si traces also showed up on two feed items, but were not seen on the poststabilization PGA analysis on the resulting 3013 containers.

Table I-1: PGA Results for Ten Rocky Flats Chloride-bearing Oxide Batches

3013 ID	IDC	Feed Item	Prompt Gamma Analysis				
			Cl	F[1]	Mg	K	Na
H000804	067	C01796	X		X	X	X
	086	C00470	X		X		X
	Poststabilization		X		X	X	X
R610285	086	C00688	X		X	X	X
	086	C00821	X		X	X	X
	Poststabilization		X		X	X	X
R610269	067	CLLANL063 [2,3]	X		X		X
	086	C01313	X		X		X
	Poststabilization		X		X	X	X
R610324	086	C00290	X		X	X	X
	086	C00299	X		X		X
	Poststabilization		X		X	X	X
H000549 [4]	086	C000129	X	X	X		X
	086	C01154 [5]	X	X	X	X	X
	Poststabilization		X		X	X	X
R610326 [6]	067	C00356	X	X	X	X	X
	067	C00655 [7]	X	X	X	X	X
	Poststabilization		X	X	X	X	X
R610439	067	CLLANL026 [2]	X	X	X	X	X
	067	CLLANL067	X	X	X	X	X
	Poststabilization		X	X	X	X	X
R610391	067	CLLANL060 [2,8]					
	086	C00876	X		X		X
	Poststabilization		X		X	X	X
H000798	086	C00877	X		X	X	X
	086	C01141	X	X	X	X	X
	086	C01154 [5]	X	X	X	X	X
	Poststabilization [9]		X	X	X	X	X
R610417	067	C00106	X				X
	067	CLLANL062 [2]					X
	Poststabilization						X

[1] All F peaks very small
[2] Original item number had a stacker can suffix Item number truncated in order to fit table
[3] Small Be peak detected
[4] Outer can failed NDT—reworked in R610427
[5] This item split between H000549 and H000798
[6] Outer can failed NDT—reworked into R610356
[7] Possible Si peak
[8] Data file blank, no results detected
[9] Small F peak

Moisture Analysis and Material Balance Before and After Stabilization

The results from the TGA/IR moisture analyses are summarized in Table I-2, along with the material balance information for the furnace tray and pre/poststabilization weight changes. Nine of the ten batches passed based on the TGA results, with 0.280% the highest weight loss observed on R610391, one of the lowest assay batches. Container R610417 had ambiguous TGA data (that is, slight gains and losses over the heat up cycle) requiring that the IR analysis be used to determine the content, which was 0.000%. Review of all the IR data showed essentially no moisture in any of the batches—the highest IR result was 0.022% for R610326. The two- and three-dimensional plots for the IR data show considerable noise interference due to being at or near the lower detection limit for water.

A rough material balance for the trays used for Cl salt stabilization, as well as the batches themselves, was performed. The furnace trays used by PuSPS normally have a tare weight in the range of 1,370–1,380 g when new. The average tray life is typically in the range of 15–19 furnace runs. The average weight loss per run is in the range of 10–20 g, and the final tray tare weights are on the order of 950–1,000 g at the time of failure, although exceptions do occur where holes have developed and trays have failed with fewer runs or higher final tare weights.

Review of the tray history data available as of March 26th shows that Tray #9 was used for three of the Cl salt batches fairly early in its life cycle (runs 4, 7, and 11) and did not show significant weight losses during the 800°C stabilization runs.

Trays #6 and #14 were used for two Cl salt batches, both at points that were approaching the average tray life for PuSPS operations. Tray #6 experienced fairly high weight losses (53 g and 71 g for runs 13 and 15, respectively). The data show that this tray was used for at least three more stabilization batches after running Cl salts, and the tare weight is approaching the point where the trays usually develop holes and have to be replaced.

Table I-2: Summary of Assay, Moisture Content, and Material Balance Information

3013 ID	Pu Assay (wt %)	TGA Moisture Content (wt %)	IR Moisture Analysis Result	Furnace Tray #/ Tray Usage	Tray Weight Change (g)[2]	Batch Weight Change (g)[3]
H000804	69.2	0.130	0.000	#9/4th Run	1.8	7.5
R610285	69.5	0.070	0.000	#14/13th Run	–4.3	93.1
R610269	72.3	0.250	0.000	#11/7th Run	13.1	8.8
R610324	71.5	0.070	0.020	#14/14th Run	tbd	–43.8
H000549[4]	61.1	0.140	0.004	#6/13th Run	53.4	33.2
R610326[5]	60.8	0.140	0.022	#9/6th Run	8.6	10.4
R610439	52.9	0.140	0.000	#9/12th Run	1.8	25.9
R610391	54.6	0.280	0.002	#3/15th Run	–21.7	49.6
H000798	63.6	0.000	0.000	#6/15th Run	71.1	–42.2
R610417	84.3	0.000	0.000	#13/26th Run	3.0	3.1

[1] Tray usage indicates the number of times that the tray had been used for oxide stabilization.
[2] The tray weight change is calculated based on the change in tray weight between the chloride run and the subsequent stabilization run. A positive number indicates a weight loss occurred.
[3] The batch weight change is based on the initial net weight of the material minus the sample weight and the net material weight in the convenience can. A positive number indicates a weight loss occurred.
[4] H000549 outer can failed NDT—reworked into R610427.
[5] R610326 outer can failed NDT—reworked into R610356.

Tray #14 was used for two Cl salt runs, consecutively (runs 13 and 14). The change in tray tare weight for the tray was not available for run #14 at the time of the data query, but it is highly likely that this tray was very near its end of life, given that the tare weight going into run #14 was 1006 g and that run #14 was the last recorded use as of February 25th. Trays #3, 11, and 13 were each used for a single batch of chloride-bearing oxide. The only point worthy of remark is that Tray #13 was on its 26th run with the Cl salt batch and was used for at least 28 runs, based on the latest data.

The pre to poststabilization batch weight changes ranged from the largest weight loss of 93 g to two batches with weight gain of about 42–44 g. While data on the tray material balance is not yet available for the largest batch weight gain, it is interesting to note that the second largest weight gain by a batch (~42 g) corresponded to the largest weight loss from the furnace tray, indicating that corrosion products from the tray sloughed off into the oxide batch. Also of interest is that the two batches with the highest weight losses corresponded to weight gains on the furnace trays, indicating that residual salt may have adhered to the trays.

Observations on IDC 061 Materials Stabilized at Rocky Flats

The PGA on the Rocky Flats 3013s that contain IDC 061 and <80 wt % Pu+eU were reviewed to determine whether Cl salt would be detected as a contaminant. As shown by the data in Table I-3, detection of Cl in some of the foundry oxide is to be expected, given that Pu metal from pyrochemical processes may have had residual salts on the button, either on the surface or as occlusions. Also, as noted previously, Mg and Na detection is ineffective as a discriminator for chloride-bearing material, since their presence is ubiquitous. Fluorine detection is fairly common and is to be expected with foundry oxide due to the calcium fluoride coating on the graphite molds. The Pu+eU assay range of the 13 items with prompt gamma data ranged from 59–79 wt %.

Table I-3: Rocky Flats IDC 061 Prompt Gamma Data

3013 ID	Prompt Gamma Analysis											
	Al	Be	Cl	Cr	Cu	F	Fe	Mg	K	Na	Si	Ta
H000808		X	X			X[1]		X		X		
H000847					X	X[2]		X		X		
H000861	X					X		X		X	X[3]	
H000862		X			X	X		X		X		
H000898						X		X		X		
H000913		X	X		X			X		X		
H000914			X[4]			X		X		X		
H000937	X	X			X	X		X		X	X?[5]	
R601780								X				
R610056		X			X			X				
R610201			X					X		X		
R610305		X			X	X		X		X		
R610319		X			X	X		X		X		

[1]Strong F
[2]Strong F
[3]Could not distinguish Al and Si. Al more likely due to sensitivity
[4]Weak Cl, strong F
[5]Definite Al signal, Si possible

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Appendix K: Author Biographies

Jeremy Boak

Dr. Jeremy Boak is project leader for Nuclear Material in the Risk Reduction and Environmental Stewardship Division at LANL. From 2000 to 2002, he was lead laboratory manager for the Nuclear Material Focus Area for EM-50. He directed the multilaboratory team providing technical support to DOE leads for the Focus Area, interacting with sites to define needs, assembling the needs into calls for proposals, reviewing proposals, preparing budgets, and managing funded projects.

From 1998 to 2000, Boak was project leader for the Environmental Science and Technology program at LANL and managed projects supporting the EM-50 mission, including development and deployment of the SuperHENC NDA system for Rocky Flats.

He served as the TRU waste lead for the Environmental Stewardship Office (ESO) from 1996 to 1998, managed upstream treatment projects for TRU waste, helped define TRU waste projections for the *Accelerated Cleanup: Paths to Closure* document for LANL, and represented the ESO on the Waste Management Steering Committee.

Boak led preparation of the Work Plan for Los Alamos and Pueblo Canyons for the Environmental Restoration Project at LANL. This plan defined the program to evaluate the potential risk on and off Laboratory property from transport of contamination through the two canyons most strongly affected by Laboratory operations.

Before coming to the Laboratory, Dr. Boak directed performance assessment and technical data management at DOE's Yucca Mountain Program. He was responsible for the first two performance assessments completed by the project, and presented the results of these efforts nationally and internationally.

Dr. Boak's scientific expertise includes geological sciences (mineralogy, petrology, petroleum geology, and environmental geology), TRU waste management and pollution prevention, and nuclear material technology development and deployment. He has authored or coauthored 18 peer-reviewed papers. Boak received a Ph.D. in geological sciences from Harvard University in 1983. Boak has held a Q-clearance since 1996.

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Elizabeth Conrad

Elizabeth Conrad is the Principal Technical Advisor—Special Nuclear Materials for the Building 371/374 Closure Project, Kaiser-Hill Company, LLC, at the Rocky Flats Environmental Technology Site. She is responsible for analysis, direction, and strategy development on technical and safety issues associated with the storage, stabilization, and shipment of Rocky Flats Pu metal, oxide, and residues. Recent initiatives include deployment of a new moisture-measurement technique for Pu oxides and the disposal of low-purity oxides to the WIPP. She instigated the original DOE complex-wide effort to show technical equivalency to the DOE Standard 3013 for lower-temperature stabilization of chloride-bearing oxides.

Prior to joining Kaiser-Hill in 2001, Ms. Conrad worked as a consultant with the Los Alamos Technical Associates, Inc. (1997–2001) and M. H. Chew and Associates, Inc. (1992–1997). She provided technical support to Kaiser-Hill, Fluor Hanford Company, and for the DOE at Headquarters (DOE-HQ), the Rocky Flats Field Office, and the Albuquerque Operations Office. She established the approach to reduce risk from high-dispersibility residues and formed the safety basis for pipe overpack container storage, performed numerous evaluations on disposition pathways for Rocky Flats residues, and facilitated Hanford's original variance to safeguards termination limits for the disposal of their sand, slag, crucible, and incinerator ash residues to WIPP.

From 1981 to 1992, Ms. Conrad worked at the Hanford site, initially for Rockwell Hanford Operations and then Westinghouse Hanford Company. Her background includes a detail as a technical advisor to Defense Programs, DOE-HQ on Pu production issues, 1989–1991. Additionally, Ms. Conrad provided technical support to the PFP and the Plutonium Uranium Extraction (PUREX) Plant, covering the technical production aspects of the nuclear fuel reprocessing cycle from fuel dissolution to Pu metal and oxide production.

Ms. Conrad received her B.S. in chemical engineering from Montana State University in 1981.

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Calvin H. Delegard

Calvin Delegard has 23 years of experience in applied, process, and nuclear materials chemistry at Hanford. He joined PNNL in 1996 after 16 years in Hanford operations, supporting the PFP, PUREX, and the waste tank farms with particular expertise in actinide chemistry; Pu process chemistry; tank waste chemistry; and U, Fe, and Zr corrosion.

He investigated the effects of waste constituents on the solubility and soil sorption of Co, Sr, Cs, U, Np, Pu, and Am. His findings on Pu dissolution from oxide, third phase formation in Pu purification at PUREX, and Pu nitrate concentrator corrosion were implemented to improve plant flow sheets and operations.

Mr. Delegard provided initial characterization of the gas-generation reactions occurring in Hanford's infamous burping waste tank. He has engaged in Hanford waste processing research and development (R&D)—hydrothermal silicate immobilization, ozonation, calcination/dissolution, electrolysis, and sludge and fractional salt dissolution. He collaborates with the Institute of Physical Chemistry, Russian Academy of Sciences, in studies of transuranium element and Tc chemistry in alkaline media. He currently is investigating the characteristics, processing, and storage of irradiated U metal-bearing sludge from the Hanford K Basins.

Mr. Delegard was appointed twice to the International Atomic Energy Agency (1976–1979 and 1987–1992), where he designed and led nuclear material safeguards inspections and methods development for destructive and nondestructive nuclear materials verification. Upon returning to the US, he was involved in efforts at the PFP for the first-ever submission of weapons materials to International Atomic Energy Agency (IAEA) safeguards. He played a key role in IAEA acceptance of the PFP operator's calorimetric NDA system for Pu verification, sharply decreasing the dose, material handling, and shipment requirements of existing IAEA safeguards.

His publications include Hanford contractor and Pacific Northwest, Los Alamos, and Brookhaven National Laboratory reports; articles in *Radiochemistry*, *Radiochimica Acta*, *Nuclear and Chemical Waste Management*, *Journal of Nuclear Materials Management*, and *Journal of Alloys and Compounds*; book chapters on actinide chemistry; and symposium proceedings. Cal earned his B.S. in chemistry (with distinction, Phi Beta Kappa) in 1970 from Washington State University.

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Alice M. Murray

Alice Murray is the manager of the Actinide Laboratory Programs (ALP) Group at the Savannah River Technology Center, SRS (6/00 to present). She was also the manager of Stabilization and Processing Product Lines of the Nuclear Material Focus Area.

Before becoming manager of the ALP Group (6/96–5/00), Dr. Murray was a researcher in the same group and worked on flow-sheet development for the dissolution of legacy materials in the F-Canyon facility at SRS. She also supported the residue characterization program at Rocky Flats through reviews of laboratory notebooks, production and experimental run sheets, laboratory analyses, and other available information.

Prior to working at SRS, Dr. Murray worked at the RFP/ RFETS. She started work at RFP in 1987 in the pyrochemical process development group. She developed and supervised the implementation of a production process to extract americium from aged Pu. She participated in several DOE complex-wide initiatives, including serving as the team leader for the multisite Disassembly/ Conversion/Purification Team for Complex 21 and participating on Trade Studies for Rocky Flats pyrochemical salts and sand, slag, and crucible residues. She managed joint research programs with LANL, LLNL, and the Colorado School of Mines.

Dr. Murray spent five years as a postdoctoral associate doing laser spectroscopy. One year was spent at the University of Kansas (1982) with the remaining time at the University of Texas at Dallas (1983–1987). At the University of Kansas, she was involved with microwave double resonance spectroscopy, and at the University of Texas at Dallas she developed methods to visualize the liquid and vapor phases of fuel sprays to improve the efficiency of fuel-delivery systems.

She received her Ph.D. in physical chemistry from the University of Arizona in 1982. Her B.A. in chemistry was obtained from Mount Holyoke College in 1975 (Magna Cum Laude, Phi Beta Kappa).

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Gary D. Roberson

Mr. Roberson is manager of the Defense Nuclear Facility Safety Board (DNFSB) 94-1 technology R&D program sponsored by the Office of Integration and Disposition. He was the team leader developing the Non-Actinide Isotope and Sealed Source project and database for the nuclear material integration program. Mr. Roberson has taken the lead in the small sites nuclear material disposition workshop preparing risk analysis of nuclear materials at small sites in the DOE complex. He is responsible for the Preparing Activity on DOE-STD-3013-2000, "Stabilization, Packaging, and Storage of Plutonium-Bearing Materials." He has responsibility for nuclear material technology integration within DOE as defined in the "Integrated Nuclear Material Management Plan" report to Congress and in international coordination with Britain (JOWOG), Russia, France, and Japan; NATO; and IAEA. Mr. Roberson has recently been asked to lead the nuclear material disposition activities for EM site closure for the Office of Science and Technology.

Mr. Roberson has over 31 years of experience in science and technology fields, the last 13 years in government positions including Headquarters Technology Representative on the Richland Source Evaluation Board; Acting Director of the Waste Tank Remediation System, Washington D.C.; Acting Deputy Director of the Regulatory and Site Evaluation Division, Yucca Mountain; and baseline manager for the Office of Waste Management, Washington D.C. He has experience in the high-level, low-level, and TRU waste programs across the DOE complex.

Prior to employment in the government, Mr. Roberson was an exploration geologist in the oil and gas industry, where he owned his own company and consulted in the fields of exploration, development, geophysics, and industrial waste management.

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Theodore J. Venetz

Ted Venetz is currently employed as a senior engineer with Fluor Hanford at the PFP, and began employment at the Hanford Site in 1981. He is currently a member of the MIS Working Group (MIS-WG) and has been a technical contributor to the DOE-STD-3013-2000 working group since 1996. He has provided technical assistance to the DOE on various initiatives related to improving integration, nuclear materials management, and Pu storage and disposition issues.

Mr. Venetz has previously been employed as part of the Nuclear Materials Strategic Planning Group, in Plutonium Disposition Planning and Solid Waste System Engineering, and is cognizant engineer for the Plutonium Reclamation Facility. He has expertise in process engineering related to nuclear materials production, Pu oxide processing and recovery, Pu stabilization and storage, and waste management and disposal.

In addition to his Pu-processing background, Mr. Venetz has experience in management, production, and project engineering in the manufacture of semiconductor feed materials using hydrogenation, distillation, and vapor deposition.

Venetz received a B.S. in chemical engineering from Montana State University in 1981.

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