DISTRIBUTION SHEET

To: Distribution From: Criticality & Radiological Analyses Date: 9/9/94

Project Title/Work Order:

CSER 94-004: Criticality Safety of Double Shell Waste Storage Tanks

EDT No.: 157940

ECN No.:

Name	MSIN	With Attachment	EDT/ECN & Comment	EDT/ECN Only
SJ Altschuler	R3-01	X		
JJ Badden	S5-01	X		
SL Bhatia	R3-01	X		
VC Boyles	R1-49	X		
DJ Braun	H4-66	X		
DR Bristol (4 copies)	R3-01	X		
T Chiao	H4-64	X		
GM Christensen	H4-21	X		
RF Christensen	S7-54	X		
JC Conner	H4-61	X		
JW Daughtry	H4-64	X		
DE Deaton	T4-07	X		
GL Dunford	R2-50	X		
TA Demitruk	H5-36	X		
RA Dodd	R2-70	X		
DB Engelman	R1-49	X		
KO Fein	H4-63	X		
HY Fouad	S1-57	X		
DE Friar	R3-01	X		
JL Geiger	R3-01	X		
RB Gelman	R2-54	X		
JM Grigsby	H4-62	X		
AL Hess	H4-64	X		
MN Islam	R3-08	X		
NW Kirch	R2-11	X		
JL Lee	S7-82	X		
WE Matheison	S6-19	X		
EM Miller	H4-64	X		
LD Muhlestein	H4-64	X		
R Ni	S5-07	X		
RJ Nicklas	R1-43	X		
LT Nirider	T5-53	X		
RE Raymond	R2-54	X		
RF Richard	H4-64	X		
SH Rifaey	S2-45	X		
CA Rogers (20 copies)	R3-01	X		
WE Ross	S5-07	X		
JS Schofield	R1-67	X		
MK Ullah	L6-57	X		
TS Vail (4 copies)	R1-51	X		
JH Wicks	T4-08	X		
JL Wilk	T3-01	X		
MD Zentner	H4-65	X		

EDT No.: 157940

Page 2 of 2

Central Files (Orig. + 2)
OSTI (2)

L8-04	x
L8-07	x

Criticality Safety of Double-Shell Waste Storage Tanks

Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
Waste Management

**Westinghouse
Hanford Company** Richland, Washington

Hanford Operations and Engineering Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930

Approved for Public Release

MASTER

ds
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

JKE 9/12/94

Page 1 of 81

1. EDT 157940

13 STA 4
SEP 22 1994
ENGINEERING DATA TRANSMITTAL

2. To: (Receiving Organization) System Engineering				3. From: (Originating Organization) Criticality & Radiological Ana.				4. Related EDT No.: N/A			
5. Proj./Prog./Dept./Div.: Tank Waste				6. Cog. Engr.: CA Rogers				7. Purchase Order No.: N/A			
8. Originator Remarks: Transmittal of Criticality Safety Evaluation Report (CSER) 94-004.								9. Equip./Component No.: N/A			
								10. System/Bldg./Facility: DST/Tank Farms			
11. Receiver Remarks:								12. Major Assm. Dwg. No.: N/A			
								13. Permit/Permit Application No.: N/A			
								14. Required Response Date: 9/9/94			
15. DATA TRANSMITTED											
(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted				(F) Impact Level	(G) Reason for Transmittal	(H) Originator Disposition	(I) Receiver Disposition
1	WHC-SD-SQA-CSA-20368		0	CSER 94-004: Criticality Safety of Double-Shell Waste Storage Tanks				S	1,2		
16. KEY											
Impact Level (F)		Reason for Transmittal (G)				Disposition (H) & (I)					
1, 2, 3, or 4 (see MRP 5.43)		1. Approval 2. Release 3. Information 4. Review 5. Post-Review 6. Dist. (Receipt Acknow. Required)				1. Approved 2. Approved w/comment 3. Disapproved w/comment 4. Reviewed no/comment 5. Reviewed w/comment 6. Receipt acknowledged					
(G)	(H)	17. SIGNATURE/DISTRIBUTION (See Impact Level for required signatures)								(G)	(H)
Reason	Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN	(J) Name	(K) Signature	(L) Date	(M) MSIN	Reason	Disp.
1	1	Cog. Eng. CA Rogers	CA Rogers	8/30/94	R3-01						
1	1	Cog. Mgr. JW Daughtry	JW Daughtry	9/14/94	H4-64						
		QA									
1	1	Safety MN Islam	MN Islam	9/13/94							
		Env.									
1	1	Tech Rev SJ Altschuler	SJ Altschuler	9/8/94	R3-01						
1	1	Crit. Saf. Rep. TS Vail	TS Vail	9/8/94							
18.		19.				20.				21. DOE APPROVAL (if required) Ltr. No.	
CA Rogers Signature of EDT Originator		TS Vail Authorized Representative for Receiving Organization				JW Daughtry Cognizant/Project Engineer's Manager				☐ Approved ☐ Approved w/comments ☐ Disapproved w/comments	

RELEASE AUTHORIZATION

Document Number: WHC-SD-SQA-CSA-20368, REV 0

Document Title: CSER 94-004: CRITICALITY SAFETY OF DOUBLE-SHELL
WASTE STORAGE TANKS

Release Date: 9/21/94

* * * * *

**This document was reviewed following the
procedures described in WHC-CM-3-4 and is:**

APPROVED FOR PUBLIC RELEASE

* * * * *

WHC Information Release Administration Specialist:

Kara Broz

(Signature)

9/21/94

(Date)

SUPPORTING DOCUMENT		1. Total Pages
2. Title	3. Number	4. Rev No.
CSER 94-004: Criticality Safety of Double-Shell Waste Storage Tanks	WHC-SD-SQA-CSA-20368	0
5. Key Words	6. Author	
Waste, Double-Shell, Waste Storage Tanks, Criticality Safety, Plutonium, Critical Parameters, Vault Tanks, DST, DCRT, Evaporator	Name: C. A. Rogers	
	Signature: <i>CA Rogers</i>	
	Organization/Charge Code 8D150/N1C62	
<p><i>KMB 9/2/94</i></p> <p>APPROVED FOR PUBLIC RELEASE</p>		
7. Abstract		
<p>This criticality safety evaluation covers double-shell waste storage tanks (DSTs), double-contained receiver tanks (DCRTs), vault tanks, and the 242-A Evaporator located in the High Level Waste (HLW) Tank Farms on the Hanford Site. Limits and controls are specified and the basis for ensuring criticality safety is discussed.</p> <p>A minimum limit of 1,000 is placed upon the solids/plutonium mass ratio in incoming waste. The average solids/Pu mass ratio over all waste in tank farms is estimated to be about 74,500, about 150 times larger than required to assure subcriticality in homogeneous waste. PFP waste in Tank 102-SY has an estimated solids/Pu mass ratio of 10,000.</p> <p>Subcriticality is assured whenever the plutonium concentration is less than 2.6 g/L. The median reported plutonium concentration for 200 samples of waste solids is about 0.01 g/L (0.038 g/gal).</p> <p>A surveillance program is proposed to increase our knowledge of the waste and provide added assurance of the high degree of subcriticality.</p>		
8. PURPOSE AND USE OF DOCUMENT - This document was prepared for use within the U.S. Department of Energy and its contractors. It is to be used only to perform, direct, or integrate work under U.S. Department of Energy contracts. This document is not approved for public release until reviewed.		10. RELEASE STAMP
<p>PATENT STATUS - This document copy, since it is transmitted in advance of patent clearance, is made available in confidence solely for use in performance of work under contracts with the U.S. Department of Energy. This document is not to be published nor its contents otherwise disseminated or used for purposes other than specified above before patent approval for such release or use has been secured, upon request, from the Patent Counsel, U.S. Department of Energy Field Office, Richland, WA.</p> <p>DISCLAIMER - This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.</p>		<p>OFFICIAL RELEASE BY WHC</p> <p>DATE SEP 22 1994</p> <p><i>SA 4</i></p>
9. Impact Level S		

CSER 94-004

Title: CRITICALITY SAFETY OF DOUBLE-SHELL WASTE STORAGE TANKS

Prepared by: CA Rogers Date: August 30, 1994
C. A. Rogers
Engineer, Criticality and Radiological Analyses

Reviewed by: S. J. Altschuler Date: 9/8/94
S. J. Altschuler
Engineer, Criticality and Radiological Analyses

Approved by: J. W. Daughtry Date: 9-14-94
J. W. Daughtry
Manager, Criticality and Radiological Analyses

Approved by: M. N. Islam Date: 9/21/94
M. N. Islam
Manager, Waste Tank Safety Assurance

This page intentionally left blank.

EXECUTIVE SUMMARY

This Criticality Safety Evaluation Report reviews storage of high-level radioactive waste in underground double-shell storage tanks and double-contained receiver tanks located in the high-level waste tank farms on the Hanford Site. Limits and controls to govern waste received and stored are spelled out, and the basis for continued safety is discussed. Justification is provided that a nuclear criticality is extremely unlikely, if not impossible, in these tanks.

Because of the difficulty in characterizing waste inside storage tanks, criticality safety depends upon demonstrating inherent characteristics of waste which ensure subcriticality. The parameter of primary importance to this evaluation is the solids/plutonium mass ratio. A related parameter is the plutonium concentration in settled solids. Subcriticality is assured whenever the plutonium concentration is less than 2.6 g/L in the settled solids or when the solids/plutonium mass ratio exceeds 476 throughout the waste. When either relationship is satisfied throughout the waste, criticality is not possible regardless of the composition, the degree of moderation or reflection, or the distribution of the waste. This remains true even in waste with multiple layers of distinctly different composition and thickness.

The average solids/plutonium mass ratio for all waste in the tank farms is estimated to be at least 74,500, about 150 times larger than required to assure subcriticality in homogeneous waste. The solids/plutonium mass ratio

for PFP waste in tank 241-SY-102 is estimated to be 10,000. This is the lowest ratio for any tank.

The median plutonium concentration for 200 analyzed samples of waste solids (Braun et al. 1994) is about 0.01 g/L (0.04 g/gal), a value 260 times smaller than the minimum critical concentration. The largest concentration found by analysis is 0.35 g/L.

Hobbs et al. (1993) reports the upper limit on plutonium solubility in alkaline salt solutions representative of tank waste to be 0.017 g/L (0.064 g/gal). The median plutonium concentration from among 306 analyzed liquid samples (Braun et al. 1994) is about 0.0001 g/L (0.0004 g/gal).

Settling of suspended particulates and evaporation of liquid are important mechanisms capable of concentrating plutonium. Mixing and the tendency to form layers are important mechanisms that disperse waste. Mechanisms tending to reduce the solids/plutonium mass ratio in one region of a tank would be counteracted by the large solids ratio for the waste as a whole. Mechanisms that might concentrate plutonium are counteracted by those that disperse and blend plutonium with other waste components.

A program of waste characterization and surveillance is recommended to increase our knowledge of waste and to monitor the stored waste to ensure compliance to discharge criteria. Analysis of waste samples will increase assurance of the waste's high degree of subcriticality.

CONTENTS

1.0	INTRODUCTION	1
2.0	SUMMARY AND CONCLUSIONS	3
3.0	SAFETY PHILOSOPHY	7
3.1	Double Contingency Principle	7
3.2	Criteria for Discharged Waste	8
3.3	Margin of Safety	8
4.0	LIMITS AND CONTROLS	11
4.1	General Limits	11
4.2	Tanks Containing Less Than 10 kg of Plutonium	12
4.3	DSTs Containing More Than 10 kg of Plutonium	13
4.4	242-A Evaporator	15
4.5	Proposed Changes to Operations	15
4.6	Surveillance Program	15
4.7	Recovery Plan For Nonconformance	16
5.0	CRITICALITY ALARM COVERAGE	17
6.0	HISTORY OF TANK CONTENTS	19
6.1	Description of Tanks	19
6.2	Description of Waste Streams	20
6.3	Estimate of Plutonium in Waste	22
6.4	Estimate of ²³³ U in Waste	23
7.0	GENERATION OF FUTURE WASTE	25
7.1	Waste Generation Projections	25
7.2	Transfer Data Sheets	26
7.3	PUREX Plant	27
7.4	Plutonium Finishing Plant	28
7.5	B Plant	30
7.6	S Plant	30
7.7	Waste Sampling and Characterization Facility	30
7.8	T Plant	30
7.9	100N Area	31
7.10	242-A Evaporator	31
7.11	Waste From Single Shell Tanks	31
8.0	CHARACTERIZATION OF TANK CONTENTS	33
8.1	TRAC	33
8.2	Analytical Samples	34
8.3	The Conservative Waste Model	35
8.4	Solubility of Plutonium in Waste	36

8.5	Density of Solids	39
8.6	Liquid Content	39
9.0	PARAMETERS IMPORTANT TO CRITICALITY SAFETY	41
9.1	Plutonium Critical Parameters	41
9.2	Absorber-to-Plutonium Ratios	44
9.3	Uranium	46
9.4	Ratio of Plutonium to Uranium	47
9.5	Chemical Separation of Plutonium From Uranium	47
9.6	Mass Ratio of Solids to Plutonium	49
9.7	Minimum Critical Mass	50
9.8	Boron and Cadmium	50
9.9	Global Parameters	51
9.10	Margin of Safety	54
10.0	MECHANISMS THAT CHANGE PLUTONIUM CONCENTRATION	55
10.1	Importance of Solids Content	55
10.2	Concentrating Mechanism: Exceeding Discharge Limits	56
10.3	Concentrating Mechanism: Settling of Suspended Material	57
10.4	Concentrating Mechanism: Evaporation	59
10.5	Concentrating Mechanism: Chemical Separation of Components	59
10.6	Dispersing Mechanism: Formation of Layers	61
10.7	Dispersing Mechanism: Mixing	61
11.0	DISCUSSION	63
11.1	Uniform Plutonium Distribution	63
11.2	Nonuniform Plutonium Distribution	64
11.3	The Improbability of Achieving Criticality	66
11.4	Intertank Transfers of Supernatant Liquid	69
11.5	Leakage of Supernate into Ground	70
12.0	LIMITS	73
12.1	Tank Farm Criticality Prevention Specification Limits	73
12.2	Double-Contained Receiver Tank Limits	76
12.3	242-A Evaporator Facility	77
12.4	Facility Discharge Limits	79
12.5	Basis for Tank Farm CPS Limits	82
13.0	SURVEILLANCE PROGRAM	91
13.1	Auditing: Historical Perspective	91
13.2	Elements of a Surveillance Program	92
13.3	Recovery Plan for Nonconformance	94
14.0	REFERENCES	97
15.0	BIBLIOGRAPHY	100

APPENDIX

A	BASIS DOCUMENTATION FOR CADMIUM ADDITION	A-1
B	REVIEW OF RECORDS FOR SOURCE OF ²³³ U IN TANK 104-C	B-1

LIST OF TABLES

1	Waste Generation Projections (Including Flushes)	26
2	Post-Evaporator Non-Routine Waste Additions	27
3	PFP Waste Generation Rate and Solids Content	29
4	Composition of Conservative Waste Model	36
5	Plutonium Subcritical Limits	43
6	Mass Ratio Subcritical Limit	45
7	Quantity of Tank Waste - August 1993	52
8	Maximum Plutonium Concentration as a Function of Solids	89

LIST OF TERMS

CAS	Criticality Alarm System
CPS	Criticality Prevention Specification
CSER	Criticality Safety Evaluation Report
CSR	Criticality Safety Representative
DCRT	Double-Contained Receiver Tank
DST	Double-Shell Tank
EIS	Environmental Impact Statement
HLW	High-Level Waste
OWVP	Operational Waste Volume Projection
PFP	Plutonium Finishing Plant
PRF	Plutonium Reclamation Facility
PUREX	Plutonium-Uranium Extraction
REDOX	Reduction Oxidation Plant
SST	Single-Shell Tank
TBP	Tributyl Phosphate
TDS	Transfer Data Sheet
TRAC	Track Radioactive Components
UNH	Uranyl Nitrate Hexahydrate
USQ	Unreviewed Safety Question
WSCF	Waste Sampling And Characterization Facility

1.0 INTRODUCTION

High-level radioactive waste from nuclear fuels processing is stored in underground storage tanks located in the high-level waste (HLW) tank farms on the Hanford Site. The older single-shell tanks (SSTs) are inactive and no longer receive waste. The newer double-shell tanks (DSTs) are active and will continue to receive waste. In addition, there are four double-contained receiver tanks (DCRTs) and two double-contained vaults of much smaller size used to hold waste on a temporary basis until it is transferred to a DST.

Waste in tank storage contains low concentrations of fissile isotopes, primarily ^{235}U and ^{239}Pu . An important safety concern is the preclusion of a self-sustaining neutron chain reaction, also known as a nuclear criticality, in the tanks. This Criticality Safety Evaluation Report (CSER) reviews operations in DSTs, DCRTs, and vault tanks and provides justification that a nuclear criticality cannot occur. Limits and controls to govern the discharge of waste are spelled out, and the basis for continued safety is discussed.

Once waste is inside storage tanks the composition and the distribution of waste components become uncertain because of the complexity of discharged waste and the mixing with previously stored tank waste. Because of this uncertainty, criticality safety depends upon demonstrating inherent characteristics of waste which ensure subcriticality. Primary among waste characteristics that support criticality safety are the large proportion of waste solids to fissile material and the relative uniform mixing of components within each waste layer.

Critical parameters for tank waste are based upon a hypothetical waste composition referred to as the conservative waste model. This waste composition is defined by Rogers (1993) and is based upon 28 waste compositions analyzed for 16 SSTs. Although only samples from SSTs were used to derive the conservative waste model, critical parameters derived from the model may be applied to all tank waste because: the physics upon which the analyses are based is identical; DST waste is similar to SST waste; and considerable conservatism is included in the waste model. The conservative waste model defines a waste composition that has a smaller absorption cross section than any actual waste.

Projected future waste sources are described to provide guidance for criticality safety reviews and to help develop limits tailored to the types of wastes likely to be present. In the past, waste-generating operations were almost always governed by flowsheets that specified precisely every aspect of the process, resulting in well-defined waste. In the future, however, much of the waste will be generated during cleanup of older facilities, and may prove even more difficult to characterize.

A program of waste characterization and surveillance is proposed to increase our knowledge of tank waste and to ensure compliance to discharge limits. The analysis of characterization data will provide added assurance of the waste's high degree of subcriticality.

Additional information on the criticality safety of tank waste can be found in *High-Level Waste Subcriticality Safety Assessment* (Braun et al. 1994), which describes process history, waste streams, waste sample data, and waste tank chemistry, and discusses the basis for criticality safety.

This CSER provides a basis for criticality prevention specification (CPS) limits to be used for waste discharges and is intended to supersede the current CSER and its addenda.

2.0 SUMMARY AND CONCLUSIONS

This report spells out criteria against which waste can be evaluated to ensure an adequate margin of subcriticality. It provides the technical basis for limits and controls to be used in CPSs to ensure that a self-sustaining neutron chain reaction (nuclear criticality) is not possible within tank waste. Specific limits and controls evaluated for DSTs are described in Section 4.0. In addition, limits and controls are evaluated for the much smaller DCRTs and vault tanks, which are used for temporary storage of tank waste.

Primary safety parameters

The parameter of primary importance in this evaluation is the solids/plutonium mass ratio. The presence of solids ensures that settling of suspended material and evaporation of liquid do not allow the plutonium concentration to increase to an unsafe level. When the solids/plutonium mass ratio exceeds 476, criticality is not possible in homogeneous waste (see Section 9.1). When specific elements, such as iron, are present, subcriticality can be assured with a smaller ratio of solids.

Subcriticality is assured whenever the plutonium concentration is less than 2.6 g/L in settled waste solids. This is the minimum plutonium concentration that can be made critical in tank waste.

Geometric and distribution considerations

Within each waste stream received into tank farms, the waste is generally well mixed and nearly homogeneous. However, the waste within a storage tank may be composed of several waste streams, and the various waste streams may be mixed together to produce a complex distribution.

The conservative waste model defines a waste composition with reduced neutron absorption for which critical parameters are conservative relative to any real waste. A subcritical limit on plutonium concentration is calculated based upon homogeneous conservative model waste. Without exceeding this limiting plutonium concentration, it is not possible to construct a critical configuration. This is true because the original configuration has a lower neutron absorption at every point than does any real waste and the moderation is optimized. When plutonium is removed, the configuration will be less reactive.

The complexity of an unknown heterogeneous distribution of waste types can be overcome by replacing the entire configuration with a single composition known to be more reactive than any of the individual waste types. Since all discharged waste is less reactive than conservative model waste, it is conservative to represent the entire volume of waste by the conservative waste model.

Estimated solids/plutonium mass ratios

Roetman et al. (1994) estimates the total plutonium in all Hanford Site waste storage tanks to be 981 kg. This is an upper limit on the total plutonium, based upon conservative assumptions of waste generation. Hanlon (1993) states that the total volume of slurries and sludge is 62.3 million liters (16.4 million gallons). These two types of solids comprise about 27 percent of the total waste volume. Based only on the volume of slurries and sludge, a conservative estimate of the average plutonium concentration is found to be 0.016 g/L (0.061 g/gal). The average solids/plutonium mass ratio is estimated to be about 74,500, about 150 times larger than required to assure subcriticality in homogeneous waste.

Nearly all PFP waste has been sent to tank 241-SY-102 and is expected to have a smaller proportion of solids than waste in other storage tanks. The solids/plutonium mass ratio for tank 102-SY is estimated to be 10,000.

Using conservative assumptions, an estimate is made of the smallest solids/plutonium mass ratio that might be expected anywhere within tank waste. An extremely high probability exists that the solids/plutonium mass ratio for any given volume of slurry or sludge will exceed 2,100, a value 4.4 times the subcritical limit of 476.

Measured plutonium concentrations

The median plutonium concentration for 200 analyzed samples of waste solids is about 0.01 g/L (0.04 g/gal) (Braun et al. 1994), a value 260 times smaller than the minimum critical concentration of 2.6 g/L (9.8 g/gal). The largest reported value is 0.35 g/L. These 200 samples have been taken over the last 20 years from many different SSTs and DSTs.

Although the validity of some analyzed sample results have been questioned, the errors found have been conservative. Regardless of the validity of individual sample results, the average values will remain virtually unchanged and the large margin of safety indicated by these analyses will remain unchanged.

Solubility of plutonium

Hobbs et al. (1993) reports the upper limit on plutonium solubility in alkaline salt solutions representative of tank waste to be 0.017 g/L (0.064 g/gal). Depending upon the makeup of the waste, the saturation concentration might be as low as 0.002 g/L (0.008 g/gal). The median plutonium concentration from among 306 analyzed liquid samples is about 0.0001 g/L (0.0004 g/gal) (Braun et al. 1994). The two largest measured concentrations for plutonium in solution were slightly above 0.01 g/L.

Mechanisms which change plutonium concentration

Settling of suspended particulates and evaporation of liquid are important mechanisms capable of concentrating plutonium. When the plutonium concentration is increased, the upper limit on concentration is determined primarily by two factors: the areal density of plutonium and the quantity of solids present.

An important mechanism of dispersal for waste entering a storage tank is the tendency to form layers. As the layers form, the incoming waste is spread over a large area, thereby preventing a large buildup of waste in a confined volume.

Unless the plutonium concentration in waste is increased by a very large factor, criticality is not possible. Mixing within the waste tends to disperse the plutonium, and none of the mechanisms capable of increasing plutonium concentration appear capable of overcoming the dispersal and blending mechanisms. No scenario has been found that might credibly lead to criticality.

Estimate of ^{233}U in Tank Waste

Hess (1994) estimates there to be 45 kg of ^{233}U at tank farms: 33 kg in tank 104-C and 12 kg in tank 102-C. ^{233}U is taken into account in the evaluation of criticality safety for these two tanks.

"Holdup" tanks

Before waste is discharged to tank storage, it is accumulated in a "holdup" tank at the processing facility. Once inside the much larger waste storage tank, the waste spreads out and mixes with the earlier waste. A region of high plutonium concentration in the holdup tank would be transformed into a thin layer and mixed with other waste. Conditions that might enhance the possibility of criticality are greatly diminished after discharge; thus, the probability of criticality in a storage tank is much less than in a holdup tank. The likelihood of criticality in a holdup tank is extremely low, and none has ever occurred.

Discharge limits

The safety philosophy for waste storage is to make the margin of safety of discharged waste sufficiently large that no specific criticality safety limits are required for storage. A primary goal is to ensure that waste will remain subcritical into the indefinite future without supervision. Limits and controls applied to discharged waste are provided in Section 4.0.

Audits and appraisals

Since the beginning of fuel production and processing at Hanford, there has been a program of periodic audits and appraisals to ensure that all operations, including the production and disposal of radioactive wastes, are conducted according to limits and controls applied to them.

Surveillance Program

A program of surveillance is recommended to monitor the stored waste to ensure compliance to discharge criteria and to characterize waste in storage. This program should establish specific criteria for determining when samples are to be taken, how samples are to be analyzed, and when further investigation is required. Rules for surveillance are provided in Section 4.6.

Criticality alarm coverage

This CSER provides documentation that the criteria permitting operations at tank farms without coverage of a criticality alarm system are met (see Section 5.0).

3.0 SAFETY PHILOSOPHY

Discharge of waste to tank storage has always been strictly controlled to ensure criticality safety. In the past, limits have been placed upon waste before discharge and also within storage tanks. In practice, however, the ability to control or to monitor waste inside a storage tank is very limited. By far the more effective criticality safety control is that exercised before discharge at the point of generation.

The philosophy used in this evaluation is that limits and controls are to be applied to discharged waste to ensure that it will have inherent characteristics which guarantee subcriticality. The primary safety goal is to ensure that waste will remain subcritical into the indefinite future without supervision. By making the margin of safety of discharged waste sufficiently large, no specific criticality safety limits are required after discharge.

3.1 DOUBLE CONTINGENCY PRINCIPLE

The basic criterion used for criticality safety is the double contingency principle, stated as follows:

At least two unlikely, independent, and concurrent changes (contingencies) in processing and/or operating conditions must happen before criticality becomes possible.

A contingency is defined as an unlikely action, event, or occurrence that causes a change in operating conditions such that a prescribed safe operating condition or limit is exceeded.

In the philosophy of the double contingency principle it is generally expected that two independent parameters will be controlled to ensure a large margin of safety. However, control of only a single parameter is sufficient at times to guarantee subcriticality. In that situation, it is acceptable to use two independent administrative controls to ensure that the limit on that single parameter is not violated. For example, when the plutonium concentration is sufficiently low, criticality is not possible regardless of the waste density or composition. Therefore, a control on concentration could be used as a single parameter limit, provided at least two controls are exercised to prevent violation of the limit.

Limits and controls are spelled out in a CPS to be used by personnel directly responsible for the discharge of waste. The CPS will contain only limits and controls that can be implemented by the operators. The basis for those limits and controls is provided in this CSER.

3.2 CRITERIA FOR DISCHARGED WASTE

To ensure a high degree of subcriticality, limits and controls will be placed upon waste discharged from generating facilities. The following criteria will be used to develop specific limits and controls.

1. Discharged waste shall conform to one of the following limits.
 - a) The concentration of fissionable material shall be less than the minimum critical concentration for an infinite system times a safety factor.
 - or
 - b) The mass ratio of solids to fissionable isotopes shall be greater than the minimum mass ratio that can be made critical in an infinite system times a safety factor.
2. A safety factor shall be used to ensure that a critical parameter will not be exceeded. This safety factor will compensate for uncertainties associated with a parameter and for the probability of exceeding the limit value (see Section 3.3 below).
3. Discharged waste shall be sufficiently well mixed to preclude localized violations of limits.
4. The pH of discharged waste will be controlled to ensure alkalinity, unless an evaluation shows that alkalinity is not important to criticality safety.

If waste discharged to tank storage is not chemically compatible with waste already in storage, a chemical explosion might occur. Although it is very important that an explosion in the receiver tank be prevented, an explosion would not produce any waste configuration capable of criticality. Since the responsibility to ensure chemical compatibility does not fall to criticality safety, no criterion for chemical compatibility is included in the above list.

3.3 MARGIN OF SAFETY

The limit value for a parameter is derived from two components: 1) a subcritical limit value below which subcriticality is assured and 2) a safety factor.

A safety factor is a multiplier used to ensure an adequate margin of safety under all normal and credible accident conditions. The operating limit is obtained by multiplying the subcritical limit by the safety factor. The safety factor should be large enough to ensure that any violation of the operating limit will not be large enough to exceed the subcritical limit.

For limits which are maximum values the safety factor is less than unity, while for limits which are minimum values the safety factor is greater than unity. The safety factor applied to a concentration limit shall not be

greater than 0.5, while the safety factor applied to a component/plutonium mass ratio shall not be less than 2.0.

The safety factor shall take into account:

1. The range of variation of the waste; i.e., the range of possible changes in composition and distribution within the tank storage environment, including variations caused by transferring waste between tanks and mixing.
2. The possibility that drainable liquids, along with their dissolved components, might be removed from the waste; i. e., that the waste will remain subcritical after loss of drainable liquid.
3. The range of credible violation of controls on discharged waste.

This page intentionally left blank.

4.0 LIMITS AND CONTROLS

Limits and controls are provided to govern Tank Farm operations, including the receipt of waste from waste generating facilities (such as fuel processing facilities) and its transfer between storage tanks. These limits and controls are to apply to high-level radioactive waste (HLW) in:

- DSTs,
- DCRTs,
- vault tanks, and
- the Rail Car Unloading Facility 204-AR.

When placed in a CPS, limits and controls may be tailored to fit specific conditions of operation.

Once waste is inside of a storage tank, little assurance of the overall configuration of waste can be obtained from direct measurement. For this reason, no limits are placed upon the plutonium concentration and plutonium mass inside storage tanks. Instead, investigation levels are established to defined a point at which concern arises that the large margin of safety may be eroding. When a parameter is outside the boundary defined by an investigation level, further investigation is undertaken to determine the quality of the analytical measurements or predictive computations used to identify the suspected infraction.

Tanks are placed in two groups: those containing less than 10 kg of plutonium and those containing more. This grouping permits routing waste containing low solids to tanks known to contain very little plutonium.

Before each transfer, chemical compatibility between incoming waste and waste already stored is verified by tank farms operations. Since an explosion would not produce any waste configuration capable of criticality, no requirement to verify chemical compatibility is considered necessary in a CPS.

4.1 GENERAL LIMITS

1. Plutonium Equivalence - The amount of ^{235}U less than or equal to the equivalent of 1 wt% enrichment may be excluded in concentration and total mass calculations. One gram of ^{235}U in excess of 1 wt% enrichment or one gram of ^{233}U shall be assumed equivalent to one gram of plutonium, unless otherwise restricted by a specification.
2. When ^{238}U is used to justify subcriticality for plutonium, the ^{235}U enrichment in the uranium must be taken into account.
3. Discharged waste shall be well mixed.
4. Discharged waste shall be alkaline (basic) with a pH of at least 9.0, unless a criticality safety evaluation shows that alkalinity

is not required. (This limit is set for the exceptional case. In practice, it is expected that the pH will exceed 12.)

5. Each facility discharging waste to tank farms shall develop procedures to ensure compliance to CPS limits.
6. Verification of compliance shall be documented before each transfer.
7. An auditable continuous inventory of plutonium and an assessment of the plutonium concentration both in the solids and supernate shall be maintained for each tank.
8. Upon identification of any failure to meet limits and controls in this CPS, the Recovery Plan For Nonconformance (Section 4.7) shall be followed.

4.2 TANKS CONTAINING LESS THAN 10 KG OF PLUTONIUM

If a double-shell tank (DST), double-contained receiver tank (DCRT), or a vault tank will contain less than 10 kg of plutonium after completion of a transfer, the following limits may be used.

1. The transfer may be made without consideration of the solids content, provided one of the following conditions is met:
 - a. The total plutonium in the transfer is less than 15 g;
 - b. The plutonium concentration in the transferred waste is less than 0.013 g/L (0.050 g/gal).
 - c. An airlift circulator is operating in the receiver tank and the transfer contains not more than 200 g of plutonium.
 - d. The transfer is made through a slurry distributor and the total plutonium added to the waste at any single position does not exceed 200 g.
2. If requirements above for transfers without consideration of solids are not met, transfers may be made in accordance with requirements for tanks containing greater than 10 kg of plutonium (Section 4.3).

ADDITIONAL LIMITS FOR DCRTS

3. For DCRTs 244-TX, 244-S, 244-U, and 244-BX, the maximum plutonium in each tank shall not exceed 2,000 g.
4. After each transfer of Z-Plant solutions from DCRT 244-TX to DST 102-SY, the transfer line shall be flushed with water.
5. For transfer of solution from DCRT 244-TX into 244-S:

- a. The solution in 244-TX shall be allowed to settle.
- b. The sluicing system in 244-TX shall be operating during the transfer.
- c. Prior to transfer, the Criticality Safety Representative for tank farms shall be notified.

4.3 DSTs CONTAINING MORE THAN 10 KG OF PLUTONIUM

When the total plutonium inventory in a DST exceeds 10 kg, the following limits apply:

1. One of the following methods may be used to determine the plutonium concentration and/or the solids/plutonium mass ratio:

- a. A computation based upon the plutonium mass, the solids volume, and the density of settled solids. Compensation shall be made for uncertainties to ensure that the calculated concentration or mass ratio is conservative.

The average plutonium concentration in precipitated (settled) solids can be found by dividing the total incoming plutonium mass by the total incoming solids volume.

The solids/plutonium mass ratio is found by dividing the density of settled solids (not including contained water) by the plutonium concentration.

$$\text{Solids/plutonium mass ratio} = \frac{\text{Solids Density (g/L)}}{\text{Plutonium Concentration (g/L)}}$$

If the measured density of settled solids is not available, assume a solids density of 1,200 g/L.

- b. A laboratory analysis of tank samples.
 - c. The minimum solids fraction and/or the maximum plutonium concentration possible as determined from a flowsheet governing the generation of the waste may be used to determine compliance.
2. When the plutonium inventory for a DST is equal to, or greater than, 10 kg, the solids/plutonium mass ratio for the tank contents shall be shown to be at least 1,000 before additional plutonium may be added. This is an average (global) value determined by dividing the total solids mass by the total plutonium mass.

3. For each batch of waste sent to a DST, one of the following sets of limits shall apply:

- a. The solids/plutonium mass ratio for waste already in receiver tank exceeds 1,000, and the plutonium content in the incoming batch of waste is less than defined in Section 4.2, item 1.

or

- b. The following conditions are satisfied for incoming waste:

1. The solids/plutonium mass ratio is at least 1,000, as determined by analysis or predictive calculation.
2. The plutonium concentration averaged over the total volume (both solids and liquid) of a batch shall not exceed 0.033 g/L (0.125 g/gal).

or

- c. A specific solids component is used as a basis for assuring subcriticality. When a specific solids component is used, the component/plutonium subcritical mass ratio, as determined by analysis or predictive calculation, shall not be less than twice the subcritical mass ratio for that component.

When a specific component is used to guarantee subcriticality, justification must be provided that the plutonium will remain mixed with that component under normal and credible abnormal conditions. Section 9.2 lists mass ratios for specific components.

or

- d. Cadmium may be added to the waste and transfer continued under the following conditions:

1. Transfer is made to tank 102-SY or 105-AW only.
2. Before transfer, the solids/plutonium mass ratio already in the receiver tank shall be at least 1,000.
3. The cadmium/plutonium mass ratio shall be at least 0.33. (In other words, there shall be at least one gram of cadmium for every three grams of plutonium.)
4. The plutonium concentration shall not exceed 30 g/L in the precipitated (settled) solids.

(Note: Chemical analysis of waste within a storage tank can not be used to verify the cadmium limit because other waste in the tank may not have been discharged with cadmium.)

4.4 242-A EVAPORATOR

242-A Evaporator operations shall conform to the following:

1. Plutonium concentration
in feed solution: < 0.005 g/L (0.019 g/gal)
2. Before an evaporator campaign begins, a determination shall be made and documented of the expected quantity and concentration of plutonium which will be in the feed and slurry tanks at completion of the run.
3. After an evaporator campaign, a determination shall be made of the actual quantity and concentration of plutonium in the feed and slurry tanks, either by analysis or calculation.

4.5 PROPOSED CHANGES TO OPERATIONS

If a proposed change to facility operating procedures will change the makeup of discharged waste:

- The change shall be reviewed for compliance to applicable CPS limits and controls and approved by the Tank Farm Criticality Safety Representative.
- If the proposed new operation is not within the existing criticality safety envelope, a CSER will be completed and a CPS will be issued to cover the operation before the operation is initiated.

4.6 SURVEILLANCE PROGRAM

A surveillance program with the following components shall be in place to monitor waste. Analysis of waste samples is intended to provide adequate information to verify that the waste is well subcritical.

- When a waste sample is analyzed, the following parameters shall be measured:
 - pH (to demonstrate alkalinity)
 - Specific gravity
 - Density and volume fraction of settled solids
 - Water content

- Concentrations of plutonium, uranium, iron, manganese, and components of greater abundance in the waste (aluminum, sodium, silicon, nitrate, carbonate, etc.), as applicable.

(If a fissionable isotope can be shown not to be present or to be exempt from criticality safety control, no analysis need be made for that isotope. A component may be exempted from analysis if its presence is not required to show an adequate degree of subcriticality.)

- Concentrations of ^{235}U when uranium with enrichment greater than 1.0 wt% might be present and ^{233}U when it might be present.

(In most tanks all uranium is depleted. Only tanks in C Farm contain measurable quantities of ^{233}U .)

- Characterization data obtained from analyses is to be compared to the following investigation levels.
 - The plutonium concentration in settled (precipitated) solids exceeds 1.0 g/L (3.8 g/gal).
 - The solids/plutonium mass ratio is less than 1,000.
 - The pH is less than 9.0.

Upon identification of a failure to meet any one of these investigation levels, the Recovery Plan for Nonconformance shall be followed.

- No surveillance is required for a 75-ft diameter tank for which the plutonium inventory is less than 10 kg.
- Waste characterization data shall be maintained to facilitate criticality safety evaluation.

4.7 RECOVERY PLAN FOR NONCONFORMANCE

If a waste sample retrieved from any double-shell tank or double-contained receiver tank is found to fail an investigation level, a recovery plan for nonconformance will be initiated according to *Nuclear Criticality Safety Manual*, WHC-CM-4-29, Section 15, "Recovery From Criticality Prevention Specification Nonconformance."

As part of this investigation, a written recovery plan is developed. The core of this recovery plan will consist of an evaluation "to determine the appropriate method of recovery." See Section 13.3 for more details.

5.0 CRITICALITY ALARM COVERAGE

The *Nuclear Criticality Safety Manual*, WHC-CM-4-29, Section 11.0, Part 5.1, states that a facility may be exempted from coverage by a criticality alarm system (CAS) if the following criteria are met:

A CAS is not required when a documented safety analysis shows that it is not needed due to the physical form and isotopic distribution of fissionable material. Such analyses shall be approved by the independent safety review organization.

DOE Order 5480.24, *Nuclear Criticality Safety*, Section 7.b states that "the requirements in ANSI/ANS-8.3 relating to the need for an alarm system are not applicable to this Order." It then provides the following requirements for operating without a criticality alarm system (CAS):

- (3) In those cases where the mass of fissionable material exceeds the limits established in paragraph 4.2.1 of ANSI/ANS-8.3, but a criticality accident is determined to be impossible due to the physical form of the fissionable material, or the probability of occurrence is determined to be less than 10^{-6} per year (as documented in a DOE approved SAR), neither a CAS nor a criticality detection systems is required. In addition, neither a CAS nor a criticality detection system is required to be installed underwater when fissionable material is handled or stored beneath water shielding that is adequate to protect personnel; however, a means to detect fission gasses or other volatile fission products should be provided in occupied areas immediately adjacent to such underwater storage areas except for fuel systems where no fission products are likely to be released. Also, neither a CAS nor a criticality detection system are required for fissionable material during shipment of fissionable material packaged in approved shipping containers, or fissionable material in approved shipping containers awaiting transport provided no other operation involving fissionable material not so packaged is permitted on the dock or in the shipment area.

High-level waste tanks are categorized as limited control facilities, as defined in the *Nuclear Criticality Safety Manual*. Criticality safety is ensured by controlling the form and distribution of fissionable material. In practice, the low concentration of plutonium and the high proportion of neutron-absorbing solids ensures a form that is highly subcritical regardless of the distribution of the waste, the degree of neutron moderation, and the presence of reflectors.

This CSER provides documentation that the criteria permitting operations at tank farms without coverage of a criticality alarm system are met.

This page intentionally left blank.

6.0 HISTORY OF TANK CONTENTS

Tank waste is a complex mixture of many chemicals. At least 49 waste streams have been routed to the tank farms since the first discharge in 1944, and many tanks contain waste from several streams mixed in various proportions.

6.1 DESCRIPTION OF TANKS

Upon discharge from a processing facility, waste may either be sent directly to a DST or to a smaller intermediate holding tank for temporary storage. The intermediate tanks are classed as double-contained receiver tanks (DCRTs) or vault tanks. These tanks are double contained to provide assurance that waste liquid would not be able to reach the soil should a leak develop.

Double-shell storage tank

All DSTs are 22.8 m (75 ft) in diameter and have a nominal capacity of 3,800,000 L (1,000,000 gal). These tanks have been used to store liquid radioactive wastes since 1971. A DST is constructed of two steel shells with an annular air space between them. The outer shell is surrounded by reinforced concrete.

All DSTs are located underground with 1.8 to 2.4 m (6 to 8 ft) of soil covering their tops. The soil layer is intended to provide shielding from radioactive waste.

Double-contained receiver tank

Waste leaving a processing facility is often routed through an intermediate DCRT for temporary storage. This waste is sometimes transferred through a second DCRT before it is sent to a DST for long-term storage. The 244-BX, 244-S, 244-TX, and 244-U tanks are DCRTs.

DCRT 244-TX is used for short term storage of PFP waste and salt-well waste (jet-pump solution) from the T, TX, and TY Tank Farms. 244-TX is 3.7 m (12 ft) diameter by 12.5 m (41 ft) long with a volume of 136,000 L (36,000 gal). Up to 95,000 L (25,000 gal) of waste is permitted. This tank is oriented horizontally with a slight slant. The inlet is at the high end and the outlet is at the low end.

DCRT 244-TX uses sluicing jets to circulate and flush the contents. Three neutron monitors located underneath the tank at regular spacing are used to detect plutonium buildup and shut off the feed pump if a high neutron level is detected.

DCRT 244-S is a 4.6-m (15-ft) diameter by 5.5 m (18-ft) long cylinder with the axis oriented vertically. This tank provides short term storage for solution from the S and SX Tank Farms and the 222-S laboratory.

244-BX and 244-U are similar in size and shape to 244-S and 244-TX. These tanks provide short term storage for jet pump solution from the B, BX, BY, and U Tank Farms.

All DCRTs are much smaller in diameter than a DST and have a capacity less than 40,000 gal.

Vault tanks

Tanks 244-A, 244-AR and 244-CR are vault tanks used for interim storage. Although these tanks possess the capacity to add chemicals, neither facility is used for waste treatment or chemical addition. Each vault consists of two 20,000 gal tanks and two 5,000 gal tanks.

6.2 DESCRIPTION OF WASTE STREAMS

A description of waste streams routed to the tank farms is provided in *A History of the 200 Area Tank Farms* by J. D. Anderson (1990), which provides the following synopsis of waste streams:

Four basic chemical operations were the source of radioactive waste solutions transferred to underground storage tanks since startup of the Hanford site. These were the Bismuth Phosphate (BiPO_4) process, the Tributyl Phosphate (TBP) process, the reduction oxidation (REDOX) process, and the plutonium-uranium extraction (PUREX) process. Three of these were chemical separations programs for the recovery of uranium and plutonium from irradiated reactor fuels. The fourth (TBP) was designed for the recovery of uranium metal waste generated by the BiPO_4 process. In all cases, the aqueous wastes were made alkaline for storage in underground steel tanks.

Anderson (1990) provides the following specific details. The plutonium and uranium content in the waste usually is specified as a percentage of the quantity processed. Although the waste streams described are the source of nearly all waste stored in the tank farms, the processes generating these wastes are no longer operating. Most waste streams have not sent waste to tank farms for a long time. An estimate of future sources of waste is provided in Section 7.0, Generation of Future Waste.

Bismuth Phosphate (BiPO_4) Process - The bismuth phosphate process generated the following waste types.

1. Alkaline coating removal waste, containing small amounts of fission products, was combined with first-cycle decontamination wastes for storage. About 0.4 percent of the plutonium and about 0.4 percent of the uranium is estimated as having gone to waste.
2. Metal waste from the extraction, containing all of the uranium and about 1 percent of the plutonium.

3. Byproduct cake solution and waste solution from the first decontamination cycle, containing about 1 percent of the plutonium.
4. Second decontamination-cycle waste, containing about 1 percent of the plutonium.

Uranium Recovery Plant - Waste from the Uranium Recovery Plant contained about the same proportion of fission products as did metal waste. This waste is referred to as TBP waste. Anderson (1990) does not specify the content of uranium and plutonium.

REDOX Plant - The REDOX Plant generated the following waste types:

1. Coating waste from the decladding of aluminum-clad fuels, containing about 0.4 percent of the plutonium and 0.4 percent of the uranium.
2. Waste from the decladding of zircaloy-clad fuels. This waste is described as containing about 0.0006 kg of uranium/L (0.001 lb of uranium/gal). The plutonium content is stated to be equal to the uranium content. This is an obvious inaccuracy because the content of the uranium should be hundreds of times greater than that of plutonium. Perhaps the intent may be to show that the uranium and plutonium are only a small fraction of the original.
3. REDOX waste was the high-level component of the process waste. It contained about 0.05 percent of the original uranium and 0.04 percent of the original plutonium.

PUREX Plant - Waste from the PUREX Plant falls into the following types:

1. Coating waste from the decladding of aluminum-clad fuels. This waste contains about 0.4 percent of the original plutonium and 0.4 percent of the original uranium.
2. Waste from the decladding of zircaloy-clad fuels. This contains the same content of plutonium and uranium as the same type waste from the REDOX Plant.
3. Organic wash waste. This contains about 0.00017 kg of uranium/L (0.0003 lb of uranium/gal). The plutonium content is very low and is not specified.
4. Neutralized PUREX Plant acid waste. The uranium and plutonium content is very low and is not specified.
5. Waste from the thorium campaigns. The uranium and plutonium content is very low and is not specified.

All of these waste streams are derived from slightly enriched uranium fuel elements that have been burned in a reactor. This fuel has an initial ²³⁵U

enrichment less than 1.3 wt%, which the burning process reduces to a level below that in natural uranium (i. e., below 0.72 wt%) while at the same time producing plutonium. The plutonium content increases to an average value of approximately 0.10 wt% of the uranium content. The maximum plutonium content will not exceed 0.15 wt% of the uranium.

Plutonium Finishing Plant - The *Safety Assessment* provides the following description of waste from the PFP:

The PFP is the only potential source of separated plutonium in the waste tanks. Fuel processing is not performed at the PFP. Its feed source is primarily the PUREX Plant and other process facilities. Waste from the PFP was not sent to the tank farms until 1973. Before that time, PFP waste was discharged to burial drums or cribs.

The PFP consists of three separate operations that generate waste containing plutonium and the Development and Analytical Laboratories. The three operations are the remote mechanical "A" (RMA) oxide line, which converts plutonium nitrate produced at the PUREX Plant and formerly at the REDOX Plant to plutonium oxide powder; the remote mechanical "C" (RMC) metal line, which converts plutonium oxide to plutonium metal via calcium reduction of plutonium fluoride; and the Plutonium Reclamation Facility (PRF), which processes a variety of plutonium scrap materials, such as crucible fragments, to plutonium nitrate to serve as feed to the RMC line (Braun et al. 1994).

For additional information on waste streams and present tank contents, see Appendix B of the *Safety Assessment* (Braun et al. 1994).

6.3 ESTIMATE OF PLUTONIUM IN WASTE

Based upon information provided by Anderson, the plutonium in waste is expected to be about 1 percent of the original plutonium processed. However, these values are estimates based upon fuel being subjected to a single process under normal conditions. In practice, fuel may be subjected to more than one process, and process conditions do not always correspond to flowsheet values.

Roetman et al. (1994) provides an estimate of the quantity of plutonium discharged as waste based upon a careful review of plutonium production and process efficiencies. In all, an estimated 67.5 metric tons of plutonium were produced at the Hanford Site, of which about 63 metric tons were processed at the Hanford Site. The difference in these number is for 4 metric tons of unprocessed plutonium in the K Basins and for 528 kg of plutonium sent offsite for processing.

Several methods were used to estimate the mass of plutonium sent to waste. The best estimate for criticality safety evaluation is a conservative estimate based upon the yearly maximum waste loss approximation. Using this method, the total plutonium sent to waste is found to be 950 kg of plutonium from the separations processes and 31 kg from PFP. This provides a total for tank farms of 981 kg of plutonium. This value is more than twice as large as the

total of the annual average estimates and sets an upper limit on the total plutonium in waste at tank farms.

6.4 ESTIMATE OF ^{233}U IN WASTE

Hess (1991) reviewed historical records to arrive at an estimate of the total quantity of ^{233}U sent to tank farms. A copy of Hess' letter report is provided in Appendix B. He summarized his review as follows:

The results of that review indicate that a total of about 45 kg of ^{233}U was discharged out of PUREX to underground tanks in C-Farms during 1966 and 1970 thoria campaigns. Although the total volume of liquid waste transferred was on the order of several million gallons, it is highly probable that the ^{233}U settled in the initial tanks of a cascade of tanks used. This would have resulted in ^{233}U accumulations of 33 kg in tank 104-C (241-C-104) from the 1970 campaign and 12 kg in 102-C from the 1966 campaign. It is recommended that these amounts be added to inventories of 104-C and 102-C, and that future sampling in all of the C-Farm tanks should include tests for thorium and to further track the waste disposition from the thoria campaigns.

Roetman (1994) makes the follow statement concerning ^{233}U :

Another fissionable isotope of criticality concern is ^{233}U . The thorium irradiation process resulted in the direct production of ^{233}U , which was then recovered with the PUREX process. The waste from this recovery was discharged to the waste tanks. Since the recovery of ^{233}U from thoria was much more difficult than the separation of plutonium from uranium, the recovery efficiency was less, approximately 95%. Approximately 45 kg of ^{233}U were discharged to the Hanford waste tanks from the 1966 and 1970 thoria campaigns.

This page intentionally left blank.

7.0 GENERATION OF FUTURE WASTE

A survey of anticipated waste sources is provided. Although an estimate is made of the future volumes of waste, it should be recognized that projected values may change and unforeseen sources of waste may develop. From a criticality safety point of view the following information is considered descriptive and is intended to help anticipate the needs of a criticality safety program. However, it is not important to know the exact composition and volumes of future waste. The description provided in this CSER need not be revised to accommodate a change in operations unless the change requires a change in CPS limits and those new limits are not covered by this CSER.

Most tank waste was generated during reactor fuel element processing. These processes, and the composition of the waste generated, were well defined. Waste was generated at a rate regulated by plutonium production. However, the mission of the Hanford Site has changed from one of production to one of environmental cleanup. The large-scale dissolution of fuel elements, accompanied by generation of large volumes of waste, is not presently envisioned for the future. In the past, waste-generating operations were governed at every step by flowsheets. In the future, cleanup of older facilities will not be governed by flowsheets. For this reason, future waste may prove more difficult to describe, and a greater potential may exist for producing unexpected compositions.

7.1 WASTE GENERATION PROJECTIONS

Waste Generation and Processing Rates With Volume Reduction Factors - 1988, WHC-SD-WM-TI-309 (Cruzan 1988), provides an exhaustive description of projected waste compositions and volumes. In the six years since it was compiled, however, many of the projections have changed. An updated estimate of future waste volumes from the various generators is provided in *Operational Waste Volume Projection (OWVP)* (Koreski 1994).

Presently, there is a shortage of unused tank space, and new waste is being held to a minimum. An evaporator in the 242-A Facility will be used to reduce the volume of liquid waste, thereby creating more space in DSTs. After restart of the evaporator, there will be an increase in the rate at which waste will be sent to storage.

Table 1 shows OWVP projections of routine waste to be generated by the various facilities. Table 2 shows projected non-routine waste additions to DSTs after restart of the 242-A Evaporator. PFP waste projections are discussed in Section 7.4.

Table 1. Waste Generation Projections (including flushes)
(Taken from OWVP)

Facility	Before restart of evaporator (kgal/month)	After restart of evaporator (kgal/month)
PUREX Plant	15	23
UO ₂ Plant	0	0
B Plant	23	23
S Plant (222-S Lab)	5	18
T Plant	6	20
300 Area	5	5
400 Area	0 ^a	1
WSCF ^b	0	0.7
Tank Farms/Misc.	10	30
TOTALS	64	~121

^aBefore 242-A Evaporator restart, one transfer of 10 kgal.

^bWaste Sampling and Characterization Facility

7.2 TRANSFER DATA SHEETS

The Transfer Data Sheet (TDS) is used to keep track of waste transfers and to ensure compliance to rules and regulations. A TDS is completed before waste is transferred into a holdup tank in a processing facility, and before each transfer to tank farms. In addition, a TDS is completed before each transfer between tanks at tank farms.

The organization making the transfer is responsible for completing the TDS. Before a transfer is made, the composition of the waste is determined and values are obtained for all parameters required by the CPS. Calculations must be independently verified, and supervision's approval must be obtained before the transfer is made. For transfers involving tank farms, the CSR for tank farms reviews the TDS to ensure compliance with CPS limits.

A comprehensive description of the waste is an important part of the TDS. For most transfers, waste samples are analyzed to determine values for parameters controlled by the CPS. In some cases, the composition is established using earlier sample analyses or from predictive computations. Agreement with the CPS limits is required before the transfer can be made.

An inventory of fissile content is maintained for each holdup tank. An estimate of the fissile content in each transfer is shown on the TDS, and this information is used to update the inventory for the storage tank.

Table 2. Post-Evaporator Non-Routine Waste Additions
(Taken from OWVP)

Facilities	Volume and Type (kgal)
PUREX Plant: deactivation waste	1500 DN ^a
B Plant: terminal clean-out waste	562 DN
100 Area: terminal clean-out waste	571 SF ^b
100 Area: sulfate waste	36 DN
300 Area: fuel supply clean-out	12 DN
400 Area ^c	0
105-F, 105-H: basin clean-out waste	225 DN
Tank 107-AN: caustic addition	50 DN
K-Basin: cleanout	unknown ^d
TOTAL	2956

^adilute non-complexed waste

^bslurry feed

^cBefore evaporator restart, one non-routine transfer of 10 kgal.

^dWater from K-Basin cleanout. This may be routed directly to evaporator.

7.3 PUREX PLANT

The primary mission of the PUREX Plant has been to process irradiated N-Reactor fuel elements to produce plutonium nitrate, uranyl nitrate hexahydrate (UNH), and neptunium nitrate. Processing operations included the dissolution of cladding and fuel, solvent extraction, conversion of plutonium nitrate to plutonium oxide, acid recovery, and solvent treatment. These operations are no longer conducted.

Procedures used to control waste discharged from the PUREX Plant are similar to those used at the PFP described in the next section. The TDS is used to keep track of transfers and to ensure compliance to CPS limits.

Transition to shutdown

The PUREX Plant is currently in a transition to shutdown status. The last transfer of waste to tank farms is projected for December 1997. During this transition period, all fissionable material will be either removed from the facility or stabilized. Fissionable material is considered stabilized when it is securely fixed in place and does not present any criticality safety hazard. An example of stabilized fissionable material is surface contamination within ducts.

PUREX waste is accumulated in holding tanks before being sent to tank farms. In the past, waste was sent to tank farms from tanks E5, G8, R8, F16, and F18. In the future, all discharged waste is expected to leave the PUREX Plant from tank F18.

The process of removing residual radioactivity from more than 100 tanks and from miles of piping is underway. Since 1990, plutonium has been flushed from vessels, gloveboxes, and equipment. Because of the change to shutdown status, flush solutions containing plutonium and UNH stored in the solvent extraction accountability tank D5, and the solvent extraction feed adjustment tank E6, will be disposed of as waste.

PUREX tanks D5 and E6 are standard PUREX flat-bottom tanks with a nominal 3.0-m (10-ft) diameter and 2.74-m (9-ft) height. Both of these tanks are large enough to hold 18,900 L (5,000 gal) of solution.

Plutonium in tank E6 was accumulated during flushes of the plutonium solvent extraction cycles and from the PuO₂ Facility gloveboxes after the stabilization run at the PUREX Plant in March 1990. Product UNH solution was transferred into tank E6 from UNH storage (P-tanks). In addition to these streams, the waste mixture in tank E6 also includes residual fission products that were already present.

If sent to tank farms, the waste material would be transferred in small batches after being neutralized and diluted with water to ensure low uranium concentration. The primary reason for dilution with water is to minimize solids settling in the pipeline during the transfer.

It is expected that some PUREX waste will require the presence of cadmium. This waste is expected to be sent to tank 105-AW, and the cadmium will meet the requirements that the cadmium/plutonium mass ratio not be less than 0.33. In practice, the cadmium/plutonium mass ratio is expected to be about 6.0.

When neutron poisons, such as cadmium, are used as a basis for control. They must be intimately mixed with the plutonium. Both the pH of the waste to be transferred and the pH of the alkaline matrix in the waste storage tanks will ensure that the uranium, plutonium, and cadmium will remain insoluble.

7.4 PLUTONIUM FINISHING PLANT

Maintenance and laboratory work is continuing at the PFP, but major process lines, including the Remote Mechanical C (RMC) Line and process lines in the PRF, have been placed on standby pending completion of an environmental impact statement (EIS). After the EIS is completed, it is expected that operations will begin to stabilize fissionable material. The EIS is expected to take between one and five years to complete.

The stabilization process will include decontamination and cleanout operations. Some projects, such as ductwork remediation, will generate practically no liquid waste. If cleanout of gloveboxes and bays in the PRF is identified as an interim action, then some liquid waste generation would be expected.

According to the OWVP:

This projection assumes that there will be approximately 50 kgal/month of waste generated while PRF is operating, and there will be approximately 6 kgal/month generated while the remote mechanical line is operating. It is assumed that the PFP labs will produce approximately 2.5 kgal/month during PFP stabilization (Koreski 1994).

Table 3 shows the OWVP projections of solids content in PFP waste and the expected rate of waste accumulation.

Table 3. PFP Waste Generation Rate and Solids Content

Solids in waste (vol%)	
Plutonium Reclamation Facility	3.5
Remote Mechanical C Line	4.4
Laboratory	4.5
Rate of waste generation (per hour of operation)	
Plutonium Reclamation Facility	261 L (69.0 gal)
Remote Mechanical C Line	36.7 L (9.7 gal)
Laboratory	15.5 L (4.1 gal)

Control of Discharged Waste

PFP waste discharged to tank farm facility 244-TX passes through the storage and treatment tank D5 located in the 241-Z Building. Waste in tank D5 is received from other tanks located in the 241-Z Building: hold-up tanks D4, D7, and D8 and process tanks 19, 39, WM-1, and 40. This information describes the present discharge pathway, but there is no guarantee it will remain unchanged in the future.

All operations are governed by detailed operating procedures. A TDS must be completed before each waste transfer to D5.

Sampling is controlled by a procedure that specifies both when and how it is to be done. Before waste is transferred to tank D5, samples are analyzed for parameters needed to characterize the waste. Adjustments are made to waste in tank D5 before discharge to tank farms if required to meet acceptance criteria.

The fissile inventory in tank D5 is determined using a calculation method described in an operating procedure. The fissile content of each batch of waste discharged into tank D5 is added to the D5 inventory to obtain a total tank content. Chemical analysis of samples from tank D5 is not normally used to estimate the tank plutonium inventory because the iron hydroxide

precipitate interferes with the analysis. An assessment of iron content in the solids may be made by chemical analysis or by performing a calculation based on knowledge of iron addition and tank volumes.

Before waste is transferred, an independent verification of the calculations is made, and the TDS is reviewed and initialed by supervision. After all steps have been completed, supervision's approval must be obtained before the actual transfer begins.

7.5 B PLANT

The OWVP states that B Plant will no longer be used for pretreatment of Hanford Site tank waste. Nevertheless, B Plant is projected to continue to generate miscellaneous waste until FY 1997. Cleanout and stabilization is estimated to take five years after that (Koreski 1994).

B Plant is classified as an exempt facility, and the waste from it should therefore contain fissionable material only in trace quantities.

7.6 S PLANT

S-Plant waste is sent to tank farms from the 222-S Laboratory and the Waste Sampling and Characterization Facility (WSCF). Liquid mixed waste from the 222-S Facility is stored in tank 102 of the 219-S Waste Handling Facility. This waste currently is being transferred in bulk tanker shipments to the 204-AR Facility.

Each time a shipment is made to tank farms, a sample is pulled for characterization purposes, and a TDS is completed. The amount of fissile material in grams is calculated from the sample results. The tank farms supervisor of the CSR for tank farms must approve the TDS and check compliance to the CPS before shipment.

7.7 WASTE SAMPLING AND CHARACTERIZATION FACILITY

The WSCF receives waste from S Plant. Liquid mixed waste from WSCF is stored in the two tanks of the 6266-A Facility. The description for S Plant waste above applies also to WSCF waste.

7.8 T PLANT

T Plant's primary mission includes decontamination of radiologically and chemically contaminated equipment and treatment of wastes. Wastes generated at T Plant are estimated to contain about 6.5 vol% solids (Koreski 1994).

Waste shipments from T Plant are handled in the same manner as shipments from S Plant. Currently, waste is being sent to tank farms through the 204-AR Facility.

7.9 100-N AREA

Decommissioning of N Reactor is projected to start in 1994 and to require six years to complete (Koreski 1994). Decommissioning is projected to generate a total of 2,161,000 L (571 kgal) of waste. This waste is expected to be concentrated in the 100 Area before shipment to DSTs.

Depending on the option used for removal, replacement or treatment of contaminated K-Basin water, the waste from these activities might end up in DSTs. At present, however, this does not appear likely.

7.10 242-A EVAPORATOR

A major problem associated with storing high-level waste is the lack of available storage space. One of the primary ways to increase available space is to reduce the volume of stored waste by evaporating off some of the water portion. Most of the waste sent to tank farms is in the form of a dilute solution primarily made up of water.

The 242-A Evaporator is designed to remove liquid from DST waste. Operation of the evaporator is described as follows:

The operation of the evaporator requires a minimum of two dedicated double-shell tanks in addition to dilute receivers. Wastes are collected in the dilute receiver tanks. If the waste streams contain any initial solids, they settle out in the dilute receivers. When the dilute receivers are full, the supernate is transferred to the evaporator feed tank. An evaporation is started when the evaporator feed tank is full. An evaporation involves taking the waste from the evaporator feed tank, running it through the evaporator to the slurry receiver tank. This waste is then transferred back to the evaporator feed tank. This cycle continues until the waste has been concentrated to the desired endpoint. The waste is then sent to the interim product tank (Cruzan 1988).

Multiple passes through the evaporator are required before the liquid removal process is complete. The concentrated waste is designated as double-shell slurry feed and is pumped to another available DST for storage.

About 3,800,000 to 7,600,000 L (1,000 to 2,000 kgal) of waste per month can be processed by the 242-A Evaporator. In the past, however, the average processing rate has been about 1,900,000 L (500 kgal)/month.

7.11 WASTE FROM SINGLE-SHELL TANKS

As part of the Waste Stabilization Program, liquid waste from SSTs will be pumped to DSTs. This liquid is obtained through salt-well pumping and should be relatively free of solids. There is a possibility that solids may be sluiced from an SST and pumped to a DST.

Although operations in SSTs are evaluated in a separate CSER, the discharge of SST waste to DSTs will be controlled according to discharge waste criteria in this CSER and in the CPS for DSTs.

8.0 CHARACTERIZATION OF TANK CONTENTS

Two sources of information on tank waste composition are available: (1) a software program known as TRAC (Track Radioactive Components), and (2) the results of chemical analyses of waste tank samples.

In practice, when assessing criticality safety of a specific storage tank, the available analytical data may be inadequate, making it necessary to use TRAC data to characterize the waste. It is generally best to review both sources of data and to use the more conservative as the basis for safety evaluation. The sources are discussed below.

8.1 TRAC

TRAC (Jungfleisch 1984) is essentially an accounting program that uses records of past waste additions and transfers to estimate the amounts and kinds of waste in storage tanks. Based on the data provided, the code follows waste components through the tanks and provides estimates of the inventories remaining in each tank. The most recent TRAC tank inventory was generated in 1985.

Two factors require that significant uncertainty allowances be used when applying TRAC data and results. These are (1) the difficulty in mathematically modeling the complex physical processes involved, and (2) the difficulty in validating TRAC-generated estimates.

Waste transfers into, from, and between tanks are complex processes that are difficult to describe accurately in a computer model. First, the computer model must take into account that waste in the Hanford Site storage tanks originates from a number of different processes. Then, it must account for the addition of stable chemicals and the removal of radionuclides. Finally, waste has been transferred between tanks, and different waste streams have been combined. These processes make it difficult to estimate tank contents.

Waste streams have at times been passed, or "cascaded," through more than one tank on their way to their destinations. Because the fraction of solids that settles out into each intermediate tank is not accurately known, it is hard to estimate the final composition of solid waste in a tank.

Because of the problems in verifying the contents of any given tank, TRAC estimates have proven difficult to validate. (Some TRAC plutonium content estimates differ significantly from estimates based on analysis of tank samples. It is unknown how much of this is caused by TRAC and how much is caused by uncertainties in the sample results.)

The TRAC computer model provides an independent estimate of the total plutonium discharged in waste of 385 kg (Jungfleisch 1983). This estimate is somewhat lower than an estimate of 407 kg made by Roetman (1994) based on annual average estimates, but it is considerably lower than Roetman's conservative estimate of 981 kg based upon annual maximum estimates. It has

long been suspected that the TRAC estimate might be too low. Records used to obtain the TRAC estimate may have provided an incomplete accounting of the plutonium.

Because of its limitations, TRAC-generated data is used conservatively in developing criticality safety models and limits.

8.2 ANALYTICAL SAMPLES

The highest quality analytical data available come from waste characterization reports that describe core samples taken from tank waste.

Because only very limited sample data are available, considerable variation in component concentrations must be expected, not only for waste in different tanks but also for waste from different locations in the same tank. Clearly, the limited number of core samples means that not all waste types present in the Hanford Site storage tanks have been sampled. Also, a single core sample might contain material from discrete waste layers that have formed in the tank. Such a sample would not represent actual conditions and might instead be a homogenized average of two or more waste types. (The samples are mixed before being analyzed.)

Data Compiled for Safety Assessment

As part of the *Safety Assessment*, a compilation was made of waste sample analyses made between 1974 and the present (Braun et al. 1994). For the 914 samples uncovered by this search, a plutonium concentration was reported for 200 of 312 solids samples and 306 of 602 liquid samples.

The greatest plutonium concentrations are reported for solids samples. The highest plutonium concentration reported is 0.35 g/L (1.3 g/gal), but the median value of all solids samples is found to be about 0.01 g/L. The larger of the reported plutonium concentrations may be significantly conservative. A review of one suspect sample providing a high plutonium concentration revealed an error indicating that the probable concentration was much less. Other samples taken from the same tank indicated a much lower plutonium concentration than that of the suspect sample.

Two liquid samples are reported with plutonium concentrations greater than 0.01 g/L. It is not known to what extent these values have been influenced by uncertainties associated with the measurements. However, the median plutonium concentration from among all 306 liquid samples is about 0.0001 g/L.

When a waste-bearing solution is made highly alkaline, much of the waste precipitates in the form of solids which settle to the bottom of the tank. A high pH will therefore tend to keep the plutonium combined with solids. The *Safety Assessment* shows a histogram of the pH for 310 liquid samples and 75 solids samples. The lowest pH values found are as follows: three values between 7.0 and 8.0 and six values between 8.0 and 9.0. The median pH from all samples is about 12.0.

An alkaline solution is one for which the pH exceeds 7. All sampled waste is therefore alkaline.

8.3 THE CONSERVATIVE WASTE MODEL

Tank waste is a complex mixture of components, and the composition of any given portion of the waste has uncertainties in every component. This uncertainty in composition introduces considerable complexity into the determination of critical parameters. For this reason, a waste model, known as the conservative waste model, has been developed (Rogers 1993). This model is used as the basis for calculating conservative subcritical limits. Subcritical limits provided by Rogers (1993) are the basis for this evaluation.

Basis for conservative model

A conservative waste model composition is determined by tabulating available waste analyses and selecting the maximum concentrations of components that are good neutron scatterers and poor neutron absorbers, and minimum concentrations of components that are good neutron absorbers. The conservative waste model was based upon 28 waste compositions analyzed for 16 SSTs. The primary goal in formulating this waste model was to provide a waste composition known to have a smaller macroscopic absorption cross section than that of any real waste. Critical parameters are calculated using the assumption of optimal water moderation. In this way, subcritical limits calculated using the conservative waste model are conservative relative to the actual critical values for any real waste.

Meaning of conservative

As used in this report, conservative values, estimates, or assumptions are ones which produce "worse" (more limiting or severe in some way) results than the actual case. Conservative estimates can be used to set limits or to simplify analyses of criticality safety. Such limits and analyses are used to make sure that, in spite of uncertainties, the real case is always as safe or safer than the model. Thus, if the model can be shown to be safe, the safety of the real situation has been shown.

The conservative waste model is intended to

- Be easier to use than more elaborate and precise descriptions.
- Address all those features of the waste that are significant with respect to criticality.
- Always produce conservative analysis results (that is, operating limits derived from the model are as safe or safer than the limits would be if derived from the actual waste).

Composition of conservative model

Table 4 shows the composition of the conservative waste model. Only the waste solids are included. The model assumes a dry solids density of 1,200 g/L. The concentrations of plutonium and water are independent variables not part of the waste model.

Table 4. Composition of Conservative Waste Model

Component	wt%
Oxygen (O)	40.7
Phosphorus (P)	6.9
Silicon (Si)	3.8
Sodium (Na)	21.5
Aluminum (Al)	7.2
Nitrogen (N)	0.0
Iron (Fe)	19.9

The basic requirement for waste to fall within the conservative waste model is that the neutron absorption in one liter of that waste after all water has been removed exceeds the neutron absorption in 1,200 g of conservative model waste solids. Although it is possible to construct theoretical models of waste having less absorption than this, it is expected that all real tank waste will satisfy this criterion.

Although only samples from SSTs were used to derive the conservative waste model, critical parameters derived from the model may be applied to all tank waste. This is because DST waste is similar to that in SSTs and there is considerable conservatism included in the waste model. The high proportion of oxygen and the absence of hydrogen in the conservative waste model also provides additional conservatism for all waste types likely to be present in the tanks, even those having a considerably different makeup from the analyzed samples used to develop the model.

8.4 SOLUBILITY OF PLUTONIUM IN WASTE

An important parameter for criticality safety is the solubility of plutonium in high-level waste. The higher the solubility the more difficult it is to control the distribution of the plutonium. If the plutonium can be dissolved, for example, separation of the plutonium from other components might be possible by preferentially dissolving the plutonium. When plutonium is in solution, there are mechanisms, such as evaporation of liquid, settling, and precipitation, that are capable of increasing the concentration.

Perhaps the main problem associated with having a large fraction of the plutonium in solution would be the difficulty in estimating how much plutonium is in each tank. When plutonium is dissolved, the quantity transferred when waste is pumped between tanks is increased, and it becomes more difficult to estimate the distribution of the plutonium. It is therefore desirable to ensure a low solubility for plutonium to keep it combined with solids and to make it less mobile. Because plutonium is less soluble in an alkaline solution, the pH of the waste is controlled to ensure alkalinity.

Concentration of Dissolved Plutonium

Four documents were examined that discuss the solubility of plutonium under the conditions present in high-level waste. C. H. Delegard is the primary author for two of these studies, and D. T. Hobbs is the primary author of the other two.

Hobbs investigated the influence of hydroxide, nitrate, nitrite, aluminate, sulfate, carbonate, and temperature on the solubility of plutonium and uranium in alkaline salt solutions and reached the following conclusion:

For salt solutions within the range considered by this study, upper 95% tolerance limits for Pu and U solubilities, estimated from analytically measured specie concentrations, are 1.68 mg/L and 17.1 mg/L (6.36 mg/gal and 64.7 mg/gal), respectively. The alkaline salt solutions considered in this study should bound those that will be treated in the in-tank precipitation process (Hobbs et al. 1993).

Hobbs also concluded that:

Conditions which increase the plutonium solubility do not necessarily increase the uranium solubility. Maximum plutonium solubility is predicted at high nitrate, high hydroxide, high carbonate, and high sulfate concentrations. Maximum uranium solubility is predicted at high hydroxide, high aluminate and high sulfate concentrations and low nitrate, low nitrite, and low carbonate concentrations (Hobbs et al. 1993).

Effects of waste components on solubility

Hobbs makes the following observation concerning the effect of other waste components upon solubility:

The solubilities reported in this document may be higher than those which will be observed in actual waste due to the coprecipitation of the plutonium and the uranium with iron, manganese, and aluminum during neutralization of fresh waste. In a single experiment in which the plutonium and uranium were coprecipitated with iron, the solubility of plutonium was decreased by a factor of about five, and that of uranium increased by about a factor of two (Hobbs et al. 1993).

Although the common understanding is that plutonium precipitates in alkaline solution, this simple understanding does not fully describe the complex nature

of the chemistry involved in waste. Delegard shows that the solubility of plutonium increases for increasing NaOH.

The solubility of Pu(IV) hydrous oxide, $\text{PuO}_2 \cdot x\text{H}_2\text{O}$, in air-equilibrated, synthetic, Hanford high-level waste (HLW) solutions was determined as a function of NaOH, $\text{NaAl}(\text{OH})_4$, NaNO_3 , NaNO_2 , and Na_2CO_3 concentrations. The solubility was found to increase with the square of the NaOH chemical activity. The components NaNO_3 and NaNO_2 increased $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ solubility by increasing NaOH activity (Delegard 1985).

Although the plutonium solubility is found to increase with addition of NaOH, the solubility nevertheless remains very low. Delegard (1985) studied the solubility of plutonium in NaOH solutions over the range of NaOH concentration between 1 and 15 molar.

For typical waste, Delegard (1985) states that the NaOH concentration is 4 molar. At this concentration the maximum plutonium concentration is found to be about 0.0005 g/L (0.0019 g/gal or 2×10^{-6} molar). When allowed to set for a long time, the plutonium concentration in solution decreases to a value about 8 times smaller. When the NaOH is increased from 4 molar to 7 molar, the concentration of dissolved plutonium increases by about 10 times, and at 11 molar it is about 100 times greater than at 4 molar. At the very high NaOH concentration of 11 molar, the plutonium concentration in solution should not exceed 0.05 g/L (0.19 g/gal) (Delegard 1985).

Upper limit on solubility

From the information above, it can be seen that the concentration of dissolved plutonium in high-level waste should never be greater than 0.017 g/L, even under the most idealized conditions for dissolution. Depending upon the makeup of the waste, the saturation plutonium concentration might be as low as 0.002 g/L. These values would be achieved only when the quantity of plutonium present is large. In practice, the quantity of available plutonium and the large quantity of intermixed solids should combine to produce a much smaller concentration of dissolved plutonium.

Suspended Particulates

When liquid is pumped from one tank to another, the quantity of plutonium transferred is a function of solubility and of suspended particulates. When the saltwell pumping method is used, the liquid is passed through a screen to remove particulates. Nevertheless, even liquid in which solids have been allowed to settle for a long time and which has been screened (filtered) will contain a small content of suspended solids. The composition of suspended particles would be expected to be the same as the composition of solids within the waste. Because the quantity of suspended particulates is generally small and the plutonium concentration in the solids is small, the total quantity of plutonium in suspended particulates should be very small. This conclusion does not apply to waste that has been stirred and for which the solids have not been given time to settle out.

8.5 DENSITY OF SOLIDS

Waste solids provide an effective way of controlling the plutonium concentration. When the plutonium is mixed with a high proportion of solids, it is very difficult, if not impossible, to separate the plutonium from the solids by mechanical means. Stirring, mixing, pumping, or any other operation performed on the waste tends to more completely mix the plutonium with the solids.

When waste contains a large fraction of liquid, it is possible for solids to be suspended in the liquid. Removal of liquid may cause the density of the solids to increase. The highest density for the solids is obtained by removing all of the liquid to obtain dry solids. The volume of dry solids provides a lower limit on the volume of waste. When all plutonium is assumed confined to the dry solids, an upper limit is obtained on the plutonium concentration. Since the maximum possible plutonium concentration is determined by the minimum density of solids, the dry solids density is an important parameter for criticality safety.

Lower limit on solids density

The lower limit on solids density obtained for the conservative waste model is 1,200 g/L. At the low solids density of 1,200 g/L, it is estimated that dry solids occupy 35 percent of the volume and the remaining 65 percent is void. For a plutonium concentration of 4.0 g/L (15.1 g/gal), optimal moderation occurs when water occupies about 19 percent of the total volume. Therefore, at optimal moderation about 46 percent of the volume is void. If the fraction of water is higher, reactivity decreases.

At optimal water content, waste is nearer to being dry than to being water-saturated. At this low water content it is not possible for solids to be suspended. This means that, for optimal water content, the smeared (i. e., average) density of solids will be the same as for dry solids. For real waste the density of solids at optimal moderation will be greater than 1,200 g/L, the lower limit established for conservative model waste.

Lesser solid densities are possible for solids suspended in water. A configuration capable of suspending solids would not contain void space. In that configuration, the water content would be greater than that which results in greatest reactivity (i. e., optimal water content). This water increases the concentration of plutonium required for criticality. As the water content in the waste increases, the minimum critical plutonium concentration increases until it reaches 7.2 g/L (27.2 g/gal), the minimum critical plutonium concentration in water.

8.6 LIQUID CONTENT

The high water content of the waste ensures that fissile material is highly overmoderated. However, there are operations designed to remove water from waste, such as saltwell pumping and passing waste through an evaporator. Although the degree of overmoderation decreases as liquid is removed, the very low plutonium concentration ensures that the waste will remain overmoderated

after completion of evaporation or pumping. Even if all water were to be removed, the scattering properties of the large fraction of material in the waste that is not fissile would provide appreciable moderation and absorption.

This evaluation assumes that optimal moderation of waste is possible. Therefore, the actual volume of liquid in the waste tank does not affect conclusions reached. No restrictions need be placed on the water content of tank waste, either as to how little or how much is allowed to be present.

9.0 PARAMETERS IMPORTANT TO CRITICALITY SAFETY

If a given parameter is to be controlled as a means of ensuring criticality safety, the range over which that parameter can be varied while maintaining the system subcritical must be known. The value of that parameter at which the system is just critical is referred to as its critical value.

For purposes of criticality safety, a subcritical limit for a parameter is defined. The subcritical limit is the largest (or sometimes the smallest) value of a parameter which will assure that a system is subcritical, after taking into account uncertainties in the method of determining the critical point. In this evaluation a "critical" parameter generally is taken to mean the subcritical limit and will therefore describe a system that is actually subcritical. The neutron multiplication constant (either k_{eff} or k_{inf}) for subcritical limits calculated for this evaluation will not exceed 0.95 with a 95 percent confidence level.

When a critical parameter is reported in an authoritative document, such as an American Nuclear Society (ANS) Standard or the *Nuclear Safety Guide* (Thomas 1978), that parameter may be used as a subcritical limit, even though it may be based upon a multiplication factor greater than 0.95.

9.1 PLUTONIUM CRITICAL PARAMETERS

Conservative assumptions

The fissionable isotopes potentially present in waste are ^{233}U , ^{235}U , ^{239}Pu , and ^{240}Pu . Because ^{235}U is always combined with a ratio of ^{238}U sufficient to ensure that the uranium is subcritical, the ^{235}U can usually be ignored. When the ^{235}U is not ignored, it is often treated as if it were ^{239}Pu and added to the plutonium inventory. ^{233}U appears only in a few tanks, and when present it can be treated as if it were ^{239}Pu , and also added to the quantity of plutonium. That is to say, the ^{233}U and ^{235}U may be considered to be equivalent to ^{239}Pu . For these reasons the nuclear criticality safety of tank waste is usually discussed solely as a function of the plutonium present.

At fissile concentrations above 50 g/L, ^{233}U can have a smaller critical mass than ^{239}Pu . However, in a large volume the minimum critical concentration for ^{233}U is larger than for ^{239}Pu . Over the range of fissile concentrations found in waste the replacement of ^{233}U with ^{239}Pu is conservative.

Plutonium is distributed non-uniformly, and there is considerable uncertainty as to the degree of non-uniformity. Conservative assumptions must be made to compensate for the lack of information.

^{240}Pu is fissionable, but not fissile. The presence of even a small quantity of moderating material increases the critical mass of this isotope very rapidly until criticality is not possible with it alone. In the tank waste environment, ^{240}Pu acts as a mild poison, and its presence increases the quantity of ^{239}Pu required to achieve criticality. Therefore, it is

conservative either to ignore the presence of ^{240}Pu or to assume all plutonium is ^{239}Pu (i.e., to replace ^{240}Pu with ^{239}Pu).

Plutonium in water

Criticality is not possible for plutonium in a plutonium-water mixture unless the plutonium concentration exceeds 7.2 g/L.

When certain materials are present whose neutron absorption cross sections are small, in addition to water, criticality becomes possible at lower concentrations. For tank waste, criticality is possible at a lower plutonium concentration when the total macroscopic absorption cross section per plutonium atom is less than for water.

Plutonium in waste

For criticality to be possible in tank waste, it is necessary for the plutonium concentration to be at least 2.6 g/L (9.84 g/gal) over a large volume. This value is based upon the conservative waste model and occurs at an hydrogen/plutonium (H/Pu) atom ratio of about 100. Alternately, criticality is possible with a higher plutonium concentration over a smaller volume.

To achieve criticality with waste having a plutonium concentration of 4.0 g/L requires a 4.7-m (15.4-ft) diameter, 53,750-L (14,200-gal) sphere containing 215 kg of plutonium. Optimal moderation occurs for an hydrogen/plutonium atom ratio of 500.

For a slab of waste to go critical with 4 g Pu/L it would have to be at least 2.1 m (7.0 ft) thick. This is a conservative value obtained by applying the formula for buckling conversion to the critical sphere.

At 10 g Pu/L the critical mass in tank waste is approximately 3.0 kg of plutonium in a volume of 300 L (79.3 gal).

The minimum critical areal density of plutonium in water is conservative when applied to waste. $2,582 \text{ g Pu/m}^2$ (240 g Pu/ft^2) is the lowest areal density that can be made critical (Carter et al. 1969). The areal density includes all plutonium above a unit area of floor, including plutonium located all the way to the top surface.

A summary of critical parameters for plutonium in conservative model waste and in water solution are shown in Table 5.

Table 5. Plutonium Subcritical Limits

Parameter	Subcritical limit ^a
Conservative waste model	
Infinite critical concentration	2.6 g Pu/L
Solids/Plutonium mass ratio	476 (min.)
Plutonium/Solids mass ratio	2.1 g/kg
Critical mass at 4.0 g Pu/L	215. kg Pu
Critical mass at 10.0 g Pu/L	3.0 kg Pu
Sphere diameter at 4.0 g Pu/L	4.7 m (15.4 ft)
Slab thickness at 4.0 g Pu/L	2.1 m (7.0 ft)
Critical areal density	> 240 g/ft ²
Plutonium-Water Solution	
Infinite critical concentration	7.2 g Pu/L
Critical areal density	240 g/ft ²

^aLimits shown are maximum subcritical limits, except for the solids/plutonium mass ratio, which is a minimum subcritical limit.

Parametric Study

Schwinkendorf (1994a) provides a parametric study for plutonium in conservative model waste. For this study the density of waste solids is varied between 0 and 75 vol% in water. This means that the upper limit on solids is assumed for these calculations to be 75 vol%. For water, the lower limit is assumed to be 25 vol%.

Calculations were made for plutonium concentrations over the range of 1 to 8 g/L. For these plutonium concentrations, k_{inf} is larger when the solids content is larger. Therefore, when the solids content is low, the water content is sufficient to overmoderate the waste.

The critical slab thickness and the areal density are calculated for plutonium concentrations between 5 and 8 g/L. When the plutonium concentration is less than 6 g Pu/L, the minimum values for these parameters occur when the solids occupy more than 75 percent of the volume and water occupies less than 25 percent. In other words, the smallest critical slab thickness and the smallest critical areal density occur when the water content is less than is considered for these calculations.

A 7.0-ft thick slab containing 75 vol% solids and 25 vol% water is critical at a plutonium concentration of 4.5 g/L. Through extrapolation, the critical

plutonium concentration for a 7.0-ft thick slab is estimated to be 4.0 g/L when the water moderation is optimal.

For a waste mixture, the plutonium critical areal density is greater than that for plutonium in pure water. This confirms that it is conservative to use the minimum critical areal density for plutonium in water for criticality safety evaluation of waste.

Schwinkendorf (1994b) calculates critical dimensions for spheres, hemispheres, and cylinders of waste over the same range of variation described above. Critical parameters are sensitive to plutonium concentration and water content. Above 6 g Pu/L critical dimensions are smallest at a water content greater than 25 vol%. At lesser plutonium concentrations optimal water content is less than 25 vol%.

9.2 ABSORBER-TO-PLUTONIUM RATIOS

When any one of the following mass ratios is met or exceeded, subcriticality is assured for all concentrations of plutonium. For consistency, all ratios are specified with the plutonium in the denominator.

1. When the ^{235}U enrichment is less than that of natural uranium (0.72 wt%), the "always safe" limit value for the U/Pu mass ratio is 770. This is the reciprocal of 0.0013 for the Pu/(Pu + U) mass ratio provided by the *Nuclear Safety Guide* (Thomas 1978).
2. When the U/Pu mass ratio is insufficient to ensure subcriticality, iron in the waste can be used in the analysis. For a given mass, neutron absorption in iron is four times that of uranium. Thus an equivalent mass ratio of (U + 4Fe)/Pu may be used to account for uranium and iron. The "always safe" value of this ratio is 770, (the same as the ratio for U/Pu).
3. Criticality is not possible for the following mass ratios:
 - a) Iron to ^{239}Pu exceeds 160
 - b) Iron to ^{235}U exceeds 77
 - c) Manganese to ^{239}Pu exceeds 32
 - d) Manganese to ^{235}U exceeds 30.
4. Cadmium and boron are strong absorbers of moderated neutrons. If the ratio of hydrogen to fissile atoms exceeds 250, subcriticality is assured when either the cadmium/fissile atom ratio exceeds 0.5 or the boron/fissile atom ratio exceeds 2.0. Fissile refers to ^{235}U , ^{233}U , and ^{239}Pu .
5. Criticality is not possible when the hydrogen-to-plutonium (H/Pu) atom ratio exceeds 3600.

Sometimes no single waste component is sufficient to demonstrate subcriticality. In this case, the waste taken as a whole may be used to demonstrate subcriticality, provided the neutron absorption in a given mass of

waste exceeds that for an equal mass of conservative model waste. If this can be shown, criticality is not possible when the plutonium/solids mass ratio is less than 2.1 g/kg.

Conversely, criticality is not possible when the reciprocal solids/plutonium mass ratio limit is greater than 476.

9.2.1 Additional Absorber-to-Plutonium Mass Ratios

Because tank waste is so variable, it is easier to provide assurance of subcriticality if the subcritical ratios are known for many different waste components. Detailed, published analyses provide a basis for subcritical limits on mass ratios for uranium, iron, and manganese. Based upon this published data, subcritical mass ratios for other components have been derived. Derived mass ratios for nickel, chromium, silicon, aluminum, nitrogen, and nitrate are shown in Table 6. Nitrate is included in the table because it is the form in which nitrogen most often occurs and is most often reported in a chemical analysis.

Table 6. Mass Ratio Subcritical Limit

Component	Absorber/fissile mass ratio limit
Aluminum (Al)	910
Chromium (Cr)	135
Nickel (N)	105
Nitrogen (N)	61
Nitrate (NO ₃)	270
Sodium (Na)	360
Silicon (Si)	1400
Water	150

Recall that k_{inf} solely depends on the macroscopic cross section for absorption in a mixture. This makes a simple method for deriving mass ratios possible. For example, if a large volume of iron and plutonium is slightly subcritical, it should remain slightly subcritical when the iron is replaced by an equivalent (in neutron absorption) quantity of another component. This equivalent quantity can then be used to define a mass ratio for the substituted element.

In these ratios, fissile material refers to the sum of ^{239}Pu and ^{235}U . However, the ^{235}U content in uranium enriched to less than 1.0 wt% need not be included in the fissile material used to determine mass ratios for components shown in Table 6.

The minimum safe absorber-to-fissile mass ratios in Table 6 are intended to be used to evaluate waste inside storage tanks to provide assurance of subcriticality. If used as the basis for setting limits on future waste additions, an evaluation should first be made of the margin of safety associated with using that specific component. For instance, an assessment should be made of the ability of chemical reactions within the waste to separate that component from the fissile component. In addition, a safety factor should be applied to compensate for possible variations in the mass ratio.

9.2.2 Combining the Effect of Several Absorbers

The total neutron absorption in waste is the combined neutron absorption of the various components. The *Safety Assessment* describes a way to assess the combined effect of the various components on criticality:

A measure of how subcritical a system is may be obtained by considering the fraction of the actual absorber-to-plutonium ratio divided by the minimum subcritical absorber-to-plutonium ratio. The fraction formed from the actual-to-minimum ratios are then totaled. The formula for the sum of fractions of actual-to-minimum subcritical absorber ratios is as follows (Braun et al. 1994).

$$\sum_{j=1}^N \frac{\left(\frac{X_j}{Pu}\right)_{actual}}{\left(\frac{X_j}{Pu}\right)_{subcritical}} \geq 1$$

When the sum of fractions is greater than 1.0, the total neutron absorption is sufficient to ensure subcriticality in an infinite system of homogeneous waste. The greater the sum of the fractions, the greater the margin of safety.

Even if the sum of the fractions for a waste sample is determined to be less than 1.0, there are numerous reasons why the waste configuration may still be well subcritical. The sample may only represent a small fraction of the actual waste, uncertainty in the analyzed composition may be high, not all of the waste components may have been included in the calculation, and so forth. However, if a value less than 1.0 is obtained, additional evaluation is required to demonstrate subcriticality.

9.3 URANIUM

In a uranium-water system that is homogenized, criticality is not possible until the enrichment exceeds 1.03 wt%. Although criticality is possible at enrichments as low as 0.72 wt% in precisely defined heterogeneous arrays with low neutron absorbing moderators, such as graphite or heavy water, these configurations would be impossible to achieve in tank waste. Nearly all uranium sent to waste storage tanks has been enriched less than 1.03 wt%.

There is no chemical or physical means by which the ^{235}U can be separated from the ^{238}U unintentionally.

The presence of uranium enriched to more than 1.0 wt% would be the only way in which uranium might contribute to criticality. Only small quantities of enriched uranium were ever sent to tank storage, and the potential for accumulation of even a very small quantity of enriched uranium at a significant concentration is very remote, if not impossible.

CPS-T-149-0010, Rev. D-0, which has been used in the past to cover operations involving tank waste, has the following limit governing ^{233}U and ^{235}U .

One gram of ^{233}U or ^{235}U in excess of 1 wt% enrichment shall be assumed equivalent to one gram of Pu, unless otherwise restricted by a specification. The amount of ^{235}U less than or equal to the equivalent of 1 wt% enrichment may be excluded in concentration and total mass calculations.

For waste configurations it is conservative to treat ^{233}U and ^{235}U as ^{239}Pu .

9.4 RATIO OF PLUTONIUM TO URANIUM

An important parameter to help justify a conclusion of subcriticality is the plutonium/uranium mass ratio. *Nuclear Safety Guide, TID-7016 Revision 2* (Thomas 1978) states that criticality is not possible for plutonium combined with natural or depleted uranium provided the ratio of $\text{Pu}/(\text{Pu} + \text{U})$ does not exceed 0.0013. Natural uranium contains 0.72 wt% ^{235}U .

For this evaluation, the inverse of the above ratio, or $(\text{Pu} + \text{U})/\text{Pu}$, is used. This inverse ratio places the plutonium in the denominator, where it appears in other ratios used to assess subcriticality. The subcritical limit for the inverse ratio is 770. Subcriticality is assured when the mass ratio exceeds this value.

Much of the uranium sent to waste storage tanks is depleted with a ^{235}U content less than that of natural uranium. Because most of the waste is a byproduct of the production of plutonium from low-enriched uranium, the uranium/plutonium mass ratio is usually larger than the subcritical limit.

The ratio of $(\text{Pu} + \text{U})/\text{Pu}$ is often simplified to U/Pu . This substitution causes the ratio to decrease slightly and is therefore conservative. Because the ratio of uranium to plutonium must be greater than 770 to justify a conclusion of subcriticality, the error introduced by this substitution is small and may be neglected.

9.5 CHEMICAL SEPARATION OF PLUTONIUM FROM URANIUM

Plutonium is obtained by chemically separating it from uranium metal fuel elements that have been irradiated in a reactor. While in the reactor, the ^{235}U is consumed in the fissioning process and plutonium is generated. Because the purpose of the separation process is to recover the valuable plutonium, nearly all of it is removed. Consequently, the discarded uranium

sent to waste tanks contains only a small fraction of plutonium and about half the original ^{235}U . Most of the plutonium sent to waste disposal is intimately associated with uranium, primarily in the form of oxide.

The possibility of chemically separating plutonium from uranium is discussed in *Properties of Potential Uranium Precipitates as Related to Chemical Processing* (Colvin 1967). Concerning the behavior of plutonium when sodium polyuranate is precipitated, Colvin provides the following information:

The major constituent of dissolver solution is uranyl nitrate with plutonium and fission products being present at much lower concentrations. When sodium hydroxide is added to dissolver solution, the behavior of plutonium is dependent upon the plutonium valence state.

The plutonium-to-uranium ratio will be higher in the precipitate than in the original solution if plutonium is in the IV valence state. Laboratory experiments, where only a portion of the uranium is precipitated, indicated an immediate 80 percent plutonium enrichment in the precipitate. A prolonged digestion period considerably increases this figure. Plutonium polymer formation is most likely the principle contributor to the observed enrichment. The above experiments were performed with a beginning dissolver solution temperature of 450° C. Variance in temperature could change the above figure considerably.

The opposite condition exists when plutonium is in the VI valence state. The Pu/U ratio in the precipitate is a factor of two less in the precipitate than in the original solution.

Analysis of dissolver solutions indicates that plutonium is normally present as 75-90% Pu(IV).

This process described by Colvin raises the possibility that at least part of the plutonium might separate from the uranium under certain conditions. For the separation process to work, the plutonium and uranium must be dissolved first; however, conditions in tank waste are controlled to prevent the dissolution of the heavy metals. Dissolution is prevented by maintaining a high pH (i.e., the waste is alkaline).

In practice, it is expected that the plutonium will remain uniformly mixed with the uranium. Conditions under which the proportion of plutonium might be increased over a sizeable volume of waste are very unlikely.

If chemical processes did somehow cause the proportion of plutonium to increase over a region within the waste, this would not by itself make criticality possible. Before criticality becomes possible, several other independent conditions would also have to be fulfilled.

- The presence of absorbers other than ^{238}U would have to be far less than usual. Under normal conditions, even with a total removal of ^{238}U , other absorbers should be more than adequate to ensure subcriticality.

- The plutonium would have to be concentrated many-fold (usually by more than a factor of 100).
- The quantity of plutonium concentrated into a small volume would have to be large enough to go critical.

9.6 MASS RATIO OF SOLIDS TO PLUTONIUM

To ensure subcriticality it is not sufficient to place an upper limit on the plutonium concentration. When this limit is used, it is also necessary to place a lower limit on the density of solids.

However, the parameter most directly related to criticality safety is the total neutron absorption cross section per atom of plutonium. This parameter is directly proportional to the ratio of the mass of waste solids to the mass of plutonium in the same volume of waste. In other words, it is proportional to the ratio of solids density to plutonium concentration, a ratio referred to as the solids/plutonium mass ratio. The units for this ratio is grams of solids per gram of plutonium.

A limit on the mass ratio of solids to plutonium eliminates the need for separate limits on the plutonium concentration and the solids density. At the same time, a limit on mass ratio is more versatile because it applies over a wider range of plutonium concentrations and solids densities.

For conservative model waste with a solids density of 1,200 g/L, the minimum critical concentration for plutonium is 2.6 g/L. This plutonium concentration, divided by the solids concentration, yields a plutonium/solids mass ratio of 2.17 g/kg. When the reciprocal ratio, the solids/plutonium mass ratio, is used, the subcritical limit is 476 (minimum). When the mass of solids exceeds 476 times the mass of plutonium, criticality is not possible. In practice, this reciprocal mass ratio is used more often than the plutonium/solids mass ratio.

For the subcritical limit on the solids/plutonium mass ratio to be valid, two conditions must be assured.

1. The neutron absorption must be at least as great as that in an equal mass of conservative model waste.
2. The plutonium and solids must be well enough mixed to guarantee that the solids/plutonium mass ratio limit is exceeded throughout the waste.

Even if the solids/plutonium mass ratio is less than the subcritical limit, criticality does not become possible until the region affected is large enough to contain more than a minimum critical mass of plutonium. In practice, waste sent to storage is well mixed, and its mass ratio is greater than the limit.

To ensure continued compliance to subcritical limits within the waste tank environment, a safety factor is applied to discharge limits. This safety factor is selected commensurate with the uncertainty.

Uranium, aluminum, and silicon, when taken alone, exhibit a solids/plutonium subcritical limit larger than that of the conservative model waste. In other words, a larger mass of these elements is required to ensure subcriticality than would be required by conservative model waste. If the proportion of these components is very high, this fact must be taken into account when setting a limit on the solids/plutonium mass ratio.

9.7 MINIMUM CRITICAL MASS

Rogers (1993) concludes that the minimum critical mass of plutonium in waste is 520 g when the density of waste solids is less than 1,200 g/L, and 750 g when the density of waste solids is more than 1,200 g/L. In practice, the composition of real waste ensures that the minimum critical mass is greater than these values.

Although the minimum critical mass is often an important parameter in assessing criticality safety, it is of limited use when evaluating tank waste because the quantity of plutonium in a tank usually exceeds it.

There are nevertheless situations in which the minimum critical mass can be used to show subcriticality. When the total tank inventory of fissionable material is known to be less than the minimum critical mass, subcriticality is assured without knowing the actual waste composition or the plutonium distribution.

To achieve criticality with a mass of plutonium equal to the minimum possible value of 520 g would require that the plutonium concentration be 30 g/L (113 g/gal). There are no known mechanisms capable of concentrating plutonium in waste tanks to such a high value.

9.8 BORON AND CADMIUM

Boron and cadmium are effective absorbers of neutrons, and their presence in tank waste can be very important. Whenever criticality evaluations are made using boron, it is important to recognize that the two primary isotopes have greatly different absorption cross sections and that a proper specification for boron is important. Boron in waste is assumed to be natural boron composed of 20 wt% ^{10}B and 80 wt% ^{11}B .

In spite of possessing very large cross sections for absorption, cadmium and boron are not included in the conservative waste model. The neutron absorption contribution of these elements would dominate the waste model. If they were included in the model, their continued presence in the tank waste would have to be guaranteed. Otherwise, critical parameters based upon the model could not be used as a basis for storage limits. As a practical matter, it would be very difficult, if not impossible, to guarantee the presence of these poisons mixed uniformly throughout the waste.

Still, the large neutron absorption of cadmium and boron means they are potentially important to subcriticality studies. If their presence is independently verified, they provide additional assurance of subcriticality.

Under special circumstances cadmium may be added to waste to permit discharge with a higher plutonium concentration than otherwise permitted. Cadmium addition is discussed in Section 12.5.8 and in Appendix A.

9.9 GLOBAL PARAMETERS

Parameters obtained from analysis of waste samples generally are applicable only to a limited volume of waste. Samples taken from a different tank, or from a different location within the same tank, would be expected to show a different value for a parameter. Although it is almost never possible to accurately predict the value of a parameter, it is sometimes possible to determine an expected value. For example, when an analysis is made of a selected parameter, such as a component concentration, the value expected is the average value. The average value can be found by dividing the total tank inventory by the volume of waste in that tank.

For the following discussion, a parameter based upon the inventory of an entire tank or upon the total inventory of tank farms is called a global parameter. Global parameters help define the range of variability of waste for individual tanks.

When the total mass of plutonium and the total volume and mass of waste solids and liquids are known, the average plutonium concentration and the average solids/plutonium mass ratio can be found. A global parameter for tank farms will remain unchanged when waste is transferred between tanks, and it will change only slightly, if at all, when new waste is sent to tank farms.

When a global parameter is known, it can sometimes be used to estimate other parameters. For instance, if the plutonium inventory for an entire group of tanks (global inventory) is known and several tanks have very little plutonium, then the average inventory for the remaining tanks will be higher than the group average. If, on the other hand, a few tanks contain most of the plutonium, then the average inventories of the remaining tanks will be less than the group average.

Roetman (1994) estimates the total quantity of plutonium discharged to tank storage to have been 981 kg since the beginning of plutonium production.

Table 7 summarizes volumes of various waste types reported by Hanlon (1993).

Table 7. Quantity of Tank Waste - August 1993
(Hanlon 1993))

	SST	DST	Total
Supernatant liquid (kgal)			
Total supernatant	575	20,709	21,284
Solids (kgal)			
Double-shell slurry	0	2,040	2,040
Sludge	12,464	1,955	14,419
Salt cake	23,169	760	23,929
Total solids	35,633	4,755	40,388

Based upon this information, an estimate can be made of the total volume of plutonium bearing waste solids. Since a smaller volume of solids projects a higher plutonium concentration, it is conservative to underestimate the volume of solids. Since the plutonium concentration in supernatant and in salt cake is usually very small, these waste types are assumed to contain no plutonium and are not included in the estimate of the volume. All plutonium is assumed to be found within the slurry and sludge. In this way the total volume of plutonium bearing solids is found to be 62,297,000 L (16,459,000 gal).

Mass ratio for tank farms

Using a volume of 62,297,000 L and a plutonium mass of 981 kg, the average plutonium concentration is found to be 0.0157 g/L of solids. Since a low estimate of volume and a high estimate of plutonium are used, this global average plutonium concentration should be larger than the actual value.

When the solids density is known, the average solids/plutonium mass ratio can be determined. Based upon 26 analyzed core samples, Rogers (1993) reports an average waste density of 1.57 g/cm³. After the liquid has been removed, the average density of the remaining solids exceeds 2.0 g/cm³. To be conservative a lower limit on the solids density is used. Since a density of 1.2 g/cm³ is found to be less than the density of 95 percent of dry solids, it provides a conservative lower limit.

Based on a conservative solids density of 1,200 g/L, the global average solids/plutonium mass ratio for tank farms is found to be 74,500.

Mass ratio for PFP waste

Processes at PFP have not been subject to flowsheet control. Waste generated at PFP has not been as predictable in composition as that for PUREX, and there has been no guarantee that the ratio of solids to plutonium would be as high. For this reason, PFP waste is expected to have a smaller proportion of solids than waste from other processing plants. Nearly all PFP waste has been sent

to tank 102-SY, for which Roetman (1994) estimates a plutonium content of less than 31 kg of plutonium. For this tank Hanlon (1993) reports the volume of solids and liquids to be 268,700 L (71,000 gal) and 2,479,000 L (655,000 gal), respectively. This shows the solids to occupy 9.8 vol% of the waste. Based only upon the volume of solids, the average plutonium concentration would be 0.12 g/L, and the solids/plutonium mass ratio becomes 10,000 (assumes a solids density of 1,200 g/L). This mass ratio is much less than that for the tank farms as a whole.

Mass ratio for tank 104-C

One of the largest fissile material inventory for any storage tank in tank farms is reported for tank 104-C. This inventory, conservatively estimated at 89 kg, is based upon an estimated 56 kg of plutonium and 33 kg of ²³³U. For this discussion the entire inventory is treated as if it were 89 kg of plutonium.

Hanlon reports that tank 104-C contains 1,117,000 L (295,000 gal) of sludge. The average plutonium concentration is found to be 0.08 g/L, and the average solids/plutonium mass ratio is 15,055.

Mass ratio for tank 105-AW

The possibility exists that a limited quantity of PUREX waste may be sent to tank 105-AW under the limit for cadmium addition. An estimate is now made of the solids/plutonium mass ratio for tank 105-AW.

Hanlon reports that tank 105-AW contains 1,124,000 L (297,000 gal) of sludge. The *Safety Assessment* (Braun et al. 1994) reports the plutonium concentration in sludge to be 0.02 g/L. In six composite samples the largest plutonium concentration is reported to be 0.024 g/L. Based upon the largest reported plutonium concentration of 0.024 g/L, the solids/plutonium mass ratio is found to be 50,000.

Lower limit on mass ratio

To ensure subcriticality, it is necessary not only for the global solids/plutonium mass ratio to exceed the subcritical limit, but it is also necessary that the ratio be exceeded within any selected subvolume within the larger volume within each tank. However, to determine if any region having a very low mass ratio actually exists would require taking analytical samples from all regions of all storage tanks. This is not practical. Therefore, it is necessary to rely upon available information to show that the presence of such a region is extremely unlikely.

An estimate of the lower limit on the solids/plutonium mass ratio is made using the following assumptions for the worst case storage tank:

- (1) The plutonium inventory is 100 kg, a value about 10 percent of the estimated total for the entire tank farms. This value is 17 times larger than the average tank inventory.

- (2) The solids volume is 176,000 L, a value half of the average.
- (3) The solids density is 1.2 g/cm^3 , a value less than 95 percent of measured solids densities.

Using these conservative assumptions, a lower limit on the average solids/plutonium mass ratio for any storage tank is found to be 2,100. The actual mass ratio in any storage tank has a high probability of exceeding 2,100. This is less than one-fourth of 10,000, the value for tank 102-SY, and the smallest found for any tank. The next smallest estimated mass ratio is 15,055 for tank 104-C.

Even a tank with an average mass ratio of 2,100 probably would be well below critical at every location within the tank. For criticality to be possible a large volume of waste would have to have a solids/plutonium mass ratio less than 476, a value only 22 percent of the average. The process by which waste is discharged and transferred between tanks tends to ensure that waste is well mixed. It is extremely unlikely that a large region having this low of a mass ratio would exist, even in a tank whose average mass ratio is only 2,100.

9.10 MARGIN OF SAFETY

Waste sent to tank storage has always been subject to limits and controls established to ensure subcriticality. However, the considerable complexity of storage creates uncertainties in waste characterization. Operations such as transferring waste between tanks and mixing change the relative distribution of components. For this reason waste must be discharged with an inherent margin of safety to ensure subcriticality over the range of possible variations in composition.

The complexity of tank waste makes it difficult to assess the margin of subcriticality. This difficulty is caused in part by waste not being homogeneous. When several waste streams are combined, layers of distinctly different composition may form. Composition may vary both vertically and horizontally.

Waste characterization studies have been conducted to verify waste composition. However, the volume of analyzed samples represents only a small fraction of the total volume of waste at tank farms. The uncertainty caused by this paucity of data makes it necessary to use conservative assumptions when characterizing waste for a criticality safety evaluation.

Safety is maintained by assuring that parameters associated with waste do not exceed the subcritical limit (i. e., the value at which criticality becomes possible). A safety factor is applied to ensure that the subcritical limit is not exceeded. The safety factor is a fraction less than unity by which the subcritical limit is multiplied to obtain an operating limit. For waste, the operating limit is usually referred to as the discharge limit. The safety program then ensures that the discharge limit is not exceeded. In the unlikely event that an discharge limit is exceeded, the margin created by the safety factor provides assurance that the subcritical limit will not be exceeded.

10.0 MECHANISMS THAT CHANGE PLUTONIUM CONCENTRATION

A primary goal of criticality safety is to ensure that tank waste will remain well below critical for an indefinite time, even after waste types have been mixed and redistributed. At the time of discharge, waste is well subcritical because of limits and controls placed upon it at the generating facility. However, conditions within the waste tank environment are not static. Waste may be transferred between tanks, and different waste streams may be mixed together. In the past, waste sent to SSTs sometimes passed through a tank in the process known as cascading. In this process the heavier components probably settled out, while the lighter components passed on into the next tank. These processes transform the waste into compositions that are not well known.

For criticality to occur, the plutonium concentration must exceed the minimum concentration for which criticality is possible. This remains true no matter how wastes are mixed together or distributed. This minimum critical concentration is much greater than the discharge limit, and to achieve such a high concentration, there must be mechanisms capable of greatly increasing the plutonium concentration. If such a high plutonium concentration can be shown to be impossible, then at the same time criticality is shown to be impossible.

There are two ways to achieve a high plutonium concentration in waste solids: to receive waste already having a high plutonium concentration or to concentrate plutonium after it reaches the storage tank. The following sections review how the plutonium concentration might be increased and the potential consequences.

10.1 IMPORTANCE OF SOLIDS CONTENT

The presence of solids greatly increases the difficulty of achieving a critical configuration. Solids not only increase the neutron absorption, but also limit the ability of the plutonium to become more concentrated. Even after all liquids have been drained from the waste, the remaining solids ensure that the average plutonium concentration remains low.

The total mass of solids in all waste tanks is known to greatly exceed what is required to maintain subcriticality for the total quantity of plutonium available. However, the components of tank waste are not uniformly distributed among the various tanks, and the possibility must be considered that a localized region of high plutonium concentration and relatively low solids concentration might exist.

The conservative waste model defines a waste for which the neutron absorption is less than for any actual waste. Any homogenized real waste cannot be made critical when the mass ratio of waste solids to plutonium exceeds 476. This is the same as stating that the plutonium must be less than 2.1 g per kilogram of solids.

For some waste components taken by themselves, a mass ratio smaller than 476 will ensure subcriticality. For example, iron will ensure subcriticality when its mass ratio to plutonium exceeds 160. Although iron is usually present, the amount is often insufficient to ensure subcriticality by itself.

Cadmium and boron are very effective neutron absorbers, and even a small quantity will greatly increase the critical plutonium concentration. Both of these elements may be present in waste, but their presence is usually ignored because it cannot be assured.

Many waste components are good absorbers of neutrons. For each of these components there is a corresponding absorber/plutonium mass ratio above which criticality is impossible. When the ratio of one particular absorber is decreased, it is likely that there will be other absorbers in the waste capable of ensuring subcriticality.

Knowledge of the plutonium and solids content is obtained through chemical analysis of waste samples. As part of the *Safety Assessment*, chemical analysis reports for over 500 waste samples were examined, and an assessment was made as to whether they contained sufficient neutron absorbers to ensure subcriticality (Braun et al. 1994). Although no single component assures subcriticality for all waste, when the effects of several components were added together, all samples were shown to represent well-subcritical waste.

Many samples examined in the *Safety Assessment* were incomplete. Sometimes concentrations were measured for only a few components. For this reason, the margin of safety is expected to be larger than reported, and in some cases it possibly is much larger.

10.2 CONCENTRATING MECHANISM: EXCEEDING DISCHARGE LIMITS

It is theoretically possible that at some time in the past an abnormally large quantity of plutonium was discharged and produced a region of higher plutonium concentration within a storage tank. The possibility of such a discharge is now examined.

A surveillance program has been in place since the beginning of waste discharge to ensure compliance with process limits and controls. No record of any abnormal discharge was found during the course of this evaluation. Nevertheless, the possibility is considered that an abnormal discharge might have been made without detection. What would be the criticality safety implications of such a discharge?

Safety factors have been applied to ensure that any credible violation of discharge limits would not lead to a nuclear criticality. In the past the plutonium concentration in discharged waste has been maintained at less than 0.013 g/L (0.05 g/gal). If waste were discharged at this maximum permitted concentration, the plutonium would still have to be concentrated more than 200 times to reach the minimum critical concentration. If the tank plutonium inventory is assumed to be no greater than 200 kg, the plutonium concentration would have to be increased 300-fold to reach the minimum critical concentration of 4.0 g/L.

Holdup Tanks

Waste has never been discharged directly to tank farms, but is sent first to a holdup tank in the process facility. Only after a predetermined volume of waste accumulates is the waste discharged. Waste holdup tanks have large diameters and are recognized as locations for a potential accidental nuclear criticality. For this reason, these tanks are closely monitored to ensure compliance to criticality safety limits and controls. Audits are made and samples analyzed on a regular basis as part of a program to prevent abnormal accumulation of plutonium. If a violation is detected, the waste is not discharged to tank farms.

Under normal conditions, the quantity of plutonium in a holdup tank is small, and it is mixed with a much larger quantity of solids. Accumulation of an abnormal quantity of plutonium, followed by its discharge to a storage tank, would require a failure of the auditing and sampling program. For the accumulation to be large, a major breakdown in both the processing operations and the auditing program would be required. For a large quantity of plutonium to escape detection would also require a failure of nuclear materials management. Multiple failures of operating and accounting procedures would have to go undetected before a large quantity of plutonium could be discharged to tank farms.

For criticality to even be possible, the plutonium would have to be separated from the uranium. A careful accounting of separated plutonium is maintained by nuclear materials management.

Holdup tanks used to collect and hold waste until it is pumped to tank farms do not have a critically safe design. If a nuclear criticality were to actually occur, the most likely location would be in the holdup tank. Because the contents of these tanks are stirred, it is unlikely that plutonium would be concentrated in a small volume within the larger volume of waste. If highly concentrated plutonium solution were erroneously sent to a holdup tank, it would not likely remain highly concentrated.

The process of separating plutonium from uranium requires a large ratio of chemicals to plutonium, thereby insuring the presence of a large quantity of neutron-absorbing solids in the waste.

See Section 11.3 for more discussion of the consequence of discharging abnormal quantities of plutonium into the much larger storage tanks.

10.3 CONCENTRATING MECHANISM: SETTLING OF SUSPENDED MATERIAL

For criticality to occur, the plutonium concentration in tank waste would have to be much greater than when discharged. Conversely, if a sufficiently high plutonium concentration cannot be achieved, criticality is not possible.

Upper limit on concentration

The most obvious, and also perhaps the most effective, mechanism for concentrating plutonium is settling. Particulates suspended in a waste

mixture can settle out over a period of time. The upper limit of the plutonium concentration in the settled layer is determined primarily by two factors: the areal density of plutonium and the quantity of solids present.

The areal density is the total mass of plutonium above a unit of floor area. As solid waste settles, the density of the solids and the concentration of plutonium increase, but the areal density remains unchanged, provided no new waste is being added to the tank.

Settling probably accounts for most of the increased concentration found in analyzed samples, as compared to discharge limits. At discharge, the maximum plutonium concentration is 0.013 g/L. However, samples have been reported with a plutonium concentration as high as 0.35 g/L. This more-than-25-fold increase was obtained from actual waste samples, and shows that plutonium concentration can increase after discharge.

Solids content is the primary limiter of concentration by settling. The highest possible plutonium concentration would be achieved when all liquid either drains or evaporates, leaving all suspended and dissolved matter on the tank floor. The upper limit on the average plutonium concentration is the mass of plutonium divided by the volume of solids. The best indicator of subcriticality is for the solids/plutonium mass ratio to exceed the subcritical limit. The presence of a sizeable ratio of solids is important to criticality safety.

Total quantity of settled plutonium

Settling of solids and evaporation of liquid can result in a layer of waste in which the plutonium concentration has increased. However, criticality is not possible unless the plutonium areal density exceeds 240 g/ft^2 ($2,582 \text{ g/m}^2$). This areal density over the area of a storage tank would require more than 1,000 kg of plutonium. There is a low probability that the inventory of any tank exceeds 10 percent of this quantity. Therefore, criticality would not be possible within a layer of settled waste, regardless of the solids content.

Transfers of settled solids

If the entire plutonium inventory of a DST were actually settled into a thin layer at the bottom, there would be a possibility that this layer would remain after the liquid above it has been removed. Although well subcritical, this liquid might be pumped into another tank. If this were done, the margin of subcriticality might be reduced in two ways:

- 1) This waste might be combined with that of another tank, thereby increasing the plutonium inventory. After the wastes have been combined, the process of settling could begin anew and the plutonium concentration further increase.
- 2) If concentrated waste were to be pumped into a smaller diameter tank, the depth and areal density of the waste would increase.

Since all DSTs are of the same diameter, the second way to increase concentration does not apply to DSTs. DCRTs, on the other hand, do have a smaller diameter than DSTs. However, they have a shorter height and a much smaller volume. Periodically the entire contents of DCRTs are transferred to DSTs, thereby preventing the buildup of solids from different DSTs.

Even without taking solids into account, combining the contents of different tanks, even assuming the most extreme scenario, would not result in criticality. This is true because for a uniform areal density the total plutonium inventory in all the tanks would not be sufficient to cause criticality. In practice, it would be unlikely that a tank would even exceed 10 percent of the total inventory.

10.4 CONCENTRATING MECHANISM: EVAPORATION

An evaporator is used to remove liquid from waste. This creates new storage space by reducing the volume of stored waste. From a criticality safety point-of-view evaporation is similar to settling discussed in Section 10.3. When only settling is considered, a liquid layer remains above the solids. After evaporation, the liquid has been removed. After either process, the worst-case composition of the solids layer should remain about the same.

The primary difference between evaporated solids and settled solids is the possibility that the evaporated solids might achieve a lower water fraction. The possibility of complete removal of liquids is considered in this evaluation.

10.5 CONCENTRATING MECHANISM: CHEMICAL SEPARATION OF COMPONENTS

In discussions of concentrating mechanisms, the mechanism usually found most difficult to understand and to describe is that of chemical separation of waste components. This is the consequence of the complexity of the chemistry and the high degree of uncertainty of the chemical makeup of any actual waste.

Alkalinity of waste

If the solubility of plutonium is high, the difficulty in controlling its distribution throughout the complex of waste storage tanks is greatly increased. On the other hand, if the solubility is low, it is easier to keep the plutonium "locked up" within selected tanks. This is true because the plutonium then settles to the bottom with the other insoluble waste components. The upper layers of liquid can then be pumped to another tank while leaving most of the plutonium behind. In this way, the solids and plutonium can be accumulated in a relatively low number of tanks.

When the waste is alkaline, plutonium solubility is low. Waste sent to tank storage is maintained alkaline to ensure that the plutonium remains combined with the solids. Based upon published data from chemical experiments with plutonium, the upper limit of the concentration of dissolved plutonium in liquid waste should not exceed 0.017 g/L (see Section 8.4). In practice, the concentration would be expected to be less than 1/10 of this.

Process capable of increasing plutonium concentration

A process capable of concentrating plutonium can be postulated theoretically: the plutonium would first be dissolved and then precipitated. In the precipitate, the proportion of plutonium might be higher than in the original waste.

For plutonium dissolution to occur, followed by precipitation, the chemical environment of the tank must change. Dissolution requires a change from alkalinity to acidity, and precipitation requires the reverse. These changes should only be possible when wastes of considerably different compositions are mixed. Because chemical compatibility is determined before waste is transferred, it is highly unlikely that such transfers would ever be made.

Conditions that prevent plutonium accumulation

For tank waste there are several conditions that tend to prevent the accumulation of a large mass of plutonium in a small, compact volume.

- First, alkaline waste permits dissolution of only a very low concentration of plutonium.
- Second, the plutonium would be mixed with a large quantity of solids. These solids would tend to shield the plutonium from the chemicals that would dissolve it. Even if dissolved, much of the plutonium would be trapped within the solids and would not move to the surface.
- Third, because there is no mechanism to force the precipitate to a localized portion of the waste, precipitated plutonium would be expected to spread out over the entire cross section of the tank. This spreading out would ensure a geometry not conducive to criticality.

Removal of neutron absorbers

Another possibility to consider is that chemicals might dissolve neutron-absorbing components and remove them to a different location. Even then, there are several natural controls preventing criticality.

- The low plutonium areal density would preclude criticality even if all absorbers were removed.
- The variety of chemicals that composes the waste would mitigate the impact of removing a specific absorber. Even if one were removed, some of the others should be unaffected. The large solids/plutonium mass ratio would continue to guarantee subcriticality even after some components have been removed.
- The natural tendency of any operation performed on waste is to cause mixing. Components removed chemically would tend to be remixed with the waste.

In conclusion, no chemical process has been identified that might credibly lead to criticality. The natural tendency of the waste is to disperse and to mix, which reduces the potential for criticality.

10.6 DISPERSING MECHANISM: FORMATION OF LAYERS

Layering is an important waste dispersal mechanism. As waste enters a storage tank, it spreads over a large area, thereby preventing a buildup of waste in a confined volume.

An investigation of the waste's tendency to form layers is reported in *Ferrocyanide Waste Tank Hazard Assessment - Interim Report* (Grigsby et al. 1992), as follows:

Evidence for the fluidity of the settled sludge can be seen from the observation of the behavior in the field and in the laboratory. The accumulated sludges in the tanks were pumped between tanks, sometimes for several miles. Settled synthetic In-Plant sludges made in the laboratory were observed to be readily pourable.....

The handling of freshly prepared synthetic In-Plant ferrocyanide sludges provides an independent way to predict conical pileup in tanks. Although a carefully controlled and scaled test was not done, incidental observations indicated that sludge poured into transparent plastic containers formed a level surface in a matter of seconds after pouring was terminated. Based on the observation that a level surface was achieved within seconds in a 0.3-m (1-ft)-diameter container, a level surface would be expected within minutes in a 22.9-m (75-ft) diameter tank.

Based on the preliminary calculations presented above, it is concluded that ferrocyanide pumped into storage tanks, for example, would form a horizontal surface within minutes. Fresh sludge would be expected to mix with sludge already in the tank in the immediate vicinity of the outfall. This mixed sludge would spread on top of the preexisting sludge surface. Therefore, while horizontal layers having compositions corresponding to specific batches would be possible, it appears that localized vertical piles of sludge are highly improbable (Grigsby et al. 1992).

Layer formation would spread an incoming waste stream into a thin layer. Any localized volume of higher plutonium concentration within the sludge would be dispersed. The spreading process would ensure a relatively uniform areal distribution within the storage tank.

10.7 DISPERSING MECHANISM: MIXING

The only operation performed for many waste storage tanks is the pumping of new waste into the tank. The incoming solids from each batch of waste settle into a layer and the liquid portion mixes with the already present supernatant liquid. In these tanks the configuration of the waste should remain relatively unchanged over long periods of time.

There are five tanks, however, that have air-lift circulators and two tanks with mixing pumps. The purpose of the air-lift circulators and mixing pumps is to mix the waste. In addition, when waste is transferred from one tank to another, the transfer process can result in mixing of waste. It is therefore possible for different waste types to be mixed together after they have been sent to tank storage.

Mixing tends to disperse a region of higher plutonium concentration. The concentration of each component in waste types that have been mixed together tends to become closer to an average value. Regions containing both higher and lower concentrations tend to become smaller. The overall waste mixture becomes increasingly uniform in composition as the mixing continues. Although the waste is initially well subcritical, mixing is expected to increase the margin of safety even farther by dispersing the plutonium and reducing the regions of higher plutonium concentration.

11.0 DISCUSSION

The distribution of waste components has a very important influence on the plutonium concentration required to achieve criticality. However, the composition of waste and distribution of components is very different from one tank to another. In Sections 11.1 and 11.2 the effect of component distribution on criticality safety are examined.

Many parameters, some independent and some interrelated, work together to determine whether a critical configuration is possible. The difficulty of achieving a critical configuration after taking into account the interplay of these parameters is discussed in Section 11.3.

The transfer of supernatant liquid from one tank to another is discussed in Section 11.4, and the criticality safety implications of a leak of liquid into the ground is discussed in Section 11.5.

11.1 UNIFORM PLUTONIUM DISTRIBUTION

In homogeneous waste, the concentration of any component remains unchanged throughout the waste.

The total quantity of plutonium sent to all tanks has been determined to be less than 981 kg (Roetman et al. 1994), an average of 5.6 kg of plutonium per tank. It is highly unlikely that the largest quantity of plutonium in any tank exceeds 100 kg.

Critical parameters

When the plutonium concentration is less than 2.6 g/L, criticality is not possible in conservative model waste. When the plutonium concentration is 4.0 g/L, criticality occurs for 215 kg of plutonium in a spherical volume of 53,700 L (14,200 gal). At this concentration, the minimum critical slab thickness is 2.1 m (7.0 ft). However, for criticality to occur in a 2.1-m (7.0-ft)-thick slab in a 22.9-m (75-ft) diameter tank, at least 3,500 kg of plutonium at 4 g/L are required.

Areal Density

The minimum areal density of plutonium that can be made critical is 2,582 g/m² (240 g/ft²). The cross sectional area of a 22.9-m (75-ft) diameter tank is 410.5 m² (4,417 ft²). At the minimum critical areal density, 1,060 kg of plutonium is required to achieve criticality. This quantity exceeds the estimated total inventories for all tanks combined, and is more than 10 times greater than the largest inventory expected in any single tank.

When the areal density is less than the minimum critical areal density, criticality is impossible for a uniform slab, regardless of the slab thickness. This remains true when the moderation is optimized.

The primary benefit of being under the minimum critical areal density is that it eliminates concerns about settling and precipitation. If the slab layer is thick, the plutonium concentration must be low. When the layer is made thinner, the plutonium concentration will increase, but the slab will remain subcritical.

In summary, criticality is found to be impossible in a 22.9-m (75-ft) diameter storage tank for any quantity of plutonium less than the estimated total for tank farms, provided only that the plutonium is distributed uniformly over the cross sectional area of the tank. This remains true regardless of the degree of moderation and whether or not any neutron absorbers are present in addition to water.

11.2 NONUNIFORM DISTRIBUTION OF PLUTONIUM

The waste within each incoming waste stream was stirred before discharge. Incoming waste is therefore nearly homogeneous. However, the waste within a single storage tank is often composed of several waste streams, and each of these may form a distinct layer. Therefore, the waste as a whole cannot be considered homogeneous.

Layers having different compositions

When the distribution of waste components is not uniform, the conditions under which criticality is possible becomes more complex. This complexity creates an obstacle to the evaluation of tank waste. It is well known that under certain conditions the critical mass of slightly enriched uranium is smaller in a heterogeneous lattice than when homogenized. How can one then be sure an evaluation is conservative when applied to heterogeneous waste of unknown composition?

It is important to recognize the difference between minimum critical mass and minimum critical concentration. The parameter used to evaluate waste is minimum critical plutonium concentration. A large homogeneous system, such as a waste tank, for which conditions are optimized to produce the smallest possible critical plutonium concentration will nevertheless have a critical mass which is extremely large. On the other hand, a configuration designed to produce the smallest possible critical mass will have a plutonium concentration several times larger than the minimum which can be made critical in a homogeneous configuration.

For example, although the minimum critical plutonium concentration in a very large volume of water is 7.0 g/L, the minimum critical plutonium mass is achieved when the plutonium concentration is 30 g/L over a volume of 17 L. The minimum critical mass is then 520 g of plutonium. Although the critical mass has been greatly reduced, the plutonium concentration is considerably increased over a limited region of the system.

Consider a homogenized critical sphere of waste at optimal moderation. When the distribution of waste components are assumed to remain unchanged, the same conclusion can be reached as was reached for plutonium in water. Plutonium and water are considered independent variables which may be arbitrarily

redistributed in the waste. A smaller critical mass is possible in waste only by increasing the plutonium concentration in some regions above the 2.6 g/L concentration at which critical becomes possible in homogenized waste at optimal water moderation.

Waste was sent to tank storage in a series of waste streams. A waste stream is defined as the waste discharged from a single process. Some processes were continued for years, and many batches of waste were discharged to storage during this time. Throughout a process, conditions remain relatively constant, and the composition of the waste remains relatively constant. Before discharge, each batch of waste was stirred to ensure a uniform mixture. In tank storage this entire volume of waste appears as a single layer of more or less uniform composition.

The conservative waste model was developed to represent all waste. The model composition was selected so that the critical parameters would be conservative when compared to those for any real waste. The total neutron absorption in a kilogram of the conservative waste will exceed that in a kilogram of real waste.

Each waste stream generally forms a distinct layer within the large storage tank. If the waste in a layer is replaced by conservative model waste, that layer becomes more conservative. If a second layer is replaced, the overall waste becomes even more conservative. If this process is continued, all waste types will be replaced by conservative model waste, and the waste will be more conservative than the original combination of waste types.

The term "minimum critical concentration" is used to refer to the smallest concentration of plutonium which can be made critical in a homogeneous configuration. In a heterogeneous system the plutonium concentration is not uniform. When a limit is placed upon the maximum permitted plutonium concentration, it means that the highest plutonium concentration at any point in the waste shall not exceed the specified value.

The limit is based upon the minimum critical concentration for a homogeneous configuration of conservative model waste. From the above, it can be seen that this limit is conservative when applied to waste composed of multiple layers of different composition, when each has a greater macroscopic neutron absorption cross section than the conservative waste model.

Composition variation within a layer

Mixing of waste streams may occur. This is especially true when waste is pumped from one tank to another. The resultant composition may not be uniform even within a given layer. Nevertheless, all of the original waste streams had a total absorption cross section per unit mass larger than that of the conservative waste model. No matter how much mixing occurs, the average absorption cross section of the resultant waste will remain unchanged and will exceed that of the conservative waste model. In addition, the total absorption cross section per unit mass for any selected portion of the waste should show a larger value than that of the conservative waste model. This is true because mixing would tend to even out the regions of higher and lower

absorption and to produce a final mixture in which the neutron absorption cross section is spatially more uniform than before mixing. Therefore, the minimum critical plutonium concentration derived from homogeneous waste will continue to apply even when waste composition is not uniform within layers.

Critical parameters

In the past, except for two tanks, the discharge limit on the plutonium concentration was 0.013 g/L (0.050 g/gal). In the two exceptional tanks a discharge limit of 0.033 g/L was used. Virtually all waste now in storage tanks was discharged under a limit of 0.013 g/L.

Based upon this CSER, the limit on plutonium concentration will be increased to 0.033 g/L (0.125 g/gal) for all tanks. At the same time a limit will be applied to the solids/plutonium mass ratio. In the past no limit was specified on the solids content.

It is extremely unlikely that the inventory of a tank would exceed 100 kg. For 215 kg criticality would be possible only if the plutonium concentration exceeds 4 g/L (15.1 g/gal). Because the plutonium limit for mixtures of discharged waste has always been 0.013 g/L, the incoming plutonium must be concentrated by a factor of at least 307 before criticality becomes possible. In practice, the plutonium concentration in the incoming waste is usually much less than 0.01 g/L, and the concentrating factor required to achieve a critical plutonium concentration is actually much greater than 307.

Even a 307-fold increase in plutonium concentration would not be sufficient to cause criticality. This high concentration would have to be exceeded over a sufficiently large, compact volume before criticality is possible. For instance, when the plutonium concentration is 4.0 g/L, criticality requires a spherical volume of 53,700 L (14,200 gal). A cube of this volume would be 3.8 m (12.3 ft) on a side. Although this is a sizeable volume, it is small relative to the total volume of the tank. Even if this much waste containing a high plutonium concentration were actually within the tank, it would be extremely unlikely for it to be confined to a compact volume.

11.3 THE IMPROBABILITY OF ACHIEVING CRITICALITY

Many parameters and mechanisms work together to determine if criticality will occur. These have been discussed independently, but in practice several factors may operate at the same time. The discussion that follows shows that several independent events of low probability are required to create a critical configuration.

Holdup tanks

Waste is accumulated in the processing facility until it is discharged as a batch. For this discussion, the tank holding waste before discharge is referred to as a holdup tank. Typically, a holdup tank is a large diameter cylindrical tank with a volume of about 18,900 L (5,000 gal).

A holdup tank is geometrically unfavorable. This means that an accidental criticality in the tank is possible if a large quantity of plutonium is present. For this reason, holdup tanks, and the processes producing waste, are carefully monitored to ensure a low plutonium concentration and an adequate quantity of solids. Criticality safety in waste storage tanks is directly related to how well the waste holdup tanks have been controlled. If the waste in the holdup tank has always been inherently safe, then the waste discharged to the storage tanks would also be inherently safe.

Important questions concerning holdup tanks are: What is the most highly reactive waste ever discharged and how much? What is the worst case discharge?

A major concern is the possibility that a past undetected violation of discharge limits might have created the potential for a criticality in the future. The following discussion considers hypothetical worst case discharges that might have been made at anytime since 1945. Although written in the past tense, the scenarios described also represent worst case scenarios for present and future operations. The quantity of waste sent to tank storage in the future is expected to be far less than in the past.

The fact that no criticality has ever occurred within a holdup tank sets an upper limit on the quantity and concentration of plutonium discharged in a batch of waste. If criticality had occurred, the waste would not have been discharged.

Breakdown of controls

If it is assumed that a batch of very nearly critical waste was discharged, then a major breakdown of controls would have had to occur. The formation of highly reactive waste would have required violation of multiple process controls. Most of the waste originated from processes governed by flowsheets (see Section 13.1) for which every stage was carefully monitored and controlled. An abnormal condition of the waste would have been the reflection of an abnormal product. A drop in the quantity or purity of the product plutonium would have been recognized and an investigation would have been undertaken to determine the cause.

There are no records of abnormal discharges. That highly abnormal process conditions could pass undetected is extremely unlikely. That a large quantity of plutonium, an extremely valuable material and the object of the entire production process, could have been improperly routed to waste without detection would be very difficult to explain. For these reasons, it seems very unlikely that quantities of plutonium in excess of the normal waste discharges were sent to waste storage tanks.

Plutonium must be separated from uranium

Most plutonium sent to tank storage has been combined with a large proportion of depleted uranium. Separation of plutonium from the uranium is very unlikely, and criticality would not be possible unless the plutonium is

separated. Therefore, for most waste, criticality would not be possible, regardless of procedural violations that might occur.

Upper limit on discharged plutonium

Nevertheless, the possibility is considered that separated plutonium might be accidentally routed to the holdup tank and then sent to tank farms. In an extreme hypothetical case, one might assume that a 18,900-L (5,000-gal) holdup tank is filled with waste containing plutonium at a concentration of 4 g/L. This concentration is hundreds of times greater than expected. The total quantity of plutonium would then be 75 kg, the quantity normally found in about 10 million liters of waste.

Formation of 2-in thick layer

Nevertheless, when this waste is discharged into the 22.9-m (75-ft) diameter storage tank, it would form a layer less than 5 cm (2 in.) thick. The areal density would be only 17 g/ft², as compared to the minimum critical areal density of 240 g/ft². This waste is clearly subcritical. In fact, it would remain well subcritical after 10 more similar discharges. Even when the minimum critical areal density is reached, the presence of neutron absorbers would still ensure subcriticality. As can be seen, discharges of extraordinary quantities of plutonium would not create a critical configuration in the storage tank.

Multiple discharge violations

Even if a region of extraordinarily high plutonium concentration (even greater than 4 g/L) in the holdup tank were postulated, this region would be transformed to a thin, flat region upon discharge to the much larger storage tank. Diffusion and circulation within the waste would continue to spread the plutonium over a larger volume, thereby further reducing the concentration and the areal density.

If a second such batch were to be discharged, the region of higher plutonium concentration would also be transformed into an thin, flat region. These regions would be randomly distributed, and the upper region would very likely not overlay the lower region. Even after many such abnormal discharges, it would be extremely unlikely to achieve a critical configuration. The random distribution of the various regions of higher concentration would tend to produce a relatively uniform areal density over the large area of the storage tank.

Special case

One special case, however, needs additional review. When incoming waste falls into deep supernatant liquid, the incoming waste might spread into a quasi-spherical or cylindrical volume. Nevertheless, no matter what the geometry, the plutonium concentration must exceed 7 g/L (26.5 g/gal) before criticality becomes possible in a liquid.

Because the incoming waste would be diluted by the supernatant already in the storage tank, the incoming plutonium concentration would have to be greater than 7 g/L, probably several times as great, to achieve criticality in the supernatant. The incoming plutonium concentration probably would have to be at least 20 g/L (75 g/gal) for criticality to be possible, and the plutonium concentration in the holdup tank would have to exceed 20 g/L. The region involved would have to be large enough to permit criticality in the supernatant, but not so large as to cause criticality in the holdup tank. Because the holdup tank is stirred, such a high configuration would be virtually impossible without criticality occurring in that tank. A plutonium concentration of 20 g/L in the discharged waste would exceed the past CPS limit of 0.013 g/L by 1,500 times and the new CPS limit of 0.033 g/L by 600 times.

Most waste is discharged with an adequate quantity of solids to ensure subcriticality. Usually the solids are far more than required to ensure subcriticality. In the presence of an abnormally high plutonium concentration the solids/plutonium mass ratio would be reduced. Nevertheless, the quantity of solids would be expected to be quite large. The presence of solids would increase the plutonium concentration required to achieve criticality. Criticality is not possible until the mass ratio falls below 476, regardless of the actual plutonium concentration.

Conclusion

Regardless of the incoming plutonium concentration, the waste would spread out over a large area and the areal density of the plutonium would become small. The highest probability of criticality exists when the waste is first discharged. If criticality does not occur immediately upon discharge, it would not be expected to occur later.

Any configuration that is subcritical in the holdup tank will be even more subcritical in the much larger storage tank. The discharge of multiple, highly abnormal batches of waste would not be capable of creating a critical configuration in the storage tank. For these reasons, a criticality in a storage tank is extremely unlikely, even following an abnormal discharge of waste.

11.4 INTERTANK TRANSFERS OF SUPERNATANT LIQUID

Occasionally, the need arises to pump waste from one tank to another. One reason for pumping is to consolidate waste from several partially filled tanks. The following discussion examines the process of pumping supernatant liquid from one tank to another.

All tank waste was originally sent to tank farms under discharge limits that were set up to ensure the waste was highly subcritical. Therefore, transfer waste contained in both the sending and the receiving tanks will have a low plutonium concentration and a large solids/plutonium mass ratio.

Before a transfer is made, waste from sending and receiving tanks must be shown to be chemically compatible.

Plutonium in pumped liquid waste

Most waste transferred between tanks is liquid. The quantity of suspended solids is usually only a small fraction of the total waste. For the evaluation of a waste transfer, the most important parameter is the concentration of plutonium.

Section 8.4 discusses the solubility of plutonium in tank waste. Based on solubility experiments, the saturation concentration of dissolved plutonium in waste liquid, under the most idealized conditions, should not be greater than 0.017 g/L. Depending on the makeup of the waste, the plutonium saturation concentration might be as low as 0.002 g/L.

The *High Level Waste Tank Subcriticality Safety Assessment* describes the results of 306 analyzed liquid samples (Braun et al. 1994); two are reported to have plutonium concentrations somewhat greater than 0.01 g/L, but the median plutonium concentration is reported to be about 0.0001 g/L.

The plutonium concentration in transferred solids should be similar to that for waste solids in general. The plutonium concentration is unlikely to be greater than 0.01 g/L. The quantity of plutonium in suspended solids in supernatant liquid will be small.

Plutonium in the receiver tank

Criticality safety concerns related to the receiving tank are more important than those related to the sending tank. While pumping waste, almost no potential exists for increasing reactivity in the sending tank; however, when this waste reaches the receiving tank, the incoming plutonium is added to that already present. In addition, the force of the incoming waste stream might stir the receiver tank waste and also cause changes in the chemical composition.

Pumping mixes the waste and makes it more uniform. For waste to be pumped, it must be in a slurry and very fluid. When it reaches the receiver tank, the waste will spread out into a layer. Waste from regions of higher plutonium concentration is dispersed when it reaches the receiver tank.

There are no known mechanisms capable of concentrating plutonium contained in receiver tanks to concentrations even remotely approaching that for which criticality becomes possible.

11.5 LEAKAGE OF SUPERNATE INTO GROUND

DSTs are designed to ensure that no waste will leak into the ground. A leak that develops in the inner wall will be contained within the outer wall. In the extremely unlikely event that a leak should permit liquid waste to drain into soil, criticality would be highly unlikely.

Minimum Critical Concentration

A conservative model of soil can be postulated based on silicon dioxide. A major component of soil, silicon dioxide is one of the least neutron-absorbing (and hence one of the most conservative) materials occurring in nature. Altschuler (1991a,b) reports that the subcritical limit concentration of plutonium in sand (silicon dioxide) is 0.70 g Pu/L of sand. At this plutonium concentration, the maximum achievable k_{inf} will not exceed 0.95 at a 95-percent confidence level. This sets a lower limit on the critical concentration of plutonium in soil.

The minimum critical plutonium concentration in silicon dioxide sand occurs when the sand contains no water. The addition of water increases neutron absorption and, at the same time, minimum critical plutonium concentration. Under the driest conditions credible, the sand would still contain some water. In addition, there would be other compounds present which would absorb neutrons. The presence of these absorbers would increase the minimum critical plutonium concentration.

Supernate leaking into the soil would carry with it neutron-absorbing materials. The mass ratio of these absorbers to plutonium would likely be very high. These absorbers would significantly increase the plutonium concentration required to achieve criticality.

If supernate were to drain to the ground, the soil would act as a filter and trap the plutonium in a relatively small volume near the source of the leak. Solids within the supernate would also be trapped by the soil. The depth to which the plutonium might penetrate the soil would depend on the size of the plutonium-bearing particles. Large particles would be filtered out in a short distance, measured in inches, while dissolved plutonium would migrate to a greater distance. For criticality to occur, both the plutonium concentration and the quantity of plutonium would have to be quite large.

Minimum Critical Mass

The plutonium concentration does not directly determine whether criticality will occur. It is also necessary that the quantity of plutonium be large enough for criticality at the plutonium concentration present. Below the minimum critical concentration criticality is not possible.

In systems of plutonium, water, and silicon dioxide, the minimum critical plutonium mass is achieved when the water content is high and the volume is small. The addition of silicon dioxide dilutes the water and reduces the degree of moderation, so that a larger volume is required for criticality. For criticality to occur for a plutonium concentration of less than 1.0 g/L, a very large sphere composed entirely of silicon dioxide would be required, and the critical mass of plutonium would be very large.

Beginning with a system composed largely of SiO_2 , the plutonium critical mass will decrease monotonically with the addition of water as the interstitial space is filled and with the replacement of SiO_2 with water. The smallest critical mass would occur when no SiO_2 is present.

The soil should trap a large fraction of the leaked plutonium in a relatively small volume near to the source of the leak. This volume should be composed largely of solids, thereby limiting the water fraction and increasing the neutron absorption. Because of the highly uncertain nature of the resulting configuration, no estimate is made of the lower limit on the critical mass. It would, however, be expected to be greater than the total plutonium contained in the leaking supernate.

Critical Slab Thickness

For plutonium confined to a slab layer, the critical thickness of the slab would be smallest when the water content is highest. If the silicon dioxide fraction is increased, the critical thickness and the minimum critical areal density would increase.

Although the subcritical limit on plutonium concentration is only 0.7 g/L in silicon dioxide, the thickness of the slab required for criticality would be large for concentrations even approaching this value, and the total plutonium required for criticality would be large.

Expected Plutonium Concentration

Even if a plutonium concentration in excess of 0.70 g/L (2.65 g/gal) could be achieved, it is extremely unlikely that the quantity of plutonium would be sufficient to achieve criticality, even under "ideal" conditions.

The plutonium concentration in supernate is generally much less than 0.001 g/L (0.004 g/gal). For criticality to become possible, the plutonium concentration would have to be increased several thousand times.

12.0 LIMITS

This section reviews limits provided in CPSs and in facility operating procedures. These limits have been the basis for maintaining criticality safety in the past. Recommended changes are discussed in Section 12.5, Basis For Tank Farm CPS Limits.

Procedures used to ensure compliance to CPS limits and controls are outlined. Because limits and controls used in the past have worked well, they provide a good basis for future limits.

An attempt is made to provide limits applicable to all anticipated waste types. Because CPS limits are generally written broadly, changes in waste sources should not require changes in the CPS limits. Nevertheless, if a future waste type falls outside of the description provided, an evaluation will provide the basis for changing the CPS.

Limits in CPSs should be tailored to the types of waste likely to be generated. Generalized limits sometimes result in unneeded conservatism when applied to specific waste types. Although it is of paramount importance to ensure a high degree of safety, at the same time care must be exercised not to increase costs by requiring the addition of unneeded waste components (such as extra water or neutron absorbers). Simple, easily understood limits are desirable, but they must also be flexible enough to respond to individual circumstances.

Details of plant operations are not provided in this discussion. If such details are needed, plant procedures governing those operations should be consulted.

12.1 TANK FARM CRITICALITY PREVENTION SPECIFICATION LIMITS

In the past discharges to tank farms have been governed by limits and controls specified in CPS-T-149-00010, *Waste Storage Tanks and Associated Equipment*. This CPS applies to the waste evaporators, to DSTs, to the vaults (244-A, 244-AR, and 244-CR), and to the Rail Car Unloading Facility 204-AR. The last revision for this specification (Revision D-0) was made June 17, 1988 (WHC 1988).

CPS-T-149-00060 and CPS-T-149-00061 have provided limits for DCRTs 244-TX, 244-S, 244-U, and 244-BX. These CPSs are discussed in Section 12.2.

Waste is mixed before discharge. Mixing provides assurance that localized plutonium concentrations will not form.

Criticality is not possible for uranium in homogeneous systems when the uranium contains less than 1.0 wt% ^{235}U (See Section 9.3). This is true because of neutron absorption by the ^{238}U . The CPS uses the following limit.

One gram of ^{233}U or ^{235}U in excess of 1 wt% enrichment is considered equivalent to one gram of plutonium, unless otherwise restricted by a specification. The amount of ^{235}U less than or equal to the equivalent of 1 wt% enrichment may be excluded in concentrations and total mass calculations (WHC 1988).

Discharged waste is maintained alkaline to prevent plutonium from dissolving and to keep the plutonium mixed with the solids. However, in the CPS no limit is placed upon pH. The lack of a limit reflects a knowledge that (1) all discharged waste is alkaline, and a limit therefore need not be stated, and (2) alkalinity is of secondary importance to criticality safety.

Plutonium in waste is either dissolved or in the form of fine particles. This permits easy mixing with waste solids.

Limits in CPS-T-149-00010 (Rev D-0)

The following limits are specified in CPS-T-149-00010 (Rev D-0), although the arrangement is different than shown here.

Concentration limits

Average concentration in feed solution to
241-A and 242-S evaporators: <0.01 g/gal

Maximum plutonium concentration in mixtures routed to:

Waste Storage Tanks (except 102-SY): 0.05 g/gal

244-AR and 244-CR vault tanks: 0.05 g/gal

102-SY: 0.125 g/gal

No transfers may be made into tanks which contain 10,000 or more grams plutonium or vaults unless the maximum plutonium density possible after in-tank concentration is shown to be as follows (except as permitted with cadmium addition):

102-SY ≤ 2 g/L plutonium in solids

All Other Waste Tanks ≤ 1 g/L plutonium in solids

Total plutonium mass limits

Total plutonium in any 75-ft diameter storage tank:

All tanks except 104-C,
106-C, and 102-SY < 50 kg

Tanks 104-C, 106-C, and 102-SY < 125 kg

Cadmium addition limits

Cadmium addition applies only to transfers into tank 102-SY.

<u>Plutonium concentration in Solids, g/L</u>	<u>Minimum required cadmium concentration (as precipitated solids) g Cd/g Pu</u>
0 < conc. ≤ 2	0.00
2 < conc. ≤ 30	0.33

Tanks containing less than 10,000 g of plutonium

Transfers into tanks which contain less than 10,000 g of plutonium are required to meet one of the following conditions:

1. The transfer contains not more than 15 g of plutonium.
2. An airlift circulator is operating in the tanks and the transfer contains not more than 200 g of plutonium.
3. The transfer is made through a slurry distributor and the total plutonium added to the waste at any single position does not exceed 200 g.
4. The maximum plutonium density is controlled in accordance with the requirements for tanks containing greater than 10,000 g of plutonium.

Tanks containing more than 10,000 g of plutonium

To demonstrate compliance with in-tank plutonium concentration limits, the plutonium concentration in the tank or vault solids shall be determined by one of the following methods:

1. Dividing the total tank or vault plutonium inventory by the total solids volume in the tank, provided that the plutonium content can be considered distributed.
2. A predictive computation.
3. A laboratory analysis of tank samples.
4. The use of the minimum solids fraction possible as determined from the flowsheet.

This concentration shall be determined after each transfer. The concentration shall be shown on an auditable continuous inventory maintained for each tank.

12.2 DOUBLE-CONTAINED RECEIVER TANK LIMITS

CPS-T-149-00060 and CPS-T-149-00061 provide limits for DCRTs 244-TX, 244-S, 244-U, and 244-BX, as follows:

Maximum plutonium concentration in solution
routed to the tanks: $\leq 0.05 \text{ g/gal}$

Maximum plutonium in each tank: 2000 g

A transfer line water flush shall be made after each 244-TX to 102-SY transfer of Z Plant solutions.

Should it be necessary to transfer solution from 244-TX into 244-S, the 244-TX solution shall be allowed to settle and the sluicing system shall be operated during the transfer. The Manager, Criticality and Radiological Analyses shall be notified of the plan to move the transfer prior to being made (WHC 1980, WHC 1987).

Basis for DCRT Limits

Altschuler (1980) provides a criticality safety evaluation of tanks 244-TX and 244-S. Both tanks are used "to collect the solutions from saltwells in the process of 'drying up' the underground waste storage tanks containing salt cake and sludges." His evaluation is summarized as follows.

Contingencies in the 244-TX tank arise from exceeding the concentration or amount of fissile material charged from the D5 tank at Z Plant or continual accumulation of fissile material because of settling or precipitation. Analysis using well-referenced data (mainly ARH-600) shows that the triple contingency criteria are met if a large deposit in one spot can be prevented from accumulating. The possibility of criticality arises not from the accumulation itself but by a sudden ineffective dispersal of the solids by a recirculation jet which enlarges and increases the moderation of the accumulation before sufficient dispersal has taken place in the 244-TX tank. The presence of the recirculation sluice jets will ensure removal of the solids when the solution is transferred out of the tank and a more uniform accumulation on the bottom then if the solids are left in the tank. Thus it is shown that the value of k-effective plus two standard deviations is less than 0.95 for all credible conditions.

Routine use of the 244-S tank does not involve the transfer of 244-TX solutions (containing Z Plant plutonium wastes) into the tank, although the solution does go through a valve pit on top of the tank in making transfers to tank 102-SY. The amount of plutonium transferred into the tank from the salt wells will be extremely small; thus, little or no buildup of plutonium is expected in the tank.

Altschuler (1980) states that a criticality safety evaluation should be made if 244-TX solution is to be transferred into 244-S.

The following contingencies were investigated.

1. Exceeding the amount of material in the uniform solution charged to the 244-TX tank. Because of the 400 g limit in the D5 tank, the maximum overbatch is considered to be 400 g in a single batch.
2. Uniform precipitation or settling of the material charged (a) as a slab and (b) as a cylindrical segment.
3. Precipitation or settling in one spot as sludge of 1.2 g/cm³.
4. Resuspension of a uniform precipitate.
5. Resuspension of a precipitate that has been accumulated in one spot.

The evaluation for these tanks does not consider neutron absorbing characteristics of solids within the waste. In reality the assumption of no neutron absorption by solids is very conservative.

The plutonium concentration in incoming waste is limited to 0.05 g/gal, the same as for waste discharged from processing plants. If the 36,000 gal 244-TX tank was completely filled with waste at this incoming concentration, the total plutonium inventory would be 1,800 g. The limit of 2,000 g was placed on the total plutonium to allow for a full tank at maximum concentration plus a small accumulation. However, in practice there is no way to determine the total inventory of the tanks with any certainty. For this reason the true basis for safety in DCRTs is the assurance that waste discharged from the processing plants has an adequate margin of subcriticality.

12.3 242-A EVAPORATOR FACILITY

Limits for the 242-A Evaporator Facility are included in CPS-T-149-00010 for the tank farms. CSAR 81-022 (Blyckert 1981) provides the basis for these limits.

Blyckert describes the evaporation process.

A conventional forced circulation vacuum-evaporation system is used to concentrate radioactive waste solutions. Feed to the evaporator is pumped to the reboiler where it is heated. The heated slurry is discharged from the reboiler to the vapor-liquid separator vessel, which is maintained at a reduced pressure. Under this process condition, a fraction of the water in the salt slurry concentrate flashes to vapor and is drawn into the primary condenser. As evaporation takes place, the concentration of salt increases in the slurry. The slurry is then pumped to underground storage tanks, allowed to settle, and the supernatant liquid is pumped back as feed to the evaporator.

Feed solutions to the evaporators are sampled and analyzed to assure that the fissile material concentration does not exceed 0.01 grams per gallon. Continuous operation of the evaporator-crystallizers

concentrate the solution by a factor of two. (A batch would be required to concentrate the solution to twenty percent of its original volume, but this is difficult to accomplish.)

Blyckert evaluates the evaporator and concludes that there is no potential for criticality.

Fissile material content in the feed is not more than 0.01 g/gal. If the concentration of fissile material in the feed to the evaporator were double that of the allowable concentration, normal operation would not result in evaporator bottoms in excess of 0.05 g/gal, while if the system were operated in a batch mode the fissile material content of that limited volume could reach 0.1 g/gal. While this fissile material content would be double the allowable concentration for feed to storage tanks, it is less than three percent of that required to be reported and less than two-thirds of one percent of fissile material concentration in waste which might become critical, 4.3 g/L (Carter 1979). There is no known way for feed available to the evaporators to be handled to cause the system to become critical. Consequently, there are no other criticality safety restrictions for the evaporator operations. It should be noted that because of the high pH (>8) of the solutions, the plutonium content of the waste being concentrated is low. It should also be noted that criticality safety with 4.3 g/L of plutonium would require over 200 kg of plutonium.

Blyckert addresses the question as to whether plutonium might plate out and concludes that the quantity of plutonium which might collect in the evaporator would be too small to create any potential for criticality.

Plating or scaling of waste on the surface of the evaporator does not occur except at high specific gravity solution (>1.67) where 80 percent of the solids are sodium nitrate; the remainder is composed mainly of carbonates and phosphate. The plutonium concentration would not be increased greater than an order of magnitude. From an experimental run, 3,000 pounds of scale were formed which would give 0.6 g of plutonium based on the feed concentration of 0.0001 g of plutonium per liter of slurry. If the feed contained the maximum concentration permitted (0.01 g Pu/gal), 16 g of plutonium would be expected to be incorporated in the scale. This amount of plutonium is of no criticality safety concern, nor is double the amount. The scale easily dissolves in water. Plating out or scaling is therefore not a criticality safety problem.

When averaged over tank farms, the mass ratio of solids to plutonium in waste is found to be 74,500. For PFP waste the solids/plutonium mass ratio is at least 10,000, the smallest value found for any tank. If all liquid were to evaporate from supernate, the suspended and dissolved portion of the waste would be deposited as solids. The mass ratio of solids to plutonium in this deposit is expected to be similar to that for the waste as a whole. The solids/plutonium mass ratio for any supernate would therefore be expected to be at least 10,000. This is more than 20 times larger than required to ensure subcriticality in homogeneous waste. This solids content would be far more

than required to guarantee subcriticality at every stage of evaporation, even should all liquid be removed.

In practice, the solids/plutonium mass ratio in supernate may not be well known. This uncertainty leads to caution manifested through use of a limit on plutonium concentration in the evaporator feed solution. This limit is set so low that criticality is not possible, even if the evaporator feed were to contain no solids and the volume of liquid removed through evaporation were to be far greater than expected.

12.4 FACILITY DISCHARGE LIMITS

Facility limits for waste discharges are dictated by the limits for the tank farms. That is to say, waste leaving a facility must fall within the limits required for waste received into a storage tank. The following discusses limits used by the PUREX Plant and the PFP, the two primary waste generating plants.

12.4.1 Limits at the PUREX Plant

At the PUREX Plant, the primary control to ensure criticality safety is limitation of plutonium concentration to a maximum of 0.013 g/L (0.05 g/gal). This low concentration provides a margin of safety to allow for an increase in concentration caused by settling in the storage tanks. This concentration is 300 times smaller than the minimum concentration that can be made critical when the plutonium inventory is 200 kg.

The solids portion of waste provides assurance that settling and liquid removal can not cause the plutonium to concentrate to unsafe levels (see Section 10.3). The volume of the solids after all liquid has been removed establishes a lower limit on the volume in which the plutonium can be concentrated.

The PUREX Plant is the source of the majority of waste in tank storage. Processes used at the PUREX Plant guarantee that waste will have a large proportion of solids. These processes have always been governed by flowsheets that are well regulated and ensure predictability. Because the processes are well regulated, waste is generated in a predictable manner. The proportion of solids in this waste is far greater than necessary to ensure subcriticality. This remains true even following upset conditions. Since the required quantity of solids was known to always be present, there was no need to specify a limit in the CPS for the solids content.

Plutonium at the PUREX Plant has always been associated with a large proportion of ^{238}U . This uranium has always been discharged with the waste, thereby providing a high assurance that the $^{238}\text{U}/\text{Pu}$ mass ratio in waste is large.

The large margin of subcriticality in PUREX-Plant waste has been verified by chemical analyses of tank waste samples. The highest plutonium concentration yet reported based upon chemical analysis is around 0.3 g/L, a value one-ninth of the minimum critical concentration. Although the accuracy of this

measurement has not been checked, it is thought to be conservative (i. e., larger than the actual value). The high solids and the low plutonium content in analyzed samples has been sufficient to guarantee a large margin of subcriticality.

When taken as a whole, the solids/plutonium mass ratio for the tank farms is at least 74,500 (see Section 9.9). This is more than 150 times larger than required to assure subcriticality. This large mass ratio provides a high level of assurance that PUREX-Plant waste in tank storage will remain well subcritical.

12.4.2 Limits at the PFP

At the PFP plutonium has been handled in a purified (separated) form. This is an important difference from PUREX-Plant waste because it raises the possibility that plutonium might be discharged with a low proportion of solids. For this reason, PFP discharge limits include a limit on the minimum solids content.

Operations in the 241-Z Solution Disposal Facility are governed by CPS-Z-165-80741, Rev. A-2, which has the following limits for waste (WHC 1992):

- * Total plutonium for any 241-Z tank (maximum): 400 g
- * Plutonium concentration of solutions transferred to tank farms (maximum): 0.05 g/gal

PFP procedure ZO-101-010, *Transfer TK-D5 to Tank Farms*, provides operators with detailed procedures to ensure compliance to the criticality prevention specifications (WHC 1993). In addition to the above limits, this procedure includes the following discharge limits:

- * The waste mix shall contain more than 0.6 percent solids by volume.
- * Iron concentration shall be at least 35 grams per liter of solids.

PFP waste is sent to tank 102-SY. CPS-T-149-00010 (Rev. D-0) for the tank farms permits tank 102-SY to receive waste containing up to 0.125 g/gal of plutonium. Although the tank farms permit receipt at this higher plutonium concentration, the PFP CPS has not been revised to permit discharge of the higher concentrations.

The limit on solids ensures that the plutonium concentration can not exceed the minimum critical concentration under any credible accident condition, including loss of all liquid. Loss of all liquid with only the solids remaining is one of the worst credible conditions that might arise. During the process of draining liquid the proportion of solids would increase from 0.6 wt% to 100 vol%. This is a 167-fold increase in solids density. If the initial plutonium concentration is the maximum permitted of 0.0132 g/L (0.05 g/gal), removal of liquid would increase the concentration to 2.2 g/L.

As can be seen, the highest plutonium concentration that can be achieved without violating discharge limits is 2.2 g/L. Since this value is only 85 percent of the minimum critical plutonium concentration (i. e., 2.6 g/L), the waste would remain subcritical even with complete loss of liquid.

A plutonium concentration of 2.2 g/L in settled solids would exceed the CPS limit of 2 g Pu/L. This means it would be theoretically possible to discharge waste from PFP within the CPS limits and to violate the plutonium concentration limit in the tank farms CPS. However, in practice it would be extremely unlikely to do so because (1) the actual volume of solids is usually considerably larger than its limit and (2) the actual plutonium concentration is usually much less than its limit.

Conservative estimates provided by Koreski (1994) of the solids content in PFP waste range from 3.5 vol% for the Plutonium Reclamation Facility to 4.5 vol% for the Laboratory (see Section 7.4). The expected solids content is therefore at least six times the minimum value permitted by the operating limits.

Since a plutonium concentration in excess of 2 g/L is possible only when the solids content is less than 0.6 vol% and the expected solids content is more than 3%, it is extremely unlikely for this limit to be exceeded. Nevertheless, it is recommended that the PFP limit on solids be increased to prevent a possible violation of tank farm limits.

Minimum solids/plutonium mass ratio

The smallest solids/plutonium mass ratio possible without violating PFP operating limits is obtained with a plutonium concentration of 0.05 g/gal and a solids content of 0.6 vol%. If the dry solids density is assumed to be 1,200 g/L (a conservative value), the smallest mass ratio is found to be 545. This is 1.1 times the subcritical limit.

Iron is one of the best elements to use to ensure subcriticality. There are two important reasons for this: iron has a relatively large neutron absorption cross section and it coprecipitates with plutonium. By coprecipitation, it is meant that both iron and plutonium will tend to remain associated with each other during precipitation.

A limit is placed on the minimum iron content of 35 g/L in the solids. Assuming the density of dry solids is 1,200 g/L, this minimum iron content comprises only 2.9 wt% of the solids. If in addition, the solids comprise only 0.6 vol% of the waste, the minimum permitted by the limit, the concentration of iron might be as low as 0.21 g/L. At this minimum, the iron/plutonium mass ratio might be as low as 15.9. This ratio is only 9.9 percent of the iron/plutonium mass ratio subcritical limit of 160. The fraction of the actual-to-minimum subcritical absorber ratio for iron is therefore only 0.1.

The total margin of safety can be found by taking into account both the iron and the non-iron component of the solids. After subtracting the 35 g/L of iron, the non-iron solids density is found to be 1,165 g/L. The fraction of

the actual-to-minimum subcritical absorber ratio for the solids is therefore and 1.1. The sum of the actual-to-minimum subcritical absorber ratios for the iron and the non-iron components of the solids is then found to be 1.2. This is only slightly greater than without the iron. Although the addition of any iron provides an increase in the safety margin, the present limit for iron addition does not increase the margin much.

Actual solids content in tank 102-SY

PFP waste in tank 102-SY is found to have a solids content of 9.8 vol% (see Section 9.9), a value 16 times greater than the minimum required by the operating limits. The solids/plutonium mass ratio is found to be 10,000, a value 21 times larger than the subcritical limit.

12.5 BASIS FOR TANK FARM CPS LIMITS

Limits and controls to be used in the CPS are spelled out in Section 4.0. This section discusses the bases for those limits with particular attention paid to changes from past CPS limits.

12.5.1 Limit on pH

A limit of 9 is placed on the minimum pH to ensure that the plutonium remains insoluble and mixed with the solids. The expected pH in tank waste is more than 12.

The primary reason for a high pH is to maintain a measure of control over the distribution of plutonium within the waste. Dissolution is prevented by maintaining a high pH (i.e., the waste is alkaline). When the pH is high, the plutonium will be combined with the solids and the quantity of dissolved plutonium will be small.

The *Safety Assessment* (Braun et al. 1994) reported 385 pH measurements. Of these, 9 samples showed a pH below 9.0, but none showed a pH below 7.0. This indicates that about 1 out of every 40 measurements might be expected to show a pH less than 9.0.

The limit on pH is a secondary limit whose violation does not create conditions which might cause criticality. Even if the pH were abnormally low, it is unlikely that more than a fraction of the plutonium would be dissolved. Even if all plutonium in a tank were to dissolve, the areal density would remain well below that for which criticality is possible.

Normally the plutonium is thoroughly mixed with uranium. Colvin (1967) raises the possibility that part of the plutonium might separate from the uranium, if allowed to dissolve. Separation of the plutonium from the uranium is one of the possibilities that a high pH is intended to prevent.

12.5.2 Water Content

As a rule, waste contains a large percentage of water. However, to ensure long-term stability and to preclude tank leaks, liquids (primarily water) are

sometimes removed from the waste. Since it is often desirable that the liquid content of waste be low, it is important that criticality safety not depend upon the water content.

In the past the plutonium concentration in discharged waste was maintained below 0.05 g/gal. It has been sometimes necessary to add water to ensure that this limit would not be exceeded. Since waste is pumped through pipes to tank farms, it is necessary that it be fluid. The water content necessary to meet the CPS limit has sometimes been greater than required to achieve the necessary fluidity. This added water occupies space in the storage tanks and reduces the available storage volume. This storage space is reclaimed by pumping supernatant liquid through an evaporator to remove water. In this way, water added to meet the discharge limits is later removed to create storage space. A long-term cost savings would be realized no additional requirements be placed upon the water content above that required to ensure fluidity for pumping.

Criticality safety limits are based upon the assumption that the water content in waste may be optimal.

12.5.3 Waste With Low Solids Content

Prior to 1983 all waste discharged from the PUREX Plant contained an adequate volume of solids. In 1983 an addendum (Carter 1983) was added to CSAR 79-007 (Carter 1979) to cover the discharge from the PUREX Plant of waste containing very little or no solids. The primary concern related to waste with low solids content is the lack of a limitation on the ability to concentrate plutonium.

Carter addresses the concern that plutonium might accumulate by drying out of the waste, by forming layers, or by filtration in the solids, as follows:

In the new waste tanks, mechanisms exist (airlift circulators and slurry distributors) which distribute the plutonium over a large area (and over a large volume in the case of tank 102-AW). Accumulations over a large area (slab) require a minimum critical areal density of at least 240 g/ft² for low density wastes (Carter 1969, p. III.A.8.100-3). If the slab is limited to only a 10-ft radius (unlikely in the 75-ft diameter tank), then 75 kg would be the minimum amount of plutonium required for critical and this is at a concentration of 15 g/L. If a slab is limited to 3.64-ft radius, the minimum critical mass is approximately 10 kg, but also at a minimum critical concentration of about 15 g/L. The critical areal density increases rapidly as the concentration approaches 7 g/L; at 10 g/L it is 290 g/ft². Limitation of the plutonium to a small area is not considered credible in these tanks because of the very liquid wastes plus the capability to spread the wastes. Layers of different concentrations will tend to increase the critical areal density. With the spreading mechanisms, localized accumulations are no longer considered a potential problem (Carter 1983).

For criticality safety the most important parameter used to characterize waste is the solids/plutonium mass ratio. This ratio may be specified in terms of

specific elements which comprise the solids or in terms of the total solids content (i. e., the aggregate of all solids components). When waste contains little or no solids, it becomes difficult to know whether the required ratio of solids to plutonium is met. Sometimes waste consists of a liquid with a low content of solids. When this is the case it may not be possible to determine a value for the mass ratio of solids to plutonium. Problems associated with low solids content are discussed in Section 12.4.2.

Since this waste with low solids content must be liquid, it will contain considerable hydrogenous compounds, primarily water, which provide a high degree of moderation. The minimum critical plutonium concentration in this liquid should be no smaller than 7 g/L, the value for a purely water solution. This is several times larger than the minimum possible critical concentration of 2.6 g/L for plutonium in conservative model waste.

In liquid waste the solubility of plutonium is very low. Therefore, even though the quantity of solids may be low, the actual solids/plutonium mass ratio would be expected to be large. However, there is no guarantee that the actual solids/plutonium mass ratio will exceed a value which ensures subcriticality. For this reason, restrictions are placed upon this waste to ensure an acceptable margin of safety.

Batches with less than 15 g of plutonium

Sometimes a batch of waste may contain so little plutonium that it can not influence the margin of safety, regardless of solids present. Accordingly, transfers of 15 g, or less, of plutonium are permitted without imposing restrictions. In this case, the plutonium is less than 3% of the minimum which can be made critical under idealized conditions.

Carter recommends that total quantity of plutonium sent to a single tank in such transfers not exceed 1,000 g.

Whenever the total plutonium in a tank exceeds 10,000 g, all transfers, even those containing less than 15 g of plutonium, must be accompanied by a determination of the plutonium concentration in the settled solids.

Batches with low plutonium concentration

Waste with low solids content may be sent to tank storage if the plutonium concentration is less than 0.013 g/L (0.050 g/gal). This limiting concentration is arbitrarily selected to be so small as not to pose any criticality safety concern. It is more than 200 times smaller than the minimum critical concentration. In the storage tank this liquid waste would spread out over a wide area and would increase the areal density of plutonium by a only very small amount. If the entire tank is filled with waste containing 0.013 g Pu/L, the areal density of plutonium would be about 11 g/ft², less than 5% of the minimum critical value. In practice the plutonium concentration in liquid waste is expected to be far less than 0.013 g/L.

Tanks with waste spreading capability

Two devices are available to spread incoming waste over a wide area of the tank: airlift circulators and slurry distributors. Carter (1983) specifies the following limits for tanks with waste spreading capability:

1. The airlift circulator (102-AW) or the slurry distributors shall be operating to spread out the plutonium-bearing waste.
2. The maximum amount of plutonium for a single transfer is 200 g (all wastes).
3. Such transfers may continue until a total of 10 kg is in the tank.
4. Upon reaching 10 kg, the plutonium concentration in the tank(s) shall be determined by dividing the total tank plutonium inventory by the total solids volume in the tank or by some other appropriate method. This concentration shall be determined after each transfer.

For a slurry distributor the quantity of plutonium discharged at any single location is limited to 200 g. After the distributor has been moved to a new location, another transfer can be made.

The fluidity of this waste would assure that it spreads out into a thin layer. The plutonium concentration in all discharged waste is considerably less than the minimum critical concentration. When liquids containing low solids are spread over a wide area, the areal density of plutonium for the tank will increase only slightly.

The total quantity of plutonium in a batch is less than 40% of the minimum critical mass for a plutonium-water system. Before the mass of plutonium exceeds the minimum critical mass, the distribution mechanism would have to fail for three batches. Before criticality becomes possible, the plutonium would at the same time have to be placed in a compact, localized configuration. Such a configuration would not even be possible until the depth of waste reaches several feet in the tank. In addition, there would have to be a failure to mix the waste uniformly before discharge and an inexplicable suspension of the natural tendency of waste to form layers. All of these factors combine to make criticality extremely unlikely, if not impossible.

Tanks with less than 10 kg of plutonium

Often for liquid waste of low solids content, such as supernate pumped from one tank to another, it may not be possible to determine the actual ratio of solids to plutonium. After examining this situation, Carter (1983) concluded that "restrictions on in-tank plutonium concentrations are unnecessary below 10 kg of tank inventory." Relative to the large mass of plutonium required for criticality in a storage tank, 10 kg is very small.

Tanks with more than 10 kg of plutonium

When the total quantity of plutonium sent to a single tank reaches 10 kg, no further waste may be added until it is assured that the solids/plutonium mass ratio is at least 1,000 for waste in the tank. It is expected that the actual mass ratio will be considerably larger than this value. This mass ratio shall be satisfied before each new batch of waste is added.

12.5.4 Plutonium Concentration in Incoming Waste

The maximum plutonium concentration in incoming waste shall not exceed 0.033 g/L (0.125 g/gal) of total waste (i. e., averaged over mixture of liquids and solids). In the past this limit was applied to only a few selected tanks, but it is now extended to all tanks. The older limit was 0.013 g/L (0.050 g/L). This limit does not apply to waste inside a storage tank.

This limit ensures that the plutonium will be spread more widely over the storage tank than it would if higher concentrations were permitted. By requiring the plutonium concentration in incoming waste to be low the difficulty of concentrating the plutonium to a critical concentration is greatly increased. It also helps ensure that the solids/plutonium mass ratio limit is met.

For criticality to occur the plutonium concentration must be increased to at least 2.6 g/L. This requires the incoming plutonium concentration to be increased by at least a factor of 78 before criticality is possible. As a rule the plutonium concentration in the incoming waste will be much smaller than the limit.

12.5.5 Plutonium Concentration in Settled Solids

Once in a storage tank it becomes difficult to determine plutonium concentration in waste. For waste inside storage tanks it is important that the waste have inherent properties which ensure subcriticality. Limits at generating facilities are established to ensure that a large margin of safety exist for waste received at tank farms. The large fraction of solids in incoming waste effectively limits the maximum plutonium concentration which can be achieved inside of the storage tank. These solids ensure a high degree of neutron absorption. The limit on the solids/plutonium mass ratio for waste sent to tank farms eliminates the need to place a limit on the maximum permitted plutonium concentration.

No limit is placed upon the plutonium concentration or the solids content within stored waste. Safety is dependent upon the solids/plutonium mass ratio which is guaranteed by discharge limits.

A surveillance program will monitor the waste. As part of this program, the plutonium concentration, solids content, and pH will be measured and compared to investigation levels. Failure to meet an investigation level will require that a recovery plan for nonconformance be developed as described in Section 4.7.

In effect, investigation levels take the place of limits, but they are not considered to be CPS limits. The reason for this is the great difficulty in verifying actual limits. Even should an investigation level be exceeded, there remains a high probability that the margin of subcriticality remains high (See Section 13.2).

12.5.6 Total Plutonium Inventory

An estimate of the plutonium inventory in a storage tank can be derived from the plutonium concentration and the waste volume. However, this estimate will have a large uncertainty. Although the volume of settled solids can be determined with reasonable accuracy, the average plutonium concentration generally cannot. The plutonium would not be expected to be uniformly distributed, and the number of measurements of concentration is always limited. Any determination of the total plutonium in a tank will have a very large degree of uncertainty associated with it.

When an inventory is used for criticality safety evaluation, the largest measured concentration is assumed to represent the entire tank. This produces an estimated inventory which is expected to be conservative. Sometimes the degree of conservatism is thought to be quite high.

The primary parameter used to determine the inventory is the plutonium concentration. Placing a limit on the total plutonium inventory does not provide any additional level of control over that provided by a limit on the plutonium concentration. For this reason, no limit will be placed upon the plutonium inventory.

Past limit on total plutonium

CPS-T-149-00010 (Rev. D-0), which has been used in the past, specifies a total plutonium mass limit of 125 kg for tanks 104-C, 106-C, and 102-SY. For all other storage tanks the mass limit has been set at 50 kg of plutonium. In reality the basis used to justify the larger limit is applicable to all tanks. However, only these three tanks are considered to have a possibility of actually containing more than 50 kg of plutonium. An 125 kg limit was not placed on other tanks because there was no need for such a limit. The 125 kg limit on tanks 104-C, 106-C, and 102-SY, clearly show that these tanks warrant closer scrutiny than other tanks.

The basis used for establishing a tank limit of 125 kg and a plutonium concentration limit of 2 g/L was as follows. At twice this concentration, or 4 g Pu/L, the critical mass for a sphere of conservative model waste is 215 kg plutonium. Therefore, a sphere of waste containing 125 kg of plutonium will remain well subcritical, even after the plutonium concentration exceeds twice the limit value. If 125 kg of plutonium were actually present, it would be extremely unlikely that even a fraction of it would occupy a spherical region small enough to produce an average plutonium concentration approaching 2 g/L.

12.5.7 Limit on Solids Content

The parameter of primary importance to criticality safety is the solids/plutonium mass ratio. For tank waste this ratio will be limited to a minimum of 1,000, a value twice that required to ensure subcriticality in a homogeneous mixture.

Although the variability in the solids/plutonium mass ratio is unknown, the average value is nevertheless expected to be much larger than required to ensure subcriticality. For the tank farms as a whole, the global value of this ratio has been conservatively estimated at 74,500 as a whole and for tank 102-SY at 10,000. In future waste, based upon these large values, it should be easy to ensure a mass ratio greater than 1,000. There is no reason to expect that the solids/plutonium mass ratio in PFP waste in the future will be significantly less than in the past.

In the past, operating procedures for PFP have required that the solids content be at least 0.6 vol%. This has ensured a solids/plutonium mass ratio of at least 570, a value 1.2 times that required for subcriticality in homogeneous waste. The solids/plutonium mass ratio for actual waste has been determined to be 10,000, a value 17 times larger than the limit. This larger ratio is not surprising because most discharged waste will contain less plutonium and more solids than permitted by the limits. When both of these parameters are conservative, the mass ratio becomes even more conservative. The actual mass ratio in discharged waste is therefore expected to be considerably larger than the limit mass ratio of 1,000 (minimum).

Table 8 shows the relationship between plutonium concentration and solids content when the mass ratio is 1,000, based upon a density of 1,200 g/L for settled solids. For example, if the settled solids occupy 1.0 percent of the volume of waste, a plutonium concentration of 0.012 g/L will result in a solids/plutonium mass ratio of 1,000.

In practice the solids density should be greater than 1,200 g/L. When Table 8 is used to obtain a limit on plutonium concentration, the actual mass ratios should be greater than 1,000.

Iron content

Iron is a desirable waste component because of its neutron absorption cross section and because it is difficult to separate from plutonium.

PFP should continue to require iron in its waste. Although the present limit of 35 g of iron per liter of solids is not sufficient to ensure subcriticality by itself, it provides added assurance that no process will be able to separate the plutonium completely from the solids.

Table 8. Maximum Plutonium Concentration as
a Function of Solids
(Solids/Plutonium Mass Ratio = 1,000)

Precipitated Solids in Volume Percent	Plutonium Concentration Maximum	
	g/gal	g/L
0.5	0.023	0.006
1.0	0.045	0.012
1.5	0.068	0.018
2.0	0.091	0.024
2.5	0.112	0.030
3.0	0.135	0.036

12.5.8 Limit on Cadmium

The limit on cadmium addition states that the plutonium concentration may be as high as 30 g/L in precipitated solids provided at least one gram of cadmium is present for every three grams of plutonium. The basis for cadmium addition is provided in Appendix A.

Cadmium addition permits discharge of waste without the addition of a large quantity of solids to lower the plutonium concentration. This limit for cadmium addition is intended to be used only in rare situations in which the plutonium concentration in settled solids has the potential to exceed 1 g/L. Most discharges are expected to have a lower plutonium concentration, and there is no reason to add cadmium. Discharges based upon cadmium addition are uncommon.

No change will be made in limits for cadmium addition (see Section 12.1), except that tank 105-AW will be added as a receiver tank to permit discharge of cadmium controlled waste from the PUREX Plant.

A concern when using cadmium as a control is whether it will remain associated with the plutonium after discharge. When using this limit, the potential that the solids might dissolve must be considered.

A cadmium/plutonium mass ratio of 0.13 is sufficient to assure subcriticality in an infinite homogeneous system. The mass ratio limit of 0.33 is 2.5 times larger than this value. In practice, the actual quantity of cadmium in the waste is expected to be significantly higher than the limit.

Discharges based upon cadmium limits will have less solids than other discharges. However, the majority of discharges will have a higher solids/plutonium mass ratio, and the average mass ratio for all discharges

will remain high. The overall solids/plutonium mass ratio for waste in the storage tank will remain greater than 1,000.

If cadmium were omitted from a batch, the impact on reactivity will not be large enough to cause a problem. This is true for several reasons. First, the volume of a single batch is very small relative to the size of the storage tank. Second, the waste would tend to spread out into a thin layer in the 22.9-m (75-ft) diameter storage tank. Third, the mass of plutonium in one batch would be less than the minimum critical mass.

12.5.9 Limits For 242-A Evaporator

In the past a limit of 0.010 g/gal was placed upon the plutonium in evaporator feed solution. Because of the high degree of subcriticality, it is acceptable to increase the limit on plutonium concentration to 0.019 g/gal (0.005 g/L).

Evaporator feed is always liquid. Normally only a fraction of the liquid is removed, and the plutonium remains highly overmoderated. Even after a hundred-fold increase in plutonium concentration, with all other components unchanged, the evaporator solution would remain well subcritical. In addition, the ratio of solids to plutonium would be expected to greatly exceed that required to ensure subcriticality. Criticality safety for 242-A Evaporator operations is discussed in Section 12.3.

Before an evaporator campaign begins, a determination shall be made of the expected quantity and concentration of plutonium which will be in the feed and slurry tanks at completion of the run.

After an evaporator campaign, a determination shall be made of the actual quantity and concentration of plutonium in the feed and slurry tanks, either by analysis or calculation.

13.0 SURVEILLANCE PROGRAM

Available information strongly supports the conclusion that nuclear criticality within the waste storage environment is extremely unlikely, if not impossible. Tank waste will remain subcritical under the worst credible postulated conditions of handling and storage. No scenario has been identified that would be capable of inadvertently removing the waste from a highly subcritical state.

The extremely low probability that a region of high reactivity exists within a tank, coupled with the low probability of it being discovered, even if it should exist makes it difficult to verify compliance to criticality safety limits placed on stored waste. True criticality safety control must be exercised before the waste is sent to tank storage. For this reason, the primary goal of this criticality safety evaluation has been to show that stored waste will remain safe by virtue of the large margin of safety afforded by limits placed upon waste at the time of receipt into the tank farms. Nevertheless, there is considerable interest in verifying the state of stored waste. This interest is driven primarily by the high degree of uncertainty in waste composition and distribution.

A program of surveillance designed to obtain information about the actual state of the stored waste enhances the criticality safety program in two primary ways: it verifies that discharge criteria are met, and it characterizes waste in storage tanks. Analyzed waste compositions support the assertion that the waste is well below critical.

13.1 AUDITING: HISTORICAL PERSPECTIVE

The criticality safety of waste streams has been maintained through adherence to process flowsheets and through control of waste component concentrations.

A detailed description of a process is called a flowsheet. To exercise flowsheet control means to monitor every step of the process to ensure that the process conforms to the flowsheet. Removal of plutonium from nuclear fuel is a complex process requiring precision to carry out. Every aspect of the process must be thoroughly understood and carefully planned. Deviation from the flowsheet might mean a drop in production and an increase in waste. A very careful overview of the plutonium removal process is required to ensure that the final product is pure and that no accidents occurred producing it. Errors are costly and are carefully guarded against. Many safeguards are used to ensure that each step of the flowsheet is met. The need to precisely control processing means that the waste product must also be well defined. Thus, in operations following a flowsheet there is a high assurance that the plutonium concentration in the waste is low and the solids/plutonium mass ratio is large.

The majority of waste in the tank farms was discharged from the PUREX Plant. Virtually all PUREX-Plant waste was generated in processes that used a flowsheet.

Tomlinson (1961) made a safety review of manufacturing and chemical processing facilities in 1961. He described the formal audits and reviews used to assure safety as follows:

Engineers involved with process technology, but not having line responsibilities for plant operation, have assigned responsibilities to perform routine audits of the plant process operations, thereby insuring operation within the limits defined by the process specifications. In addition, nuclear safety practices are formally reviewed once per year by a Senior Engineer specializing in nuclear safety, and twice a year by a qualified engineer within the Technology Operation (Tomlinson 1961).

Plutonium discharged to waste storage tanks has been maintained at less than 0.013 g/L. Plutonium in the discharged waste would have to be concentrated more than 200 times before criticality becomes possible. For this to occur requires a breakdown in procedural control at the processing plant. The high level of control maintained in the processing plants makes failure to detect such an off-normal condition highly unlikely. Once a violation is detected, the waste will not be discharged until after it has been brought back into conformance with CPS limits.

13.2 ELEMENTS OF A SURVEILLANCE PROGRAM

This section discusses the elements of a surveillance program.

Schedule of surveillance

When setting up a schedule of surveillance, the following factors should be taken into account:

- the cost of obtaining and analyzing samples
- the uncertainty on the composition of the waste
- the total estimated plutonium inventory
- the operations being performed
- the data already available
- the length of time since the last sample analyses.

When the waste composition and distribution is to be changed, the need for waste characterization takes on added importance. At times of change there is a greater chance that an unexpected, more highly reactive configuration will develop. Although no credible scenario capable of even approaching a critical configuration has been found, analytical data provides reassurance that the margin of safety continues to remain large. Reassurance is important with tank waste because of its great complexity and the great difficulty in its characterization.

After liquid has been removed to stabilize the waste in a tank, the need for surveillance will diminish. When the waste is dry, it should continue to remain unchanged in the future.

Data to be obtained from samples

The primary goal of a surveillance program is to ensure that the waste maintains a high degree of subcriticality. Analysis of waste samples is intended to measure parameters which verify applicable criticality safety limits.

The pH is measured to ensure that the waste is alkaline. This provides assurance that the plutonium is insoluble and mixed with the solids.

The specific gravity and the solids density make it possible to determine the proportion of solids and the proportion of water.

The plutonium concentration provides an immediate way to know the degree of subcriticality by comparison with the minimum critical concentration. In addition, the solids/plutonium mass ratio can be obtained. This mass ratio can be compared with the mass ratio subcritical limit to obtain assurance that subcriticality will be maintained no matter the water content.

When the concentrations of uranium, iron, manganese, and other important components, such as aluminum, sodium, silicon, nitrate, and carbonate, are known, specific mass ratios can be obtained. From these, the fraction of the corresponding subcritical limit can be obtained for each component. The sum of the fractions then provides a more precise way to measure the degree of subcriticality.

When it is known that a specific component is not present in a tank or can be shown to be exempt from criticality safety control, no analysis need be made for that component.

When uranium with ^{235}U enrichment greater than 1.0 wt% might be present or when ^{233}U might be present, the concentration of these isotopes should be obtained as part of the chemical analyses. In most tanks all uranium is depleted. Only tanks in C Farm contain measurable quantities of ^{233}U .

Investigation levels

No limits are placed in the CPS for waste inside of storage tanks. Nevertheless, analysis of waste samples can be used to verify that the waste is well below critical. This is done by comparing selected measured parameters to a set of criteria for acceptability. These criteria are called investigation levels.

Investigation levels for waste surveillance are defined as follows:

- The plutonium concentration exceeds 1.0 g/L (3.8 g/gal).
- The solids/plutonium mass ratio is less than 1,000.
- The pH is less than 9.0.

If sample analysis shows an investigation level to be crossed, the recovery plan for nonconformance shall be followed as described in Section 4.7. The goal is to determine if the apparent reduction in safety margin is real.

An investigation level is not considered a CPS limit. Rather, it is considered a point at which concern is raised over the potential erosion of the safety margin. An investigation level may be viewed as a trigger point at which concern is raised that the margin of safety appears to be eroding.

Maintenance of surveillance data

Compiled waste characterization data should be maintained in a centralized location to facilitate safety evaluations. This data should be updated as new data is available.

Tanks not needing monitoring

When it is known to a high degree of certainty that criticality is not possible in a tank, there may be no need to monitor the waste in that tank. Tanks which satisfy one of the following criteria need not be monitored.

- The total quantity of fissionable material in the tank is less than 10 kg.
- The waste has been stabilized so that there is very little drainable liquid and no waste is being added.

13.3 RECOVERY PLAN FOR NONCONFORMANCE

Nonconformance may be placed into two groups: CPS infractions or limit violations found before discharge and suspected investigation level violations found from analysis of waste samples from within a storage tank.

Nonconformance before discharge

Prior to discharge, waste is controlled by the CPS for the generating facility. If waste is found not to meet CPS limits, a recovery plan will be undertaken and appropriate changes will be made to bring the waste into compliance before discharge.

If the pH is less than 9.0, the pH will be adjusted to bring it the desired level.

Nonconformance of tank waste sample

After discharge, if a waste sample taken from a DST, DCRT, or vault tank is found to fall outside of an investigation level, a recovery plan will be undertaken.

Recovery Plan

When a suspected nonconformance is detected, an investigation will be conducted according to procedures described in WHC-CM-4-29, *Nuclear Criticality Safety Manual*, Section 15, "Recovery From Criticality Prevention Specification Nonconformance."

A suspected nonconformance shall be immediately brought to the attention of the immediate manager who, in turn notifies the Criticality Safety Representative (CSR) and obtains other technical assistance as required to determine if a nonconformance has occurred. At this time an immediate review is made to determine if a limit [or an investigation level] has been violated (WHC-CM-4-29).

If violation of a limit or an investigation level cannot be ruled out (i. e., it cannot be determined that a violation has not occurred), the

immediate manager notifies the manager of the operating organization (Tank Farms) and the manager of the independent safety review organization, and promptly informs the manager of Criticality and Radiological Engineering and the building administrator (if different from the operating manager), and as appropriate, the manager of the engineering support organization (WHC-CM-4-29).

Evaluation

An evaluation shall be made "to determine the appropriate method of recovery" (WHC-CM-4-29). Details of the recovery process, including a diagram, are provided in Section 15 of WHC-CM-4-49.

The discovery of a nonconformance will be based upon an analytical analysis of a sample or on a predictive calculation. The foremost question at this time is the quality of the analyses upon which the discovery is based. An evaluation will be made to determine the quality of the waste sample and of the method used to analyze it.

Waste has a large degree of complexity associated with it, and the procurement of accurate characterization data is difficult. Uncertainties are usually reflected in assumptions which ensure conservatism in analytical results. For these reasons, there is a tendency to overestimate the plutonium concentration and to underestimate the quantity of solids presence. When a measurement shows an investigation level to be exceeded, it will be probable that the high value results from analytical uncertainty and the use of conservative assumptions. The recovery plan will examine the way in which the data was obtained to determine what errors or conservative assumptions might have been incorporated in the process of obtaining it.

An assessment of the degree of subcriticality should be made. This generally is done by comparing the measured plutonium concentration and measured component/plutonium mass ratios to their respective subcritical limits. When the composition of the waste is known, the sum of the measured

component/plutonium mass ratios divided by their respective subcritical limits can be used to show subcriticality.

As part of this evaluation, it may become necessary to obtain new samples and to make an independent assessment of the waste composition.

If after this investigation it is concluded that an investigation level has actually been exceeded, then a violation of the CPS limits will be declared.

The CSR is required to document the technical basis for the evaluation of the nonconformance.

Approval of Recovery Plan

According to WHC-CM-4-29, Section 15, Part 5.3.2:

The recovery plan shall be agreed upon and signed by the manager of the independent safety review organization (or delegate), the manager of the operating organization and, as appropriate, the engineering manager (or delegate). When recovery actions begin, the written plan shall be followed.

Although not specifically designated in WHC-CM-4-29, it is appropriate for the CSR to also sign the recovery plan.

14.0 REFERENCES

- Altschuler, S. J., 1980, *CSAR 80-015: 244-TX and 244-S Salt Well Receiver Tanks*, SD-SQA-CSA-20110, Rockwell Hanford Operations, Richland, Washington.
- Altschuler, S. J., and P. C. Doto, 1991a, *Minimum Critical Safety Limits For Nuclear Waste*, Transactions of the American Nuclear Society, Vol. 64, pp. 339-340.
- Altschuler, S. J., 1991b, *CSER 91-011: Minimum Critical Safety Limits for Nuclear Waste*, WHC-SD-SQA-CSA-20339, Westinghouse Hanford Company, Richland, Washington.
- Anderson, J. D., 1990, *A History of the 200 Area Tank Farms*, WHC-MR-0132, Westinghouse Hanford Company, Richland, Washington.
- Braun, D. J., L. D. Muhlestein, T. B. Powers, and M. D. Zentner, 1994, *High Level Waste Tank Subcriticality Safety Assessment*, WHC-SD-WM-SARR-003, Westinghouse Hanford Company, Richland, Washington.
- Blyckert, W. A., 1981, *Waste Evaporators 242-A, 242-S*, CSAR 81-022, SD-SQA-CSA-20112, Rockwell Hanford Operations, Richland, Washington.
- Carter, R. D., G.R. Kiel, and K. R. Ridgway, 1969, *Criticality Handbook*, ARH-600, Vol. II, p. III.A.8.100-3, Atlantic Richfield Hanford Company, Richland, Washington.
- Carter, R. D., 1979, *Underground Waste Storage Tanks and Associated Equipment*, CSAR 79-007, SD-SQA-CSA-20108, Rockwell Hanford Operations, Richland, Washington.
- Carter, R. D., 1983, *Underground Waste Storage Tanks and Associated Equipment*, Addendum 1, CSAR 79-007, SD-SQA-CSA-20109, Rockwell Hanford Operations, Richland, Washington.
- Colvin, C. A., 1967, *Properties of Potential Uranium Precipitates as Related to Chemical Processing*, ARH-147, Atlantic Richfield Hanford Company, Richland, Washington.
- Cruzan, T. L., D. C. Riley, R. L. Shaver, and J. N. Strode, 1988, *Waste Generation and Processing Rates With Volume Reduction Factors - 1988*, WHC-TI-309, Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Delegard, C. H., and S. A. Gallagher, 1983, *Effects of Hanford High-Level Waste Components on the Solubility of Cobalt, Strontium, Neptunium, Plutonium, and Americium*, RHO-RE-ST-3 P, Rockwell International, Richland, Washington.

- Delegard, C. H., 1985, *Solubility of $PuO_2 \cdot xH_2O$ in Alkaline Hanford High-Level Waste Solution*, RHO-RE-SA-75 P, Rockwell International, Richland, Washington.
- DeNeal, D. J., 1970, *Historical Events - Single Pass Reactors and Fuels Fabrication*, DUN-6888, Douglas United Nuclear, Inc., Richland, Washington.
- DOE Order 5480.24, *Nuclear Criticality Safety*, August 12, 1992, U. S. Department of Energy, Washington, D. C.
- DOE Order 5480.21, *Unreviewed Safety Questions*, U. S. Department of Energy, Washington, D. C.
- Grigsby, J. M., D. B. Bechtold, G. L. Borsheim, M. D. Crippen, D. R. Dickinson, G. L. Fox, D. W. Jeppson, M. Kummerer, J. M. McLaren, J. O. McCormack, A. Padilla, B. C. Simpson, and D. D. Stepnewski, 1992, *Ferrocyanide Waste Tank Hazard Assessment - Interim Report*, WHC-SD-WM-RPT-032 Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Hanlon, B. M., 1993, *Tank Farm Surveillance and Waste Status Summary Report for August 1993*, WHC-EP-0182-65, Westinghouse Hanford Company, Richland Washington.
- Hess, A. L., 1991, *Review of Records for Source of ^{233}U in Tank 104-C* (Letter 29210-91-030 to S. D. Godfrey), Westinghouse Hanford Company, Richland, Washington. This is attached as Appendix B.
- Hobbs, D. T., T. B. Edwards, and S. D. Fleischman, 1993, *Solubility of Plutonium and Uranium in Alkaline Salt Solutions (U)*, WSRC-TR-93-056, Savannah River Technology Center, Westinghouse Savannah River Company, Aiken, South Carolina.
- Koreski, G. M. and J. N. Strode, 1994, *Operational Waste Volume Projection*, WHC-ER-029 Revision 19, Westinghouse Hanford Company, Richland, Washington.
- Jungfleisch, F. M., 1983, *Supplementary Information to the Preliminary Estimation of the Waste Inventories in Hanford Tanks Through 1980*, SD-WM-TI-058, Rockwell Hanford Operations, Richland, Washington.
- Jungfleisch, F. M., 1984, *Preliminary Estimation of the Waste Inventories in Hanford Tanks Through 1980*, SD-WM-TI-057, Rockwell Hanford Operations, Richland, Washington.
- Roetman, V. E., S. P. Roblyer, and H. Toffer, 1994, *Estimation of Plutonium in Hanford Site Waste Tanks Based on Historical Records* WHC-EP-0793, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

- Rogers, C. A., 1993, *CSER 92-009: An Analytical Model For Evaluating Subcritical Limits For Waste in Hanford Site Storage Tanks*, WHC-SD-SQA-CSA-20356, Westinghouse Hanford Company, Richland, Washington.
- Thomas, J. T., 1978, *Nuclear Safety Guide, TID-7016, Revision 2*, NUREG/CR-0095, ORNL/NUREG/CSD-6, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Schwinkendorf, K. N., 1994a, *Criticality Analysis of Homogeneous Pu-Water-Waste Systems*. This is Appendix A.6.0 of Braun et al., *High Level Waste Tank Subcriticality Safety Assessment*, WHC-SD-WM-SARR-003, March 1994.
- Schwinkendorf, K. N., 1994b, *Criticality Analysis of Various Idealized Waste Geometries* (Appendix A.7.0 of Braun et al, *High Level Waste Tank Subcriticality Safety Assessment*, WHC-SD-WM-SARR-003, March 1994).
- Tomlinson, R. E., 1961, *Safety Review of Manufacturing Facilities - Chemical Processing Department*, HW-69586, General Electric Company, Richland, Washington.
- WHC, 1980, *Operations of Tanks 244-TX and 244-S*, CPS-T-149-00060, Rev. A-0, Westinghouse Hanford Company, Richland, Washington.
- WHC, 1987, *Operation of Tanks 244-U and 244-BX*, CPS-T-149-00061, Rev. B-0, Westinghouse Hanford Company, Richland, Washington.
- WHC, 1988, *Waste Storage Tanks and Associated Equipment*, CPS-T-149-00010, Rev. D-0, Westinghouse Hanford Company, Richland, Washington.
- WHC, 1992, *241-Z Solution Disposal Facility*, CPS-Z-165-80741, Rev. A-2, Westinghouse Hanford Company, Richland, Washington.
- WHC, 1993, *Transfer TK-D5 to Tank Farms*, PFP Procedure Z0-101-010, Rev/Mod C-0, Westinghouse Hanford Company, Richland, Washington, December 1993.
- WHC-CM-4-29, *Nuclear Criticality Safety Manual*, Westinghouse Hanford Company, Richland, Washington.

15.0 BIBLIOGRAPHY

- Clemmons, J. S., and A. Q. Goslen, 1992, *Minimum Safe Ratios of Fe and Mn to U-235 in an Infinite System (U)*, Nuclear Criticality Safety Analysis, WM-92-3, WER-MER-921143, Westinghouse Savannah River Company, Aiken, South Carolina.
- Clemmons, J. S., and A. Q. Goslen, 1992, *Minimum Safe Ratios of Fe and Mn to Pu-239 in an Infinite System (U)*, Nuclear Criticality Safety Analysis, WM-92-5, WER-MER-921353, Westinghouse Savannah River Company, Aiken, South Carolina.
- Hey, B. E., 1993, *Dose Consequence for Postulated 350 MJ Hanford Site Underground Radioactive Liquid Waste Tank Criticality*, WHC-SD-WM-TI-527, Westinghouse Hanford Company, Richland, Washington.
- Hobbs, D. T., and T. B. Edwards, 1993, *Solubility of Plutonium in Alkaline Salt Solutions (U)*, WSRC-TR-93-131, Savannah River Technology Center, Westinghouse Savannah River Company, Aiken, South Carolina.
- Stratton, W. R., 1983, *The Myth of Nuclear Explosions at Waste Disposal Sites*, LA-9360, UC-70, Los Alamos National Laboratory, Los Alamos, New Mexico, October 1983.

APPENDIX A
BASIS DOCUMENTATION FOR CADMIUM ADDITION

This page intentionally left blank.

Addendum 2A for Criticality Safety Analysis Report (CSAR) 79-007 provides the basis for permitting larger plutonium discharge limits for tank 241-SY-102 when cadmium is added as a neutron poison. Although written in 1984, this addendum was not formally distributed. In 1994 it was transmitted on EDT 157914 as Supporting Document WHC-SD-SQA-CSA-20365.

The text of Addendum 2A for CSAR 79-007 is provided with some minor changes to enhance clarity. Attachments and graphs are omitted.

ADDENDUM 2A - CSAR 79-007

Criticality Safety Analysis Report for Miscellaneous Facilities
Criticality Prevention Specification CPS-T-149-00010
Title: Waste Storage Tanks and Associated Equipment

Prepared by: R. D. Carter	Date: 4/16/84
Reviewed by: W. A. Blyckert	Date: 4/16/84
Approved by: C. L. Brown	Date:

Recommended for approval by the Nuclear Criticality Safety Committee
Approved by Approval Authority: Date: 9/30/83

INTRODUCTION

This Addendum 2 to CSAR 79-007 modifies the requirements for plutonium-bearing wastes which are introduced into the waste storage tanks. The EGGNIT-2 Computer code was used to calculate material buckling values for various conditions.

The addition of plutonium-bearing solids which result in an excess of 2 g Pu/L in the storage tank waste may be done safely when the required cadmium is added to the solids and positive measures are taken to ensure that the required amount of cadmium* is maintained in association with the plutonium-bearing solids. The minimum required weight ratios of cadmium to plutonium are 0.25 and 0.33 for plutonium concentrations of: $2 < \text{Pu} < 17$ and $17 < \text{Pu} < 30$, respectively. The analysis shows that the resultant systems meet the safety requirements of RHO-MA-136.

DESCRIPTION

Recent activities within the Plutonium Finishing Plant are producing plutonium-bearing liquid waste streams which will result in concentrations of plutonium in excess of 1 g/L in waste storage tank 241-SY-102. The current estimate of plutonium in solids in the waste is 2.6 g/L of solids, which include aluminum hydroxide as 85 percent of the solids volume.

* Cadmium is assumed to be natural cadmium which contains 12.2 atomic percent ^{113}Cd .

Possible solutions to the storage problem include (1) the removal of the plutonium before it is transferred to the waste tanks; (2) the addition of solids to the waste to reduce the plutonium concentration; or (3) the addition of a neutron poison, such as cadmium, to be precipitated with plutonium in the solids. Cadmium will be added to tank 241-TX-244 and transferred to tank 241-SY-102. This action is designed to prevent the dissolution of cadmium from solids from the PFP which contains plutonium in excess of 2 g/L of solids and to which cadmium will be added.

ACCIDENT OR ERROR CONDITIONS

The following accident or error conditions were considered as contingencies:

1. Cadmium is added to the plutonium-bearing waste in insufficient quantities.
2. Cadmium is dissolved from the solids waste which contains plutonium in excess of 2.0 g/L.
3. Solid fraction of waste in storage tank exceeds 70 percent.
4. Plutonium is concentrated in the tank by some means.
5. Plutonium is overbatched in any addition to the tank.

Assumptions made in the analysis include:

1. Composition of waste is that provided by Waste Management Process Technology personnel.
2. Cadmium is added to the plutonium-bearing waste in accordance with the specification limits.
3. The presence of cadmium as associated with plutonium solids is maintained.
4. Plutonium and cadmium are precipitated before being added to tank 241-SY-102.
5. Plutonium concentration is within specification limits.

ANALYSIS AND SUMMARY

The reactivity of the waste from the Plutonium Finishing Plant in an underground storage tank was calculated using hand calculations and the EGGNIT-2 computer code based on composition of 2.6 g Pu/L and solids data (0.5 percent) provided by Waste Management Process Technology personnel. The hydrogen-to-plutonium ratio was calculated at various plutonium concentrations and at various percent solids concentrations from 60 to 95 percent. The material buckling was then calculated for the systems without and with the addition of cadmium.

In error number one, a large total mass of unpoisoned plutonium waste would be required to present a problem because (1) the suggested concentrations of cadmium to be added are twice those required for poisoning an infinite system and (2) it is not foreseeable that insufficient quantities of cadmium will be added as a routine operation so that short term accidental deficiencies will be compensated for by other additions.

The second postulated error, dissolving cadmium solids, would required large amounts to be removed before a problem is encountered. It is not foreseeable that this error could cause a problem because the presence of cadmium is normally in excess of twice as much as is required for poisoning an infinite system, the quantity of plutonium required for a critical system is large and not affected by small volumes with reduced poison, and the addition of adverse chemicals is monitored.

The third postulated error, increasing the volume percent of solids beyond 70 percent, is not credible. Deliberate efforts to compress powders to form fuel elements have achieved a maximum density of 70 percent of theoretical. The neutralization of waste will take place before it enters storage tanks; therefore, no increase in solids fraction beyond 70 percent is foreseeable.

The fourth postulated error is that of concentration of the plutonium in the solids. If T Plant wastes are added to tank 241-SY-102, the aluminum hydroxide, $Al(OH)_3$, could be redissolved. Since aluminum hydroxide can be 85 percent of the total solids volume (1,210 g out of $193 + 1,210 + 4 + 10 = 1,417$ g), any plutonium solids could have the plutonium concentration increase by $1/(1-0.85)$ or 6.7 times. This would also require consolidation of the solids in the tank. If plutonium is increased by 6.7 times and the maximum original concentration is 2.6 g/L then the concentration of plutonium could be as high as 17 g Pu/L. The requirements of cadmium poison will compensate for this reactivity increase if such an event were to take place.

The fifth postulated error condition is that of overbatching plutonium when 2.6 g Pu/L is the normal maximum concentration. Then, an error could increase the mass of plutonium in tank 241-TX-244 by 400 g in excess of that normally expected (e.g., from 800 to 1,200 g), because a double batch of plutonium is in a D Farm tank in the Plutonium Finishing Plant. A single concentration or mass error should not be a problem since such large masses are required for a critical system (i.e., the total storage tank mass is affected very little.)

In the safety evaluation, the long-term effect was considered. Results of the EGGNIT-2 calculations show that:

1. At 17 g Pu/L it will take a weight ratio of cadmium to plutonium of 0.11 to poison a 150 kg sphere to critical, 0.12 to poison a 300 kg mass to critical, and 0.13 to poison an infinite mass to critical.
2. The difference in requirements are negligible; the poisoning should be done to make an infinite system subcritical.

This page intentionally left blank.

APPENDIX B

REVIEW OF RECORDS FOR SOURCE OF ^{233}U IN TANK 104-C

This page intentionally left blank.

From: Criticality Engineering Analysis (CEA)
Phone: 3-2982 R3-01 2751E/C-104
Date: August 19, 1991
Subject: REVIEW OF RECORDS FOR SOURCE OF ²³³U IN TANK 104-C

29210-91-030

To: S.D. Godfrey R1-51

cc: S.L. Bhatia R3-01 J.G. Propson R2-18
C. Defigh-Price H4-23 L.E. Thomas R3-08
R.A. Dodd R1-51 R.K. Tranbarger R1-49
K.D. Fowler R2-11 T.S. Vail R1-43

- References: 1) Memo, Tank 104-C Investigation Team to H.D. Harmon, "TANK 104-C INVESTIGATION TEAM REPORT", #76400-91-023, July 15, 1991.
- 2) Letter, R.D. Carter to G.C. Oberg, "WASTE TANK CRITICALITY PARAMETERS", ARHCO, Oct. 22, 1976.
- 3) Letter, G.C. Oberg to J.L. Deichman, "Tank Farm Sludge and Salt Cake Samples", Oct. 31, 1976.
- 4) ARH-2127, "PUREX PROCESS OPERATION AND PERFORMANCE: 1970 THORIA CAMPAIGN", R.R. Jackson and R.L. Walser, March 1977.
- 5) RHO-SA-37, "PUREX PROCESS OPERATION AND PERFORMANCE --1970 THORIA CAMPAIGN", R.L. Walser, February, 1978.

SUMMARY

Reference 1 recommends an action item for CEA entitled "Review historical records for Tank 104-C and provide recommendations for adjusting the fissile material inventory based upon evidence that U-233 is also present in the tank". The results of that review indicate that a total of about 45 kg of ²³³U was discharged out of PUREX to underground tanks in C-farms during 1966 and 1970 thoria campaigns. Although the total volume of liquid waste transferred was on the order of several million gallons, it is highly probable that the ²³³U settled in the initial tank of a cascade of tanks used. This would have resulted in ²³³U accumulations of 33 kg in tank 104-C from the 1970 campaign and 12 kg in 102-C from the 1966 campaign. It is recommended that these amounts be added to inventories of 104-C and 102-C, and that future sampling in all of the C-Farm tanks should include tests for thorium and ²³³U to further track the waste disposition from the thoria campaigns.

DISCUSSION

For this review, records were searched for files about processing, handling, shipping and storage of ²³³U materials, and about disposal of wastes bearing

S. D. Godfrey
August 19, 1991
Page 2

29210-91-030

such materials. The 1976 references 2 and 3 (attachments #1 and #2)) are the only CEA memos found concerning ^{233}U contaminated sludges in the large waste tanks. Reference 2, the memo discovered during previous team activities, indicates that Tank 104-C supposedly contains 28 kg of ^{233}U . Reference 3 is a 1976 recommendation by CEA that analyses of core samples from 104-C include tests for ^{233}U content. Other memos to/from CEA were found pertaining to waste tank total fissile material inventories, but these were predominately accounts of Pu content.

CEA is not normally informed about details of transfers of fissile-bearing slurries into and between the waste tanks. There are memos from tank farm operations to CEA in instances where it was perceived that tank total Pu contents were approaching CPS limits; in these cases, requests of CEA to increase the fissile limits were granted (to 125 kg for certain tanks in 1979). The evaluations for these changes were documented as CSARs. None of the evaluations specifically calculated for ^{233}U , because it has been assumed, conservatively, that ^{233}U would be included as equivalent to ^{239}Pu .

Hundreds-of-kg quantities of ^{233}U were handled at PUREX during two Thoria campaigns, in 1966 and in 1970. The processing of the thoria target elements were part of production programs to supply ^{233}U to the Naval Reactor program. Records of CEA activities at the time contain several files pertaining to analyses of criticality safety limits for vessels used in the processing, storage and shipping of ^{233}U solutions. However, none of these CEA analyses addressed the discharge of PUREX-processing waste contaminated with ^{233}U out to the underground waste tanks.

W. Matheison, the Criticality Safety Representative for PUREX, identified References 4 and 5 as providing extensive details of the 1970 Thoria campaign, including losses to waste. The assertion that there are significant amounts of ^{233}U in the large waste tanks is substantiated in these documents. Waste discharges from the thoria campaigns were contaminated with fissile elements to a degree comparable to discharges from Pu production runs.

Reference 4 alludes first to the initial Thoria campaign in 1966. The Introduction includes the statements - -*"The first Purex production scale campaign was conducted in 1966. Approximately 165 tons of thorium and 220 kilograms of uranium-233 were recovered."* Charging of thoria targets to the dissolver began in May of 1966, the campaign was completed in July, and turnaround to uranium-plutonium production was completed in August of 1966.

About the 1970 campaign, the Summary of Reference 4 states - -*"The campaign was successfully conducted and resulted in the recovery of about 600 kgs of ^{233}U from approximately 470 tons of irradiated thoria (ThO_2) target elements. The overall recoveries based on reactor input data were 95.2 percent for uranium and 94.9 percent for thorium"*. This campaign consisted of two different runs, the first one for non-specification material (high ^{238}U thoria), and then another run for specification-grade material. The initial non-specification charge was made August 5, 1970. After completing the

S. D. Godfrey
August 19, 1991
Page 3

29210-91-030

processing for specification-grade material, post-thorium flushing was conducted until January 16, 1971.

Attachments #3 and #4 are tables summarizing the material balances for the Non-Specification and Specification portions, respectively, of the 1970 campaign. These tables were extracted from Section VI-B, ACCOUNTABILITY AND MATERIAL BALANCE, of Reference 4. The waste losses for thorium and uranium (which is predominately ^{233}U) are listed by the tanks at PUREX which receive the waste streams from the various treatment lines. The four major PUREX tanks listed in the tables, tanks F18, E5, G8, and R8, are all cited in various earlier sections of the report (sections IV-C through IV-L) as staging tanks for holdup and sampling of waste solutions and slurries for subsequent disposal to underground storage tanks.

In Attachment #3 it will be noted that 8.9 kg total ^{233}U is listed as lost to waste for the Non-Specification portion of the campaign. However, only 8.0 kg can be said was routed to the underground tanks, the other 0.9 kg of ^{233}U remained as contamination of the output thorium. Likewise, in Table 2, for the Specification portion only 25.0 kg of the 28.9 kg uranium listed as Total Waste Loss can be considered transferred to the tank farms, because 3.9 kgs are listed as retained with the thorium. Thus, the total ^{233}U output channelled during the 1970 thoria campaign to underground waste tanks by the reference-4 accounting is $8.0 + 25.0 = 33.0$ kg.

It is probable that the 28 kg ^{233}U value cited in Attachment #1 as supposedly in tank 104-C was derived from earlier drafts of Reference 4, or other campaign summaries, reporting on total losses from the Specification portion.

A tabulation of liquid wastes sent to non-boiling underground tank storage from PUREX during the 1970 campaign is given in Attachment #5; this table is from Section VI-C (WASTE VOLUMES) of Reference 4. The waste volumes are listed by PUREX tank and source waste stream, and the summary shows a total of 2,795,000 gallons was discharged during the 1970 campaign. However, all of the ^{233}U lost to the liquid stream was essentially from TK-F18, TK-E5, and TK-G8, which provided a total of 2,155,000 gallons.

Evidence that 1970 thoria campaign wastes were routed to tank 104-C was obtained in discussions with Francis Jungfleisch. A review of the TRAC data base at his office shows that during two quarters of 1970, when the second campaign was in progress, some thoria bearing wastes were channeled into 104-C. However, considering that the C-farm tanks 101 through 112 are 500,000 gallons capacity each, the two million gallons of ^{233}U -contaminated liquid waste discharged from PUREX in 1970 would have to been routed to several tanks.

Further scanning of the TRAC data base revealed that during 1966 tank 102-C also received waste transfers labeled "thorium". It is noted in reference 5 that the process characterization and efficiency for the 1970 campaign were very similar to the first production-scale runs in 1966. It is surmised that

S. D. Godfrey
August 19, 1991
Page 4

about a million gallons of discharge would have been routed to tank farms in the 1966 campaign, based on the relative campaign outputs of ^{233}U (ratio of 220kg/600kg). The waste liquids in 1966 also would have been sent to a number of tanks.

The amount of ^{233}U sent to 102-C in 1966 also can be estimated on the basis of the performance data for the 1970 campaign. Given that the 1970 output of 600 kg of ^{233}U (as nitrate solution shipped to ORNL) resulted in 33 kg loss to the tank farm waste stream, the 220 kg ^{233}U produced in 1966 would entail waste stream contents totalling $33/600 \times 220 = 12.1$ kg ^{233}U .

Discussions with staff familiar with the tank farms operations indicate that the PUREX liquid discharges at the time probably went through a cascade of tanks; first into tank 104-C, from which then the overflows cascaded into 105-C, 106-C, etc.. At some stage after the first tank there may also have been some concentration of overflow liquids in an evaporator. It is most likely that the solids (which would include thorium and uranium as insoluble compounds) slurried out with the liquids from PUREX would have settled in the first tank of the cascade series, into 104-C for the 1970 discharges. Likewise, in 1966 the uranium and thorium would have settled in 102-C and the overflow liquids passed on to other C-farm tanks. Further investigation of tank transfer records for these periods would have to be undertaken to determine which other tanks may have received uranium and thorium in solution.

It is therefore warranted that future core samplings and analyses for all the C-farm tanks include assays for ^{233}U contents. The previous request (in the attached 1977 memo) from CEA for ^{233}U analysis of a tank 104-C core apparently was not accommodated.

A. L. Hess
Principal Engineer, Criticality Engineering Analysis

P. C. Doto
Manager, Criticality Safety Analysis

db

attachments (5)

Date: October 22, 1976

To: G. C. Oberg

From: R. D. Carter *RDC*

ATTACHMENT #1

Subject: WASTE TANK CRITICALITY PARAMETERS

- References: (1) Letter, J. D. Anderson to G. C. Oberg,
"Location of Plutonium Accumulations",
July 29, 1976
- (2) Letter, J. E. Horton to O. R. H. Rasmussen,
"Analysis and Characterization of Sludge
Sample from Tank 106-C", January 6, 1975

The large waste tanks such as 106-C contain fissile material (primarily plutonium) in diluted form. Some of the tanks have kilogram quantities. The 106-C tank is reported to have 52 to 57 kilograms in it (reference) and the 104-C tank supposedly has at least 28 kilograms of U-233 and 10 kilograms of plutonium.

Because of the dilution, no criticality hazard exists. These tanks are 75 feet in diameter, which results in a volume of approximately 125,000 liters per foot of depth. Since the waste depth in these tanks is several feet, even 100 kilograms would be less than one gram of fissile material per liter. An analysis of the 106-C tank waste composition (reference 2) shows that the infinite multiplication factor is less than 1.0 up to 3.5 grams of plutonium per liter, under the worst moderation, and therefore criticality is impossible below this concentration. No neutron absorbers other than iron were included in the calculation.

The above analysis assumes an infinite system. A somewhat more conservative approach is to determine the critical areal density by assuming that the fissile material is spread uniformly in the horizontal direction (it can be layered vertically without affecting the validity of the analysis). The minimum critical areal density for plutonium-water systems is 240 grams of plutonium per square foot at 20 grams of plutonium per liter. Mixtures of plutonium and water with non-absorbing scatterers, such as oxygen, aluminum and silicon can reduce this to 185 grams per square foot at 3.5 grams of plutonium per liter. This would require at least 800 kilograms of plutonium for a criticality. Of course,

G. C. Oberg
Page 2
October 22, 1976

the analysis in the second paragraph shows that an infinite amount of plutonium would be required at 3.5 grams per liter using an actual composition of the waste. However, in this case the limiting values would cover any tank waste composition that could realistically be expected.

RDC:j1

Date: . October 31, 1977

No: . 72120-77-70

TO: (Name, Organization, Internal Address)

. J. L. Deichman

FROM: (Name, Organization, Internal Address, Phone)

. G. C. Oberg

. 2-2246

ATTACHMENT #2

Subject: . Tank Farm Sludge and Salt Cake Samples

The criticality analysis for 75 foot diameter underground storage tanks assumes a uniform horizontal distribution of plutonium in the sludge and salt cake within tanks. The purpose of this letter is to request complete core samples from Tanks 106-C, 104-C, 118-TX, and 111-S to supply additional information as to the plutonium content, the distribution of plutonium within the tank solids, and the composition of the wastes. In addition, a core sample is requested from the top four feet of either TK-102-U or TK-105-U.

Except for the U-Farm tanks, the entire thickness of the solids within the tanks should be sampled. A separate sample is required from at least each two feet of solids (one foot for the U-Farm tank), or more often if required to obtain a representative distribution as determined by visual observation. Three core locations should be chosen in each tank as follows: (1) center, (2) under or as close as possible to the fill line discharge, and (3) one randomly spaced elsewhere in the tank at least 20 feet from either of the other samples, if possible. Locations in each tank should be communicated to Criticality Engineering and Analysis prior to sampling.

All samples should be analyzed for plutonium and uranium. Other analyses to be requested on samples from one core per tank should include Na, Fe, N, O, Si, and Al. Uranium-233 should be run on the samples from one core from Tank 104-C. All sample results should be reported as grams per liter. The proportion of solids and liquid in the sludge should be determined as should the amount of dissolved salts in the liquid.

If an existing sampling program will produce analytical data on the solids in tanks, perhaps some of the above needs can be filled by such a program. Please let me know the action that will be taken.

G.C. Oberg

G. C. Oberg
Manager,
Criticality Engineering and Analysis

GCO/jl

cc:

W. A. Blyckert
R. D. Carter
R. R. Eggleston
G. C. Oberg (2)

LIQUID WASTE VOLUMES AND ESTIMATED SALT MASS TO NON-BOILING
UNDERGROUND TANK STORAGE
1970 THORIA CAMPAIGN

ATTACHMENT #5

Source	Non-Specification Portion		Specification Portion		Total	
	Gallons	Tons of Salt	Gallons	Tons of Salt	Gallons	Tons of Salt
Pre-Campaign Flushes TK-F18	360,000	150			360,000	150
LWW	85,800	70	141,000	120	226,800	190
Sumps	91,800	50	213,000	120	304,800	170
Interim Flushes	43,900	40	25,000	30	68,900	70
Post Campaign Flushes			45,000	20	45,000	20
TK-E5						
Coating Waste	140,900	40	229,000	160	369,900	200
Post-Campaign Flushes			65,000	60	65,000	60
TK-G8						
OWW	278,400	20	314,000	30	592,400	50
Post-Campaign Flushes			80,000	6	80,000	6
TK-R8						
OWW	195,100	5	193,000	10	398,100	15
Post-Campaign Flushes			14,000	1	14,000	1
TK-U3 & U4						
Lab. Waste plus Stack drainage, etc.	30,100	1	250,000	6	280,100	7
Total	1,226,000	380	1,569,000	560	2,795,000	940

Table I from Section IV-C,
WASTE VOLUMES,
of ARH-2127 (reference #4)

WMC-SD-SQA-CSA-20368, Rev. 0

B-12

Date: . October 31, 1977

No: . 72120-77-70

TO: (Name, Organization, Internal Address)

. J. L. Deichman

FROM: (Name, Organization, Internal Address, Phone)

. G. C. Oberg

. 2-2246

ATTACHMENT #2

Subject: . Tank Farm Sludge and Salt Cake Samples

The criticality analysis for 75 foot diameter underground storage tanks assumes a uniform horizontal distribution of plutonium in the sludge and salt cake within tanks. The purpose of this letter is to request complete core samples from Tanks 106-C, 104-C, 118-TX, and 111-S to supply additional information as to the plutonium content, the distribution of plutonium within the tank solids, and the composition of the wastes. In addition, a core sample is requested from the top four feet of either TK-102-U or TK-105-U.

Except for the U-Farm tanks, the entire thickness of the solids within the tanks should be sampled. A separate sample is required from at least each two feet of solids (one foot for the U-Farm tank), or more often if required to obtain a representative distribution as determined by visual observation. Three core locations should be chosen in each tank as follows: (1) center, (2) under or as close as possible to the fill line discharge, and (3) one randomly spaced elsewhere in the tank at least 20 feet from either of the other samples, if possible. Locations in each tank should be communicated to Criticality Engineering and Analysis prior to sampling.

All samples should be analyzed for plutonium and uranium. Other analyses to be requested on samples from one core per tank should include Na, Fe, N, O, Si, and Al. Uranium-233 should be run on the samples from one core from Tank 104-C. All sample results should be reported as grams per liter. The proportion of solids and liquid in the sludge should be determined as should the amount of dissolved salts in the liquid.

If an existing sampling program will produce analytical data on the solids in tanks, perhaps some of the above needs can be filled by such a program. Please let me know the action that will be taken.

G. C. Oberg
Manager,
Criticality Engineering and Analysis

GCO/jl

cc:

W. A. Blyckert
R. D. Carter
R. R. Eggleston
G. C. Oberg (2)

TABLE 1

ATTACHMENT #3

MATERIAL BALANCE
NON-SPECIFICATION PORTION

Waste Loss	<u>Th, Tons</u>	<u>% R.R.*</u>	<u>U, Kgs</u>	<u>% R.R.*</u>
F18				
1WW	.3	.2	1.4	.8
Sumps	.5	.4	1.7	1.0
Flushes	.1	.07	1.8	1.0
E5	.1	.07	1.0	.6
G8	.3	.2	2.0	-1.1
R8	.1	.07	.1	.06
U3 & U4	0	0	0	
U in Th Product	—	—	.9	.5
TOTAL	1.4	1.0	8.9	5.1
Product Input				
Reactor Receipts	130.4	100.0	174.9	100.0
TK-D5	125.2	96.0	167.9	96.0
Product	119.8	91.9	161.3	92.2
Product & Waste Loss	121.2	92.9	170.2	97.3
Reactor MUF	-9.2	7.0	-4.7	2.7
TK-D5 MUF	-4.1	3.1	+1.3	.7

* % R.R. = percent of reactor receipts

Table I from Section IV-B,
ACCOUNTABILITY AND MATERIAL BALANCES,
of ARH-2127 (reference #4)

TABLE 2

ATTACHMENT #4

MATERIAL BALANCE
SPECIFICATION PORTION

Waste Loss	<u>Th, Tons</u>	<u>% R.R.*</u>	<u>U, Kgs</u>	<u>% R.R.*</u>
F18				
LWW	3.7	1.3	2.9	.6
Sumps	2.0	.7	5.5	1.2
Int. Flushes	.1	.04	.6	.1
Post Flush.	.6	.2	.7	.1
E5				
Coating Waste	.3	.1	2.7	.6
Post Flush	2.4	.8	8.7	1.9
G8				
CWW	.9	.3	3.0	.7
Post Flush	0	0	.4	.09
R8				
CWW	.1	.04	.3	.07
Post Flush	0	0	0	
U3 & U4				
Lab Waste	0	0	.2	.04
U in K6 Product	—	—	<u>3.9</u>	<u>.9</u>
TOTAL	10.1	3.5	28.9	6.4
Product Input				
Reactor Receipts	285.5	100.0	452.6	100.0
TK-D5	280.6	98.3	449.3	99.3
Product	274.9	96.3	436.2	96.4
Product & Waste Loss	285.0	99.8	465.1	103.8
Reactor MUF	-.5	.2	+12.5	2.8
TK-D5 MUF	+1.7	.6	+4.4	1.0

* % R.R. = percent of reactor receipts

LIQUID WASTE VOLUMES AND ESTIMATED SALT MASS TO NON-BOILING
UNDERGROUND TANK STORAGE
1970 THORIA CAMPAIGN

ATTACHMENT #5

Source	Non-Specification Portion		Specification Portion		Total	
	Gallons	Tons of Salt	Gallons	Tons of Salt	Gallons	Tons of Salt
Pre-Campaign Flushes	360,000	150			360,000	150
TK-F18						
1WW	85,800	70	141,000	120	226,800	190
Sumps	91,800	50	213,000	120	304,800	170
Interim Flushes	43,900	40	25,000	30	68,900	70
Post Campaign Flushes			45,000	20	45,000	20
TK-E5						
Coating Waste	140,900	40	229,000	160	369,900	200
Post-Campaign Flushes			65,000	60	65,000	60
TK-G8						
OWW	278,400	20	314,000	30	592,400	50
Post-Campaign Flushes			80,000	6	80,000	6
TK-R8						
OWW	195,100	5	193,000	10	398,100	15
Post-Campaign Flushes			14,000	1	14,000	1
TK-U3 & U4						
lab. Waste plus Stack drainage, etc.	30,100	1	250,000	6	280,100	7
Total	1,226,000	380	1,569,000	560	2,795,000	940

Table I from Section IV-C,
WASTE VOLUMES,
of ARH-2127 (reference #4)