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ENGINEERING CHANGE NOTICE

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------------- A-7900 -------------

2. ECN Category (mark one)	3. Originator's Name. Organization, MSIN, and Telephone No.		4. USQ Required?	5. Date
Supplemental[] Direct Revision [X] Change ECN [] Temporary [] Standby Supersedure Cancel/Void []	H.R. Risenmay, Stabilization, T5-55, 373-3503		[X] *Yes* [] No	June 12, 2001
	6. Project Title/No./Work Order No.		7.Bldg./Sys./Fac.No.	8.Approval Designator
	Thermal Stabilization		PFP/73T/234-5Z	QS
	9. Document Numbers Changed by this ECN (includes *sheet* no. and rev.)		10. Related ECN No(s).	11. Related PO No.
	HNF-SD-CP-OCD-040. Rev. 3		N/A	N/A

12a. Modification Work	12b. Work Package No.	12c. Modification Work Complete	12d. Restored to Original Condition (Temp. or Standby ECN only)
[] Yes (fill aut Blk. 12b) [X] No (NA Blks.12b, 12c, 12d)	N/A	N/A	N/A
		Design Authority/Cog. Engineer Signature & Date	Design Authority/Cog. Engineer signature & Date

The referenced document was changed to include section on stabilized material packaged for bagless transfer with accompanying addendum. A letter that states that alloy processing is bounded by metal processing was also added as an addendum.

14a. justification (mark one)

Criteria Change[X]	Design Improvement[]	Environmental[]	Facility Deactivation[]
As-Found []	Facilitate Const[]	Const. Error/Omission[]	Design Error/Omission[]

14b. Justification Details

In order to package stabilized material for bagless transfer the applicable documentation needed to be updated. The referenced document is the basis document for the operating specifications for thermal stabilization and a new section for the specifications related to bagless transfer of stabilized material was added.
For the USQ see the comprehensive USQ for Oxide into BTC PFP-2001-14.

15. Distribution (include name, MSIN, and no. of copies)
See Distribution Sheet

RELEASE STAMP

JUN 18 2001

DATE:

STA: 5

HANFORD RELEASE

(12)

ID:

App 6-15-0

16. Design verification Required	17. Cost Impact					18. Schedule Impact (days)	
	ENGINEERING		CONSTRUCTION				
[] Yes	Additional	[] $	Additional	[] $		Improvement	[] N/A
[X] No	savings	[] $ N/A	Savings	[] $ N/A		Delay	

Block 20.

SDD/DD	[]	Seismic/Stress Analysis	[]	Tank Calibration Manual	[]
Functional Design Criteria	[]	Stress/Design Report	[]	Health Physics Procedure	[]
Operating Specification	[X]	Interface Control Drawing	[]	Spares Multiple Unit Listing	[]
Criticality Specification	[]	Calibration Procedure	[]	Test Procedures/Specification	[]
Conceptual Design Report	[]	Installation Procedure	[]	Component Index	[]
Equipment Spec.	[]	Maintenance Procedure	[]	ASME Coded Item	[]
Const. Spec.	[]	Engineering Procedure	[]	Human Factor Consideration	[]
Procurement Spec.	[]	Operating Instruction	[]	Computer Software	[]
Vendor Information	[]	Operating Procedure	[X]	Electric Circuit Schedule	[]
OM Manual	[]	Operational Safety Requirement	[]	ICRS Procedure	[]
FSAR/SAR	[]	IEFD Drawing	[]	Process Control Manual/Plan	[]
Safety Equipment List	[]	Cell Arrangement Drawing	[]	Process Flow Chart	[]
Radiation Work Permit	[]	Essential Material Specification	[]	Purchase Requisition	[]
Environmental Impact Statement	[]	Fac. Proc. Samp. Schedule	[]	Tickler File	[]
Environmental Report	[]	Inspection Plan	[]	None	[]
Environmental Permit	[]	Inventory Adjustment Request			

20. Other Affected Documents: (NOTE: Documents listed below will not be revised by this ECN.) Signatures **below** indicate that the signing organization has been notified of other affected documents listed below.

Document Number/Revision	Document Number/Revision	Document Number Revision
OSD-Z-184-00006	ZO-160-044	
OSD-Z-184-00045		

21. Approvals

Signature	Date	Signature	Date
Design Authority H.R.Risenmay	6-6-01	Design Agent	
Cog. Eng. H.R.Risenmay		PE	
Cog. Mgr. R.A. Burk	6/11/1	QA	
QA D.R.Groth	6-07-01	Safety	
Safety S.E.Nunn	6-2-01	Design	
Environ.		Environ.	
Other.		Other	

DEPARTMENT OF ENERGY

Signature or a Control Number that tracks the Approval Signature

ADDITIONAL

UNREVIEWED SAFETY QUESTION (USQ)

Jentification Number: PFP-2001-14	**USQ EVALUATION**	**Page** 1 of 6

Title: Document Changes Required for Implementation of Safety Basis Changes Authorized by Safety Evaluation Reports for 2736-ZB JCO/Plutonium Oxides Powders in Bagless Transfer System and Increase in Glovebox HC-230C-3 and HC-230C-5 Inventory Limits for Magnesium Hydroxide Precipitation Process.

DESCRIPTION:
DOE-RL recently issued Safety Evaluation Report (SER) amendments to the PFP Final Safety Analysis Report, HNF-SD-CP-SAR-021 Rev. 2. The Justification for Continued Operations for 2736-ZB and plutonium oxides in BTCs Safety Basis change (letter DOE-RL ABD-074) was approved by one of the SERs. Also approved by SER was the revised accident analysis for Magnesium Hydroxide Precipitation Process (MHPP) gloveboxes HC-230C-3 and HC-230C-5 containing increased glovebox inventories and corresponding increases in seismic release consequence. Numerous implementing documents require revision and issuance to implement the SER approvals.

The SER authorizing plutonium oxides into BTCs specifically limited the SER authorization scope to "'pure' or clean oxides, i.e., 85 wt% or grater Pu, in this feed change" (SER Section 3.0 Base Information paragraph 4 [page 11]). Comprehensive USQ Evaluation PFP-2001-12 addressed the packaging of Pu alloy metals into BTCs, and the packaging of Pu alloy oxides (powders) into food pack cans and determined that the activities did not represent an USQ. The same information used to make the PFP-2001-12 negative USQ determination is applicable to packaging Pu alloy powders (DOES NOT INCLUDE STABILIZED MHPP MATERIALS OR OXIDES OF MOLYBDATES) into BTCs. Information from USQ Evaluation PFP-2001-12 is included in this USQ Evaluation for packaging of relatively pure Pu oxides and Pu alloy oxides into BTCs.

INTRODUCTION:
Comprehensive USQ Evaluation PFP-2001-12 addressed the packaging of Pu alloy metals into BTCs, and the packaging of Pu alloy oxides (powders) into food pack cans and determined that the activities did not represent an USQ. The same information used to make the PFP-2001-12 negative USQ determination is applicable to packaging Pu alloy powders. Information from USQ Evaluation PFP-2001-12 is included in this USQ Evaluation for packaging of Pu alloy oxides into BTCs.

Numerous implementing documents require revision to implement changes authorized by the SERs. These documents and description of changes are:

HNF-SD-CP-SAR-021. Rev. 2 - Supplemental ECN written to:
- add MHPP inventory increase dose consequence to Table 2-5,
- add the MHPP gloveboxes to Table *5-5,*
- revise the release consequence discussion in Section 9.2.4.10 to reflect the increased glovebox inventories,
- add MHPP inventory increase dose consequence to Table 9-1,
- add the MHPP gloveboxes and maximum Pu allowed values to Table 9-25, and revise Tables 9-31 and 9-33 to reflect the increased release quantities and dose consequences.

WHC-SD-CP-OSR-010, Rev. 0-Q - Because the OSR changes were reviewed and approved by DOE-RL, a USQ evaluation of the document changes is not required by procedure, but it is included here for completeness.
- The complete ZB fire hazard analysis JCO Limiting Condition for Operation (LCO) and Administrative Controls (ACs) set and OSR Appendix C discussion of fire protection procedures approved by the JCO SER is added to the OSR as revision 0-R.
- The MHPP SER authorized increase in maximum plutonium allowed in gloveboxes HC-230C-3 and HC-230C-5 is added to OSR AC 5.22 Table 5.22.1 and the effective date of criticality prevention specifications referenced is updated to June 2001.

HNF-SD-PRP-HA-002 is revised to include a discussion of the ZB fire scenario contained in the drafl fire hazard analysis document and the ZB JCO. The discussion provides the basis for a revised emergency preparedness action level for fire in 2736-ZB.

UNREVIEWED SAFETY QUESTION (USQ)

CPS-Z-165-80101, "Flat-Bed and Fixed Array Wagons" - Revised to add:
- up to 4,400 g nonmetal allowed in a BTC/3013,
- cans must be closed before entering the wagon position,
- allow movement of one container over top of another during loading/unloading,
- no more than 25 wagons parked in one array,
- U-235 restricted to 50 wt% if U H/X >2,
- Five wagons, 2 position wagons, or lard can wagons can be intermixed in an array,
- fissionable material ≥ 100 g Pu no closer to receptacles than wagon edge except during loading/unloading wagon,
- minimum of 18 inch spacing from transition operations except for loading/unloading wagon,
- minimum 18 inch spacing from wagon array and fissionable material ≥ 100 g except when moving a wagon into or out of an array,
- one item may be left unattended or, one wagon left unlatched as the result of off-normal or emergency situations. The loose item is to be spaced according to General Storage, Transition, and Transportation limits. This item is to be placed into an approved storage location during recovery from the off-normal or emergency event.

The changes to CPS-Z-165-80101 have been reviewed against and written to be consistent with CSER 99-005. The Criticality Safety Representative, Criticality Safety Engineer, and independent Nuclear Safety Engineer have approved the CPS as compliant with CSER requirements and assumptions.

CPS-2-165-80642 "Glovebox HC-230C-3 and HC-230C-5" - Revised to:
- delete the # of poly jars that may be used to load precipitate instead of furnace boats,
- split out Glovebox HC-230C-3 Mass and Container limits out into Limit Sets A and B depending upon the types of containers in use, both limit sets increasing the maximum glovebox mass to 16,500 g as approved by the MHPP SER,
- split out the Glovebox HC-230C-5 Mass and Container limits into Limit Sets A and B depending upon the types of containers in use, both limit sets increasing the maximum glovebox mass to 7,100 g as approved by the MHPP SER,
- added poly-jars to process controls spacing limits with the HC-3 conveyor glovebox.
- poly jars are to be handled one at a time or in a poly-jar rack,
- added section on dealing with filtrate.

The changes to CPS-2-165-80642 have been reviewed against and written to be consistent with CSER 00-003 (HNF-6537), CSER 00-026 (HNF-7548), CSER-00-001 and technical adequacy determination forms. The Criticality Safety Representative, Criticality Safety Engineer, and independent Nuclear Safety Engineer have approved the CPS as compliant with CSER requirements and assumptions.

ZAP-000-003 for dispersible Pu inventory - Revised to incorporate the increased Glovebox HC-230C-3 and HC-230C-5 inventories.

ZAP-000-008 for periodic criticality safety inspection - Revised to:
- add PFP vault and room 638 and 641 combustible material accumulation inspection,
- reference to revised OSR AC 5.20.

OSD-Z-184-00013, Operating Specification for vault storage - Revised to:
- include the BTC lid deflection program required by OSR AC 5.25,
- to reflect the combustible material control inspections required by revised OSR AC 5.20

ZO-200-032 for periodic inspection of containers in vaults - Revised to incorporate the BTC lid deflection program contained in OSD-2-184-00013.

ZSE-23E-001 - new procedure issued to demonstrate compliance with new LCO 3.2.4.1 and Surveillance Requirements SRs 3.2.4.1.1, SR 3.2.4.1.2, SR 3.2.4.1.3. The procedure incorporates the SR requirements verbatim.

ZSE-23E-002 - new procedure issued to demonstrate compliance with new LCO 3.2.4.1 and Surveillance Requirement SR 3.2.4.1.6. The procedure incorporates the SR requirements verbatim.

ZSE-26A-001 - new procedure issued to demonstrate compliance with new LCO 3.2.4.1 and Surveillance Requirements SR 3.2.4.1.4, SR 3.2.4.1.5, and SR 3.2.4.1.7. The procedure incorporates the SR requirements verbatim

ZSE-26A-002 - new procedure issued to demonstrate compliance with new LCO 3.2.4.2 and Surveillance Requirements SR 3.2.4.2.1 through SR 3.2.4.2.8. The procedure incorporates the SR requirements verbatim.

ZO-160-044, Package Stabilized Material for Bagless Transfer. This is a new procedure, the same as ZO-160-034, except that it packages the stabilized oxide and mixed oxide (alloy oxides) material in a BTCC for welding into a BTC in the bagless transfer system. In the body of the procedure where ever Pu element weight is documented or calculated a duplicate set of instructions have been included for the U element weight. The procedure is written to be consistent with plutonium bearing material thermal stabilization descriptions contained in FSAR Chapter 6, and Chapter 9 abnormal events, accident analyses as modified by ECN 666901 (approved by the JCO SER) that makes FSAR changes to allow oxide packaging in addition to metal items in BTCs, and to be consistent with criticality prevention specification requirements for handling uranium in RMNRMC line gloveboxes.

OSD-Z-184-00045, Bagless Transfer Material Process. The changes are to add the words "or alloy" where "Pu metal" is found in the document to expand the application of the document to cover alloy processing, and to add packaging oxides or mixed oxides into a BTC.

HNF-SD-CP-OCD-040, Basis Document For Thermal Stabilization. Changes are to include new documentation for metal or alloy processing with basis for the operating specifications. The basis for including oxide into a BTC is covered.

Metal Oxide into BTC/3013 Blend Plan. This is a classified document that lists the metal oxide that was generated during the packaging of metal when a pyrophoric item was thermally stabilized and packaging for bagless transfer to vault storage. The Metal Oxide Blend Plan has not been issued a document number at this time.

Before issuance, the documents described above must be reviewed and approved by one or more qualified USQ evaluators to verify document changes are within the scope of this USQ Evaluation.

AFFECTED SSC:
Affected systems, structures, and components include the entire 2736-ZB Building structure and contents, 2736-ZB fire sprinkler and detection and alarm systems, PFP radiological facilities where flat bed and fixed array wagons are present, Magnesium Hydroxide Precipitation Process gloveboxes HC-230C-3, HC-230C-5 and the HC-3 conveyor glovebox in 234-52 Room 230-C. 234-5Z RMC and RMA Line areas where oxides and mixed oxides are processed into BTCs, PFP areas where BTCs are stored or staged, and PFP facility radiological areas affected by revised combustible control program requirements.

Technical expert assessment has determined that Pu alloy oxides, with exception of molybdates, behave the same as relatively pure Pu oxides when packaged. The changes have been screened or otherwise evaluated for criticality safety and nuclear safety impacts, and the changes have been authorized by Safety Evaluation Report. Technical expert assessment has determined that Pu alloy oxides, with exception of molybdates, behave the same as relatively pure Pu oxides when packaged. Therefore no measurable adverse effects upon the SSCs is postulated.

SAFETY BASIS:
The Safety Basis documents listed in FSP-PFP-5-8 Section 2.23 Appendix A applicable to the changes are:
HNF-SD-CP-SAR-021, Plutonium Finishing Plant Final Safety Analysis Report Rev. **2** as appended by:
- Supplemental ECN 658096 incorporating the Magnesium Hydroxide Precipitation Process (MHPP) and Change ECN 660563 to MHPP ECN 658096.
- Supplemental ECN 665381 incorporating the Bagless Transfer System (BTS) process
 DOE/DP-0130 Supplement 6 approving the MHPP and Supplement 7 approving ECN 660563 to the MHPP.
WHC-SD-CP-OSR-010, Plutonium Finishing Plant Operational Safety Requirements, Rev. 0-Q.

In addition to the Safety Basis documents listed above, the following are also Safety Basis documents as defined in DOE and HNF Unreviewed Safety Question programs that are being implemented by the document changes:
■ DOE-RL letter 01-ABD-074, "Contract Number DE-AC06-96RL-13200 - Unreviewed Safety Question (USQ) "Fire Hazard Analysis for the Plutonium Finishing Plant (PFP) (Occurrence Report RL-PHMC-PFP-2001-001)" with attached Safety Evaluation Report supplement approving HNF-7616 Rev. 0, "Justification for Continued Operation for

UNREVIEWED SAFETY QUESTION (USQ)

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the 2736-ZB Building at the Plutonium Finishing Plant" and approving plutonium oxide powders to be processed in BTCs.

- DOE-RL letter 01-ABD-070, "Contract Number DE-AC06-96RL-13200 - Engineering Change Notice 666938 "Magnesium Hydroxide Precipitation Process" and attached SER supplement approving increased plutonium inventories in MHPP Gloveboxes HC-230C-3 and HC-230C-5.

The stabilization of Pu alloys will be incorporated in Rev 3 of the PFP FSAR or in a future ECN to Rev 3 of the FSAR

CONCLUSION:
Barney G. S. I T. D. Cooper letter to D. R. Speer, May 9, 2001, Water Reabsorption and Safety Questions on *Alloy* Stabilization, 1AC00-PPSL-01-24 Rev.1, Fluor Hanford. Inc., Richland Washington responded to the question on alloys listed below:

Are the alloys different enough from the high quality oxides to cause us to implement new controls to assure that moisture reabsorption won't cause the stabilized materials to exceed the 0.5% moisture criteria?

In response to question 1 [there were 2 questions **he** was asked to answer], it is concluded that the best information available on water reabsorption on calcined alloys indicates that significant amounts of water will not be absorbed on these oxides in the time required to handle them before repackaging them in the glove boxes. This the same conclusion as was reached for Pu metal oxides in Barney, G. S. (2001). Letter to T. W. Halverson, January 2, Water Readsorption Rates on Relatively Pure PFP Calcined *Plutonium* Dioxide, I ACOO-01-001, Fluor Hanford, Inc., Richland Washington. Therefore, water reabsorption of calcined alloys is considered the same as for calcined metals.

The document changes being made are within the PFP Safety Basis as established by the current FSAR as modified by outstanding engineering change notices, supplements to safety evaluation reports, approval letters, and the conclusions of this USQ Evaluation. The changes are within the scope of existing approved criticality safety analyses. All Evaluation questions are answered "No". No additional PRC or DOE approvals are required for the changes.

REFERENCES:
USQ Evaluation PFP-2001-12, "Stabilization of Pu Alloys"
Barney G. S. I T. D. Cooper letter to D. R. Speer, May 9, 2001, Water Reabsorption and Safety Questions on *Alloy Stabilization,* 1AC00-PPSL-01-24 Rev.1, Fluor Hanford. Inc., Richland Washington
Barney, G. S. (2001). Letter to T. W. Halverson, January 2, Wafer Readsorption Rates on *Relatively* Pure PFP Calcined Plutonium Dioxide, 1AC00-01-001, Fluor Hanford, Inc., Richland Washington.
CSER 00-026, "3 Boat Limit for Magnesium Hydroxide Glovebox 5
CSER 00-003, "CSER for Magnesium Hydroxide Process Glovebox 3"
CSER 00-001, "CSER for Cementation Operations at the PFP"
CSER 99-005, "CSER for Plutonium Transfer Wagon".

Instructions: to each   and   for each   A restatement of the question does not constitute a satisfactory justification or basis. An adequate justification provides sufficient explanation such that an independent reviewer could reach the same conclusion based on th   formati   provided.

1. Does the PROPOSED ACTIVITY or PISA increase the probability of occurrence of an accident previously evaluated in the Safety Basis?
   [X] No   [ ] Yes/Maybe

   Basis: Technical expert safety assessment has determine that for packaging purposes, Pu alloy oxides, with exception of molybdates, behave the same as relatively pure Pu oxides. The new documents and document changes listed above implement recently approved changes in the plant Safety Basis. In addition, field level implementing procedures and criticality prevention specification changes have been reviewed and by criticality safety staff documenting that the document changes are consistent with requirements and assumptions in applicable criticality safety evaluation reports. Because the documents implement and are consistent with recently approved by DOE Safety Basis accident analyses as modified by this USQ Evaluation, and are consistent with criticality safety

UNREVIEWED SAFETY QUESTION (USQ)

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evaluation report requirements and assumptions, there can be no increase in the probability of any accident previously evaluated in the Safety Basis.

Does the PROPOSED ACTIVITY or PISA increase the consequences of an accident previously evaluated in the Safety Basis?
[X] No   [ ] Yes|Maybe

Basis: The type of Pu powder being packaged into BTCs and 3013 containers does not affect the consequence of a burst container. Because the documents being issued or changed implement and are consistent with recently approved by DOE Safety Basis accident analyses as modified by this USQ Evaluation, and are consistent with criticality safety evaluation report requirements and assumptions, there can be no increase in the consequences of any accident previously evaluated in the Safety Basis.

Does the PROPOSED ACTIVITY or PISA increase the probability of occurrence of a malfunction of EQUIPMENT IMPORTANT TO SAFETY (ITS EQUIPMENT) previously evaluated in the Safety Basis?
[X] No   [ ] Yes|Maybe

Basis: Because the documents being issued or changed implement and are consistent with recently approved by DOE Safety Basis accident analyses as modified by this USQ Evaluation, and are consistent with criticality safety evaluation report requirements and assumptions, there can be no increase in the probability of occurrence of malfunction of ITS equipment previously evaluated in the Safety Basis.

Does the PROPOSED ACTIVITY or PISA increase the consequences of a malfunction of ITS EQUIPMENT previously evaluated in the Safety Basis?
[X] No   [ ] Yes|Maybe

Basis: Because the documents being issued or changed implement and are consistent with recently approved by DOE Safety Basis accident analyses as modified by this USQ Evaluation, and are consistent with criticality safety evaluation report requirements and assumptions, there can be no increase in the consequence of occurrence of malfunction of ITS equipment previously evaluated in the Safety Basis.

Does the PROPOSED ACTIVITY or PISA create the possibility of an accident of a different type than any previously evaluated in the Safety Basis?
[X] No   [ ] Yes|Maybe

Basis: The only accident of a different type represented by the document changes is a BTC containing Pu oxide or Pu Alloy oxide with a significant (> 0.2%) water content bursting due to the influence of heat or flame from a fire. The JCO and SER approved FSAR ECN analyze this event. Technical expert safety assessment has determined that Pu alloy oxides, with exception of molybdates, present no more hazard than relatively pure Pu oxide. Because the documents being issued or changed implement and are consistent with recently approved by DOE Safety Basis accident analyses as modified by this USQ Evaluation, and are consistent with criticality safety evaluation report requirements and assumptions, there is no possibly of an accident of a different type than previously evaluated in the Safety Basis represented.

Does the PROPOSED ACTIVITY or PISA create the possibility of a malfunction of ITS EQUIPMENT of a different type than any previously evaluated in the Safety Basis?
[X] No   [ ] Yes|Maybe

Basis: The only accident of a different type represented by the document changes is a BTC containing plutonium oxide with a significant (> 0.2%) water content bursting due to the influence of heat or flame from a fire. The BTC bursting would be a malfunction of ITS equipment. The JCO and SER approved FSAR ECN analyze this event. Technical expert safety assessment has determined that Pu alloy oxides, with exception of molybdates, present no more hazard than relatively pure Pu oxide. Other documents being issued either have no affect upon, or enhance the performance of ITS equipment (e.g., LCOs and SRs on the fire systems to assure their operability). Because the documents being issued or changed implement and are consistent with recently approved by DOE Safety Basis accident analyses as modified by this USQ Evaluation, and are consistent with criticality safety evaluation report requirements and assumptions, there is no possibly of a malfunction of ITS equipment of a different type than previously evaluated in the Safety Basis represented.

UNREVIEWED SAFETY QUESTION (USQ)

Identification Number: 'FP-2001-14	**USQ EVALUATION (continuation)**	**Paae 6 of 6**

. Does the PROPOSED ACTIVITY or PISA reduce a margin of safety?
[X] No   [ ] YeslMaybe

Basis: The FSAR, HNF-SD-CP-SAR-021 (including supplemental ECN 662390, Tank 241-Z-361 Addendum), the OSR. WHC-SD-CP-OSR-010, and the SER, DOEIDP-0130, however, use different terms like "margin of safety", "safety margin", "margin of strength". "margin of protection" and "margin of subcriticality" or "subcritical margins" in an entirely different context to refer to:

- general safety for the public, i.e., in the remoteness of the site and the ability to control access (see FSAR Section 2.1.2),
- structural resistance of components to natural forces (see FSAR Sections 5.2.2.1.2, 5.2.8.1.1, 5.2.8.2.1, 5.2.8.3.1, 9.2.4.1.1, and 9.2.8 and SER Appendix A and SER section 9.2.4A.1),
- analysis of effects and consequences of excessive building pressurization (see FSAR Sections 9.1.7A.3.3, 9.1.7B.3.2, 9.1.7C.3.2, and 9.1.7D.3.2),
- analysis of effects and consequences of loss of ventilation (see FSAR Section 9.1.8.3.3),
- hydrogen flammability potential in PR cans (see FSAR Sections 9.1.2A, 9.1.2A.1.4),
- evaporation analysis of chemicals from the 2735-Z retention basin (see FSAR Section 9.2.8 and SER Appendix A), and,
- criticality safety and criticality safety evaluations (see FSAR Sections 4.4.4.2, 6.2.9.1, 6.2.9.1.1, 6.2.9.1.2, 6.4.2.9.1, 9.2.4.2.11.J, 9.2.4.2.11.M. Appendix 9F-Table 9F.2, Table 9F.15, Table 9F.21, Appendix QG-Table 9G.2 and OSR Appendix C - Feature 4 and SER section 11.6).

There are no other implied margins of safety discussed in any of the Safety Basis documents. The packaging of Pu alloy oxides, with exception of MHPP products and molybdates, into BTCs and 3013 containers, and issuance of new documents and document changes needed to implement SER approvals for oxides in BTCs and increases in MHPP glovebox inventories do not affect general public safety or structural strength or ventilation system upsets or hydrogen flammability in PR cans or the 2735-Z retention basin or the margins of subcriticality in existing criticality safety limits derived from approved criticality safety evaluations, or any perceived margins of safety contained in the ZB FHA JCO and SERs. Therefore none of these perceived "margins of safety" are reduced.

JSQE #1 _J. P. King_
(Print Name)
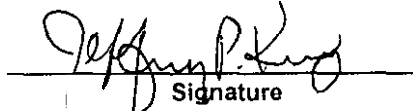
Signature   Date: _6/6/01_

USQE #2 _DR GROTH_
(Print Name)

Signature   Date. _6 07-0J_

PRC REVIEW (If Required)

Meeting No.: _____   Date _____

PRC has determined the Proposed Activity or PISA involves a **USQ:** [ ] No   [ ] YeslMaybe

PRC Chairman Concurrence: _____   Date: _____
Signature

Fluor Hanford, Inc.
TS-12
Richland, WA 99352

373-2419 phone
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gary_s_scott_barney@rl.gov

FLUOR GLOBAL SERVICES

Memorandum

To:	D. R. Speer	**Date:**	May 9, 2001
Location:	T5-50	**Reference:**	1AC00-PPSL-01-24Rev.1
Telephone:	373-1110	**Client:**	
From:	G. S. Barney/ T. D. Cooper	**Subject:**	WATER REABSORPTION AND SAFETY QUESTIONS ON ALLOY STABILIZATION
Location:	T5-12		

cc: J. R. Ewalt
     L. F. Perkins

The purpose of this letter is to provide responses to questions you had concerning stabilization of the alloy items. The questions are listed below:

1. Are the alloys different enough from the high quality oxides to cause us to implement new controls to assure that moisture reabsorption won't cause the stabilized materials to exceed the 0.5% moisture criteria?

2. Are the alloys different enough from the metals to cause us to implement new controls to manage the hazards associated with opening and stabilizing them?

Our responses are as follows:

Water Reabsorption on Stabilized Plutonium-Uranium Alloy Items (G. S. Barney)

Stabilization treatment of the Pu-U metal alloys items in the PFP production furnaces will yield a mixture of oxides that will absorb small amounts of moisture from the humid glove box air in contact with the oxides. The objective of this summary **is** to estimate the amount of water that might be reabsorbed over a reasonable time period for exposure to glove box air. This must be less than 0.5 wt. percent to meet the 3013 Standard. According to literature references the oxides produced by heating the alloys in air at 1000°C **will** be a mixture of PuO_2, U_3O_8, U_3O_{8-x}, **and** possibly UO_3 (Haschke et al., 1997). For alloys containing molybdenum, molybdates of plutonium and uranium would also be expected. Plutonium dioxide fired at 1000°C has been shown to absorb very small amounts of water. The equilibrium water content of pure PuO_2 treated by the 3013 Standard will be typically less than 0.2 wt. percent (Barney, 2001). Equilibrium with the glove box air will be reached in several hours.

Date   May 23, 2001
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Information on adsorption of water on the other oxides is much more scarce. Equilibrium thermodynamic calculations (Taylor et al., 1993) show that at 25°C, all of the uranium oxide products listed above, **are** unstable in glove box air. This instability is caused by *the* adsorption of water to form $UO_3 \cdot 2H_2O$ and β-$UO_2(OH)_2$. Formation of these hydrated compounds is no doubt very slow, since U_3O_8 is used **as** a primary standard for uranium gravimetric analyses (Greenwood and Earnshaw, 1985). The most relevant moisture absorption data that was found was **for** a sample of mixed oxide fuel (UO_2-PuO_2) that **was** calcined at 750°C for three hours and then exposed to glove box air (Kerraker, 1995). After nine days the weight gain was determined to be 0.10 wt. percent and leveled off at this **value** for **three** more days. X-ray diffraction analysis of this sample showed that not all of the solid solution of the cubic dioxides was converted to PuO_2 + U_3O_8 even after heating at 900°C for one hour in air.

A Chinese article (Feng and Chen, 1986) reports that during storage of U_3O_8, increases in weight were observed due to formation of hydrates by reaction with atmospheric water. The method of preparation and length of storage was not specified in the abstract, so the information is of little value.

Although most molybdates are non-hygroscopic, the compound, $Y_2Mo_3O_{12}$, hydrates in air to form $Y_2Mo_3O_{12} \cdot 4H_2O$ (Fournier et al., 1970). Yttrium is a rather **rare** element and is not **known** to exist in our alloy inventory, therefore, $Y_2Mo_3O_{12}$, is not anticipated in the oxide product. No information on water absorption on plutonium or uranium molybdates was found. We therefore cannot state with certainty the degree of moisture readsorption that will occur on plutonium or uranium molybdates. Readsorption of moisture on plutonium or uranium molybdates is not expected to be a significant phenomenon, however if it occurs, the extent of readsorption will be bounded by the readsorption behavior of MgO found in the product from the magnesium hydroxide process. Several tests with CeO_2 as surrogate plutonium dioxide along with molybdenum oxide would help to identify any readsorption problems. These tests could be performed in the PPSL in a relatively short time.

In conclusion, the best information available on water reabsorption on calcined alloys indicates that significant amounts of water **will** not be absorbed on these oxides in the time required to handle them before repackaging them in the glove boxes. Only 0.10 weight percent water was reabsorbed on a calcined MOX sample over 12 days.

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Safety Review for Handling Pu Alloy Materials (T.D. Cooper)

The Plutonium Finishing Plant (PFP) is tasked with ensuring the stability of plutonium (Pu) bearing materials within the PFP vaults. PFP has already gone through a safety review for handling plutonium metal and plutonium metal corrosion products that lasted several years. Numerous attempts to prove the safety in handling these materials through theoretical and mathematical analysis failed due to the complex nature of these problems and lack of data. We finally resorted to documenting the extensive history of processing throughout the DOE complex and the historical safety for handling kg sized samples of metal as buttons and/or ingots and up to 200 grams of pure plutonium hydride within a glovebox. This documentation is contained in the Denver Workshop notes and in several letters prepared by T. D. Cooper.

In addition to pure plutonium metal, PFP also possesses many metal alloy items wherein Pu is alloyed with other metals such as aluminum, molybdenum, etc. The question has been raised as to the safety of handling these alloys and their relative hazard as compared to Pu.

Plutonium forms a spallable oxide coating that allows continuing oxidation. It is also more electronegative than many other alloying metals. The rather large reaction enthalpy and the relatively fast surface reaction rates, results in large temperature increases. This temperature increase also serves to drive the reaction rates.

The factors affecting the reaction rate of an element are the inherent reactivity of that element, the reactant concentrations, the temperature, the specific surface area, and the presence of catalytic agents.

Since Pu is the primary reactant within the alloy the concentration will always be less than in pure plutonium metal. As a general rule of thumb, an alloy's reactivity follows the reactivity of the dominant metal in the alloy.

The reaction temperature for alloys will typically be less than for pure plutonium metal. Factors that could increase the alloy reactivity are high specific surface area, and/or the presence of catalytic agents.

From the above discussion, one can see that for items of similar specific area, the behavior of pure plutonium bounds the behavior of the alloys. We can thus adopt the same general rules for handling alloys as currently exist for handling Pu metal.

These rules are:

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- Handling kg -sized monoliths with the glovebox is permissible,

- Up to 200 grams of potentially reactive powder is permissible

Adequate rules for handling large quantities of turnings and shavings of Pu metal within the glovebox have not been promulgated. This **area** will now be discussed.

It is known (Ref. 1) that any configuration of metal is safe as long as it remains within a standard slip lid can with a diameter less than **5** inches. Natural diffusion or convection rates into this container cannot move oxygen fast enough to cause unacceptable pressures or temperatures to arise within the glovebox.

If metal with high specific surface area is removed from the can, and the metal heats pyrophorically, the main heat transfer path is through conduction through the bottom and radiation to the remainder of the glovebox. Air is notoriously inefficient in absorbing radiation energy since only a very **small** percentage of the gas molecules are poly-atomic. Modeling shows that the increase in temperature of the glovebox is limited to less than 75 °C for a **2** kg sample assuming instantaneous and evenly distributed heat transfer. Since the combustion event is not instantaneous, it is very unlikely that the glovebox temperature increase would exceed 10 °C. The glovebox pressure never departs from the normal negative regime, for any condition other than very fine powder being explosively distributed throughout the air.

We therefore conclude that with the exception of the fine powder case, less than 2000 grams of Pu metal or any of its alloys (in any configuration) has been analyzed and cannot increase the general temperature of a typical C-Line glovebox beyond 75 °C. **This** 2000 gram value is not meant to be an absolute limit. Larger amounts in specific configurations will be permissible with appropriate analysis. For fine pyrophoric powders, **an** experience-based limit of *200* grams is used.

Reference:

1. Letter 15F00-99-054, " Scientific Evaluation Of Safety In Processing Pu Metal", Thurman Cooper, May **25,** 1999

Basis Document for Thermal Stabilization

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Project Hanford Management Contractor for the
U.S. Department of Energy under Contract DE-AC06-96RL13200

Fluor Hanford
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Flour Hanford. Inc.

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BASIS DOCUMENT FOR THERMAL STABILIZATION

CHANGE CONTROL RECORD			
(3) Revision	(4) **Description** of Change - **Replace,** Add, and Delete Pages	Authorized for **Release**	
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4 **RS**	Added section 8, Plutonium Bearing Material for Bagless Transfer; Attachment F, Lead Nitrate Reactions in Scrap Heels; Attachment G, Bagless Transfer For Plutonium Oxides. *Per EcN 665398* *ARY 6-15-01*	H.R.Risenmay *H.Res Risening* *6-6-01*	R.A. Burk *RAburk* *6/11/1*

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1.0 INTRODUCTION

The HC-21C and HA-211 gloveboxes will be used to stabilize plutonium bearing material. This will be accomplished by heating plutonium oxide, plutonium metal or alloy, magnesium hydroxide precipitated plutonium or plutonium/uranium oxide/hydroxide, reactive incinerator ash, oxalate precipitated plutonium or plutonium/uranium, plutonium oxalate conversion product (oxycarbonate from previous processing in RMN RMC lines), and ~~PRF and other organic (~~tributyl phosphate) bearing sludges.~~, plutonium oxide, reactive incinerator ash, plutonium metal, and plutonium oxalate conversion product (oxycarbonate)~~. Heating to a temperature of $1000\,^{\circ}C$ in an air stream will drive off residual volatile components and convert residual plutonium~~-organic~~ bearing materials to PuO_2.

This technical basis covers the Operation Specification Document (OSD-Z-184-00006) and explains the limits necessary for criticality prevention, protection of personnel and environmental safety, minimizing equipment damage, and attempting to maximize process efficiency.

The following equipment, along with associated instrumentation, interlocks, piping, etc., is covered.

Equipment

- Furnace
- Temperature Controller
- Temperature Alarm Switches
- Off-gas Filter
- Sieve

2.0 Feed Specifications

2.1. Feeds Permitted

Limit: Plutonium oxide, plutonium metal or alloy, magnesium hydroxide precipitated plutonium or plutonium uranium oxide hydroxide, oxalate precipitated plutonium or plutonium/uranium, tributyl phosphate (TBP) bearin& ~~sludges,~~ ~~from other wet process gloveboxes,~~ ~~plutonium oxide,~~ plutonium oxalate (oxycarbonate from previous processing in RMA/RMC lines), ~~plutonium metal~~ and incinerator ash. Glovebox HA-211 cannot be used to process ~~plutonium metal or~~ any material that may ~~have organic content~~ contain TBP, i.e., PRF sludge and sludges from other wet process gloveboxes ~~that may contain tributyl phosphate (TBP)~~.

Basis: Processing has been limited to the above feeds because analysis has shown the off-gases produced will not be a safety hazard.

Plutonium metal items will be oxidized at 550 degrees C, a temperature below the melting point of the metal. This is done to prevent the molten plutonium metal from forming an alloy with the boat material, which could melt a hole in the bottom of the boat. Plutonium alloys should be bounded by the metal processing as described in the Barney/Cooper Letter on Processing Plutonium Alloys as found in Appendix I.

Magnesium hydroxide precipitated plutonium or plutonium/uranium oxideihydroxide will have been dried on a hot plate to remove the water before processing in the furnaces. The furnaces will be run on the programming used for TBP type organic bearing sludges to t'urther dry the material before thermal stabilization.

Testing of the oxalate precipitation process for solution stabilization by PPSL has shown that the filter cake dries on the hot plate without boiling and just gives off steam during the process. The dried filter cake is then very tine powder that is loaded into the boat for thermal stabilization at 1000 degrees C. In the regular production process for this material the sludge program will be used to thermally stabilize the dried oxalate precipitate to ensure that the drying process is complete before ramping the furnace on up to 1000 C.

Glovebox HA-211 is not equipped with a CO_2 purge system, and therefore, it cannot be used to process any item that may contain ~~organic material~~ (TBP). ~~The Authorization Basis does not allow plutonium metal to be processed in Glovebox HA-211.~~

Over time the Pu Oxalate (that was produced in previous processing in the RMNRMC lines) will degrade to PuOCO, $2H_2O$ (plutonium oxycarbonate) with a reaction half-life of 64 days. Considering the length of time the oxalate has been in storage (in excess of 4 years), this results in essentially all of the oxalate having degraded to the carbonate form. (Reference: The Chemistry of Plutonium, J. M. Cleveland, pages 407-408)

Incinerator ash is primarily made of material from the Rocky Flats incinerator. A small portion of the material is from the 232-Z incinerator. The ash contained an average of 22% carbon and therefore was re-burned in glovebox HA-40F to remove the carbon. A portion of the material was not processed in HA-40F and this material will be stabilized in the muffle furnaces.

The material that came from Rocky Flats is broken into three categories, Old, Middle and Current. The Old material typically has the high carbon content (up to 42%) and the lowest plutonium content. The Current material typically has the lowest carbon content and the highest plutonium content.

A potential concern with the incinerator ash from Rocky Flats is the presence of lead in the form of lead nitrate which can react violently with graphite. TGA/DTA testing performed with lead nitrate in the presence of graphite indicated that only a small exothermic reaction occurred between $340°C$ and $420°C$ (Appendix H). The material was heated to over $450°C$ prior to being shipped to Hanford, therefore the presence of lead nitrate is not expected.

Any other feeds will be evaluated by PFP Stabilization engineers on a case by case basis.

2.2. Feeds NOT Permitted

Limit: Plutonium bearing materials (PBM) with greater than 10 grams maximum TBP or its degradation products ——— in each charge.

Basis: Feed items that originated in PRF have a potential to contain tributyl phosphate (TBP). One of the decomposition products of TBP is butene. Butene, in certain concentrations, can be flammable. Controlling the organic content to ≤ 10 grams is one of the barriers which prevents butene generation from reaching flammable levels. (See Attachment A, Table 1 and Figures 1 and 2.)

The 10 gram TBP type organic limit is specified in the Addendum to WHC-SD-CP-SAR-021, Revision 0-K, "Plutonium Finishing Plant Final Safety Analysis Report", 1999, Section 5.2.2

2.3. Charge Size

Limit: Shall not exceed a charge depth in boat of 1 ½ inches or a mass of

- $\leq 1000g$ Pu for TBP bearing sludge material

- $\leq 500g$ reactive incinerator ash

- $\leq 2400g$ for Pu + U in metal and alloy items and magnesium hydroxide precipitated Pu or Pu/U oxidelhydroxide and oxalate precipitated plutonium or plutoniumiuranium

- ≤ 150-gram accumulations of Pu metal or alloy brushings with no more than 200 grams of brushings exposed to the air in the glovebox at any time.
  Exception
  Any amount of brushings from any one item are permitted to be processed together.

- Brushing accumulations may be mixed with >85% Pu product quality oxide or oxide from burned metal or alloy (including any residual metal) for processing.

- 2400 g of Pu for feed material except organic bearing sludge and reactive incinerator ash.

- , 1 ½ inches depth in the boat and

- a maximum amount of 10 grams TBP type organic in the charge.

Basis: Charge size (depth) was determined to allow for oxidation of the material in the boat and to allow for safe operation of the process. Safety calculations have been done using 20 grams TBP. If the charge size is limited to 10 grams TBP type organic, then the amount of butene gas generated during processing will be within safe limits (below flammability limits).

Laboratory tests showed that charges containing oxalate (oxycarbonate produced in previous processing in the RMA/RMC lines) liquefied and

foamed. The charge must fit into the boat, which has been designed to fit inside the furnace without interference with thermocouples or purge and vent lines. The boat allows generous free board to avoid boil over. CSER 94-007 and 94-008 assess the boat size for criticality and allows material to fully load the boat.

Feed material charges other than organic bearing sludges and reactive incinerator ash are limited to 2725g total weight with a restriction of 2400g Pu. The criticality limit for glovebox HC-21C is 5000g Pu when processing feed material with a H/X < 20. Reducing the boat charge size to 2400g from the CPS allowed 2500g allows 200g for the glovebox holdup. Typical glovebox holdup is around 50g Pu.

To eliminate the necessity of doing calculations to determine the allowable charge that meets the 2400g Pu limit that can be placed in a furnace boat during charge preparation, the maximum charge size will he based on a product quality oxide that contains about 88% Pu. This results in a maximum charge size of 2725g of material in each boat for stabilization.

3.0 Controller Specifications

3.1. Furnace Ramp Rate Settings

Limit: Maximum Furnace Ramp Rate

Temperature Range	Ramp Rate (C/hr)	SCR Output (Amps)
25 - 500	300	13
500 - 700	200	13
700 - 900	125	13
900 - 1000	75	13

Basis: The furnace is ramped up slowly to avoid damaging the furnace heating coils. The manufacturer recommends that the furnace should not he operated at full power (17 amps) for extended periods of time (over 4 hours). Process tests indicate that complying with the specified ramp rates will prevent overloading the heating coils. (See Attachment C), "Scrap Stabilization Furnace Test Results", WHC-SD-CP-TRP-059, J. A. Compton. April 5, 1994)

Consideration was also given to optimize process time within the safety envelope and to protect the furnace heating coils from overheating causing failure and short lifetime.

These ramp rates are a safety feature and are programmed into the controller. The specified ramp rates ensure that gases will be exhausted as they are generated so combustible mixtures will not be accumulated. (See Attachment A, Table 1 and Figures 1 and 2)

The ramp rates cited are maximum rates. Ramp rates can he adjusted to avoid overshooting the *soak* temperatures.

3.2. Furnace Temperature Deviation Band Settings

Deviation Limit: $\pm 20 \, ^\circ C$

Basis: Low deviation alarm can detect a removed thermocouple, burnt out heater element, poorly tuned controller, etc. High deviation alarm will detect too high a ramp rate by activating when temperature exceeds the expected ramping temperature. Exceeding the ramp rate could generate excess butene gas when processing an organic charge or overheat the heating coils causing failure and short lifctiine.

The deviation hand alarm will also detect soak temperatures either above or below the set point. The butene curves in Figures 2 and *6* of Attachment **A** show the effect of exceeding the *soak* temperature set point of $175 \, ^\circ C$ by 20 degrees.

3.3. Heating Cycle PRF Sludge <u>and Magnesium Hydroxide or Oxalate Percipitate</u> Settings

Limit: 1st Soak - 1 ½ hr at $175 \, ^\circ C$

2nd *Soak* - 2 hr at $1000 \, ^\circ C$

Basis: The ramp rate and temperature limit for the first soak time was selected because this parameter keeps the rate of butene generation outside of the flammable range. The one and a half hour soak time was determined by calculating the amount of time it would take to thermally decompose 20 grams of TBP to butene. 'Twenty grams is double the amount of TBP allowed in a batch. (See Attachment **A,** Table 1 and Figures 1 and 2).

Laboratory test results were used to determine the temperature limit and one hour soak time for the second soak. The tests showed that by heating material at $1000 \, ^\circ C$ for one hour, essentially all of the volatiles will be removed, thus meeting the vault storage specification. In addition, the higher temperature reduces the absorptivity of the processed sludge making it more stable. (See Attachment B)

These *soak* rates are specified in the Addendum to WHC-SD-CP-SAR-021, Revision 0-K, "Plutonium Finishing Plant Final Safety Analysis Report", 1999, Section 5.2.2.

<u>This heating cycle was also chosen for magnesium hydroxide or oxalate precipitate. The 1.5 hour dwell at 175 degrees C finishes drying the precipitate before ramping up to 1000 degrees C for thermal stabilization of the material.</u>

3.4. Heating Cycle Pu Oxalate (Oxycarbonate) Settings

Limit: 1st Soak - 1 hr at 110°C

2nd Soak – ½ hr at 175°C

3rd Soak – Minimum – 2 hrs at 1000°C

Basis: 1st Soak - Before start of operation, laboratory tests with oxalate (oxycarbonate produced in previous processing in RMA/RMC lines) showed that it became liquid above 100°C. A soak at this temperature removes the water of hydration and allows the evaporation of the free liquid portion of the charge to evaporate without foaming over the edge of the boat. Operating experience has shown that boil-over was not avoided at the previous soak setpoint of 175°C. Upon further research it was found that the dehydration temperatures start at 90°C (Reference: J.M. Cleveland, The Chemistry of Plutonium, 1979, p. 403,404). In order to evaporate water, the soak temperature must exceed the boiling point of water. To avoid boil-over and still evaporate water, a new setpoint of 110°C was selected for the first soak. Even with the lower soak time, some of the material may boil over. This is not a major concern in that the material can be easily scraped and brushed out of the furnace. The material is then placed in a can with the rest of the charge material in HC-18M.

2nd Soak – Laboratory test results were used to determine the temperature limits for the second and third soaks. The second soak separates the remaining water of hydration from the oxycarbonate (oxalate) and continues evaporation of free liquids.

3rd Soak – The DOE Standard 3013-96, Long Term Storage Criteria for >50% Pu oxides, requires that materials be heated to 950°C or higher for 2 hours and meet a <0.5% LOl @ 1000°C. Tests showed that by heating material at 1000°C for one hour, essentially all of the volatiles will be removed, thus meeting the vault storage specification of <0.5% LOI for material less than 50% Pu. In addition, the higher temperature reduces the absorptivity of the processed sludge making it more stable. (See Attachment B)

Testing of the oxalate precipitation process for solution stabilization by PPSL has shown that the filter cake dries on the hot plate without boiling and just gives off steam during the process. The dried filter cake is then very fine powder that is loaded into the boat for thermal stabilization at 1000 degrees C. In the regular production process for this material the sludge program will be used to thermally stabilize the dried oxalate precipitate to ensure that the drying process is complete before ramping the furnace on up to 1000 C

3.5. Heating Cycle Pu Oxide Setting

Limit: *Soak* – Minimum 2 hrs at $1000\,^\circ$C

Basis: Laboratory test results were used to determine the temperature limit and *soak* time. The DOE Standard 3013-96, Long Term Storage Criteria for >50% Pu oxides, requires that materials be heated to $950\,^\circ$C or higher for 2 hours and meet a <0.5% LOI @ $1000\,^\circ$C. Tests showed that by heating material at $1000\,^\circ$C for one hour, essentially all of the volatiles will be removed, thus meeting the vault storage specifications of <0.5% LOI for material less than 50% Pu. In addition, the higher temperature reduces the absorptivity of the processed sludge making it more stable. (See Attachment B)

3.6. Heating Cycle Incinerator Ash Setting

Limit: Reactive Ash *Soak* - 4 hr at $1000\,^\circ$C

Nonreactive Ash – Minimum 2 hrs at $1000\,^\circ$C

Basis: Process testing indicates that a 4 hour soak time at $1000\,^\circ$C along with a one and one half inch depth in the boat will allow oxidation of sufficient carbon to meet vault specifications. (Reference: WHC-SD-CP-TP-087 Rocky Flat Ash Test Procedure (Sludge Stabilization), 9/14/05).

The 2 hrs at $1000\,^\circ$C heating cycle is to be used with nonreactive incinerator ash that has been processed through HA-40F or the stabilization furnaces. Because the material was previously processed to $600\,^\circ$C, 2 hours at 1000 "C is sufficient to meet the Long Term Storage Criteria.

3.7. Heating Cycle for Pu Metal or Alloys

Limit: 1" *Soak* - 550°C until metal or alloy is oxidized ~~for 6 hours~~

2nd *soak* - 1000°C for 2 hours

Basis: A laboratory experiment heated a metal button to 550°C in a crucible furnace. Oxidation of the button was completed in 6 hours. The metal or alloy charge will be examined and recycled on the metal program with the 550°C dwell until all metal or alloy will pass through a 4 mesh sieve. (Reference: SD-CP-PTR-008, Burning Plutonium Metal Buttons Using an Igniter, 10/23/85) The second *soak* is identical to the *soak* performed on other plutonium oxide items.

The *soak* temperature of 550°C was selected for the first *soak* because it is below the melting point of plutonium metal. If the metal melts, it will form an alloy with the Hastelloy boat and ruin the boat.

found in the Barney/Cooper Letter on Processing Plutonium Alloys in Appendix I.

3.8. High Furnace Temperature Setting

Limit: 1050°C

Basis: The high furnace temperature alarm system provides an independent backup to prevent over-heating the furnace if the Controller fails. The maximum furnace temperature recommended by the manufacturer is 1093°C. Operating the furnace at the full output of power required to maintain this temperature for an extended period of time (>4 hours) can shorten the lifetime of the furnace element and cause failure.

Specification limit is set to allow for over-shooting during ramp time. The set point changed from 1025°C to 1050°C in September, 1995 because the lower temperature was found to be more conservative than required and caused unnecessary process cycle shut-downs. There were no safety reasons for the lower limit of 1025°C and the new setpoint of 1050°C is still well below the manufacturers recommended guidelines.

3.9. Glovebox High Temperature Alarm Setting

Limit: 70°C (158°F)

Basis: This alarm is in place to provide sufficient warning of off-standard conditions which could cause the glovebox to heat up and reach the Fire Suppression System activation temperature of 93°C (200°F).

Glovebox HC-21C has a Halon fire suppression system, and Glovebox HA-211 has a dry chemical suppression system. It is desirable that activation of the Halon system in Glovebox HC-21C he avoided unless there is an uncontrolled fire in the glovebox, because once the Halon has been released, there will he no tire suppression system for the glovebox. Halon is a regulated material and may be difficult to replace. (Reference drawing H-2-97481, sheets 26, 27, 28, 29.)

4.0 OFF-GAS SYSTEM

4.1. Off-gas Flow Rate

Limit: 120 to 180 std. ft³/hr. for Sludge, /oxalate, and magnesium hydroxide or oxalate precipitate.

60 to 90 std. ft³/hr. for Oxide/MOX/Pu Metal

A flow rate of 60 - 90 std. ft³/hr shall be used when processing reactive incinerator ash.

Exception:

Off-gas tlow was specified for sludge charges because of the possibility of butene which could be generated when PRF Sludge containing tributyl phosphate (TBP) is processed. Its purpose is to dilute and remove flammable off-gases during the period butene can be generated. This period is ended before the furnace reaches a temperature of 250°C. The same flow rate was specified for oxalate and magnesium hydroxide or oxalate precipitate charges to aid the evaporation of free liquids.

Basis: In glovebox HC-21C, off-gases are vented to the 26" Hg vacuum system. In glovebox HA-211, off-gases are vented to the 5" Hg vacuum system. A flow rate of 120 - 180 std. ft³/hr will provide enough circulation to dilute the flammable gases generated when processing PRF Sludge to within safe concentrations. It will also provide greater air circulation through the furnace to aid oxidation and remove volatiles from the charges. (See Attachment **A,** Figures 3, 4, 5, and 6 and associated tables.)

During stabilization of reactive incinerator ash, carbon will oxidize to both CO and CO,. CO is flammable (though not explosive) in concentrations greater than 12%. Calculations were performed which indicated that CO concentrations will remain below 12% as long as sufficient oxygen is present (0.6 scfm is sufficient to convert almost all carbon to CO,) (Attachment E).

The incinerator ash is very flighty and therefore is susceptible to being pulled into the off gas line and plugging the filter. The off gas tlow rate will be reduced to 60 - 90 scfh while processing this material.

The sludge/oxalate/magnesium hydroxide or oxalate percipitate and oxide/MOX off-gas flow rates are specified in the Addendum to WHC-SD-CP-SAR-021, Revision 0-K, "Plutonium Finishing Plant Final Safety Analysis Report", 1999, Section 5.2.2.

4.2. Filter Differential Pressure

Limit: ≤ 10 psi for Glovebox MC-21C

≤ 50 in.-H,O for Glovebox HA-211

Exception

PFP Stabilization engineers can allow continued operation of a cycle with

greater dP as long as the required exhaust flow is maintained

A filter is installed in the exhaust line after it leaves the furnace. The filter's function is to remove airborne particulate matter in the off-gas.

Basis: Any particulate matter remaining **in** the filter can absorb moisture at the beginning of the cycle. Once the particulate matter absorbs moisture, it hardens into a solid piece. This reduces the permeability of the filter which decreases the air flow rate through the furnace. Low air flow increases the possibility of combustible gas build-up. (See Attachment C, Internal Memo 15530-94-DMB-070, D. M. Bershaw to W. S. Lewis, "Pressure Drop Analysis for Filter on 26 Inch Vacuum Line in Glove Box HC-21C", Westinghouse Hanford Company, Richland, Washington, June 1, 1994). The limit for Glovebox HC-21C is also specified in the Addendum to WHC-SD-CP-SAR-021, Revision 0-K, "Plutonium Finishing Plant Final Safety Analysis Report". 1999, Section 5.2.2.

5.0 PURGE SYSTEM

5.1. Purge Flow Rate

Limit: $\geq$ 45 std. ft^3/hr CO_2

The carbon dioxide purge flow will be used only for charges originating in PRF or other wet process gloveboxes with a potential for containing TBP. The CO_2 purge is only available in Glovebox HC-21C.

Basis: Carbon dioxide was chosen because it was found to be more effective on a molar basis. Minimum purge flow with carbon dioxide during the ramp and *soak* times (about 2 ½ hours) for PRF sludge charges, assures flammable gas concentration in the furnace remains below minimum safe limit. (See Attachment A, Figures 3, 4, 5, and 6 and associated tables).

The 45 scfh CO_2 flow rate is specified in the Addendum to WHC-SD-CP-SAR-021, Revision 0-K, "Plutonium Finishing Plant Final Safety Analysis Report", 1999, Section 5.2.2.

6.0 FIRE SAFETY

6.1. Combustible Material

Limit: Glovebox gloves near furnace fixed in position with bungi cord during processing cycle.

Minimal non-engineered combustible materials such as plastic bags, polyjars, or rags in Gloveboxes HC-21C and HA-211 during the heating cycle.

Basis: This limit is set both to prevent contacting of combustible materials with hot surfaces and accumulating of significant quantities of combustibles. Surface temperatures of the lines exiting the furnace can exceed 400°C during the heating cycle. The exhaust line which carries the hot gasses is insulated to the offgas filter which is a significant heat sink. The CO_2 line is not insulated and portions of the line near the furnace could reach temperatures over 400°C.

Radiant heat transfer should reduce the line temperature to below $200 \,^\circ C$ by the time the line exits the glovebox. Combustible materials contacting these surfaces may ignite and the resulting fire may breach glovebox containment if these materials are present in sufficient quantity.

These requirements are specified in the Addendum to WHC-SD-CP-SAR-021, Revision 0-K, "Plutonium Finishing Plant Final Safety Analysis Report", 1999, Section 5.2.2.

7.0 Product Specifications

7.1. Particle *Size*

Limit: Particles must go through 4 mesh sieve

Exception:

PFP Stabilization engineers can allow larger chunks of material to be canned with the concurrence of the Product Handling and Storage Cognizant Engineer.

Basis: A fairly uniform particle size is required to assure that samples taken for LOI are representative. Larger chunks also may not be completely dried. If no large chunks of material are present in product, sieving will not be required.

8.0 PLUTONIUM BEARING MATERIAL FOR BAGLESS TRANSFER

8.1. Permitted Feeds - Metal

Limit: DOE-STD-3013-2000 requires that Metal pieces to be packaged shall each weigh at least 50 grams net weight. Foils, turnings, and wires shall not be packaged under this Standard. Metal items packaged shall be visually free of non-adherent corrosion products (including oxide). liquids, and organic materials such as plastics and oils.

Basis: The surface area per gram of plutonium metal will be large enough that pyrophoric reactions will be unlikely. Turnings, foils. and wires have too large a surface area per gram of plutonium metal and probably will be pyrophoric.

'The elimination of the non-adherent corrosion products, liquids, and organic materials such as plastics and oils will prevent adsorbed water in amounts that could pressurize the storage container above the working pressure.

8.2. Permitted Feeds - Oxide

Limit: Well-characterized, high purity product quality oxide resulting from known processes including, Oxidization of metal, Oxidation of metal brushings, Oxalate derived oxide – that is produced by calcination of Pu oxalate.

Basis: A literature search as documented by PPSL staff based on technical research and testing concludes that plutonium dioxide from metal burning and oxalate calcinations will not reabsorb enough moisture to fail the 3013 criterion as long as it has been tired at 950C for at least two hours (Barney 2001). Additionally it concludes that moisture reabsorbtion is relatively rapid and equilibrium water contents are expected to be less than 0.1 wt%. It can be concluded that this readsorbtion is likely to occur during cooling and handling of the process furnace charge and will be detected in the LOI or SFE analysis. For relatively pure oxides, calcined at 1000C, the effect of relative humidity on readsorbtion was not significant, the reference memo discusses readsorption tests done with RH as high as 74%. These conclusions are well known and form the basis for the DOE –STD-3013 (DOE 2000, Bailey 2000, Haschke 1995)

The 3013 STD limits the total mass of package content to no more than 5 kg and indicates that mass may be further limited to ensure that the bounding pressure does not exceed the outer container design pressure. Alternatively analysis can be done to show the free gas volume of the package is at least 0.25 l/kg of oxide. (DOE 2000, Section 6.3.2.).

See Attachment J: Bagless Transfer for Plutonium Metal and Oxides.

8.3. Feeds Not Permitted

Limit: Any feeds not specifically allowed, including all impure oxides and oxide from the magnesium hydroxide or oxalate precipitation process.

Basis: Although reduction in the surface area of plutonium in these materials is also expected, re-adsorption of moisture is expected to be of concern due to the presence of salts and such as CaO and MgO. In additional, the magnesium hydroxide product is also shown to adsorb Carbon Dioxide and behavior of the adsorbed CO_2 is not yet well understood. Additional limits and controls will have to be developed before canning impure oxides, including the potential for dry air or dry inert atmospheres.

8.4. Water Content

Limit: The water content in stabilized oxide should be below 0.2 wt %

Basis: The percent moisture of the permitted feeds (relatively pure oxide) should be very low after calcinations, because of the reduction in specific area. (DOE 1999 and Haschke 1995). Since oxides less than 5 m^2/gm arc routinely expected to result after calcination at 950C, regardless of the method of preparation, any oxide from the permitted feeds that is analyzed above 0.2 % moisture should be considered unusual and subject to additional review. For the permitted feeds allowable moisture content in the stabilized oxide should be below 0.2 wt %. Material discovered with a water content of greater than 0.2 wt% would indicate that the material is not thermally stabilized and should be rc-sampled or reprocessed as needed.

Sample results for stabilized oxides between 0.5 wt% and 0.2 wt% can be accepted after evaluation and documentation by the Vault cognizant engineer.

See Attachment J: Bagless Transfer for Plutonium Metal and Oxides.

8.5. BTCC Contents

Limit: Limit BTC contents to Hanford BTCC with oxide and no foreign objects allowed

Basis: The 3013 STD limits the total mass of package content to no more than 5 kg and indicates that mass may be further limited to ensure that the bounding pressure does not exceed the outer container design pressure. Alternatively analysis can be done to show the free gas volume of the package is at least 0.25 l/kg of oxide. (DOE 2000, Section 6.3.2.). Section 6.5.2 of DOE-STD-3013 requires measurement of the particle density or reference to a model that demonstrates a limitation on mass loading is not needed. It will be necessary, to limit the inners cans in the overall package to the BTCC and BTC that were analyzed and prohibit any foreign objects, such as metal spacers or pressure sensing devices, unless analysis shows minimum free volume requirements are maintained.

See Attachment J: Bagless Transfer for Plutonium Metal and Oxides,

This series of figures was developed from data obtained from laboratory tests performed with uranyl nitrate-trihutyl phosphate adduct ("Behavior of Tributyl Phosphate in A-Line Processes", DP-1418, August 1976, H.D. Harmon, et al). The physical and chemical properties were studied to define optimum, safe operating conditions for denitration of uranyl nitrate solutions containing low concentrations of adduct. A conservative kinetic factor (KF) of 3 was used when the data was applied to plutonium hearing material, which will be used in the sludge stabilization process, to account for the fact that plutonium nitrate has two times as much nitrate as uranyl nitrate. Figures 1 and 2 show the expected results calculated if the process is operated at conditions defined in the Operating Specification Document. Figure 1 shows the relationship of the decomposition curve of 20 grams of TBP and the butene generation curve to the temperature cycle. Figure 2 shows the flammability curves. The butene concentration is well below the lower flammability limit.

Changes in inputs for Table 2 and reflected in Figures 3 and 4 are: (1) a hold temperature of 155 °C, which is 20 °C less than setpoint temperature hut still within the OSD limits; (2) furnace purge flow rates at 5% less than OSD limits: and (3) the off-gas flow rate of 90 scfh, which is 25% less than OSD limits. Figure 3 shows a part of the butene is generated at a temperature of about 150 °C and dissipated slowly during the hold time. The remainder is generated at the time of the second ramp up. However, as can be seen in Figure 4 the concentration level of the highest peak is much less than the lower flammability limit. These results indicate that the carbon dioxide purge flow needs to continue for at least 140 minutes to compensate for this deviation.

Figures 5 and *6* reflect the input changes as follows: (1) the hold temperature of 195 °C, which is 20 °C greater than setpoint temperature, hut still within the OSD limits; (2) the furnace purge rate at 5% less than OSD limits; and (3) the off-gas flow rate of 90 scfh, which is 25% less than OSD limits, The butene peak for these conditions reaches its highest concentration at the set point (See Figure 5). This is the point most likely to have an overshoot so the upper deviation limit should not exceed this temperature. The highest butene concentration (as shown in Figure **6)** is about 75% of the flammable limit. This concentration is acceptable due to the four other conservative inputs used in the calculations.

Temperature over-shoots of 3 to 13 degrees were observed in the initial furnace tests. Therefore, a hold temperature of 20 °C less than the upper deviation hand will he set to allow for overshoot without activating the furnace shutdown interlock.

Calculations to show the lower flammability limit for butene compared to normal operating conditions.

Butene is generated at 0.648 mol/hr   (Table #1. Row 9, Columns 1 and 2)
Offgas flow rate is 139.006 mol/hr   (Table #1, Last Row, Columns 1 and 2)

$$\frac{0.648 \text{ mol/hr butene}}{139.006 \text{ mol/hr offgas}} = 0/0046 \times 100 = 0.46\% \frac{\text{butene}}{\text{total offgas}}$$

For conservatism, calculations were made for a double batch, with the amount of TBP (20 grams) See Table #1, Row 1, Columns 3 and 4.

Normal operations will process a charge of 500 grams with a maximum of 2% TBP which equals 10 grams TBP. The percent butene is divided by 2.

$$\frac{0.46}{2} = 0.23\%$$

The lower flammability limit at $25 \,^{\circ}C$ as shown in Figure 2 is from Figure 68 on page 54 of Bureau of Mines Bulletin 627, "Flammability Characteristics of Combustible Gases and Vapors", M. G. Zabetakis, 1965.

The lower flammability limit at $250^{\circ}C$ is calculated by using the temperature correction equation on page C-67 of AIChE Today Series, "Fundamentals of Fire and Explosion Hazards Evaluation", C. Grelecki, 1976.

$$L, / L_{25} = 1 - 0.000721 (t - 25)$$

where

$L,$ = lower limit of gas mixture at temperature of interest
L_{25} = lower limit of gas mixture at $25 \,^{\circ}C$
t   = temperature of interest

$$L_{25} = 1 - 0.000721 (250 - 25) (2)$$

$$L_{25} = 1.675$$

The percent of butene which could be generated at normal conditions as compared to the lower flammability limit at $250 \,^{\circ}C$ is as follows:

$$\frac{0.23}{1.675} = 0.1373 \times 100 = 13.73\%$$

TABLE # 1

Initial Ramp Rate	5 [Cimin]	Initial TBP Wt.	20 [grams TBP]
Time Interval	1.5 [min]	Initial TBP mols	0.0751 [mol TBP]
Temp @ Time 0	30 [C]	TBP Conv Factor	3 [mol C4/mol TBP]
Time/new Ramp Rate	120 [min]	Inert **Kzn** Gen Fact	1 [mol inert/mol C4]
New Ramp Rate	3.333333 [C/min]	Kin Factor Input	3
Frn Hold Temo	175 [C]	Kin Factor Min	1
Frn Min Temo	25 [C]	Kin Factor Used	3
Frn Max Temp	400 [C]		
Max C4 Gen Rate	0.648 [mol C4/hr]		
Max Inert Rate	0.648 [mol inert/hr]		
Max Tot Flow	36.047 [(C4+inert+Purge)/hr]		
Min Frn OG Req'd	31.118 [cfh @ 298 & 1 atm]		
Time at Frn Purge Change	400 [min]		
Furn Purge Rate	30 [scth]		
O2 in Furn Purge	0.1% [% O2]		
Inert in Frn Puree	99.9% [% N2]		
Mol Frn Purge Rate	34.751 [mol purgeihr] 0.035 [molO2 purgeihr] 34.717 [mol Inert purgeihr]		
Time When OG Rate Changes	400 [min]		
Furn OG Rate	120 [scth]		
Mol Frn OG Rate	139.006 [mol Tot OG/hr]		

Unreacted TBP & C4H8 Rate

FIGURE 1

Unreacted TBP, C4H8 Rate, & Temperature
OSD Nominal Conditions, KF = 3.0

TBP Rem'g [gm TBP] —— Charge Temp [C] —— C4H8 Rate [mol/hr]

Furnace Off-gas Flammability
OSD Nominal Conditions, KF = 30

FIGURE 2
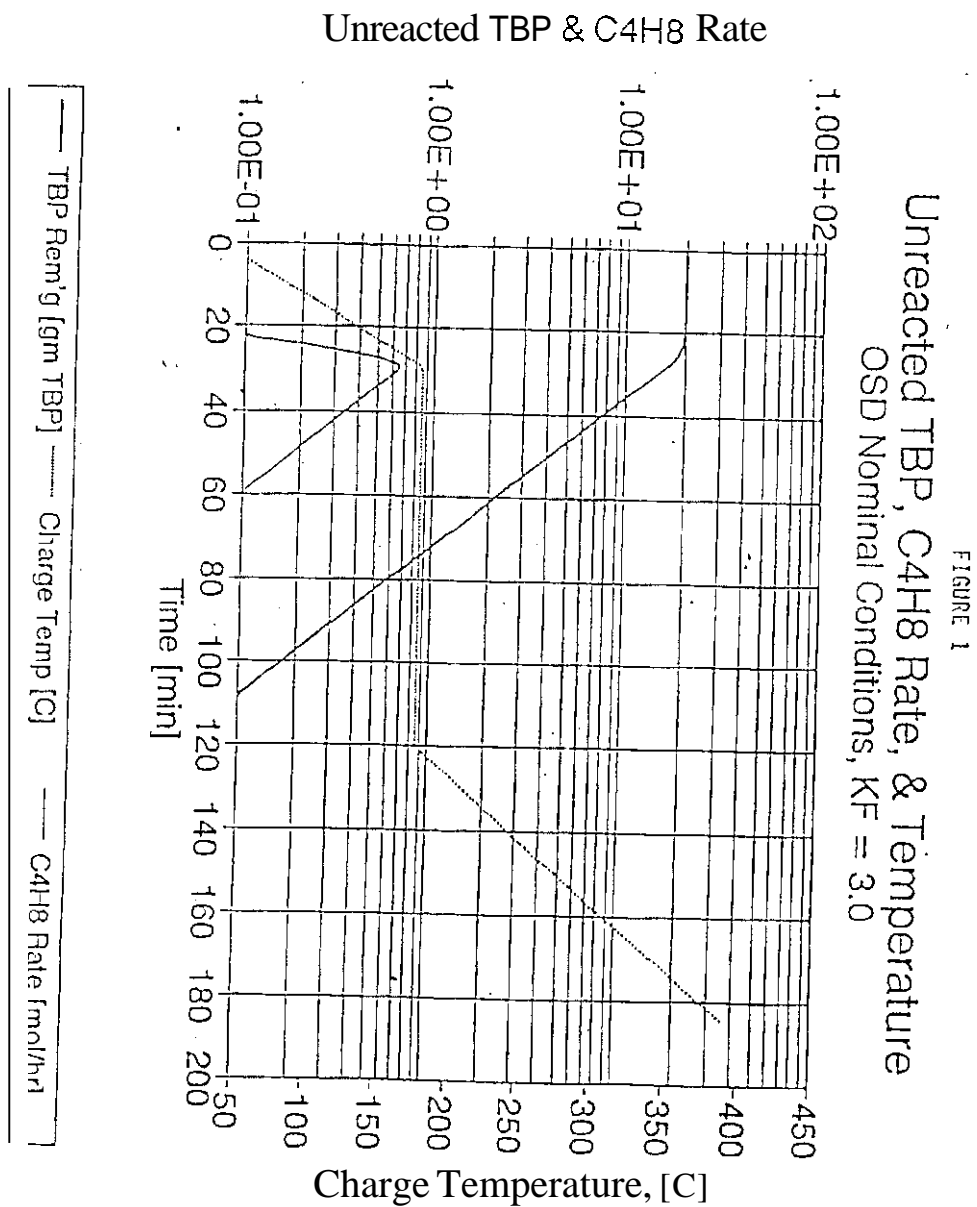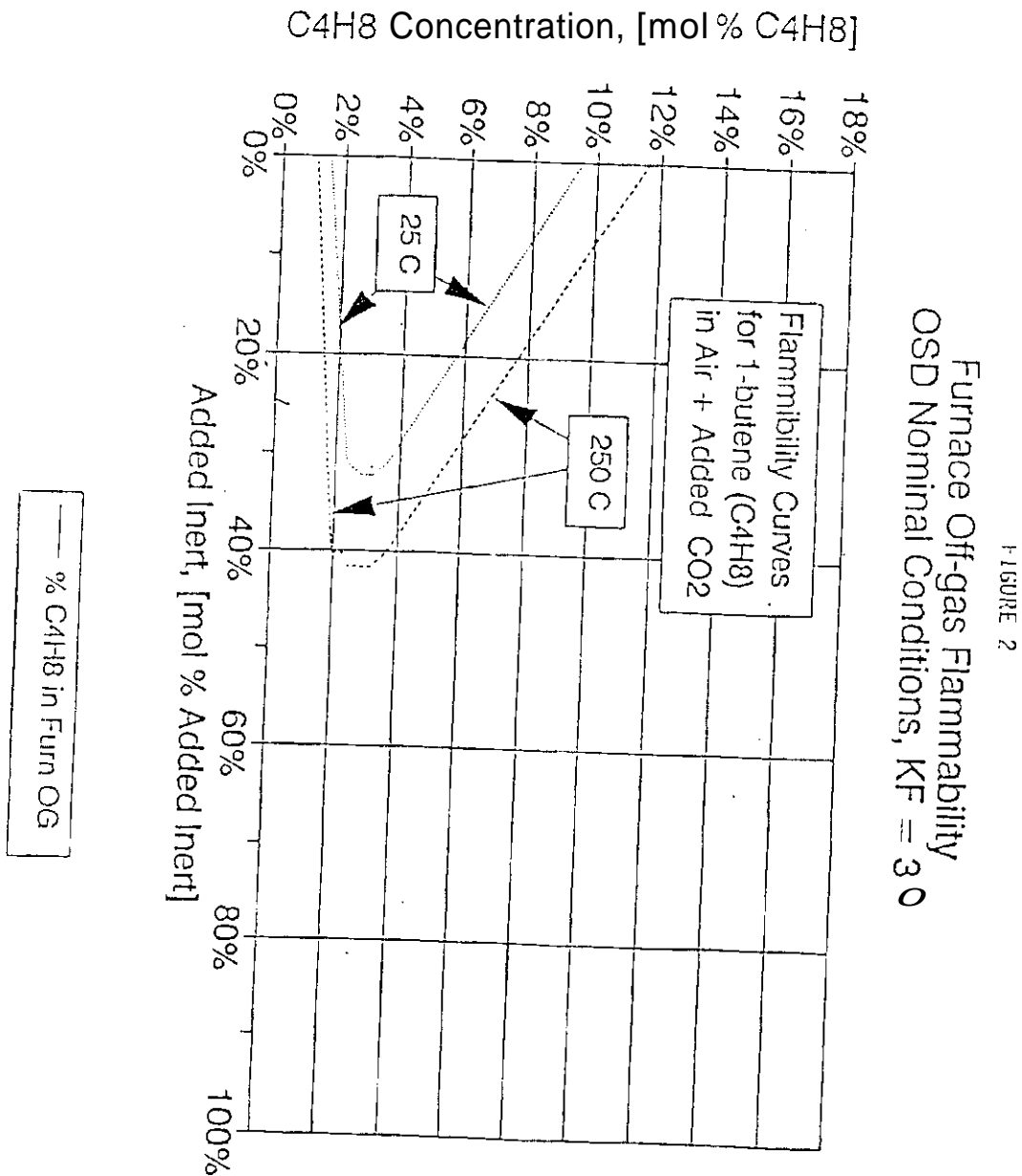
TABLE # 2

Initial Ramp Rate	5 [Cimin]	Initial TBP Wt	20 [grams TBP]
Time Interval	1.5 [min]	Initial TBP mols	0.0751 [mol TBP]
Temo til Time 0	30 [C]	TBP Conv Factor	3 [mol C4/mol TBP]
Time/new Ramp Rate	120 lminl	Inert Rzn Gen Fact	1 [mol inert/mol C4]
New Ramp Rate	3.333333 [Cimin]	Kin Factor Input	~
Fm Hold Temp	155 [C]	Kin Factor Min	1
Frn Min Temp	25 [C]	Kin Factor Used	3
Frn Max Temp	400 [C]		
Max C4 Gen Rate	0.234 [mol C4/hr]		
Max Inert Rate	0.234 [mol inertihr]		
Max Tot Flow	33.482 [(C4+inert+Purge)/hr]		
Min Frn OG Rea'd	28.904 [cfh @ 298 & 1 atml		
Time at Frn Purge Change	400 [min]		
Furn Purge Rate	28.5 [scfh]		
O2 in Furn Purge	0.1% [% O2]		
Inert in Frn Purge	99.9% [% N2]		
Mol Frn Purge Rate	34.751 [mol purgeihr] 0.033 [mol O2 purgeihr] 32.981 [mol Inert purgeihr]		
Time When OG Rate Changes	400 [min]		
Eurn OG Rate	90 [scfh]		
Mol Frn OG Rate	104.254 [mol Tot OG/hr]		

Unreacted TBP & C4H8 Rate

Figure 3. Unreacted TBP, C4H8 Rate, & Temperature OSD Error Conditions, KF = 3.0

FIGURE 4

Furnace Off-gas Flammability
OSD Error Conditions, KF = 3.0

Flammibility Curves
for 1-butene (C4H8)
in Air + Added CO2

25 C

250 C

C4H8 Concentration, [mol % C4H8]

Added Inert, [mol % Added Inert]

—— % C4H8 in Furn OG

TABLE # 3

Initial Ramp **Rate**	5 [C/min]	Initial TBP Wt.	20 [grams TBP]
Time Interval	1.5 [min]	Initial TBP mols	0.0751 (mol TBP]
Temp @ Time 0	30 [C]	TBP Conv Factor	3 lmol C4/mol TBP]
Time/new Ramp Rate	120 [min]	Inert Rzn Gen Fact	1 lmol inert/mol C41
New Ramp Rate	3.333333 [C/min]	Kin Factor Input	3
Frn Hold Temp	195 [C]	Kin Factor Min	I
Frn Min Temp	25 [C]	Kin Factor Used	3
Frn Max Temo	400 [C]		
Max C4 Gen Rate	1.387 [mol C4/hr]		
Max Inert Rate	1.387 [mol inert/hr]		
Max Tot Flow	35.788 [(C4+inert+Purge)/hr]		
Min Frn OG Req'd	30.895 [cfh @ 298 & 1 atm]		
rime at Frn Purge Change	400 [min]		
Furn Purge Rate	28.5 [scfh]		
0 2 in Furn Purge	0.1% [% O2]		
Inert in Frn Purge	99.9% [% N2]		
Mol Frn Purge Rate	33.014 [mol purge/hr] 0.033 [mol O2 purge/hr] 32.981 [mol Inert purge/hr]		
Time When OG Rate Changes	400 [min]		
Furn OG Rate	90 [scfh]		
Mol Frn OG Rate	104.254 [mol Tot OG/hr]		

Unreacted TBP & C4H8 Rate, & Temperature
OSD Error Conditions, KF = 3.0
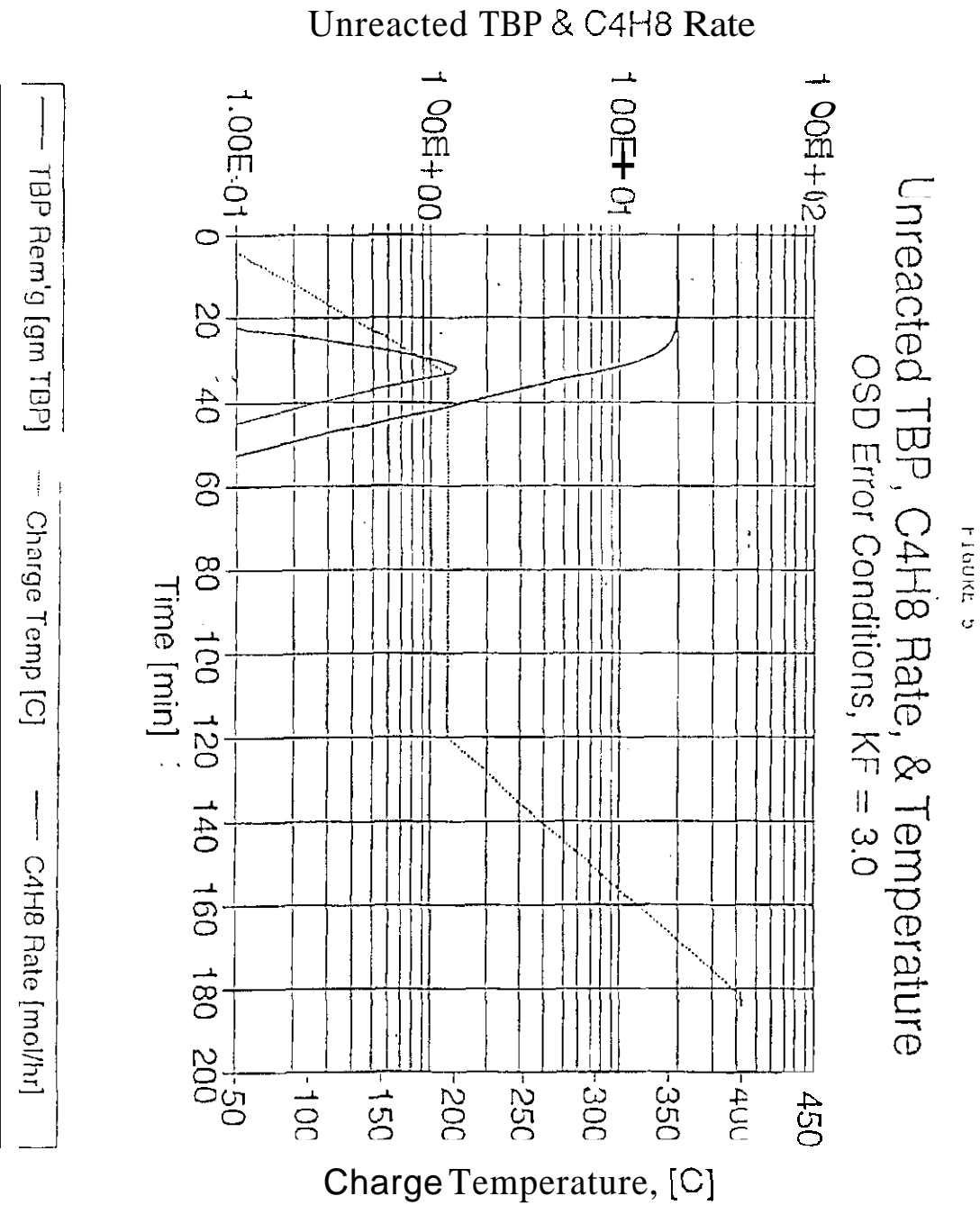
FIGURE 5

FIGURE 6

Furnace Off-gas Flammability
OSD Error Conditions, KF = 3.0
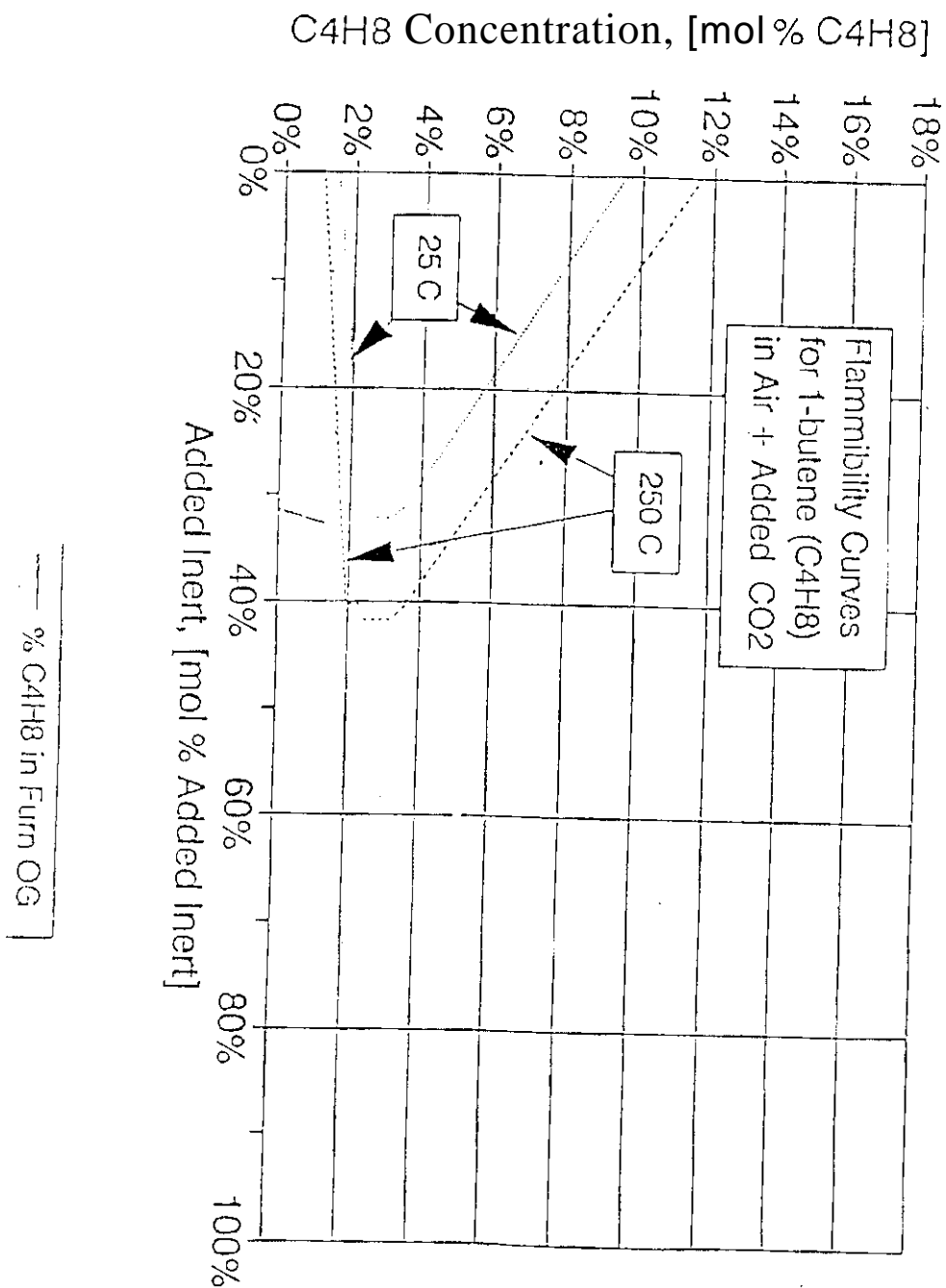
BASIS DOCUMENT FOR THERMAL STABILIZATION
ATTACHMENT B: TEST PERFORMED BY PPSL 1994

TABLE # 1, Centrifuge Sludge

ITEM a	BONE DRY NET WEIGHT	WT. ITEM + CAN W/LID	WT. OAN	% WT. OAIN	T	T-T₀	(T-T₀)²
760 C FIXED							
PPSL-213A	45.94	131.23g	0.0	0.0	0738 4/14	0 hrs	0
		131.26	0.03	0.0653	0810 4/14	0.534	0.731
		131.29	0.06	0.131	0842 4/14	1.067	1.033
		131.33	0.10	0.218	1020 4/14	2.867	1.603
		131.33	0.10	0.218	1120 4/14	3.697	1.923
		131.36	0.13	0.283	1604 4/14	8.434	2.904
		132.39	1.03	2.24	0730 4/20	102.275	10.118
		133.97	2.74	5.96	1045 4/27	315.037	17.74
1000 C FIXED							
PPSL-213B	74.32	159.78	0.0	0.0	0740 4/20	0	0
		159.81	0.03	0.040	0810 4/10	0.500	0.707
		159.87	0.04	0.054	0849 4/20	1.150	1.077
		159.85	0.07	0.094	0900 4/20	1.333	1.154
		159.87	0.09	0.121	0920 4/20	1.333	1.154
		159.88	0.100	0.135	0940 4/20	2.000	1.414
		159.89	0.110	0.148	0955 4/20	2.250	1.500
		159.92	0.140	0.188	1030 4/20	2.833	1.683

a	BONE DRY NET WEIGHT	WT. ITEM + CAN W/LID	WT. GAIN	% WT. GAIN	T	T-T$_0$	(T-T$_0$)$^{-2}$
		159.94	0.160	0.215	1100 4/20	3.333	1.876
		159.96	0.180	0.242	1155 4/20	4.250	2.061
		159.97	0.190	0.256	1220 4/20	4.666	2.160
		160.00	0.220	0.296	1315 4/20	5.583	2.363
		160.03	0.250	0.336	1510 4/20	7.500	2.739
		160.34	0.560	0.753	0635 4/21	22.913	4.786
		160.37	0.590	0.794	0730 4/21	23.83	4.880
		160.55	0.770	1.036	1430 4/21	30.83	5.553
		161.07	1.290	1.736	1045 4/27	171.00	13.08

Centirfuge Sludge
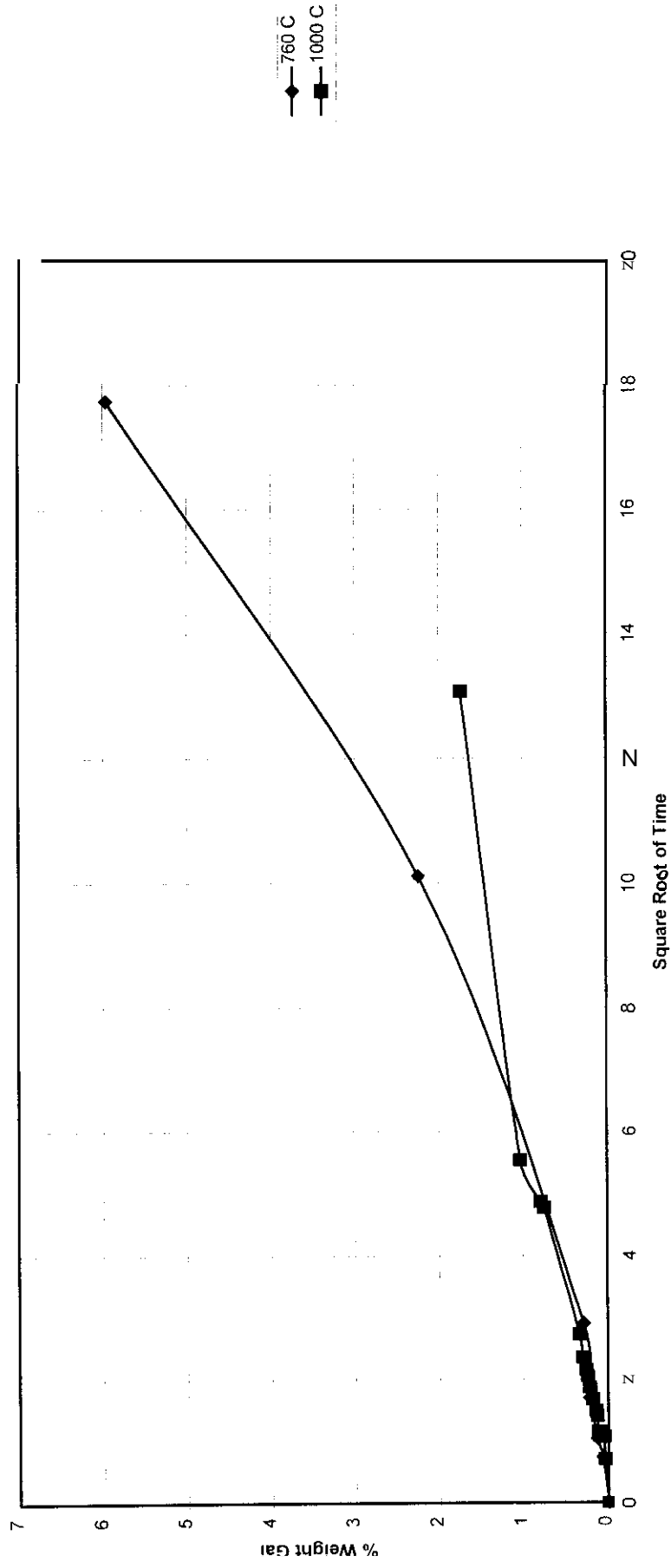
BASIS DOCUMENT FOR THERMAL STABILIZATION
ATTACHMENT B: TEST PERFORMED BY PPSL 1994

TABLE #2. Oxalate Sludge

	ITEM ID	BONE DRY NET WEIGHT	WT. ITEM + CAN w/lid	WT GAIN	% WT. GAIN	T	T-T₀	(T-T₀)^{1/2}
760 C FIXED	PPSL-213B	105.11	155.85	0.0	0.0	0800 4/5	0 hrs	0
			155.86	0.010	0.00951	0910 4/5	1.167	1.080
			155.90	0.050	0.0476	1005 4/5	2.083	1.443
			155.91	0.060	0.0571	1020 4/5	2.333	1.527
			155.96	0.110	0.104	1220 4/5	4.333	2.082
			155.98	0.130	0.124	1350 4/5	5.667	2.380
			155.99	0.140	0.133	1440 4/5	6.667	2.582
			156.33	0.480	0.457	1310 4/6	29.167	5.481
			156.44	0.590	0.561	0755 4/7	47.917	6.922
			157.62	1.770	1.684	0630 4/12	166.50	12.904
			162.76	6.910	6.574	1045 4/27	534.67	23.55
1000 C FIXED	PPSL-214A	109.67	193.60	0.0	0.0	1020 4/27	0	0
			193.63	0.030	0.0274	1235 4/27	2.250	1.500
			193.63	0.030	0.0274	1300 4/27	2.667	1.633
			193.66	0.060	0.0547	1445 4/27	4.334	2.082
			193.81	0.210	0.1915	0650 4/28	20.500	4.528

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ITEM ID	BONE DRY NET WEIGHT	WT. ITEM + CAN W/LID	WT. GAIN	% WT. GAIN	T	T-T₀	$(\overline{T}-\overline{T}_0)^{1/2}$
		193.82	0.220	0.2006	0850 4/28	22.500	4.743
		192.96	0.260	0.237			
		192.01	0.210	0.293			
						140.167	11.839

Oxalate Sludge

BASIS DOCUMENT FOR THERMAL STABILIZATION
ATTACHMENT B: TEST PERFORMED BY PPSL 1994

TABLE # 3   Canyon Floor Solids

	ITEM ID	BONE DRY NET WEIGHT	WT. ITEM + CAN W/LID	WT. GAIN	% WT. GAIN	T	T-T₀	(T-T₀)$^{1/2}$
760 C FIXED	PPSL-215A	71.08	145.99	0.0	0.0	1320 4/6	0 hrs	0
			146.02	0.030	0.0422	1350 4/6	0.500	0.707
			146.87	0.880	1.238	0630 4/12	137.17	11.712
			148.45	2.460	3.46	1045 4/21	357.337	18.900
1000 C FIXED	PPSL-215B	74.55	159.60	0.0	0.0	0800 4/21	0	0
			159.64	0.040	0.0537	0810 4/21	0.167	0.409
			159.69	0.090	0.1207	0830 4/21	0.500	0.707
			159.72	0.120	0.1610	0840 4/21	0.667	0.817
			159.76	0.160	0.2116	0900 4/21	1.000	
			159.77	0.170	0.2780	0910 4/21	1.165	
			78		0.2415	0920 4/21	1.333	1.155
			81					
			159.82	0.220	0.2951	1000 4/21	2.000	1.414

ITEM ID	BONE DRY NET WEIGHT	WT. ITEM + CAN W/LID	WT. GAIN	% WT. GAIN	T	T-T$_0$	(T-T$_0$)$^{1/2}$
		159.84	0.240	0.3210	1050 4/21		
		159.85	0.250	0.3353	1100 4/21		
		159.86	0.260	0.3488	1130 4/21	3.500	1.871
		159.87	0.270	0.3622	1250 4/21	4.833	2.198
		159.88	0.280	0.3756	1430 4/21	6.500	2.550
						146.75	12.114

Canyon Floor Solids
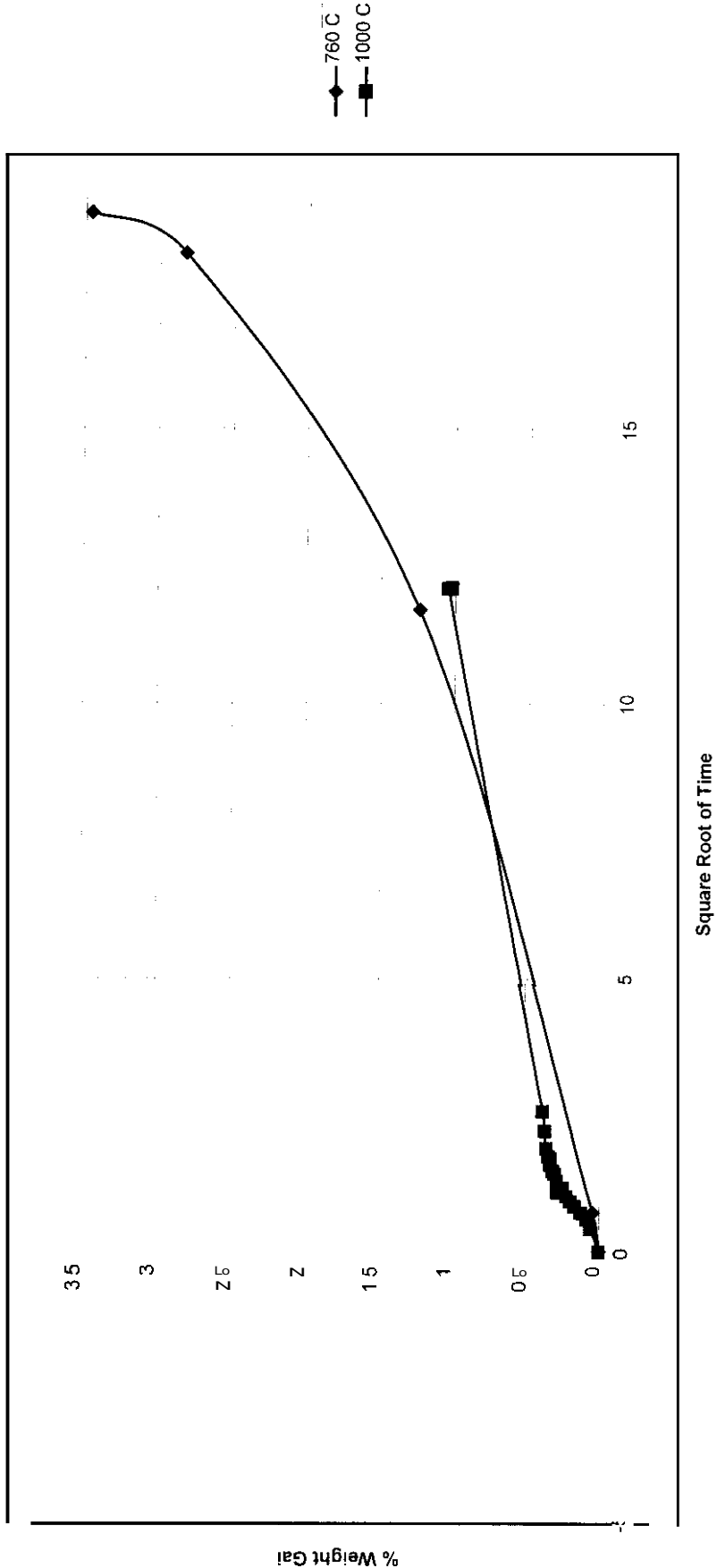
WestInghouse　　　　　　　　　　　　　　　　　　　　　　　　　　**Internal**
Hanford Company　　　　　　　　　　　　　　　　　　　　　　　　Memo

From:　　PFP Process Engineering　　　　　　　　　　　　15530-94-DMB-070
Phone:　　373-5092　55-55
Date:　　June 1, 1994
Subject:　PAESSURE DROP ANALYSIS FOR FILTER ON 26 INCH VACUUM LINE IN GLOVE
　　　　　BOX HC-ZIC

To:　　　W. S. Lewis　　　　　　T5-55

　　　　cc:　,L. Dayley　　　　15-55
　　　　　　M. W. Gibson　　　15-55
　　　　　　DMB File/LB

(1)　CRANE Co. Flow of Fluids Throuoh Valves. Fittinos. and Pioe. Technical
　　　Paoer No. 410. Crane Co. King of Prussia, PA. 1988.

(2)　Rockwell Hanford Operations. plutonium Finishing Plant Safety Analysis
　　　Reoort (SD-HS-SAR-007). Pages 5-21 through 5-26. 1987.

This memo documents an analysis of the 26" vacuum line and filter in glove
box HC-21C. A minimum flow rate of 2 cfm through the vacuum line during
sludge stabilization is necessary to ensure the glove box is properly
vented. A differential pressure gauge has been installed across the 26"
vacuum line filter. The normal operating pressure drop across this ceramic
filter is 1 psi. It is expected that with use the pressure drop across the
filter will increase, thus reducing flow through the line. Ey approximating
how much vacuum is necessary to sustain the minimum flow rats, a guideline
may be established to determine when the filter should be changed out.

Analysis of this system indicates the vacuum required for a 2 cfm flow
through the vacuum line is 0.12 psi (0.25 in. Hg). However. this analysis
does not take into account the pressure drop for all the piping From the
glove box to the 26" vacuum pumps located in building 291-Z. Therefore a
safe operating limit for the pressure drop across the filter would be in the
8-10 psi (16-20 in. Hg) range.

In order to calculate the pressure drop a flow rate of 2 cfm (120 cfh),
observed 5 ft. from the end of a 1/2" s.s. pipe, was plugged into a version
of the Bernoulli equation for compressible fluid flow in pipe. The ideal
gas law and a temperature of 70°F were used to determine the density of air
under a 26" vacuum. Correction factors for the compressibility of air were
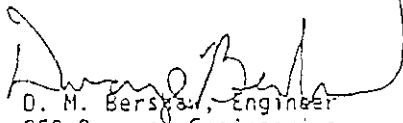
W. S. Lewis   **ATTACHMENT** C   15530-94-DMB-073
Page 2
June 1, 1994
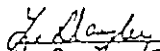
found in the Crane Manual. These factors were approximated to salve the
flow equation and then were refined after several iterations.

Any questions concerning this analysis may be addressed to Dwayne Bershaw at
373-5092 (T5-55).

D. M. Bershaw, Engineer
PFP Process Engineering

Concurrence:

L. DayVey, PFP Process Engineer
PFP Process Engineering

cse

Attachments 3

W. S. Lewis
Page 1 of 1
June 1, 1994

Attachment 1

Determination Reynold's Number

$$Re = \frac{Dv\rho}{\mu}$$

$D = 0.5\ inches$

$$\rho = \frac{PM}{RT} = \frac{100mmHg\ mol\ K}{62.36L\ mmHg\ 294K}\frac{28.85g}{mol}\frac{kg}{1000g}\frac{2.205lbm}{kg}\frac{1000L}{m^3}\frac{m^3}{35.313ft^3} = 9.83*10^{-3}\frac{lb}{ft^3}$$

$$v = \frac{q}{A} = \frac{2ft^3}{min}\ \frac{1}{(\frac{0.25}{12}ft)^2\pi}\ \frac{min}{60s} = 24.4\frac{ft}{s}$$

$\mu = 0.018cP\ (air\ at\ 70°F,\ 1\ atm)\ Crane\ Manual\ pg.\ A-5$

$$\mu = 0.018cP\ \frac{P}{100cP}\ \frac{N\ s}{10P\ m^2}\ \frac{kg\ m}{N\ s^2}\ \frac{2.205lbm}{kg}\ \frac{m}{3.2808ft} = 1.21*10^{-5}\frac{lb}{ft\ s}$$

$$Re = \frac{Dv\rho}{\mu} = 0.5inch\ \frac{ft}{12inch}\ \frac{24.4ft}{s}\ \frac{9.83*10^{-3}lb}{ft^3}\ \frac{ft\ s}{1.21*10^{-5}lb} = 825$$

.94-DMB-070

W. S. Lewis
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June 1, 1994

Attachment 2

Flow Equation for Compressible Fluid through pipe
(Crane Manual, Equation 3-20, pg. 3-4)

$$q'_m = 678 \, Y \, d^2 \sqrt{\frac{\Delta P \, P'_1}{K \, T_1 \, S_g}}$$

$$q'_m = 2 \frac{ft^3}{min} \qquad T_1 = 530R \ (70°F) \qquad S_g = 1.0$$

$P'_1 = -1.1$ inches H_2O gauge = 0.997 atm = 14.7 psi   (Ref.2)

For Laminar Flow (Re < 2300) friction factor $f = \frac{64}{Re} = \frac{64}{825} = 0.0776$

$$K_{pipe} = f \frac{L}{D} = 0.0776 \frac{5ft}{0.5inch} \frac{12inch}{ft} = 9.31 \qquad K_{expansion} = 1.0 \qquad K_{tot} = 10.3$$

$$d^2 = (0.5inch)^2 = 0.25 \qquad Y = 0.99^{(1)}$$

(1) found in Crane Manual pg. A-22 and solved for after several iterations

$$\Delta P = \frac{K \, T_1 \, S_g}{P'_1} \left(\frac{q'_m}{678 \, Y \, d^2} \right)^2 = \frac{10.3(530)(1)}{14.7 \, psi} \left(\frac{2}{678(0.99)(0.25)} \right)^2 = 0.0528 psi$$

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Attachment 3

Total Possible Pressure Drop Across 26" Vacuum Line

$$\Delta P = (26\ inch\ Hg - 0.081\ inch\ Hg) \times \frac{1000\ mmHg}{39.37\ inch\ Hg} \times \frac{14.7\ psi}{760\ mm\ Hg} = 12.7\ psi$$

Pressure needed to maintain 2 cfm flow rate
$$\Delta P = 0.052A\ psi = 0.107\ inches\ Hg$$

Acceptable Pressure Drop Across Filter
$$\Delta P = 8\text{-}10\ psi = 16\text{-}20\ inches\ Hg$$

(Normal) operating pressure drop for the ceramic filter = 1 psi

For Glovebox HA-21I

Total Possible Pressure Drop Across 5" H Vacuum Line

$$\Delta P = (5\ inch\ Hg - 0.081\ inch\ Hg) \times \frac{1000\ mmHg}{39.37\ inchHg} \times \frac{14.7\ psi}{760\ mm\ Hg} = 2.4\ psi$$

Pressure needed to maintain 2 cfm flow rate is = 0.0528 psi

Acceptable Pressure Drop Across Filter
$$\Delta P = 15\text{-}19\ psi = 415\text{-}52.6\ in\text{-}H_2O \approx 50\ in\text{-}H_2O$$

W S Lewis

checked by David _____

15530-94-DMB-070

HC-21C
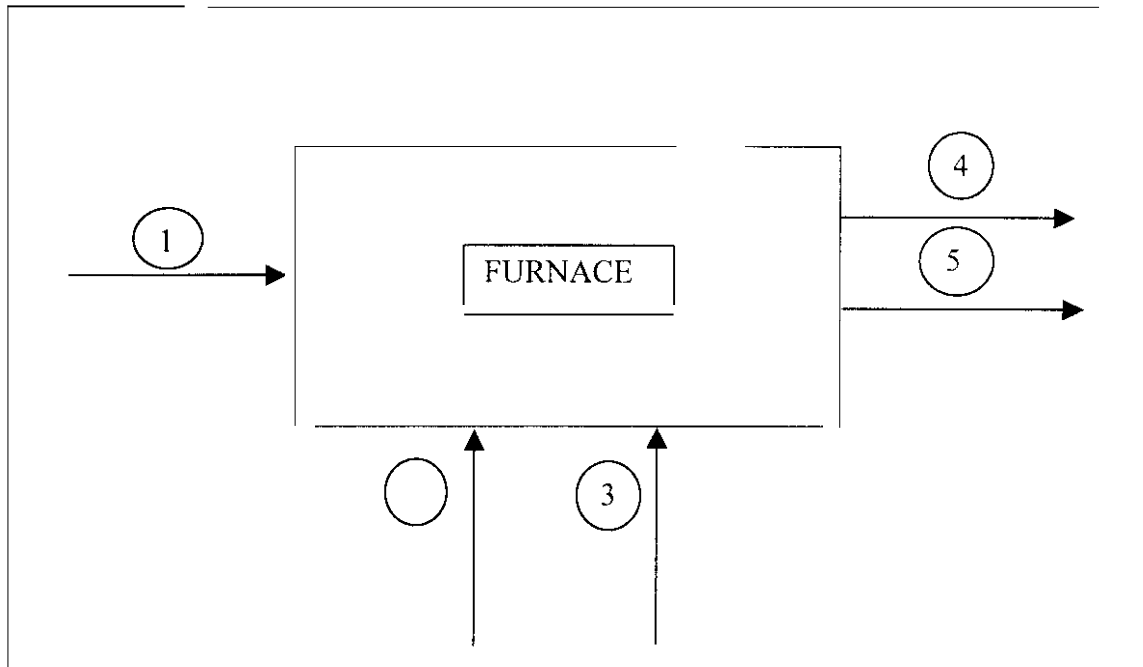
Material Balance

Feed 1 (Pu Oxalate)

$PuOCO_3 * 2H_2O + \text{heat} \longrightarrow PuO_2 + 2H_2O \text{ (g)} + CO_2 \text{ (g)}$

95% HNO_3 driven off as acid

$HNO_3 \longrightarrow HNO_3 \text{ (g)}$

5% reacts as follows:

$2 HNO_3 \longrightarrow H_2O \text{ (g)} + NO \text{ (g)} + NO_2 \text{ (g)} + O_2 \text{ (g)}$

$H_2O \longrightarrow H_2O \text{ (g)}$
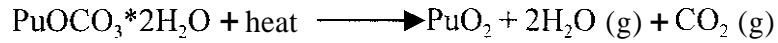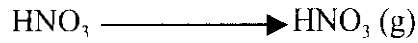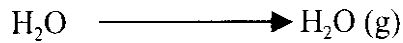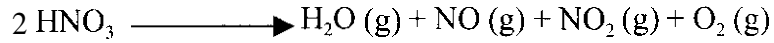
Charge Size (grams)   500

Grams					
	1	2	3	4	5
$PuOCO_3 * 2H_2O$	472.5				
HNO_3	5.5			5.23	
O_2			624.4	624.4688	
CO_2				59.4	
PuO_2					365.85
NO				0.0645	
NO_2				0.0989	
H_2O	22			70.779	
N_2			2497.6	2497.6	

Feed 2 (PRF Sludge)

$(C_4H_9O)_3PO + heat \longrightarrow 3\ C_4H_8\ (g) + \frac{1}{2}\ H_4P_2O_7 + \frac{1}{2}\ H_2O\ (g)$

$H_4P_2O_7 + heat \longrightarrow 2\ H_2O\ (g) + P_2O_5\ (g)$

$2\ Fe(NO_3)_3*2H_2O \longrightarrow Fe_2O_3 + 4\ HNO_3 + NO\ (g) + NO_2\ (g) + O_2\ (g)$

$Pu(NO_3)_4* H_2O \longrightarrow 4\ HNO_3 + NO\ (g) + NO_2\ (g) + PuO_2 + O_2\ (g)$

95% HNO_3 driven off as acid

$HNO_3 \longrightarrow HNO_3\ (g)$

5% reacts as follows:

$2\ HNO_3 \longrightarrow H_2O\ (g) + NO\ (g) + NO_2\ (g) + O_2\ (g)$

$H_2O \longrightarrow H_2O\ (g)$
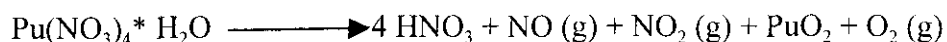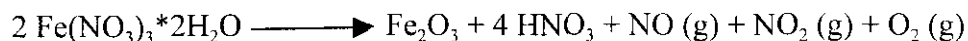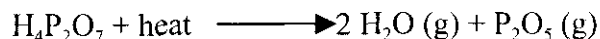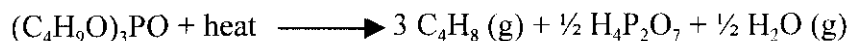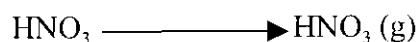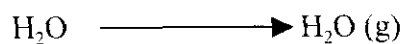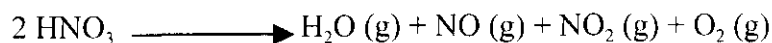
Charge Size (grams)   500

	Grams				
	1	2	3	4	5
$Pu(NO_3)_4$	130				
HNO_3	165			258.495	
O_2			624.4	645.616	
CO_2		4658		4658	
PuO_2	35				105.46
NO				19.89	
NO_2				30.5	
H_2O				2.457	
N_2			2497.6	2497.6	
$Fe(NO_3)_3$	165				
$(C_4H_9O)_3PO$	5				
P_2O_5				1.35	
C_4H_8				2.96	
Fe_2O_3					46.95

Feed 1

$$PuOCO_3 * 2H_2O + heat \longrightarrow PuO_2 + 2H_2O \text{ (g)} \uparrow + CO_2 \text{ (g)} \quad \textbf{4}$$

$$HNO_3 + heat \longrightarrow HNO_3 \text{ (g)} \quad \textbf{4}$$

$$2\,HNO_3 \longrightarrow H_2O \text{ (g)} + NO \text{ (g)} + NO, \text{ (g)} + O_2 \text{ (g)} \quad (5\% \ HNO_3 \text{ does this)}$$

$$H_2O + heat \longrightarrow H_2O \text{ (g)} \uparrow$$

Feed 2

$$(C_4H_9O)_3PO + heat \longrightarrow 3\,C_4H_8 \text{ (g)} \uparrow + \tfrac{1}{2}\,H_4P_2O_7 + \tfrac{1}{2}\,H_2O \text{ (g)} \uparrow$$

$$H_4P_2O_7 + heat \longrightarrow 2\,H_2O \text{ (g)} \uparrow + P_2O_5 \text{ (g)} \uparrow$$

$$2\,Fe(NO_3)_3 * 2H_2O \longrightarrow Fe_2O_3 + 4\,HNO_3 + NO \text{ (g)} + NO_2 \text{ (g)} + O_2 \text{ (g)}$$

$$Pu(NO_3)_4 * H_2O \longrightarrow 4\,HNO_3 + NO \text{ (g)} + NO_2 \text{ (g)} + PuO_2 + O_2 \text{ (g)}$$

$$HNO_3 + heat \longrightarrow HNO_3 \text{ (g)} \uparrow$$

$$2\,HNO_3 \longrightarrow H_2O \text{ (g)} + NO \text{ (g)} + NO_2 \text{ (g)} + O_2 \text{ (g)}$$
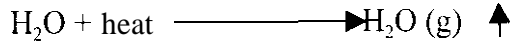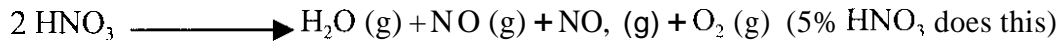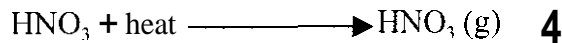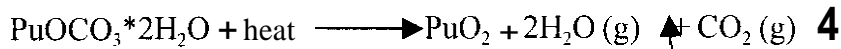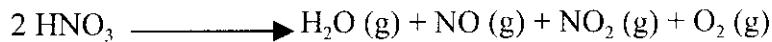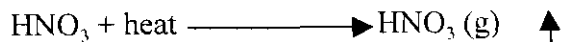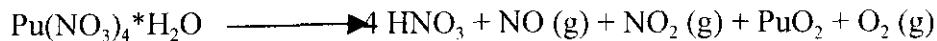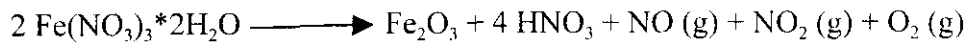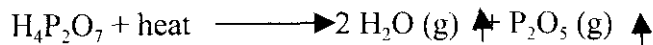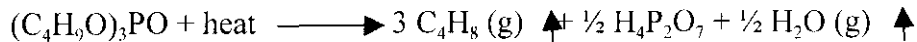
Off gas flow rate

Based on 1 hr @ 20°C 760 mmHg BDA density 1.225 Kg/m^3

$$\frac{90\ ft^3}{} \ \frac{0.02832m^3}{ft^3} \ \frac{1.225 Kg}{m^3} = 3.122\ g\ of\ BDA$$

Assume air is 20% O_2 + 80% N_2

$$O_2 = 624.4 \ g$$

$$N, = 2497.6 \ g$$

CO, (used only with PRF sludge for 3 hours of the rampup time)
Specific volume = 8.76 ft^3/lb

$$\frac{30\ ft^3}{hr} \ \frac{ft^3}{8.67\ lb} \ \frac{3\ hrs}{cycle} \ \frac{2.205\ lb}{Kg} = 22.654\ Kg = 22654\ g\ /\ cycle$$

Feed 1

$Pu = 239 = 239\,(1)$ $\dfrac{472.5 \text{ grams}}{349 \text{ g/mole}} = 1.35$ g-moles $PuOCO_3*2H_2O$

$O = 16 - 16\,(6)$

$C = 12 = 12\,(1)$

$H = 1 = 1\,(2)$

349 grams/ mole

$$\dfrac{1.35\,moles\ PuOCO_3*2H_2O}{}\ \dfrac{2\ mole\ H_2O}{PuOCO_3*2H_2O} = \dfrac{2.71\ moles\ H_2O}{}\ \dfrac{18\ grams}{mole\ H_2O} = 48\ grams\ H_2O$$

$$\dfrac{1.35\ moles\ PuOCO_3*2H_2O}{}\ \dfrac{1\ mole\ CO_2}{PuOCO_3*2H_2O}\ \dfrac{44\ grams}{mole\ CO_2} = 59.4\ grums\ CO_2$$

$O = 16\,(3)$

$N = 14$ $\dfrac{0.27 \text{ grams } HNO_3}{63 \text{ g/mole}} = 0.0043$ moles HNO_3

$H = \underline{1}$

$\quad 63$

$$0.0043\,moles\ HNO_3\ \dfrac{mole\ H_2O}{2\ moles\ HNO_3}\ \dfrac{18\ grams}{mole\ H_2O} = 0.039\ grums\ H_2O$$

$$0.0043\,moles\ HNO_3\ \dfrac{mole\ NO}{2\ moles\ HNO_3}\ \dfrac{30\ grams}{mole\ NO} = 0.0645\ grams\ NO$$

$$0.0043\,moles\ HNO_3\ \dfrac{mole\ NO_2}{2\ moles\ HNO_3}\ \dfrac{46\ grums}{mole\ NO_2} = 0.0989\ grams\ H_2O$$

$$0.0043\,moles\ HNO_3\ \dfrac{mole\ O_2}{2\ moles\ HNO_3}\ \dfrac{32\ grams}{mole\ O_2} = 0.0688\ grums\ O_2$$

$$1.35\,moles\ PuOCO_3*2H_2O\ \dfrac{1\ mole\ PuO_2}{mole\ PuOCO_3*2H_2O}\ \dfrac{271\ grams}{mole\ PuO_2} = 365.85\ grams\ PuO_2$$

Feed *2*

Fe = 55.85

H = 1

C = 12

O – 16

P = 30.97

Pu = 239

N = 14

NO, = 46

moles $Pu(NO_3)_4 * 2\ H_2O = \dfrac{130}{505} = 0.26$ moles $Pu(NO_3)_4$

moles $HNO_3 = \dfrac{165}{63} = 2.62$ moles HNO_3

moles $Fe(NO_3)_3 * 2\ H_2O = \dfrac{165}{277.85} = 0.59$ moles HNO_3

moles $(C_4H_9O)_3PO = \dfrac{5}{265.47} = 0.019$ moles $(C_4H_9O)_3PO$

$H_4P_2O_7 = 177.94$, $Pu(NO_3)_4 = 505$, $HNO_3 = 63$

$Fe(NO_3)_3 * 2\ H_2O = 277.85$

$(C_4H_9O)_3PO = 265.97$

$NO = 30$, $PuO_2 = 271$

$$0.26\ moles\ Pu(NO_3)_4\ \frac{2\ moles\ HNO_3}{mole\ Pu(NO_3)_4}\ \frac{63\ grums}{mole\ HNO_3} = 32.76\ grams\ HNO_3$$

$$0.26\ moles\ Pu(NO_3)_4\ \frac{moles\ NO}{mole\ Pu(NO_3)_4}\ \frac{30\ grums}{mole\ NO} = 7.8\ grams\ NO$$

$$0.26\ moles\ Pu(NO_3)_4\ \frac{moles\ NO,}{mole\ Pu(NO_3)_4}\ \frac{46\ grams}{mole\ NO,} = 11.96\ grams\ NO,$$

$$0.26\ moles\ Pu(NO_3)_4\ \frac{moles\ PuO_2}{mole\ Pu(NO_3)_4}\ \frac{271\ grams}{mole\ PuO_2} = 70.46\ grums\ PuO_2$$

$$0.26\ moles\ Pu(NO,)\,,\frac{moles\ O,}{mole\ Pu(NO_3)_4}\ \frac{32\ grams}{mole\ O,} = 8.32\ grams\ O,$$

$$0.019\ moles\ (C_4H_9O)_3PO\ \frac{3\ moles\ C_4H,}{mole\ (C,H_9O),PO}\ \frac{52\ grums}{mole\ C_4H_8} = 2.96\ grums\ C_4H,$$

$$0.019\ moles\ (C_4H_9O)_3PO\ \frac{0.5\ moles\ H_4P_2O_7}{mole\ (C_4H_9O)_3PO}\ \frac{2\ moles\ H,O}{mole\ H_4P_2O_7}\ \frac{18\ grams}{mole\ H,O} = 342\ grams\ H,O$$

$$0.019\ moles\ (C_4H_9O)_3PO\ \frac{0.5\ moles\ H_4P_2O_7}{mole\ (C_4H_9O)_3PO}\ \frac{moles\ P_2O_5}{mole\ H_4P_2O_7}\ \frac{141.99\ grums}{mole\ P,O_5} = 1.35\ grams\ P_2O_5$$

$$0.019\ moles\ (C_4H_9O)_3PO\ \frac{0.5\ moles\ H,O}{mole\ (C,H_9O)_3PO}\ \frac{18\ grams}{mole\ H_2O} = 0.171\ grams\ If,O$$

$$0.59\ moles\ Fe(NO_3)_3 * 2H_2O\ \frac{moles\ Fe,O,}{mole\ Fe(NO_3)_3 * 2H,O}\ \frac{159.7\ grams}{mole\ Fe,O,} = 47.11\ grums\ Fe,O,$$

$$0.59 \, moles \, Fe(NO_3)_3 * 2H_2O \, \frac{4 \, moles \, HNO_3}{mole \, Fe(NO_3)_3 * 2H_2O} \frac{63 \, grams}{mole \, HNO_3} = 74.34 \, grums \, HNO_3$$

$$0.59 \, moles \, Fe(NO_3)_3 * 2H_2O \, \frac{moles \, NO}{mole \, Fe(NO_3)_3 * 2H_2O} \frac{30 \, grams}{mole \, NO} = 8.85 \, grums \, NO$$

$$0.59 \, moles \, Fe(NO_3)_3 * 2H_2O \, \frac{moles \, NO_2}{mole \, Fe(NO_3)_3 * 2H_2O} \frac{46 \, grams}{mole \, NO_2} = 13.57 \, grams \, Fe_2O_3$$

$$0.59 \, \textbf{moles} \, Fe(NO_3)_3 * 2H_2O \, \frac{moles \, O_2}{mole \, Fe(NO_3)_3 * 2H_2O} \frac{32 \, grams}{mole \, O_2} = 9.44 \, grums \, O_2$$

Grams HNO_3 $\dfrac{13.605}{63 \text{ g/mole}}$ = 0.216 moles

$$0.216 \, moles \, HNO_3 \, \frac{moles \, H_2O}{2 \, mole \, HNO_3} \frac{18 \, grums}{mole \, H_2O} = 1.944 \, grums \, H_2O$$

$$0.216 \, moles \, HNO_3 \, \frac{moles \, NO}{2 \, mole \, HNO_3} \frac{30 \, grams}{mole \, NO} = 3.24 \, grums \, NO$$

$$0.216 \, moles \, HNO_3 \, \frac{moles \, NO_2}{2 \, mole \, HNO_3} \frac{46 \, grums}{mole \, NO_2} = 4.97 \, grums \, NO_2$$

$$0.216 \, moles \, HNO_2 \, \frac{moles \, O_2}{2 \, mole \, HNO_3} \frac{32 \, grams}{mole \, O_2} = 3.45 \, grums \, O_2$$

Westinghouse   Internal
Hanford Company   Memo

From: PFP **Process** Engineering   15530-95-1TC-039
Phone: . 373-3685 T5-55
Date: May 10, 1995
Subject: AIR FLOW REQUIREMENTS FOR STABILIZATION OF POCKY FLATS ASH

To: W.S. lewis   T5-55

            cc: M.W. Gibson   T5-55

The purpose of this memo is to present the results of
calculations for determining the air flow requirid through
the HC-21C muffle furnaces when stabilizing Rocky Flats **Ash.**
The air flow must be great enough to provide sufficient
oxygen to oxidize the carbon in the ash.

Observations from 2 TGA don.; by the PPSL with granular
activated carbsn indicate that a minimum reaction time of
1.9 hours is required to oxidize a carbon charge. This time
was used to perform the remaining calculations.

As seen in Attachment 1, calculations show that an zir flow
of 0.679 scfn is required to oridize 2 charge of 500 grams
with **37%** carbon to carbon dioxide (CO_2).

Formation of carbon monoxide (CO) due to deficient supply of
oxygen is undesirable since CO concentrations of 12.5% to
74.2% ai-e flammable. Evaluation of the PPSL analysis does
not show formation of CO with an air flow of 20 cc/min.
This is equivalent to an air flow of 1 scfn through the
muffle furnaces in HC-21C using the carbon mass to air ratio
used for the TGA analysis.

Even if the carbon in a charge were to forn exclusively CO,
the air flow can be set to ensure the CO concentration is
below the lower flammability limit of 12.5%. An air flow cf
0.86 scfn was found to maintain the CO level below the LFL.

Therefore, an air flow of 1 scfm is sufficient for charges
of Pocky Flats Ash. This flori rate is adequate to oxidize
the carbon to CO_2 and also ensures that CO concentrations
will remain below the LFL for CO of 12.5%.

L. T. Cunningham
PFP Process Engineer

att

Carbon Monoxide Generation Calculations

Assumptions:

- Charge weight is 500 grams hulk weight
- Maximum carbon content is 37% (average is 22%)
- Carbon homogeneously mixed throughout charge
- Oxygen diffusion into charge is sufficient to maintain carbon oxidation at maximum rate
- Efficiency of Oxygen utilization is 75%
- Standard Temperature and Pressure

1.   Calculate the rate at which carbon will oxidize.

   ⇨ Used the TGA run of granular activated carbon (GAC) done in the PPSL laboratory. TGA run done with 130.8 mg GAC and from 20°C to 1000°C at 5°C/min.

   *   Find the greatest slope of the TG curve.

Data points: 10% weight loss at 590°C and 24% weight loss at 670°C

$$\frac{dT}{d(Weight\ Loss)} * \frac{100\%}{5"C/\min} = \frac{80°C'}{14\%\ weight\ loss} * \frac{100\%}{5"C/\min} = 114\ \min$$

2.   Calculate the amount of carbon is a charge.

   ⇨ The maximum carbon content in the Rocky Flats Ash is 37%. The average carbon content is 22%. Charge size is currently limited to 500 grams.

Maximum Carbon in charge:

500 g * 0.37 g C/g material = 185 g carbon or 15.417 g-moles

Average carbon is charge:

500 g * 0.22 g C/g material = 110 g carbon or 9.167 g-moles

3.   Calculate the flow rate of air needed to oxidize carbon completely to carbon dioxide

   ⇨ Reaction: $C + O_2 \longrightarrow CO_2$
   ⇨ Assume efficiency of O_2 use as 75%
   ⇨ O_2 used produces an equal volume of CO,

Oxygen needed:

$$15.417\ g-moles\ C * \frac{1\ g-mole\ O_2}{1\ g-mole\ C} * \frac{1}{0.75} = 20.556\ g-moles\ O_2$$

Air needed:

$$20.556\ g-moles\ O_2 \frac{22.4\ liters}{g-mole\ air} \frac{ft^3}{28.316\ liters} \frac{100\ g-moles\ air}{21\ g-moles\ O_2} = 77.43\ ft^3\ air$$

$$\frac{77.43 \, ft^3 \; air}{1.9 \, hours} = 40.76 \; ft^3 \, / \, hr = 0.679 \; scfm$$

4.   Calculate the air flow rate to maintain the CO level below the LFL if only CO is produced.

⇨ Reaction: $2C + O_2 \longrightarrow 2CO$
⇨ LFL of CO is 12.5%
⇨ O_2 used produces twice the volume of CO

Oxygen needed to make CO:

$$15.417 \, g - moles \, C * \frac{1 \, g - mole \, O_2}{2 \, g - mole \, C} * \frac{1}{0.75} = 10.278 \, g - moles \, O_2$$

Air needed to make CO:

$$10.278 \, g - moles \, O_2 \; \frac{22.4 \, liters}{g - mole \, air} \; \frac{ft^3}{28.316 \, liters} \; \frac{100 \, g - moles \; uir}{21 \, g - moles \, O_2} = 38.72 \; ft \; uir$$

$$\frac{38.72 \, ft^3 \; air}{1.9 \, hours} = 20.38 \; ft^3 \, / \, hr = 0.340 \; scfm$$

Carbon Monoxide Produced:

$$\frac{15.417 \, g - moles \, C}{1.9 \, hours} \; \frac{1 \, g - mole \; CO}{1 \, g - mole \, C} \; \frac{22.4 \, liter}{g - mole} \; \frac{ft^3}{28.316 \, liter.s} = 6.42 \; ft^3 \, / \, hr \; CO$$

Air flow rate needed to maintain CO concentration below 12.5%:

$$\frac{6.42 \, ft^3 \, / \, hr \; CO}{12.5\%} = 51.35 \; ft^3 \, / \, hr = 0.86 \; scfm$$
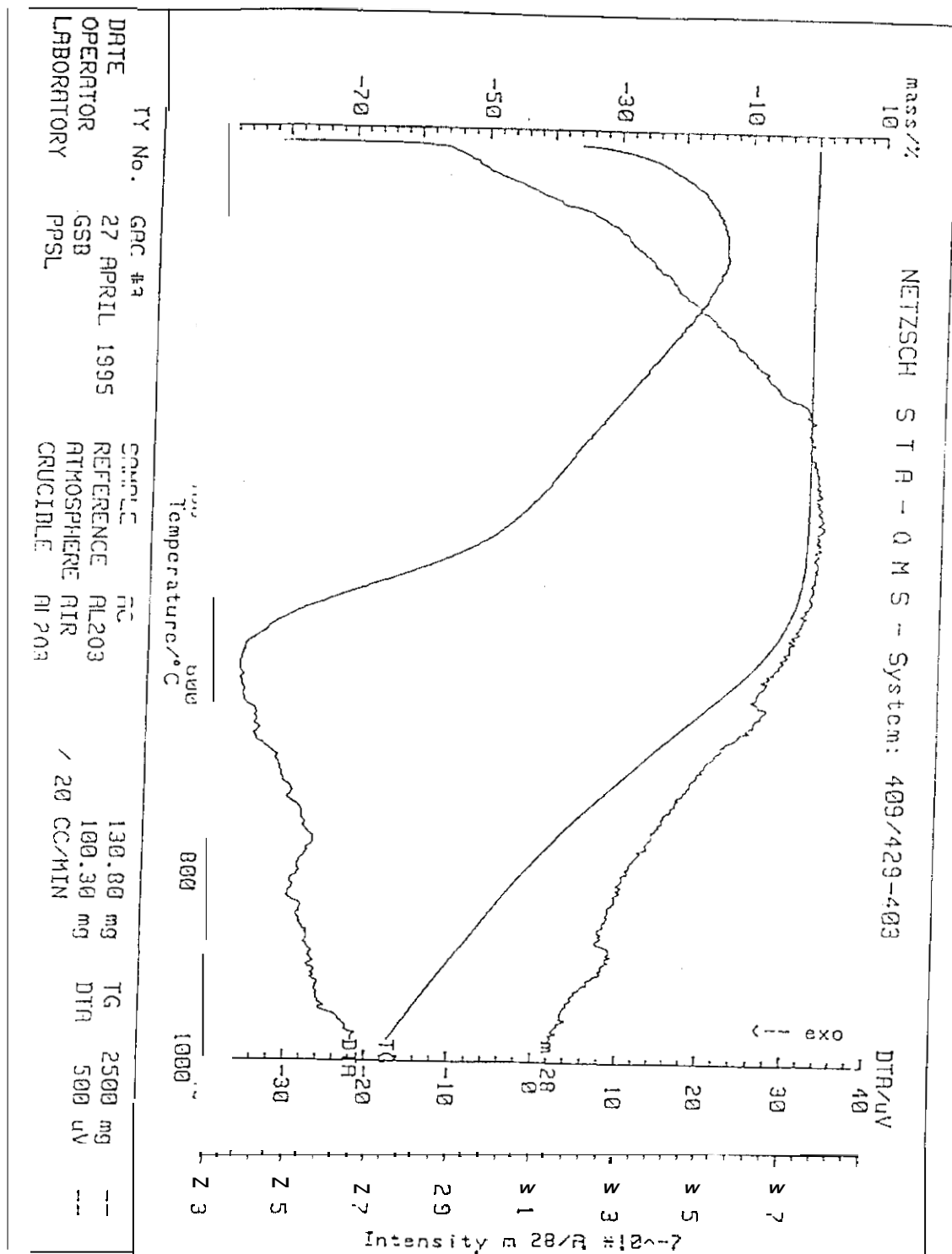
Internal Letter

Rockwell International

Date. November 8, 1985

No .65454-85-156

TO: *(Name, Organization, Internal Address)*
- P. Certa
- Process Engineering
- 234-5/200 W

FROM: *(Name, Organization, Internal Address, Phone)*
- C. H. Delegard/D. G. Bouse
- Plutonium Process Development Unit
- 234-5/200 W
- 3-3723/3-2419

Subject: • Lead Nitrate Reactions in Scrap Heels

References:?

1) T.C. Johnson and J.W. Lindsay, "Flammability of Leaded Dry-Box Gloves". RFP-1354 (June 1969).

2) J.W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. VII, p. 862, Longmans, Green and Co. (1947).

3) L. Bretherick, Handbook of Reactive Chemical Hazards, 2nd Edition, p. 1077, Butterworths (1979).

4) N.I. Sax, Dangerous Properties of Industrial Materials, 6th Edition, p. 1696, Van Nostrand Reinhold Co. (1984).

5) Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition, Vol. 14, p. 168, John Wiley and Sons (19811.

Recently, concern has been expressed that lead nitrate, $Pb(NO_3)_2$, may react violently with oxidizable materials in scrap heels and cause safety problems in heel stabilization. Lead nitrate has been found as a precipitate from nitric acid dissolution of lead-bearing Rocky Flats incinerator ash. Oxidizable material such as rags, paper, and graphite (also found Rocky Flats scrap) may also be fed, with the lead nitrate, to a furnace for thermal stabilization. In the present study, literature was reviewed and lab tests performed which showed the reactions were exothermic. While explosive reactions were described in the literature, no explosions were found in the lab tests.

The investigations were prompted by J. J. Roemer who recalled a study conducted at Rocky Flats concerning the flammability of leaded glove box gloves (Reference 1). The cause of the gloves' flammability was attributed to lead nitrate forming in cracks in the Hypalon or Neoprene gloves and, with time or heat, reacting with the degraded glove material to ignite or explode. Lead nitrate. found to precipitate from solutions produced by nitric acid dissolution of lead-bearing Rocky Flats ash, has a relatively low solubility in nitric acid solution (Ref. 2), dropping to about 4 g $Pb(NO_3)_2$ per liter at 11 $\underline{M}$ HNO_3. On the other hand, lead nitrate's solubility in water is about 100 times higher. This solubility offers a simple way to remove lead nitrate from the scrap.

**Rockwell
International**

P. Certa
Page **2**

References in chemical safety (Refs. **3,** 4) indicate violent reactions of lead nitrate with among other things, graphite, potassium acetate and ammonium thiocyanate. Lead nitrate also is a component in the manufacture of matches, pyrotechnics (fireworks) and explosives (Ref. 5).
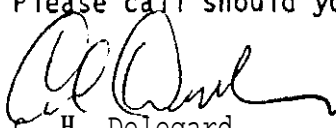
The most likely lead nitrate reactions in PFP were considered to be with TBP, paper, and graphite. Mixtures of lead nitrate and **TBP** were placed in a muffle furnace at 500°C. The mixture began to smoke as the temperature rose and the fumes eventually ignited. The flames subsided and some "pops" occurred to leave a gray-yellow deposit of lead oxide. A paper filter soaked with lead nitrate solution also was placed in the 500°C furnace. The paper did not burst into flames but instead burned from the edges-in along a glowing front. Mechanically mixed blends of lead nitrate and graphite were placed in the 500°C furnace. Small pops were noted as the mixture heated but were no different in quality from the pops noted for heating lead nitrate alone.

Thermal analyses were run of a lead nitrate-graphite mixture intimately blended according to the following stoichiometry:

$$Pb(NO_3)_2 + 2C \rightarrow PbO + N_2O + 2CO_2$$
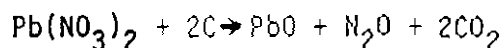
The results of the thermal analysis are presented in the Figure. Weight loss, complete at 550°C, correspond to production of PbO or Pb_2O_3. Small, mild exothermic events occurred at ~340, 380, and 420°C.

Please call should you have further questions or requests.

C. H. Delegard
Senior Chemist

D. G. Bouse
Senior Chemist

CHD:DGB:gij

att.

cc: T. W. Kruppa
　　T. A. Lane
　　J. J. Roemer
　　J. P. Sloughter
　　C. R. Stroup

ORIGINAL

ockwell Hanford Operations $\quad RE$ $5 \cdot 1 \cdot 13 \cdot 5$

SUPPORTING DOCUMENT		Number	Rev. Ltr./ Chg. No.	Page A of 17 Total Pages
PROGRAM: CHEMICAL PROCESSING		SD— CP-PTR-008	0	

Document Title: PROCESS TEST REPORT: Burning Plutonium Metal Buttons Using An Igniter	Baseline Document ☐ Yes ☒ No
	WBS No. or Work Package No. K6H3A
Key Words: Plutonium metal, Glovebox HC-21-C and Glovebox HA-21-1, oxidation, igniters. Hoskins furnace	Prepared by (Name and Dept. No.) *Lisa Weissbach* Lisa D. Weissbach/65930 See reverse side for additional approvals

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Abstract

Four (4) process tests were performed in Glovebox HA-21-1 to determine the safest and most effective method of oxidizing plutonium metal. The final process, which used the button igniter as a heat source, was performed on 08-21-85 and was the most successful in terms of safety, processing time, and ease of operation.

Plutonium metal oxidation is accomplished by contacting a heat source with the button to raise the surface temperature of the button to approximately 550°C. At this temperature, ignition occurs and the plutonium metal burns to form a plutonium oxide powder.

The first three process tests involved ignition in a Hoskins crucible furnace. Because of poor air supply to the burning oxide and the awkward handling of hot crucibles using tongs, improvements in safety and operating time were needed. An alternative processing method, a button igniter, was fabricated for the fourth process test. The igniter was designed to sit on the button surface and supply sufficient heat to initiate oxidation. Besides reducing processing time from approximately 9 hours to approximately 2 hours, no transferring of hot material was necessary.

The procedure and equipment outlined in the fourth process test. PTP-Z-995-0004, "Oxidation Process", will be used as a basis for future plutonium oxidation processing in Glovebox HC-21-C.

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A-6400-073 (7-85)

Page	Number	SUPPORTING DOCUMENT
B	SD-CP-PTR-008	

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DESCRIPTION OF CHANGE

A-6400-073R (7-85)

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2.0   DESCRIPTION OF TEST

Plutonium (Pu) metal oxidation is accomplished by contacting a heat source to the metal., which raises the surface temperature of the button to approximately 550°C. A t this temperature, ignition occurs and initiates the oxidation of Pu metal to Pu oxide.

A series of four (4) tests, total, were performed to evaluate processing time and ease of operation.   The processing details for each test are described below.

2.1   First Test

The first test examined button ignition and oxidation of Pu metal in a crucible furnace.   Besides successful oxidation of the plutonium metal in a crucible furnace, the processing time, ignition temperature, and cooling times, associated with this apparatus was a question answered by this process test.

2.2   Second Test

The second test was an attempt to ignite the plutonium metal button using a soldering iron as an alternative heat source to the crucible furnace.   The button was placed in a 6" x 6" x 1" burning pan and the soldering iron held on the button surface.   When the soldering iron failed to ignite the plutonium metal, the button was placed in the crucible furnace, heated to ignition, and transferred to the burning pan to complete conversion to the oxide form.

2.3   Third Test

Verification of NMIC calorimetry results and increasing the air supply to the burning plutonium metal were the object of this process test. The button ignition was accomplished in the crucible furnace and then transferred to the 6" x 6" x 1" burning pan to oxidize.   After about 30 minutes the burning metal was transferred to an 11" x 11" x 1-1/2" pan which was being tested to see if processing time could be reduced. When sufficient time was allowed to complete cooling of the oxide product, it was transferred to packaging cans.

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24   Fourth Test

An additional heat source, an igniter designed and fabricated for this process test, initiated oxidation of the plutonium button without the use of a Hoskin furnace. The button was placed in an 11" x 11" x 1-1/2" burning pan and the igniter rested on the button surface supplying enough heat through a circular shaped element to initiate oxidation. The plutonium oxide product, once formed in the pan, was allowed to cool and then packaged. As with the other tests, criteria such as total processing time and ease of operation were considered.

In addition, heat dissipation from the burning button was measured using heat crayons. The results of these observations will be discussed in the "test results" section of this docum ment.

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3.0 TEST METHOD AND TEST EQUIPMENT

All four (4) process tests involved plutonium metal oxidation in Glovebox HA-21-1.   The following summarizes equipment used in each test.

Test 1	Test 2	Test 3	Test 4
Furnace (Hoskins model FD-104	Furnace (Hoskins mode FD-104	Furnace (Hoskins model FD-104	Igniter (H-2-95860)
Crucible	Crucible	Crucible	SS stirrer
SS sheathed chrom-alumel	SS sheathed chrom-alumel	SS sheathed chrom-alumel	Electronic balance
			SS 11"x11"x1-1/2" pan
Electronic balance	Electronic balance	Electronic balance	Leather gloves
			Heat crayons
Leather gloves	Soldering iron	S.S. 11"x11"x1-1/2" pan	
	S.S. 6"x6"x1" pan		
	Leather gloves	Leather gloves	

*S.S. = Stainless steel

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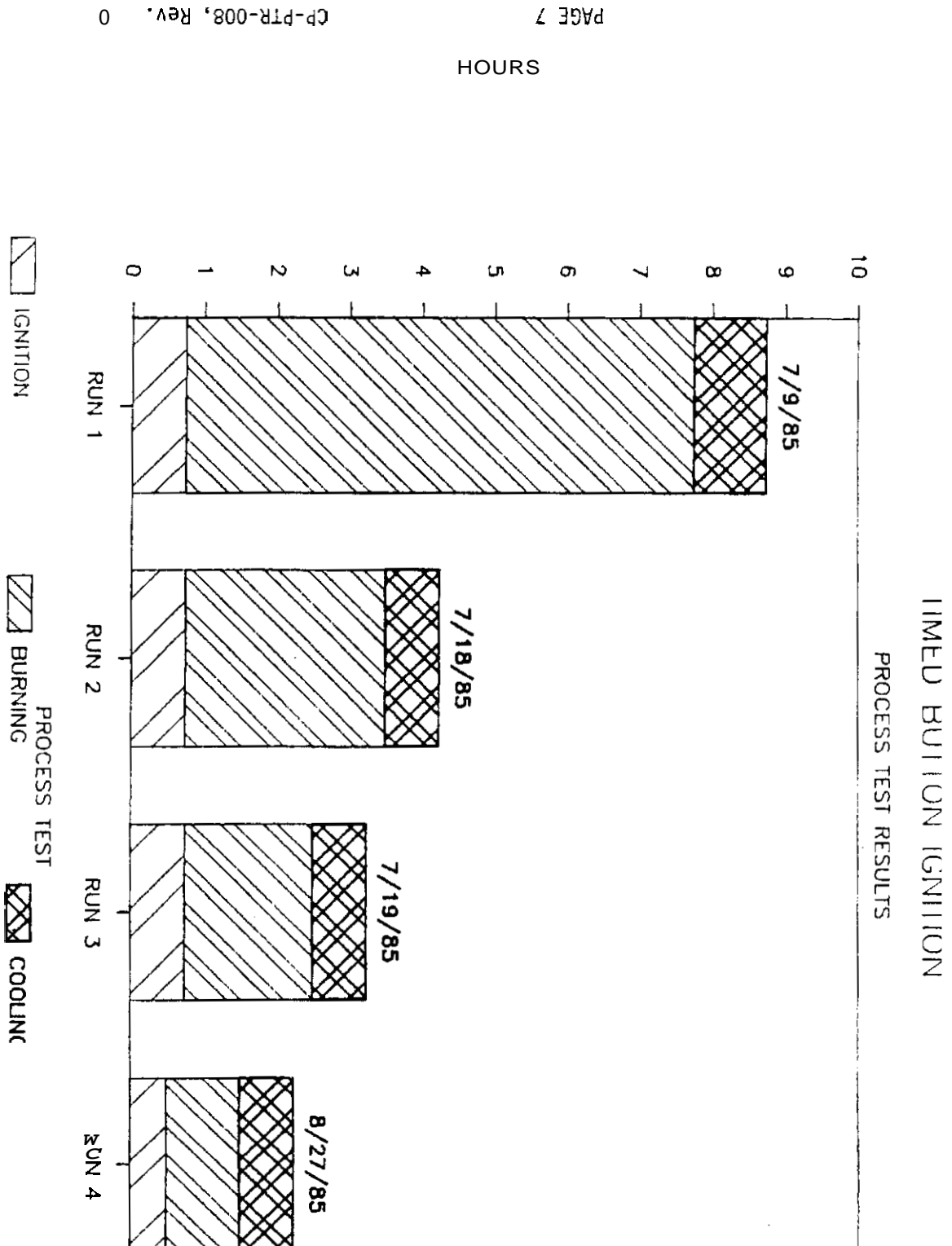| SUPPORTING DOCUMENT	Number	Rev. Ltr./Chg. No	Page
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4.0   TEST RESULTS

Processing time and operator safety were major criteria for choosing the most desirable processing method. The results for processing time in terms of ignition, burning, and cooling times are summarized in Figure 1. A significant decrease in processing time between the first and fourth run is illustrated by the drop from 8.75 hours to 2.25 hours. This is a decrease of 74%, which translates to a 200% - 300% increase in processing capability. For Runs 1, 2, and 3, the use of the furnace increased ignition time because of of poor air supply to the metal. In Run 1, since the conversion of Pu metal to oxide was performed completely in the crucible furnace, the air supply problem was even more evident by the drastic increase in reaction time. For tests 2 and 3, transferring Pu metal and oxide in a hot crucible was awkward and ignition time took longer because of air supply problems. For these reasons, Process Tests 2 and 3 took longer than the fourth process test.

In terms of safety and ease of operation, Process Test 4 was the best processing alternative. The results are presented in tabular form on Table 1. In summary, Run 4 was the safest and easiest process test to perform because the igniter, instead of the crucible, was the heat source. There was no transferring of thermally hot material, no awkward and heavy crucible handling and no air circulation problems around the burning Pu metal. The first test was the next best alternative, since all transfers were made while the plutonium was cool. The worst alternatives were Runs 2 and 3. Because of operating difficulties and transferrance of hot plutonium metal, these two operating schemes were considered poor choices.

Using the heat crayons during Process Test 4 revealed no heat dissipation problems around or above the burning pan. Temperatures close to normal were observed because of good air circulation. However, the area of contact below the pan, which sat directly on the glovebox floor, became quite hot, reaching approximately $400^\circ C$. Because of this finding, a change in the burning pan design wasincorporated which added 1" legs. The introduction of an insulating layer of air between the pan and glovebox should prevent future hot spots on the glovebox.

HOURS

TIMED BUTTON IGNITION
PROCESS TEST RESULTS

IGNITION

BURNING

COOLING

PROCESS TEST

RUN 1   7/9/85

RUN 2   7/18/85

RUN 3   7/19/85

RUN 4   8/27/85

0 1 2 3 4 5 6 7 8 9 10

TABLE I
OBSERVATIONS ON SAFETY AND EASE OF OPERATION

	ACTIVITY	EASE OF OPERATION	SAFETY	LL RATING
Run 1	Placed button in crucible furnace	Simple	No problems	
	Ignition, oxidation, & cooling	Simple	Furnace is hot; caution around heat source	
	Removal of crucible from furnace after run completion for weighing & packaging	Difficult; crucible with button oxide is heavy, hard to hold with tongs	May be problem if crucible breaks, glove rips or loss of Pu oxide inventory	Poor
Run 2	Placed button in pan	Simple	No problems	
	Attempted use of soldering iron	Simple	Caution around heat source	
	Placed button in crucible furnace	Simple	No problems	
	After ignition transferred button from crucible to burning pan	Difficult; crucible with button is heavy (approx. 5 lbs.), very hot (550ºC), could burn gloves	Dangerous if button should fall out or if crucible dropped & broke, possibility of uncontrolled Pu metal fire, burning of gloves	Poor
Run 3	Placed button in crucible furnace	Simple	No problems	
	After ignition transferred button from crucible to burning pan	Difficult; crucible with button is heavy (approx. 5 lbs.), very hot (550ºC), could burn gloves or organics	Dangerous if button should fall out or if crucible dropped & broke, possibility of uncontrolled Pu metal fire, ...	Poor
Run a	Placed button in burning pan	Simple	No problems	
	Ignited button with igniter	Simple	Caution around heat source, potential to burn gloves	
	Removal from pan after cooling	Simple	No problems	Excellent

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5.0   RECOMMENOATIONS/CONCLUSIONS

In terms of safety, ease of operation, and processing time, using the igniter to initiate burning was the optimum alternative.   The crucible furnace made transfers of plutonium metal, or oxide, a problem and lengthened processing time. This was due to the awkward handling of the crucible with tongs and to the poor air supply available to the burning metal in the crucible.   Using the furnace alone, as in the first process test, the operation was both safe and easy to perform, but the processing time was too long and therefore unacceptable.

The second and third process tests were acceptable in terms of processing time, but were considered neither safe nor easy to perform.

Since the fourth process test, which evaluated the igniter, met all the criteria deemed essential for button burning, the process test procedure PTP-Z-995-0004, "Oxidation Process" will be the basis for future plutonium oxidation processing in Glovebox HC-21-C. The operating procedure which will provide instructions for processing is: **20-160-033,** Rev 3.

As for heat dissipation, continued monitoring of the operation is planned. Initial operation will involve two (2) buttons burning simultaneously in HC-21-C. With the availability of additional heat sources and increased operator familiarity with the button burning process, Z-Plant Process Engineering can approve simultaneous ignition of up to four (4) buttons.

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6.0   REFERENCES

Process Test Plans

PTP-Z-995-0004, Rev. 0 - Rev. 2, "Oxidation Process"

Operating Procedure

ZO-160-033, Rev. A-0, "Oxide Pu Metal in Glovebox HC-21-C"

Process Specification

OSO-A-184-00005, "Miscellaneous Treatment"

Drawings

H-2-95860, Button Igniter Assembly

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APPENDIX A

DATA SHEETS

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OXIDATION PROCESS TEST DATA SHEETS

0 Z A-45-06-384 (07-09-85)

1. Weight of button/%240:   content: **2064.3**

2. Time of starting furnace: **10:50** am

3. Time oxidation begins: **11:25** am

4. Temperature oxidation begins: **550°C**

5. Time oxidation is complete: **5:45** pm

6. Time furnace is cooled to **50°C**:   **6:45** pm

7. Tare weight of slip lid can(s):   **87.7 – 94.0** grams

8. Gross weight of can(s):   **1432.4 – 1172.0** grams

9. Net weight **(8-7)**:   **1344.7 – 1078.0** grams   wt. gain: **359.4** grams

10. Estimated plutonium value to can(s): **(0.88** x net wt. **(9.))**   **2132** grams

11. Measured Pu value (calorimeter/N DAIA)

NOTES: o   Once oxidation started, the metal burned slow due to lack of oxygen.

o   Material stuck to the sides of pot crucible; operators had to reheat crucible to clean out remaining metal

o   Metal would arc when temperature reached **220°C**

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OXIDATION PROCESS TEST DATA SHEET

DZA-45-06-426 (07-18-85)

1. Weight of button/% 240 content: 2054 grams

2. Time soldering iron turned on: 10:00 am

3. Time oxidation begins: 10:43 am

4. Temperature oxidation begins: 575°C

5. Time oxidation complete: 1:30 pm

6. Tare weight of slip lid can(s):   88.2 g/91.3 g

7. Gross weight of can(s):   1331.1 g/1260.2 g

8. Net weight (8-7):   1242.9 g/1168.9 g

9. Estimated plutonium value to can(s):   1093.8 g/1028.6 g

   (0.88 x net weight (9.))   Total: 2122.4 g

10. Measured Pu value (calorimeter/ND AIA)

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OXIDATION PROCESS TEST DATA SHEET

D Z A-45-06-425 (07-19–85)

1. Weight of button/% 240 content: 2068.8 grams

2. Time soldering iron turned on: furnace time: 10:15 am

3. Time oxidation begins: 10:55 am

4. Temperature oxidation begins: 550°C

5. Time oxidation is complete: 12:45 pm

6. Tare weight of slip lid can(s):   128.0 g

7. Gross weight of can(s):   2475.3 g

8. Net weight (8-7):   2347.3 g

9. Estimated plutonium value to can(s):   2065.6 g

   (0.88 x net weight (9.))

10. Measured Pu value (calorimeter/N DAIA)

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OXIDATION PROCESS TEST DATA SHEET

OZA-45-06-401 (08-27-85)

1. Weight of button/%240 content: 2037 grams

2. Time ring heater turned on: 11:30 am

3. Time oxidation begins: 1200 pm

4. Temperature oxidation begins: 550°C

5. Time oxidation is complete: 12:55 pm

6. Tare weight of slip lid can(s): 124.5 g

7. Gross weight of can(s):   2461.0 g

8. Net weight (8-7):   2336.5 g

9. Estimated plutonium value to can(s):   2056.12 g

   (0.88 x net weight (9.))

10. Measured Pu value (calorimeter/ND AIA)

11.

Heat Crayon Types	Melt? (y/n)	Time	Location
52°C	N	12:30	1' from pan inside glovebox
150°C	Y	1230	Under glovebox, under pan
260°C	Y	1235	Under glovebox, under pan
371°C	Y	12:40	Under glovebox, under pan
427°C	N	1245	Under glovebox. under pan

Summary of Proposed limits and controls to allow oxide packaging in a BTC

These limits and controls will not prevent a BTC failure (i.e., make it incredible), they are intended to make a failure extremely unlikely and provide adequate worker protection should a failure occur.

Limit/Control	Basis	Detection/Control
Permitted feeds- Pure oxide from metal oxidation or calcinations of oxalate	PPSL memo (Barney 2001) documenting literature search concluding that pure, well characterized oxides will not reabsorb after calcination at 1000C, plus other documents	Blend Plan for packaging will specify what oxide items will be packaged. Source and method of preparation must be known. Feeds not permitted include impure oxides and oxides from MgOH precipitation.
Surveillance Check can for lid deflection (pressurization), initially, within 30 days, and periodically	Pressure models indicate BTC working pressure could be exceeded with loading to 3013 limits of % water	Surveillance procedures. Cans that develop over 100 psia may be subject to additional surveillance. Cans that exceed 350 psia will require reprocessing.
Limit BTC contents to Hanford BTCC with oxide and no foreign objects allowed	To comply with 3013 standard requirement demonstrating through measurement or analysis that 3013 working pressure will not be exceeded.	Canning procedures control can configuration and contents. Analysis demonstrates gas particle density measurement not required, as per DOE-STD 3013 requirements
Allowable moisture content	For the permitted feeds allowable moisture content in the stabilized oxide should be below *0.2* **wt** %	Stabilized oxides between *0.5* wt% and *0.2* wt% can be accepted after evaluation and documentation by the Vault cognizant engineer.

General Process Description:

Stabilized oxide from the permitted feed sources will be removed from the furnace, screened and collected in a BTCC. Alternatively, stored product oxides previously stabilized at 1000C and currently stored in food pack cans may be opened and the contents from one or more cans placed into the BTCC. After filling the BTCC will be blended and sampled. After sampling the lid will be reinstalled. When acceptable stability test results are received the BTCC will be transferred for welding/sealing as soon as possible. During the welding process the BTCC atmosphere will be exchanged with dry helium.

Permitted oxide feeds

Source and method of preparation must be known

Well-characterized, high purity product quality oxide resulting from known processes
including:
Oxidization of metal
Oxidation of metal brushings
Oxalate derived oxide – that is produced by calcination of Pu oxalate

Applicable source codes
Oxalate derived product oxides includes:
- PBO-
- BLO-
- LAO-
* Oxidization of metal
  o Includes historical Brushed button oxide (BBO)

  o Burned Oxide (BO)

  o recent metal brushing

  o oxidized metal (461 Prefix)

- DZO (includes oxalate derived oxide and oxide produced by metal burning)

- (GEO source method is unknown)

Other high purity oxides, greater than 85 wt% Pu before stabilization, may be accepted
after evaluation on a case-by-case basis and approval of the Vault Storage Cognizant
engineer. This evaluation must be recorded in the documentation/database file for each
item.

Basis: A literature search as documented in by PPSL staff concludes that based on
technical research and testing that plutonium dioxide from metal burning and
oxalate calcinations will not reabsorb enough moisture to fail the 3013 criterion as
long as it is fired at 950C for at least two hours (Barney 2001). Additionally it
concludes that moisture reabsorbtion is relatively rapid and equilibrium water
contents are expected to be less than 0.1 wt%. It can be concluded that this
readsorbtion is likely to occur during cooling and handling of the process furnace
charge and will be detected in the LOI or SFE analysis. For relatively pure
oxides, calcined at 1000C, the effect of relative humidity on readsorbtion was not
significant, the reference memo discusses readsorption tests done with RH as high
as 74%. These conclusions are well known and form the basis for the DOE –
STD-3013 (DOE 2000, Bailey 2000, Haschke 1995)

Additionally the following controls will be in place as matter of good practice.
1. The stabilized oxide, when stored in the BTCC after blending and sampling,
will have the lid installed.
2. The BTCC atmosphere will be replaced with dry helium during the canning
process.

Detection/Control:

> The Blend plan for oxide canning will only allow relatively pure oxide feed materials from the approved sources.

Feeds not Currently Permitted

Any feeds not specifically allowed, including all impure oxides and oxide from the MgOH precipitation.

Basis: Although reduction in the surface area of plutonium in these materials is also expected, re-adsorption of moisture is expected to be of concern due to the presence of salts and potentially moisture adsorbing metal oxides, such as CaO and MgO. In addition. the MgOH product is also shown to adsorb Carbon Dioxide and behavior of the adsorbed CO, is not well yet understood. Additional limits and controls will have to be developed before canning impure oxides, including the potential for dry air or dry inert atmospheres.

Detection/Control:

> The Blend plan for oxide canning will not allow impure oxide feed materials.

Pressurization Analysis and Models and Oxide Particle Density Measurement

Note: All the following pressure models are conservative and therefore predict "worst case" pressure values and do not reflect realistic, anticipated pressures. Actual pressures are expected to be low, i.e., no more than a few atmospheres, but are difficult to predict because of the complexity of the situation and lack of a definitive pressurization model.

3013 Pressurization Model

> The 3013 STD limits the total mass of package content to no more than 5 kg and indicates that mass may be further limited to ensure that the bounding pressure does not exceed the outer container design pressure. Alternatively analysis can be done to show the free gas volume of the package is at least 0.25 l/kg of oxide. (DOE 2000, Section 6.3.2.). The database, as required by section 6.5.2 of DOE-STD-3013 requires measurement of the particle density or reference to a model that demonstrates a limitation on mass loading is not needed.

> The Hanford 3013 oxide package container description is given as:

Container	Interior volume (liters)	Mass (grams)	Container Material Volume (liters)	Free Volume (liters)
BTCC	1.560	1475	0.187	1.560
BTC	2.105	1690	0.214	1.918
BNFL outer	2.602	4026		2.204

Determination of the gas volume of the Containers

The worst-case oxide can loading is that where the bulk material fills the convenience container.

Therefore an oxide where 5.0 kg mass/1.56 liters = 3.2 kg/l is the worst-case oxide bulk density. The 3013 STD allows use of a packaging fraction method, in lieu of gas pycnometer measurement, which states that the ratio of bulk density to particle density does not exceed 0.62. Thus particle density is determined by bounding estimate to be 3.2/0.62 or 5.17 kg/l. This gives a maximum material volume as 5.0 kg/5.17 kg/l= 0.967 liters.

The worst-case gas volume of the containers (V_1) are:

V_1 for a BTC only = 1.918-0.967 =   0.95 liters
V_1 for the overall Hanford 3013 Package = 2.204-0.967=1.237 liters

Therefore to eliminate the need for particle density measurement on oxides it can be shown that the free volume requirement, section 6.2.3 of the DOE-STD-3013 is met, specifically that the free gas volume shall be at least 0.25 l/kg of oxide. Though the calculated minimum free volume is just slightly under this, (0.013 liters), it is based on worst case assumptions of can filling and the bulk density to particle density ratio. In practice, the can will not be filled 100% full, as the current procedure specifies it is filled to ½ inch below the threads in the mouth of the BTCC, providing additional free volume not credited in the analysis above. It will be necessary, however to limit the inners cans in the overall package to those analyzed above and limit any foreign objects, such as metal spacers or pressure sensing devices, unless analysis shows that minimum free volume requirements are maintained, or expected pressures will not exceed container working pressures.

Estimate of Maximum Pressure in a BTC with 5 kg of oxide.

From the 3013 STD equation to calculate the maximum theoretical pressure in a BTC

Values of Parameters used to Calculate Pressure

Symbol	Quantity	Units	Symbol	Quantity	Units
P	Container Pressure	Psia	V_1	Gas Volume of Container*	0.95 l
P_0	Fill Gas Pressure at Filling	Psia	M	Mass of Oxide	5.0 kg
T_1	Evaluation Temperature (Determined by thermal analysis)	438 K (165C)	ρ	Density of Oxide	3.2 kg/l
T_0	Fill Gas Temperature at Filling	298 K (25 C)	Q_0	Container Energy Generation	19 w
L	Water in Container	0.5 wt%	τ	Storage Time	50 yr.

* The gas volume is determined by subtracting the material volume (mass of 5.0 kg divided by particle density of **5.17kg/l**, determined by the from the bulk density by the packing fraction method to yield 0.967liters) from the 1.918 liter free volume of the BTC/BTCC container system.

$$P_{max\ in\ BTC} = P_0 \cdot (T_1/T_0) + 0.67\ ml \cdot T_1/V_1 + 7.517x10^{-5}\ Q_0 \cdot \tau \cdot T_1/V_1$$
$$P_{max\ in\ BTC} = 14.7*(438/298) + 0.67*5*0.5*438/0.95 + 7.517X10^{-5}*19*50*438/0.95$$
$$P_{max\ in\ BTC} = 71.6 + 777.3 + 37.9 = 827\ psia$$

For the maximum pressure in a 3013 outer can, only the gas volume is different. previously determined to be 1.237 liters. This assumes the BTC has failed.

$$P_{max\ in\ 3013\ outer} = P_0 \cdot (T_1/T_0) + 0.67\ ml \cdot T_1/V_1 + 7.517x10^{-5}\ Q_0 \cdot \tau \cdot T_1/V_1$$
$$P_{max\ in\ 3013\ outer} = 14.7*(438/298) + 0.67*5*0.5*438/1.237 + 7.517X10^{-5}*19*50*438/1.737$$
$$P_{max\ in\ 3013\ outer} = 21.6 + 593.1 + 25.3 = 640\ psia$$

Rate Based Radiolysis Model

The 3013 model, which assumes 100% radiolysis, with no time factor can be converted to a time based prediction with inclusion ofradiolysis rate data. The overall radiolysis/recombination equation is given as:

$$PuO_2\ (s) + x\ H_2O\ (adsorbed) \rightarrow PuO_{2+x}\ (s) + x\ H_2\ (g)$$

An experimentally derived rate, determined by LANL (Haschke 1995), is given as 3.3 nanomoles/m²-day. A comprehensive decay program developed by Hoyt includes this rate based pressure buildup, applied at a constant value until all available water is reacted. This approach, while resulting in lower pressures initially, will eventually reached the same pressures as the 3013 model, because it assumes all the water is reacted. This is conservative for two reasons:

First, the radiolysis reaction will not realistically run to full completion.

Second, the LANL rate data, which was developed for the initial rate. measured in

Case	%water	% 240	Total Mass	Wattage	Comments
1	0.05	16.5%	2.85 Kg	19	High heat oxide, typical of most of
2	0.20	16.5%	2.85 Kg	19	PFP pure oxides, additional free volume due to reduced mass.
3	0.05	11.5%	5 Kg	19	FG oxide (lower power generation)
4	0.20	11.5%	5 Kg	19	allow loading to mass limit
5	0.50	16.5%	5 Kg	33	High heat oxide loaded to 5 Kg exceeds allowable wattage, also unrealistic residual moisture content

Case /Time	He Pressure (from alpha decay) psi	Hydrogen (from radiolyislrecombination) Psi	Cover Gas (mostly He) psi	Total Pressure psi
1/ 50yrs	22.5	30.6	20.7	73.8
2/50 yrs	22.5	122.2	20.7	165.5
3/50yrs	33.8	77.2	20.7	137.8
4/50yrs	33.8	308.8	20.7	363.4
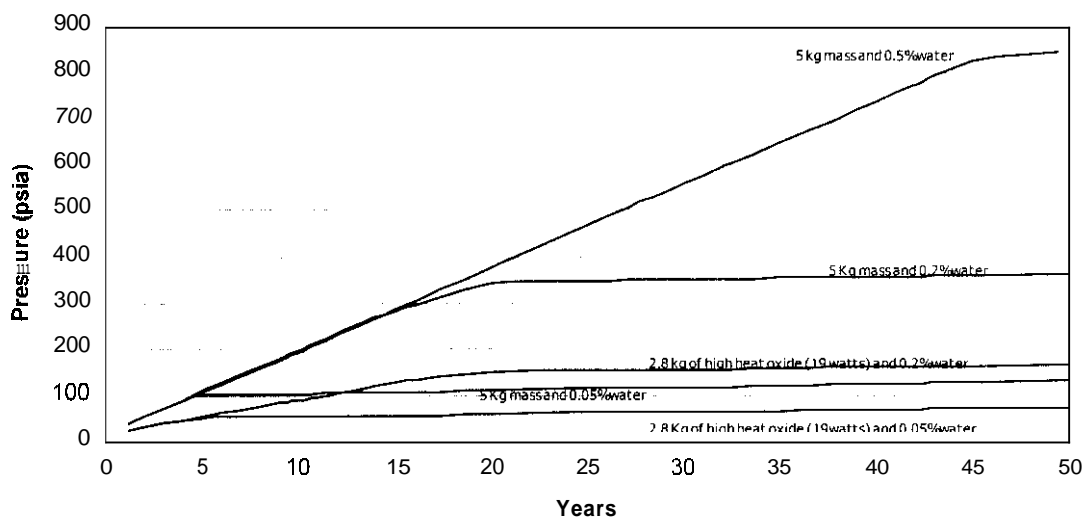
From this figure, for the normal maximum expected residual water content (0.2wt%) and using the conservative assumptions for particle density (developed earlier) and the

conservative rate based model, the calculated pressure does not exceed the BTC working pressure of 350 psig until 25 years.

Pressure determined by Vapor Pressure Model

Current research suggests that expected pressures are less than the maximum theoretical pressures predicted by the DOE-STD-3013-99 (Veirs). Radiolysis of adsorbed water is not expected to determine pressures. Current and historical research on moisture adsorption on PuO_2 indicates that water is adsorbed in layers, The first two layers, called chemisorbed or molecularly absorbed water are very tightly bound and will not be desorbed at expected storage temperatures. Water layers above these two, called physisorbed water can behave like free water and can be expected to be released as vapor at expected storage temperatures, i.e., above 100C. The amount of water available to vaporize and create pressure is therefore dependent on the specific surface area of the oxide. The mass of water per layer has been determined experientially to be 0.22 mg $H20/m^2$. (Haschke). Predicted storage pressures using this model are essentially determined by the amount of water adsorbed above two monolayers and the temperature of the gas phase in the storage container. Previous thermal modeling of BTCs in storage, loaded to 19 watts, has estimated gas phase storage temperatures at 165C. The numbers of monolayers that would result for various surface oxides packaged with differing moisture contents is given in Table XX ., although the oxide is not expected to load to more than two monolayers. These values are provided because the standard allows up to 0.5wt% water

Table XX

Total number of monolayers of water present of oxide

Specific Surface Area	Weight Percent Water					
m²/gm	0.5	0.4	0.3	0.2	0.1	0.05
10	2.3	1.8	1.4	0.9	0.5	0.2
5	4.5	3.6	2.7	1.8	0.9	0.5
1	22.7	18.2	13.6	9.1	4.5	2.3
0.5	45.5	36.4	27.3	18.2	9.1	4.5
0.1	227.3	181.8	136.4	90.9	45.5	22.7

Results of a LANL model developed in support of the LANL MIS program for pressure in BNFL style 3013 containers is shown in Figure YY (Viers 2000)

Figure YY – LANL Vapor Pressure Model for 3013 cans

Pressure vs. Temperature as a Function of Surface Area
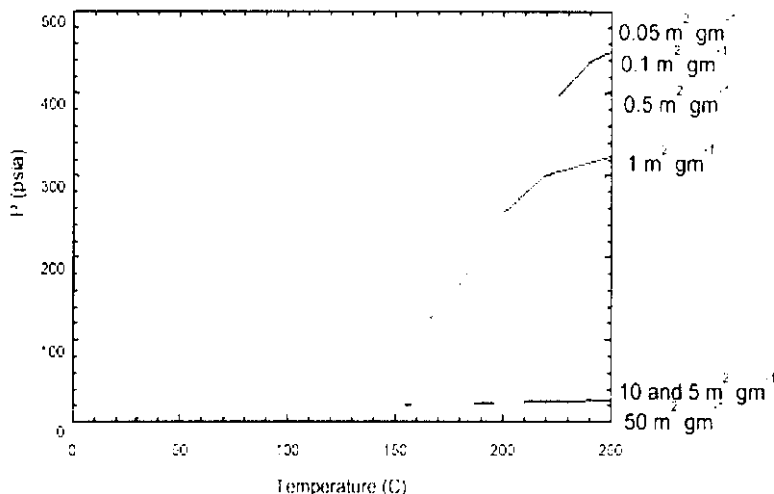
A simplified model for the Hanford BTC is shown in Figure ZZ. With increasing moisture content pressures rise in accordance with the ideal gas law, until saturation pressures are reached. With oxides with surface areas of 5 m^2/gm and less, and with the DOE-STD-3013 allowable moisture content, there is sufficient moisture available to reached saturation. There is no time constant in the model; pressures are realized as soon as the can reaches thermal equilibrium, which is expected to be within hours after canning. As such, helium generation from alpha decay is not included; but it would be expected to continue to slowly increase pressures, typically on the order of 15 to 30 psia after 50 yrs.

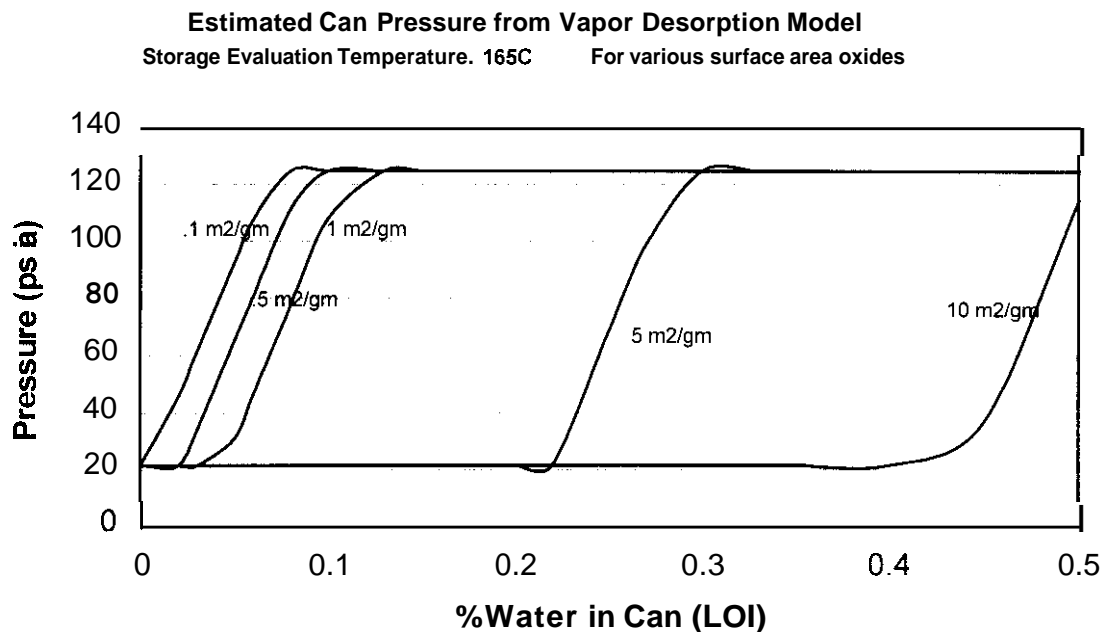Other Values used in the this model are:

Gas Constant -R	82 cm3-atmlgmol–K
BTC free volume	950 cm3
Evaluation Temperature	165 C
Initial Pressure	14.7 psia of He gas at 25C
Saturation Pressure at 165C	103 psia

Figure ZZ – Vapor Pressure Model Results for Hanford BTC

Estimated Can Pressure from Vapor Desorption Model
Storage Evaluation Temperature. 165C   For various surface area oxides

Allowable moisture content on oxides

As a control measure only oxides that measure less than 0.2 wt% moisture will he routinely accepted. Oxides that have between 0.2 and 0.5 wt % moisture may he packaged after evaluation and approval of the Vault Cognizant Engineer.

Basis: The percent moisture of the permitted feeds (relatively pure oxide) should be very low after calcinations, because of the reduction in specific area. (DOE 1999 and Haschke 1995). In addition analysis of data related to moisture readosorbtion

and ½ monolayers. (Haschke 1995) Dependent on surface area of the oxide, this would result in % adsorbed moisture as shown in Table Z.

Table Z

Percent Moisture for Equilibrium Water Concentration for Pure Oxides

Specific Surface Area (m²/gm)	Percent moisture
10	0.310
5	0.155
1	0.031
0.5	0.016
0.1	0.003

Since oxides less than 5 m^2/gm are routinely expected to result after calcination at 950C, regardless of the method of preparation, any oxide from the permitted feeds that is analyzed above 0.2 ‰ moisture should be considered unusual and subject to additional review.

Analysis of material with greater than 0.2 **wt%** moisture may include review of source of the material and stabilization results of similar material, and stabilization run data. Potentially specification of additional surveillance requirements could result. The disposition of these items should be documented and recorded in the database/documentation file for the specific item.

Surveillance for pressurization while stored as BTC only (No outer can)

Limits: The containers will be checked for pressurization by use of a dial indicator to measure lid deflection.

The surveillance frequency of the BTCs containing oxide will be:

- Baseline taken with 2 hrs of welding
- Initial taken at nominally 30 days in storage (**+/** 5 days)
- Periodic done every 12 months (+/1 one month)

After a significant positive experience basis is accumulated the surveillance frequency may be relaxed.

Basis: The baseline lid deflection must be taken quickly as the vapor pressure model indicates pressure above 100 psia may occur as soon as thermal equilibrium occurs. The initial lid deflection, taken at 30 days, is a DOE-STD-3013 requirement to check for "infant mortality" type failures. The periodic inspection is done to accumulate an experience base to demonstrate that can pressurization is not occurring and to detect any latent failures.

Detection/Control:

Any BTCs that exhibit pressurization above 100 psia will be subject to enhanced surveillance as deemed appropriate by the vault storage cognizant engineer. Any BTC with pressures above the working pressure of 350 psia will be opened. analyzed for moisture content, restabilized and repackaged.

References

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Mason 1999: R.E. Mason, et. al., " Materials Identification and Surveillance: June 1999 Characterization Report", Los Alamos National Laboratory Report LA-UR-99-3053

Veirs 2000: K. Viers, et al, "Vapor Pressure and Moisture Sorption and Material Moisture Content by Measuring the Relative Humidity'' Los Alamos National Laboratory MIS Working Group Meeting, October 2000

FLUOR *GLOBAL SERVICES*

Memorandum

To	**D.** R. Speer	Date	May 22, 2001 ~~May 21, 2001~~
Location	T5-50	Reference	IAC00-PPSL-01-24Rev I
Telephone:	373-1110	Client	
From:	G. S. Barney/ T. D. Cooper	Subject	WATER REABSORP'I'ION AND SAFETY QUESTIONS ON ALLOY STABILIZATION
Location:	T5-12		

cc: J. R. Ewalt
L. F. Perkins

The purpose of this letter is to provide responses to questions you had concerning stabilization of the alloy items. The questions are listed below:

1. Are the alloys different enough from the high quality oxides to cause us to implement new controls to assure that moisture reabsorption won't cause the stabilized materials to exceed the 0.5% moisture criteria?

2. Are the alloys different enough from the metals to cause us to implement new controls to manage the hazards associated with opening and stabilizing them'?

Our responses are as follows:

Water Reabsorption on Stabilized Plutonium-Uranium Alloy Items (G. S. Barney)

Stabilization treatment of the Pu-U metal alloys items in tlie PFP production furnaces will yield a mixture of oxides that will absorb small amounts of moisture from the humid glove box air in contact with the oxides. The objective of this summary is to estimate tlie amount of water that might be reabsorbed over a reasonable time period for exposure to glove box air. This must be less than 0.5 wt. percent to meet the 3013 Standard. According to literature references tlie oxides produced by heating tlie alloys in air at 1000°C will be a mixture of PuO_2, U_3O_8, U_3O_{8-x}, and possibly UO_3 (Haschke et al., 1997). For alloys containing molybdenum, inolybdates of plutonium and uranium would also he expected. Plutonium dioxide fired at 1000°C has been shown to absorb very small amounts of water. The equilibrium water content of pure PuO_2 treated by tlie 3013 Standard will be typically less than 0.2

wt. percent (Barney, 2001). Equilibrium with tlie glove box air will he reached in several hours

Information on adsorption of water on the other oxides is much more scarce. Equilibrium thermodynamic calculations (Taylor et al., 1993) show that at 25°C, all of the uranium oxide products listed above are unstable in glove box air. This instability is caused by the adsorption of water to form $UO_3 \cdot 2H_2O$ and $\beta\text{-}UO_2(OH)_2$. Formation of these hydrated compounds is no doubt very slow, since U_3O_8 is used as a primary standard for uranium gravimetric analyses (Greenwood and Earnshaw. 1985). The most relevant moisture absorption data that was found was for a sample of mixed oxide fuel (UO_2-PuO_2) that was calcined at 750°C for three hours and then exposed to glove box air (Kerraker, 1995). After nine days the weight gain was determined to he 0.10 wt. percent and leveled off at this value for three more days. X-ray diffraction analysis of this sample showed that not all of the solid solution of tlie cubic dioxides was converted to $PuO_2 + U_3O_8$ even after heating at 900°C for one hour in air.

A Chinese article (Feng and Chen, 1986) reports that during storage of U_3O_8, increases in weight were observed due to formation of hydrates by reaction with atmospheric water. The method of preparation and length of storage was not specified in tlie abstract, so the information is of little value.

Although most molybdates are non-hygroscopic, the compound, $Y_2Mo_3O_{12}$, hydrates in air to form $Y_2Mo_3O_{12} \cdot 4H_2O$ (Fournier et al., 1970). Yttrium is a rather rare element and is not known to exist in our alloy inventory, therefore, $Y_2Mo_3O_{12}$, is not anticipated in the oxide product. No information on water absorption on plutonium or uranium molybdates was found. We therefore cannot state with certainty the degree of moisture readsorption that will occur on plutonium or uranium molybdates. Readsorption of moisture on plutonium or uranium molybdates is not expected to be a significant phenomenon, however if it occurs, the extent of readsorption will he hounded by the readsorption behavior of MgO found in the product from the magnesium hydroxide process. Several tests with CeO_2 as surrogate plutonium dioxide along with molybdenum oxide would help to identify any readsorption problems. These tests could be performed in the PPSL in a relatively short time.

In conclusion. tlie best information available on water reabsorption on calcined alloys indicates that significant amounts of water will not be absorbed on these oxides in tlie time required to handle them before repackaging them in tlie glove boxes. Only 0.10 weight percent water was reahsorhed on a calcined MOX sample over 12 days.

References:

Barney, G. S. (2001), Letter to T. W. Halverson, January 2, *Water Readsorption Rules on Relatively Pure PFP Calcined Plutonium Dioxide,* 1AC00-01-001, Fluor Hanford, Inc.. Richland Washington.

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Safety Review for Handling Pu Alloy Materials (T. D. Cooper)

The Plutonium Finishing Plant (PFP) is tasked with ensuring tlie stability of plutonium (Pu) bearing materials within tlie PFP vaults. PFP has already gone through a safety review for liandling plutonium inetal and plutonium metal corrosion products that lasted several years. Numerous attempts to prove the safety in handling these materials through theoretical and mathematical analysis failed due to the complex nature of these problems and lack of data. We finally resorted to documenting the extensive history of processing throughout the DOE complex and tlie historical safety for handling kg sized samples of metal as buttons and/or ingots and up to 200 grains of pure plutonium hydride within a glovebox. This documentation **is** contained in the Denver Workshop notes and in several letters prepared by T. D. Cooper.

In addition to pure plutonium metal, PFP also possesses many metal alloy items wherein Pu is alloyed with other metals such as aluminum, molybdenum, etc. The question has been raised as to tlie safety of handling these alloys and their relative hazard as compared to Pu.

Plutonium forms a spallable oxide coating that allows continuing oxidation. It is also more electronegative than many other alloying metals. The rather large reaction enthalpy and the relatively fast surface reaction rates, results in large temperature increases. This temperature increase also serves to drive the reaction rates.

The factors affecting the reaction rate of an element are the inherent reactivity of that element. tlie reactant concentrations, tlie temperature, tlie specific surface area, and tlie presence of catalytic agents.

Since Pu is the primary reactant within tlie alloy the concentration will always he less than in pure plutonium metal. **As** a general rule of thumb, an alloy's reactivity follows tlie reactivity of the dominant metal in the alloy.

The reaction temperature for alloys will typically he less tliaii for pure plutonium metal. Factors that could increase the alloy reactivity are higli specific surface area, and/or the presence of catalytic agents.

From tlie above discussion, one can see that for items of similar specific area, tlie behavior of pure plutonium bounds the behavior of the alloys. We can thus adopt the same general rules for handling alloys as currently exist for handling Pu metal.

These rules are:

- Handling kg -sized monoliths with tlie glovebox is permissible.

- Up to 200 grains of potentially reactive powder is permissible.

Adequate rules for handling large quantities of turnings and shavings of Pu metal within the glovebox have not been promulgated. This area will now be discussed.

It is known (Ref. 1) that any configuration of metal **is** safe as long as it remains within a standard slip lid can with a diameter **less** than *5* inches. Natural diffusion or convection rates into this container cannot move oxygen fast enough to cause unacceptable pressures or temperatures to arise within the glovebox.

If metal with high specific surface area is removed from the can, and tlie metal heats pyropliorically, the main heat transfer path is through conduction through the bottom and radiation to the remainder of the glovebox. Air is notoriously inefficient in absorbing radiation energy since only a very small percentage of tlie gas molecules are poly-atomic. Modeling sliows that tlie increase in temperature of the glovebox is limited to less than **75** ^{0}C for a 2 kg sample assuming iiistantaneous and evenly distributed heat transfer. Since the combustion event is not instantaneous. it is very unlikely that the glovebox temperature increase would exceed 10 ^{0}C. The glovebox pressure never departs from the normal negative regime, for any condition other than very tine powder being explosively distributed throughout the air.

We therefore conclude that with the exception of the tine powder case. less than 2000 grams of Pu metal or any of its alloys (in any configuration) has been analyzed and cannot increase the general temperature of a typical C-Line glovebox beyond 75 ^{0}C. 'This 2000 grain value is not meant to be an absolute limit. Larger amounts in specific configurations will be permissible with appropriate analysis. For fine pyrophoric powders, an experience-based limit of 200 grams is used.

Reference:

1. Letter 15F00-99-054, " Scientific Evaluation Of Safety In Processing Pu Metal", Thurman Cooper, May 25, 1999

To	From	Page 1 of 1
Distribution	PFP Process Engineering	Date March 27, 2001
Project Title/Work Order		EDT No. NA
Basis Document for Thermal Stabilization		ECN No. 665398

Name	MSIN	Text With All Attach.	Text Only	Attach./ Appendix Only	EDT/ ECN Only