

Sto B
JUN 28 1999

12 ENGINEERING DATA TRANSMITTAL

Page 1 of 1
 1. EDT **620681**

2. To: (Receiving Organization) PFP		3. From: (Originating Organization) PFP TRANSITION ENGINEERING		4. Related EDT No.: N/A	
5. Proj./Prog./Dept./Div.: PFP/15C00		6. Design Authority/Design Agent/Cog. Engr.: K. R. HERZOG		7. Purchase Order No.: N/A	
8. Originator Remarks: This is a report on the status of plutonium storage ES&H vulnerabilities at PFP. Update On The Department Of Energy's 1994 Plutonium Vulnerability Assessment For The Plutonium Finishing Plant				9. Equip./Component No.: N/A	
11. Receiver Remarks:				10. System/Bldg./Facility: 234-5Z/2736-Z	
11A. Design Baseline Document? <input type="radio"/> Yes <input checked="" type="radio"/> No				12. Major Assm. Dwg. No.: N/A	
				13. Permit/Permit Application No.: N/A	
				14. Required Response Date: N/A	

15. DATA TRANSMITTED					(F)	(G)	(H)	(I)
(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	Approval Designator	Reason for Transmittal	Originator Disposition	Receiver Disposition
1	HNF-3541		0	Update on the Department O	N/A	1	1	1

16. KEY		
Approval Designator (F)	Reason for Transmittal (G)	Disposition (H) & (I)
E, S, Q, D OR N/A (See WHC-CM-3-5, Sec. 12.7)	1. Approval 2. Release 3. Information 4. Review 5. Post-Review 6. Dist. (Receipt Acknow. Required)	1. Approved 2. Approved w/comment 3. Disapproved w/comment 4. Reviewed no/comment 5. Reviewed w/comment 6. Receipt acknowledged

17. SIGNATURE/DISTRIBUTION (See Approval Designator for required signatures)											
(G) Reason	(H) Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN	(G) Reason	(H) Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN
1	1	Design Authority K. R. Herzog	<i>[Signature]</i>	3/31/99	T2-12	1	1	M. W. Gibson	<i>[Signature]</i>	4/5/99	TS-55
1	1	Design Agent P. E. Roeger	<i>[Signature]</i>	4/5/99	TS-50	1	1	R. D. Redekopp	<i>[Signature]</i>	4/5/99	TS-25
1	1	Cog. Eng. K. R. Herzog	<i>[Signature]</i>	3/31/99	T2-12	1	1	R. E. Heineman Jr	<i>[Signature]</i>	6/2/99	
1	1	Cog. Mgr. T. E. Huber	<i>[Signature]</i>	3/31/99		1	1	F. R. Crawford	<i>[Signature]</i>	6/2/99	
		QA									
		Safety									
		Env.									

18. Signature of EDT Originator <i>[Signature]</i> Date: 3/31/99		19. Authorized Representative for Receiving Organization <i>[Signature]</i> Date: 6/14/99		20. Design Authority/Cognizant Manager <i>[Signature]</i> Date: 6/14/99		21. DOE APPROVAL (if required) Ctrl No. _____ <input type="radio"/> Approved <input type="radio"/> Approved w/comments <input type="radio"/> Disapproved w/comments	
--	--	---	--	---	--	---	--

S

Update On The Department Of Energy's 1994 Plutonium Vulnerability Assessment For The Plutonium Finishing Plant

K. R. HERZOG
B&W Hanford Co
PO Box 1200 MSIN T5-45
Richland, WA 99352
U.S. Department of Energy Contract DE-AC06-96RL13200

EDT/ECN: 620681 UC:
Org Code: 15C00 Charge Code: 103403
B&R Code: Total Pages: 50

Key Words: PFP, plutonium, environment, safety, health, storage, vulnerability, characterization, Plutonium Finishing Plant, 234-5Z, 2736-Z, metal, oxide, solution, residues, inventory, MOX, fuel, SNM

Abstract: A review of the environmental, safety, and health vulnerabilities associated with the continued storage of PFP's inventory of plutonium bearing materials and other SNM. This report re-evaluates the five vulnerabilities identified in 1994 at the PFP that are associated with SNM storage. This new evaluation took a more detailed look and applied a risk ranking process to help focus remediation efforts.

TRADEMARK DISCLAIMER. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors.

Printed in the United States of America. To obtain copies of this document, contact: Document Control Services, P.O. Box 950, Mailstop H6-08, Richland WA 99352, Phone (509) 372-2420; Fax (509) 376-4989.

DOES NOT CONTAIN CLASSIFIED OR UNCLASSIFIED CONTROLLED NUCLEAR INFORMATION

Reviewing Official / ADC: *[Signature]*

Date: *6/28/99*

[Signature]

Release Approval

6/28/99

Date

JUN 28 1999		12
Release Stamp DATE:	HANFORD RELEASE	
STA: 5		ID:

Approved For Public Release

Update On The
Department Of Energy's 1994
Plutonium Vulnerability Assessment For
The Plutonium Finishing Plant

HNF-3541
Revision 0

January 1999

Prepared By:
B&W Hanford Company

Under Contract Number:
DE-AC-0696-RL13200

TABLE OF CONTENTS

EXECUTIVE SUMMARY	1
1.0 INTRODUCTION	7
1.1 BACKGROUND	7
1.2 GOAL AND PURPOSE	8
1.3 OBJECTIVES	8
1.4 SCOPE	8
2.0 METHODOLOGY	9
2.1 APPROACH	9
2.2 VULNERABILITY CRITERIA	10
2.3 DEFINITION OF UNSTABLE	10
3.0 STATUS AND RESULTS FOR THE ORIGINAL VULNERABILITIES	11
3.1 HYDROGEN GENERATION IN UNVENTED SOLUTION STORAGE CONTAINERS -- RL-3.1.3.1	11
3.2 PLUTONIUM STORED IN UNSTABLE FORMS -- RL-3.1.3.2	11
3.2.1 Mitigation Actions Completed To Date	12
3.2.2 Issues Regarding Unstable Plutonium Items Stored At PFP That Are Not Described In The 1994 Assessment	12
3.3 DETERIORATION OF STORAGE CONTAINERS -- RL-3.1.3.3	15
3.3.1 Mitigation Actions Completed To Date	16
3.3.2 Issues Associated With Deterioration of Storage Containers That Are Not Described In The 1994 Assessment	16
3.4 INSUFFICIENT KNOWLEDGE OF PACKAGING CONFIGURATION AND MATERIALS AT PFP -- RL-3.1.3.4	17
3.4.1 Mitigation Actions Completed To Date	18
3.4.2 Issues Associated With Packaging And Characterization That Are Not Described In The 1994 Assessment	18
3.5 REACTIVE CHEMICALS STORED IN PFP GLOVEBOXES □ RL-3.1.4.2	21
4.0 VULNERABILITY REVIEW BY MATERIAL FAMILY	22
4.1 ISSUES ASSOCIATED WITH THE SOLUTION INVENTORY AT PFP	22
4.2 ISSUES ASSOCIATED WITH THE PLUTONIUM METAL INVENTORY AT PFP	23
4.3 ISSUES ASSOCIATED WITH THE PLUTONIUM ALLOY INVENTORY AT PFP	25
4.4 ISSUES ASSOCIATED WITH THE NUCLEAR FUELS INVENTORY AT PFP	26
4.5 ISSUES ASSOCIATED WITH THE MOX INVENTORY	27
4.6 ISSUES ASSOCIATED WITH THE POLYCUBES INVENTORY AT PFP	27

4.7 ISSUES ASSOCIATED WITH NON-POLY-CUBE COMBUSTIBLES INVENTORY.....	28
4.8 ISSUES ASSOCIATED WITH THE REDUCTION RESIDUES (SS&C) INVENTORY AT PFP.....	28
4.9 ISSUES ASSOCIATED WITH THE PLUTONIUM COMPOUNDS INVENTORY AT PFP.....	29
4.10 ISSUES ASSOCIATED WITH THE MISCELLANEOUS ITEMS PLUTONIUM INVENTORY AT PFP.....	30
4.11 ISSUES ASSOCIATED WITH THE SOURCES AND SAMPLES INVENTORY AT PFP.....	30
4.12 ISSUES ASSOCIATED WITH THE PLUTONIUM OXIDES INVENTORY AT PFP.....	31
4.13 ISSUES ASSOCIATED WITH THE ASH INVENTORY AT PFP.....	32
4.14 ISSUES ASSOCIATED WITH THE URANIUM INVENTORY AT PFP.....	32
4.15 ISSUES ASSOCIATED WITH THE SPECIAL ISOTOPES INVENTORY AT PFP.....	33
5.0 RISK BASED PRIORITIZATION.....	34
6.0 SUMMARY AND CONCLUSIONS.....	38
7.0 REFERENCES.....	41

~~This Page Is Intentionally Blank~~ dp for KR H 6/28/99

EXECUTIVE SUMMARY

Background

In 1994, the Department of Energy (DOE) evaluated vulnerabilities associated with plutonium storage at Hanford's Plutonium Finishing Plant (PFP) as part of a complex-wide initiative. The purpose of the 1994 assessment was to identify degradation in plutonium materials and packaging, and weaknesses in facilities and administrative controls that could potentially result in inadvertent releases of plutonium, exposing workers or the public, or contaminating the environment. The 1994 assessment identified 5 vulnerabilities associated with plutonium storage at PFP that required further evaluation and action (Refs. 1 and 2). These were:

- RL-3.1.3.1 Hydrogen generation in unvented solution storage containers (PFP).
- RL-3.1.3.2 Plutonium stored in unstable forms.
- RL-3.1.3.3 Deterioration of storage containers.
- RL-3.1.3.4 Insufficient knowledge of packaging configuration and materials at PFP.
- RL-3.1.4.2 Reactive chemicals stored in PFP gloveboxes.

The Department of Energy, Richland Operations Office (RL) requested that the vulnerabilities reported in the 1994 plutonium vulnerability study be updated and re-evaluated in 1998. The goal of this effort was defined in a June 13, 1998 letter: "The review will allow us to more thoroughly understand the risk reduction impact and/or benefits of our overall technical approach." (Ref 4).

Objectives

Three objectives have been established for this vulnerability reassessment. They are:

- Identify those vulnerabilities that have been fully resolved for which no further action is needed,
- Document newly identified and changed vulnerabilities that need to be incorporated into the scope of current programs, and
- Provide a basis for risk-based prioritization of the remaining stabilization efforts at PFP.

Status of Previously Identified Vulnerabilities

Of the original 5 vulnerabilities associated with plutonium storage at PFP, two vulnerabilities have been closed. The first, "RL-3.1.3.1, Hydrogen generation in unvented solution storage containers (PFP)" was closed in May of 1995 following venting of the previously unvented containers. Since vent-clips were required by procedure to be installed on the outer container, the effort in 1995 focused on storage containers that were designed with a manual vent valve. The storage containers in question were inspected and the vented where necessary. With the vent valves in the open position, all solutions at PFP were believed to be stored in continuously vented configurations. A spot check conducted in December 1998 identified solution storage containers that did not have the required vent-clips installed. The number of containers in this condition was still being determined at the time of this report. Due to this new information, vulnerability "RL-3.1.3.1, Hydrogen generation in unvented solution storage containers (PFP)" is being reopened. Although beyond the scope of this vulnerability, plutonium solutions in storage at PFP were also assessed for the potential for leaking to result in a criticality event. The leaking of solution from their storage containers has been shown through analysis not to present a criticality concern. The second, "RL-3.1.4.2, Reactive chemicals stored in PFP gloveboxes" was also closed following the successful stabilization of PFP's inventory of approximately 236 plutonium-bearing organic sludge items from the Plutonium Reclamation Facility in June of 1996. However, PFP has a small amount of residual sludge in glovebox storage that was not within the scope of the original vulnerability.

The remaining 3 findings are being addressed through DOE's Implementation Plan for Defense Nuclear Facility Safety Board (DNFSB) Recommendation 94-1. (Additional information may be found in Reference 2.) To date progress has included stabilization of the high-risk ash (46 items), stabilization of the 27 containers of chloride and fluoride solutions stored in polybottles, cementation and discarding of 219 kg of SS&C, as well as stabilization of some additional nitrate solutions and metals/oxides. The primary hazard associated with PFP's remaining plutonium storage vulnerabilities is PFP facility worker exposure to plutonium resulting from a plutonium storage container failing. As described in the PFP Final Safety Analysis Report (ref. 28), current PFP plutonium storage vulnerabilities do not pose a significant hazard to the public or on-site (non-PFP) workers and do not represent a significant threat to the environment.

Additional Vulnerabilities Identified

Plutonium characterization, analysis, and stabilization efforts performed at PFP and elsewhere in the DOE complex, have yielded new information for better defining the potential hazards to workers from plutonium storage at PFP. This information, together with the different methodology used to prepare this report, has resulted in the identification of issues not specifically identified in the original 1994 assessment. The additional potential plutonium storage and handling issues (Attachment A provides a table summary of the issues.) include:

- Additional unvented solution storage containers have been identified.
- PFP has more families of plutonium-bearing materials that exhibit the potential for some type of instability than was previously recognized. These include:
 - Solutions
 - Alloys
 - Selected Oxides and Mixed Oxides
- Plutonium-bearing material packaged before 1980 may not achieve the same plutonium storage barrier performance as material packaged after 1980. As a consequence, the risk of storage container failure may be higher than that previously perceived.
- Thirty-year storage of plutonium at PFP has resulted in the formation of reactive compounds such as plutonium hydrides and plutonium nitrides. These reactive compounds may represent new hazards for plutonium storage and processing not previously recognized.¹
- Characterization data is not complete for plutonium in storage at PFP. Furthermore, plutonium inventory records may not always completely or accurately describe the storage container contents. Thus potentially delaying the processing of unstable materials (because they were assumed to be stable) or cause the selection of inappropriate stabilization methods or stability tests. This could result in container failure in storage due to pressurization, corrosion or collapse.
- Based on radiography, mixed plutonium oxides from one source may be corroding the inner storage containers. This may cause unexpected failure of the inner plutonium storage container.
- A few plutonium metal items are stored in direct contact with plastic. Other plutonium metals and alloys are packaged in the same air space as plastic. The presence of hydrocarbons in contact with or in the same air space as plutonium metal and certain alloys may cause accelerated storage container failure. They also provide a source of hydrogen for the formation of plutonium hydrides, which may in turn catalyze the formation of plutonium nitrides.
- The vault storage surveillance program may not be sufficient to detect and identify warning signs associated with failing plutonium storage containers. In some cases, no warning signs may exist for the impending failure of a plutonium storage container.

¹DOE-RL declared an Unreviewed Safety Question (USQ) in 1997 (RL letter 97-TPD-210) because of the potential for reactive compounds to be formed and the potential hazard they represent to workers upon opening.

- The hazards associated with fuel fabricated for reactors other than the Fast Flux Test Facility (FFTF) need evaluation to ensure appropriate contamination barriers have been provided.
- The storage configuration for polycubes does not ensure contamination control in all circumstances.
- Loss-on-ignition (LOI) testing may not provide the best indication of the suitability of processed materials for long-term storage. Materials that have "passed" LOI testing could be the source of future storage container failure.

Recommended Priority Approach

This report also proposes a risk-based approach for prioritizing the remaining efforts to stabilize plutonium at PFP. The criteria used to establish the priority of a plutonium material family were:

1. Ability to challenge storage container containment because of reactions occurring within the sealed container.
2. Ability to cause an energetic reaction when released from storage container.
3. Ability to detect warning signs of impending plutonium storage container breach.

The results of this risk-based approach indicate that PFP efforts should be prioritized as:

- 1 Venting solution storage containers
- 2 Unalloyed plutonium metals stabilization,
- 3 Evaluating (and venting if pressurized) three potentially pressurized sealed neutron sources (PuF4)
- 4 Stabilizing Oxides containing incompletely stabilized plutonium metal & "ZQM" oxides,
- 5 Stabilizing plutonium-bearing solutions
- 6 Stabilizing Polycubes and other combustibles.
- 7 Stabilizing High-assay, alloyed plutonium metal
- 8 Stabilizing Glovebox stored items

- 9 Cementation and/or discarding of residues (SS&C, ash, low-grade oxides, & miscellaneous)
- 10 Restabilization of oxides, MOX, sources, standards, and compounds
- 11 Repackaging of low-assay, alloyed plutonium metal and fuel pins.

Path Forward

Individual stabilization project plans are being prepared for each of the material categories to be stabilized. The stabilization project plans will address the issues identified in this report applicable to the categories of material being stabilized by the project. The stabilization project plans form one foundation for the PFP Integrated Project Management Plan (IPMP) and detailed resource-loaded project schedules completed in April 1999. The stabilization project plans also provide a basis for the December 1998 revision to PFP's input to the Department of Energy's DNFSB Recommendation 94-1 Implementation Plan.

Information from this report will be used to update PFP's material characterization program, and it will be used to modify PFP's plutonium storage container surveillance program. The information from this report will also be used within PFP's system engineering efforts to develop an optimized stabilization schedule that maximizes risk reduction. Plans of action developed to address broader, cross-cutting issues, such as characterization will also be incorporated into a revision of the *DNFSB Recommendation 94-1 Hanford Site Integrated Stabilization Management Plan (SISMP)* (Ref. 3)

This Page Is Intentionally Blank

1.0 INTRODUCTION

1.1 BACKGROUND

In 1994, DOE conducted a complex-wide assessment to identify and prioritize the environment, safety, and health vulnerabilities that arise from the storage of plutonium in the DOE facilities and determine which present the most urgent risks to worker, the public and/or the environment. Vulnerabilities were defined as conditions leading to degradation in plutonium materials and packaging, and weaknesses in facilities and administrative controls that could expose workers or the public, or contaminate the environment. The results of that effort were published in the *Plutonium Working Group Report on Environment, Safety and Health Vulnerabilities Associated with the Department's Plutonium Storage* (Ref. 1). The plan of action for addressing the identified vulnerabilities was established in *Plutonium Vulnerability Management Plan* (Ref. 2). Complex-wide, 299 vulnerabilities were identified, with 35 of these at Hanford. Of the Hanford vulnerabilities identified, 5 are directly associated with plutonium storage at the Plutonium Finishing Plant (PFP). These are:

- RL-3.1.3.1 Hydrogen generation in unvented solution storage containers (PFP).
- RL-3.1.3.2 Plutonium stored in unstable forms.
- RL-3.1.3.3 Deterioration of storage containers.
- RL-3.1.3.4 Insufficient knowledge of packaging configuration and materials at PFP.
- RL-3.1.4.2 Reactive chemicals stored in PFP gloveboxes.

Two of these vulnerabilities have been closed. The first, "RL-3.1.3.1, Hydrogen generation in unvented solution storage containers (PFP)" was closed in May of 1995 following venting of the previously unvented containers. Since vent-clips were required by procedure to be installed on the outer container, the effort in 1995 focused on storage containers that were designed with a manual vent valve. The storage containers in question were inspected and the vented where necessary. With the vent valves in the open position, all solutions at PFP were believed to be stored in constantly vented configurations. However, a spot check conducted in December 1998 identified some solution storage containers that did not have the required vent-clips installed on the outer container (drum). This configuration could allow hydrogen gas to build up in the drum creating an explosion hazard. Due to this new information, this vulnerability is being reopened. The second, "RL-3.1.4.2, Reactive chemicals stored in PFP gloveboxes", was also closed following the successful stabilization of PFP's inventory of approximately 236 plutonium-bearing organic sludge items from the Plutonium Reclamation Facility in June of 1996.

Closure of the remaining three vulnerabilities requires completion of PFP's stabilization program resulting from DNFSB Recommendation 94-1. This program requires the stabilization and packaging of all PFP's plutonium-bearing materials to DOE-STD-3013 or equivalent criteria, or packaging for disposal at WIPP. Originally, the entire program was scheduled to be completed by May 2002. A combination of factors including funding shortfalls and a fissile material movement hold imposed by the operating contractor has delayed completion by up to 38 months.

Because of this delay, PFP was requested (Ref. 4) to re-evaluate the original vulnerabilities associated with the continued storage of plutonium-bearing materials and determine if there were any significant changes in the original vulnerabilities that might affect the execution of the program. This report provides the re-evaluation that has been requested.

1.2 GOAL AND PURPOSE

The goal of this report is to review the issues associated with a delay in stabilization of plutonium-bearing materials and their continued storage in their current configuration based upon currently available information. This review provides a basis to more thoroughly understand the risk reduction impact and/or benefits of the plutonium stabilization approach at PFP, and it identifies issues that should be considered during the development and implementation of PFP stabilization projects.

The purpose of this report is to evaluate the 5 vulnerabilities noted above and determine how they have changed, how the understanding of the vulnerabilities has changed, what additional vulnerabilities may exist, and determine the impact of the delay in the stabilization program from the perspective of the identified vulnerabilities.

1.3 OBJECTIVES

Three objectives have been established for this report:

- 1) Identify those original vulnerabilities that have been closed for which no further action is needed;
- 2) Identify changed vulnerabilities or additional information that needs to be incorporated into the scope of current project planning activities to ensure stabilization programs comprehensively address PFP's plutonium storage vulnerabilities; and.
- 3) Provide a basis for risk-based prioritization of the remaining stabilization efforts at PFP.

1.4 SCOPE

To complete these objectives, the scope of effort for this report included the following activities:

- Defining criteria for classification of conditions as plutonium storage vulnerabilities,
- Identifying issues that affect storage, stabilization, or disposition of plutonium at PFP,
- Providing a definition for unstable materials, and
- Establishing a risk-based prioritization methodology and ranking for processing materials.

2.0 METHODOLOGY

2.1 APPROACH

The re-evaluation of the five originally identified vulnerabilities consisted of reviewing the 1994 plutonium vulnerability assessment and management plan, inventory data, radiography data, selected PFP procedures and specifications, and other information currently available at PFP to determine how the vulnerabilities (or understanding of the vulnerabilities) have changed, if at all, since 1994. The steps in the approach undertaken in preparing this report were:

- Collect data from documents,
- Compare collected information with the vulnerability criteria established,
- Identify changes in the previously identified (1994) 5 vulnerabilities,
- Identify any new vulnerabilities,
- Evaluate the risk of identified vulnerabilities against established risk criteria, and
- Develop recommendations for preventing or mitigating the vulnerability.

This evaluation uses a different approach than was used in the 1994 plutonium vulnerability assessment (Refs. 1 and 2) to identify issues of concern. The 1994 evaluation provided a high-medium-low ranking of hazards to the worker, public or environment for each of the broadly scoped vulnerabilities. The approach used in this report refines this information, using the criteria developed in Section 2.1, to identify specific characteristics of the material or packaging that potentially results in risk to facility workers for that plutonium material group. Where the original Pu vulnerability study addressed potential vulnerabilities for broad categories of materials, this reassessment addressed specific families and sub-groups of materials. This approach yields a more detailed list of issues by plutonium material groups in storage at PFP. This approach was adopted so that facility hazard prevention and mitigation efforts can be tailored for the specific

hazards of the plutonium material groups at PFP. This more detailed effort was also necessary so that a risk-based sequence of actions could be developed that recognizes the differences between the various plutonium material groups at PFP.

As a result of the methodology used to prepare this report, some different issues were identified in this report as compared to those identified in the 1994 plutonium vulnerability assessment. To allow comparison with the 1994 plutonium vulnerability assessment, issues in this report are grouped into two categories. First, are examples of issues that were discussed in the 1994 vulnerability assessment. The second are issues that are not discussed in the original 1994 report. Because of the broad Pu categories originally assessed, the more detailed issues identified in this report were in some cases not previously identified or the issues were grouped into the broader vulnerabilities identified.

2.2 VULNERABILITY CRITERIA

Because PFP's plutonium is stored inside seismically qualified, filtered confinement structures, the plutonium storage vulnerabilities (both original and newly identified) addressed in this report do not affect the public or the environment. However, if plutonium storage containers (contamination barriers) fail, the facility worker is potentially affected. Specific criteria were established to help determine if an issue represented a vulnerability potentially affecting facility workers. The criteria used in preparing this report were:

- Does the material have the potential to challenge its containment?
- Has the material previously demonstrated the ability to challenge its containment?
- Will the material react vigorously if containment is breached?
- Are there reliable early warning signs that would indicate an impending breach of the material's containment?

2.3 DEFINITION OF UNSTABLE

The 1994 plutonium vulnerability assessment report did not provide a definition of the characteristics that would cause materials to be classified as unstable. For the purpose of this report, an unstable material is defined as one that presents a hazard to its container such that it should not be stored in a standard sealed food pack can, presents a hazard during processing, or reacts vigorously when exposed to the environment: air, water, elevated temperatures consistent with shipping and handling, etc. However, being unstable does not mean the item is unsafe. For example, proper packaging can mitigate the risks associated with a material's instability, (e.g. venting plutonium-bearing solutions containers can mitigate the risks associated with hydrogen buildup).

3.0 STATUS AND RESULTS FOR THE ORIGINAL VULNERABILITIES

This section provides a reassessment of each of the 5 vulnerabilities identified in the 1994 plutonium vulnerability assessment. Each section identifies issues addressed in the 1994 report followed by new issues identified as a result of this evaluation. Mitigation actions completed to date are also presented. In Section 4.0, the issues identified in this section will be further broken down into specific issues associated with each of the plutonium material groups present at PFP.

3.1 HYDROGEN GENERATION IN UNVENTED SOLUTION STORAGE CONTAINERS -- RL-3.1.3.1

"RL-3.1.3.1, Hydrogen generation in unvented solution storage containers (PFP)" was closed in May of 1995 following confirmation that all inner containers were unvented. All solutions at PFP were believed to be stored in constantly vented configurations. However, a spot check conducted in December 1998 identified some solution storage containers that did not have the required vent-clips installed on the outer container (drum). Further evaluation indicated that outer containers with or without vent clips could allow hydrogen gas to build up in the drum creating an explosion hazard. Due to this new information, this vulnerability is being reopened.

The vulnerability identified in the 1994 report (Ref.1) was limited to a small number of solution storage containers that had vent valves on the inner container (stainless steel bottle). These valves were to be closed during shipment and opened for storage. All the suspect containers were opened and the vent valves opened or verified that they were in the open (vented) position.

In the original vulnerability, the hydrogen could build up in the inner container to a high pressure. In newly identified case, the container design allows hydrogen to escape the inner container through filters/vents but without adequate venting of the outer container (drum) hydrogen concentration is expected to build up in drum. During drum handling or opening, the worker is at risk of injury due to the explosive potential of hydrogen gas.

3.2 PLUTONIUM STORED IN UNSTABLE FORMS -- RL-3.1.3.2

The 1994 plutonium vulnerability assessment does not provide a clear definition of what characteristics/criteria were used to categorize a plutonium material as unstable, although the report does state that hydrogen generation/accumulation is the primary issue. The *Plutonium Vulnerability Management Plan* (Ref. 2) also lists hydrides and metal fines as significant issues. The report concludes that there were approximately 700 items in the PFP vaults that were unstable and listed four categories of unstable materials: polycubes - 260 items; sand, slag, and crucible (SS&C) - 266 items, reactive ash - 46 items, and plutonium metal - 352 items.

In the 1994 plutonium vulnerability assessment, the primary focus on material stability was placed

on plutonium-bearing solids in cans (food pack or lard cans) and their ability to rupture their storage container. Other key attributes included not corroding the container and not reacting violently when exposed to air or water.

Drawing on the considerations noted above, the apparent basis for placing these materials into the unstable category were:

- Reactive ash releases gases that typically include hydrogen that result in container pressurization.
- SS&C contain calcium metal in the form of pellets and powders. SS&C is therefore water reactive. SS&C may also contain plutonium metal fines, which are pyrophoric.
- Polycubes generate hydrogen and hydrocarbon gases.
- Plutonium metals may have formed plutonium nitrides and plutonium hydrides. Both of these compounds are pyrophoric.

3.2.1 Mitigation Actions Completed To Date

Polycubes are being stored in vented and filtered containers with strict movement restrictions imposed. Food pack cans are routinely monitored for deformation that would indicate pressure buildup or formation of hydrogen gas. The 46 items of reactive ash were stabilized in January 1996. Also, 219 kg (of a total of 2422 kg) of sand, slag and crucible (SS&C) material has been cemented. The balance of the issues identified in the plutonium vulnerability assessment are being addressed as part of the Department's Implementation Plan for Defense Nuclear Facility Safety Board (DNFSB) Recommendation 94-1.

3.2.2 Issues Regarding Unstable Plutonium Items Stored At PFP That Are Not Described In The 1994 Assessment

Based on review of available data and the definition provided in Section 2.3, the following 6 plutonium material categories may also contain unstable items:

- Plutonium-uranium alloys and plutonium rich (>~90 wt% Pu) alloys (69 items) may be unstable, and potentially as reactive as plutonium metal [Ref. 6 and 7]. During prolonged storage, alloys with a high plutonium-to-alloy ratio may have formed plutonium hydrides/nitrides. Like plutonium metal, hydrogen from degradation of organic materials (e.g., plastic bags) may react with the plutonium in the alloy to form hydrides. The plutonium hydrides could then catalyze the formation of plutonium nitrides. Plutonium hydrides and plutonium nitrides are pyrophoric. Also, with available air, or in-leakage of air, plutonium alloys may have partially oxidized in storage, which may result in container failure and cause

the metal to spall and produce pyrophoric plutonium metal fines. Similar chemical changes to pyrophoric compounds or spalling might occur with the uranium metal in the alloys. One alloy item has bulged in storage. This item is identified as a Pu/Al-Y vycor melt residue with 6.9% Pu-240. It is identified as 90% plutonium. The cause of the bulge has not been determined. Based on their low plutonium-to-alloy ratio and the inherent stability of aluminum, the 7% Pu-Al alloy items (~57 items [Ref 8]) are likely stable [Ref. 7].

- The 28 items categorized as Miscellaneous Materials (Ref. 7) do not have characterization data or process histories that enable excluding the possibility that these containers may contain plutonium alloy or plutonium metal. Accordingly, these 28 items may be unstable because they could contain alloy or plutonium metal scrap that would pose the same risks as discussed above.
- Non-FFTF fuel pins and assemblies contain plutonium metals and/or alloys (4 pins), plutonium and uranium carbides (5 pins), enriched uranium metal and/or alloys (76 pins) that may not be stable (Ref 9). Plutonium carbides are known to be friction and pressure sensitive. Additionally, some of these pins are sodium-bonded. Sodium metal is water reactive. The condition of the fuel pin cladding will determine if the metals, alloys, and carbides are safe for continued storage, but the condition of the cladding is not known. If the pins were cut up to make them fit into the containers or the cladding has corroded, the fuel could be exposed to plastic or the atmosphere in the container, leading to fuel degradation. Degraded fuel could be water reactive, pressure and friction sensitive, and pyrophoric.
- PFP received shipments of oxides that were created by burning plutonium metal buttons from the Savannah River Site. This set of oxides may not be stable. One container has buckled inward (paneled) which implies plutonium corrosion products such as nitrides, oxides, hydrides etc may have formed. Metal fines also are likely to be present in oxides where the plutonium weight is identified as being greater than stoichiometric (88-wt%). The summary inventory report (Ref 8) shows that there are 19 oxide items that are greater than 88-wt% plutonium, and, therefore, were not completely converted to oxide. Because of the Pu metal content, this set of oxides would have similar issues as those discussed above for Pu metal.
- Non-polycube combustibles may be unstable (Ref. 6) as they may generate hydrogen similar to polycubes.
- One item of plutonium metal turnings was found during radiography. Plutonium metal turnings are pyrophoric. It is possible that metal turnings may also be present in non-metal items such as lab samples, scrap, and reduction residues (Ref. 24).

Additional examples:

- Although addressed in the 1994 assessment and PFP actions under DOE's implementation

plan for DNFSB Recommendation 94-1, the specific potential for hydrogen generation from plutonium-bearing solution containers did not result in solutions being identified as a “unstable plutonium item.” Hydrogen gas is generated from plutonium-bearing solutions as a result of radiolysis of the nitric acid, water, and any residual organic. The hydrogen gas can cause storage container failure if the container is not vented to relieve pressure, and the hydrogen is a flammability hazard. PFP has stringent controls that address hydrogen hazards that include providing continuous venting for solution containers, use of non-sparking tools, use of drum lid restraints devices, and grounding straps. (Note: this represents a clarification in definition of unstable material and does not represent a newly identified hazard.)

- The potential for generating flammable gasses from the degradation of the plastic bag(s) used in the packaging of plutonium oxides and metals was not described as a specific vulnerability in the 1994 assessment (Ref. 10). Because of the degradation of plastic bags in the storage containers, hydrogen and other flammable gases (e.g., methane) may be present in the atmosphere of sealed plutonium storage containers. The gases produced may pressurize the container causing it to fail, and the flammable gases could potentially ignite when the container is opened.
- Items packaged prior to October 31, 1980 may not have been tested for stability (loss on ignition test or equivalent) (Ref. 11). PFP did not require stability testing for all types of plutonium-bearing materials until after the 1980 plutonium carbide burning incident (that occurred in Building 234-5Z, Room 230-C). As a result, pre-1980 materials may not be fully stabilized and may prematurely cause storage container failure.
- Loss-on-ignition testing may not provide good indication in all cases of the suitability of processed materials for long-term storage. If a sample being tested contains Pu metal, the weight gain associated with metal oxidation during LOI testing can mask the weight loss occurring due to water loss. This situation would lead to the erroneous conclusion that the weight loss on ignition was acceptably small. As such, even materials that have “passed” LOI testing may cause future storage container failure (Ref. 30)
- Items that do not meet PFP's vault storage criteria are stored in gloveboxes. Glovebox stored items are therefore generally categorized herein as unstable. PFP stores a limited number of a wide-range of unstable items in gloveboxes. One such item is a PuF_3/UF_6 compound. The UF_6 compound has recently been identified as a potential vulnerability (Ref. 7) because UF_6 is a gas near room temperature. Glovebox storage mitigates the potential hazards associated with UF_6 -bearing materials.

3.3 DETERIORATION OF STORAGE CONTAINERS -- RL-3.1.3.3

The 1994 plutonium vulnerability assessment identified that the design life of all of PFP's storage

containers has not been determined; however, PFP had a sufficiently strong monitoring program to detect problems before containers failed.

Failure mechanisms for the plutonium storage containers include buckling inward (paneling) and causing a breach of the seal, bulging outward resulting in breach of the seal, or container corrosion, embrittlement, or seal and/or filter (including glue used to attach the filter) failure from corrosive constituents, radiation exposure, high temperatures, and the extended length of storage.

The following are examples identified of the container deterioration issue described in the 1994 plutonium vulnerability assessment report:

- Radiography has identified containers of plutonium metal that are buckling inward, potentially as a result of the formation of plutonium nitrides (Refs. 12, 13, 14, and 15). Buckling inward can cause a breach of the plutonium storage container.
- Corrosion of stainless steel solution containers by acids over a long period of time, specifically HCl and HF (Refs. 1 and 2).
- Some items, such as plutonium nitrate solutions, are known to be corrosive and thus may cause the deterioration of their containers.
- The effect radiation has on the container is also discussed in the 1994 assessment in the context of radiation breaking down plastics such as are found in some of the solution storage containers (Ref. 16).
- Based on weight gain data, the seals on some plutonium metal containers have leaked allowing the metal to oxidize and gain weight. One item of metal has gained greater than 25 grams (Ref. 17).
- Food pack can gaskets fail at approximately 140° C (Ref. 18). Gasket failures (leaks) would also be expected as a result of exposure to radiation and elevated temperatures for extended periods of time. High temperature and radiation conditions exist for some food pack cans in storage.
- The filters used on the top of the polycube storage cans may become dislodged during handling due to degradation of the glue that holds the filter in place. The glue would be expected to degrade as a result of exposure to radiation and elevated temperatures for extended periods of time. High temperature and radiation conditions exist for some cans in storage.

3.3.1 Mitigation Actions Completed To Date

Radiography has been performed to start identifying problem containers. Twenty-seven items of chloride/fluoride solutions have been stabilized or discarded. Closing vulnerability "RL-3.1.3.3 Deterioration of Storage Containers" requires stabilization and/or repackaging additional plutonium items. In general, repackaging efforts will be conducted in parallel with the actions being undertaken for DOE's implementation plan for DNFSB Recommendation 94-1.

3.3.2 Examples Associated With Deterioration of Storage Containers That Are Not Described In The 1994 Assessment

Additional examples were identified that are associated with the deterioration of storage containers that were not discussed in the 1994 assessment. These need to be incorporated into DNFSB 94-1 planning and include:

- Radiography information indicates that at least some items of "mixed oxides" from one source are exhibiting signs of corrosion of the inner container (Refs. 12, 13, 14, and 15). Corrosion of mixed oxide storage containers was not anticipated.
- None of the 431 plutonium-bearing solution containers are currently being inspected, and there is little information that can be used to predict future solution storage container performance. (Note: Monthly visual inspections of these containers was initiated January 1999.) Continuous air monitors will provide warning of contamination only after a solution container leak occurs.
- The concentration of HCl in the 16 items of chloride solutions is unknown, therefore the length of time the product receiver (PR) can contain the solution is unknown.
- 156 of 431 plutonium-bearing solution storage containers are completely characterized. Most of the rest are characterized by process knowledge. There are about 10 plutonium solution storage containers without characterization information. The deterioration rate for solution containers with inadequately characterized contents cannot be quantified (Ref. 16).
- The integrity of the polybottles inside 99 of the 431 plutonium solution storage containers is unknown (Ref. 16). Failed polybottles would leak solution into the surrounding stainless steel container and would therefore be contained for some extended period of time depending on the type of solution involved. If polybottles fail, an increased risk of worker contamination during handling or spills would exist. However, no deterioration was noted during the 1995 downloading and stabilization of 27 polybottles of chloride and fluoride solutions.
- Weight gains for plutonium metals and alloys were not routinely measured until 1998 (Ref. 19). PFP's new weight gain limit prior to repackaging is 5 grams. Based on items weighed to date, approximately 5% of the inventory of plutonium metal has gained more than 5 grams (Ref. 17), indicating that some air in-leakage is occurring.

- The VSIS system, which is used to continually monitor food pack cans for bulging, is not designed to detect container failures caused by formation of plutonium nitride (which causes cans to buckle inward) or to detect corrosion. Items on VSIS require an annual visual inspection. Since the VSIS is not designed to detect cans that buckle inward, and one year can elapse from the time the plutonium storage container first deforms to when it is detected in the annual visual inspection, an undetected container failure could occur resulting in vault contamination.
- Inspection criteria (including surveillance frequency) did not exist for the surveillance of solution storage containers, solids stored in FL-10, L-10, shipping containers, and "bird cages," but the criteria has been developed since this report was originally drafted (Ref 43). The inspection criteria for lard cans may need to be more comprehensive (Refs. 20 and 21). Without these inspection criteria, there is no basis to formally evaluate the adequacy of the storage containers before failure.

3.4 INSUFFICIENT KNOWLEDGE OF PACKAGING CONFIGURATION AND MATERIALS AT PFP -- RL-3.1.3.4

The 1994 plutonium vulnerability assessment report (Ref. 1) states that 95% of PFP's plutonium is stored in triple can configuration, and that only the solutions, SS&C, ash, and polycubes are stored in alternate configurations. The 1994 assessment further indicates there is incomplete information on the contents and packaging for about 17 % of the PFP inventory. This evaluation identified single containment, plastic containers (i.e., polybottles), or unvented containers as the key packaging issues at PFP. This report also concludes there is uncertainty about the actual packaging, material, and storage configuration for materials at PFP.

The list of issues identified during this evaluation that are associated with the 1994 vulnerability regarding insufficient knowledge of packaging and characterization are:

- The Plutonium Recovery database (PRE) was developed to support accounting for special nuclear material. Over time, additional information was captured in this database to support plutonium processing needs, and the PRE currently represents PFP's plutonium material characterization database.² However, the PRE apparently contains suspect information on PFP material characteristics and packaging.

² The PRE will be replaced in the near future with a system that tracks safeguards data. Efforts are now underway to develop a new database for maintaining processing and analysis (characterization) data.

- A U-233 oxide item is listed as a solution (Ref. 22).
- PFP has approximately 40 items of Pu-Enriched Uranium (EU) incorrectly identified as Pu-Europium (Eu) in the PRE. Additionally, numerous items are listed as category code 950 “Plutonium/europium scrap from 324 building”. These too are likely plutonium-uranium oxides (Ref. 23).
- Items in the PRE are assigned to categories (such as metals, alloys, sources, reduction residues, etc.) based on process knowledge. Some categories are broad and do not provide useful characterization data (such as "solution", scrap, etc) (Refs. 8 and 16). The operating definition regarding which plutonium materials were assigned to these categories has varied over the years. As a result an item of plutonium metal may be categorized as a metal, source, reduction residue, or miscellaneous material (Ref. 24). This leads to confusion on the inventory and thus in monitoring, characterization, and stabilization planning.

3.4.1 Mitigation Actions Completed To Date

Some characterization, including radiography, has been performed focusing on areas of significant uncertainty. As part of this re-evaluation, extensive review of the available characterization data has also been performed, which will provide input to a new database now under development.

3.4.2 Examples Associated With Packaging And Characterization That Are Not Described In The 1994 Assessment

Additional issues have been identified that are associated with packaging and characterization that are not discussed in the 1994 assessment. These need to be incorporated into DNFSB 94-1 planning and include:

- Approximately 85 items are stored in shipping containers, which have not been opened and inspected and/or assayed since receipt. The plutonium material receipt dates range from 1967 to 1971 (Refs. 25 and 26). Materials received during this time frame may not be adequately characterized and the packaging configurations may vary from currently accepted practices.
- Characterization data is not retained in a retrievable manner and does not appear to be maintained under configuration control, although efforts are underway to create such a system.
- PFP has a few metal items stored in direct contact with plastic (Refs. 13, 14, and 15). Five potential items have been identified to date. One was confirmed to be metal in direct contact with plastic. One other was found wrapped in aluminum foil before placing in the plastic bag. Three others remain in vault storage. One of these items still in storage was apparently packaged at PFP in 1982 (Ref. 14), even though this storage configuration would not have

been allowable at that time (Ref. 5, Rev A).

- Radiographs show that 7 of 64 plutonium metal items examined (Ref. 15) have plutonium metal stored in the same air space as plastic, that is, the metal is separated from the plastic bag by a screw lid or slip lid can. This storage configuration may lead to the formation of plutonium hydrides. This packaging method was allowed by the PFP storage specification for both metals and alloys through 1992 (Ref. 27).
- The PFP storage specification allowed organic and epoxy coatings on the inside of cans used to store metals and alloys (Ref. 5). This allows organic to come in direct contact with essentially all of PFP's metals and alloys. Although the total quantity of hydrogen contained in this coating is small, it provides a catalyst for the formation of the plutonium nitrides that are now believed to have formed in some of PFP's inventory of metals and perhaps alloys.
- No defined path forward currently exists for some plutonium-bearing solution items, specifically: 1 item of "organic," 16 items of "chloride," and, 16 items of "caustic." Although efforts are underway to better identify these materials and develop an action plan, the potential hazards associated with these non-plutonium nitrate solutions are not well defined.
- At least one PFP operating procedure (Ref. 29) allowed for packaging in a single contamination barrier configuration until at least 1982 even though the PFP storage specification (Ref. 5) specifically called for two barriers. As a result, it is possible some containers may be handled that have only a single contamination barrier, that is only a single metal storage can barrier between the contaminated surface of the plutonium storage container and the vault atmosphere.
- One item of oxide from burned metal had an LOI of 0.5 wt% and was packaged for vault storage. During calorimetry of the item, it became apparent that a reaction was occurring. Upon subsequent unpacking, the inner container was found to have bulged. This indicates that the oxide was not as stable as the LOI indicated. DOE has identified (Ref. 30) that use of an LOI test for items that gain weight as they are stabilized may not be appropriate because the weight gain during stabilization can mask the weight loss from driving off moisture or other volatiles.
- Product oxide from the prototype vertical denitration calciner (VDC) has had low LOI (.25 to .78 wt% LOI). Accordingly, this product material was determined to be acceptable for vault storage. At least 4 of 9 containers of plutonium oxide from the prototype vertical calciner had surface rust in the vapor space of the slip lid can when opened even though they had LOIs of 0.78 wt% or less. After a short period in vault storage, one of these items pressurized. This item had condensate (water droplets) in the bag-out bag around the slip lid can even though the LOI was 0.78 wt%, which should indicate the item was very dry (Ref. 31). The cause for this behavior has not been confirmed, but additional testing is planned for the VDC to ensure

the product will meet stability criteria.

- Container design criteria were not consistently defined and implemented in the past (Ref. 32). The 1979 storage technical basis (Ref. 33) for plutonium oxide only evaluated one container and material configuration: 1 kg of oxide in a slip lid can, in a tomato can in a 7" can. An LOI limit of 1 wt% was based on this configuration. The controlling factors in the technical basis are: 1) material mass which governs how much gas can be generated, 2) available free volume in the container, and 3) the fraction of moles of gas of a particular type that can be created (e.g., CO₂, O₂, and H₂). An additional criterion in the technical basis is the maximum weight for the container. Limiting the weight ensures containers will be within the limits of the drop test certification. For some period of time between 1979 and 1998 not all of these features assumed in the technical basis were preserved when plutonium oxide was packaged. As a result, PFP has plutonium oxide stored with a weight that exceeds the weight analyzed in the technical basis. Records show items are stored in 7" cans that weigh up to 3.5 kg. Items packaged prior to 1998 will be restabilized and/or repackaged as part of the DNFSB 94-1 Program using packaging criteria that are consistent with the technical basis.
- Not all solution storage containers were fabricated to the same criteria. Some PR cans were "emergency" fabricated using pipe with plates welded to the ends (Ref. 28). The design life of these storage containers is not known.
- The PRE lists many Pu-EU items in inventory but often only gives a gram quantity for one or the other of the fissile components. Many of these items have not been assayed since receipt at PFP (in mid-1970's) (Ref. 25). If there is an error in the fissile material quantity, this may lead to violation of one of the contingencies to prevent criticality.
- Storage containers for plutonium metals, oxides, and residues may build-up hydrogen or other flammable gases from thermal and radiolytic degradation of plastic used in packaging materials (Ref. 10). These gases may pressurize the storage container causing failure. The flammable gases may ignite when the storage container is opened.

3.5 REACTIVE CHEMICALS STORED IN PFP GLOVEBOXES -- RL-3.1.4.2

The fifth PFP vulnerability identified in 1994, "RL-3.1.4.2, reactive chemicals stored in PFP gloveboxes," was closed following the successful stabilization of PFP's inventory of approximately 236 plutonium-bearing organic sludge items from the Plutonium Reclamation Facility in June of 1996. However, PFP still has a small amount of sludge and other unstable materials in glovebox storage that was outside the scope of the original vulnerability.

4.0 VULNERABILITY REVIEW BY MATERIAL FAMILY

This section of the report groups the issues identified in Section 3.0 (both original and newly identified) according to their applicability to the specific families of plutonium materials in storage at PFP. This grouping of issues by material family will be used in Section 5.0 to develop a recommended risk-based priority for the processing of material groups at PFP. The material groups addressed in the following sections are the primary material groups identified in PFP inventory records. Specific examples of the previously identified issues for the individual material groups have also been provided to assist DNFSB 94-1 planning efforts.

4.1 ISSUES ASSOCIATED WITH THE SOLUTION INVENTORY AT PFP

Issues identified for solutions in storage include:

- Some containers of solutions were identified as not having the required vent-clips. Vent-clips are necessary to prevent the buildup of hydrogen in the outer container (drum) due to radiolytic decay of the liquids. Preliminary information indicates that some of these drums were loaded in 1996. The number of solution storage containers that are not vented was still being determined when this document was written (Ref. 43). The buildup of hydrogen gas from the radiolytic decay of solutions creates an explosion hazard (Ref. 1). Inadequate storage criteria and procedures combined with a lack of a surveillance program contributed to the creation of this vulnerability and the long delay in identifying it. (Note: Monthly visual inspections of these containers was initiated January 1999.)
- The 1994 plutonium vulnerability assessment (Ref. 1) expressed a concern about criticality safety if the containers of solutions leaked. This issue is addressed in criticality safety evaluation reports (CSER): 79-010, 79-011, and 79-030. These CSER show there that there is a triple contingency to preclude criticality (Ref. 34).
- Not all solution storage containers were fabricated to the same criteria. Some PR cans were "emergency" fabricated using pipe with plates welded to the ends (Ref. 28). The design life for these containers is not known.
- The concentration of HCl in the chloride solutions is unknown therefore the length of time the PR can is able to contain the solution is unknown.
- There is no monitoring program for solution containers (Refs. 20 and 21). As such, there is no early warning mechanism for container failure and leakage (Ref. 1). (Note: Monthly visual inspections of these containers was initiated January 1999.)
- About 156 of 431 plutonium-bearing solution storage containers are completely characterized.

Most of the rest are characterized by process knowledge. There are about 10 plutonium solution storage containers without characterization information. The deterioration rate for solution containers with inadequately characterized contents cannot be quantified (Ref. 16).

- Because of a lack of characterization data, no defined path forward currently exists for several items, specifically: 1 item of "organic," 16 items of "chloride," and, 16 items of "caustic."
- Product oxide from the prototype vertical denitration calciner (VDC) has had low LOI (.25 to .78 wt% LOI). Accordingly, this product material was determined to be acceptable for vault storage. At least 4 of 9 containers of plutonium oxide from the prototype vertical calciner had surface rust in the vapor space of the slip lid can when opened even though they had LOIs of 0.78 wt% or less. After a short period in vault storage, one of these items pressurized. This item had condensate (water droplets) in the bag out bag around the slip lid can even though the LOI was 0.78 wt%, which should indicate the item was very dry (Refs. 31 and 33). The cause for this behavior has not been confirmed, but additional testing is planned for the VDC to ensure the product will meet stability criteria.
- The integrity of the polybottles (99 items) inside storage containers is unknown (Ref. 16). Failed polybottles would leak solution into the surrounding stainless steel container and would therefore be contained for some extended period of time depending on the type of solution involved. If polybottles fail, an increased risk of worker contamination during handling or spills would exist. However, no deterioration was noted during the 1995 downloading and stabilization of 27 polybottles of chloride and fluoride solutions.

4.2 ISSUES ASSOCIATED WITH THE PLUTONIUM METAL INVENTORY AT PFP

Issues associated with PFP's plutonium metal inventory include:

- PFP's plutonium metal is typically high Pu-240 (16 to 18%) and typically more than 20 years old. This results in a high decay heat and increased radiological dose due to americium buildup. In addition to higher operator exposures, elevated temperatures may accelerate degradation of plutonium storage container seals. Higher temperatures also promote the formation of plutonium nitrides.
- Based on the buckling inward of plutonium storage containers on some (estimated to be 7%) plutonium metal items, it has been concluded that plutonium corrosion products including plutonium nitrides have been formed (Ref. 13). Since plutonium hydrides are believed to catalyze the formation of these plutonium nitrides, at least some of these containers would also be expected to contain plutonium hydrides. This set of chemical reactions may be more prevalent for some plutonium metal items. Before 1992 PFP procedures allowed plutonium metals and alloys to be wrapped in aluminum foil, bagged out of the glovebox in a plastic bag,

and then canned in food pack cans (Ref. 5). This places the plutonium in the same air space as the plastic. As such, hydrogen would be readily available in these cases to react with the plutonium metal and form plutonium hydride.

- Some plutonium metal storage containers may also contain plutonium metal fines that spilled from the surface of the plutonium metal. Plutonium metal fines are pyrophoric (Ref. 6).
- The VSIS system, which is used to continually monitor food pack cans for bulging, is not designed to detect container failures caused by formation of plutonium nitride, which causes cans to buckle inward. Items on VSIS require an annual visual inspection. Since the VSIS is not designed to detect cans that buckle inward, and one year can elapse from the time the plutonium storage container first deforms to when it is detected, an undetected container failure could occur that results in vault contamination.
- Approximately 40% of the plutonium metal inventory are stored in a two metal can configuration with the plastic bag in the annular space (Ref. 35). Two contamination barriers are required by procedure (Ref. 5).
- One item of plutonium metal turnings was found during radiography. It is possible that other metal turnings may be present in non-metal families such as lab samples, scrap, or SS&C (Ref. 24). Plutonium metal turnings are not allowed in storage due to their potential for pyrophoric reaction.
- One item of plutonium metal was found in direct contact with plastic and was subsequently thermally stabilized (oxidized). Radiographs indicate 4 more plutonium metal items may be in direct contact with plastic that are currently stored in the vaults (Refs. 13, 14, and 15).
- Based on samples to date, approximately 5% of the plutonium metal items in storage have gained more than 5 grams. This indicates that some of the metal is oxidizing in storage as a result of air in-leakage. Assuming the weight gain/time function is linear, the rate of oxidation is very slow (Ref. 17).
- Loss-on-ignition testing may not provide good indication in all cases of the suitability of processed materials for long-term storage. As such, even materials that have “passed” LOI testing may cause future storage container failure (Ref. 30). One item of oxide from burned metal had an LOI of 0.5 wt% and was packaged for vault storage. During calorimetry of the item, it became apparent that a reaction was occurring. Upon subsequent unpacking, the inner container was found to have bulged. This indicates that the oxide was not as stable as the LOI indicated. DOE has identified (Ref. 30) that use of an LOI test for items that gain weight as they are stabilized may not be appropriate because the weight gain during stabilization can mask the weight loss from driving off moisture or other volatiles.

- The potential for generating flammable gases due to radiolysis of the plastic bags used in packaging containers of plutonium metals was not described in the 1994 assessment (Ref. 10). These gases produced may cause the storage container to pressurize and fail. The flammable gases may ignite when the storage container is opened.

4.3 ISSUES ASSOCIATED WITH THE PLUTONIUM ALLOY INVENTORY AT PFP

Issues associated with PFP's plutonium alloy inventory include:

- None of the four items (of a total of 126 alloys) radiographed showed signs of deterioration. However, two containers (50% of those radiographed) were found to be packaged using a single contamination barrier, that is only a single metal storage can barrier between the contaminated surface of the plutonium storage container and the vault atmosphere (Refs. 13, 14, and 15). Two contamination barriers are currently required (Ref. 5).
- Some alloys, especially the plutonium-uranium alloys, may be as reactive as PFP's plutonium metal (Ref. 6). Some alloys have higher Pu-240 contents than PFP's plutonium metals, up to 25.8% Pu-240 (Ref. 8). As such, some of the plutonium alloys may exhibit the same concerns as noted above for high Pu-240 plutonium metal.
- One plutonium alloy item has bulged in storage. This item is identified as a Pu/Al-Y vycor melt residue with 6.9% Pu-240. It is identified as 90% plutonium. The cause of the bulge has not been determined (Ref. 14).
- The constituents of the plutonium alloy "scrap" are not identified. Many items are of non-Hanford origin and are pre-1980 packages. The acceptance criteria for these items are unknown, and they have not been characterized.
- Through at least 1992, PFP procedures allowed plutonium alloys, like metals, to be wrapped in aluminum foil then bagged out of the glovebox and then canned in food pack cans (Ref. 4). This places the plutonium alloy in the same air space as the plastic, which may lead to the formation of plutonium and uranium hydrides and nitrides.
- Many plutonium alloy items were packaged prior to the issuance of PFP's storage specification. The packaging configuration of many of the plutonium alloys is unknown. Many items are listed as stored in slip lid, lard cans, or shipping containers versus food pack cans (Ref. 26). Without data on packaging, risks associated with hydrogen generation, formation of nitrides and hydrides, or the potential for oxidization of the item in storage can not be adequately evaluated or ruled out.
- Loss-on-ignition testing may not provide good indication in all cases of the suitability of

processed materials for long-term storage. As such, even materials that have “passed” LOI testing may cause future storage container failure (Ref. 30).

- The potential for generating flammable gasses due to radiolysis of the plastic bags used in packaging containers of plutonium alloys was not described in the 1994 assessment (Ref. 10). The gases produced may pressurize the container causing it to fail. The flammable gases may ignite when the container is opened.

4.4 ISSUES ASSOCIATED WITH THE NUCLEAR FUELS INVENTORY AT PFP

PFP stores a range of nuclear fuel pin types. Standard Fast Flux Test Facility (FFTF) fuel pins are composed of sintered mixed oxide (MOX) pellets in stainless steel cladding. These pins are stable and the pellets are not reactive. The storage configuration is expected to be adequate for storage for at least 50 years. PFP also stores a wide variety of other types of fuel pins. The specific issues associated with these items include:

- Five pins of mixed plutonium and uranium carbide sintered pellets in stainless steel pins are stored at PFP. Plutonium carbide sintered pellets are potentially friction and pressure sensitive (Ref. 10). Uranium carbide pellets may exhibit the same characteristics (Ref. 6).
- The PFP inventory also includes 76 enriched uranium-metal or zirconium-alloyed items and 4 plutonium, enriched-uranium, zirconium alloy items in stainless steel tubes (Ref. 9). These items are believed to be sodium bonded. Sodium is water reactive. The packaging configuration for these items is unclear at this time.
- PFP has three NaK bonded fuel rods stored in "birdcages" (Ref. 9). The condition of these rods is unknown. NaK is water reactive.
- PFP also stores some spent nuclear fuel (Ref. 3). The configuration of this material is unclear at this time.

4.5 ISSUES ASSOCIATED WITH THE MOX INVENTORY AT PFP

Specific issues associated with the MOX inventory at PFP include:

- The inventory of MOX scrap is not well characterized. The constituents of the plutonium storage containers are not fully identified. Many of the items were received before current acceptance criteria were established.
- Based on limited radiography there are items of MOX that are not packaged in accordance with current requirements, that is only a single metal storage can barrier exists between the contaminated surface of the plutonium storage container and the vault atmosphere.
- Included in the MOX items that are stored in a single contamination barrier configuration are a family of MOX identified as "ZQM." Some of the MOX items from the "ZQM" family were radiographed. The radiographs suggest that the inner storage cans have deteriorated significantly. The corrosion mechanism is unclear, but it is likely to be a result of some unidentified corrosive contaminant in the MOX scrap (Refs. 13, 14, and 15).
- The potential for generating flammable gasses due to radiolysis of the plastic bags used in packaging of containers of plutonium mixed oxides was not described in the 1994 assessment (Ref. 10). The gases produced may pressurize the container causing it to fail. The flammable gases may ignite when the container is opened.
- Loss-on-ignition testing may not provide good indication in all cases of the suitability of processed materials for long-term storage. As such, even materials that have "passed" LOI testing may cause future storage container failure (Ref. 30).

4.6 ISSUES ASSOCIATED WITH THE POLYCUBES INVENTORY AT PFP

PFP's inventory of polycubes is well characterized but not well packaged. Polycubes are high Pu-240 and over twenty years old. High contact dose fields (up to 9 RAD) have been measured (Ref. 36). They off-gas hydrogen and hydrocarbon gasses as a result of the radiolytic decay of the polystyrene plastic. To accommodate the off-gas, the polycubes are stored in vented, filtered containers. Typically, polycubes are stored in single food pack cans that have a small hole in the top. A filter is glued (taped) to the top of the can over the hole. Polycubes are also stored in vented polyjars in gloveboxes. A contamination spread occurred in 1987 as a result of inverting a container of deteriorated polycubes and the filter failing. The glue that held the filter in place had apparently deteriorated. The deterioration was likely due to the effects of radiation and age. Since the incident, new filters have been added to the cans and movement restrictions imposed.

In 1996, approximately 15 glovebox-stored polycubes were moved from one glovebox to another. The operator who handled the items noted that most of the polycubes were fairly intact. Deterioration was noted around the edges and corners and powder was noted in the bottom of the polyjars (Ref. 37). One item was observed to be all powder with no obvious cube left. It is believed that this item was partially stabilized years ago in Plutonium Reclamation Facility, Glovebox MT-4 pyrolysis furnaces (Ref. 38). Based on the past contamination spread, and the potential for the polycube to be disintegrated, the polycubes can potentially cause a spread of contamination during handling even though additional measures have been implemented to reduce the likelihood of contamination being released.

4.7 ISSUES ASSOCIATED WITH NON-POLYCUBE COMBUSTIBLES INVENTORY AT PFP

PFP has 12 containers of non-polycube combustibles in storage (Ref. 8). This inventory requires additional characterization to enable determining the specific hazards that may be present and the path forward for disposition.

The potential for generating flammable gasses due to radiolysis of the plastic bags used in packaging of containers of non-polycube combustibles was not described in the 1994 assessment (Ref. 10). The gases produced may pressurize the container causing it to fail. The flammable gases may ignite when the container is opened.

Loss-on-ignition testing may not provide good indication in all cases of the suitability of processed materials for long-term storage. As such, even materials that have "passed" LOI testing may cause future storage container failure (Ref. 30).

4.8 ISSUES ASSOCIATED WITH THE REDUCTION RESIDUES (SS&C) INVENTORY AT PFP

SS&C has been previously identified in the DOE implementation plan for DNFSB Recommendation 94-1 (RL-3.1.3.2) as a high risk residue due to the presence of unreacted calcium metal, the possible presence of plutonium metal fines from failed metal reductions, and the presence of other reactive or corrosive constituents.

SS&C is typically stored in un-tinned food pack cans that are inside of lard cans. (The lard cans are nominally 5-gallon slip lid cans that are taped shut.) Although there is no specific inspection criteria for lard cans in storage, observations made during the cementing of approximately 219 kg of SS&C in 1996 did not identify any significant issues with the packaging of the SS&C in lard cans (Refs. 13, 14, and 15).

The second group of SS&C containers is 7" food pack cans. The 7" food pack cans are used for higher plutonium assay items. These 7" food pack items may also contain plutonium oxide and fluoride powders and/or plutonium metal. They may also contain lab scraps and samples including metal fines and turnings (Ref. 24). The characterization of these storage containers is not complete.

The potential for generating flammable gases in containers of SS&C was not described in the 1994 assessment (Ref. 10). The gases produced may pressurize the container causing it to fail. The flammable gases may ignite when the container is opened. Furthermore, unreacted calcium metal may react with available moisture to form calcium hydroxide and hydrogen gas. Since the 7" food pack cans are better sealed, the potential for hydrogen build up is greater in these cans than for lard cans.

4.9 ISSUES ASSOCIATED WITH THE PLUTONIUM COMPOUNDS INVENTORY AT PFP

PFP's inventory of compounds can be grouped into four families. Plutonium fluorides, Pu-Zr scrap, Pu-Be scrap, and Pu-Th scrap. The plutonium fluorides are grouped into PuF₃ and PuF₄.

Specific issues associated with the plutonium compounds at PFP include:

- To meet DOE-STD-3013 (Ref. 39), plutonium fluorides must be converted to plutonium oxides. Fluorides must be converted to oxides by processing such as dissolution/precipitation, direct oxidation, pyrohydrolysis, or reduction to metal.
- Five items of PuF₃ are coded with the same code as would be used for UF₆. UF₆ is a concern because it is a gas at near room temperature (Ref. 7). Four of the five items have been confirmed to be PuF₃ with no UF₆. The fifth item is described as "BNW U Scrap WG." This item is mixed PuF₃/UF₆ and is stored in a vented configuration in a glovebox. This storage arrangement appears adequate for the hazard, but stabilization is required prior to moving the item to vault storage.
- The constituents of the plutonium compound scrap require additional characterization to ensure the hazards are fully identified and to enable a disposition path forward to be established.
- The potential for generating flammable gases due to the degradation of plastic materials in containers of plutonium compounds was not described in the 1994 assessment (Ref. 10). The gases produced may pressurize the container causing it to fail. The flammable gases may ignite when the container is opened.

- Loss-on-ignition testing may not provide good indication in all cases of the suitability of processed materials for long-term storage. As such, even materials that have “passed” LOI testing may cause future storage container failure.

4.10 ISSUES ASSOCIATED WITH THE MISCELLANEOUS ITEMS PLUTONIUM INVENTORY AT PFP

There is limited information upon which to determine what issues might exist for the miscellaneous plutonium items inventory at PFP. Based on the inventory records, the miscellaneous inventory likely contains spent nuclear fuel (Ref. 3), metal, and alloy scrap (Ref. 8). As such, items in the miscellaneous category may have all of the issues associated with each of these material families (Ref. 9). Additional characterization will be necessary to fully evaluate the hazards of these materials and to develop the disposition path forward.

The potential for generating flammable gases due to the degradation of plastics in containers of miscellaneous plutonium items was not described in the 1994 assessment (Ref. 10). The gases produced may pressurize the container causing it to fail. The flammable gases may ignite when the container is opened.

Loss-on-ignition testing may not provide good indication in all cases of the suitability of processed materials for long-term storage. As such, even materials that have “passed” LOI testing may cause future storage container failure.

4.11 ISSUES ASSOCIATED WITH THE SOURCES AND SAMPLES INVENTORY AT PFP

There is limited information upon which to determine what issues might exist for the plutonium sources and samples in storage at PFP. Concern has been raised that sealed containers of PuF₄ used as neutron sources might fail due to the pressure buildup from alpha radiolysis of contained moisture and/or alpha decay (helium generation). Three of these sources are over 30-years old (Ref. 40). Also, two of the items are potentially plutonium metal (Ref. 26). The packaging configuration for these metal items is unclear. Additional characterization will be necessary to fully evaluate the hazards of these materials and to develop the disposition path forward.

The potential for generating flammable gases due to degradation of plastics in containers of plutonium sources and samples was not described in the 1994 assessment (Ref. 10). The gases produced may pressurize the container causing it to fail. The flammable gases may ignite when the container is opened.

Loss-on-ignition testing may not provide good indication in all cases of the suitability of

processed materials for long-term storage. As such, even materials that have "passed" LOI testing may cause future storage container failure.

4.12 ISSUES ASSOCIATED WITH THE PLUTONIUM OXIDES INVENTORY AT PFP

Oxides are typically considered stable as long as they are properly dried and have been completely converted to oxide (Ref. 41). The standard test to ensure stability has been the loss on ignition (LOI) test (Ref. 4). For most oxide generation methods, this is a valid test. However, the LOI test may not be completely valid for oxides that are created by burning plutonium metal buttons because metal gains weight as it oxidizes thus masking the weight loss due to gas generation. Gas generation can lead to container over pressurization, while un-oxidized metal can be pyrophoric or can lead to the formation of plutonium nitrides and plutonium hydrides, which are also pyrophoric. PFP began restricting weight gains on ignition in 1998 (Ref. 5, current revision). As a result, the satisfactory LOI tests performed on that portion of the PFP inventory of "product oxide" generated by burning metal buttons do not necessarily provide assurance that this oxide is stable for long-term storage (Ref. 30).

Container design criteria were not consistently defined and implemented in the past (Ref. 32). The 1979 storage technical basis (Ref. 33) for plutonium oxide only evaluated one container and material configuration: 1 kg of oxide in a slip lid can, in a tomato can in a 7" can. An LOI limit of 1 wt% was based on this configuration. The controlling factors in the technical basis are: 1) material mass which governs how much gas can be generated, 2) available free volume in the container, and 3) the fraction of moles of gas of a particular type that can be created (e.g., CO₂, O₂, and H₂). An additional criterion in the technical basis is the maximum weight for the container. Limiting the weight ensures containers will be within the limits of the drop test certification. For some period of time between 1979 and 1998 not all of these features assumed in the technical basis were preserved when plutonium oxide was packaged. As a result, PFP has plutonium oxide stored with a weight that exceeds the weight analyzed in the technical basis. Records show items are stored in 7" cans that weigh up to 3.5 kg. Items packaged prior to 1998 will be restabilized and/or repackaged as part of the DNFSB 94-1 Program using packaging criteria that are consistent with the technical basis.

One item (of a lot of potentially 106 items) of plutonium oxide received from the Savannah River Site produced by burning metal buttons has had the outer storage container buckle inward, similar to the effect observed for plutonium metal items. The cause of the buckling inward in plutonium metal items is believed to be the formation of plutonium corrosion products such as nitrides, oxides, hydrides etc. The inventory summary report (Ref. 8) lists 19 items as having plutonium concentrations greater than 88 wt% indicating they may not have been completely oxidized, and, as a result, these items may also contain corrosion products such as plutonium nitrides and plutonium hydrides as well.

PFPP also stores a large quantity of oxides that contain large percentages of chloride salt impurities. These chloride salts may cause corrosion of storage containers and may cause off-gas line plugging during thermal stabilization (Ref. 35).

Other issues identified with oxides include improper packaging (single contamination barriers), improper or incomplete characterization, and bulging of the inner containers. Also, the potential for generating flammable gasses due to radiolytic decay of plastic used in packaging in containers of plutonium oxides was not described in the 1994 assessment (Ref. 10).

4.13 ISSUES ASSOCIATED WITH THE ASH INVENTORY AT PFP

The inventory of ash from Rocky Flats has been thermally stabilized to at least 450° C, 1-wt% LOI at PFP. This should provide sufficient stability to allow for continued storage as-is until cementation and discard can be accomplished.

The thermal stability and packaging of the Hanford-produced ash are less documented (Ref. 42). The Hanford origin ash is typically stored in taped lard cans (Ref. 35). No specific problems have been noted with this material in storage. This ash should be acceptable for continued storage as-is until cementation and discard can be accomplished.

The potential for generating flammable gas in containers of plutonium-bearing ash was not described in the 1994 assessment (Ref. 10).

4.14 ISSUES ASSOCIATED WITH THE URANIUM INVENTORY AT PFP

Uranium (without plutonium) storage vulnerabilities at PFP were not part of the 1994 assessment. Much of this material will be shipped from PFP in the next 12 months. The balance needs to be better evaluated before disposition plans can be established.

4.15 ISSUES ASSOCIATED WITH THE SPECIAL ISOTOPES INVENTORY AT PFP

The PRE (Ref. 22) lists 3 americium-241, 3 californium, 3 uranium-233, 1 neptunium, and 22 thorium items in inventory at PFP. The configuration of these special isotopes needs to be determined. No data was available that characterizes these items. Stability and storage criteria have not been defined.

5.0 RISK BASED PRIORITIZATION

The specific issues identified for each of PFP's material families developed in Section 4.0 are used in this section of the report to develop a risk-based priority and sequence for processing PFP materials.

The goal of prioritization is to sequence stabilization and repackaging activities to achieve the most rapid reduction of risk possible. Risk reduction is achieved by stabilizing material and/or placing the material in more suitable containers. The risk at PFP that is being prevented or mitigated by this action is the risk to workers associated with a container failure in storage or handling that results in exposure to radionuclides. There is no way of predicting exactly when an item will fail in storage or during handling, and the approach used does not quantify the risks associated with the failure of one container versus another. Accordingly, the total time needed to process all of the containers (aggregate rate of processing plutonium storage containers) and the specific risks each of the families of material represent are the key factors in defining the rate of risk reduction in the approach used. Developing a risk ranking method without the ability to quantify the risk of each item or the ability to precisely predict when each container will fail is not possible. Therefore, a subjective, probabilistically based risk ranking method was developed. This method is not a guarantee that items assigned the lower risk rankings will not fail before stabilization. This method simply applies engineering judgement in a systematic way to attempt to identify the highest items.

An assumption made during the development of this report is that the failure during storage or handling of any plutonium container storage container is unacceptable, and the potential consequences of any such plutonium storage container failure to PFP workers is unacceptable. Accordingly, the first consideration made in identifying the risk various plutonium material families represent is the potential for this plutonium material family to challenge its storage container or containment boundaries. For example, plutonium metals and solutions can challenge their storage container boundaries, and they are therefore identified as higher risk. There are few credible storage hazards that would place the worker at undue risk for items stored in gloveboxes. Items stored in gloveboxes would pose a lower risk than vault stored items. Items that do not pose a credible threat to their container are defined to have a still lower priority.

In the approach used, the risk a material family presents to its storage containers is further graded based upon whether the risk has been demonstrated or is suspected. Demonstrated ability to breach a container is ranked higher than that of a suspected or potential threat to the container. Where potential or suspected threats exist, additional characterization and analysis is required to understand the risk of this material. The materials that pose the greatest potential threats to their containers would appropriately receive higher priority for characterization and analysis.

The second broad consideration is the potential for plutonium uptake (inhalation) by workers if a container failure occurred. Materials that could react vigorously when the container fails (e.g.,

plutonium hydrides) and pressurized items are more likely to cause significant plutonium uptake by workers because vigorous reactions and/or pressurization will tend to rapidly spread the radionuclides into a larger air volume. More workers may be affected and there will be less reaction time available.

The third major consideration is the early warning characteristics of the container. The test applied in this risk-based approach is whether there are detectable warning signs that will enable PFP to identify pending container failure so that action can be taken to prevent container failure. Where pending container failure cannot be reliably detected, the risk of this plutonium material family is ranked higher than those where the primary failure mechanisms can be detected.

Seven material types were identified that have the ability to challenge their storage containers or confinement boundaries: unvented solution containers, metals, non-nitrate solutions, polycubes, ZQM oxides, the Pu-Al-Y alloy item, and oxides from incompletely burned buttons. Unvented solution storage containers can build up hydrogen to potentially explosive concentrations and/or over pressurize the container. Metals have demonstrated their ability to cause their storage containers to fail either by pressurizing or buckling inward. Oxides from incompletely burned metal buttons may also cause their storage containers to fail by buckling inward. The Pu-Al-Y source has pressurized in storage. Non-nitrate Solutions in storage have the potential to cause their storage containers to fail through corrosion. Although polybottles containing solutions have failed in the past, there have not been any reported instances of the stainless steel containers failing. The vented storage configuration provided for polycubes may cause an effective breach of the storage container if the storage containers are tipped or jarred. Radiographs of the ZQM oxides show indications of significant corrosion of the inner container.

Three material types were identified that will react vigorously if released from their storage containers: unvented solutions, metals and the incompletely oxidized metal resulting from burning metal. Solutions containers have failed in the past due to over pressurization and others have exploded or ignited upon opening causing worker injuries and/or contamination spreads. In the case of metals and oxides from incompletely burned metals, the plutonium hydrides and plutonium nitrides potentially present may rapidly react creating heat and hydrogen. The hydrogen produced may further react (burn) thus intensifying the reaction. In combination, these reactions may rapidly disperse plutonium. Additional data is required to determine if the ZQM oxides may react if the container fails.

Applying the third consideration, unvented solutions have the greatest potential for causing container failure, injury, and/or contamination spread with no early warning. Currently there is no routine surveillance of solution storage containers (Note: Monthly visual inspections of these containers was initiated January 1999, however due to the limits of the visual inspection, this surveillance may not provide sufficient response time prior to contamination spread occurring.). Metals have a greater potential than oxides from incompletely burned metals for causing a failure with little time to respond. Current PFP surveillance systems (VSIS) and surveillance procedures

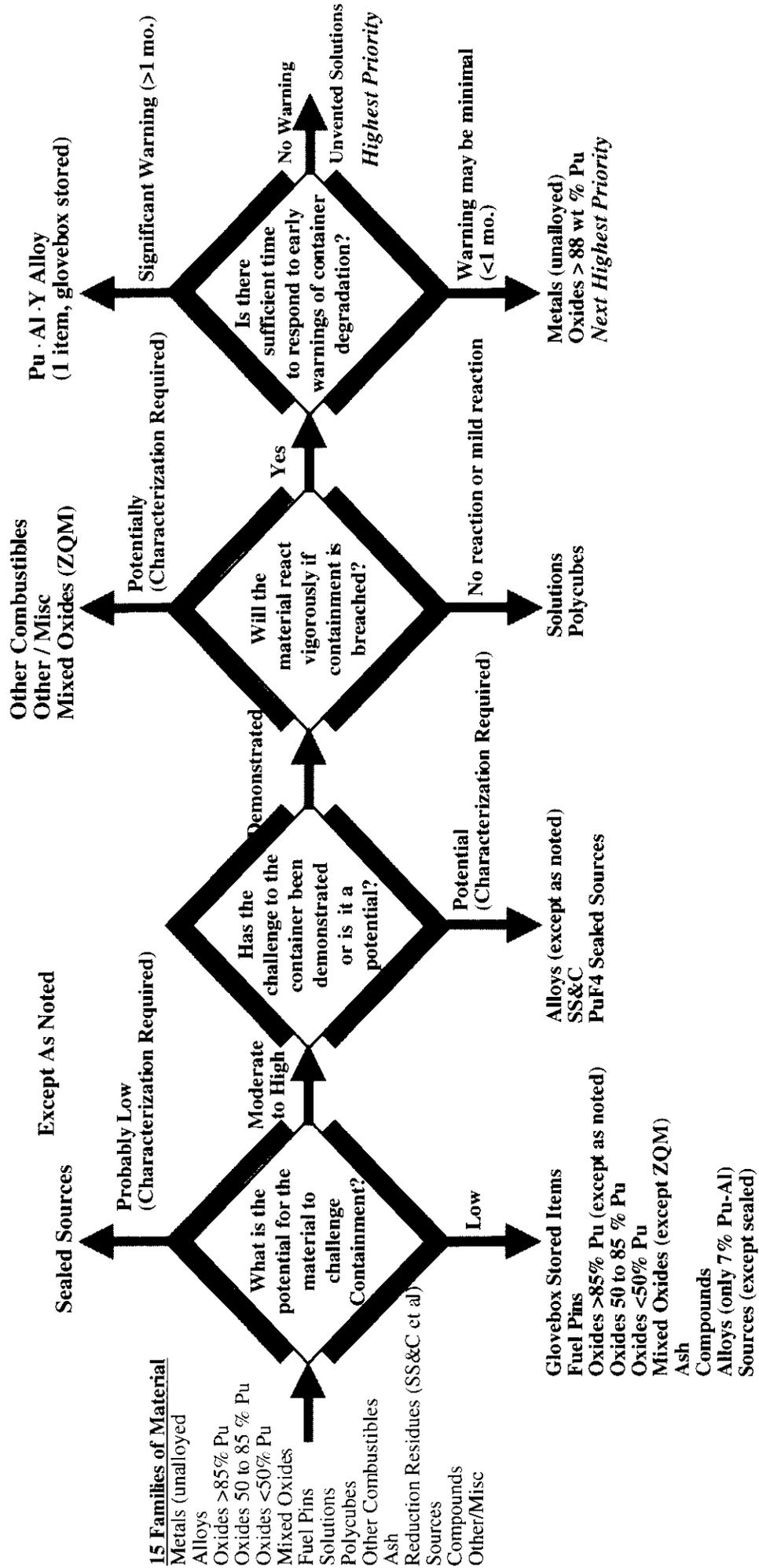
may not detect a pending container failure resulting from buckling inward. This phenomenon is believed to be the result of the formation of plutonium nitrides catalyzed by the formation of plutonium hydrides. This phenomenon would be more likely to occur with a plutonium metal item than an incompletely burned plutonium oxide. Furthermore, there are more cases of buckled inward metal items than oxide items. As a result, plutonium metal items were judged to be a higher risk than oxides from incompletely burned metal items.

Using this approach, as a result of the compounding risk factors, unvented solutions were judged to be the greatest safety risk. Plutonium metals were judged to be the next highest risk material family at PFP. Oxides from incompletely burned buttons were found to be the third highest risk, as this material family was determined to possess all of the same risk factors as the plutonium metals but in smaller quantity (amount of potentially hydrided metal) per can. The ZQM oxides would be the fourth priority based on the demonstrated container degradation and the lack of data to show they will not react if the container fails. Solutions (specifically the solutions in polybottles, the chloride solutions, the organic solution, and the approximately 10 solution items which data has not been located to determine the type of acid(s) stored) were evaluated to be fifth priority. This is based principally on the lack of detectable early warning indication of pending storage container failure. Polycubes were determined to be the sixth highest risk.

Significant uncertainties remain with some families and sub-families of materials that may alter the relative risk ranking. Characterization emphasis should be placed on resolving/answering potential issues such as:

- The three PuF₄ sealed neutron sources were fabricated for use at Hanford over 30 years ago and little data are available on their construction. The concern with these three items is the potential for pressurization and catastrophic failure. While the three PuF₄ sealed neutron sources may pressurize and potentially fail with out warning, repackaging will mitigate the hazard. These three items should therefore be given priority just behind metal stabilization to determine if they are pressurized and to repackage them if necessary (if pressurized).
- Determining if plutonium alloys have corroded and formed hydrides or nitrides in storage.
- Determining the corrosion potential of the non-nitrate solutions and the makeup of the organic solution.
- Determining if plutonium metal or alloys are present in material families such as "miscellaneous".
- Determining the characteristics (material and packaging) of the non-polycube combustibles.

PFP Risk Based Prioritization Logic



6.0 SUMMARY AND CONCLUSIONS

Since the 1994 assessment of plutonium vulnerabilities was completed, 2 of the 5 vulnerabilities associated with the storage of plutonium at PFP have been addressed and were closed. One of these (unvented solution storage containers) is being reopened. The other three vulnerabilities remain open and are being addressed through the implementation of the DNFSB 94-1 program at PFP. As a result of the information developed in this report, additional issues have been identified within the three open vulnerabilities that need to be considered as the balance of the DNFSB 94-1 program at PFP is completed. These issues will be addressed during the development and implementation of the project plans for each of the stabilization projects. Attachment A summarizes PFP plutonium vulnerabilities.

Some of the issues identified, such as characterization, cut across several stabilization projects. An approach for addressing the broader issues will be prepared that maps the issues identified in this plan to the path forward that will be adopted for addressing these issues at PFP. The plan of actions will be incorporated into the Site Integrated Stabilization Management Plan (SISMP).

In some cases, defining the path forward and necessary actions requires conducting further characterization. The information developed in this report provides a guide for defining future PFP characterization efforts. The materials identified in this report that need additional characterization and analysis to determine their interim acceptability and/or stabilization processes include:

- Solutions,
- Alloys,
- Miscellaneous materials,
- Non-polycube combustibles,
- Sources and samples,
- Non-FFTF fuel pins,
- Glovebox stored items,
- Materials packaged prior to October 1980 that may have not been tested for stability and all items packaged prior to issuance of the PFP storage specification (1979), and
- Special isotopes.

The information developed in this report also indicates there are some failure modes and mechanisms for plutonium materials in storage that may not be detected by current surveillance procedures and equipment. Specific examples include plutonium metal and incompletely burned oxide storage containers buckling inward and corrosion failure of plutonium solution storage containers. Interim compensatory measures, including additional surveillance, may need to be developed to address these storage issues.

The results of this risk-based approach indicate that PFP efforts should be prioritized as:

- 1 Venting solution storage containers,
- 2 Unalloyed plutonium metals stabilization,
- 3 Evaluating and venting if necessary, three PuF₄ sealed neutron sources,
- 4 Stabilizing Oxides containing incompletely stabilized plutonium metal & "ZQM" oxides,
- 5 Stabilizing plutonium-bearing solutions
- 6 Stabilizing Polycubes and other combustibles.
- 7 Stabilizing high-assay, alloyed plutonium metal
- 8 Stabilizing glovebox stored items
- 9 Cementation and/or discarding of residues (SS&C, ash, low-grade oxides, & miscellaneous)
- 10 Restabilization of oxides, MOX, sources, standards, and compounds
- 11 Repackaging of low-assay, alloyed plutonium metal and fuel pins.

However, the characterization and analysis program may identify new information that alters this prioritization. Also, there may be practical barriers to processing materials strictly in accordance with this sequence.

Using the priorities established in this report and the current plant status, the best sequence from a risk reduction perspective for stabilizing and packaging PFP materials starts with plutonium metals and then proceeds to the incompletely burned plutonium oxides and the ZQM oxides. Additional work crews will be needed to begin processing other high priority material families. However, the critical parameter is progress toward completing DNFSB 94-1 since every

plutonium storage container represents some risk of failing that could lead to PFP worker exposure to radionuclides. The information developed in this report will be used in the ongoing PFP systems engineering effort to continue to improve the stabilization schedule to ensure that risk reduction is maximized.

7.0 REFERENCES

1. DOE/EH-0415, DOE, "Plutonium Working Group Report," Volume 1 and 2 Appendix part 2, dated November of 1994.
2. DOE/EM-0199, DOE, "Plutonium Vulnerability Management Plan," dated March of 1995.
3. HNF-EP-0853. Rev. 5, BWHC, "DNFSB Recommendation 94-1 Hanford Site Integrated Stabilization Management Plan," dated May 1997.
4. Memorandum (DRAFT), L. Olguin, to L. Romine, "Description of deliverable for July 30 Update of Plutonium Vulnerability Study," dated June 9, 1998.
5. Operating Specifications (OSD-Z-184-00013 Rev E-0), T. B. Veneziano, "Special Nuclear Material Storage," dated December 1, 1983.
6. O. J. Wick, Pacific Northwest Laboratories, "Plutonium Handbook A Guide To The Technology," Vol. 1, dated 1967.
7. Letter, L. J. Olguin to L. D. Romine, "Contract No. DE-AC06-96RL-13200 - Delivery of the report: data requirements and criteria for establishing risk judgements for stabilization of plutonium materials at PFP "Al Williams Report," FDH-9856537, dated August 4, 1998.
8. WHC-SD-CP-TI-212, M. W. Gibson, "Planning Data for Plutonium Finishing Plant Special Nuclear Material Inventory," EDT 619159, dated September 19, 1996.
9. Table, "Pu Inventory Chemical Composition Data", T. Venetz, dated 4/9/97.
10. Plustor.htm@www3.dp.doe.gov, "Assessment of Plutonium Storage Safety Issues at Department of Energy Facilities," U.S. Department of Energy, undated.
11. Report, "DOE Investigation Committee Report on Ignition and Pressurization of Plutonium Scrap Container in Z Plant on October 9, 1980." December 1980.
12. WHC-SD-CP-TRP-067, G. R. Wittman, "Plutonium Inventory Characterization Technical Evaluation Report," EDT 609908, dated July 1, 1996.
13. WHC-SD-CP-TRP-068, G. R. Wittman, "Plutonium Inventory Characterization Technical

- Evaluation Report 2," EDT 609909, dated August 30, 1996.
14. HNF-SD-CP-TRP-070 (DRAFT), E. P. Bonadie and G. R. Wittman, "Plutonium Inventory Characterization Technical Evaluation Report 3," 1996.
 15. WHC-SD-CP-TRP-065 (DRAFT), "Plutonium Inventory Characterization Technical Evaluation Report Appendix," Rev. 0, dated July of 1996.
 16. L. H. Rodgers, "PFP Liquid Inventory," 15500-96-LHR-024, dated May 1, 1996.
 17. Presentation graph, "Plutonium Metal Weight Gains," R. Szempruch.
 18. Internal Letter, W. J. Anderson, to File, "Evaluation of Internal Pressure in Food Pack Cans during Storage and Shipment of Plutonium Oxide," 65240-79-150 R1, dated October 26, 1979.
 19. DNFSB/TECH-1, "Plutonium Storage Safety at Major Department of Energy Facilities," Defense Nuclear Facility Safety Board, Washington, D.C., April 14, 1994.
 20. Operating specifications document (OSD-Z-184-00013), "Special Nuclear Material Storage," Plutonium Finishing Plant, Richland, WA, Jan 1998.
 21. Operating procedure (Z0-200-032), "Monitor For Pressurized Or Suspect Containers," Plutonium Finishing Plant, dated 30 July 1998.
 22. Plutonium Retrieval System (PRE, safeguards computer database).
 23. WHC-CM-4-50, Safeguards Accounting Manual, Section Appendix B, Rev 4, "Table B-8. Category Code Listing," dated September 2, 1991.
 24. ccMail, T. J. Venetz to K. R. Herzog, "Comments on Risk Write-up," dated April 16, 1998.
 25. Paper, "Poorly Measured Items," Westinghouse Hanford Company, dated 1996.
 26. Document, K. R. Herzog, "Herzog Request on Containers, [Receipt date before October 31, 1981]," dated July 1998.
 27. Operating Specifications OSD-Z-184-00013 Rev G-0, L. A. Garner, "Special Nuclear Material Storage," dated November 5, 1992.
 28. WHC-SD-CP-SAR-021, "Plutonium Finishing Plant Final Safety Analysis Report,"

- Revision O-J, Westinghouse Hanford Company, dated 1995.
29. Standard Operating Procedure ZO-160-032 Rev B-1, S. Laguna, "Document Acceptance Review Form: *Stabilize Reactive Scrap*," dated July 23, 1982.
 30. Document, H. H. Van Tuyl, "Packaging of Plutonium for Storage or Shipment," dated March of 1981.
 31. Chart, J. Compton, "Comparison of Rusted Cans to their Run Conditions Prototype Calcliner," dated May 26, 1998.
 32. Letter BWHC-9756810, E. P. Bonadie, to L. J. Olguin, "Review of Internal Staff Technical Questions Regarding Special Nuclear Material Storage," BWHC-9756810, dated August 1, 1997.
 33. Internal Memo 12242-88-JHK-051, C. S. Sutter to File RE 5.4.1 OSD-Z-184-00013 "Basis For OSD-Z-184-00013 Loss-On-Ignition Specification"
 34. CSAR 79-010, 79-011, and 79-030, "Criticality Safety Analysis Report for RHO-MA-165 Criticality Specifications 80.10 and 80.11 (L-10 and FL-10 Containers Only), Criticality Safety Analysis Report for RHO-MA-165, Criticality Specifications 80.10 and 80.11 (10L Container Only), Criticality Safety Analysis Report for RHO-MA-165, Criticality Prevention Specification 80.10," dated 31 January 1979, 2 February 1979, and 24 July 1979.
 35. Conversation with R. Szempruch.
 36. Conversation D. Bogen.
 37. Conversation with J. Price.
 38. Conversation with R. Redekopp.
 39. DOE-STD-3013-94, "Criteria for Safe Storage of Plutonium Metals and Oxides," U.S. Department of Energy, December 1994.
 40. ccMail, C. M. Kronvall to R. D. Redekopp, "Regarding another pressurized container...", dated August 6, 1997
 41. J. M. Haschke and T. E. Ricketts, "Plutonium Dioxide Storage: Conditions for Preparation and Handling," LA-12999-MS/UC-721 & UC-722, Los Alamos National Laboratory, issued August of 1995.

42. cc:Mail, T. Venetz to K. Herzog, "RE: Pu Vulnerability Update," dated July 17, 1998.
43. Conversations with M. Gibson December 14 and 28, 1998, and March 9, 1999.

Attachment A

PFM Plutonium Vulnerabilities

Vulnerability Identification Number	Description	Status	Reference
RL 3.1.3.1	Hydrogen generation in solution storage containers which are not vented	Reopened	Plutonium Working Group Report
RL 3.1.3.2	Plutonium stored in unstable forms	Open	Plutonium Working Group Report
3.1.3.2.a	SS&C is water reactive and may contain pyrophoric materials	Open	Section 3.2
3.1.3.2.b	Polycubes generate hydrogen and hydrocarbon gases	Open	Section 3.2
3.1.3.2.c	Plutonium/uranium metals and alloys may have formed pyrophoric nitrides and hydrides	Open	Section 3.2
3.1.3.2.d	Miscellaneous items in storage may contain pyrophoric plutonium metal or alloys	Open	Section 3.2.2
3.1.3.2.e	Cladding condition for non-FFTF fuel pins is unknown and may be degraded leading to possible water reactivity, pressure sensitivity, or pyrophoricity	Open	Section 3.2.2
3.1.3.2.f	Oxides from incompletely burned plutonium metal in storage may be forming pyrophoric plutonium hydrides and plutonium nitrides	Open	Section 3.2.2
3.1.3.2.g	Plutonium-bearing combustibles in storage may generate hydrogen and hydrocarbon gases	Open	Section 3.2.2
3.1.3.2.h	At least one container of pyrophoric plutonium metal turnings was found in storage. Others may exist	Open	Section 3.2.2
3.1.3.2.i	Plutonium bearing solutions in storage	Open	Section 3.2.2
3.1.3.2.j	Pre-1980 items in storage may not be fully stabilized	Open	Section 3.2.2
3.1.3.2.k	LOI may not provide a good indication of material stability	Open	Section 3.2.2
3.1.3.2.l	Unstable materials stored in glovebox	Open	Section 3.2.2
RL 3.1.3.3	Deterioration of storage containers (unknown package design life)	Open	Plutonium Working Group Report
3.1.3.3.a	Plutonium storage containers buckling inward	Open	Section 3.3.
3.1.3.3.b	Solution storage containers corroding and the design life not quantified.	Open	Section 3.3.
3.1.3.3.c	Seals (all) on some plutonium metal containers may be failing based on weight gains observed	Open	Section 3.3.

3.1.3.3.d	High temperatures and radiation conditions exist for some food pack cans which can lead to food pack can gasket failure	Open	Section 3.3.
3.1.3.3.e	Some mixed oxide containers are corroding the inner storage container	Open	Section 3.3.2
3.1.3.3.f	Plutonium-bearing solution storage containers are not being inspected on a periodic basis	Open	Section 3.3.2
3.1.3.3.g	Storage container life for chloride solutions is unknown because the chloride concentration is unknown	Open	Section 3.3.2
3.1.3.3.h	Some plutonium-bearing solution storage containers have not been adequately characterized. As such, the deterioration rate for these solution storage containers cannot be quantified.	Open	Section 3.3.2
3.1.3.3.i	The integrity of polybottles inside 99 of 431 plutonium-bearing solution storage containers is unknown	Open	Section 3.3.2
3.1.3.3.j	At least 5% of the inventory of plutonium metal has gained more than 5 grams indicating that some air-leakage is occurring	Open	Section 3.3.2
3.1.3.3.k	The VSIS system will not detect failures resulting from storage containers buckling inward, e.g., plutonium nitride formation	Open	Section 3.3.2
3.1.3.3.l	Inspection criteria do not exist for all PFP storage containers	Open	Section 3.3.2
3.1.3.3.m	Deterioration of glue holding the filters on the polycube storage containers	Open	Section 3.3
RL 3.1.3.4	Insufficient knowledge of packaging configuration and characterization of material.	Open	Plutonium Working Group Report
3.1.3.4.a	PFP inventory database (PRE) contains suspect data	Open	Section 3.4
3.1.3.4.b	PFP inventory data base categories are too broad and do not always contain useful characterization data. Different criteria have been applied to determine which materials are assigned to each category.	Open	Section 3.4
3.1.3.4.c	85 items are stored in shipping containers which have not been opened and inspected and/or assayed since receipt	Open	Section 3.4.2
3.1.3.4.d	Characterization data is not retained in a retrievable manner and does not appear to be maintained under configuration control	Open	Section 3.4.2
3.1.3.4.e	PFP has a few metal items stored in direct contact with plastic	Open	Section 3.4.2
3.1.3.4.f	PFP has metal items stored in the same air space as plastic	Open	Section 3.4.2

3.1.3.4.g	PFP storage specification allowed organic and epoxy coatings on the inside of storage containers for metal and alloys	Open	Section 3.4.2
3.1.3.4.h	Some plutonium-bearing solutions (33 items) have no identified disposition path and the hazards associated with these containers have not been evaluated	Open	Section 3.4.2
3.1.3.4.i	PFP procedures allowed storing plutonium with only a single contamination barrier	Open	Section 3.4.2
3.1.3.4.j	Despite low LOI, some containers of plutonium oxide produced by the prototype VDC had surface rust	Open	Section 3.4.2
3.1.3.4.k	Plutonium storage container design criteria were not consistently defined and implemented in the past	Open	Section 3.4.2
3.1.3.4.l	Not all solution storage criteria were designed to the same criteria, some were "emergency" fabricated using pipe with plates welded to the ends	Open	Section 3.4.2
3.1.3.4.m	Storage containers for plutonium may build-up hydrogen or other flammable gases causing the storage container to fail	Open	Section 3.4.2
RL 3.1.4.2	Reactive chemicals in PFP gloveboxes	Closed	Plutonium Working Group Report

