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STABILIZING PLUTONIUM MATERIALS AT HANFORD: SYSTEMS ENGINEERING FOR PFP TRANSITION PROJECT EFFORT ON DNFSB 94-1

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Abstract: This report discusses the basic objectives of the stabilization and packaging activities at the Plutonium Finishing Plant that satisfy the Defense Nuclear Facility Safety Board Recommendation 94-1 by transforming the plutonium materials at Hanford into forms or conditions which are suitable for safe storage to appropriate storage criteria; or discard that meets appropriate waste acceptance criteria., Rev.

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TABLE OF CONTENTS

1.0 INTRODUCTION	1-1
2.0 SCOPE	2-1
3.0 OBJECTIVES	3-1
4.0 APPROACH	4-1
5.0 OVERALL FUNCTIONAL DESCRIPTION	5-1
5.1 ANALYZE MISSION	5-1
5.2 FUNCTIONAL DECOMPOSITION	5-1
5.3 RELATIONSHIP OF PLUTONIUM STABILIZATION TO HANFORD CLEANUP MISSION	5-5
6.0 REQUIREMENTS	6-1
6.1 SOURCES OF REQUIREMENTS	6-1
6.2 CONVERT PLUTONIUM MATERIALS	6-1
6.3 CHARACTERIZE PLUTONIUM MATERIAL	6-5
6.4 PACKAGE STABILIZED PLUTONIUM MATERIAL	6-6
7.0 ALTERNATIVES	7-1
7.1 INTEGRATED STABILIZATION PROCESS	7-1
7.2 STABILIZATION	7-3
7.2.1 Reduction Residues	7-3
7.2.2 Fluoride Residues	7-4
7.2.3 Sludges	7-4
7.2.4 Potential Residues	7-5
7.2.5 Ash	7-5
7.2.6 Oxalate Residues	7-7
7.2.7 Oxide Residues	7-7
7.2.8 Oxides	7-8
7.2.9 Alloys	7-8
7.2.10 Nitrate, Chloride and Basic Aqueous Plutonium Solutions	7-9
7.2.11 Combustibles	7-15
7.2.12 Polycubes	7-17
7.2.13 Oil and Organic Solutions	7-19
7.2.14 Pu-Contaminated Metals	7-24
7.3 IMPLEMENTATION TO REDUCE OPERATOR EXPOSURE	7-25
8.0 DECISION CRITERIA	8-1

TABLE OF CONTENTS

(continued)

9.0 ALTERNATIVE COMPARISONS	9-1
9.1 ALTERNATIVE DESCRIPTIONS	9-1
9.2 EVALUATION APPROACH	9-4
9.3 EVALUATION OF ALTERNATIVES ONE THROUGH THREE FOR SOLID RESIDUES AND SOLUTIONS	9-6
9.3.1 Evaluation	9-6
9.3.2 Sensitivity of Result to Weighting of Decision Criteria	9-8
9.4 EVALUATION OF ALTERNATIVES 4 THROUGH 7 FOR COMBUSTIBLES ..	9-9
9.4.1 Evaluation	9-9
9.4.2 Sensitivity of Result to Weighting of the Decision Criteria	9-14
10.0 RECOMMENDED INTEGRATED BASELINE	10-1
10.1 INTEGRATED STABILIZATION BASELINE	10-1
10.2 INTEGRATED CHARACTERIZATION, STABILIZATION, AND PACKAGING SYSTEM	10-5
11.0 ISSUES	11-1
11.1 ULTIMATE DISPOSITION OF PLUTONIUM MATERIAL	11-1
11.2 RELATIONSHIP TO PFP STABILIZATION EIS	11-1
11.3 PFP TRANSITION PROJECT PRIORITIES	11-1
11.4 MATERIAL STATUS AND DISCARD LIMITS	11-5
12.0 RECOMMENDATIONS FOR FURTHER STUDY	12-1
13.0 REFERENCES	13-1
APPENDIX A DNFSB RECOMMENDATION 94-1	
APPENDIX B DOCUMENTS USED TO COMPILE DECISION CRITERIA	
APPENDIX C SUMMARY OF PACKAGING REQUIREMENTS FROM DOE-STD-3013-94	
APPENDIX D SENSITIVITY ANALYSIS CROSSOVER DIAGRAMS	
APPENDIX E INITIAL DRAFT OF POLICY MEMORANDUM ON TREATMENT AND DISPOSITION OF PLUTONIUM BEARING RESIDUES	

LIST OF FIGURES

4-1. Hanford Systems Engineering Core Process	4-2
5.1-1. Mission Context Diagram	5-2
5.2-1. Functional Hierarchy	5-3
5.2-2. Functional Block Flow Diagram	5-6
5.3-1. Functional Hierarchy Hanford Site Cleanup	5-7
5.3-2. Functional Hierarchy PFP Store, Treat, Disposition	5-8
7.1-1. Hypothetical Example of Six Alternatives from Various Options in Three Unit Operations	7-2
7.2-1. Residue Dissolution and Solution Stabilization by Precipitation Process	7-12
7.2-2. Vertical Calciner for Direct Denitration	7-14
7.2-3. Molten Salt Oxidation Flow Schematic	7-18
7.2-4. Simplified Wet Air Oxidation	7-22
7.2-5. Simplified DETOX SM Process Diagram	7-23
9.3-1. Ranking of Alternatives 1 and 2 Including Average of Two Evaluation Teams	9-10
9.3-2. Diagram of Percent of Weight on Req./Waste Minimization Measure versus Utility for Alternatives 1 and 2	9-11
9.4-1. Ranking of Alternatives 4 through 7 including Average of Two Evaluation Teams	9-15
9.4-2. Cross Over Point for End Point Characteristics	9-16
9.4-3. Cross Over Point for Process Capability	9-17
9.4-4. Cross Over Point for Stakeholder Perceptions	9-18
10.1-1. Selected, Preferred Integrated Stabilization System has Five Processes	10-2
10.1-2. An Integrated Process with Direct Denitration does not reduce the Number of Process	10-3
10.1-3. Molten Salt as the Core Process is the Simplest with Only Three Processes	10-4
11.1-1. Plutonium Disposition Schedule for PEIS	11-2

LIST OF TABLES

2-1. Summary of Plutonium Materials Addressed in this Report	2-2
6.1-1. Sources of Requirements for Pu Stabilization	6-2
6.2-1. Requirements from DOE-STD-030-94 Related to the Treatment of Plutonium Material ≥ 50 weight %	6-3
6.4-1. Schedule Commitments Associated with Packaging made to Support DOE's Response to DNFSB 94-1	6-7
8.1-1. Decision Criteria for Alternative Evaluation and Ranking	8-2
9.1-1. Illustration of the Alternatives 1-3 For Stabilizing Solid Residues and Solutions	9-2
9.1-2. Illustration of the Alternatives 4-7 for Combustibles	9-3
9.2-1. Matrix of the Identified Alternatives and the Proposed Feed Material Categories	9-5
9.3-1. Evaluation Data Matrix for Alternatives 1 & 2	9-7
9.4-1. Evaluation Data Matrix for Alternatives 4 through 7	9-13
11.3-1. The Site Goals used to Evaluate the Relative Importance of PFP Near Term Activities	11-3
11.3-2. PFP TP Strategic Priorities List	11-4

1.0 INTRODUCTION

The elements of DNFSB Recommendation 94-1 are summarized, and the impact to the Plutonium Finishing Plant (PFP) Transition Project is discussed. In order to alleviate the concerns expressed in DNFSB 94-1, material must be characterized, stabilized and packaged for safe interim storage. Many alternative systems can be developed that stabilize the materials. However, finding an alternative that meets the variety of requirements while providing the desired performance requires a technical and disciplined approach. This report documents that approach. This report discusses the programmatic and technical requirements for DNFSB 94-1 compliance. Alternative systems for implementing the recommendation will be discussed. The relationship of other issues and initiatives to the implementation of DNFSB 94-1 will also be explained. The report aims to provide backup information and the systems engineering approach that is the basis for the plutonium-bearing materials portion of the *DNFSB Recommendation 94-1 Hanford Site Integrated Program Plan* (WHC 1994).

The Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 94-1 (Conway 1994) expressed concern that the storage of plutonium materials and spent nuclear fuel was not safe and strongly recommended that this concern be addressed and corrected quickly. DNFSB Recommendation 94-1 stated that the halt of nuclear weapons material production around 1989 basically "froze the manufacturing pipeline" in a state that was unsafe; this unsafe state "should not be left unremediated" and DNFSB 94-1 concluded that "imminent hazards could arise within two to three years unless certain problems are corrected." The Department of Energy (DOE) agreed, accepted DNFSB's recommendation on August 31, 1994, and began efforts to address DNFSB's concerns and correct the identified problems.

DNFSB Recommendation 94-1 addressed five specific concerns about specific liquids and solids containing fissile material and radioactive substances located at specific sites in the DOE complex. Hanford was mentioned, specifically, for the spent fuel located in the K-Basins and for plutonium-bearing liquids and solids. DNFSB made eight specific recommendations: three apply to Hanford. The first is that within 8 years, all storage of plutonium metal and oxide should be in conformance with DOE's long-term storage criteria documented in DOE-STD-3013-94. The second is that the program to place the K-Basin reactor fuel in a stabilized condition for interim storage until ultimate disposition occurs should be accelerated such that the fuel is in safe interim storage within 2 to 3 years. The final recommendation states that facilities that may be needed for future handling and treatment of the materials in question be maintained in a usable state. Hanford Site is identified as one of those facilities.

Prior to DNFSB's release of Recommendation 94-1 on May 26, 1994, DNFSB published a report titled *Plutonium Storage Safety at Major Department of Energy Facilities* (DNFSB 1994). This report was based on DNFSB staff and DNFSB outside expert visits to Rocky Flats, Hanford's PFP, Savannah River Site F-Area, and Los Alamos National Laboratory and on conversations with local plutonium experts. The concerns in the report that are specific to Hanford are:

- Bottled solutions are not safe for long-term storage.
- Polycubes generate gas and are not suitable for long-term storage.
- Unstable precipitation and solvent extraction residues are stored in glove boxes.

-
- Incinerator ash from Rocky Flats requires action to improve long-term stability.
 - Sand, slag and crucible stored in lard cans is not stable.
 - Plutonium metals and oxides are stored in food pack cans, which have elastomer seals and an unknown design life.
 - The material in storage should comply with DOE long-term storage criterion.

DOE issued an Implementation Plan on February 28, 1995, that includes the planned efforts for resolving DNFSB 94-1 issues regarding plutonium material at Hanford. This Implementation Plan (DOE 1995) is also the Integrated Program Plan (IPP), which was requested in DNFSB Recommendation 94-1. The Implementation Plan sets schedule commitments for specific Hanford material. The plan calls for a DOE complex-wide integrated approach to resolve DNFSB's concerns. DOE's complex-wide integrated approach is consistent with DNFSB's recommendation to use a systems engineering approach when remediating the identified concerns. DOE's Implementation Plan defines and requires Site Integrated Stabilization Management Plans (SISMP's). This report, "Stabilizing Plutonium Materials at Hanford: Systems Engineering for DNFSB 94-1 and PFP Transition Project," provides the basis and the systems engineering approach for the plutonium materials portion of the *Hanford Site Integrated Stabilization Management Plan* (WHC 1994).

2.0 SCOPE

While DNFSB 94-1 only addresses specific materials, the DOE has broadened the scope to include additional bulk liquids and solids containing fissile material and other radioactive substances in reprocessing canyons, processing lines and various facilities that require conversion to forms, or establishing conditions, suitable for safe interim storage. The scope was broadened to ensure that similar materials under similar conditions receive the same degree of attention as those noted by DNFSB in its Recommendation.

The materials to be stabilized are plutonium-bearing materials at the Hanford Site, excluding the items currently held by the Pacific Northwest National Laboratory. Plutonium in spent fuel, solid waste, tank waste and contaminated soils is also excluded. The materials can be found at PFP and Plutonium Uranium Extraction Facility (PUREX). PUREX is scheduled to be completely deactivated in 1997, and all plutonium material will be relocated to PFP or to the Tank Waste Remediation System (TWRS). The inventory of plutonium materials at Hanford is extremely diverse and contains approximately 200 different material source or description codes and categories. The material is a collection of scrap, processing residues, residual material from glove box type operations, product forms, and etc. Some materials are residuals from the Remote Mechanical C-Line (RMC) and Plutonium Reclamation Facility (PRF) processing lines, and miscellaneous glove box operations at PFP and Hanford. Significant amounts of material are from other sites in the DOE complex such as Rocky Flats and Savannah River. The plutonium material can be classified in a number of ways: according to chemical properties, physical properties, their source and history, potential stabilization method or their evaluated hazard level or risk for incident. Table 2-1 summarizes the materials addressed in this report. The grouping of the material was made with the intent of determining stabilization processes. The table has a classification, potential residues, that indicates the potential for additional inventory items as a result of terminal clean out (TCO) and decontamination of Hanford facilities, such as PFP and PUREX. The quantity has been estimated and is expected to be minimal compared to the amount of the current inventory. The table and this report do not include plutonium metal, fuel pin assemblies, and sources.

Table 2-1. Summary of Plutonium Materials Addressed in this Report
Based on June 1995 Inventory Information.

Item Classification	Description	Number of Items	Weight of Pu (Kg)	Relationship to HSISMP Material Type ¹
Reduction residues	Residues (includes sand, slag & crucible) from the plutonium metal reduction process (the RMC line), containing plutonium metal fragments, slag, calcium fluoride, excess calcium, manganese oxide, sand and crucible pieces.	266	43	Equivalent to the material type. Slag and Crucible.
Fluoride residues	Residues containing PuF_4 in high levels if from RMC line or in low levels if from dried dissolver heels.	12	3	Part of the material type. Compounds.
Sludges	The primary origin of sludges is PRF and typical consists of 33% Fe_2O_3 and $\text{Fe}(\text{NO}_3)_3$, 1% TBP, 26% $\text{Pu}(\text{NO}_3)_3$, 7% PuO_2 and 3 to 5M HNO_3 .	N/A	N/A	Part of the material type. Other/ Miscellaneous.
Potential residues	This is material collected from PFP and PUREX decontamination and terminal clean out operations.	N/A	N/A	Not included in the HSISMP.
Ash	The composition of the ash is varied, because it is from the combustion of discarded glovebox sweepings. Ash is from both the 232-Z incinerator and "reburned" ash from Rocky Flats that was stabilized in the HA-40F furnace. Past analyses show high levels of silicon oxide and metal oxides such as calcium, lead, iron, aluminum, chromium, manganese, and zinc.	551	81	Equivalent to the material type. Ash.
Oxalate residues	Sludges containing plutonium oxalate from the RMC precipitation step. Some of these were removed from PRF tankage and centrifuges.	N/A	N/A	Part of the material type. Other/ Miscellaneous.
Oxide residues	Scrap containing plutonium oxide including burned metal oxide. The purity is highly variable and less than 50%.	553	91	Equivalent to the material type. Oxide < 50%.

Item Classification	Description	Number of Items	Weight of Pu (Kg)	Relationship to HSISMP Material Type ¹
Oxides	These are plutonium oxides >50% including, PUREX and other product oxides that have been thermally stabilized in either the 9A calciner or the HA-21A furnaces.	2647	1849	Equivalent to the material type, Oxide > 50%.
Alloy	All alloys in the inventory: Pu-U-Mo, Pu-U, Pu-Al, Pu-Zr & Pu-Th. Twenty-eight items are uncharacterized and five items are anode heels.	125	34	Equivalent to the material type, Alloys.
Solutions, nitrate	Plutonium nitrate solutions including: PUREX product from PUREX cleanout, fuels grade product nitrate, concentrated filtrate from RMC line including potassium nitrate, manganese dioxide, plutonium nitrate, and PRF flush solutions.	422	330	Part of the material type, Solutions.
Solutions, chloride	Solutions received from Argonne Material Lab that are nitric acid and hydrochloric acid mixtures, some as high as 6M HCl.	19	3	Part of the material type, Solutions.
Solutions, basic	Sodium carbonate solutions that were down loaded from PRF.	16	1	Part of the material type, Solutions.
Combustibles	Filters, plastics, and other combustible material contaminated with plutonium.	22	1	Equivalent to the material type, Other Combustibles.
Polycubes	Composed of polystyrene and plutonium oxide. Most have been formed into cube shape (called polycubes), and some is present as loose material from the cube forming process or is partially processed in the past pyrolysis process.	251	34	Equivalent to the material type, Polycubes.
Solutions, oil and organic	Solutions containing degraded tributylphosphate.	2	1	Part of the material type, Solutions.

Item Classification	Description	Number of Items	Weight of Pu (Kg)	Relationship to HSISMP Material Type ¹
Pu contaminated metal	Non plutonium metal that is contaminated with plutonium.	1	0.9	Part of the material type. Other/ Miscellaneous.

¹ This column explains the relationship to the inventory given in WHC-EP-0853, DNFSB Recommendation 94-1 Hanford Site Integrated Stabilization Management Plan (HSISMP). The HSISMP includes inventory not addressed in this report such as metal, fuel, sources and compounds.

3.0 OBJECTIVES

The basic objectives of the stabilization activities discussed in this report are to satisfy DNFSB and to successfully resolve the issues in DNFSB Recommendation 94-1 by transforming the plutonium materials at Hanford into forms or conditions which are suitable for safe interim storage. Interim storage is defined in DOE's Implementation Plan for Recommendation 94-1 (DOE 1995) as storage, which is compliant with approved safety basis, for the time period waiting for final, ultimate disposition. This interim time period is also defined in DOE's Implementation Plan as long-term which could last up to 40 years. However, DOE-STD-3013-94, *Criteria for Safe Storage of Plutonium Metals and Oxides*, (DOE 1994) defines the duration of safe, interim storage as at least 50 years. The DNFSB also requests that worker exposure be limited and additional waste generation and effluent emissions to the environment be minimized. In addition to DNFSB, the Hanford Site also has overall objectives in addition to stabilizing plutonium material for safe, interim storage. These objectives relate to Hanford's ability to carry out the work required to clean up Hanford according to its commitments with the State of Washington and its stakeholders. The objectives are listed below:

- Stabilize all plutonium materials for safe, interim storage which could be as long as 50 years.
 - Discard materials with low plutonium content according to all applicable state and federal regulations and with DOE approval, when the costs for stabilization and continued storage are higher than costs for disposal as waste.
 - Limit worker exposures and maintain a safe and compliant facility.
 - Minimize risks associated with stored plutonium.
 - Minimize waste generation and emissions to the environment.
 - Involve stakeholders in stabilization decisions through the appropriate NEPA documentation process.
 - Satisfy all commitments to DOE, State of Washington, etc.
 - Comply with all applicable laws, regulations, and policies.
 - Provide a flexible stabilization system which will successfully treat the diverse plutonium inventory which will be placed into storage.
 - Provide a packaging system which complies with DOE-STD-3013-94 *Criteria for Safe Storage of Plutonium Metals and Oxides*.
 - Comply with the newly released DOE-STD-3013-94 and residue standards and policy by the end of stabilization activities. DNFSB recommended that this occur in a reasonable time period such as eight years, which is 2002.
 - Consider other PFP commitments for future resources when determining the cost and schedule of stabilization activities.
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4.0 APPROACH

DNFSB recommends that a systems engineering approach be used to ensure that activities are integrated and to provide a technical, defensible basis for the proposed stabilization activities. The implementation plan accepts DNFSB's recommendation and commits to using a basic systems engineering approach. The described approach focuses on having key information available to support program decisions. As this systems engineering approach is executed, information is available to make key program and management decisions.

Figure 4-1 illustrates the Hanford Systems Engineering Core Process which is contained in the draft *Hanford Systems Engineering Management Plan* (WHC 1994). The figure shows a multi- step approach that begins with purpose definition and ends with a decision between proposed systems. This decision is based on defined criteria and is necessary to ensure that the necessary requirements are met and that the desired system performance will be achieved. This systems engineering model stresses the following:

- Development of an engineering description of the "customer's" stated needs or of the performance deficiencies in an existing system.
- Function definitions of the system and dependencies among system's parts and with other systems.
- Identification of all system requirements.
- Test and verification of the emerging system designs to ensure the right design and management choices are being made.

Figure 4-1 is also annotated to indicate which steps are addressed in the specific sections of this report. The figure provides a "road map" to the interpretation and purpose of each section of the report. This report will not include the final step, which is completing the engineering baseline. This engineering baseline is the portion, relevant to plutonium materials, of WHC-EP-0853, *DNFSB Recommendation 94-1 Hanford Site Integrated Stabilization Management Plan (HSISMP)*, Rev. 1, October 1995.

Figure 4-1. Hanford Systems Engineering Core Process

5.0 OVERALL FUNCTIONAL DESCRIPTION

5.1 ANALYZE MISSION

The mission discussed in this plan is to stabilize plutonium bearing materials for safe interim storage. Safe interim storage is defined as safe, controlled, inspectable storage that is compliant with approved safety basis for the time period prior to the ultimate disposition. This time period could be decades and is assumed to be 40 years in DOE's Implementation Plan for Recommendation 94-1 (DOE 1995). However, DOE's Criteria for Safe Storage of Plutonium Metals and Oxides, DOE-STD-3013-94 (DOE 1994), defines the interim duration as at least 50 years. The proposed approach is graded and risk-based by stabilizing the most hazardous materials first, depending on necessary process availability, and will limit worker exposure and minimize the generation of additional waste. At completion of the stabilization activities, all plutonium material will be safely stored.

Figure 5.1-1 illustrates this mission as a "black box" transformation process where the inputs, which enter from the left, are transformed into the outputs, which exit to the right. The inputs to the system are all the plutonium materials located at PFP, both in vault storage and glove boxes. Some of these materials are considered unstable and reactive. Other material meets Hanford's storage specifications and has been stable in storage for many years, but does not conform to DOE-STD-3013-94. Some plutonium materials will be collected during future terminal cleanout activities at PFP and PUREX. Unirradiated fuel, which contains plutonium, from FFTF and other reactors is stored at PFP and more FFTF fuel will be added in the future. The final condition of all materials will allow for safe interim storage. The material will be packaged and conform with applicable storage criteria or applicable disposal criteria. Some material, like FFTF fuel, may not explicitly conform with the criteria. Provisions will be made and documented to ensure that the material is safe for interim storage.

Figure 5.1-1 also shows resources entering from the bottom. These allow the transformation process, titled stabilize plutonium materials, to be executed. The resources are the allocated funding and mission essential capabilities. Mission essential capabilities are defined as skilled people, current technology, and physical structures and equipment. All are necessary to accomplish the stabilization process. Entering from the top of Figure 5.1-1 are controls and constraints. These will be discussed in further detail in Section 6.0. The final element of Figure 5.1-1 is the boundaries and interfaces. These help define the scope of these stabilization activities and develop the relationship between other functions and programs.

5.2 FUNCTIONAL DECOMPOSITION

The transformation process, titled stabilize plutonium materials, is a function that can be divided into a more detailed set of functions. These functions can be arranged in a hierarchy diagram where the main function is at the top and successively more detailed functions are arranged below in layers, similar to an organization chart. Figure 5.2-1 is the functional hierarchy diagram for the stabilization of plutonium materials. Each of the lower functions must be performed in order to accomplish the higher function.

Figure 5.1-1. Mission Context Diagram

Figure 5.2-1. Functional Hierarchy

While the first function is titled "Stabilize Pu Material for Storage, Disposal or Shipment," DNFSB Recommendation 94-1 strictly defines the stabilization associated with storage only. Disposal and shipment are not a DNFSB 94-1 concern. However, stabilization for disposal and possibly for shipment should also be considered. Disposal is needed, because some of the plutonium materials currently held in the inventory only contain small amounts of plutonium. Shipment should be considered, because integration between sites is being investigated on request of the Under Secretary to the Department of Energy. Each of the functions shown in Figure 5.2-1 are listed below with their detailed definitions.

Stabilize Pu Material for Storage, Disposal or Shipment -- Characterizes, treats and packages the plutonium materials to permit safe storage, disposal or shipment. The storage is for the interim time period while the methods for final disposition are being determined. Safe disposal will be allowed only when authorized and only when the material meets the appropriate waste acceptance criteria. Safe shipment is a possibility, if the capabilities do not currently exist at Hanford but do exist at other DOE sites.

Characterize Pu Material to Determine the Stabilization Needs -- Examines the existing material information and may collect additional information in order to determine if and what treatment is necessary for the safe storage, disposal or shipment of the material.

Collect Additional Material Information -- Collects additional information, if necessary, by analysis, inspection, assay, or sampling to assist in the stabilization of the materials.

Evaluate Available and Collected Material Information to Determine the Required Treatment -- Analyzes the existing and collected information and determines the appropriate treatment method, process sequencing, process requirements, and process parameters to successfully stabilize the material.

Assess Hazards to Determine the Urgency and Prioritize -- Orders the stabilization activities and determines which materials to stabilize first to effectively apply resources to activities that eliminate the most risk to workers, public and the environment at the earliest time.

Convert the Pu Material for Storage, Disposal or Shipment -- Processes the material to make it suitable for safe storage, disposal or shipment. This may involve pre-treatment, thermal treatment, calcining, denitration and/or burning.

Convert Solutions -- Processes solutions to make them stable.

Convert Residues and Oxides (<50%) -- Processes residues and oxides that are less than 50% plutonium by weight, making them safe for interim storage.

Convert Metals and Oxides (>50%) -- Processes metals and oxides that are greater than or equal to 50% plutonium by weight to make them conform to storage, disposal, or shipment criteria.

Package Stabilized Pu Material for Storage, Disposal or Shipment -- Performs the verification, packaging, documentation for transfer of the stabilized materials to safe storage, disposal, or shipment.

Verify the Stabilized Material Meets Criteria -- Inspects, measures, samples, and analyzes the stabilized material to ensure that it complies with the appropriate storage, disposal or shipment criteria.

Package Stabilized Material -- Places the stabilized material in a package that conforms with the applicable standards.

Document Packaging and Material Form Information -- Records the required information in the necessary forms and systems, properly labels the package, and certifies that packing criteria have been met.

The relationship between these functions is illustrated in Figure 5.2-2, a functional block flow diagram that includes all of the physical material flows, but may not include all of the necessary information flows between the functions. Figure 5.2-2 has the three main functions of characterize, convert, and package. This diagram also indicates the sources of all the materials or information that are inputs to the system. It also indicates the destination of the materials or information that exit from the system. This diagram is a general, pictorial representation of the stabilization systems. It does not indicate the methods, techniques or processes that will be used, but generically defines the systems for each of the three main functions.

5.3 RELATIONSHIP OF PLUTONIUM STABILIZATION TO HANFORD CLEANUP MISSION

WHC-EP-0722, *Systems Engineering Functions and Requirements for the Hanford Cleanup Mission: First Issue* (WHC 1994d) was developed by senior executives from Westinghouse Hanford Company, Pacific Northwest Laboratory, Kaiser Engineers Hanford, Boeing Computer Services, Richland, and the Hanford Environmental Health Foundation. The work was later continued by executive level delegates, and a functional hierarchy was developed which covered all of the basic functions necessary to Cleanup Hanford. Beginning with Cleanup Hanford, each function is divided into smaller functions. This forms the hierarchy, which looks similar to an organization chart.

The functional model is contained in a database using RDD-100®, a systems engineering software program by Ascent Logic. The database is called Hanford Site Integrated Technical Baseline (HSITB) and has been updated and maintained approximately every quarter. The activities that are required in DNFSB's recommendation can be found in the lower levels of the hierarchy.

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Figure 5.2-2. Functional Block Flow Diagram

Figures 5.3-1 and 5.3-2 indicate where stabilizing plutonium materials can be found. Hanford has a variety of nuclear materials on site, which are not considered waste. These materials must be properly handled, stored and eventually dispositioned according to the decision of the Secretary of Energy. These activities are on the same level as the disposal and remediation of Hanford's waste including tank waste and solid waste as indicated in Figure 5.3-1. The storage, handling and treatment of plutonium bearing materials can be found in the function block numbered 4.7.1. It is also shown in thicker, darker line size. The functional block numbered 4.1 Deactivate Facilities is also shown thicker on Figure 5.3-1. This is because PFP's mission also includes deactivating the facilities to prepare them for decontamination and decommissioning by DOE's environmental restoration contractor, Bechtel. More information on the deactivation of PFP can be found in PFP's Mission Analysis report, WHC-SD-CP-MAR-001 (WHC 1994c). The engineering baseline and the associated schedule baseline in WHC-EP-0853 (WHC 1995a) Hanford Site Integrated Stabilization Management Plan contains some clean up elements that are relevant to the stabilization efforts discussed here, but are, strictly speaking deactivation type functions. Further down in the hierarchy the need to stabilize the residual, deteriorating material is identified as indicated in Figure 5.3-2. The hierarchy defines the boundaries for all stabilize activities. DNFSB Recommendation 94-1 is just one source of requirements, constraints and priorities for stabilization activities. This functional framework provides a way to manage all of the activities relating to the stabilization of plutonium materials.

* Reference: WHC-SD-CP-MAR-001 PFP Transition Project
Mission Analysis Report

Figure 5.3-1. Functional Hierarchy Hanford Site Cleanup

Figure 5.3-2. Functional Hierarchy PFP Store, Treat, Disposition

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6.0 REQUIREMENTS

6.1 SOURCES OF REQUIREMENTS

In order to define a system to stabilize materials containing plutonium at Hanford, the various sources of requirements need to be determined. The sources discussed here are those which apply to either the stabilization process, the specific physical end state characteristics, or the specific packaging requirements. The activities at Hanford are governed and controlled by many regulatory agencies, both at a federal level and a state level. These requirements are not included in this list. However, National Environmental Policy Act (NEPA) calls for an Environmental Impact Statement (EIS), and the PFP Stabilization EIS is in preparation. Before any recommendations made in this report on DNFSB's Recommendation 94-1 are implemented, any necessary additional NEPA documents such as an EIS, EA or Categorical Exclusion shall be completed. In addition to the federal and state regulations which apply to all companies and activities within the State of Washington, the Department of Energy has entered into legally-binding and specific commitments for the Hanford cleanup operation. The Tri-Party Agreement (Ecology et al. 1989) is one such commitment. In addition to these commitments, DOE has also committed to resolve concerns from other groups with authority to audit and assess safety and health concerns. Examples of these groups are DNFSB and ES&H Vulnerability Assessments. Corrective action plans have been generated to address these issues. These commitments are included in these requirements. The specific sources are listed in Table 6.1-1.

6.2 CONVERT PLUTONIUM MATERIALS

This section discusses and defines the requirements related to the activities on processing the material to make it suitable for safe storage, disposal or shipment. The conversion activities may include pretreating, calcining, oxidizing, precipitating, denitrating, or thermally treating. The requirements discussed here address all three dimensions of success: performance, schedule and cost. The source documents listed in Table 6.1-1 only include a few performance requirements, more schedule requirements, and limited cost requirements. The requirements are summarized in Table 6.2-1, and the commitments are summarized in Table 6.2-2. The source of the requirement and the specific page and paragraph are included when applicable. The requirements from the DOE long-term storage criteria apply to only the plutonium materials with 50% or greater content of plutonium by weight.

Review of the tables indicates that very few requirements exist that define the acceptable end state of the material. What is safe for interim long-term storage? Plutonium metal and plutonium oxide are two forms safe for interim long-term storage. DOE-STD-3013-94 indicates that both forms are appropriate if they are 50% by weight of plutonium or greater. Efforts are under way to develop a criteria for plutonium residues, those materials that are less than 50% by weight. The 50% is not necessarily based on any technical limitation. Any amount and variety of impurities increases uncertainty regarding long-term stability for storage. Because most forms of plutonium are reactive, impurities and other constituents complicate the analysis of its behavior over the expected 40 to 50 year storage period. Potential safety problems can arise from the interaction of the plutonium with air, moisture, or radiolytic breakdown products. The breakdown products can come from the

container impurities or other constituents in the stored material. Solutions are not considered safe for storage.

Table 6.1-1. Sources of Requirements for Pu Stabilization

DNFSB's Recommendation 94-1, May 1994 (Conway 1994).

DOE's Implementation Plan for Defense Nuclear Facilities Safety Board's Recommendation 94-1, February 28, 1995 (DOE 1995).

DOE-STD-3013-94 Criteria for Safe Storage of Pu Metals and Oxides. December 1994 (DOE 1994).

Initial Draft of Policy Memorandum on Treatment and Disposition of Plutonium Bearing Residues (contained in Appendix E).

OSD-Z-184-00013 Special Nuclear Material Storage, June 1995 (WHC 1995).

DOE/EM-0199 Plutonium Vulnerability Management Plan, March 1995.

Corrective Action Plan to Plutonium Vulnerability Assessment Hanford Site, Prepared by Westinghouse Hanford Company, September 1995.

Hanford Federal Facility Agreement and Consent Order, 1994, as amended. Milestone M-83-02 on interim actions including sludge stabilization (Ecology et.al. 1989).

WHC-EP-0063-4 Hanford Site Solid Waste Acceptance Criteria Document, September 1991 (WHC 1991).

WIPP/DOE-069 TRU Waste Acceptance Criteria for Waste Isolation Pilot Plant, January 1989.

The condition of the oxide (for 50% Pu and greater residues) is to have a less than 0.5% loss on ignition (LOI). Loss on ignition is a standard test of purity originating as a quality test for pure plutonium oxides. The definition according to the storage standard is "the percentage of mass loss measured when a representative sample of thermally processed plutonium-bearing oxide is heated at a specified temperature for the time period required (as demonstrated by certification procedures) to remove residual moisture and other volatile species from the sample." The storage standard DOE-STD-3013-94 does not specify methods, temperatures or durations to thermally stabilize material for storage nor does it specify a particular LOI method or temperature.

Thermally stabilizing at 1000°C is the current approach for sludge stabilization actions at PFP. Treating the oxide at 1000°C causes some sintering of the particles which reduces the fraction of dispersible and respirable particles.

Table 6.2-1. Requirements from DOE-STD-030-94 Related to the Treatment of Plutonium Material ≥ 50 weight %

Description of Requirement	Reference*
The material form shall be solid metal or conditioned oxide (powder or compacted) forms and contain a minimum of 50 weight percent plutonium.	9. 2
The forms shall be readily retrievable from the containers.	9. 4.1.A.2
The stored plutonium shall have a thermal output of less than 30 Watts per primary containment vessel.	9. 4.1.B
The steady-state plutonium metal temperature shall not exceed 100 °C (212 °F).	9. 4.1.B
The quantity of stored plutonium oxides and plutonium metal should be as close as possible to, but shall not exceed 5.1 kg (11.2 lbs) and 4.5 kg (9.9 lbs), respectively.	9. 4.1.B
Actual operating limits on thermal output, quantity or temperature shall be facility specific considering criticality, radiation and heat output constraints.	9. 4.1.B
Metal pieces shall have thicknesses greater than 1.0mm (0.04 in.) or have specific surface areas less than 1.0 cm ² /g (72 in ² /lb). Metal pieces with greater surface areas shall be converted to an oxide form.	9. 4.1.C.1
Plutonium metal shall be free of loose oxide.	9. 4.1.C.2
Plutonium oxides shall be thermally stabilized to less than 0.5% loss on ignition and retain this characteristic through final packaging.	9. 4.1.D.1

* Page number and paragraph number.

Table 6.2-2. Schedule Commitments Associated with Treatment made to Support DOE's Response to DNFSB 94-1

Description of Commitment ¹	Page Number ²	NMSTG Milestone Number
Begin processing solutions at PFP in June 1997.	37	IP-3.1-022
Stabilization of 4800 liters at PFP completed in January 1999.	3, 36, 37	IP-3.1-017
Start restabilizing the high assay oxides at PFP in July 1999.	48	IP-3.2-033
Complete restabilizing high assay oxides at PFP in May 2002.	48	IP-3.2-034
Thermally stabilize and repackage all plutonium oxide to meet the metal and oxide storage standard by May 2002.	41, 50	IP-3.2-018
Stabilization of polycubes begins in July 1999.	67	IP-3.3-028
Stabilization of polycubes completed in January 2001.	67, 73	IP-3.3-029
Stabilize 46 cans of selected ash from RF in muffle furnaces by March 1996.	4, 67, 73	IP-3.3-032
Stabilize and package all remaining residues to safe interim storage standards by May 2002.	4, 67, 73	IP-3.3-033

¹ The commitments are taken from the NMSTG (Nuclear Material Stabilization Task Group) milestone numbers. These commitments are being tracked and monitored by the group.

² The milestones originated from DOE's DNFSB Recommendation 94-1 Implementation Plan. The referenced page numbers are from this plan.

In *The Rocky Flats Environmental Technology Site Integrated Program Plan* (IPP 2995), seven characteristics are listed which define the suitable end state for plutonium residues: 1) no liquid components, 2) no hydrogenous matrix material, 3) no hydrogenous materials as primary or first layer of containment, 4) no reactive metals including plutonium and RCRA reactive metals like sodium and calcium, 5) no chemically unstable or chemically incompatible constituents, 6) no corrosive gases or any gas generating capability through either chemical or radiological means, and 7) no ignitable, flammable or shock-sensitive constituents.

6.3 CHARACTERIZE PLUTONIUM MATERIAL

Characterization is an important function necessary to stabilize the plutonium-bearing materials at PFP. Characterization can be performed to satisfy many questions: how safe are the materials currently in storage; are they safe enough for long-term storage; which material items pose the most risk to safe long-term storage; which treatment technique is the appropriate way to stabilize the materials, and does the material meet the necessary standards for storage, waste acceptance, or shipping? Both the material itself as well its container and packaging configuration can be characterized. In order to characterize, information must be evaluated and assessed and new information should be collected. Reviewing all of the different questions of interest before a characterization effort is undertaken is necessary to avoid multiple handling occurrences, thereby limiting worker exposure and maximizing the effectiveness of characterization activities.

The specific outcome of characterization activities will be information indicating the priority and the order of material to be stabilized, information needed to determine stabilization processes and process parameters, and will result in updated process knowledge. The purpose of the priority is to stabilize the most risky and potentially hazardous material first. This would allow early focus on the materials posing the highest risk, so that limited resources are used to eliminate the most risk. The priority will be determined from information on the materials' packages in addition to information regarding the material itself. The need to collect this information is documented in an assessment of the vulnerabilities associated with DOE's plutonium storage (DOE/EH-0415; DOE Draft 1994). A *Plutonium Inventory Characterization Implementation Plan* (Szempruch 1995) describes a model to evaluate risk and a plan to supplement the model with data collection. WHC-SD-CP-TP-086 *Plan to Examine special Nuclear Material and the Foodpack Can Storage Containers at the PFP Storage Vaults*, August 1995 is the first plan to perform characterization. When this plan is executed, information should be available to establish priorities for stabilization efforts.

The second kind of information that will be produced from characterization activities is the needed data to define which processes will be used to stabilize the material. This information will be primarily about the material itself and will likely include the identification and composition of the non-plutonium constituents. Any characterization needed for environmental compliance may be performed at the same time. Finally, all information that is collected both on the material and the package will be added to the existing process knowledge and will be documented and maintained as required for the future storage and disposition of the material.

The available and potential resources for material characterization are the following:

- Non-destructive assay systems (gamma energy spectroscopy).

-
- Calorimeter.
 - Loss on ignition (LOI) equipment.
 - Solution counter.
 - Thermal gravimetric analyzer (TGA)/mass spectrometer.
 - Ion chromatography.
 - X-ray fluorescence.
 - Total organic carbon (TOC) analyzer.
 - Digital radiography equipment.

6.4 PACKAGE STABILIZED PLUTONIUM MATERIALS

Packaging is important to the safe long-term storage of plutonium-bearing materials and is the subject of the majority of the new DOE storage standard, DOE-STD-3013-94. This standard calls for a minimum of a boundary container and a primary containment vessel (PCV). The boundary container fits inside the PCV. Both containers have specifications on size, material of construction, design pressure and testing requirements. The standard allows for a third container, called a material container, which fits inside the boundary container. The current Hanford packaging does not meet DOE-STD-3013-94. The primary concerns about the current Hanford packaging are found in assessments of plutonium storage safety by DNFSB and the ES&H group in DOE. They are elastomer seal degradation, can material compatibility, and the unknown design life.

Two more issues are important in this discussion. The first is that DOE-STD-3013-94 is only applicable to material containing 50 wt% and greater of plutonium. In the PFP inventory, only 30% of the items by number and 40% by plutonium weight are estimated to be in this range. DOE complex efforts are underway to develop a standard for the plutonium material less than 50% by weight. The second issue is that none of the existing packages used throughout DOE will meet the criteria and the packaging systems under development may or may not meet the standard. Hanford has committed to performing engineering studies and to making a new repackaging line. These commitments are summarized in Table 6.4-1.

The following packaging alternatives are possible:

- Continue packaging according to the Hanford criteria until a packaging system which conforms with DOE-STD-3013-94 is developed by DOE and is available. DOE-HQ is leading a site-wide packaging procurement.
- Modify the Hanford packaging method in the interim until a packaging system which conforms with DOE-STD-3013-94 is available.
- Develop, design and construct own packaging system to meet DOE-STD-3013-94. In the interim time before this option is available, the current Hanford criteria or modified criteria can be used for packaging.

The second alternative has several approaches, as indicated below:

- Eliminate the elastomer seals.
 - Change the can material.
 - Size a package to fit into the boundary container that meets the DOE-STD-3013-94 requirements for a material container.
-

The last alternative has a couple of approaches:

- Implement a design for a boundary container only. Wait for DOE development of the *outer container, the PCV*.
- Implement both a boundary container and PCV design.

Table 6.4-1. Schedule Commitments Associated with Packaging made to Support DOE's Response to DNFSB 94-1

Description of Commitment ¹	Page Number ²	NMSTG Milestone Number
Complete detailed design, equipment procurement, and installation of a new repackaging system at Hanford in 1998.	47	IP-3.2-029
Train staff, prepare procedures, and perform operational readiness testing (prior to commencing operations) in September 1999.	47	IP-3.2-030
Commence repackaging operations at Hanford in October 1999.	47	IP-3.2-031
Complete metal repackaging at Hanford in September 2000.	47	IP-3.2-032

¹ The commitments are taken from the NMSTG (Nuclear Material Stabilization Task Group) milestone numbers. These commitments are being tracked and monitored by the group.

² The milestones originated from DOE's DNFSB Recommendation 94-1 *Implementation Plan*. the referenced pages are from this plan.

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7.0 ALTERNATIVES

7.1 INTEGRATED STABILIZATION PROCESS

The plutonium inventory is in a variety of forms and has been categorized into sixteen groups that are identified by description from the inventory listing. Items are categorized into groups by material type such that stabilization process options can be identified for each group. Some items listed in the inventory, such as compounds, are not sufficiently described to identify appropriate potential process options. Further characterization, which is planned, will likely find that one or more of the evaluated processing options will have the capability to stabilize a currently uncharacterized inventory item. The inventory, summarized in Section 2.0, represents the various aspects of past PFP operations, the various types of recycle materials produced in recovery processes, and material from other DOE operations at other sites. Therefore, it is unlikely that further characterization of the plutonium inventory will identify a material that requires a stabilization process totally different from processes discussed in this evaluation.

A suite of processes is required to stabilize the solutions, residues and combustibles found in the PFP plutonium inventory. While the inventory has been categorized into sixteen groups, each inventory group will not require a different process. In the process of reviewing each inventory item for stabilization processes, some processes appear again and again. For example, thermal treatment may be a process for the stabilization of Rocky Flats ash; and it is also part of a stabilization process for solutions. Precipitation of plutonium as an insoluble compound from solution is a common process for the treatment of plutonium effluents streams and an initial processing step in the production of plutonium metal and oxide. The precipitate produced is thermally treated, which is also a stabilization process option. The suite of processes becomes alternative process systems with most processes having the capability to handle more than one inventory item. The process systems that come out of the review of plutonium inventory items and the processes that can be used to stabilize these items can be broken down into three possible unit operations or functional processing steps: preparation or pretreatment; stabilization treatment; and thermal treatment.

Within each of these three functional processing steps, multiple alternatives can exist as is illustrated in Figure 7.1-1. Hypothetically, preparation may include two options, S and T; stabilization treatment may have three options, X, Y, and Z; and thermal treatment may have only one option. In this hypothetical case, six different process systems can be assembled. The evaluation of this process system then becomes one of assessing it in terms of the number and variety of inventory items that it can process. Evaluating it against the defined decision criteria will lead to identifying the process systems which are the most desirable. Some of the potential processing systems may not require all of the above functional processing steps. For example, thermal treatment for Rocky Flats ash, which was mentioned previously, does not require preparation or stabilization treatment. Some inventory items may fall outside of the capability of the basic, functional process systems and will require unique preparation or stabilization treatment. These inventory items will be identified when possible. The focus of this study is an integrated process system made up of unit processes and is not a detailed evaluation of each unit process. Table 9.1-1 is a matrix summarizing the alternatives for each plutonium category. The alternatives are discussed in detail in the following sections.

Alternatives:

1. S → X → U
2. S → Y → U
3. S → Z → U
4. T → X → U
5. T → Y → U
6. T → Z → U

Figure 7.1-1. Hypothetical Example of Six Alternatives from Various Options in Three Unit Operations

The following discussion of the process options (Section 7) and the selection of an option (Section 10) should complement laboratory testing to supplement and confirm or invalidate the identified option. For example, based on this evaluation, the option for a particular inventory item might be thermal treatment. However, laboratory testing may find that the thermal treatment of this material may result in unacceptable corrosion to the thermal treatment equipment or may find unacceptably long processing times. The results of this evaluation can provide guidance for the final testing by directing laboratory experiments or engineering studies toward refining the options evaluated here.

7.2 STABILIZATION

7.2.1 Reduction Residues

Sand, slag and crucible (SS&C) is a recycle stream from the plutonium tetrafluoride reduction to plutonium metal. A charge of plutonium tetrafluoride and calcium metal and a small quantity of elemental iodine is loaded into a magnesium oxide crucible that is bedded in magnesium oxide sand in a pressure vessel and the pressure vessel is placed in an induction furnace. After the reduction process is completed, the slag and crucible are broken and the plutonium metal button removed. The sand, slag and crucible are broken up in a hammer mill. The slag remaining after the reduction step is largely composed of calcium fluoride, calcium iodide, unreacted calcium metal, plutonium oxide, unreduced plutonium fluoride and small plutonium metal droplets. The molten plutonium penetrates several millimeters into the wall of the magnesium oxide crucible.

One alternative for the stabilization of the SS&C is a variation of the recovery process used at all plutonium processing sites, including Hanford. The sand, slag and crucible material was first dissolved and then the plutonium was recovered from the solution using ion exchange or solvent extraction. This same process can be used to stabilize both the unreacted calcium metal and the plutonium metal droplets, but without purifying the plutonium. Dissolving the sand, slag and crucible material forms a feed stock that can be processed in the same equipment which will be used for the solutions in the PFP inventory, direct denitration or precipitation. The precipitate formed from the precipitation process needs final stabilization such as thermal treatment. The precipitate is an impure plutonium hydroxide if hydroxide precipitation is used. The impurities consists of other metal ions precipitated in the process.

The SS&C can be dissolved by heating 60% aluminum nitrate nonahydrate (ANN) and 64% nitric acid in a vessel with the sand, slag and crucible material. Hanford used both the MT-5 pot dissolver and a continuous dissolver in PRF. At the Savannah River Site, this step was performed in a slab dissolver in 200 L batches. Continuous dissolution in glass and Kynar® airlift cascade dissolvers, similar to those used at the Rocky Flats site, is an option if the quantities of materials requiring dissolution are large enough. The solution is then digested to convert any fluorosilicic acid (H_2SiF_6) to the less soluble silicon dioxide (SiO_2). The solution is passed through primary filters to remove any solids such as silica (SiO_2) and is collected in a filtrate tank. The filters are cleaned by back flushing with hot caustic (12.5% NaOH) to a backwash waste tank.

* Registered Trademark of Elf Atochem North America, Inc., Philadelphia, PA

The alternative to dissolution followed by precipitation and thermal treatment or direct denitration is to proceed directly to thermal treatment. In terms of simplicity, this approach is obviously preferable; but some process related questions need to be addressed before an informed decision can be rendered. The process of dissolution dissolves the potentially reactive calcium and plutonium metal. A thermal treatment process would convert the unreacted metals to the respective oxides. However, metals occluded in the slag and crucible matrix may be prevented from reacting completely. Additional grinding of the SS&C may be required before proceeding with thermal stabilization. Processing rate should also be considered in comparing these processes.

For stabilizing by only thermal treatment, the SS&C is first placed into a tared "boat" and weighed. The boat contains the SS&C material during the thermal treatment process. The use of CO₂ to dilute oxygen leaking into the unit and combustible gases may be warranted to prevent a rapid exothermic reaction with calcium metal and or other reactive compounds. Steam introduced into the controlled furnace atmosphere reacts with the materials including PuF₃ at a controlled rate without the risk of a burn or an explosion. A vacuum system removes the off gas. The temperature cycle including the rate of increase or decrease and the hold time and temperature are controlled by a preset program.

7.2.2 Fluoride Residues

The previously described dissolution process for stabilizing SS&C can also be used to stabilize fluoride residues. Dissolution of SS&C is a preparatory process to solution stabilization which is either direct denitration or precipitation followed by thermal treatment. The alternative is heating the fluoride residues in the muffle furnace in the presence of steam.

A dissolver system as previously described for SS&C can readily accept fluoride residues. Plutonium powders, plutonium trifluoride (PuF₃), plutonium tetrafluoride (PuF₄) and plutonium oxide (PuO₂) are process materials in the Savannah River plutonium finishing facility (FB Line) glovebox for the calciothermic reduction to plutonium metal. In the process of handling these powders, some were spilled on the floor of the glove box or on the process equipment. These powders were, in the past, collected and placed in a slag and crucible container for eventual solid scrap dissolution. Feedstock for solid scrap dissolution consisted of SS&C, floor sweepings, metal turnings from button sampling and some offsite scrap. Aluminum nitrate nonahydrate (60% ANN) and 64% nitric acid are heated with SS&C and other solid scrap including the floor sweeping with the plutonium trifluoride and the plutonium tetrafluoride. The Savannah River dissolver is of slab construction which is a geometry that is favorable for leakage of neutrons that could initiate a chain reaction and has a maximum capacity of approximately 260 liters. The SS&C dissolution process was operated at PFP in MT-5 pot dissolver and a continuous dissolver in PRF. The dissolver solution is a feed stream to the precipitation process. In precipitation the plutonium precipitates as a solid, leaving the fluoride in solution.

Another process applicable to stabilization of fluoride residues is molten salt oxidation. Fluorine corrosion of the refractory is controlled in molten salt oxidation of fluoride residues by the continuous overflow of molten salt to remove the fluoride as the sodium salt. The sodium fluoride concentration is maintained at 10% (Sevigny et al. 1994). Section 7.2.11, on the treatment of combustibles, contains additional information on the molten salt process.

7.2.3 Sludges

Sludge is a term used to identify material that originates in PRF and has an average consistency of 33% ferric oxide and ferric nitrate, 1% tributylphosphate, 26% plutonium nitrate, 7% plutonium oxide and 3-5M nitric acid. The cleanout of PRF glovebox and the process cell in PRF that contains the solvent extraction equipment will remove additional sludge.

This material is being stabilized in the muffle furnaces. Sludges with tributylphosphate concentration of greater than 2% will be blended with sludges with tributylphosphate concentration of less than 2%. The restriction on tributylphosphate is to prevent a rapid exothermic reaction. Hydrolyzation is an alternative for sludges with tributylphosphates concentration greater than 2%. Hydrolyzation process description is included in Section 9.2.

The operation of the molten salt oxidation process in a pulsed continuous mode, described as packaging the sludge in small size packages similar to toilet paper rolls, which by virtue of size would prevent the rapid decomposition of tri-n-butyl phosphate and feeding the packaged sludge pneumatically or mechanically to the molten salt reactor is another alternative (Sevigny et al. 1994). Developing such a remote packaging system and a pulsed continuous feed system are significant efforts and are not the best use of molten salt oxidation.

7.2.4 Potential Residues

Material collected from PFP and PUREX decontamination and terminal clean-out operations will also require stabilization. The types of residues from terminal clean-out are expected to be similar to the PFP inventory items that have been listed in Table 2.1. PFP and PUREX Plant operated similar processes for the production of plutonium oxide. The process intermediaries and products from the PUREX clean-out will include plutonium nitrate, plutonium oxalate and plutonium oxide. These process intermediaries and products that have been accumulated and require stabilization are assumed to be the same material types materials that will be removed in the PFP clean-out. Residues removed during decontamination efforts will include plutonium fluorides, oxalate, oxide and SS&C. Because the potential residues are similar to existing inventory items, appropriate stabilization processes should be in place to stabilize this material as it is removed and characterized. Those materials not requiring long-term storage will be packaged as TRU waste for discard.

7.2.5 Ash

The SS&C alternatives discussed in Section 7.2.1 are also applicable with some modification to the treatment of ash. In terms of process operations, one unit operation, dissolution of solids, could be added to the proposed processes for stabilizing the solutions by precipitation and direct denitration. Another alternative, thermal treatment, which is the final step in the solution stabilization process, may be adequate to stabilize ash. Determining factors in process selection are the ability of the process to meet storage criteria, process throughput rate and processing problems that could require extensive maintenance and increased operator exposure.

One concept for a dissolution process would be to continuously dissolve the ash in heated nitric acid containing fluoride ions in glass and Kynar® airlift cascade dissolvers. The resulting slurry from the dissolution process is filtered, and the filtrate is vacuum-transferred to the filtrate tank. Feed could

be delivered to the dissolution glove box by a chain conveyor. The plutonium-bearing solids are mixed with calcium fluoride (CaF_2), which provides the fluoride ion to promote plutonium dissolution and are sifted through a screen removing chunks and foreign objects. A variable speed screw feeder moves the solid material at a controlled rate into the first dissolver vessel where it is contacted with nitric acid.

The various residues require different acid strengths for optimum dissolution/leach. Incinerator ash is dissolved in 9M nitric acid and ash residues in 12M nitric acid. The airlift circulator cascades the nitric acid slurry from one dissolver to the next. An internal steam coil maintains the dissolver solution at an elevated temperature.

Incinerator ash typically contains large amount of silica which reacts with hydrogen fluoride (HF) to produce volatile silicon tetrafluoride (SiF_4). The silicon tetrafluoride is exhausted in the air used for agitation through an off-gas condenser where it will cool and react with water to form silica and hydrofluorosilicic acid. Acid vapors from the off gas are condensed and the condensate drains to the dissolver filter. Uncondensed vapors and condensable gases pass through the condenser, a demister, before being exhausted by the process vacuum system to the building ventilation system. The slurry containing both dissolved solids, and undissolved solids, overflows the last dissolver in the train, is cooled, and flows onto a Nutsche type filter. Vacuum draws the solution through the filter and a polishing filter into the filtrate receiver while the solids are retained on the filter. The retained solids are removed and placed in a separate filter where they are washed with 0.35N nitric acid to remove excess fluorides. The washed solids can be dried on hot plate, assayed, and then packaged to meet the Waste Receiving and Processing Facility solid waste acceptance criteria. An alternative to hot plate drying is thermal treatment at relatively low temperatures and relatively shorter cycle times than required for the thermal treatment of SS&C.

Silica builds up in the off-gas condensers which require occasional clean-out. Cleaning consists of flushing with caustic solution and steam. This caustic wash solution is filtered and transferred to the waste collection tank. The silica cake is dried like the ash residue, assayed and packaged to meet the Waste Receiving and Processing Facility waste acceptance criteria.

The alternative to preparation by dissolution and treatment by precipitation or direct denitration is to directly proceed with thermal treatment. This eliminates liquid waste and the problems associated with the filtration of gelatinous silica slurry. If for some reason the thermal treatment of ash is found to be highly corrosive to the thermal treatment system (more corrosive than the nitric acid-hydrofluoric acid used as a dissolvent) or to produce unacceptable material for storage, then the dissolution alternative is the preferred option. An advantage to the dissolution option is that any material left, is disposable as TRU wastes. Vault storage or treatment and packaging to meet the standards of the plutonium storage criteria (DOE-STD-3013-94) is not required for TRU.

Muffle Furnace. The thermal treatment of ash is assumed to be similar to the thermal treatment of oxides. The ash is placed into a tared boat and weighed. The boat is placed in the thermal treatment unit and the vacuum system on the thermal treatment unit is adjusted to maintain an off-gas flow rate of approximately 60 cfh. Some incinerator ash has been stabilized at PFP by thermal treatment.

The heat as regulated by the controller slowly increases the ash and boat temperature to 1000°C and the boat and ash are held at this temperature for 1 hour. The heat to the thermal treatment unit is

then shutoff, and the furnace is allowed to cool. The cool down time is roughly 5 ½ hours for a total process time of 12 hours (Sevigny et al. 1995).

Thermal treatment equipment could be a batch-type operation; another option is semi-continuous operation in a tunnel furnace. Boats used to carry the material to be treated enter the tunnel furnace through an airlock. Opening the inner airlock door to move the boat into the furnace pushes the boats in the furnace ahead and eventually out as boats are processed. Pushers can be driven by electric motor, compressed air, or hydraulic systems, and can be automatically timed and synchronized with door-opening timers (Perry 1963). Ceramic tunnel kilns handling large irregular-shaped ceramic objects are equipped for precise control of temperature and humidity to prevent cracking (Perry 1963).

Some compounds in the ash melt below 1000°C or form low melting eutectics that can volatilize and interfere with loss-on-ignition (LOI) measurements. Agitation of feed materials during thermal treatment may also improve the processing rate by breaking up agglomerates and improving heat transfer, thus producing a product consistently within LOI specifications.

Molten Salt Oxidation. The molten salt oxidation treatment is not suitable for high contents of ash or noncombustible solids in the material feed; excessive amounts of the carbonate salt would be removed as residues in order to remove these solids (Haas, et al. 1994).

7.2.6 Oxalate Residues

Plutonium oxalate is an intermediary in the preparation of plutonium oxide or plutonium metal, which is described here. The nitric acid concentration of the plutonium nitrate feed to the oxalate precipitation process is adjusted to 3M HNO₃, and the plutonium oxidation state to plus four (IV). Oxalic acid is added over a 30 to 45 minute period until the endpoint concentration of 0.15M is reached causing the precipitation of plutonium oxalate. The resultant precipitate is filtered and air dried prior to transferring to a thermal treatment unit for drying and calcination. Calcination converts the plutonium oxalate to plutonium oxide as shown in the following equation:

The oxalate residue is an intermediary in the process to produce a stable oxide. Thermal treatment is the necessary process step to complete this process. An alternative other than simply heating to decompose the oxalate to a stable oxide would be a more circuitous path to meet the same end.

In the furnace oxide process, the oxalate or low fired oxide is placed in a boat that is placed in the furnace and the furnace off gas rate is adjusted to draw 120 to 125 cfm via the vacuum system. The material forms a liquid phase above 100°C which boils over at 180°C unless the temperature is held at 170°C for 1 hour, then the temperature is increased to 1000°C. Then, the power is shutoff, and the furnace is allowed to cool to 200°C. Total process time per batch is approximately 14 hours. The boat and its contents are placed in a desiccator to cool to room temperature. The product is ground and sieved to get a representative sample for an LOI analysis. If the LOI is less than 0.50%, the product is weighed, canned, packaged and sent to the vaults for storage.

7.2.7 Oxide Residues

The oxide residues are in an acceptable form under the DOE storage criteria, but the LOI criteria are likely higher than the new criteria requirement of 0.50%¹ hence, firing these residues will be required. LOI is a measure of the amount of volatile compounds present in the residue which are a concern because radiolysis of this material results in pressurization of the storage containers. The PFP oxides require thermal treatment at the newly specified conditions to meet the long-term storage criteria. There are no reasonable alternatives, other than repeating a final thermal treatment step, which is comparably simple with no technological risk.

7.2.8 Oxides

Other solids stable by form are both high and low fired oxides. Further characterization by making LOI measurements will identify those solids that require additional thermal treatment to meet the long-term storage criteria. Once the low fired oxides are identified, they can be included in batches of oxide residues for thermal treatment. Using a tunnel furnace instead of a batch furnace would accelerate the rate at which this material could be treated. The operating parameters for the treatment of low fired oxides are similar, hence the heating zones in a tunnel furnace could be programmed to take each boat of material as it is pushed through the airlock door and through each heating zone to the correct temperature and for the time required to produce an acceptable product. A reasonable assumption would be that the oxalate residue, the oxide residue, and the other stable oxide requiring thermal treatment could be processed in the tunnel as a batch with different heat zone settings. The calcining completes the conversion of what little oxalate that may remain and reduces the water content to less than the LOI requirement.

7.2.9 Alloys

If an alloy is determined to be stable and non-reactive through characterization, then repackaging to meet the standard may be all that is necessary. Plutonium metal is considered stable under the new standard (DOE-STD-3013-94). Plutonium-beryllium, an alloy in PFP inventory, causes high exposures in handling because of the alpha-neutron reaction. The stabilization of this material may be required to meet the Hanford ALARA requirements if reducing reactivity of this material is not an issue. A purification step of ion exchange or solvent extraction would be necessary to remove the beryllium.

If any or all of the alloys in the PFP inventory of plutonium-uranium-molybdenum (Pu-U-Mo), plutonium-uranium alloy (Pu-U), plutonium-thorium alloy (Pu-Th), plutonium-aluminum (Pu-Al), plutonium-zirconium alloy (Pu-Zr), and anode heels from electrorefining of plutonium are determined to be too reactive for long-term storage, then there appear to be at least two treatment options: dissolution followed by the solution treatment (see Section 7.2.10), or oxidation via thermal treatment. The latter is preferred if it is possible to ensure that the oxidation is complete, and no unoxidized metal remains. The Pu-U, Pu-Th, Pu-Al, and Pu-Zr are dissolvable in the nitric acid - hydrofluoric acid solution. A dissolvent of nitric acid and hydrofluoric acid is formed in the SS&C dissolution by the SS&C material (contains fluoride) and the nitric acid addition. The actual concentrations of nitric acid and hydrofluoric acid will differ with the alloy being dissolved. Those alloys that form more refractory type materials will require higher acid concentrations.

A source of Pu-U-Mo alloy is the scrap rejects from the fabrication of Zero Power Plutonium Reactor (ZPPR) fuel. This ternary alloy is approximately 20-25 wt% plutonium, 75-80 wt% uranium and 1 wt% molybdenum. Thermal treatment is the processing alternative that is capable of preparing an oxide from the Pu-U-Mo alloy. In order to justify the necessity of the thermal treatment, the resulting oxide should have improved long-term stability over its existing form, the ternary alloy.

Thermal treatment of the ternary alloy begins with size reduction of large pieces. If the material is too hard, making size reduction difficult, then repeated thermal treatment of the entire piece followed by bushing to remove the oxide may be required. The desired size metal is placed in a boat and loaded in a thermal treatment unit. Air to oxidize the ternary alloy is supplied to the unit at a flow rate of 120 to 125 cfh (Sevigny et al. 1994). The size is expected to increase up to 40%. The off gas generated in the oxidation process is exhausted by the vacuum system.

A temperature-time cycle program for the thermal treatment of non-organic containing substances is applicable to the oxidation of the ternary alloy. Thermal treatment of the ternary alloy requires testing to develop processing times and parameters. The temperature is increased after the initial hold to 1000°C which is maintained for 1 hour (Sevigny et al. 1994). The timer shuts off the power, and the thermal treatment unit is allowed to cool to 200°C for roughly 5½ hours. Approximate total processing time is 12 hours.

The anode heels from electrorefining of plutonium are oxidized as follows: the material is placed inside the thermal treatment unit with an air supply. As the temperature is increased and the material begins to oxidize, air flow is provided. When oxidation is complete the heat is turned off and the material cooled.

Thermal treatment is the only stabilization alternative for the treatment of the ternary, Pu-U-Mo alloy. However, dissolution followed by precipitation or direct denitration is an option if characterization of the ternary alloy indicates that molybdenum trioxide is undesirable. If that were the case, then the molybdenum trioxide can be leached from ternary alloy using a 1M sodium hydroxide solution.

7.2.10 Nitrate, Chloride and Basic Aqueous Plutonium Solutions

The processing options for converting plutonium solutions to a stable form are precipitation with various chemicals and direct denitration. Precipitation is a preparation process because the precipitate requires thermal treatment prior to packaging for long-term storage. Direct denitration operation at 800°C may not meet current LOI requirements without subsequent thermal treatment. Direct denitration by injection of the nitrate solution into the molten salt bath of a molten salt oxidation reactor is an option that has no distinct advantage over the options of precipitation or direct denitration in a vertical calciner. The operation of a molten salt oxidation process is sensitive to the feed rate; rapidly expanding steam and nitrogen oxides from a high feed rate can blow the molten salt out of the reactor.

Precipitation is well established, because it is an integral part of the process for the production of plutonium metal and plutonium oxide. Direct denitration and microwave drying have existed primarily in the laboratory and had not replaced precipitation at the time that plutonium recovery operations at Hanford, Savannah River, and Rocky Flats were conducted. Plutonium precipitations

using different precipitating agents have been developed and provide some flexibility in stabilizing the diverse PFP solution inventory. The same equipment of precipitator, precipitant add tank, filtrate collection tank, and vacuum system with filter boats is used in all precipitation processes regardless of the precipitating agent. The fluoride used in the dissolution of sludges and residues remains in solution during precipitation, thus a precipitate that is largely fluoride-free is the feed to thermal processing. Process parameters like filtration time, digestion time and pH can be easily changed if necessary based on laboratory tests or past precipitation operations. The objective of this process evaluation is not to discriminate between precipitation processes, but to briefly discuss the general process chemistry of all processes and to focus specifically on magnesium hydroxide precipitation, a process that has received attention in the DOE complex because of some advantages associated with stabilizing impure aqueous plutonium solutions.

Magnesium Hydroxide Precipitation. The recovery of plutonium from scrap solutions involves purification of the solution followed by precipitation: oxalate precipitation (Hanford), plutonium trifluoride precipitation (Savannah River), and hydrogen peroxide precipitation (Rocky Flats). The plutonium concentration in the filtrate and waste effluents from many of these operations is reduced to less than the discard limits by hydroxide precipitation. Producing a filtrate that can meet the discard limit is an objective of any process considered for the stabilization of aqueous plutonium solutions.

Hydroxide precipitation is a proven, mature technology for achieving a discard limit of 5×10^9 c/m/L¹. Typical is the Carrier Precipitation process in Building 774 at Rocky Flats. Solutions with less than 0.0245 g/L of actinide are treated in this building. Acid solutions containing large quantities of metal ions insoluble in basic solutions is neutralized to reduce corrosivity and to precipitate metal hydroxides. Acidic chloride solutions is also treated with hydroxide to reduce equipment corrosion and to precipitate metal ions. Hydroxide precipitation is equally effective in treating a mixture of uranium and plutonium nitrate. All wastes after neutralization are introduced into a flash mixer with ferric sulfate, calcium chloride, and magnesium sulfate. The intimate contact between these reagents and the solution improves the clarity of the supernatant thus enhancing the decontamination achievable in this process.

Precipitation of metal ions with hydroxide results in the formation of a gelatinous precipitate that is difficult to filter. The addition of potassium hydroxide as a 10M solution makes available for reaction a large number of hydroxide ions resulting in nearly instantaneous precipitation producing small particle sizes. This precipitate layer is not highly permeable to trapped water. A potassium hydroxide precipitation produces a filtrate with a pH that varies from 8 to greater than 14 and co-precipitates unwanted magnesium and calcium, which increases the quantity of material requiring calcination and storage.

When magnesium hydroxide is used as the precipitating agent, it is added as powder rather than liquid. Scrap magnesium oxide crucibles used in the metallurgical process to produce plutonium metal are being tested as an alternative precipitating agent. Neutralization occurs as the acid, nitric or hydrochloric, consumes the magnesium hydroxide powder or the magnesium oxide crucibles. The particulates formed in the neutralization process have a larger size than those produced by the

¹ Palmer, M.J. and K.W Fife. *Use of Mg (OH)₂ as a Replacement for KOH in the Neutralization of Radioactive HCl Solutions*. Draft.

addition of potassium hydroxide and do not as easily entrap water. A flocculent effect is produced, and the particulates agglomerate into a larger mass. The sharp increase in pH that is observed in precipitation with potassium hydroxide makes it difficult to control to the pH endpoint which results in the precipitation of calcium and magnesium. The filtrate from the precipitation with magnesium hydroxide has a steady pH of 9 or less which does not allow the precipitation of calcium or magnesium.

In a magnesium hydroxide precipitation process, the aqueous plutonium-bearing solution is vacuum transferred from the load-in glove box to the precipitator tank (see Figure 7.2-1). There precipitation of the plutonium from solution is accomplished by the slow addition of solid magnesium hydroxide, which continues until a pH of approximately 8 is reached. Air sparging aids crystal growth and promotes particle agglomeration. The solution is digested for an hour, and the agitation turned off, allowing the precipitate to settle. A filter boat with a sintered metal filter is attached to the bottom of the precipitator by a pneumatic lift. Vacuum is applied to the filter draining the mother liquor from the precipitator leaving a wet filter cake on the filter boat. The filtrate collects in a filtrate tank where it is sampled to determine if it meets the waste disposal criteria before being transferred to the tank farm.

The filter boat containing the plutonium precipitate is removed from the precipitator tank and is transferred to the drying station where dry, warm air is passed through the cake removing residual moisture. After air drying, the precipitate is calcined in the muffle furnace.

Oxalic Acid Precipitation. Oxalic acid precipitation is a possible alternative to magnesium hydroxide precipitation provided it can be shown to meet the discard limit. Precipitation of purified solutions with oxalic acid is a standard, proven technique that produces a precipitate with large particulates that are easily drainable. Impure plutonium-bearing solutions, however, may not form readily drainable filter cake like that which is formed from pure solutions. Rocky Flats has been testing an oxalic acid precipitation that may be applicable to the treatment of some aqueous plutonium-bearing solutions. Plutonium oxalate, which can be formed in the plus three or four oxidation state, has the lowest solubility in the plus three state. A two-stage oxalate precipitation process is being demonstrated and tested at Rocky Flats. Most of the plutonium is removed from solution in the plus four oxidation state by the addition of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$). The plutonium remaining in solution is precipitated in the plus three state by the addition of ascorbic acid. The two-stage precipitation avoids the large addition of ascorbic acid required to change the plutonium oxidation state from the four to three if a single precipitation step was performed.

Dicesium Hexachloroplutonate Precipitation. Plutonium can be precipitated as dicesium hexachloroplutonate from high normality chloride solutions with cesium chloride. This precipitation technique produces a pure plutonium precipitate from relatively impure solutions. A relatively large scale production of dicesium hexachloroplutonate was operated at Rocky Flats, but not at Hanford, for the molten salt extraction process. The chloride concentration must be high, 8 M, to avoid high losses of plutonium to the filtrate. Any solutions requiring stabilization that are below 8 M chloride would require the addition of concentrated hydrochloric acid. The plutonium in dicesium hexachloroplutonate precipitation filtrates tends to be higher than the filtrates from the other precipitations processes. A dilution may be needed to reduce the plutonium concentration in the filtrate and a dilution increases the waste volume to be processed. The dicesium hexachloroplutonate is very stable if properly dried but is not a form recognized for the long-term storage criteria. Final stabilization of the dicesium hexachloroplutonate would have to occur at

Figure 7.2-1. Residue Dissolution and Solution Stabilization by Precipitation Process

Rocky Flats where processes for the stabilization of pyrochemical salts are planned. This option was not evaluated further because of the relatively high plutonium losses to the filtrate, the relatively high waste volume, and a resulting form that would require offsite processing.

Direct Denitration. Nitrate solutions of plutonium, uranium and thorium can be successfully converted to oxides by heating the solutions to a sufficiently high temperature $>250^{\circ}\text{C}$ (Stiffler 1962) to effect decomposition of the nitrates to oxides. This denitration has been demonstrated in continuous feed calciners, both vertical and horizontal (Stiffler 1962, Felt 1965, and Lehmkuhl 1976). The process is simple, requires no additives or pretreatment of feed streams, has an easily treated offgas, and produces a stable oxide product (see Figure 7.2-2). The process space requirements are small and the equipment costs are low. Chloride is volatilized as hydrogen chloride. However, the concentration of chloride must be less than the nitrate to result in the plutonium nitrate decomposing to plutonium oxide.

The composition of the feed must be controlled to maintain a hard, dry bed of solids in the vertical denitrator. The vertical denitrator produces a calcine at the operating temperature of 800°C . There are some parallels in the feed requirements for the vertical calciner and the test results from the Spray Calciner/In Can Melter (SC/ICM). Alkali metal nitrate salts may not decompose to solid oxides. Tests of SC/ICM found that PW-4b (low-sodium) simulated waste was still free-flowing after being heated at 900°C , whereas PW-6 (high-sodium) simulated waste agglomerates above 310°C (Larson 1980). Sodium can be a problem in industrial fluidized bed incineration because low melting eutectics that are formed. Sodium chloride in the presence of sodium sulfate has a low eutectic melting point of 623°C (Wall 1975). Organic in the feed to the evaporator is also limited to prevent a rapid exothermic reaction caused by the rapid decomposition of tributylphosphate-nitrate complexes.

Operating the present design to give a residence time of 4 hours at 800°C should result in less than 0.5% LOI required by the DOE Order on long-term storage but this operating temperature is lower than the current practice of tempering the oxide at 1000°C for 1 hour. Since the calciner cannot be pushed to meet this requirement, an additional firing step of the calciner product in the thermal treatment unit is needed. The testing plans of the calciner will start with cold tests of $\text{Mg}(\text{NO}_3)_2$ followed by glovebox testing of plutonium nitrate solutions.

The overall calcination reaction is:

The calciner off gas is a mixture of air, water, nitric acid, oxides of nitrogen and fine plutonium oxide particulates. The offgas is filtered to remove the plutonium particulates, cooled in the condenser removing most of the water and the nitric acid, and exhausted to the plant ventilation system.

For the denitration to be controllable, the feed is slowly metered into the bottom of a heated, stirred bed of previously generated product solids. The liquid is rapidly evaporated and quickly undergoes the drying, denitration and conversion to stable plutonium oxide. This is accomplished in a vertical vessel (see Figure 7.2-1) with an agitator that classifies and moves the particles upward, overflowing into a receiver. The vertical calciner is operated at 800°C and has a capacity of 2 liter per hour for concentrated feeds and 4 liters per hour for dilute feeds. Criticality concerns limit the in-calciner

Figure 7.2-2. Vertical Calciner for Direct Denitration

residence mass of oxide to less than 3.25 kg (Stiffler 1962). The existing laboratory test unit is a design that is safe by geometry.

Plutonium nitrate solution, including filtrates, plutonium-uranium nitrate solutions, chloride solutions, nitric acid digestible solids and plutonium-thorium nitrate solutions are treatable by thermal denitration to form stable, dry solids (Sevigny et al. 1994). Minor amounts of fluoride can be tolerated in the vertical denitrator.

7.2.11 Combustibles

The solid combustible category includes 32 containers of assorted combustible material such as rags, chemical wipes, wood, plastic and graphite contaminated with both plutonium and uranium (Sevigny et al. 1994). Combustibles as a general category include plastic filters, graphite and acid-soaked rags. Graphite can also be treated in a preparation process that dissolves the plutonium which is then stabilized (see Section 7.2.5). Because the polycubes are a large fraction of the combustibles inventory, the application of the basic options of pyrolysis, molten salt oxidation and fluidized bed combustion for the stabilization of this material is discussed separately. Oils and solvents are also the subject of separate discussion.

Pyrolysis and oxidation by molten salt or fluidized bed are alternative incineration methods for stabilizing and thus preparing these materials for long-term storage. Wet oxidation processes are active areas of interest as alternatives to incineration. Application of two recent wet oxidation technologies, supercritical water oxidation and the DETOX process, are discussed as a means of stabilizing combustibles.

One particular concern associated with nitric acid-contaminated combustibles is the formation of readily ignitable or shock-sensitive compounds. At Rocky Flats there is an effort underway to identify materials that are potentially spontaneously combustible and to denitrate those materials using a process being developed at LANL. Segregating for treatment only those combustibles that are reactive then stabilizing these materials is a possible alternative to the oxidation processes. However, complete combustion does assure a stable product.

A common problem for the equipment used in the incineration of combustible materials is to assure the need to maintain criticality safety. Equipment with geometries favorable for leakage of neutrons is not always compatible with the bulk of the solids and volumetric requirements for efficient combustion. The combustion process produces flyash that can accumulate in the off-gas system making accountability difficult and periodic cleanouts a necessity.

Pyrolysis. In pyrolysis, the combustible material is pyrolyzed in the primary chamber and the off gas is sent to a secondary afterburner for complete combustion. In the first stage, pyrolysis of the organic material occurs under oxygen deficient conditions, with partial oxidation of the pyrolysis products. The gaseous products of pyrolysis from the first stage are completely oxidized in the second stage, which is operated with excess oxygen. Heat is supplied electrically to the dual chambers. Air is introduced into the primary chamber to oxidize and produce a noncarbonaceous ash. A combination of steam and air can be used to hydrolyze the off gas and thus control primary chamber temperatures. The electrically heated secondary chamber, the afterburner, completes the combustion of the primary chamber off gas. The chamber is fueled with preheated combustion air which is controlled by an oxygen concentration feedback loop. The oxygen concentration is

controlled at 8 mole percent to ensure complete combustion. A burner cone and baffles are used to cause ignition and create turbulence within the chamber. Turbulence is an important parameter because it drives the process to complete combustion.

The off gas from the process is cooled and filtered in two stages. Downstream of the secondary chamber, the gases are cooled with dilution air then filtered through sintered metal filters. In the second stage, a closed-loop air heat exchanger cools the off gas from the first stage of cooling and filtration to 200°C. The initial stage filtering prevents fouling of the second stage air heat exchanger. A High Efficiency Particulate Air (HEPA) filter has a rated efficiency for 0.3 micron size particle and is the final stage of filtration before the off gas is exhausted to the building ventilation system.

The pyrolysis process can treat a variety of plastics: polypropylene, Viton®, neoprene, Teflon®, PVC, hydraulic oil and both anion and cation resin. A shredder would be required to reduce the size of large objects to 2 inch pieces.

A primary chamber sized to process a 5.5 kg, 18.9 liter batch will completely incinerate the material at a rate of approximately 2 kg/hr for a total of 4 hours for the entire batch. The burn rate will produce an off gas rate of 100 scfh. A system that incorporates geometries that are favorable for the leakage of neutrons, hence critically safe, can be allowed for in the design.

Molten Salt Oxidation. In the molten salt oxidation process (see Figure 7.2-3), the combustible material is introduced with oxygen under the surface of a molten salt bath consisting of a suitable mixture of carbonates, chlorides, or sulfates of sodium, potassium, lithium or calcium (Sevigny et al. 1995). The molten salt is both the heat transfer medium and the reaction medium for the combustibles with oxygen to produce an off gas of carbon dioxide, nitrogen, and steam. The inorganic components of the combustibles and any plutonium in the combustible matrix are retained in the molten salt. The acid gases produced by the pyrolysis of halogenated organic compounds react with the alkaline carbonates in the molten salt bath to form the corresponding salt. An ash consisting of dissolved solid and retained particulates builds up in the melt and is continuously removed to maintain an ash concentration of less than 20 wt% in the melt (Sevigny et al. 1995). At an ash concentration of less than 20 wt% the fluidity of the melt necessary for contacting the feed material with oxygen, wetting the material and heat transfer to the material is maintained. The melt with the ash is dissolved in water to form an aqueous slurry. The oxides and salts of actinides are insolubles in the alkaline solution and are removed by filtering and are subsequently stabilized by thermal treatment. The alkaline filtrate is transferred to Tank Farms.

The molten salt oxidation process is operated at 800°C to 1000°C and at atmospheric pressure with a residence time in the molten salt bath of hours (Sevigny et al. 1995). Air is added in excess of 20% to 30% of that required for combustion. Equipment modifications to the feed system are required to get the feed size to one-eighty inch or less (Martin Marietta 1993). Size reduction of combustible material may require a combination of equipment to shred and pulverize the combustible material to feed specification.

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Figure 7.2-3. Molten Salt Oxidation Flow Schematic

The process has been successfully demonstrated on mixed combustible feed materials in bench and pilot-plant scale studies, with actinide removal efficiencies exceeding 99.9999% (Cooper et al. 1991; Technology Index 1994). Application of the molten salt oxidation process to PFP combustibles has been demonstrated (Wojdac 1994). Oxidation of nuclear-grade graphite is difficult, requiring the addition of sodium sulfate to the molten sodium carbonate bath to act as a catalyst.

Fluidized Bed. The Rocky Flats Integrated Program Plan (IPP 1995) states that the current plans for dealing with combustibles is to stabilize them by incinerating in an existing pilot-scale fluidized bed incinerator in Building 776. Fluidized-bed processing is excellent for thermal processing of particulate materials (Rossi 1984). The technique of levitating solids in an upward-flowing gas stream transforms the solids into a highly mobile state that creates an intimate gas/solids contact and solid-gas reaction of corrosive combustion gases with various alkali metal compounds that make up bed solids. The hydrogenous materials and any oil, grease, or solvents will be converted primarily to carbon dioxide and water vapor. Ash resulting from the combustion process is removed from the combustion chamber and packaged. Particulates in the off-gas stream are removed by cyclone separators, sintered metal filters and HEPA filters. Removed particulates are packaged with the spent bed material. Chlorinated materials generate hydrochloric acid and an in-situ fluidized bed reaction with sodium carbonate prevents this corrosive gas from entering the off-gas system. A retrofit of the Rocky Flats fluidized bed is estimated to cost \$20 million and a planned startup within three years may be optimistic.

7.2.12 Polycubes

There are 251 containers of polycubes (Sevigny et al. 1995). Polycubes are small blocks of polystyrene containing dispersed plutonium or uranium oxide. The cubes were used in criticality experiments which altered the molecular structure of the polystyrene. Those cubes that experienced neutron flux approaching what might be experienced in a chain reaction show a high degree of cross-linkage of the polystyrene matrix. The long-term stability of these cubes is a concern.

Molten Salt Oxidation. Polycubes heated above the softening point are fed to the molten salt oxidation unit using a pneumatic injector (Sevigny et al. 1995). The rate of oxidation is controlled by regulating the oxygen supply to the molten salt bath. The plutonium oxide in the polystyrene matrix is left as an ash in the molten salt. The degree of the completeness of the reaction of the styrene in the molten salt reactor is unknown; if the plastics are incompletely reacted then it would be necessary to route the off gas from the molten salt oxidation unit to a secondary combustion unit.

The recovery of the plutonium oxide ash from the molten salt bath will require additional research. The Oak Ridge report on mixed waste (Haas et al. 1994) states that molten salt oxidation is not suitable for high content of noncombustible solids in the feed; excessive amounts of the carbonate salt would be removed as residues in order to remove these solids. This statement would seem to rule out the use of molten salt oxidation to treat polycubes because the plutonium oxide particulates that are dispersed throughout the plastic matrix will be retained as an ash in the molten salt. Considerations driving a decision to another option are the amount of high ash material that requires processing and the difficulty in removing the ash-laden salt from the molten salt oxidation unit. A molten salt oxidation unit processing large amount of mixed waste, which was the focus of the Oak Ridge test, would produce an excessive amount of molten salt with ash that would have to be removed and disposed of as mixed waste. High density plutonium oxide may settle out in the bottom of the reactor rather than being homogeneously dispersed throughout the melt. A freeze

valve on the bottom of the reactor opened periodically would drain the plutonium oxide and a portion of the molten salt in the form of cullettes. These cullettes would then be dissolved and the plutonium oxide particulates filtered out of the solution and the filtrate disposed to the Tank Farm.

Fluidized Bed. Fluidized bed is another possible technique for the treatment of polycubes as demonstrated by the following industrial application. The conversion of scrap polypropylene and polyethylene into usable petrochemical fuels using indirect heated fluidized bed pyrolysis is reported by Rossi (1984). In this process, a pressurized molten stream of polymer is passed through a tubular-pipe reactor immersed in a fluidized bed of inert silica sand. The medium is fluidized with hot combustion products that provide a high bed-side coefficient. The endothermic heat of reaction is, therefore, totally input indirectly across an isothermal front, resulting in a very tightly controlled cracking reaction. The pyrolyzate is separated into various gas and liquid fractions via downstream flash-separation and condensation operations. Unlike direct-heated fluid pyrolysis processes, this process is performed in the complete absence of air or other gases, thereby yielding little coke (Rossi 1984).

In the above process, the liquids and gases have economic value but in an adaptation of this process to the treatment of polycubes the gases have no economic value and are considered waste. Combustible gases produced in the fluidized bed are incinerated after mixing with excess air in a turbulent mixing zone that ensures complete combustion. The ash consisting of the plutonium oxide particulates left from the combustion process is removed from the combustion chamber and packaged. Particulates in the off-gas stream are removed by cyclone separators, sintered metal filters and HEPA filters are collected and packaged.

Tube Furnace Modified for Pyrolysis. Polycubes have been thermally treated in a purged, scaled Linberg Tube Furnace. In this process, the tube furnace pyrolyzed the polycubes and the off gas was cooled and contacted with carbon tetrachloride in a packed scrubber. The styrene vapors are soluble in the carbon tetrachloride. The operation was plagued by loss of vacuum on the tube furnace because of condensing styrene solidifying and plugging the off-gas system. Installing a secondary combustion chamber downstream of the tube furnace for the combustion of the organics in the offgas would prevent solid accumulation and plugging. Secondary combustion eliminates solid waste disposal that would be required in any system where the organic vapors are recovered. The tube furnace in the modified system is the pyrolysis or primary combustion chamber of an incineration unit. The offgas treatment system downstream of the secondary combustion chamber as described previously in Section 7.2.11 is two stages of filtration.

The DETOX Process. See Section 7.2.13, Oils and Organic Solutions.

7.2.13 Oil and Organic Solutions

Oil and organic solutions include degraded tributylphosphate in carbon tetrachloride diluent and approximately 16 to 20 liters of lard oil with 239g of Pu. Molten salt oxidation and the fluidized bed combustion previously discussed options for stabilizing combustibles and polycubes have the flexibility to also process oils and organic solutions. One additional option for treating the organic liquids is wet air oxidation which has been widely used for more than 50 years (Flynn 1979) operates on the principle that aqueous suspensions or solutions of organic materials can react with oxygen contained in a gas such as compressed air or pure oxygen, at conditions of elevated temperature and pressure. Supercritical water oxidation a more recent development that has been

under development since the late 1970s is an extension of the more traditional wet air oxidation. A highly efficient destruction of a wide variety of hazardous chemicals suspended in water is achieved by supercritical water oxidation at relatively low temperatures above the critical point of water (374°C and 22.13 MPa) (CEP 1995).

Molten Salt Oxidation. The composition of the melt is controlled by removing dissolved salts and the insoluble oxides and salts in the melt and by the addition of fresh sodium carbonate. The molten salt removed is dissolved and filtered to recover insoluble plutonium. The advantage of molten salt oxidation is the high destruction efficiency.

The molten sodium carbonate reacts with acidic combustion products, such as hydrochloric acid or chlorine from organic compounds. For example, simple chlorinated hydrocarbons react readily with molten sodium carbonate to produce sodium chloride and carbon dioxide.

Sodium chloride in the melt is more volatile than sodium carbonate, and in test of organic feeds to an Oak Ridge molten salt oxidation bench scale test unit, the knockout pot chloride concentrations were much higher than in the melt. Two types of condensed salt deposited in the test unit between the molten salt reactor and the knockout pot. The first was formed by depositions of solid particles formed in the gas and resulted in fine particles that were easily removed (Haas et al. 1994). The second occurred through the condensation of liquid melt on the walls and freezing to form hard deposits that in the second series of Oak Ridge tests had obstructed the offgas system sufficiently to require removal (Haas et al. 1994).

In the Oak Ridge test system, the feed was pumped down the center of two concentric tubes; air was supplied through the annulus. The concentric tube assembly is enclosed in an alumina pipe that carries the liquid and gases into the salt (Haas et al. 1994). A plug in the feed tube occurred when solutions of acetic acid containing metal salts were introduced into the melt. It is believed that the acetic acid was vaporized before reaching the bottom of the injector, and hard, crystalline deposits were formed inside (Haas et al. 1994).

Fluidized Bed. Fluidized bed combustion burns solids, liquids and sludges in the presence of dry limestone to control acid gases without wet scrubbers that produce a secondary waste stream requiring disposal. Effluent from the combustion consists of a stabilized ash. Incineration of the organics in a fluidized bed results in these benefits being realized:

- Destruction of hazardous compounds
- Retention of acid gases such as hydrogen chloride
- Reduction of volume (Rickman et al. 1985).

In a development program preceding installation of a fluidized bed unit, operating under conditions resulting in a circulating bed increases turbulence. Turbulence is key to any combustion process and increases the throughput. Pilot-plant units have been configured as fluidized beds or in circulating bed modes (Rickman et al. 1985). The bubbling fluidized bed, which is the combustion zone in the typical fluidized bed, is extended in the circulating bed. High air velocity and

circulating solids creates a highly turbulent combustion zone. Solids entrained in the off gas are separated by an integral cyclone and returned to the combustor. The circulating gases and solids create turbulence and uniform temperature throughout the loop that avoids the ash slugging encountered in other types of incinerators. Nitrogen oxide and carbon dioxide emissions are controlled by good mixing, relatively low temperatures (1,450 to 1,600°F - 790 to 870°C), and staged combustion by injecting secondary air at higher locations in the combustor (Rickman et al. 1985). The combustion temperature of 790°C to 870°C is below the temperature recommended in the long-term storage criteria of 1000°C. This criterion is predicated by the LOI requirement necessary to prevent pressurization of storage containers. Testing of the ash will be necessary to determine if the LOI can be consistently met without an increase in temperature. Lower combustor temperature reduces maintenance and increases equipment life. Higher temperatures increases the efficiency of hazardous chemical destruction. At the indicated temperatures, the highly turbulent combustion zone effects a highly efficient destruction of hazardous chemicals (99.99%) and the limestone bed retains 99% of the acid vapors (Rickman et al. 1985).

System component failures such as the fan or a power failure cause the bed to slump, trapping pollutants in the limestone and ash. The slumped bed is easily and quickly brought back to a fluidized condition.

Wet Air Oxidation, Supercritical Water Oxidation and The DETOX Process. Aqueous chemical oxidation is an alternative in the event that efforts to permit incineration are unsuccessful. Wet air oxidation (see Figure 7.2-4), a process widely used for more than 50 years, operates on the principle that aqueous suspensions or solutions of organic materials can react with the oxygen contained in a gas such as compressed air or pure oxygen, at conditions of elevated temperature and pressure (Flynn 1979). Oxidation takes place in an aqueous environment at temperatures ranging from about 177 to 315°C. The high solubility and diffusivity of oxygen in aqueous solutions at elevated temperatures enables a strong chemical driving force for oxidation. Supercritical water oxidation, under development since the late 1970s is wet air oxidation above the critical point of water (374°C and 22.13 Mpa). Under supercritical conditions, water becomes dense with gas-like transport properties that allow rapid reactions. Solvent properties of supercritical water change from those of liquid water so that gases and non-polar oily compounds become soluble and salts become insoluble (CEP 1995). With the addition of an oxidant, hazardous organic waste such as polychlorinated biphenyls (PCBs), solvents and pharmaceutical wastes are destroyed rapidly and completely (CEP 1995).

Catalyzed wet oxidation has been demonstrated to have potential application to waste treatment. The DETOX process (see Figure 7.2-5), which uses iron(III) oxidant in the presence of small quantity of platinum and ruthenium ions in an aqueous acid solution oxidizes a variety of organics to carbon dioxide and hydrochloric acid (from halogenated hydrocarbons) while containing and concentrating metals in the acidic catalyst solution (Dhooge and Eisberry 1993). Iron(III) oxidizes the organic compounds and is then regenerated to iron(II) by oxygen. DETOX is distinguished from other types of wet oxidation by its relatively high organic destruction efficiencies at relatively low temperature (408 K to 523 K) and pressures (100 to 1500 Kpa) (Dhooge et al. 1994). The oxidation process is highly tolerant of feed material composition, form, water content, and particle size, but because of the corrosivity of the solution, the DETOX reactor vessel must be fabricated from tantalum or at minimum be lined with tantalum.

Figure 7.2-4. Simplified Wet Air Oxidation

Figure 7.2-5. Simplified DETOXSM Process Diagram

Three metals of interest in contaminated organic material are plutonium, uranium and mercury. Cerium and neodymium have been used as substitutes for plutonium and uranium because of similar chemistries in the DETOX catalyst solution. The solubilities of neodymium and cerium are similar to the solubilities of plutonium and uranium in chloride solution with neodymium solubility of about 80 g/L in the catalyst solution and cerium solubility of about 200 g/L (Dhooge and Eisberry 1993).

The solubility of mercury which is a possible contaminant in vacuum pump oil is 400 g/L (Dhooge and Eisberry 1993). Neodymium solubility is adversely affected by any sulfate in the organic matrix and mercury is adversely affected by phosphate. When organics containing cerium and neodymium were oxidized in the catalyst solution, the analytical method for these metals gave a minimum of 97% solvation but actual values are probably much higher (Dhooge and Eisberry 1993). An advantage of the DETOX process is the solvation of plutonium and uranium which makes this process preferable to supercritical water oxidation.

Several supercritical water oxidation research groups are seeking to improve supercritical water oxidation reactor design and prevent corrosion and plugging by the formation of salts, common when highly chlorinated contaminants are treated (CEP 1995). Carbon tetrachloride contaminated with uranium and plutonium salts, common in the organic materials at PFP, could cause recurrent pluggage of the supercritical water oxidation reactor. Supercritical water oxidation was dropped from consideration because the process is incapable, unlike the DETOX process, of solvating plutonium and uranium. Paper, cotton, and wood are apparently completely oxidized in the DETOX process solution at the atmospheric boiling temperature for the solution of 408 K. Particles of up to 1.0 cm can be processed with the same observed rate as smaller particles; shredding rather than grinding or macerating, provides sufficient sizing. Activated carbon, polyethylene and Tyvek® require higher temperatures of 423 K (140 Kpa -20 psi) to 443 K to achieve reasonable reaction rates (Dhooge et al. 1994). HEPA filter material can be decontaminated, leaving clean glass fiber for disposal. Based on the observed reaction rates, a 200 L of DETOX solution in a reactor could treat Trim™ Sol (45% mineral oil, 28% chlorinated paraffin and 15% sodium cyclic alkane sulfonate) at a rate of 3.5 kg/hr, cellulosic material at 35 kg/hr and polyethylene and like materials at a rate of 0.7 kg/hr (Dhooge et al. 1994). All rates are at a temperature of 443 K. A large reactor is required if the DETOX process is used to treat low level mixed waste rather than stabilizing special nuclear materials (SNM).

The DETOX process, like the dissolution processes, requires further processes to complete the task of producing a stabilized product. It may be possible to separate the radioactive metals and toxic metals from the DETOX solution as the hydroxides and isolate as the oxides (Dhooge et al, 1994). If this is verified then the precipitation process as previously described can be used as an intermediary process to produce a stabilized oxide. An alternative is to evaporate the hydrochloric acid in the process solution leaving iron oxide and the radioactive metal. The evaporation equipment would have to be determined. This may be an application for the vertical denitrator which in this case would function as a dryer/calcliner.

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7.2.14 Pu-Contaminated Metals

Vibratory Decontamination. Vibratory finishing is a commercial mechanical surface finishing process that can be used on both metallic and nonmetallic solids. Rapidly vibrating ceramic or metallic media abrade the surface and dislodge surface contamination. A cleaning solution flushes the contamination from the media followed by filtration and/or evaporation to concentrate the contamination. The process is often very effective at reducing contamination levels to below the TRU definition but is not often sufficient to reduce levels below background. A particular advantage of the process is that it removes paint, grease, rust or other corrosion products, tape etc., whereas electropolishing requires that the above be absent. A two step process of vibratory finishing as a pretreatment step to electropolishing is extremely effective for decontaminating metal surfaces.

The vibratory finisher is basically a tub with vibrations imparted at frequencies ranging from 750 to 2150 vpm and amplitudes ranging from 1/64 to 1/4 in. (McCoy 1980). The media are plastics or ceramics (with imbedded abrasives) or metals. The plastic or ceramic media are formed into precise geometric shapes (triangles, cones, cylinders, spheres, etc.) and range in size from 3/16 in. to several inches. The metal shapes (spheres, diamonds, cones, pins, diagonal cuts of cylinders, etc.) vary from 1/6 to 11/16 in. and because they have virtually no self wear, they produce little secondary waste. Metals used are normally case-hardened steel, stainless steel, or zinc.

Vibrators can be designed to operate in flow-through or batch mode. They can be operated to remove most of the contamination in approximately 20 minutes of residence time. The process variables that control processing time are media selection (both material, shape and size), amplitude, and frequency. Because of geometry limitations of the media, some regions of the objects being decontaminated might not be accessible. In these "tough" cases the objects might have to be sectioned into smaller pieces (Allen 1982 and Fetrow 1982).

Electropolishing. Electropolishing is an commercial electrochemical process whereby metal is removed from a surface, the exact opposite of electroplating. The usual desired result is a smooth and/or bright surface. For decontamination purposes the desired result is the removal of surface contamination. Electropolishing would be the method of choice for metal surfaces that are free of rust or other corrosion products, paint, tape, and grease. For such surfaces the degree of decontamination attainable is "less than background". Pre-treatment to remove such surface material would otherwise be necessary.

For decontamination purposes, 5 to 50 micrometers of the metal surface must be removed (Allen 1982). The process is applicable to all metals except those that form highly insulating oxides (e.g. Zircaloy). Normally the metal to be cleaned is the anode in a DC circuit, with current densities ranging from 50-500 amp/ft² (1978 Metal Finishing Guidebook and Directory). The cathode is usually larger than the anode, however, small movable cathodes have been used inside metal pipes and tanks. Also AC and reverse polarity processes have been developed.

Each metal type (steel, stainless, copper, aluminum etc.) requires a unique electropolishing solution (electrolyte). Also metal parts might have to be sectioned to permit current access or just to fit the bath. Depending on the application, baths might require heating (to enhance the reaction) or cooling (excess ohmic heating). Certainly the contaminated electrolyte would require cleaning and/or disposal and rinsing the metal is a necessary part of the process.

A number of electropolishing decontamination studies are reported by PNL (1982). The experience reported indicates that a typical application could be a stainless steel glovebox that would be sectioned into small pieces, vibratory finished, and then electropolished. For stainless steels the electrolytes are usually based on phosphoric acid alone or in combination with hydrochloric or sulfuric acids.

7.3 IMPLEMENTATION TO REDUCE OPERATOR EXPOSURE

Plutonium with a low percentage of plutonium-241 has been traditionally processed in gloveboxes that protect the operator from any physical contact with the plutonium. This concept, while minimizing the opportunities for inhalation or ingestion, has not provided all the protection sometimes needed from the radiation produced by the plutonium-241 and its decay daughter, americium-241. The plutonium in the PFP inventory is high in plutonium-240, 241 and americium-241. Two fundamental approaches to reduce operator radiation exposure are to reduce operator involvement by automating equipment, which makes it possible for the operator to perform the operations at a location that is at a distance from the operation. The other approach is to keep the operator closely involved but shield the process.

Savannah River used both approaches. The dose at the Savannah River FB-Line is not so much from gamma radiation but from neutrons from the alpha-n reaction of the plutonium trifluoride produced in the process. Exposure is reduced by automating the glovebox transfer operations. Conveyor systems move filter boats and roasting pans between process stations in the glove box thereby reducing operator exposure by reducing handling. Conveyors can be operated from local control, operated remotely from other locations, or stopped from any station. Cross conveyors move objects between the main conveyor and process stations in the wing (side) gloveboxes.

Positioning filter boats and roasting pans transferred to a process station is the function of a hydraulic system. Hydraulic lifts are used to move and remove filter boats from the precipitation system, to move and remove roasting pan from the thermal treatment unit, and to transfer these vessels from the main conveyor to a cross conveyor.

Another example of shielding is the Intermediate Level Cells in the Savannah River 773 Technical Area which were used most recently to process scrub alloy from Rocky Flats, and in the past to process plutonium isotopes with mass weights of 238 and 239, also americium-241, curium-244 and californium-252. The scale of operation was small; the scrub alloy process was performed in laboratory glassware. Uranium/plutonium solutions and plutonium chloride solutions in the 771 Building at Rocky Flats will be stabilized by hydroxide precipitation in 4 L glass beakers. The production rate is low but the scale of the operation and the flexibility that it provides makes it simple to switch from one operation to another. The intermediate level cell consists of a containment box within an air annulus that is vented to the building ventilation system. In-cell operations are accomplished with light duty master-slave manipulators that enter the cell through the roof of the cell. The operations are performed with laboratory equipment with the flexibility to change quickly from one process scheme to another. Metering pumps and tanks located outside the containment are used to introduce nonradioactive solutions. Stabilized material and waste are removed from the intermediate cell through inner door-airlock-outer door and containment bag systems. Aqueous waste solutions are disposed of via the laboratory waste disposal system. Replacement of manipulators or other in-cell equipment is accomplished through the cell roof.

8.0 DECISION CRITERIA

Decision criteria were developed to evaluate the relative desirability of the proposed alternatives. The evaluation will result in a ranking of the alternatives from the most to the least desirable. The criteria were compiled from a variety of source documents. The subjects of the referenced documents range from those specific to stabilizing plutonium material to general criteria for the operation of PFP. Some recent decision analysis has been performed for K-Basins; these criteria were also considered. The documents used to compile the following decision criteria are listed in Appendix B. Table 8.1-1 lists all of the defined criteria, which are grouped into eight general categories.

Each of the eight categories is discussed in the following paragraphs. A numeric scale is defined for each category. The scale is from 1 to 5, where 5 is the most desirable and 1 is the least desirable. Descriptions are provided for both the 1 and 5 levels. This allows for some differentiation, approximately three steps, between the two extreme descriptions. Looking at the relative desirability for each alternative in each criteria category is helpful in evaluating between 1 and 5.

End Product Characteristics The desired end product is stable, non-reactive and safe for interim storage as determined by applicable storage standards. The product must not be combustible or shock sensitive. The product must be non-corrosive and compatible with the packaging, both the current Hanford can system and the proposed stainless steel welded configuration. It should not generate significant amounts of gas by thermal, chemical or radiological processes as determined by the applicable storage standard. The end product volume should not be substantially greater than its original volume before processing. If the end product is shippable considering DOT regulations and meets the solid waste acceptance criteria, it is considered beyond the average expected performance. The product should not preclude any possible final processing and disposal options, such as continued long-term storage, placement in deep borehole, immobilization with placement in a repository, and conversion to fuel for reactors.

5- Meets all of the characteristics described above.

1- The product is acceptable for safe interim storage. It is not shippable considering DOT regulations and does not meet the solid waste acceptance criteria. Final processing for disposition may be more difficult, and the end product volume may be substantially greater than original volume before processing.

Technical Factors The desired processes will be based on mature technical processes that have been successfully demonstrated on a pilot scale or larger. The equipment needed should not require any significant development; and if the equipment can be purchased off-the-shelf, the process is considered to be beyond the expected performance. The proposed system should require minimal maintenance and have high reliability. The process should have the flexibility to incorporate improved technology. The process should be simple and easy to operate with the existing skill base. The process should be standardized so that the operator controlled parameters are uniform for all feeds.

Table 8.1-1. Decision Criteria for Alternative Evaluation and Ranking

General Category	Specific Decision Criteria
End Product Characteristics	<ul style="list-style-type: none"> - Stable, Non combustible, Not reactive - Shippable considering DOT regulations - Meets applicable storage standard - Safe for Handling - Safe for Interim Storage - Consider End Product Volume and Available Storage Capacity - Consider Proliferation Potential - Does Not Preclude Possible Final Disposition Options
Technical Factors	<ul style="list-style-type: none"> - Consider the Maturity of the Process Technology - Demonstrated to be Successful on a Pilot Scale or Larger - Consider Equipment Development - Avoid Unproven or Theoretical Processes - Consider the System Reliability - Consider the Ease of Maintenance in a Glove Box or Canyon Installation - Flexibility to Incorporate Improved Technology - Simplicity and ease of operation, considering existing skill base
Process Capabilities	<ul style="list-style-type: none"> - The process is capable of stabilizing a large portion of the diverse inventory - Ability to effectively stabilize the most hazardous items - Standardization of the process
Risk Reduction and Minimization	<ul style="list-style-type: none"> - Worker Radiological Dose - Consider Risks from Routine Activities and Accidents - Consider Worker Toxicological and Industrial Safety Risks - Consider Risks to Environment - Consider Risks to Public
Regulatory and Waste Minimization	<ul style="list-style-type: none"> - Meet Federal, State, and any associated Compliance Regulations and Agreements - Volume and Hazards of Waste - Consider the Benefits of Limiting Effluents to those Currently Covered in Existing PFP FSAR, WHC-SD-CP-SAR-021 - Generating Mixed Waste

Schedule	<ul style="list-style-type: none"> - Total Duration meets all Commitments - Proposed Implementation Durations are Feasible - Considers the Restrictions Due to Other Facility Schedules for D&D, ER, Infrastructure - Maximize progress by minimizing the period of performance
Life-cycle Cost	<ul style="list-style-type: none"> - Operation and Maintenance Cost Savings realized because stable material has less operating and maintenance needs - Include Capital Cost for Equipment & Facility Modification and Upgrades - Include Operating and Maintenance Cost - Include Costs for D&D and Waste Disposal - Total Life-Cycle Costs fit within target funding levels
Stakeholder Acceptance	<ul style="list-style-type: none"> - Consider Current Public Perception of Process - Consider Stakeholders Perceptions Regarding Transportation, Tri-Party and Economic Benefit.

5- Meets all of the characteristics described above.

1- The process may rely on unproven or theoretical processes. The necessary equipment would require development and extensive design and modeling efforts. It would require a highly trained, responsive, and knowledgeable operators and support system. The expected maintenance would occur frequently and the equipment reliability is uncertain or low.

Process Capabilities The desirable process will be capable of stabilizing a large portion, 90% or more, of the existing inventory by volume and by number. The inventory items which have been identified as the most hazardous are all treatable by this process. The process is standardized for a variety of material categories.

5- Meets the criteria described above.

1- The process is only capable of stabilizing less than half of the existing inventory by volume or number. The most hazardous inventory items may not be stabilized by this process.

Risk Minimization The most desirable process will result in minimization of the radiological dose exposure for workers. The process is amenable to dose minimization features such as automation, manipulators and shielding. The risk to the environment and public will be minimal. Toxicological and industrial safety risks will also be minimal. The potential risk from accidents and routine activities will be small.

5- Meets the criteria listed above.

1- The described risks are bigger.

Regulatory and Waste Minimization All federal and state regulations are met. The volume and hazards of the waste streams are smaller than expected levels from an average process. The

effluents are limited to those which are currently covered in the FSAR. The effluents meet the acceptance criteria and have an approved method for disposition. Mixed waste is avoided.

5- Meets the criteria listed above.

1- The volume and hazard of the waste streams are larger than expected levels from an average process. The effluents may not be covered in the FSAR. The effluents may not meet the acceptance criteria and may not have an approved disposition method. Mixed waste is minimal, but not avoided.

Schedule The total duration meets all of the commitments. The proposed implementation durations are considered feasible with a high degree of confidence. Other plant activities such as transition, deactivation, and terminal cleanout are not effected. The total duration is minimal and progress is maximized. If line item funding is needed, the schedule is likely too long to meet commitments.

5- Meets the criteria listed above.

1- The total duration does not meet the commitments and the proposed duration are feasible with a low degree of confidence. Other plant activities are effected and delayed. The total duration longer than the minimum and progress less than maximum.

Life-cycle Cost The stabilization process results in lower operating and maintenance costs. The required costs to maintain and store the stable material is significantly less than those required for unstable material. The capital cost for equipment and facility modifications are less than \$2 million, which will drive to line item funding. Line item funding will also impact schedule. The total life cycle costs including operation, maintenance, decontamination, and waste disposal are less than the average expected amount, should be minimized, and fit within targeted budgets.

5- Meets the criteria listed above.

1- The stabilization process does not lower the operating and maintenance costs associated with maintaining and storing the material. The capital cost for equipment and facility modifications exceed \$2 million, and need line item funding. The total life cycle costs are larger than the average expected amount.

Stakeholder Acceptance The expected perceptions from the public will be favorable. The activity has a high likelihood of being covered in the currently, planned NEPA efforts. Any of the past issues collected from the public are not evident in the stabilization process.

5- Meets the criteria listed above.

1- The stabilization process has some characteristics similar to past negative public perceptions. The activities needed to implement the process require NEPA efforts different from those planned.

9.0 ALTERNATIVE COMPARISONS

9.1 ALTERNATIVE DESCRIPTIONS

Section 7.2 is organized by material categories, and each category description contains descriptions of treatment alternatives. Some the treatment alternatives are applicable to several different material categories. Because of these similarities or duplications, seven basic treatment alternatives are identified. These alternatives are illustrated in Tables 9.1-1 and 9.1-2. This section discusses those seven alternatives.

Alternative 1: Dissolution/Precipitation. This process is illustrated as a block diagram (Alternative 1) in Table 9.1-1, and Figure 7.2-1 contains a schematic of the dissolution and precipitation process. Dissolution is a preparation step for processing solid residues that is not required when processing solutions. Precipitation is the stabilization treatment step and is followed by thermal treatment.

When thermal treatment alone is not adequate to meet the DOE guidelines, dissolution of solid residues may be required. This dissolution would involve nitric acids and fluoride of strengths determined by the type of residue being processed. The dissolution can be performed in small batches in slab dissolvers; or if the quantities to process are large, glass and Kynar airlift cascade dissolvers may be used. Hot caustic wash solutions may be used to back flush filters and clean off-gas condensers to remove silica cake. The dissolved residues would be filtered before precipitation to remove any solids. The solids would be dried and packaged per solid waste acceptance criteria.

Depending on the types of plutonium materials to be processed, the number of precipitation steps needed and the chemicals used in the precipitation may be varied. Magnesium hydroxide precipitation (single stage using solid magnesium hydroxide) has received some attention in the DOE complex because of some advantages in stabilizing impure solutions. Rocky Flats is demonstrating a two stage, oxalic acid precipitation. In either process, aqueous plutonium solution is transferred by vacuum into the precipitator tank. Once the precipitation process is complete, the precipitate is vacuum filtered through a filter boat and the filtrate is collected in a receiver vessel. The wet filter cake is dried and then calcined in a furnace to meet the storage requirements. The filtrate is sampled to determine if it meets the acceptance criteria before it is transferred to tank farms. This alternative could potentially be used to stabilize the following materials: sand, slag & crucible; sludge; ash; fluoride residues; graphite; alloys and solutions (chloride, nitrate, and basic).

Alternative 2: Dissolution/Direct Denitration. This process is the second process illustrated as a block diagram in Table 9.1-1, and Figure 7.2-2 contains a simplified schematic representation of the vertical calciner used for direct denitration. The feed which is either plutonium solutions or dissolved and filtered solid residues is slowly metered into the bottom of a heated, stirred bed of previously generated product solids. An agitator classifies and moves the dry particles through, an overflow into a receiver. The calciner is proposed to operate at 800 °C, and the final product may or may not meet the requirements of DOE-STD-3013-94 of an LOI of less than 0.5% at 1000 °C. Product from the vertical calciner may need thermal stabilization. This alternative could potentially be used to stabilize the following materials: sand, slag & crucible; residues with minor amounts of fluorides; sludge and solutions (nitrate and basic).

Table 9.1-1. Illustration of the Alternatives 1-3 For Stabilizing Solid Residues and Solutions

	<u>Potential Material Feed</u>	<u>Preparation</u>	<u>Stabilization Treatment</u>	<u>Thermal Treatment</u>
(1)	SS&C, Ash, Fluoride residues, Graphite, Alloys & Solutions (chloride, nitrate, & basic)	Dissolution batch or continuous	Precipitation	Thermal Treatment
(2)	SS&C, Ash, residues with minor amounts of fluoride, & Solutions (limited chloride, nitrate, & basic)	Dissolution	Direct Denitration	Thermal Treatment
(3)	SS&C, Sludge Ash, Oxalate & Oxide residues, Alloy (Pu-U-Mo) & Oxides	Grinding	None	Thermal Treatment

Alternative 3: Thermal Treatment Only. This process is the final process (Alternative 3) illustrated as a block diagram in Table 9.1-1. Depending on the residue to be treated, grinding may be required to break up the material sufficiently to get complete oxidation. Thermal treatment can be batch, continuous or semi-continuous processes depending on the type and amount of material to be processed. Inert gases may be introduced in order to guard against the risk of burn or explosion. The temperature cycle, such as the rates of temperature change, the length of the hold times and the set temperatures, can be controlled using preset programs. This alternative could potentially be used to stabilize the following materials: sand, slag & crucible; ash; sludge; oxalate & oxide residues; alloy (Pu-U-Mo); and oxides.

Alternative 4: Molten Salt Oxidation. This process is illustrated as a block diagram (Alternative 4) in Table 9.1-2. A schematic representation can be found in Figure 7.2-3. The feed material would need to be of a certain size depending on the feed system, but size reduction is probably necessary by shredding or pulverizing. The feed material is introduced with oxygen under the surface of a molten salt bath consisting to a mixture of carbonates, chlorides, or sulfates of sodium, potassium,

lithium or calcium. The organic portions of the feed are reacted with oxygen to produce carbon dioxide, nitrogen and steam. The inorganic components of the combustibles and any plutonium are retained in the molten salt. The acid gases produced react with the alkaline carbonates in the bath. The dissolved solids and the retained particles build up in the melt. This is then dissolved in water. The oxides and salts of actinides, which are insoluble in the alkaline solution, are filtered and then stabilized by thermal treatment. The alkaline filtrate is transferred to tank farms. This alternative could potentially be used to stabilize the following materials: fluoride residues, solutions (nitrate, chloride & basic), combustibles, rag/pkg-acid soaked, polycubes, graphite, and solutions (oil & organic).

Table 9.1-2. Illustration of the Alternatives 4-7 for Combustibles

<u>Alternative</u>	<u>Preparation</u>	<u>Stabilization Treatment</u>	<u>Thermal Treatment</u>
(4)	Shredder	Molten Salt	Dissolution, Filtration & Thermal
(5)	Shredder	Pyrolysis	None
(6)	Shredder	Fluidized Bed	None
(7)	Shredder	Catalyzed Wet Oxidation	Precipitation & Thermal Treatment

* All alternatives can treat combustibles, polycubes, and rags/pkg (acid soaked). In addition molten salt, fluidized bed and wet air oxidation, Alternatives 4, 6 & 7, can stabilize oil and organic solutions.

Alternative 5: Pyrolysis. This process is illustrated as a block diagram (Alternative 5) in Table 9.1-2. The feed material may require preparation such as shredding. The pyrolysis occurs in two chambers. In the first stage, the organic material is pyrolyzed under oxygen deficient conditions, and the second chamber completely oxidizes the products from the first chamber. Heat is required for both chambers. The design includes a burner cone and baffles to cause ignition and create turbulence, which is important for complete combustion. The off gas from the second chamber is

cooled and filtered. This alternative could be used to stabilize the following materials: combustibles, graphite, and polycubes.

Alternative 6: Fluidized Bed. This process is illustrated (Alternative 6) as a block diagram in Table 9.1-2. As with the other alternatives in this diagram, the feed may need to be prepared to be effectively stabilized with this method. Plastic materials have been used by melting them and introducing them as a liquid. Feed may also be pulverized into particles. Fluidized bed combustion burns solids, liquids, and sludges in the presence of dry limestone to control acid gases without wet scrubbers that produce a secondary waste stream. Effluent from the fluidized bed is a stabilized ash. High air velocities and circulating solids create a highly turbulent combustion zone with uniform temperatures. The ash, including plutonium compounds, would be retained in the bed materials. The off-gas stream is filtered through cyclone separators, sintered metal filters and HEPA filters. The combustion temperature of 790 °C to 870 °C may or may not produce a product that meets the requirements of DOE-STD-3013-94 of an LOI of less than 0.5% at 1000 °C. This alternative could potentially be used to stabilize the following materials: combustibles, rag/pkg-acid soaked, graphite and polycubes.

Alternative 7: Catalyzed Wet Oxidation (DETOX). Table 9.1-2 illustrates Alternative 7 as a block diagram, and Figure 7.2-5 shows a schematic representation. Again feed preparation is required to reduce the size, but shredding is adequate to 1.0 cm pieces and pulverization may not be necessary. The oxidation process occurs in a stirred tank where solutions of organic materials react with gaseous oxygen or air, at elevated temperature (408 K (135 °C) to 523 K (250 °C)) and pressure (100kPa (14.5 psi) to 1500 kPa (217 psi)). Organic material would be completely oxidized and the plutonium and uranium would be soluble in the chloride solution containing a catalyst. The solutions are highly corrosive and tantalum reaction vessels would be required. This process needs additional steps to produce a stabilized product. It may be possible use the precipitation process. An alternative to precipitation is to evaporate the hydrochloric acid in the process solution leaving the iron oxide and the radioactive metal. This alternative could potentially stabilize combustibles, polycubes and solutions (oil & organic).

9.2 EVALUATION APPROACH

Table 9.2-1 is a matrix of the identified alternatives and the material categories. The check mark indicates the material categories that can be stabilized by each of the identified alternatives described above. No single alternative is capable of stabilizing every material category; therefore, a combination of alternatives is needed. For the following evaluation the alternatives are divided into two groupings. Alternatives 1 through 3 primarily stabilize residues, solids and solutions, and alternatives 4 through 7 stabilize the combustible materials. The coordinates on Table 9.2-1 matrix shows that the two regions are fairly independent. Only a handful of checkmarks lie in the other two quadrants, and the majority of those are in the molten salt column. These check marks represent the flexibility of the molten salt alternative to process a variety of material categories. This topic is further discussed in Section 10.1 (see Figure 10.1-3).

By selecting one alternative from the first grouping and combining it with an alternative from the second grouping, the combination of two alternatives would stabilize the entire set of material categories found in the plutonium inventory. For this evaluation, the two groupings will be evaluated and compared separately and then integrated to make the recommended integrated

baseline as discussed in Section 10.0 of this report. Two independent data evaluation teams were involved. Alternatives 1 through 3 are discussed in Section 9.3, and Alternatives 4 through 7 are discussed in Section 9.4.

Table 9.2-1. Matrix of the Identified Alternatives and the Proposed Feed Material Categories

Material Category/Alternatives	1	2	3	4	5	6	7
Reduction residues (SS&C)	✓	✓	✓				
Fluoride residues	✓	✓	✓	✓			
Sludge	✓	✓	✓				
Incinerator Ash	✓	✓	✓				
Oxalate residues			✓				
Oxide residues			✓				
Oxides			✓				
Alloy	✓		✓				
Solutions, nitrate	✓	✓		✓			
Solutions, chloride	✓	✓		✓			
Solutions, basic	✓	✓		✓			
Combustibles				✓	✓	✓	✓
Rag/pkg-acid soaked (F, CCl ₄)				✓	✓	✓	✓
Polycubes				✓	✓	✓	✓
Graphite	✓			✓	✓	✓	
Solutions, oil & organic	✓*			✓		✓	✓

ALTERNATIVE KEY

- 1 Dissolution/Precipitation
- 2 Dissolution/Direct Denitration
- 3 Thermal Treatment Only
- 4 Molten Salt
- 5 Pyrolysis
- 6 Fluidized Bed
- 7 Catalyzed Wet Oxidation (DETOX)

* Hydrolyze in Dissolution Equipment

9.3 EVALUATION OF ALTERNATIVES ONE THROUGH THREE FOR SOLID RESIDUES AND SOLUTIONS

9.3.1 Evaluation

The third alternative of only thermal stabilization is currently being used at PFP to stabilize sludges. Two muffle furnaces are being used ramp up temperature at a safe prescribed rate and then bake the material at 1000 °C for an hour. This method is established and should be maintained to process residues. Because thermal treatment is a relatively simple process, with only one processing step, it should be used, when possible, to stabilize residues. Solutions, however, cannot be stabilized by thermal treatment alone. Precipitation and direct denitration are two stabilization alternatives for solutions. Adding dissolution capability, a preparation step, to the two solution alternatives would allow any residues that cannot be stabilized by thermal treatment alone to be first dissolved and then stabilized like solutions by either precipitation or possibly direct denitration. The second alternative is dissolution followed by direct denitration and thermal treatment, and the first alternative is dissolution followed by precipitation and thermal treatment.

The third alternative, thermal treatment only, is discussed first. The possible feeds to this process are quite diverse. Residues containing fluorides will be corrosive, especially at the 1000°C operating temperature. The corrosion could damage the thermal chambers and furnace boats containing the material. Heating plutonium fluoride compounds with steam will convert it to the oxide. Hydrogen fluoride gas produced in the steam reaction is highly corrosive. Therefore, residues containing plutonium fluoride are not best suited for stabilization by thermal treatment alone. The characteristics of the end product would depend on the characteristics of the feed material. For example, plutonium and calcium metal and plutonium fluoride may be occluded in a residue matrix like the SS&C. This metal may not be fully oxidized during thermal treatment, and it may not be detectable in an LOI measurement. The end product from this third alternative is expected to be stable and safe for interim storage, depending on feed characteristics. Firing the oxide materials to 1000°C furnace temperature will increase the difficulty of future dissolution that would be required to use the plutonium in reactor fuel. This is a final treatment and disposal option being considered, and the decision criteria did indicate a desire to not preclude any possible final treatment and disposal options. The technology is mature and proven by both past residue processing practices and the current sludge stabilization efforts. The process is simple and the equipment is available from vendors, off the shelf. Vapors from the furnace are vented to the stack through a heat exchanger. Condensate is evaporated and is also vented to the stack. Particulate is captured in HEPA filters, an integral part of PFP facilities. Sludge stabilization was performed following an EA (environmental assessment) where public and stakeholder opinions were collected. Future thermal stabilization efforts are not expected to be viewed negatively by the stakeholders.

Table 9.3-1 shows a summary of the evaluation of Alternatives 1 and 2. Alternative 3 was not evaluated, because of its current use and its obvious application for some residues. Because thermal treatment is a relatively simple process, with only one processing step, it should be used, when possible, to stabilize residues. Therefore, the evaluation between Alternative 1, precipitation and thermal treatment, and Alternative 2, direct denitration and thermal treatment, is the most relevant.

The second option, direct denitration, is evaluated next. The initial feed products are conceptually all solutions (except the oil and organic) and potentially residues which have been dissolved. Direct denitration has limited capacity for feed solutions containing chloride and fluoride. The chloride

Table 9.3-1. Evaluation Data Matrix for Alternatives 1 & 2**Averages of Evaluation Data Sets**

Criteria	(1)	(2)
End Product	5.0	4.5
Technical	5.0	3.5
Process Capability	4.5	3.5
Risk	3.5	3.5
Regulatory/Waste Min.	3.5	3.0
Schedule	4.5	3.5
Cost	4.5	3.0
Stakeholder	4.0	4.0
Mean	4.3	3.6
Std. Dev.	0.4	0.4

Evaluation Data Set #1

Criteria	(1)	(2)
End Product	5	4
Technical	5	3
Process Capability	5	3
Risk	3	3
Regulatory/Waste Min.	3	3
Schedule	4	3
Cost	4	3
Stakeholder	3	3
Mean	4.0	3.1
Std. Dev.	0.9	0.3

Evaluation Data Set #2

Criteria	(1)	(2)
End Product	5	5
Technical	5	4
Process Capability	4	4
Risk	4	4
Regulatory/Waste Min.	4	3
Schedule	5	4
Cost	5	3
Stakeholder	5	5
Mean	4.6	4.0
Std. Dev.	0.5	0.7

Alternative Key

1. Dissolution/Precipitation
2. Dissolution/Direct Denitration

concentration must be less than the nitrate to result in the plutonium nitrate conversion to oxide. The variable concentrations and impurities in the feed may tax the system. The final end product needs to be demonstrated to meet the LOI of less than 0.5 weight percent. If the end product does not meet the LOI, then thermal treatment may be required. The process has been demonstrated in the laboratory for plutonium nitrate materials of various concentrations. Alkali metal salts can cause agglomeration phase and operational difficulties. Laboratory vertical denitrator equipment exists, but use in a production type environment for stabilizing solutions will require modification at a minimum and complete development at a maximum. The stirred pot denitrator is critically safe. These undetermined development needs and the uncertainty that the variety of feed solutions poses no significant problems makes relying solely on direct denitration risky. Direct denitration will produce a filtered offgas and condensate. Solid particulate entrained in the off gas will be collected in the facility HEPA filtration system.

The first alternative, precipitation followed by thermal treatment, is evaluated next. The initial feed products are conceptually all solutions (except the oil and organic), and potentially solid residues which have been dissolved can be treated using this third option. Precipitation will produce damp plutonium solids from a variety of solutions including chloride solutions, but it is not a one step process to stabilization. Additional steps of filtration and thermal treatment are required. The final end product, following thermal treatment, will be dry impure plutonium oxides. The technology is fully developed and was used for past plutonium recovery processes. It has been used in full scale operations. The equipment that is needed has known reliability and maintenance requirements. The equipment can be utilized with different precipitating agents that may be needed to treat the diverse feeds. The process in this alternative is flexible. Even organic substances can be hydrolyzed and subsequently stabilized by aqueous processing.

Organic processing was not included in the stabilization options, because of its limited application, but the dissolution and solution treatment capability described in this alternative is flexible and is applicable to organic processing. Solids that are primarily the phosphate esters of plutonium and dibutyl phosphate (DBP) are degradation products of tri-butylphosphate, and extractant in the PRF plutonium recovery operation. The esters saponify (decompose, forming the corresponding alcohol and acid or salt) when heated with dilute sodium hydroxide solution. This plutonium ester undergoes metathesis to form $\text{Pu}(\text{OH})_x\text{H}_2\text{O}$, Na_3PO_4 and NaOC_4H_9 . After filtration, the solids can be treated again to remove all the phosphate. The purified plutonium hydroxide is dissolved in concentrated nitric acid containing 0.1 M hydrofluoric acid.

As indicated by the averages found in Table 9.3-1, the precipitation process ranked higher than the direct denitration process. Alternative 1, the precipitation process, is more favorable in terms of the end product characteristics, process capability, and the technical factors. The end product characteristic of the direct denitrator has not been demonstrated to meet the desire LOI without further thermal stabilization. The process capability for direct denitration is not capable of treating material high in chlorides and fluorides. The precipitation process is capable of stabilizing all feeds. The need for some development of the direct denitration process also caused it to rank lower on technical factors as well as cost and schedule.

9.3.2 Sensitivity of Result to Weighting of Decision Criteria

The evaluation of the alternatives performed in the previous sections treated all of the decision criteria as equal. For example, cost was equally important as technical factors, risk and all other

criteria. Graphs can be prepared to illustrate how sensitive the ranks are to the importance or weight of a particular decision criteria. This weight can be varied from 0% to 100% and the overall desirability of the alternatives is plotted on a graph, one line for each alternative. Figure 9.3-2 contains one of these graphs. If the lines crossed, one alternative becomes more desirable than another and the ranking changes. Graphs prepared for each of the decision criteria are contained in Appendix D.

For the evaluation between precipitation and direct denitration, Alternatives 1 and 2, none of the graphs showed intersections, called cross over points. Because none of the graphs intersect, precipitation always is more desirable than direct denitration. The importance or weighting of the decision criteria would not change the ranking. The difference between the two independent evaluation teams in the utility also called *desirability for direct denitration* indicates that the first data set is significantly lower (utility of 0.53 (reference Figure 9.3-1)) than the second data set (utility of 0.75 (reference Figure 9.3-1)). This lower evaluation may contribute to the absence of cross over points in the graphs. Because of the large variability or difference in the two data sets, the average of the two data sets may not be truly representative of the potential performance. It may be due to uncertainty in the information used when making the evaluation or the direct experiences and perspectives of the evaluators.

9.4 EVALUATION OF ALTERNATIVES 4 THROUGH 7 FOR COMBUSTIBLES

9.4.1 Evaluation

The evaluation of Alternatives 4 through 7 can be found in Table 9.4-1, and the processes are illustrated in Table 9.1-2. All of the four processes have the same preparation step, a shredder. Size reduction and feed uniformity needs may differ according to the feed material and the process, but feed preparation whether it is shredding or melting is needed for all of the processes. Two of the alternatives, molten salt and DETOX, require some additional processing steps to complete the stabilization. The fourth alternative, molten salt, results in unburned portions such as plutonium metal as ash distributed in the salt bed. In order to remove the unburned constituents, the salt bath must be dissolved and filtered. The filtered material must then be thermally stabilized for storage. The process evaluated includes the steps necessary to dissolve, filter and thermally stabilize the salt bed. The seventh alternative, DETOX, will result in a plutonium-bearing solution that must be processed by the alternatives for solutions, precipitation followed by thermal treatment or direct denitration. The other two alternatives, pyrolysis and fluidized bed do not require any additional steps except maybe thermal treatment.

The fourth alternative is molten salt. The possible feeds to this process are quite diverse. Combustibles, polycubes, rags, solutions (oil and organic) as well as graphite are all potential feed for the process. The salt bed will retain ash material (all that does not decompose) either dissolved in the salt bed or as insoluble material mixed in the bed. To remove the ash material, the salt bed must be further processed, by dissolution and filtration. The dissolution process needs development. Since the polycube material is unique to Hanford, testing may be necessary. The size may be directly applicable to that needed for PFP. Therefore, development of the molten salt unit should be minimal. The feed may need to be reduced to 1/80th of an inch. Some tests have resulted in feed tube plugging. The temperature of the molten salt process is 800 to 1000°C which may pose some unique safety concerns regarding rapid flashing when using liquid feeds. The waste products from

Ranking for OVERALL Goal for Preference Set Equal Weights

Average of Evaluation Data Sets

Alternative	Utility
(1) Precipitation	0.8281
(2) Denitration	0.6406

Evaluation Data Set #1

Alternative	Utility
(1) Precipitation	0.75
(2) Denitration	0.5312

Evaluation Data Set #2

Alternative	Utility
(1) Precipitation	0.9062
(2) Denitration	0.75

Figure 9.3-1. Ranking of Alternatives 1 and 2 Including Average of Two Evaluation Teams

Figure 9.3-2. Diagram of Percent of Weight on Reg./Waste Minimization Measure versus Utility for Alternatives 1 and 2

this process are liquid sodium carbonate solution and the off gas of decomposed material and will presumably be only carbon dioxide, water, nitrogen and oxygen.

The fifth alternative is pyrolysis. The possible feed products are polycubes, combustibles, rags and possibly graphite. This method has been used in the past at PFP. The proposed process is a two-stage process which is a modification of past process and will require evaluation, design, and testing. Ash will be the product from the pyrolysis process and will consist of unburned carbon, plutonium oxide, and impurities which may need further thermal treatment. Unlike molten salt, where the product requires additional processing to get to a storable form, pyrolysis could directly produce a storable form. The only waste stream will be off gas. Liquid waste will not be generated.

The sixth alternative is fluidized bed. The possible feeds are polycubes, combustibles, rags and maybe graphite. The feed size must be particles suspended in the bed material. The final product is ash and the spent bed material which have a larger mass and volume than the feed materials. Rocky Flats currently has identified using an existing fluidized bed for their combustible materials; however, the cost to retrofit is high, \$20 million. Criticality control may be difficult, because of the geometry of the vessels may be larger than the general criticality guideline of not larger than 5-6 inches. The off gas will have entrained particulate matter which requires cyclone separators in addition to sintered metal filters and HEPA filters.

The seventh alternative is DETOX, a wet air oxidation process. The possible feeds to the process are solutions (oil and organic), polycubes and combustibles. The DETOX process, like the dissolution processes, requires additional processes to get to a stable, storable product. The DETOX must be followed by magnesium hydroxide precipitation and thermal treatment. The final product is dry, thermally stabilized plutonium oxide. The process is pressurized (100 psig), which may make it riskier to personnel and workers than the other alternatives. However, robust safe designs should be possible. One advantage of the DETOX process is the solvation of plutonium and uranium. Wet air oxidation process as have been widely used for more than 50 years. Recent experiments are focusing on the use for mixed wastes including radioactive wastes. Oxidation efficiencies have been greater than 99% for organics. The DETOX process has shown sufficient promise in tests at Rocky Flats, and at this time it has replaced fluidized bed incineration as the preferred option for combustibles.

The evaluation of cost and schedule is dependent on the amount of development required; more development causes longer schedule and higher costs. The pyrolysis requires the least development, but existing equipment needs to be modified for a two stage process. The DETOX process has been successful in testing and the equipment required is simple; therefore it would follow pyrolysis for the amount of development required. The molten salt process and the fluidized bed are more complex processes and would require process and equipment development.

The evaluation of stakeholders primarily reflects the perceived idea that incineration and burning would be less favorable than other process. This perception would favor DETOX and possibly molten salt over fluidized bed and pyrolysis.

Table 9.4-1 summarizes the evaluation for all of the decision criteria for Alternatives 4 through 7. Two independent data evaluation teams evaluated the alternatives. Both data sets are included in

Table 9.4-1. Evaluation Data Matrix for Alternatives 4 through 7**Averages of Evaluation Data Sets**

Criteria	(4)	(5)	(6)	(7)
End Product	4.5	4.0	3.0	4.5
Technical	2.5	4.0	2.5	2.5
Process Capability	3.5	3.5	3.5	3.0
Risk	3.0	3.5	3.0	3.0
Regulatory/Waste Min.	3.0	3.5	3.0	3.0
Schedule	1.5	4.0	1.5	2.0
Cost	1.5	3.0	1.5	2.0
Stakeholder	3.5	2.5	2.5	4.0
Mean	2.9	3.5	2.6	3.0
Std. Dev.	0.6	0.5	0.6	1.0

Evaluation Data Set #1

Criteria	(4)	(5)	(6)	(7)
End Product	5	4	2	5
Technical	2	4	3	3
Process Capability	5	5	5	5
Risk	3	4	2	2
Regulatory/Waste Min.	4	4	4	4
Schedule	2	4	2	3
Cost	2	4	2	3
Stakeholder	4	2	2	5
Mean	3.4	3.9	2.8	3.8
Std. Dev.	1.2	0.8	1.1	1.1

Evaluation Data Set #2

Criteria	(4)	(5)	(6)	(7)
End Product	4	4	4	4
Technical	3	4	2	2
Process Capability	2	2	2	1
Risk	3	3	4	4
Regulatory/Waste Min.	2	3	2	2
Schedule	1	4	1	1
Cost	1	2	1	1
Stakeholder	3	3	3	3
Mean	2.4	3.1	2.4	2.3
Std. Dev.	1.0	0.8	1.1	1.2

Alternative Key

4. Molten Salt
5. Pyrolysis

6. Fluidized Bed
7. Catalyzed Wet Oxidation (DETOX)

Table 9.4-1 and the final chart tabulates the average of the two. The totals indicate that Alternative 5, pyrolysis, is more desirable than the DETOX, molten salt, and fluidized bed alternatives. Alternative 7 DETOX averages to the second best. This process was rated almost even with pyrolysis in the first data set and was rated last in second data set. The average of the two may not reflect the actual expected performance of the DETOX system. Figure 9.4-1 shows bar charts of the overall desirability of the alternatives: (a) is the first data set, (b) is the second data set, and (c) is the average of the two. Pyrolysis is rated highly because it has been used in the past at PFP and the equipment is already available, even though it requires modification. It is also the only option with demonstrated use for polycube treatment. The DETOX process, though more complicated because of the number of processing steps, rates highly on anticipated stakeholder acceptance and end product characteristics. The stakeholders are expected to favor this process, because it is cleaner than incineration type processes. The end product is mostly plutonium oxide; the impurities have been efficiently oxidized. The equipment is basically a stirred reactor which is quite simple.

9.4.2 Sensitivity of Result to Weighting of the Decision Criteria

The evaluation of the alternatives performed in the previous sections treated all of the decision criteria as equal. For example, cost was equally important as technical factors, risk and all other criteria. Graphs can be prepared to illustrate how sensitive the rankings are to the importance or weight of a particular decision criteria. This weight can be varied from 0% to 100% and the overall desirability of the alternatives is plotted on a graph, one line for each alternative. Figures 9.4-2, 9.4-3, and 9.4-4 contain three of these figures. When the lines cross, one alternative becomes more desirable than another and the ranking changes.

For Alternatives 4 through 7, three of the graphs indicate cross over points. If the criteria called end product characteristics were 56% to 58%, both wet oxidation (DETOX) and molten salt would begin to rank higher than pyrolysis (ref. Figure 9.4-2). If the criteria called process capability were 30% and 52% molten salt and fluidized bed would begin to rank higher than oxidation, but not higher than pyrolysis (ref. Figure 9.4-3). At 34% and 46% of the stakeholder criteria wet oxidation (DETOX) and molten salt, respectively, would begin to rank higher than pyrolysis. Therefore: if end product characteristics and stakeholder perceptions were considered more important than the other criteria, wet oxidation (DETOX) and molten salt may become more preferable to pyrolysis. The diagrams for the remaining six decision criteria are contained in Appendix D.

Ranking for OVERALL Goal for Preference Set Equal Weights

Average of Evaluation Data Sets

Evaluation Data Set #1

Evaluation Data Set #2

Figure 9.4-1. Ranking of Alternatives 4 through 7 including Average of Two Evaluation Teams

Figure 9.4-2. Cross Over Point for End Point Characteristics

Figure 9.4-3. Cross Over Point for Process Capability

Figure 9.4-4. Cross Over Point for Stakeholder Perceptions

10.0 RECOMMENDED INTEGRATED BASELINE

10.1 INTEGRATED STABILIZATION BASELINE

The process evaluation identifies the unit processes that will stabilize the PFP inventory presented in Table 2-1. Together these processes will treat the variety of SNM in the PFP inventory. These are not just a collection of distinct unit operations where each operation stabilizes a single inventory item. They are an integrated sequence of processes and unit operations where the material prepared in one process becomes the feed for the next. Some inventory items may go directly to the stabilization function and other items may require several processing steps before the final stabilized form is produced. Most of the individual unit operations taken alone are not capable of stabilizing material, but their virtues are that they can chemically prepare the inventory item making it acceptable for another downstream process. The strategy is to identify a minimum number of unit processes that in concert can process the wide variety of PFP inventory items.

The evaluation and selection process discussed in Section 9.0 indicates that one integrated process of dissolution, precipitation and thermal treatment and pyrolysis is the most preferred. The DETOX process can be included as a specialized dissolution and would require additional equipment. If the DETOX process was not included, the oil and organic solutions would not have a stabilization option and the combustibles including polycubes would be limited to only pyrolysis. Figure 10.1-1 illustrates how that integrated process would be linked together. Ignoring the preferred integrated process arrived at through the selection process in Section 9.0, the vertical denitration process and muffle furnaces could be implemented. This choice could limit the feed stream, most possibly not including materials with high chlorides and high fluorides. The only other option to stabilize these solutions is the proposed process at both Rocky Flats and Los Alamos, hydroxide precipitation. Therefore, the addition of precipitation is required to ensure that the integrated system has the flexibility to process the variety of PFP inventory items, the choice of direction denitration process does not limit the number of processing units in the integrated process. This process, illustrated in Figure 10.1-2, includes dissolution, vertical denitration, precipitation, thermal treatment, and pyrolysis.

A more radical option, which disregards the results of the evaluation performed in Section 9.0, would be to make molten salt oxidation the centerpiece of the integrated stabilization process. The major processing equipment required for molten salt oxidation is the molten salt oxidation unit, a dissolver, and a filter. Because the molten salt process can stabilize a variety of feed materials, this integrated process has less process units than the ones previously discussed. The Plutonium Stabilization Study (Sevigny et al. 1995) describes treatment of combustibles, polycubes, sludges, oils and organics, graphite, fluorine bearing material, and nitrate solutions. Processing data are also listed for processing chloride solutions. The following process units are not necessary in an integrated molten salt option: precipitation (filtration is required to process the molten salt ash); pyrolysis/DETOX process, and thermal treatment by muffle furnaces. Figure 10.1-3 illustrates this integrated molten salt process. Therefore, the molten salt process is the one integrated process which has the minimum number of process units. Detailed costing and schedule analysis of this option, which was not performed in the evaluation, might prove to rank it at the top when reevaluated. However, any development efforts that would be required to validate this process and demonstrate capability to stabilize all of the proposed material would be required. Given the available time, the necessary development effort may be too much to successfully implement this process.

Figure 10.1-1 Selected, Preferred Integrated Stabilization System Has Five Processes

Figure 10.1-2 An Integrated Process with Direct Denitration Does Not Reduce the Number of Processes

Figure 10.1-3 Molten Salt as the Core Process is the Simplest with Only Three Processes

10.2 INTEGRATED CHARACTERIZATION, STABILIZATION, AND PACKAGING SYSTEM

The stabilization process described in the previous section is only one part of the overall stabilization system defined in Section 5.2. Characterization is required to collect, evaluate and assess information regarding the material composition and characteristics as well as the packaging configuration and condition. Packaging is also required in order to safely store plutonium bearing materials for interim, though long-term duration.

The characterization system will be quite complex; and as the stabilization treatment system evolves from conceptual design through implement and operation, the information required from the characterization system will also evolve. The baseline characterization process should focus on the activities necessary to understand the level of safety of the materials currently in storage and the characterization needs and requirements to support the recommended treatment baseline. Two specific tasks are being pursued to provide this information:

- Implementation of the plutonium inventory characterization implementation plan, which was written in response DOE's complex wide vulnerability assessment, will evaluate the risk of the current inventory. The evaluation will be supplemented with data collected through inspection.
- A (PFP Laboratories Upgrade) task, which has been identified and staffed. The task will begin with identifying requirements for providing supporting information for material characterization, stabilization process control, and waste disposal. The task will be complete once the selected instruments are installed and operated.

The baseline packaging system is to develop a Hanford food-pack can that meets the requirements of the material container defined in the DOE-STD-3013-94. The material container can be placed in side of the boundary container when it becomes available. The packaging system will presumably be developed by DOE and could possibly be the bagless transfer system from Savannah River.

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11.0 ISSUES

11.1 ULTIMATE DISPOSITION OF PLUTONIUM MATERIAL

On a national policy level, efforts are underway to determine the ultimate disposition of excess fissile material. The material which is discussed in this report is within the scope of that policy. The Office of Fissile Material Disposition (MD) within the Department of Energy is preparing a Programmatic Environmental Impact Statement. This process is scheduled to be complete in the fall of 1997. An implementation plan (DOE 1995), which summarizes the extensive scoping meetings held across the country in 1994, has been completed. It establishes decision criteria and narrows the universe of disposition actions to a manageable collection of possible practical disposition actions. While the PEIS may conclude in 1997, the ultimate disposition actions may not begin until 2002 at the earliest and due to the large amount of material may last through 2035. The timeline in Figure 11.1.1 indicates the rough basis behind these dates. The major 94-1 milestones are also included on the timeline. The outcome from the PEIS in fall of 1997 may define the final form of the plutonium material, which may effect the stabilization activities such as the furnace firing temperature or the packaging strategy. Since the ultimate disposition decision may occur before the stabilization activities are completed, opportunity will exist to align the stabilization activities with the activities proposed to prepare and package the material for final disposition.

11.2 RELATIONSHIP TO PFP STABILIZATION EIS

In the fall of 1994, a Notice of Intent was issued to prepare an EIS to stabilize materials and to clean out PFP. The EIS is a decision making process where environmental and other studies are used to develop and evaluate alternatives. The public and stakeholders are involved through out the process to provide comment. The EIS process results in a Record of Decision which selects the preferred alternative. The requirement to file an EIS is part of the NEPA process. The NEPA process is a key element of DOE's planning process and a principal means of achieving stakeholder involvement.

The draft of the PFP Stabilization EIS was made available for public comment in November of 1995. The ROD is expected in mid 1996. This EIS is expected to provide PFP with a range of stabilization methods for plutonium bearing materials at PFP. Before any recommendations made in this report on DNFSB's Recommendation 94-1 are implemented, any necessary additional NEPA documents, such as an EIS, EA or Categorical Exclusion, shall be completed.

11.3 PFP TRANSITION PROJECT PRIORITIES

The stabilization of plutonium material is only one of the activities for which the PFP Transition Project has responsibility, and DNFSB's Recommendation 94-1 is only one of the sources of requirements to which the PFP Transition Project must respond. Examples of other activities are the terminal cleanout of past processing systems and the decontamination of glove boxes and canyons and the Plutonium Working Group Report on the Environmental, Safety and Health Vulnerabilities Associated with the Department's Plutonium Storage is another source of requirements. Because the PFP Transition Project has limited personnel, resources and facilities, other activities and issues must be considered when planning work.

From DOE/EIS-0229-IP, "Long-Term Storage and Disposition of Weapons Usable Fissile Materials Programmatic Environmental Impact Statement EIS Implementation Plan", March 1995.

Figure 11.1-1. Plutonium Disposition Schedule for PEIS

A ranking of major activities, projected to take place in the next few years was developed by PFP Transition Project Management. This was performed using a Kepner-Tregoe® technique. Thirty-two activities were identified and were evaluated against thirteen site goals. The thirteen goals were weighted to take into account their relative importance. Table 11.3-1 lists the goals and their weighting. The resulting ranking is summarized in Table 11.3-2 and will be used to allocate the limited resources of personnel and budget, as well as the limited facility space.

Of the 32 activities, 5 involved the stabilization of material cited in the DNFSB 94-1 Recommendation. The five activities, listed in order of importance, are sludge, solution, combustibles, reactive solids, and interim stable solids. The sludge and solution stabilization fell into the top ten of the ranking. Combustibles and reactive solids were in the middle and interim stable solids were in the bottom portion of the ranking.

This prioritization was an effort to encompass all activities at PFP Transition Project and to provide a planning and budget allocation so that activities can be planned realistically, not necessarily with the assumption that unlimited resources will be available to accomplish the plutonium material stabilization associated with Recommendation 94-1.

Table 11.3-1. The Site Goals used to Evaluate the Relative Importance of PFP Near Term Activities

Site Goals	Description	Goal Weight
Facility Reliability and Safety Boundary	Maintain the reliability of the facility systems to allow for work continuity and maintain the boundary for safety and security.	10
Meet Regulatory Requirements	Meet all applicable regulatory requirements from federal, state, and local agencies/departments.	9
Milestone Commitments	Meet the commitments made in all applicable documentation.	
	To DOE both HQ & RL (including IAEA)	6
	TPA (including EIS activities & scope)	8
	Long-term strategic commitments for SNM and according to PEIS	8
	Safe storage in 8 years according to DOE RL commitments regarding 94-1 and Plutonium Vulnerabilities	4
Risk Reduction	Reduce the risks to workers, environment and public.	8
Dose Reduction	Reduce the exposure of workers to radiation from stored materials and contaminated areas.	7
Cost Savings	Completion of the activities will reduce the maintenance and operation costs.	5
Accomplish the Cleanout/Transition	Completion of the activities will accomplish necessary steps in the facility clean out in preparation for transfer to D&D.	5
Support Site wide Mission	The activity will support other project's activities according to the Hanford site mission.	4
Waste Minimization	Minimize the generation of wastes.	2

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Table 11.3-2. PFP TP Strategic Priorities List

PRIORITY	ACTIVITY	COMMENTS
1	SLUDGE STABILIZATION	94-1
2	GLOVE BOX TCO	Plutonium Vulnerability
3	SOLUTION STABILIZATION	94-1
4	SAS UPGRADES	Plant
5	STABILIZE 46 ITEMS OF RFA	Plutonium Vulnerability
6	PFP LAB UPGRADES	Plant
7	232-Z DEACTIVATION	Plutonium Vulnerability
8	DUCT REMEDIATION	Plutonium Vulnerability
9	ELECTRICAL UPGRADES	Plant
10	241-Z CLEAN OUT	DEACTIVATION
11	TANK FARMS ISOLATION	Hanford
12	CANYON TCO	Plutonium Vulnerability
13	PROJECT B-610	Plant
14	COMBUSTIBLE STABILIZATION	94-1
15	241-Z-361 CLEAN OUT	Plutonium Vulnerability
16	REACTIVE SOLIDS STABILIZATION	94-1
17	STEAM SYSTEM REPLACEMENT	Hanford
18	FFTF FUEL MOVE	Hanford
19	SEWAGE SYSTEM REPLACEMENT	Plant
20	231-Z Cell Clean out	Plant
21	242-Z CLEAN OUT	Plutonium Vulnerability
22	IAEA	Plant
23	291-Z HOLDUP REMEDIATION	Plutonium Vulnerability
24	WRAP PILOT PROJECT	Hanford
25	INT. STABLE SOLID STABILIZATION	94-1
26	WRAP SAMPLING SUPPORT	Hanford
27	FUEL FABRICATION PILOT PROJECT	Hanford
28	231-Z CLEAN OUT (E-4 DUCTS)	Plutonium Vulnerability
29	DRAIN LINE CLEAN OUT	Plutonium Vulnerability
30	GENERAL PLANT TCO	Plutonium Vulnerability
31	216-Z-9 CLEAN OUT	Plutonium Vulnerability
32	DEACTIVATION	DEACTIVATION

11.4 MATERIAL STATUS AND DISCARD LIMITS

All of the plutonium materials currently at Hanford, the materials in the inventory and the plutonium held up in the processing equipment and facilities, are not needed to support current and potential defense needs. This material is not "waste" and is being controlled and accountability is being maintained for the International Atomic Energy Agency (IAEA) and others. The material is excess fissile material and is within the scope of the national policy efforts to determine the method for final disposition and storage discussed in Section 11.1. However, some of the material has low concentrations of plutonium making it less attractive for stabilization and interim long-term storage and more attractive for immobilization and eventual placement at a disposal site. Economic discard limits were used when plutonium was being purified to establish the value, expressed in dollars, of scrap and non-conforming materials for eventually reprocessing into plutonium products. The limit was a balance of the costs associated with producing the plutonium from raw material with the costs of reprocessing the scrap materials. Since purified plutonium is no longer produced, the basic reason for the discard limit as well as the criteria used to calculate discard limit have changed. A letter from DOE sets the new criteria which should be used to determine which is more desirable, discarding or stabilizing. Before any discard limit is used or implemented, peer and expert reviews will be conducted and DOE approval will be required.

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12.0 RECOMMENDATIONS FOR FURTHER STUDY

Characterization

- A characterization program needs to be developed to accommodate the diverse needs for additional information about the PFP inventory. Information is necessary to support the future design and implementation of the planned stabilization systems. Other information is necessary to determine the current risks of continued storage, so that the stabilization efforts are prioritized to ensure the most risky materials are stabilized first. Characterization Plan WHC-SD-CP-TP-086 is the first test plan addressing these concerns.
- During the evaluation presented in this report, some information on the material was considered insufficient to identify appropriate stabilization processes. Sludges, compounds and residues are terms loosely applied to plutonium-bearing solids which do not give any information on the material composition or characteristics.
- Further consensus, protocol, or policy is necessary to truly define what is and what is not stable or suitable for safe, long-term, interim storage. The Plutonium Strategic Plan which is currently being developed according to WHC-ID-1183 *Hanford Site Plutonium Strategic Plan-Program Plan* (WHC Draft 1995) could include this activity. Baseline material balances need to be established not only for future design and implementation efforts but also to establish the appropriate relationship to cost and schedule baselines. Since the stabilization and storage requirements are continuing to be established, a baseline is necessary to understand cost and schedule impacts.
- Develop the appropriate discard criteria which will be important for the material balance and baseline processing described previously.
- Perform a study to ensure that laboratory capabilities exist or that plans are in place for the stabilization processes defined. Ensure that the capabilities have enough capacity and are located properly to integrate into the overall stabilization system.

Regulatory

- Regulatory implications need to be evaluated early in the program planning process to allow for the time necessary and to provide the appropriate regulatory controls and documentation early in the process implementation phase.

Packaging

- The packaging system defined in DOE-STD-3013-94 needs to be completely developed and available to PFP to ensure compliance by the necessary time frame 2002. Continue efforts to interface with the DOE complex wide activities, specifically, the working group on a site-wide packaging system procurement.

Stabilization

- Evaluate the precipitation process and produce a conceptual design which includes regulatory issues, life-cycle cost and schedule analyses. Both Rocky Flats and LANL are including precipitation in their baselines, combining efforts and sharing information is *recommended*.
- Study the potential, the expected performance and the applicability to PFP materials of the DETOX, wet oxidation process. Cost and schedules should also be prepared to *determine if it is promising enough to justify further development*. Since DETOX is the baseline stabilization process at Rocky Flats, combining efforts and sharing information is recommended.
- The disposal option needs further evaluation. Possible technical and regulatory issues must be identified.

Interfaces

- Continue to interface with related DOE activities: PEIS on Disposition of Excess Fissile Material, Nuclear Materials Stabilization Task Group, Research Committee, Residue Standard, etc.

13.0 REFERENCES

1994. *Technology Index - Molten Solids Processing - Molten Salt Process.*
- Szempruch 1995, *Plutonium Inventory Characterization Implementation Plan*, 9551735 Attachment Draft, Westinghouse Hanford Company, Richland, WA.
- 9456866 ATTACHMENT Draft, *Plutonium Finishing Plant Interim Plutonium Stabilization Engineering Study*, Pacific Northwest Laboratory, Richland, WA.
- Allen, R.P., L.K. Fetrow, and M.W. McCoy, 1982, *An Integrated Decontamination System for Surface-Contaminated TRU Waste. Proceedings of the ANS Topical Meeting on the Treatment and Handling of Radioactive Wastes*, Battelle Press, Columbus, Ohio.
- ANSI N14.5-1987, January 16, 1987, *American National Standard for Radioactive Materials - Leakage Tests on Packages for Shipment*, American National Standards Institute, Inc.
- DNFSB, 1994, *Plutonium Storage Safety at Major Department of Energy Facilities*, April 14, 1994 Defense Nuclear Facilities Safety Board, Washington D.C.
- CEP, 1995, "Supercritical Water Oxidation Aims for Wastewater Cleanup." *Chemical Engineering Progress*, April 1995.
- Cooper, J., W. A. Brummond, J. Farmer, C. Hoenig, O.H. Krikorian, R. S. Upadhye, R.L. Gay, A. Stewart, and S. Yosim, 1991, *Molten Salt Processing of Mixed Wastes with Offgas Condensation*. UCRL-JC-107288, Lawrence Livermore National Laboratory, Livermore, California.
- Dhooge, P.M. and K.D. Eisberry, *Treating Contaminated Organics Using The DETOX Process*, Mixed Waste Symposium, Baltimore MD, August 17-20, 1993, LA-UR-93-1206.
- Dhooge, P.M., J.E. Moslander and J.A. Zigmond, *Year End Report for Advanced Development of the DETOX Process in Application to Low Level Combustible Mixed Waste at the Rocky Flats Environmental Technology Site*, Delphi Research Inc., September 16, 1994, Subcontract #ASC 235757PA.
- DOE/EH-0415, November 1994, *Plutonium Working Group Report on Environmental, Safety and Health Vulnerabilities Associated with the Department's Plutonium Storage*, U.S. Department of Energy.
- DOE/EIS-0244-D, November 1995, *Plutonium Finishing Plant Stabilization Draft Environmental Impact Statement*, U.S. DOE Richland Operations Office.
- DOE/EIS-0229-IP, March 1995, *Long-Term Storage and Disposition of Weapons-Usable Fissile Materials Programmatic Environmental Impact Statement Implementation Plan*, U.S. Department of Energy Office of Fissile Materials Disposition.
-

-
- DOE/MD-0002, March 29, 1995, *Summary Report of the Screening Process to Determine Reasonable Alternatives for Long-Term Storage and Disposition of Weapons-Usable Fissile Materials*, U.S. Department of Energy Office of Fissile Materials Disposition.
- DOE, 1994, *Criteria for Safe Storage of Plutonium Metals and Oxides*, DOE-STD-3013-94, U.S. Department of Energy, Washington D.C.
- DOE, 1995, *Defense Nuclear Facilities Safety Board Recommendation 94-1 Implementation Plan*, February 28, 1995, U.S. Department of Energy, Washington D.C.
- WHC, 1994, *Hanford Site Systems Engineering Management Plan*, Draft, June 30, 1994, Westinghouse Hanford Company, Richland, WA.
- (WHC Draft 1995) *Hanford Site Plutonium Strategic Plan Program Plan*, Draft, March 31, 1995, WHC-ID-1183, Westinghouse Hanford Company, Richland, WA.
- Felt, R.E., 1965, *Equipment for the Direct Calcination of Plutonium Nitrate*, RL-SEP-674, Hanford Atomic Products Operation, Richland, Washington.
- Fetrow, L.K., R.P. Allen, and M.W. McCoy, 1982, *Sectioning Techniques for Plutonium Contaminated Glove Boxes*, Proceedings of the ANS Topical Meeting on the Treatment and Handling of Radioactive Wastes, Battelle Press, Columbus, Ohio.
- Flynn B.L., 1979, "Wet Air Oxidation of Waste Streams," *Chemical Engineering Progress*, April 1979.
- Haas, P.A., J.C. Rudolph, and J.T. Bell, *Molten Salt Oxidation Of Mixed Wastes: Preliminary Bench-Scale Experiments Without Radioactivity*, June 1994, ORNL/TM-12765).
- Lehmkuhl, G.D., 1976, *Light Water Reactor Fuel Recycle Program Plutonium Nitrate-to-Oxide Conversion Project Progress Report*, July-September 1976, RFP-2590, Rocky Flats Plant, Golden, Colorado.
- Martin Marietta Energy Systems, Inc., U.S. Department of Energy, Oak Ridge National Laboratory and RUST Geotech, Inc. 1993, *Mixed-Waste Treatment - What About the Residuals? A Comparative Analysis of MSO and Incineration*, U.S. Department of Energy, Grand Junction, Colorado.
- Conway, J.T., 1994, *Recommendation 94-1 to the Secretary of Energy*, letter, John T. Conway, Chairman of Defense Nuclear Facilities Safety Board, to Secretary Hazel O'Leary.
- McCoy, M.W., H.W. Arrowsmith, and R.P. Allen, 1980, *Vibratory Finishing as a Decontamination Process*, PNL-3336, Pacific Northwest Laboratory, Richland, Washington.
- WHC, 1995, *Special Nuclear Material Storage*, OSD-Z-184-00013, Westinghouse Hanford Company.
-

-
- Perry, J.H., Ed., 1963, *Chemical Engineer's Handbook*, 4th Edition, McGraw-Hill Book Company, New York.
- Response to Defense Nuclear Facilities Safety Board Recommendation 94-1 Implementation Plan for Plutonium Materials*, October 23, 1994, Westinghouse Hanford Company.
- Rickman, W.S., et al. 1985, *Circulating Bed Incineration of Hazardous Wastes*, CEP March 1985.
- Rossi, R.A., 1984, *Indirect Heat Transfer in CPI Fluidized Beds*, Chemical Engineering Progress, October 15, 1984.
- Sevigny, G.J., et al., 1995, *Plutonium Finishing Plant Interim Plutonium Stabilization Engineering Study (FINAL DRAFT PNL-10507)*, Pacific Northwest Laboratory, Richland, WA.
- Stiffler, G.L. and H.H. Hopkins, Jr., 1962, *A Vertical Calciner for Converting Plutonium Nitrate Solution to Plutonium*.
- IPP 1995, *The Rocky Flats Environmental Technology Site Integrated Program Plan* Version 1.0, Rocky Flats Plant, Golden, CO.
- WHC 1994d, *Systems Engineering Functions and Requirements for the Hanford Cleanup Mission: First Issue*, WHC-EP-07222, Rev. 0, January 1994, Westinghouse Hanford Company, Richland, WA.
- WHC 1995a, WHC-EP-0853, Rev. 1, October 1995, *DNFSB Recommendation 94-1 Hanford Site Integrated Stabilization Management Plan*, Westinghouse Hanford Company;
- WHC 1994c, *Plutonium Finishing Plant Transition Project Mission Analysis Report*, WHC-SD-CP-MAR-001, Rev.0, September 21, 1994, Westinghouse Hanford Company.
- WHC-SD-CP-TP-077, Rev.1, December 5, 1994, *Precipitation of Plutonium from Acidic Solutions Using Magnesium Oxide*, Westinghouse Hanford Company.
- WHC-SD-CP-TP-086, Rev. 0, August 4, 1995, *Plan to Examine Special Nuclear Material and the Foodpack Can Storage Containers at the Plutonium finishing Plant Storage Vaults*, Westinghouse Hanford Company.
- WHC-SD-CP-VES-001, June 1993, *Summary Report on Hanford Plutonium Disposition Workshop*, Westinghouse Hanford Company.
- Wojdac, L. F. 1994, *18th Annual Actinide Separations Conference in Durango, Colorado - Molten Salt Technology Applications*, Westinghouse Hanford Company, Richland, WA.
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APPENDIX A

DNFSB RECOMMENDATION 94-1

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May 26, 1994

The Honorable Hazel R. O'Leary
Secretary of Energy
Washington, DC 20585

Dear Secretary O'Leary:

On May 26, 1994, the Defense Nuclear Facilities Safety Board, in accordance with 42 U.S.C. § 2286a(5), unanimously approved Recommendation 94-1 which is enclosed for your consideration. Recommendation 94-1 deals with Improved Schedule for Remediation in the Defense Nuclear Facilities Complex.

42 U.S.C. § 2286d(a) requires the Board, after receipt by you, to promptly make this recommendation available to the public in the Department of Energy's regional public reading rooms. The Board believes the recommendation contains no information which is classified or otherwise restricted. To the extent this recommendation does not include information restricted by DOE under the Atomic Energy Act of 1954, 42 U.S.C. §§ 2161-68, as amended, please arrange to have this recommendation promptly placed on file in your regional public reading rooms.

The Board will publish this recommendation in the Federal Register.

Sincerely,

John T. Conway
Chairman

Enclosure

Copy to: Mark B. Whitaker, EH-6

Approved for Release by NSA on 05-10-2014 pursuant to E.O. 13526

RECOMMENDATION 94-1 TO THE SECRETARY OF ENERGY
pursuant to 42 U.S.C. § 2286a(5)
Atomic Energy Act of 1954, as amended.

Dated: May 26, 1994

The halt in production of nuclear weapons and materials to be used in nuclear weapons froze the manufacturing pipeline in a state that, for safety reasons, should not be allowed to persist unremediated. The Board has concluded from observations and discussions with others that imminent hazards could arise within two to three years unless certain problems are corrected.

We are especially concerned about specific liquids and solids containing fissile materials and other radioactive substances in spent fuel storage pools, reactor basins, reprocessing canyons, processing lines, and various buildings once used for processing and weapons manufacture.

It is not clear at this juncture how fissile materials produced for defense purposes will eventually be dealt with long term. What is clear is that the extant fissile materials and related materials require treatment on an accelerated basis to convert them to forms more suitable for safe interim storage.

The Board is especially concerned about the following situations:

- Several large tanks in the F-Canyon at the Savannah River Site contain tens of thousands of gallons of solutions of plutonium and trans-plutonium isotopes. The trans-plutonium solutions remain from californium-252 production; they include highly radioactive isotopes of americium and curium. These tanks, their appendages, and vital support systems are old, subject to deterioration, prone to leakage, and are not seismically qualified. If an earthquake or other accident were to breach the tanks, F-Canyon would become so contaminated that cleanup would be practically impossible. Containment of the radioactive material under such circumstances would be highly uncertain.
- The K-East Basin at the Hanford Site contains hundreds of tons of deteriorating irradiated nuclear fuel from the N-Reactor. This fuel has been heavily corroded during its long period of storage under water, and the bottom of the basin is now covered by a thick deposit of sludge containing actinide compounds and fission products. The basin is near the Columbia River. It has leaked on several occasions, is likely to leak again, and has design and construction defects that make it seismically unsafe.
- The 603 Basin at the Idaho National Engineering Laboratory (INEL) contains deteriorating irradiated reactor fuel from a number of sources. This basin also

contains sludge from corrosion of the reactor fuel. The seismic competence of the 603 Basin is not established.

- Processing canyons and reactor basins at the Savannah River Site contain large amounts of deteriorating irradiated reactor fuel stored under conditions similar to those at the 603 Basin at INEL.
- There are thousands of containers of plutonium-bearing liquids and solids at the Rocky Flats Plant, the Hanford Site, the Savannah River Site, and the Los Alamos National Laboratory. These materials were in the nuclear-weapons manufacturing pipeline when manufacturing ended. Large quantities of plutonium solutions are stored in deteriorating tanks, piping, and plastic bottles. Thousands of containers at the Rocky Flats Plant hold miscellaneous plutonium-bearing materials classed as "residuals", some of which are chemically unstable. Many of the containers of plutonium metal also contain plastic and, in some at the Rocky Flats Plant, the plastic is believed to be in intimate contact with the plutonium. It is well known that plutonium in contact with plastic can cause formation of hydrogen gas and pyrophoric plutonium compounds leading to a high probability of plutonium fires.

We note that removal of fissile materials from the 603 Basin at INEL has begun. We are also following the plans for remedying several of the other situations listed. In general, these plans are at an early stage. In addition, we are aware of steps DOE has taken to assess spent fuel inventories and vulnerabilities. We also note that a number of environmental assessments are being conducted in relation to the situations we have listed above. Finally, we note that a draft DOE Standard has been prepared for methods to be used in safe storage of plutonium metal and plutonium oxide.

These actions notwithstanding, the Board is concerned about the slow pace of remediation. The Board believes that additional delays in stabilizing these materials will be accompanied by further deterioration of safety and unnecessary increased risks to workers and the public.

Therefore the Board recommends:

- (1) That an integrated program plan be formulated on a high priority basis, to convert within two to three years the materials addressed in the specific recommendations below, to forms or conditions suitable for safe interim storage. This plan should recognize that remediation will require a systems engineering approach, involving integration of facilities and capabilities at a number of sites, and will require attention to limiting worker exposure and minimizing generation of additional waste and emission of effluents to the environment. The plan should include a provision that, within a reasonable period of time (such as eight years), all storage of plutonium metal and oxide

should be in conformance with the draft DOE Standard on storage of plutonium now being made final.

- (2) That a research program be established to fill any gaps in the information base needed for choosing among the alternate processes to be used in safe conversion of various types of fissile materials to optimal forms for safe interim storage and the longer term disposition. Development of this research program should be addressed in the program plan called for by (1) above.
- (3) That preparations be expedited to process the dissolved plutonium and transplutonium isotopes in tanks in the F-Canyon at the Savannah River Site into forms safer for interim storage. The Board considers this problem to be especially urgent.
- (4) That preparations be expedited to repackage the plutonium metal that is in contact with, or in proximity to, plastic or to eliminate the associated existing hazard in any other way that is feasible and reliable. Storage of plutonium materials generated through this remediation process should be such that containers need not be opened again for additional treatment for a reasonably long time.
- (5) That preparations be expedited to process the containers of possibly unstable residues at the Rocky Flats Plant and to convert constituent plutonium to a form suitable for safe interim storage.
- (6) That preparations be expedited to process the deteriorating irradiated reactor fuel stored in basins at the Savannah River Site into a form suitable for safe interim storage until an option for ultimate disposition is selected.
- (7) That the program be accelerated to place the deteriorating reactor fuel in the K-East Basin at the Hanford Site in a stable configuration for interim storage until an option for ultimate disposition is chosen. This program needs to be directed toward storage methods that will minimize further deterioration.
- (8) That those facilities that may be needed for future handling and treatment of the materials in question be maintained in a usable state. Candidate facilities include, among others, the F- and H-Canyons and the FB- and HB-Lines at the Savannah River Site, some plutonium-handling glove box lines among those at the Rocky Flats Plant, the Los Alamos National Laboratory, and the Hanford Site, and certain facilities necessary to support a uranium handling capability at the Y-12 Plant at the Oak Ridge Site.

- (9) Expedited preparations to accomplish actions in items (3) through (7) above should take into account the need to meet the requirements for operational readiness in accordance with DOE Order 5480.31.

John T. Conway, Chairman

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APPENDIX B

DOCUMENTS USED TO COMPILE DECISION CRITERIA

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DOCUMENTS USED TO COMPILE DECISION CRITERIA

1. PNL Draft EIS Report for the Stabilization of Material at PFP.
2. DOE Response to Recommendation 94-1: Implementation Plan.
3. DOE Letter, J.E. Mecca to President Westinghouse Hanford Company, "Pu Disposition Plans," dated August 9, 1994.
4. K-Basin Sludge Stabilization Report.
5. DOE/RL-93-0100, Predecisional Draft Revision 1, Hanford Site Data for the Weapons Complex Reconfiguration Programmatic Environmental Impact Statement
6. PFP Workshop which utilized a Kemper-Tregoe Approach to Prioritize Activities Competing for Limited Resources.
7. Source of the "Objectives and Criteria of Cleanup." It begins with Clean up Hanford Site.

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APPENDIX C

SUMMARY OF PACKAGING REQUIREMENTS FROM DOE-STD-3013-94

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SUMMARY OF PACKAGING REQUIREMENTS FROM DOE-STD-3013-94

Requirement Description	Page Number
The package shall have a minimum of two barriers. For in-line storage the material shall be in a container that meets the requirements for a boundary container. The second barrier will be provided by the plutonium handling enclosure. For out-of-line storage, the material shall be either stored in a material container nested in a boundary container (until a primary containment vessel can be used) or sealed in a boundary container nested in a primary containment vessel.	10, 4.2
Design of the container should allow for inspection and surveillance.	10, 4.2
The contents of each container shall be identified on the container's exterior and noted in the data base referred to in section 4.4. The markings shall be permanent in nature such as etched, or engraved.	10, 4.2
The inner-most sealed container shall be filled with an inert gas or a glovebox atmosphere what will not create a need for restabilizing the material.	10, 4.2
Material container shall be free of organic materials such as plastics, elastomeric gaskets, and organic coatings.	10, 4.2.1
Boundary container shall be sized to fit into the primary containment vessel. Recommended dimensions are maximum outer diameter of 12.5 cm (4.9 in.), maximum external height of 25.4 cm (10.0 in.); with a hemispherical bottom the maximum height can be 27.9 cm (11.0 in.).	10, 4.2.2.A.
The boundary container shall be sealed and tested after initial fill for leak-tightness as defined in ANSI N14.5.	11, 4.2.2.B.
The boundary container shall be fabricated of material that will be corrosion-resistant in environmental conditions expected in a plutonium storage facility.	11, 4.2.2.C.
The loaded boundary container shall remain leak-tight as defined by ANSI N14.5 after the following one-time, abnormal occurrences: a 122cm (4 ft.) drop onto a flat, essentially unyielding, horizontal surface, a 61 cm (2 ft) crush in which boundary containers collide, and the compression weight of 5 boundary containers.	11, 4.2.2.C.
The boundary container shall be proof-tested to 1.5 times (ASME Boiler & Pressure Code 1992, Section VIII, Division 1, Part UG-99) the theoretical maximum internal pressure.	11, 4.2.2.D.
The boundary container shall be free of organic materials such as plastic bags, organic coatings, and elastomeric gaskets.	11, 4.2.2.E.
The primary containment vessel shall be designed for dual use, for safe storage and as the primary containment vessel for shipping.	11, 4.2.3.A.1)
The primary containment vessel shall be compatible with the shipping envelope as defined by the following: 10 CFR 71, 49 CFR 173, 49 CFR 178 and DOE 5408.3.	11, 4.2.3.A.2)

Requirement Description	Page Number
The space between the boundary container and the primary containment vessel shall be free of removable contamination as defined by DOE Rad. Con. Manual. DOE/EH-0256T.	12, 4.2.3.A.3)
The primary containment vessel shall be designed to allow for leak testing and gas sampling.	12, 4.2.3.A.4)
The primary containment vessel design shall be compatible with automated handling equipment.	12, 4.2.3.A.5)
The primary containment vessel's dimensional requirements are based on size limitations set by an existing secondary shipping container. The primary containment vessel shall be maximum inside diameter of 13.3 cm (5-1/4 in.), maximum outside diameter 15.2 cm (6 in.), and a max external height in shipping configuration of 43.2 cm (17 in.).	12, 4.2.3.B.
The primary containment vessel shall have provisions for purge and backfill of the primary containment vessel.	12, 4.2.3.C.1)
The primary containment vessel shall be resealable to the original integrity after a gas sampling operation is completed.	12, 4.2.3.C.2)
Non destructive examination of the resealed primary containment vessel shall be possible to establish the integrity of the resealed vessel.	12, 4.2.3.C.3)
The sealed primary containment vessel shall be leak-tight as defined by ANSI N14.5.	12, 4.2.3.C.4)
The primary containment vessel shall meet the following requirements ASME Boiler and Pressure Vessel Code as specified by UCID-21218-Rev.1, NUTREG/CR03019 Recommended Welding Criteria for Use in the Fabrication of Shipping Containers for Radioactive Materials, and NUTREG/CR-3854 Fabrication Criteria for Shipping Containers.	12, 4.2.3.D.1)
The primary containment vessel shall be designed for reuse.	13, 4.2.3.D.2)
The primary containment vessel's minimum design life shall be 50 years with no required maintenance.	13, 4.2.3.D.3)
The primary containment vessel shall be fabricated of materials that would provide a corrosion-resistant barrier in environmental conditions expected in a plutonium storage facility.	13, 4.2.3.D.4)
The primary containment vessel shall meet the dimensional and containment requirements following anticipated handling occurrences: 122 cm (4 ft.) drop onto a flat, essentially unyielding, horizontal surface, 61 cm (2 ft.) crush in which primary containment vessels collide, handling shock, and compression weight of 5 primary containment vessels.	13, 4.2.3.D.5)

Requirement Description	Page Number
A loaded primary containment vessel shall remain leak-tight as defined by ANSI N14.5 after the following one-time, abnormal occurrences: 9 meter (30 ft.) drop onto a flat, essentially unyielding, horizontal surface; 9 meter (30 ft.) crush in which primary containment vessels collide, vehicle crush and puncture.	13, 4.2.3.D.6)
The primary containment vessel shall be designed to withstand 5,175 kPa (750 psig) internal pressure at 204 °C (400 °F) and to withstand 147 kPa (21 psig) external pressure.	13, 4.2.3.E.
The packing material within the primary containment vessel shall be noncombustible as defined in NFPA, Life Safety Code.	13, 4.2.3.F.1)
The packing material within the primary containment vessel shall be inorganic material without plastic.	13, 4.2.3.F.2)
The steady state plutonium metal temperature shall not exceed 100 °C (212 °F).	13, 4.2.3.F.3)
The primary containment vessels shall be capable of holding a boundary container with 4.5 kg (9.9 lb.) of plutonium metal or 5.1 kg (11.2 lb.) of plutonium oxide, with a minimum required free volume of 2.5 liters (153 in ³) remaining to prevent container pressure from exceeding the design limit.	14, 4.2.3.F.4)
Include numerous requirements for inspection and surveillance for safety. Need to know baseline package weight, boundary container or sealed container dimensions.	14, 4.3
Includes numerous requirements for documentation. Need to know the following: chemical form & isotopic content, quantity (mass), source of stored material (facility that generated the material), specific processing conditions, LOI test results and conditions of test, back fill gas composition and pressure on sealing, package configuration, date and condition of packaging, initial radiation field (gamma and neutron at contact and 30 cm), surveillance results, other relevant material characteristics, documentation of inspection tests including names of individuals performing inspections and the date of inspections, records of safety inspections, and location of stored materials.	15, 4.4
This section includes numerous requirements on quality assurance and control requirements.	15, 4.5

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APPENDIX D

SENSITIVITY ANALYSIS CROSS OVER DIAGRAMS

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* This appendix contains diagrams that show the sensitivity of alternative rank or importance of the selection criteria.

WHC-SD-CP-RPL-016 Rev. 0

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APPENDIX E

INITIAL DRAFT OF POLICY MEMORANDUM ON TREATMENT AND DISPOSITION OF PLUTONIUM BEARING RESIDUES

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MEMORANDUM FOR THE DEPUTY SECRETARY

FROM: Thomas P. Grumbly
Assistant Secretary for
Environmental Management

SUBJECT: ACTION: To establish Department of Energy policy for the treatment and disposition of plutonium residues.

BACKGROUND: Residues are a broad class of plutonium-bearing solids with plutonium concentrations below 50 weight-percent, which are either by-products of past weapons production or were unprocessed at the time production ceased. These materials exist at many Department sites in a wide variety of forms including metal alloys, impure oxides, salts, organic and inorganic compounds, and plutonium-contaminated solids. There are approximately 120 metric tons of these residues across the complex, containing approximately 6 metric tons of plutonium. Ninety-nine percent of them are at Rocky Flats, Hanford, Los Alamos, and Savannah River.

The current Departmental strategy for plutonium residues is expressed in the Implementation Plan for Defense Nuclear Facilities Safety Board Recommendation 94-1, i.e., to mitigate risks to workers associated with the residues by putting them in a state for safe interim storage. Known hazards include pressurization of containers, presence of reactive material, and degradation of containers. In implementing Recommendation 94-1, the Department has committed to stabilize the higher risk residues by May 1997 and the remainder by May 2002.

ISSUE: No departmental policy exists for treating these residues for disposal. There is, therefore, no framework for evaluating the proposals or plans of various sites and activities regarding treatment and disposal. The attached memorandum will supply that policy framework.

DISCUSSION: The proposed policy is to concentrate the actinide constituents in plutonium residues and separate the non-actinide material as

transuranic or low-level waste. Actinide separation immediately reduces hazards caused by the plutonium in non-actinide matrices, lowers surveillance costs due to decreased volume of nuclear material to manage, and takes advantage of existing infrastructure prior to dismantlement.

During weapons production, there was an Economic Discard Limit that allowed the disposal (discard) of plutonium-bearing materials if the cost to separate the plutonium from the matrix was greater than the cost to produce plutonium in reactors. That formula has no relevance today, except to explain that many of the residues existing today fell under the Economic Discard Limit, but were not disposed.

Exception to the proposed policy would be granted for classes or batches of residues having low plutonium concentrations or are unusually difficult to separate. In these cases, if it can be shown to be cost effective, an acceptable alternative to actinide separation is to prepare the material as waste for direct disposal to a geologic repository as waste. The performance factors for cost effectiveness analysis will be worker exposure, cost, and waste generation. These factors will be used when comparing the disposal alternative with separation and long term storage of the separated plutonium.

SENSITIVITIES: Separation of plutonium from weapons production residues may arouse non-proliferation concern. There are, however, already 16 metric tons of excess plutonium metal and oxides of sufficient purity that they will be prepared and packaged for storage per the Department's Standard and stored, awaiting disposal decision.

POLICY IMPACT: Establishes a much needed policy in this area.

RECOMMENDATION: Sign the attached memorandum establishing policy for treatment and disposition of plutonium-bearing residues.

Concurrences:

Defense Programs/Reis	/	/95
Environmental Management/Grumbly	/	/95
Environment, Safety and Health/O'Toole	/	/95
Materials Disposition/Rudy	/	/95
Field Management/Pearman	/	/95
Nonproliferation and National Security/Rohling	/	/95
Policy/Reicher	/	/95

Attachment

~~NUCLEAR MATERIALS STABILIZATION TASK GROUP - Department of Energy~~informal memo

December 20, 1995

From: Hank Dalton, (NMSTG:EM-66, 6-5266)

To: Distribution

Re: Initial Draft of Policy Memorandum on TREATMENT AND DISPOSITION
OF PLUTONIUM-BEARING RESIDUES

I am forwarding this initial draft memo to you for comment. The final outcome may take some time, because there are strong opinions for and against, in and outside the Department. Nonetheless, we need a policy to guide the treatment of these residues.

Please give me your initial comments by January 19, on both technical and policy issues.

Attachment

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MEMORANDUM FOR FIELD OFFICE MANAGERS

ALBUQUERQUE OPERATIONS OFFICE
OAKLAND OPERATIONS OFFICE
OAK RIDGE OPERATIONS OFFICE
OHIO FIELD OFFICE
RICHLAND OPERATIONS OFFICE
ROCKY FLATS OPERATIONS OFFICE
SAVANNAH RIVER OPERATIONS OFFICE
IDAHO OPERATIONS OFFICE

DIRECTORS

LOS ALAMOS NATIONAL LABORATORY
LAWRENCE LIVERMORE NATIONAL LABORATORY
IDAHO NATIONAL ENGINEERING LABORATORY

FROM: CHARLES B. CURTIS

SUBJECT: Treatment and Disposition of Plutonium-bearing Residues

Plutonium-bearing residues are a broad class of materials with plutonium concentrations below 50 weight-percent, which are either by-products of past weapons production or were unprocessed at the time production ceased. These materials exist at many Department sites in a wide variety of forms including metal alloys, impure oxides, salts, organic and inorganic compounds, and plutonium-contaminated solids. There are approximately 120 metric tons of these residues across the complex, containing approximately 6 metric tons of plutonium. Ninety-nine percent of them are at Rocky Flats, Los Alamos, and Savannah River.

Plutonium will be separated from these residues (not necessarily refined) and packaged for storage in accordance with the Department's Standard "Criteria for Safe Storage of Plutonium Metals and Oxides" (DOE-STD-3013-94). Exceptions to this policy will be granted by the responsible Secretarial Officer if, for a given quantity, batch, or category of residues, it is more cost-effective to prepare the material for direct disposal in a geologic repository as waste. The performance factors for cost-effectiveness are worker exposure, waste generation, and cost.

Plutonium recovered from the residues addressed here is not for weapons use. It will be available for storage under international safeguards awaiting the decision on ultimate disposition. If you have questions regarding this policy, please contact Mr. Henry F. Dalton, Director, Nuclear Materials Stabilization Task Group at 202/586-7503.