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Annual Report of Tank Waste Treatability

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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



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Annual Report of Tank Waste Treatability

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Date Published
September 1993

Prepared for the U.S. Department of Energy
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Hanford Company**

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LIST OF TERMS

ALARA	as low as reasonable achievable
ALC	airlift circulation
ANL	Argonne National Laboratory
BDAT	best demonstrated available technology
BNL	Brookhaven National Laboratory
CC	complexant concentrate (waste)
CMPO	octyl(phenyl)--N,N-diisobutylcarbamoyl-methylphosphine oxide
CPU	compact processing unit
CRW	cladding removal waste
CVS	composition variability study
CY	calendar year
DBE	design base experiment
DC	dilute complexed
DF	decontamination factor
DOE	U.S. Department of Energy
DOE-HQ	U.S. Department of Energy-Headquarters
DOE-RW	U.S. Department of Energy-Civilian Radioactive Waste Management
DST	double-shell tank
DSS	double-shell slurry
DSSF	double-shell slurry feed
EA	environmental assessment
Ecology	Washington State Department of Ecology
EDTA	ethylenediaminetetraacetic acid
EIS	Environmental Impact Statement
EM	(Office of) Environmental Management
EPA	U.S. Environmental Protection Agency
FSAR	Final Safety Analysis Report
FY	fiscal year
GAO	General Accounting Office
GDF	Grouted Waste Disposal Facility
GPF	Grout Processing Facility
GTF	Grout Treatment Facility
GTM	Generic TRUEX Model
HDNNS	didodecyl-naphthalenesulfonic acid
HEDPA	1-hydroxyethane-1,1-diphosphonic acid
HEDTA	hydroxyethylenediaminetriacetate
HLW	high-level waste
HVAC	heating, ventilating, and air conditioning
HWVP	Hanford Waste Vitrification Plant
INEL	Idaho National Engineering Laboratory
IPM	initial pretreatment module
LFL	lower flammability limit
LANL	Los Alamos National Laboratory
LLW	low-level waste
MFT	melter feed tank
MIT	multi-functional instrument tree
MVSTS	Melton Valley Storage Tank
NCAW	neutralized current acid waste
NCPLX	non-complexed waste

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LIST OF TERMS (continued)

NCRW	neutralized cladding removal waste
NEPA	<i>National Environmental Policy Act of 1969</i>
NESHAP	<i>National Emission Standards for Hazardous Air Pollutants</i>
NPF	New Pretreatment Facility
NRC	Nuclear Regulatory Commission
NTA	nitriiloacetate
OCRWM	Office of Civilian Radioactive Waste Management
ODT	Office of Technology Development
ORNL	Oak Ridge National Laboratory
PA	performance assessment
PFP	Plutonium Finishing Plant
PIH	portable instrument house
PNL	Pacific Northwest Laboratory
PRF	Plutonium Reclamation Facility
PSW	phosphate/sulfate waste
PUREX	Plutonium/Uranium Extraction (Plant)
RL	U.S. Department of Energy, Richland Operations Office
SA	safety analysis
SAR	Safety Analysis Report
SEIS	supplemental environmental impact statement
SI	safety issues
SME	slurry mix evaporator
SPM	second pretreatment module
SRAT	slurry receipt and adjustment tank
SREX	strontium extraction
SRL	Savannah River Laboratory
SRTC	Savannah River Technical Center
SST	single-shell tank
TAPS	toxic air pollutants
TBP	tributyl phosphate
TC	thermocouple
THFTCA	2,3,4,5-tetrahydro-furantetra-carboxylic acid
Tri-Party Agreement	<i>Hanford Federal Facility Agreement and Consent Order</i>
TRU	transuranic (waste)
TRUEX	transuranium extraction
TWG	technology working group
TWRS	Tank Waste Remediation System
U.S.	United States
UST/ID	Underground Storage Tank/Integrated Demonstration
WAC	<i>Washington Administrative Code</i>
WAPS	Waste Acceptance Preliminary Specifications
WASRD	Waste Acceptance Systems Requirements Document
WFQ	waste form qualification
WHC	Westinghouse Hanford Company
WSCP	water-soluble chelating polymers

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Metric Conversion Chart

Into Metric			Out of Metric		
If You Know	Multiply By	To Get	If You Know	Multiply By	To Get
Length			Length		
in.	2.54	cm	mm	0.04	in.
ft	30.48	cm	cm	0.4	in.
Mass (weight)			Mass (weight)		
lb	0.453515	kg	kg	2.2	lb
Volume			Volume		
gal	3.78541	L	L	0.264172	gal
Temperature			Temperature		
Fahrenheit (°F)	Subtract 32 then multiply by 0.55555...	Celsius (°C)	Celsius (°C)	Multiply by 1.8, then add 32	Fahrenheit (°F)

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ANNUAL REPORT OF TANK WASTE TREATABILITY

R . A. Kirkbride
A. G. Lane

ABSTRACT

This report has been prepared as part of the Hanford Federal Facility Agreement and Consent Order (Tri-Party Agreement) and constitutes completion of Tri-Party Agreement milestone M-04-00D for fiscal year 1993. This report provides a summary of treatment activities for newly generated waste, existing double-shell tank waste, and existing single-shell tank waste, as well as a summary of grout disposal feasibility, glass disposal feasibility, alternate methods for disposal, and safety issues which may impact the treatment and disposal of existing defense nuclear wastes.*

This report is an update of the 1992 report and is intended to provide traceability for the documentation by statusing the studies, activities, and issues which occurred in these areas listed above over the period of March 1, 1992, through February 28, 1993. Therefore, ongoing studies, activities, and issues which were documented in the previous (1992) report are addressed in this (1993) report.

*Hanford Federal Facility Agreement and Consent Order, 2 Vols., as amended, Washington State Department of Ecology, U.S. Environmental Protection Agency, and U.S. Department of Energy, Olympia, Washington.

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ANNUAL REPORT OF TANK WASTE TREATABILITY

1.0 INTRODUCTION

1.1 TRI-PARTY AGREEMENT

The *Hanford Federal Facility Agreement and Consent Order* (Tri-Party Agreement) (Ecology et al. 1990), established in 1989 by the U.S. Department of Energy (DOE), the U.S. Environmental Protection Agency (EPA), and the Washington State Department of Ecology (Ecology), provides the basis for this report. The Tri-Party Agreement contains milestone M-04-00, which addresses tank waste treatability, issues, and concerns.

Milestone M-04-00 requires that reports of tank waste treatability studies be submitted annually beginning in September 1990.

1.2 MILESTONE M-04-00A, ANNUAL TANK WASTE TREATABILITY 1990 REPORT

The 1990 *Annual Report of Tank Waste Treatability* (Karnesky 1990) documented the first of an annual series of reports required by milestone M-04-00. In addition to presenting an historical perspective of tank waste treatment at the Hanford Site, this report described planned treatment of existing double-shell tank (DST) and single-shell tank (SST) wastes, and provided the technical basis for selection of grout and borosilicate glass as disposal forms.

1.3 MILESTONE M-04-00B, ANNUAL TANK WASTE TREATABILITY 1991 REPORT

The 1991 report (Giese 1991) represented the first statusing report in the series of these annual reports. The organization of the 1991 report was the same as that of the 1990 version. Two additional sections were added to the 1991 report. Section 7.0 summarized alternative treatment/disposal technologies which could have an impact on future disposal. Section 8.0 contained pertinent issues which may affect either treatability of tank waste or the feasibility of using grout or glass (or another viable alternative) as a final disposal option.

1.4 MILESTONE M-04-00C, ANNUAL TANK WASTE TREATABILITY 1992 REPORT

The 1992 *Annual Report of Tank Waste Treatability* (Barker and Lane 1992) also follows organization of the previous reports, comprising the second statusing report in this series of milestone reports. Section 7.0, Alternative Treatment/Disposal Technology, was revised to incorporate the activities of DOE's Underground Storage Tank - Integrated Demonstration (UST-ID) program.

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1.5 MILESTONE M-04-00D, ANNUAL TANK WASTE
TREATABILITY 1993 REPORT

The 1993 *Annual Report of Tank Waste Treatability*, following the organization of the previous reports, comprises the third statusing report in this series of milestone reports. Section 3.0, Re-evaluation of Tank Waste Treatment and Disposal Plans, was added to the 1993 report.

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2.0 SUMMARY

This fourth annual report satisfies the Tri-Party Agreement milestone M-04-00D for fiscal year (FY) 1993.

2.1 RE-EVALUATION OF TANK WASTE TREATMENT AND DISPOSAL PLANS

Re-evaluation of the treatment and disposal plans for Hanford Site tank wastes became necessary to (1) provide an integrated systems approach for achieving safe storage, (2) resolve tank safety issues, and (3) treat and dispose all Hanford Site tank wastes. As a result of the rebaselining, Tank Waste Remediation System (TWRS) management has proposed a new technical strategy for disposing of all Hanford Site tank waste. Two parallel bounding alternative strategies or approaches to the disposal program would be evaluated for implementation in the proposed new technical strategy. The first approach (extensive separations) uses yet-to-be developed technologies to separate the waste into a small volume high-level waste (HLW) fraction and a large volume low-level waste (LLW) fraction. The second approach (high capacity vitrification) uses current technologies to separate the tank waste into HLW and LLW fractions.

2.2 DOUBLE-SHELL TANKS

Existing waste in ten DSTs will be pretreated to separate the waste into HLW, transuranic (TRU) waste, and LLW volumes. Recent pretreatment technology development activities for four DST waste types (i.e., neutralized current acid waste (NCAW), neutralized cladding removal waste (NCRW), Plutonium Finishing Plant (PFP) waste, and complexant concentrate (CC) waste), is presented. The existing waste in the remaining eighteen DSTs is part of the DSS family of wastes. Until recently, this family of wastes was planned to be grouted directly. The proposed new technical strategy recommends that these wastes be pretreated to remove additional radionuclides to achieve a Class A LLW waste.

Treatment of the separated HLW and TRU waste fractions will consist of vitrification in the Hanford Waste Vitrification Plant (HWVP) before disposal in a geologic repository. Treatment of the LLW consists of solidification in cement-based grout before disposal in near-surface vaults at the Hanford Site. These treatment processes are in various stages of development and are discussed in Section 4.0.

A new pretreatment technology plan presents a strategy for identifying, evaluating, and developing technologies for pretreatment of both DST and SST wastes at the Hanford Site. This strategy includes recent planning activities for the development of pretreatment processes and the deployment of facilities. Section 4.0 also presents the status of TWRS pretreatment systems development for (1) a reference pretreatment technology development system, (2) an enhanced pretreatment technology development system, and (3) an alternative pretreatment technology development system.

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2.3 SINGLE-SHELL TANKS

Existing waste in SSTs continues to be characterized to enable appropriate treatment options to be developed. This information is needed for a supplemental environmental impact statement (SEIS) leading to a decision on final SST waste disposal.

The status of activities included in the reference pretreatment technology development system is presented in Section 5.0. Emphasis is placed on the development of pretreatment technology options for the removal of organic and ferrocyanide compounds so important to the resolution of major tank safety issues that could affect the remediation of many of the SST wastes. Several functions currently identified as being unique to SSTs are presented as potential enhancements to the reference pretreatment technology system.

2.4 GROUT AND GLASS

The current grout treatment process for LLW is described in Section 4.8. Major processing requirements for waste vitrification of the HLW in HWVP are also discussed in Section 4.8.

2.5 CURRENT WASTE GENERATORS

Currently, the following ten major facilities generate waste subject to this study report.

1. 100-N Area
2. 300 Area
3. 400 Area
4. Tank farms
5. Evaporators
6. Plutonium Finishing Plant (PFP)
7. Plutonium/Uranium Extraction (PUREX) Plant
8. B Plant
9. S Plant
10. T Plant.

Treatment of these wastes is addressed in Appendix A.

2.6 WASTE TANK SAFETY ISSUES

The pertinent waste tank safety issues that may affect either the treatability of tank waste or the feasibility of using glass or grout (or another viable alternative) as a final disposal option are presented in Section 9.0. This section provides a description, status, and plans for resolving these important safety issues.

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2.7 ALTERNATIVE TREATMENT/DISPOSAL TECHNOLOGIES

A summary of the alternative waste treatment and disposal technology systems under development within the UST-ID Program is in Section 8.0. Many of these ongoing activities are important to the implementation of TWRS Program for treatment and immobilization of tank wastes at the Hanford Site.

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3.0 RE-EVALUATION OF TANK WASTE TREATMENT AND DISPOSAL PLANS

The Assistant Secretary for Environmental Restoration and Waste Management and the director of the Washington State Department of Ecology agreed to the need to re-evaluate treatment and disposal plans for Hanford Site tank wastes (Duffy 1992). Re-evaluation of the tank waste treatment and disposal plans (referred to as rebaselining) was necessary to (1) provide an integrated system approach for achieving safe storage, (2) resolve tank safety issues, and (3) treat and dispose all Hanford Site tank wastes. Rebaselining evaluated new approaches to remediate Hanford Site tank wastes and, thus, reaffirm existing plans or recommend a new technical strategy. To facilitate this integrated system approach for managing the program elements, the DOE formed the TWRS with a mission to store, treat, and immobilize highly radioactive Hanford waste (including the current and future tank waste and the strontium and cesium capsules) in an environmentally sound, safe, and cost-effective manner.

While conducting this re-evaluation, the DOE agreed to continue supporting the existing plan for treatment and disposal of Hanford Site tank waste as detailed in the *Hanford Federal Facility Agreement and Consent Order* (Ecology, EPA, and DOE 1992).

As a result of the rebaselining, The TWRS management has proposed a new technical strategy for disposing of all Hanford Site tank waste. The selection of a proposed new technical strategy for the TWRS Program is a complex task involving the evaluation of a large body of data. Currently, the data that is available to support the selection of a proposed new technical strategy is based on engineering estimates and preliminary technology development. The dynamic nature of technology development further complicates the reliability of the data used.

To accommodate this complex, dynamic situation, a systems engineering approach is being applied to structure and analyze technical strategies and to manage the TWRS program. Systems engineering is usually applied at the problem definition phase of a project. It is normally a sequential process for system definition and implementation. However, elements of the TWRS Program are in various stages of development from preconceptual to operation. Existing information, which was developed outside the normal systems engineering process, has been used in the TWRS application of the systems engineering process. This has resulted in tailoring the formal systems engineering methodology to the TWRS application. In addition, some programmatic considerations also have been applied to the decisions made during baseline development.

A series of reports that define the scope and plans for implementing the proposed new technical strategy include the following:

- Program plan (being developed)
- Program management plan (being developed)

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- Tank Waste Remediation System Functions and Requirements (DOE/RL 1993)
- Tank Waste Remediation System Integrated Technology Plan (DOE/RL 1993)
- Tank Waste Technical Options Report (Boomer et al. 1993)
- Tank Waste Decision Analysis Report (Johnson et al. 1993)

3.1 SELECTION OF A NEW TECHNICAL STRATEGY

The analyses to support selecting a proposed new technical strategy were evaluated by the TWRS Program Leadership Council using the tailored systems engineering approach. The TWRS Leadership Council consists of senior management representatives from Westinghouse Hanford Company (WHC), Pacific Northwest Laboratory (PNL), U.S. Department of Energy-Headquarters (DOE-HQ), and U.S. Department of Energy, Richland Operations Office (RL). The Leadership Council guided the development of specific criteria and performance measures and synthesized a suite of seven technical strategies that were evaluated. These alternative strategies were synthesized from a broader set representing a diverse spectrum of technologies for accomplishing the TWRS disposal mission.

This activity produced a recommendation to proceed with activities to resolve tank safety issues, modify and upgrade existing facilities (e.g., storage tanks, evaporator), and bring the infrastructure into compliance with current standards. This is done to ensure the safety of the public and TWRS Program workers.

Two parallel bounding alternative technologies (approaches) to the disposal program execution that were selected by the leadership council will be carried forward. A selection between the two approaches will be made when supporting technologies have been sufficiently developed to understand the technical uncertainties associated with each approach. This is anticipated to be in 3 to 6 years. Technology development activities associated with each approach are described in the *Tank Waste Remediation System Integrated Technology Plan* (DOE/RL 1993). The two approaches, summarized below, provide for early resolution of tank safety issues.

The *National Environmental Policy Act of 1969* (NEPA) strategy for implementing these actions will be described in a program management plan, which is currently being developed.

The proposed new technical strategy for managing the tank waste will focus first on the mitigation or resolution of tank safety issues and the establishment of safety and environmental basis envelopes for continued operations. The tank farm infrastructure also will be upgraded to be in compliance with today's standards using a graded approach. Also, a major new project (not in the original Tri-Party Agreement) to construct new DSTs to support tank safety resolution and to be reused for future disposal will proceed.

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The two bounding alternative technologies are as follows.

1. **Extensive separations.** In this approach, pretreatment uses yet-to-be developed technologies to separate the tank waste into a small volume HLW fraction and a large volume LLW fraction. The HLW could be processed into glass in a vitrification plant smaller than HWVP. The radionuclide concentration in the LLW fraction would be within (10 CFR 61) Class A limits and would have reduced chemical toxicity.
2. **High-capacity vitrification.** In this approach, pretreatment uses current technologies to separate the tank waste into HLW and LLW fraction. A capacity greater than the currently sized HWVP melter would be required to effectively immobilize the larger volume of HLW. The LLW fraction would meet regulatory requirements, but contain higher radionuclide concentrations than for the extensive separations approach.

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The proposed new technical strategy for processing waste and managing system-generated waste addresses early progress towards disposal by initiating retrieval of supernatant liquids and salt cake. Then, the waste is processed through either distributed compact processing units (CPUs) or the initial pretreatment module (IPM). For the more difficult sludge waste, the two bounding alternative technologies will be developed in parallel until sufficient technical data are available for the decision makers to select a disposal approach. As the two bounding alternative technologies are developed and evaluated, an optimized alternative technology may develop that is in between the two approaches and uses an intermediate level of separations and an appropriately sized vitrification facility. The future of the HWVP will be determined when the total technical path forward is clear enough for decision makers to commit.

The recommended new technical strategy includes public involvement in support of the decision process. This involvement will allow for consensus on the proposed new technical strategy and guide revisions to the *Hanford Federal Facility Agreement and Consent Order*.

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4.0 TREATMENT OF EXISTING DOUBLE-SHELL TANK WASTES

This section documents the studies, activities, and issues that occurred in this area from March 1, 1992, through February 28, 1993.

4.1 INTRODUCTION

Treatment of existing DST wastes is required before permanent disposal (Augustine 1989). The existing treatment strategy is to separate DST wastes into three portions: HLW, TRU waste, and LLW. Ten DSTs will be pretreated to separate the waste into HLW, LLW, and TRU volumes. LLW from seven DSTs has previously been planned to be sent directly to grout disposal as follows: 102-AP (was 106-AN), 105-AP, 106-AP (dilute noncomplexed), 101-AW, 104-AN, 105-AN, and, following retrieval, 103-AN. One may include an eighth tank as 104-AP; however, it is essentially empty. Other dilute noncomplexed wastes contained in 101-AN, 106-AN (nearly empty now that contents have been moved to 102-AP), 101-AP, 103-AP, 107-AP, 108-AP, 102-AW, 104-AW, 106-AW, and 102-AY are either receiver tanks or contain dilute wastes to be evaporated. Other wastes have previously required pretreatment.

Treatment of the separated HLW and TRU waste fractions will consist of vitrification in the HWVP before disposal in a federal geologic repository. Treatment of the LLW currently consists of solidification in cement-based grout before disposal in near-surface vaults at the Hanford Site.

These treatment processes are in various stages of development as discussed below. The planned treatment activities will be discussed according to the waste types of double-shell slurry feed (DSSF), double-shell slurry (DSS), NCAW, NCRW, PFP waste, and CC waste.

The current waste volume inventory of the Hanford Site tank farms as of February 1993 is listed in Table 4-1. This information is available from the *Tank Farm Surveillance and Waste Status Summary Report for February 1993*, WHC-EP-0182-59 (Hanlon 1993). The volumes of both solids and liquids are recorded in cubic meters and thousands of gallons.

Tables 4-1 and 4-2 contain references to designations for waste types other than NCAW (designated as aging), NCRW (designated PN/PD), PFP (designated PT), CC, DSS, and DSSF. The concentrated phosphate (designated CP) waste has previously been planned to be grouted directly. The dilute complexed (designated DC) waste will become CC waste and the dilute noncomplexed (designated DN) will become DSSF or Dilute-DSSF (DDSSF). No plans currently exist to create further DSS by overconcentrating the waste.

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4.2 PLANNED TREATMENT OF DOUBLE-SHELL SLURRY FEED AND DOUBLE-SHELL SLURRY

4.2.1 Definition of Double-Shell Slurry Feed and Double-Shell Slurry

Many streams that enter DSTs consist of dilute liquids low in radioactivity. These streams are so concentrated by Evaporator 242-A that a second pass through the 242-A Evaporator would increase the sodium aluminate concentration past the sodium phase boundary, and the stream would solidify when cooled. At this point the waste is called DSSF. When the DSSF is processed through Evaporator 242-A, the DSSF is concentrated past the sodium aluminate phase boundary. The hot slurry is pumped to a DST where it forms solids as it cools. The waste is then called DSS.

4.2.2 Planned Treatment of Double-Shell Slurry Feed and Double-Shell Slurry

The DSSF will be pumped from DSTs to the Grout Treatment Facility (GTF) for pretreatment to achieve Class A and eventual conversion into grout. The DSS will be treated in the same manner, except for one additional treatment step to remove the DSS solids from the DSTs.

Milestone M-01-01 of the Tri-Party Agreement (Ecology et al. 1990) calls for the completion of three grout campaigns of DST waste. One campaign of phosphate-sulfate LLW has been completed. The following two campaigns will use CP and DDSSF/DN.

Currently, grout treatment of DSSF and DSS will begin when tank space is needed and/or when class A waste is available.

Treatment of DSSF and DSS has been studied in the laboratory as part of the Grout Formulation Program to develop and qualify grout formulae for the solidification of the Hanford Site's DST waste. A formula consists of measured quantities of up to four dry materials (e.g., fly ash, blast-furnace slag, and portland cement), up to three liquid additives, and the LLW liquid waste stream. The dry materials are blended together and then the liquids are added to the solids.

Qualification consists of verifying grout performance as a function of the following expected process variabilities:

- Changes in DSSF and DSS waste composition
- Dry material composition variables
- Changes in dry material storage conditions
- Dry material blending variables
- Variables in the mixing of DSSF and DSS waste with the dry blend
- Variables in grout curing conditions
- Changes in the long-term vault conditions (grout aging).

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Table 4-1. Double-Shell Tank Inventory as of February 1993. (2 sheets)

Tank Number	Waste material ^a	Volume in kgal (m ³)				
		Total waste	Supernatant ^b	DSS	Sludge	Salt cake
101-AN	DN	637 (2,411)	637 (2,411)	0	0	0
102-AN	CC	1,103 (4,175)	1,014 (3,838)	0	89 (337)	0
103-AN	DSS	952 (3,603)	15 (57)	937 (3,546)	0	0
104-AN	DSSF	1,061 (4,016)	797 (3,017)	0	264 (999)	0
105-AN	DSSF	1,127 (4,266)	1,127 (4,266)	0	0	0
106-AN	CP	23 (87)	6 (23)	0	17 (64)	0
107-AN	CC	1,068 (4,042)	934 (3,535)	0	134 (507)	0
101-AP	DN	1,061 (4,016)	1,061 (4,016)	0	0	0
102-AP	DN	1,103 (4,175)	1,103 (4,175)	0	0	0
103-AP	DN	1,132 (4,285)	1,132 (4,285)	0	0	0
104-AP	DN	19 (72)	19 (72)	0	0	0
105-AP	DSSF	822 (3,111)	822 (3,111)	0	0	0
106-AP	DN	1,130 (4,277)	1,130 (4,277)	0	0	0
107-AP	DN	1,116 (4,224)	1,116 (4,224)	0	0	0
108-AP	DN	899 (3,403)	899 (3,403)	0	0	0
101-AW	DSSF	1,148 (4,345)	1,064 (4,027)	0	84 (318)	0
102-AW	DN	809 (3,062)	808 (3,058)	0	1 (4)	0
103-AW	DN/DP	645 (2,441)	282 (1,067)	0	363 (1,374)	0
104-AW	DN	1,123 (4,251)	833 (3,153)	0	179 (678)	111 (420)
105-AW	DN/DP	977 (3,698)	680 (2,574)	0	297 (1,124)	0
106-AW	DN	1,024 (3,876)	728 (2,755)	0	211 (799)	85 (322)
101-AY	DC	923 (3,493)	840 (3,179)	0	83 (314)	0
102-AY	DN	714 (2,702)	682 (2,581)	0	32 (121)	0
101-AZ	AGING	969 (3,667)	934 (3,535)	0	35 (132)	0
102-AZ	AGING	927 (3,509)	832 (3,149)	0	95 (360)	0
101-SY	CC	1,111 (4,205)	21 (79)	530 (2,006)	0	560 (2,120)
102-SY	ON/PT	685 (2,593)	614 (2,324)	0	71 (269)	0
103-SY	CC	748 (2,831)	171 (647)	573 (2,169)	0	4 (15)

^aSee next page for description.

^bIncludes interstitial liquid.

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Table 4-1. Double-Shell Tank Inventory as of February 1993. (2 sheets)

Waste type abbreviation	Waste type	Description
AGING	Aging waste	High-level, first cycle solvent extraction waste from PUREX (NCAW).
CC	Concentrated complexant	Concentrated produce from the evaporation of dilute complexed waste.
CP	Concentrated phosphate	Waste originating from the decontamination of 100 N Area Reactor. Concentration of this waste produces concentrated phosphate waste.
DC	Dilute complexed	Characterized by a high content of organic carbon including organic complexants: EDTA, citric acid, and HEDTA are the major complexants used. Main sources of DC waste are saltwell liquid inventory.
DN	Dilute noncomplexed	Low-activity liquid waste originating from T and S Plants, the 300 and 400 Areas, PUREX facility (decladding supernate, and miscellaneous wastes), 100 N Area (sulfate waste), B Plant, saltwells, and PFP (supernate).
DSS	Double-shell slurry	Waste evaporated almost to its sodium aluminate saturation boundary or 6.5 molar hydroxide in the evaporator. For reporting purposes, DSS is considered a solid.
DSSF	Double-shell slurry feed	Waste evaporated just before reaching the sodium aluminate saturation boundary of 6.5 molar hydroxide in the evaporator. This form is not as concentrated as double-shell slurry.
PN/DP	PUREX decladding	PUREX Neutralized Cladding Removal Waste (NCRW) is the solids portion of the PUREX Facility neutralized cladding removal waste stream, received in tank farms as a slurry. Classified as TRU waste.
PT	PFP TRU Solids	TRU solids from 200 West Area operations.

EDTA = ethylenediaminetetraacetic acid
 HEDTA = hydroxyethylenediaminetriacetic acid
 NCAW = neutralized current acid waste
 PFP = Plutonium Finishing Plant
 PUREX = Plutonium-Uranium Extraction (Plant)
 TRU = transuranic (waste)
 DSS = double shell slurry.

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Grout formulation qualifications for Campaign 102 are expected to be completed in calendar year (CY) 1993.

More recently, the new technical strategy proposes to implement limited pretreatment capabilities to provide suitable feed for the grout disposal of LLW, in order to make available DST space. Early pretreatment will strive to provide feeds to the LLW disposal facility sufficiently free of radionuclides to result in a grout product which meets 10 CFR 61 Class A limits. Processes will focus on DSS, DSSF, and other DST waste. The specific process functions envisioned for this early pretreatment phase are alkaline-side cesium removal and organic /nitrate destruction (DOE/RL 1993). These functions will likely be performed in-tank or within CPUs external to and near the tank. Certain alkaline-side processes (e.g., ion exchange and precipitation) possibly could be used to reduce the content of strontium, technetium, and TRU in alkaline supernates. Additional technologies will be deployed if needed in the near-term for the destruction of organics and nitrates. However, the need for these additional technologies is not clearly established at this time, based on regulatory requirements.

4.3 PLANNED TREATMENT OF NEUTRALIZED CURRENT ACID WASTE

4.3.1 Definition of Neutralized Current Acid Waste

The NCAW is the aqueous high-salt waste from the first-cycle solvent extraction column in the Plutonium/Uranium Extraction (PUREX) Plant. This waste is neutralized to prevent corrosion of the tank farm carbon-steel tanks.

4.3.2 Planned Treatment Process of Neutralized Current Acid Waste

The first step in the proposed treatment process is to separate the solids from the supernatant (Figure 4-1) (Karnesky 1990a, 1990b). Solid-liquid separation has been demonstrated in the laboratory using a settle-decant process (Wong 1989). The solid-liquid separation step has previously been demonstrated in a plant test.

The supernatant liquid stream contains most of the cesium that will be removed by ion exchange leaving a LLW fraction destined for the GTF. Cesium will be eluted from the ion-exchange column and is destined for the HWVP. The solids will be washed and either sent directly to HWVP in the minimum pretreatment strategy or separated further in the extensive pretreatment strategy.

4.3.3 In-Tank Sludge Washing

A major goal in selecting the pretreatment process is to reduce the disposal costs by reducing the volume of waste that must be vitrified and

disposed of in a deep geologic repository. To accomplish this goal, consideration is given to processes that efficiently separate the waste segments into lower cost grout disposal and the much higher cost repository disposal. In-tank washing was evaluated (Place 1991) and determined to be the preferred alternative for this pretreatment, which was incorporated into the tank-waste-disposal strategy (Grygiel 1991). In-tank washing was identified as the minimum pretreatment process in the new technical strategy. In-tank washing of the solids or sludge with water removes soluble salts, which can be decanted to LLW disposal (grout). Another advantage of in-tank washing is that it is a proven technology that can provide early feed to the HWVP without further development. Even if the minimum pretreatment strategy is not chosen, sludge washing of NCAW as well as other wastes will probably be the first step in an extensive pretreatment strategy.

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A study to evaluate alternatives and identify the equipment and cost to implement pretreatment operations (i.e., in-tank sludge washing) for NCAW in aging-waste tanks 241-AZ-101 and -102 has been conducted (Schroeder and MacLean 1993). Tanks 241-AZ-101 and -102 each contain approximately one million gallons of NCAW, which includes about 20 inches of solids settled on the bottom of the tank with additional solids suspended in the liquid supernate by the airlift circulators (ALC). Solids in these tanks can be conveniently separated from associated liquid phases by a combination of gravity settle, decant, and filtration process steps. The settle-decant process provides the bulk separation of solid and liquid phases. The addition of a flocculant either accelerates or improves the settling process. Filtration (e.g., pneumatic hydropulse filtration) can remove finely divided solids from the partially clarified liquid phase. Washing the separated sludge (after initial decanting) with water removes soluble components (e.g., sodium, potassium salts), reducing the amount of waste that must be vitrified. Another cycle of the settle-decant-wash process provides further dilution of the soluble salts. The water wash also removes soluble sulfate ions that interfere with the vitrification process. With respect to the radioactive components, the pretreatment process will allow the TRUs and strontium to settle out of the liquid supernate into the solids below. As previously mentioned, the cesium in the decanted supernate is soluble and must be removed by basic-side ion exchange before the supernate becomes the feed stream for the GTF.

4.3.4 Schedule

The NCAW treatment technology has been demonstrated in the laboratory. Plant-scale testing in vault 244-AR and B Plant was scheduled to begin in October 1993. However, as a result of recent tank waste disposal program redefinition studies in 1991, it was recommended that B Plant, 244-AR vault, and other existing Hanford processing facilities be excluded from further consideration as pretreatment processing facilities because of the high risk in achieving environmental and safety compliance (Grygiel et al. 1991). A revised schedule for pilot plant operations needed to support HWVP melter tests will be developed on the basis of an ongoing tank waste disposal program rebaselining activity which was completed in FY 1993. The development of a revised program baseline responds to the Secretary of Energy's Decision

Statement dated December 28, 1991, to resolve an urgent program need to resolve Hanford tank waste safety issues and to prepare high-level radioactive defense waste for final treatment in grout and borosilicate glass form (DOE 1991).

4.4 PLANNED TREATMENT OF NEUTRALIZED CLADDING REMOVAL WASTE

4.4.1 Definition of Neutralized Cladding Removal Waste

Cladding removal waste (CRW) results from the dissolution of the N Reactor spent-fuel zircaloy cladding using the zirflex process in the PUREX Plant. Neutralization of this waste causes most of the zirconium to precipitate as a hydrated oxide, essentially removing all of the actinides and fission products from the solution. However, sufficient quantities of fine plutonium particles are entrained with the precipitated zirconium that the waste collected in the DSTs is considered to be a TRU waste. The waste sludge and supernate as stored in the DSTs is known as NCRW.

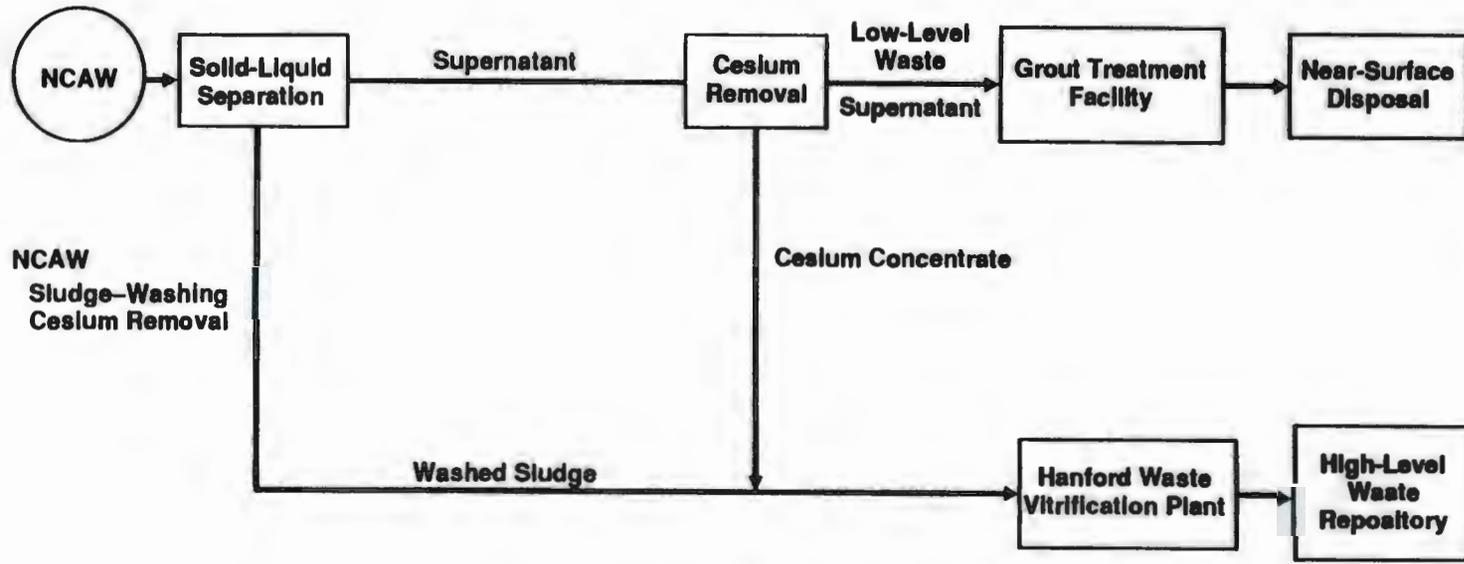
4.4.2 Planned Treatment Process of Neutralized Cladding Removal Waste

A flowsheet has recently been proposed for pretreating NCRW sludge that should meet the overall objectives of separating the TRUs from the bulk sludge components (including uranium), and not introduce additional glass-limiting components into the HLW stream (Lumetta and Swanson 1993a). Although this flowsheet is proposed for pretreating NCRW sludge, it can be easily modified to pretreat other sludges. This flowsheet (Figures 4-2 and 4-3) involves the following steps: (1) sludge washing to remove water-soluble components, (2) dissolution of the sludge in HNO_3/HF , (3) extraction of the uranium with tributyl phosphate (TBP), using what is essentially the PUREX solvent extraction process, and (4) extraction of the TRUs with octyl(phenyl)--N,N-diisobutylcarbamoyl-methylphosphine oxide (CMPO), using the transuranium extraction (TRUEX) process (Horwitz et al. 1985).

The sludge washing and dissolution portions of the flowsheet are shown in Figure 4-2. The sludge is washed four times with 3 volumes of 0.1 M NaOH at ambient temperature. Efficient solid/liquid separation is assumed to be achieved after each wash, so that interstitial liquid occupies 30% of the washed sludge volume. The wash solution will contain approximately 98% of the ^{137}Cs from NCRW sludge (Lumetta and Swanson 1993b), but the amount of this isotope is expected to be low enough that the wash solution can be handled as LLW.

The washed sludge is dissolved in two steps. In the primary dissolution step, water is added to yield a final volume of primary dissolved sludge 5 times greater than the volume of sludge being processed. Then 10 M HF is added to reach a F/(Zr+Al) ratio of 2, assuming all fluoride ion is removed from the sludge in the wash step. Finally, 12 M HNO_3 is added to form a

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NCAW = neutralized current acid waste

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Figure 4-1. Neutralized Current Acid Waste Pretreatment and Disposal.

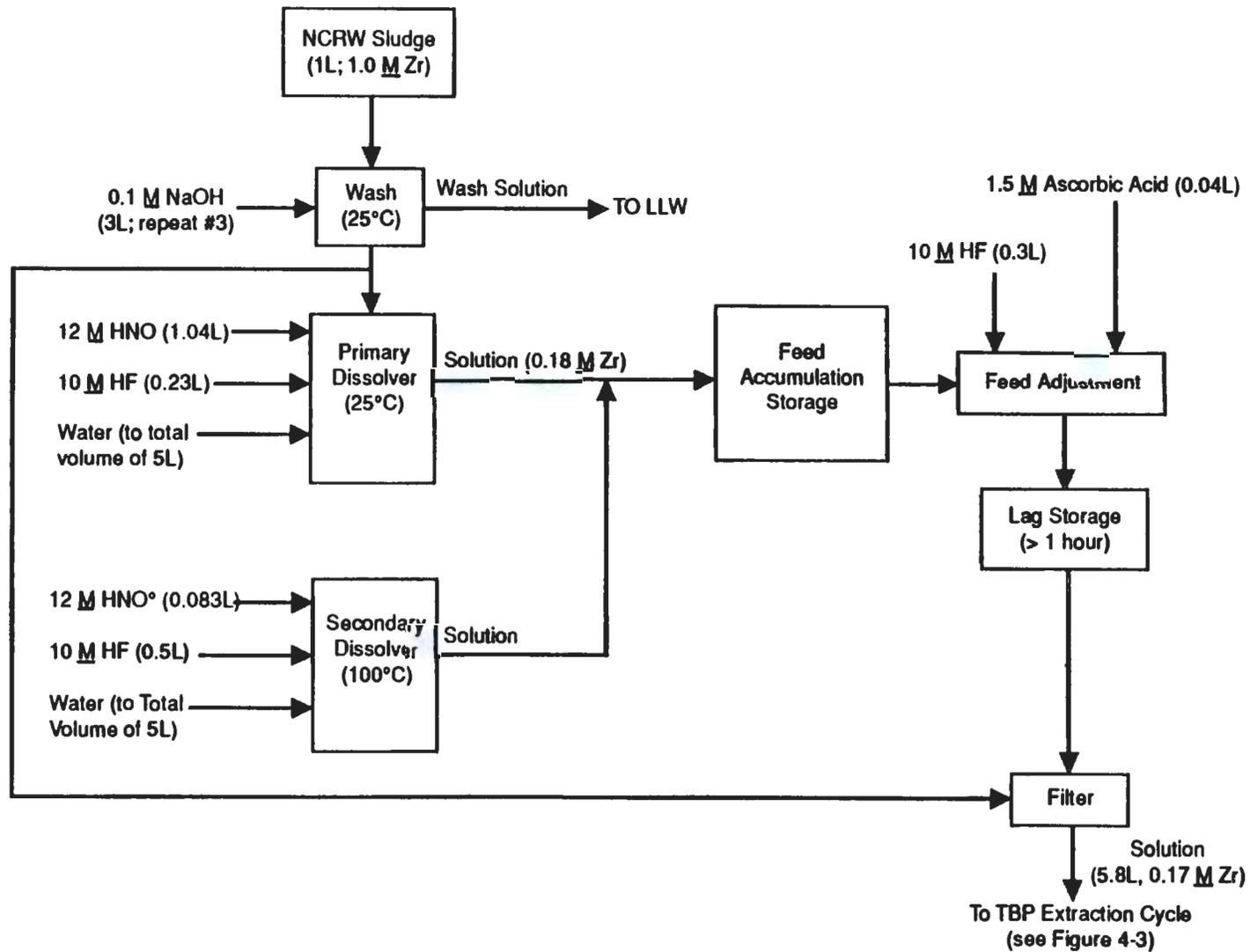


Figure 4-2. Sludge Washing and Dissolution Steps of the NCRW Pretreatment Flowsheet.

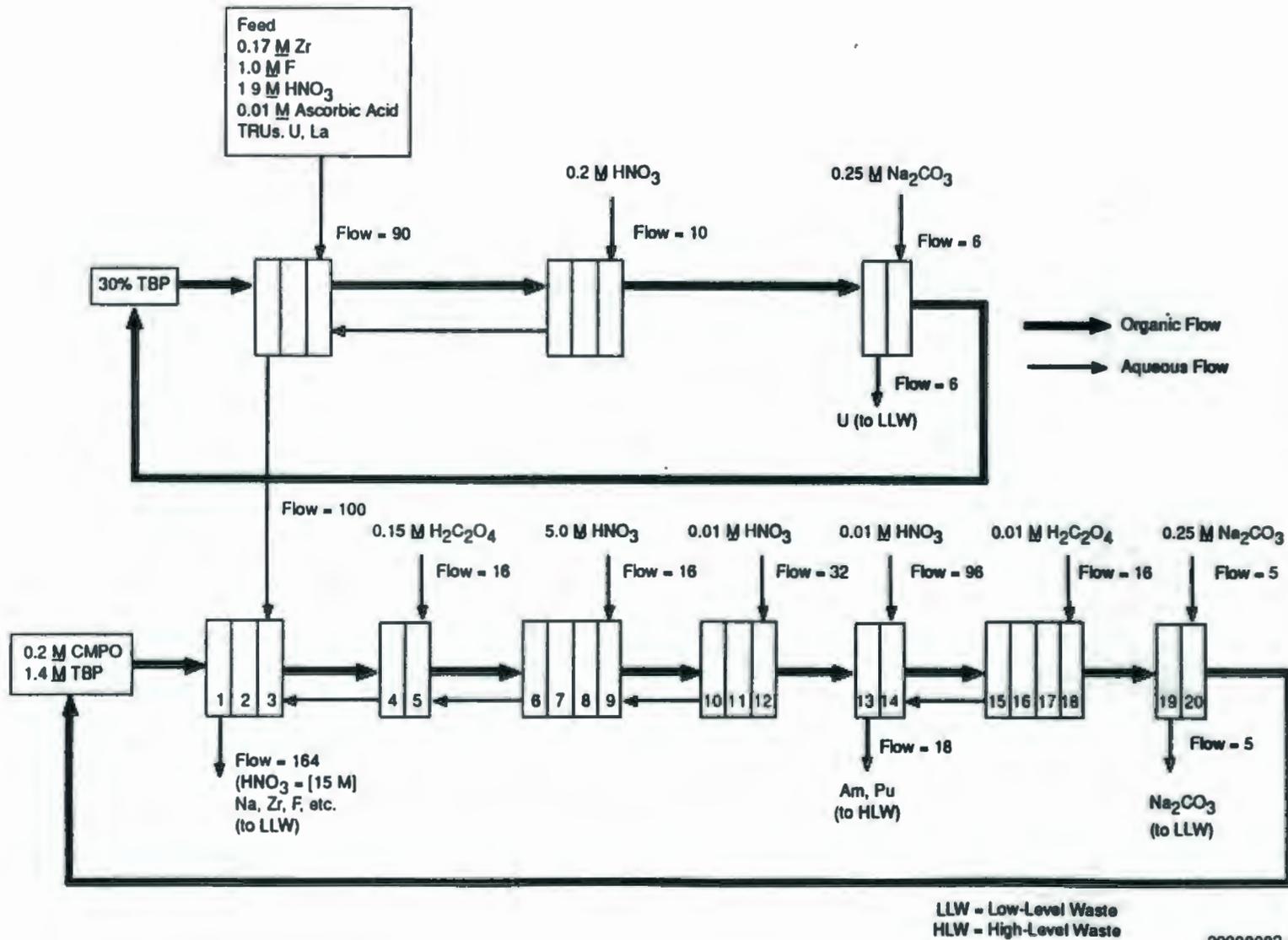


Figure 4-3. TBP and CMPO Cycles for Extraction of Uranium and Transuranics - NCRW Flowsheet.

solution that is 2 M HNO_3 . After several hours at ambient temperature, a solid/liquid separation is performed, and the solids are subjected to a secondary dissolution step.

In the secondary dissolution step, the sludge is treated at 100 °C with a small volume of a solution consisting of 2M HNO_3 and 1M HF. According to laboratory results to date, this treatment should result in complete dissolution of the remaining NCRW solids. Any undissolved solids will be routed to the vitrification facility.

The TBP and CMPO cycles for extraction of uranium and TRUs from the dissolved NCRW sludge are shown in Figure 4-3.

The solutions from the primary and secondary dissolution steps are combined, and HF is added to adjust the F/(Zr+Al) ratio to 5. This feed adjustment prevents formation of interfacial crud, since crud formation was observed at low F/(Zr+Al) ratios in the laboratory CMPO extraction stages and might also be a problem under similar conditions in the TBP extraction stages. Next, ascorbic acid is added to adjust the plutonium valence to +3, so that plutonium is not coextracted with the uranium in the TBP cycle. After the solution is stored for ≥ 1 hour, it is clarified by filtration and then sent through the TBP extraction cycle. Any filtered solids are routed to the primary dissolver to be redissolved.

The TBP extraction cycle consists of three extraction stages, three scrub stages (0.2 M HNO_3) and two strip stages (0.25 M Na_2CO_3). This cycle should extract >95% of the uranium from the dissolved sludge solution, while leaving 100% of the americium and plutonium. Improved extraction could be achieved with additional extraction stages. The uranium is stripped from the TBP solvent with Na_2CO_3 , which also serves to wash the solvent. The uranium is routed to the LLW stream, while the raffinate is routed to the CMPO extraction cycle.

The CMPO extraction cycle consists of extraction, scrubbing, stripping, and solvent washing operations. The extraction and scrubbing operations involve three extraction stages, two scrub stages using 0.04 M $\text{H}_2\text{C}_2\text{O}_4$ + 1.2 M HNO_3 (to scrub out Zr), four scrub stages using 1.7 M HNO_3 (to scrub out $\text{H}_2\text{C}_2\text{O}_4$), and three scrub stages using 0.01 M HNO_3 (to lower the HNO_3 content). The stripping and solvent washing operations involve two strip stages using 0.01 M HNO_3 , four strip stages using 0.01 M $\text{H}_2\text{C}_2\text{O}_4$, and two solvent wash stages using 0.25 M Na_2CO_3 . The relative flow rates for each stream are shown in Figure 4-3. The dilute HNO_3 strip removes the trivalent actinides and lanthanides from the CMPO solvent, while the dilute $\text{H}_2\text{C}_2\text{O}_4$ strip removes any Pu(IV) that might be present. In this step, the $\text{H}_2\text{C}_2\text{O}_4$ was chosen rather than 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) to avoid adding phosphorus to the HLW stream (Horwitz et al. 1985). With the high concentration of lanthanum in the NCRW sludge, lanthanum oxalate may potentially precipitate in the strip stages (i.e., stage 13, Figure 4-3). If this were the case, the aqueous phase from stage 15 could be collected as an effluent rather than be fed into stage 14 or the 0.01 M $\text{H}_2\text{C}_2\text{O}_4$ solution can be replaced with 0.0001 M HEDPA at this point in the process without causing production of additional HLW glass canisters.

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Workers at Argonne National Laboratory (ANL) recently have suggested that 2,3,4,5-tetrahydro-furantetra-carboxylic acid (THFTCA) could be used to strip the TRUs from the process solvent, without stripping uranium at the same time. Thus, the uranium could be separated from the TRUs without using a TBP extraction cycle. However, results obtained with THFTCA by workers at PNL have not been as encouraging as those obtained by workers at ANL. This may be caused by differences in this material from lot to lot. Further development work is needed on this and other potential stripping agents to gain confidence that they will selectively strip TRUs from the TRUEX process solvent.

4.4.3 Schedule

In FY 1991, pilot plant tests with NCRW were scheduled through FY 1996. Operation of the full-scale TRUEX process using a NCRW feed currently is being studied and a revised schedule will be issued in 1993 to reflect the results of the previously cited program rebaselining effort. However, a laboratory design basis experiment (DBE) will be performed to test the NCRW flowsheet described in the preceding section in FY 1993 using actual NCRW sludge.

4.5 PLANNED TREATMENT OF PLUTONIUM FINISHING PLANT WASTE

4.5.1 Definition of Plutonium Finishing Plant Waste

The PFP waste, stored in tank 241-SY-102 on the Hanford Site, originates from the conversion of plutonium nitrate to oxide or metal and includes TRU laboratory wastes. The PFP waste also includes Plutonium Reclamation Facility (PRF) waste consisting of high-salt solvent extraction waste and organic wash waste. Because the quantities of plutonium and americium in the PFP sludge are greater than 100 nCi/g, this sludge must be classified as a HLW. Approximately 6,000 glass canisters would result from vitrifying this waste directly. Sludge washing would reduce the required number of glass canisters to about 2,500 with the volume of glass being driven by the allowable concentration limit for chromium in the HWVP feed. Thus, an economic incentive exists to develop methods of pretreating the sludge to reduce the number of glass canisters needed to contain the final vitrified product.

4.5.2 Planned Treatment Process of Plutonium Finishing Plant Waste

Two approaches to pretreating the PFP sludge are being investigated: (1) selective leaching of chromium from the sludge and (2) dissolution of the sludge by separating the TRU elements with CMPO using the TRUEX process (Lumetta and Swanson 1993b).

The chromium leach approach offers the advantage of greater simplicity. Although a detailed analysis of the impact of this pretreatment option has not

yet been performed, it is estimated that about 1,250 HLW glass canisters would be produced if chromium is removed from PFP sludge. The number of HLW glass canisters can be further reduced to about 700 if the phosphorus and sulfur also are removed from the sludge. Removal of aluminum from the sludge would result in a further reduction of HLW glass canisters.

In the laboratory tests and analyses conducted by PNL workers from October 1990 to March 1992 on PFP sludge samples, it was found that 20 to 34 percent of the chromium present exists as Cr(VI), which can be removed from the sludge by washing with water or dilute sodium hydroxide. Most of the remaining insoluble chromium can be converted to Cr(VI) by treatment with alkaline permanganate solution. If the leach with KMnO_4 is done at room temperature, approximately 85 percent of the chromium can be removed from PFP sludge; up to 96 percent of the chromium can be removed if the leaching operation is done at 100 °C. In addition, if the sludge wash (with 0.1 M NaOH) and chromium leach are done at 100 °C, 99 percent of the Al and 100 percent of the P present in the PFP sludge can be removed. The latter two elements become significant in terms of the number of HLW glass canisters required to vitrify the PFP sludge if the Cr is removed. This approach may compete economically with the acid dissolution/TRU solvent extraction approach in reducing the number of glass canisters required to vitrify the PFP sludge. Currently, no development work is underway to remove sulfur from this waste.

Although excellent results have been achieved in the chromium leach studies, additional development is required before this process can be implemented. In particular, the TRU content of some of the sludge wash solutions has exceeded the current Class C limits (10 CFR 60) for disposal of aqueous waste in grout. Further work will be required to ensure that these solutions are non-TRU.

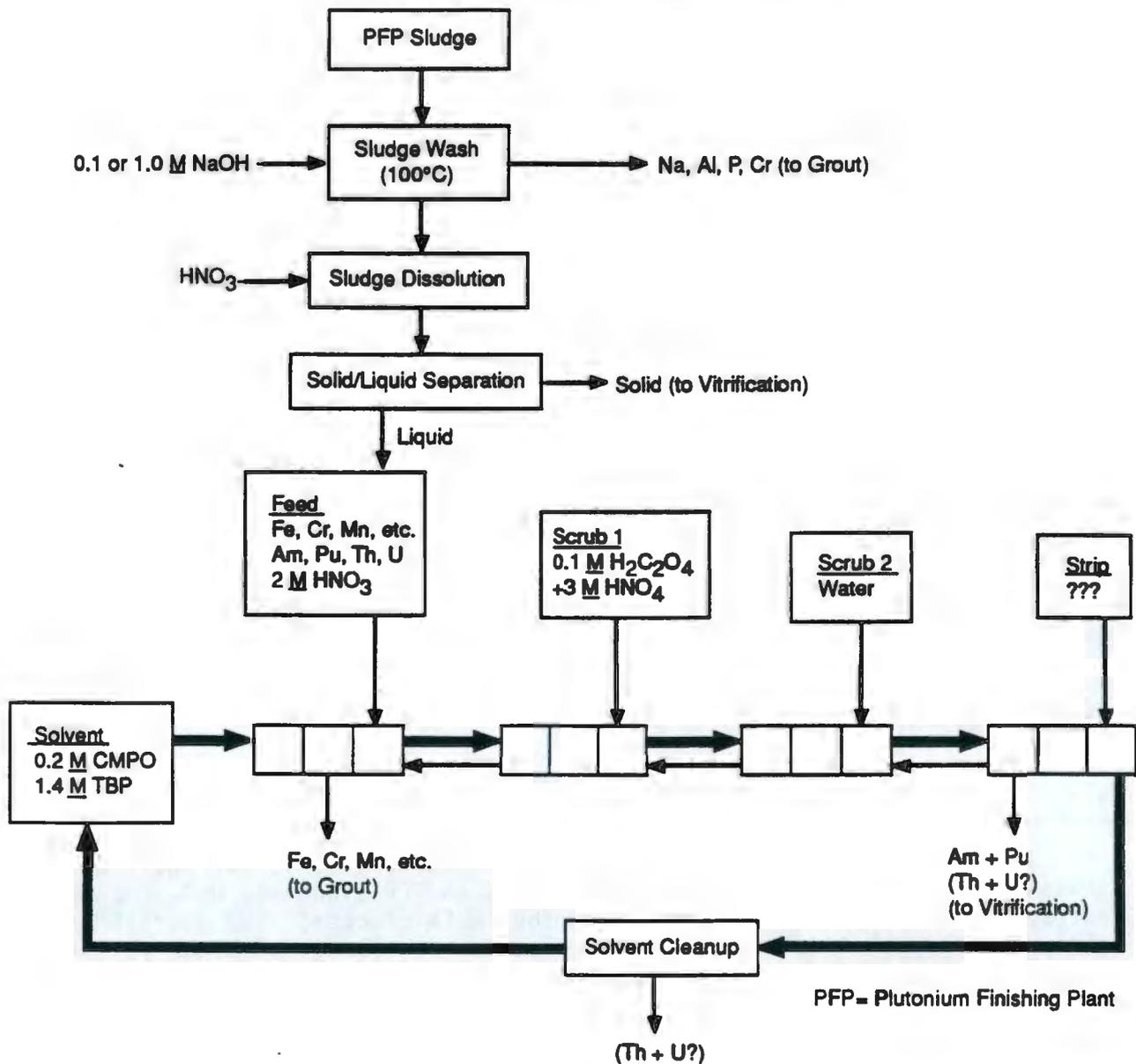
Furthermore, if the Cr leach approach is pursued, the leach solution itself would constitute a LLW which must be disposed in grout.

The second approach for pretreating PFP sludge that is currently being investigated involves dissolution of the washed PFP sludge in HNO_3 and then extraction of the TRUs with CMPO using the TRUEX process. The overall process (Figure 4-4) will involve the following steps: (1) sludge washing, (2) sludge dissolution, and (3) extraction of the TRUs with CMPO.

Good dissolution of the washed PFP sludge in dilute (2 to 3M) nitric acid has been demonstrated; for most sludge components, greater than 90 percent dissolution was achieved. Solvent extraction experiments have indicated that the TRUs (i.e., plutonium and americium) can be extracted from the dissolved sludge to low levels, with adequate decontamination factors easily achievable. If the PFP sludge is dissolved and the TRUs separated by solvent extraction, it is estimated that about 150 canisters of glass would be produced in the disposal of the PFP sludge.

In some initial tests, long phase disengaging times were observed, which could cause problems in the solvent extraction equipment. However, adding complexants (e.g., oxalic acid or acetohydroxamic acid) seems to overcome this problem without seriously affecting the efficiency of the TRU extraction.

Figure 4-4. Plutonium Finishing Plant Waste Pretreatment Conceptual Flowsheet.



PFP = Plutonium Finishing Plant

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Also, heating the dissolved PFP sludge solution (then allowing it to cool to ambient temperature prior to the solvent extraction contact) leads to improved phase disengagement behavior.

Thus, the two pretreatment options for PFP sludge investigated, chromium leaching and TRU solvent extraction, both show promise for reducing the volume of borosilicate glass required to vitrify this waste. Further investigations of these two options are planned.

4.5.3 Schedule

In FY 1991, pilot plant testing of the PFP waste treatment flowsheet using the TRUEX process was scheduled for FY 1997. However, the current tank waste disposal rebaselining activity will develop updated schedules for the PFP waste treatment laboratory, bench-scale, and pilot plant analysis and testing in FY 1993.

4.6 PLANNED TREATMENT OF COMPLEXANT CONCENTRATE WASTE

4.6.1 Definition of Complexant Concentrate Waste

Complexant concentrate waste results from concentration of wastes containing large amounts of organic complexing agents. These organic compounds were introduced to the waste during strontium recovery processing in B Plant. This waste contains complexants such as ethylenediaminetetraacetate (EDTA), hydroxyethylenediaminetriacetate (HEDTA), nitriloacetate (NTA), and citrate; also present are degradation products of these complexants. Because of these complexants, certain ions, including Fe^{3+} , Sr^{2+} , and TRUs, are in solution that would have otherwise precipitated under the alkaline conditions present in this waste. The effects of these complexants on separation processes are not fully known. Because most radionuclide separation processes are driven by complexation phenomena, it is expected that the presence of complexants hinders rather than enhances separations. Also, CC waste is one of the more voluminous of the Hanford Site DST wastes currently considered to require pretreatment. For these reasons, CC waste has been chosen as the subject of an ongoing and continuing series of exploratory studies. Many of the chemical separation processes successfully used for CC waste will likely be applicable to other Hanford Site wastes.

4.6.2 Planned Treatment Process of Complexant Concentrate Waste

During 1991, the goal of treatment was given the added scope to resolve the safety issues of watch list tanks by destroying organics and ferrocyanides. Two of the watch list tanks (101-SY and 103-SY) are complexed wastes in DSTs. Because the resolution of safety issues has priority over preparing grout and glass feeds, these tanks will be treated first by destroying the organics using one of several oxidation processes currently being evaluated. After removing cesium from the liquid phase of the oxidized

waste, the remaining liquid is a candidate for grouting. The sludge may undergo further pretreatment. The extent of the pretreatment has not yet been determined.

Figure 4-5 summarizes three possible scenarios for the pretreatment of the CC waste. The first step in Option I is the destruction of the complexants under alkaline conditions, which would result in the precipitation of the TRUs and ^{90}Sr . After removal of ^{99}Tc and ^{137}Cs , the supernatant solution might qualify as Class A LLW. The precipitated solids and the solids originally present are dissolved and the various radionuclides (TRUs, ^{90}Sr , ^{137}Cs , and ^{99}Tc) are separated. Toxic metals such as chromium might also be removed from the LLW stream before nitrate separation/destruction. Option II involves the separation of the CC supernate from the solids. The alkaline supernate is treated to remove TRUs, ^{90}Sr , ^{137}Cs , and ^{99}Tc . The complexants are then destroyed and nitrate ion removed or destroyed. The solids are dissolved and treated much the same as those in Option I. Option III involves direct acidification of the CC supernate/solids mixture to dissolve the solids. TRUs, ^{90}Sr , ^{137}Cs , ^{99}Tc , and possibly toxic metals are removed, then the complexants are destroyed and nitrate is removed or destroyed.

Possible technologies for each required separation appear in Figure 4-5. This information is not exhaustive, but serves as a guideline to identify those areas where established separation methods are not available. These areas are identified by bold boxes in Figure 4-5. Recent work has focused on five separation problems: separation of (1) Cs from acid solution, (2) Tc from acid solution, (3) TRUs from alkaline solution, (4) Sr from alkaline solution, and (5) Tc from alkaline solution. In addition to these separation problems, the problem of dissolution of CC waste solids has also been recently studied (Lumetta et al 1993a).

A conceptual flowsheet based on the work performed in recent studies is shown in Figure 4-6. The first step on the flowsheet is separation of the solids and liquids. Then, the process splits. The processes on the left side of the flowsheet are performed on alkaline supernate; the processes on the right side, on acidified waste. There are two advantages in splitting these processes. First, direct acidification of the CC waste to dissolve the solids (Option III, Figure 4-5) would greatly increase the volume of the LLW remaining after the separation of the radionuclides and reneutralization (for interim storage in carbon steel tanks). Second, the large quantities of sodium present in the supernate interfere with the radionuclide removal efficiency of some of the acid-side separation processes.

As illustrated on the left side of the flowsheet (Figure 4-6), methods were identified for removing cesium, plutonium, and technetium from the alkaline wastes. Two materials, one an organic (resorcinol-formaldehyde) resin (BSC-187) and the other a titanium-loaded zeolite (TIE-96), provide for removal of the cesium and Pu from the supernate. These materials could be vitrified directly. Essentially, the organic resins could be burned in the melter, although modifications to the construction and operation of the melter would be required. The loaded zeolite resin could more readily be vitrified with the existing design, but might result in a significant number of glass canisters being produced. Technetium could be removed from the alkaline liquid either with zeolite loaded with TCMA (TIE-96A) or by solvent extraction methods. Technetium tends to volatilize during vitrification, but a recycle

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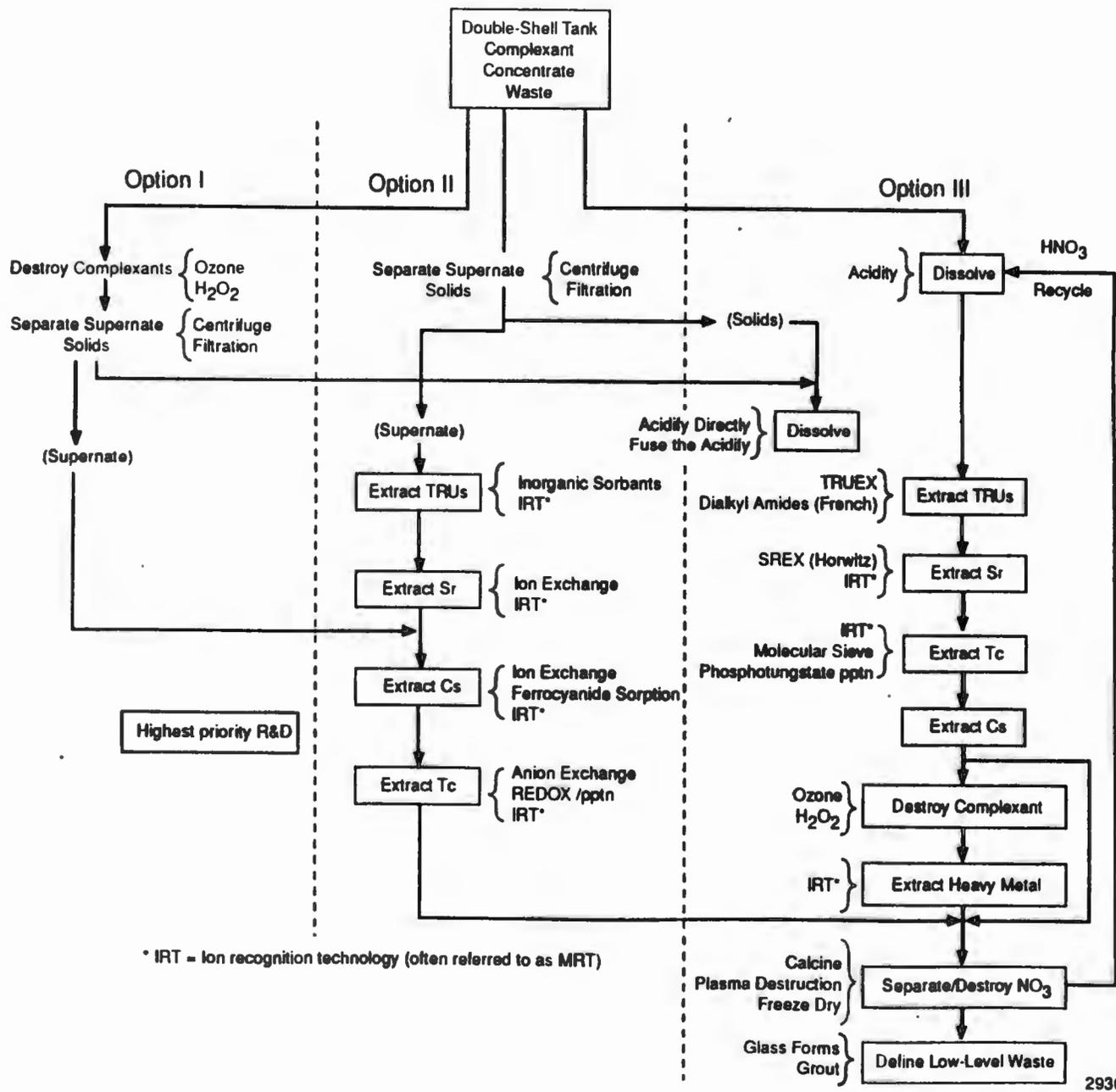


Figure 4-5. Options for Pretreatment of Complexant Concentrate Waste.

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HWVP = Hanford Waste Vitrification Plant
 TRUEX = Transuranium Extraction
 SREX = Strontium Extraction

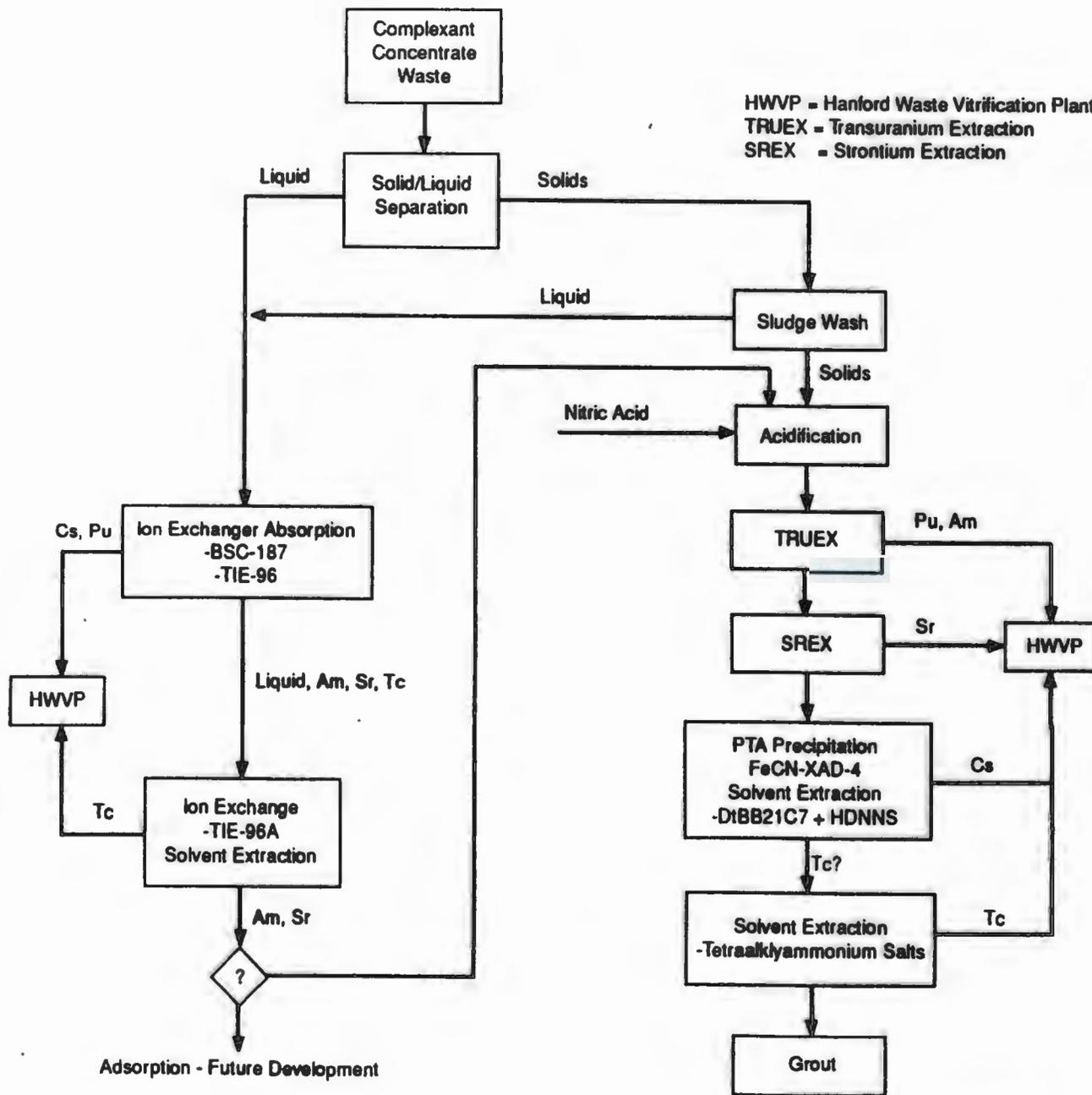


Figure 4-6. Conceptual Processing Flowsheet for Complexant Concentrate Waste.

stream from the off gas back to the feed would allow the concentration of technetium to build up in the feed stream so that it can be satisfactorily loaded in the glass. Methods have not been identified to remove complexed americium or strontium from alkaline liquids.

Promising methods were identified for removing all of the radionuclides of interest from the acidic dissolved sludge solution (right hand side of Figure 4-6). The TRUEX and the strontium extraction (SREX) solvent extraction processes are suitable for removing plutonium, americium TRUEX, and strontium SREX, although SREX might not remove ^{90}Sr to a level acceptable for Class A LLW criteria. These processes have the potential to remove technetium, but results obtained recently by PNL workers with actual CC waste indicate that technetium is not extracted by TRUEX or SREX (Lumetta et al. 1993d). Removal of technetium, if necessary, could be achieved by solvent extraction using tetraalkylammonium salts or possibly tertiary amine extractants. Cesium can be removed by precipitation with phosphotungstate or sorbed onto Amberlite XAD-4 impregnated with FECN-XAD-4 (providing adequate removal of sodium by sludge washing has been achieved). Also, it may be possible to remove cesium by solvent extraction using dibenzo-21-crown-7 (DtBB21C7) and didodecyl-naphthalenesulfonic acid (HDNNS) in a suitable diluent.

Given the lack of suitable technologies for removal of complexed americium and strontium from alkaline solution, the best approach at present for removal of these radionuclides appears to be acidification of the entire CC waste followed by the use of the TRUEX and SREX processes (Lumetta et al. 1993a).

4.6.3 Schedule

In the FY 1991 tank waste treatability report (Giese 1991), pilot plant testing of the CC waste treatment process was scheduled for FY 1997 through FY 1999. However, a new schedule was being developed in 1992 to reflect the results of the ongoing rebaselining activities. The full-scale processing schedule for CC waste also is currently being reviewed to evaluate the impact of cesium removal from the low activity portion of the treated waste on the overall treatability of CC wastes.

4.7 SUMMARY OF TANK WASTE TREATMENT

Although this section has been included under the DST chapter, it is applicable to the SST and DST. A national technology workshop was held in June 1992 as part of the TWRs technology planning efforts. During this workshop, a pretreatment technology working group (TWG) met to identify, evaluate, and prioritize candidate technologies in a systematic manner, as was done by each of the other TWRs program elements (i.e., waste tank safety and operations, characterization, retrieval, LLW waste immobilization and disposal, and HLW immobilization). This process, the working participants, and the results are summarized in the *Proceedings* from the workshop, *TWRs National Technology Workshop* (DOE-RL 1992). Nine pretreatment systems were presented to the TWG, which had previously been evaluated on the basis of cost, schedule, and institutional acceptance. The TWG identified functional needs, which are specific capabilities required to implement a pretreatment

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system, and evaluated on the basis of centrality to the system, uncertainty reduction, urgency, and enhancement potential. Then, the known technologies were identified for each functional need and evaluated on the basis of needs met, technical feasibility, schedule compatibility, and cost.

A Pretreatment Technology Plan (Barker 1993), based on the results of the workshop and other working group meetings, was developed that is applicable to both DST and SST waste pretreatment. The plan identifies the objectives for waste pretreatment processes, evaluates the pretreatment systems to satisfy those objectives, determines the functional needs for each system, and prioritizes the technologies for each of the functional needs.

4.7.1 Pretreatment Strategies Options

Several options are being evaluated for disposal of the DST and SST wastes to establish the preferred program. These options include pretreatment processes ranging from minimal separations of the HLW and LLW to advanced separation processes that dramatically reduce the volume of HLW and LLW produced and/or reduce the chemical toxicity of the LLW. Each of the options described below addresses one or more pretreatment objectives.

- **Developed (or Minimum) Pretreatment Technology System.** This option incorporates sludge washing and cesium ion exchange to remove the bulk of the nonradioactive elements soluble in a basic solution from most radioactive elements, which are insoluble in basic solution. Destruction of organics and ferrocyanides to resolve tank safety issues is also included. This option incorporates blending of waste streams to minimize the volume of HLW and to minimize the number of unique feed types to the HWVP. Sludge washing, cesium ion exchange, organic/ferrocyanide destruction, and blending are included in all waste tank options. This option produces approximately 38,000 HLW canisters 0.6 m (2 ft) diameter by 3.05 m (10.5 ft) long and 180 grout vaults.
- **Draft Reference Pretreatment System.** This option includes the minimum pretreatment technologies and adds sludge dissolution followed by TRU and strontium removal. These processes are based on acid dissolution of the metal hydroxide sludge followed by TRU and strontium extraction. This increases the LLW fraction while reducing the volume of HLW. Several process options are candidates to provide these more aggressive separations, although a development program is needed to investigate and select the appropriate processes. This option would be deployed in phases to resolve tank safety issues as a priority and to bring mature technologies online in the near term, while required technology development activities are completed. This option produces approximately 11,000 HLW canisters and 270 grout vaults.
- **Extensive Pretreatment with Material Recycle (CLEAN).** The CLEAN option uses technology requiring extensive research and development to provide minimum volumes of HLW and LLW by destroying and/or separating many of the components not treated by the first two

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options. Sludge dissolution, organic destruction, and advanced radionuclide extraction are the basic processes. Extensive chemical recovery and recycling are added to avoid generating additional chemical waste to the LLW stream.

The TWRS pretreatment strategy also includes possible deployment of several different facility options, which include the following.

- **In-Tank Processing.** Some pretreatment operations will be conducted in new or existing DSTs (see Section 4.3.3), thus minimizing the extent of the need for new operating facilities. This would require new equipment to support the processing and could require waste retrieval and transfer between tanks.
- **Compact Processing Unit.** CPUs are modular systems targeted to accomplish a single function and would be located in the vicinity of the tank (or tank farm) being remediated. This concept currently is being evaluated for the removal of cesium from DSS/DSSF feed to the grout facility. However, other CPUs could be deployed as standalone production facilities if the CPU concept proves feasible and offers cost and/or schedule advantages over the reference approach.
- **Large, Centralized Pretreatment Facilities.** Many processes, because of their complexity and/or needs to treat large volumes will have to be deployed in new, centralized treatment facilities. Two types of Central facilities are being considered for deployment:
 - **Initial Pretreatment Module (IPM).** Initial pretreatment targeted at resolving tank safety issues (i.e., organic/ferrocyanide destruction) may be conducted in a new modular facility, which could be deployed on a faster schedule than a new radiochemical processing facility (i.e., a canyon-type facility). Decisions may be made to include other process functions, such as cesium ion exchange, in the IPM.
 - **New Pretreatment Facility (NPF).** Processes will be deployed in a new pretreatment facility when (1) significant development work is required before deployment and/or (2) the processes are not suitable for operations in a modular facility because of their complexity. This would be the last pretreatment facility to be deployed and would require the greatest capital expenditure. The scope depends on the pretreatment processes selected and the feasibility of the other processing options.

4.7.2 Pretreatment Technology Program Development

As a result of the pretreatment program planning activities discussed in Section 4.7.1, a technology development program has been identified (Barker 1993). Planned activities by functional need for each of the identified pretreatment systems are presented in this section for FY 1993 and beyond.

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4.7.2.1 Reference Technology. The reference pretreatment system comprises a three-phased deployment strategy. The first phase consists of organic/ferrocyanide destruction to mitigate tank safety concerns, sludge washing, and cesium ion exchange. The second phase adds tank blending and selective leaching of the sludge. The third and final phase adds sludge dissolution and TRU and strontium extraction. The technology development program for each of these functions is summarized below.

Sludge Washing. Sludge washing is the minimal pretreatment that can be done on any tank sludge. It is expected that sludge washing will be performed on the sludge from each Hanford Site tank, except for CC sludges. Sludge washing is defined as mixing the sludge with raw or inhibited water (dilute sodium hydroxide and sodium nitrite added), then separating the undissolved solids from the wash liquor.

The primary benefit of sludge washing will be a reduction in the volume of HLW. Sludge washing will remove the soluble components (e.g., NaNO_3 , NaNO_2 , and NaOH) from the sludge. Included in the soluble portion of the sludge and salt cake is a large fraction of the ^{137}Cs . Necessary information to be determined includes the disposition of various radionuclides in the washed solids and the wash liquor phase. This information will be used to determine what additional processing will be needed to minimize glass canister production in the HWVP.

Additional processing concerns to be addressed include, evaluation of solid-liquid separation, measurement of natural settling rate, evaluation of safety issues, such as the effect of turning off the airlift circulators on heat generation in the aging waste tanks.

The washed sludge could be handled in one of three ways.

- Vitrify
- Subject to some form of intermediate processing (e.g., aluminum leaching, chromium leaching, and TRU leaching)
- Dissolve in acid and subject to an advanced pretreatment process (e.g., TRU extraction and strontium extraction).

The option chosen will depend on the final program strategy.

A secondary benefit of sludge washing is the removal of nitrite ion. The presence of nitrite ion in the sludge would lead to NO_x generation when the sludge is dissolved in acid or when heated in the vitrification process. The removal of nitrite by sludge washing would eliminate NO_x generation during those processing steps. Also, removal of carbonate ion by sludge washing would eliminate foaming associated with the release of CO_2 during acid dissolution.

Additional work scope included under sludge washing involves the development and testing needs for performing sludge wash operations. Equipment to be tested/developed includes interface monitoring equipment for evaluation of settling progress, and an online TRU monitor for continuous

monitoring of the alpha activity within the supernate liquors. Additionally, methods of improving solids settling by controlling crystallization will be investigated.

Finally, a pilot-scale facility will be constructed and operated to produce 150-kg samples of washed sludges for HWVP waste form qualification feed. This facility will then be operated for the duration of the tank waste remediation program.

In previous years, testing of individual sludges has been performed to determine separation factors for the various components. This testing has been limited to the small (approximately 2-gm) samples of tanks previously cored. This information is limited and continued testing of this material is warranted and planned. Additional testing of small samples has been performed in conjunction with acid-dissolution studies. These tests also included monitoring of solids settling rates and the effect of dilute sodium hydroxide on settling rates.

Previously, a device to continuously measure the concentration of TRUs in the sludge liquor was constructed and tested. A full-scale TRU monitor has also been constructed and operated to determine the proper internal configuration for good liquid and solids flow. Final testing is to be performed in conjunction with large-scale washing operations to test a full-size TRU monitor with aging-waste material (i.e., NCAW).

Cesium Removal by Ion Exchange. The separation of alkaline supernatant liquids, washing of HLW sludges, and retrieval of tank wastes will generate liquid containing radioactive cesium (^{137}Cs). Before disposal in grout, these liquids could be treated at the IPM, for example, by exchange to remove the majority of the cesium. Extensive studies to characterize the equilibrium behavior of selected ion exchange media over a wide range of conditions have also been completed. The remainder of the ion-exchange technology program entails defining, verifying, and recommending an ion exchange process for the IPM through laboratory-scale column studies, ion-exchange resin stability studies, and pilot-plant process demonstrations.

The concentration of liquid wastes processed through the IPM ion-exchange system will vary. Some feeds could be full strength supernatant liquors decanted directly from the tanks; other feeds will include wash waters that could vary widely in concentration. Variations will also occur in the relative concentrations of cesium and significant constituents (Na, K, Rb, hydroxides) from one type of waste to another. These and other independent variables that affect the performance of ion-exchange columns need to be characterized to support the design and subsequent operation of the ion-exchange system.

In previous years, screening studies were conducted to identify ion exchangers for use in B Plant for the pretreatment of NCAW supernate and wash waters. The selection criteria were a high capacity for cesium in the presence of a high concentration of sodium and a reasonable stability in a harsh radioactive and chemical environment. Those screening studies narrowed the choices to a Rohm and Haas phenolic resin (CS-100) and a Savannah River Technical Center-developed resorcinol resin.

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During FY 1992, an extensive test program was started to quantify the equilibrium behavior of the above resins. These tests established the equilibrium capacity of the resins under a wide range of concentrations and over the temperature range that would be encountered during processing. For the sake of comparison, identical tests with an inorganic exchanger (IE-96) were completed at the same time. Although IE-96 is the ion exchanger in use at the West Valley Demonstration Project, it is not in contention for use at the IPM because it is unstable in Hanford Site highly alkaline waste solutions.

Approximately 500 experiments were completed with CS-100 and the resorcinol resin. The primary conclusions of the FY 1992 work were that (1) the ion-exchange capacity of CS-100 and IE-96 doubles over the temperature range from 40 to 10 °C, while the capacity of the resorcinol resin improves only slightly; (2) the capacity of the resins for cesium correlates with the total sodium and equilibrium sodium-to-cesium ratio; (i.e., capacity in simulated NCAW and simulated CC waste were found to be the same, implying that generic ion-exchange data can be applied to a broad range of waste types); and (3) that the capacity of the exchangers has the following order: resorcinol > IE-96 > CS-100, although the difference in capacity diminishes as the sodium/cesium ratio diminishes. The interference effects from potassium and rubidium were only partially characterized in these experiments.

The studies being conducted during FY 1993 include a bench-scale column-loading study to define the breakthrough behavior of selected ion-exchange resins with emphasis on the operation of a multiple-column system and establishing the "maximum" volumetric throughput for the subject resins. In FY 1993 or FY 1994, in conjunction with the loading studies, there also will be experiments to optimize and verify the conditions for elution and regeneration of the columns. A study of the effects of radiation on two resins produced by Boulder Scientific Co. (resorcinol-formaldehyde polymer) and the Rohm and Haas Co. (CS-100) also will be completed. This study will examine the degradation of resin performance, the gas releases during irradiation, the water-soluble organic degradation products, the corrosive effects during irradiation, and a comparison of results for irradiation that occurs under both static and flow conditions.

In addition to the above laboratory- and bench-scale work, preparations for an ion-exchange pilot plant will be initiated in FY 1993. This will include a task to document the objectives of a pilot plant and an assessment of pilot plant facilities that are available within the DOE complex. By the end of FY 1993, a decision will be made on the course of action (e.g., pilot plant at PNL versus SRTC) and documentation of the functions and requirements for the pilot plant.

Organic/Ferrocyanide Destruction. Problems associated with those classes of tanks considered to have the highest safety risks (i.e., explosive gas generating tanks, organic tanks, and ferrocyanide tanks) could be lessened dramatically if the organic or ferrocyanide constituents of the waste could be destroyed or removed. Near-term processing to accomplish this destruction or removal may be needed to ensure continued safe storage of these wastes until final disposal process operations can be initiated. However, the scope of the organic destruction requirement currently is not well understood, nor are the technologies that can accomplish the eventual objectives well developed.

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Thus, the present objective of this task is to evaluate and develop organic destruction technologies to be incorporated into the IPM or, possibly, into a standalone CPU. Ensuring that the organic destruction process selected meets the current grout feed specification of 1,500 ppm organic carbon is a technical concern. Unless destroyed before grouting, organic complexants may greatly facilitate unacceptable transport of radionuclides or toxic metal leached from the grouted waste to the environment. Certain organic compounds also may be listed as hazardous constituents.

Laboratory studies will be conducted on selected technologies to provide data necessary to narrow technology choices. The tasks include establishing testing standards, and performing preliminary laboratory tests with actual wastes (based on the contents of an organic and a ferrocyanide watch list tank), and preliminary laboratory tests with actual wastes (from both an organic and a ferrocyanide watch list tank). Based on the results of these studies, a pilot plant will be designed and built for one or more of the selected technologies. Operation of the pilot plant on actual Hanford Site tank waste will support IPM goals by providing data for operation and full-scale IPM design that cannot be obtained by tests of waste simulants. Data will be collected and compared to batch and cold pilot plant data in the areas of chemical kinetics, element phase distribution, offgas composition, destruction efficiencies, and safety.

A separate composition variability study is being conducted by Grout Technology. The available grout formulas and validated core sample data will be used to develop a formulation for grouting treated wastes. This study will determine the effects that treating simulated and actual watch list tank waste will have on grout quality.

A technology plan was developed and implemented in FY 1993. Some of the preliminary laboratory work has been performed and will be discussed in greater detail in the Section 5.0, Treatment of Existing Single-Shell Tank Wastes.

Selective Leaching of Sludge. It is expected that advanced sludge pretreatment processes, such as the TRUEX process, will not be available until approximately 5 to 10 years after the startup of HWVP. Thus, there is a possibility that gaps may occur in the feedstock for the HWVP before startup of a second pretreatment module (SPM). Selective leaching processes may be implemented on certain wastes (e.g., CC wastes) to provide continuity of the feed to HWVP if a gap occurs between the feeds provided by sludge washing and the startup of the SPM. Leaching processes are not expected to reduce the HLW volume to the extent advanced pretreatment methods will, but they may be easily implemented in the IPM at modest cost. The costs of performing such processes may be offset by the cost of having IPM idle from lack of feed.

Two general types of leaching methods are currently being considered (1) leaching of nonradioactive components (e.g., aluminum, silicon, chromium) from the tank sludges, and (2) leaching of TRUs from the sludges. In the first approach, the volume of HLW is reduced by dissolution of certain sludge components, while the TRUs remain in the sludge. The leached sludge would be handled as HLW. In the second approach, the HLW volume is reduced by dissolution of the TRU portion of the waste, while the bulk waste material

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remains undissolved. If sufficiently decontaminated, the remaining solids could be handled as LLW. The leachate could be vitrified directly or processed further to concentrate the TRUs.

Intermediate processing studies will be ongoing through FY 2002. The scope of this work will involve (1) identifying the tank sludges that might be amenable to pretreatment by leaching methods, (2) developing the process chemistry needed to leach the desired components from the sludge, (3) developing the process flowsheets needed to leach the desired components from the sludge, (4) testing the leaching processes at laboratory-, bench-, and pilot-plant scales. Investigations will focus on removing aluminum and silicon by caustic leaching, removing chromium by oxidation to CrO_4^{2-} , or by selectively leaching with complexants, leaching TRUs with dilute HNO_3 (possibly in the presence of an oxidant), and leaching TRUs from alkaline tank sludges (e.g., with complexants and water-soluble chelates). For planning purposes, it is assumed that TRU leaching will be investigated for all sludges that are TRU wastes, but those wastes that have borderline TRU contamination levels (e.g., 100 to 150 nCi/g) will be given priority. Aluminum and silicon leaching would be done on those tanks that contain significant quantities of these elements. Chromium leaching will only be done on wastes with significant chromium content. It is expected that as more tank wastes are investigated, other wastes will be identified that could be pretreated using leaching methods.

Blending. Many waste streams expected as feed to the HWVP and the Grout Treatment Facility have components that limit the waste loading. Blending of waste feed streams is being considered as a simple, but effective, method of increasing the waste loading in grout and glass. The basic concept is that a feed high in one component will be mixed with another feed that contains a high level of a different component, producing a blended stream with a lower concentration of both components.

Development of computer software to examine benefits of blending which incorporates all of the tank waste compositions and explores the impact of various assumptions will be continued. This software is being developed to access a tank waste database and interface with databases or other software containing information on pretreatment and waste disposal processes.

An initial study was completed in FY 1993 that identified the magnitude of benefits from blending (Geeting and Kurath 1993). This study indicates that the waste loading in grout and glass can be increased and that the number of components exceeding the grout and glass specifications can be greatly reduced but not completely eliminated. This study also identified limiting case grout components (fluorine, lead) that could result in more grout vaults than current estimates. Blending is viewed as a supplemental strategy that should be considered as part of all waste pretreatment systems.

The initial study focused on blending wastes from pretreatment with sludge wash and selective leaching and did not consider more aggressive pretreatment methods. The software that is currently being developed incorporates an improved model for estimating glass waste loading. It will design a specific component frit for each waste feed, which will maximize waste loading to determine an optimum blend.

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Sludge Dissolution. In some cases (e.g., NCAW), separated and washed DST sludges can be vitrified without further pretreatment. However, to implement the SPM separation processes (e.g., TRU extraction, strontium removal) required for other sludges (e.g., PFP, CC, or NCRW), it would be necessary to dissolve the components to be separated. The washed sludges will be treated (dissolved) to prepare an aqueous HNO_3 feed for the SPM. Thus, the sludge dissolution is critical to the success of the reference and CLEAN pretreatment systems.

Sludge dissolution studies must be done on a tank-by-tank basis using actual tank samples. Sludge simulants are not suitable for such studies because of uncertainties regarding the specific species present in the wastes. A systematic study of sludge dissolution will be conducted at a laboratory scale; these tests will be ongoing through FY 2000.

The tank sludges investigated in any fiscal year will be obtained from tank core samples taken in the previous year. The results from the laboratory-scale dissolution tests will be used to plan scale-up. The sludge dissolution tests will be an integral part of the bench- and pilot-plant scale solvent extraction tests.

Sludge dissolution laboratory studies have been conducted on NCRW sludge (Lumetta and Swanson 1993c) and on PFP sludge (Lumetta and Swanson 1993b). The results from these preliminary sludge dissolution studies of DST sludges were very promising. However, laboratory studies are needed on many more tank sludges to gain confidence that the wastes to be treated in the SPM can be dissolved for processing.

TRU Removal by Solvent Extraction. System studies have indicated that the overall disposal volume for the Hanford Site tank wastes can be reduced by implementing advanced pretreatment processes (Grygiel et al. 1991; Boomer et al. 1993). In particular, partitioning of the wastes into a small volume of HLW and a large volume of LLW will result in a significant cost savings. The key element of this partitioning scheme is the separation of TRUs from the bulk sludge components. The baseline process for achieving this process is dissolution of the tank sludges in acid followed by extraction of the TRUs with CMPO, often referred to as the TRUEx process (Horwitz et al. 1985).

The scope of the solvent extraction laboratory studies will include (1) preliminary batch contacts of actual dissolved sludge solutions with the TRUEx process solvent, (2) design of the TRUEx process flowsheets for individual waste streams, and (3) testing of these flowsheets using batch contacts. The process flowsheets will then be demonstrated using bench-scale continuous counter-current solvent extraction equipment. Shakedown tests of the process flowsheets will be conducted using simulated waste (on a cold bench-scale solvent extraction unit); then tests will be done using actual wastes (on a hot bench-scale solvent extraction unit). It is expected that these bench-scale tests will be done on 1- to 25 L portions of the waste. The bench-scale tests will focus primarily on process chemistry, but some engineering information will also be obtained. The pilot-plant tests will be designed to address both process chemistry and process engineering. It is expected that the pilot plant will be capable of processing 30L of waste per hour.

The TRUEX process was invented by E. P. Horwitz at ANL and development of this process has been ongoing at ANL, PNL, and WHC. (Horwitz et al. 1985; Schulz and Horwitz 1988; Swanson 1991a, 1991b, 1991c; Lumetta et al. 1992; Lumetta and Swanson 1993a, 1993b, 1993c). Japanese workers have conducted tests of the TRUEX process for treating high-level liquid waste from plutonium-uranium (PUREX) reprocessing plants (Ozawa et al. 1992).

TRUEX test results to date have been encouraging. For example, batch testing with actual dissolved NCRW sludge solutions suggests that greater than 99 percent of the TRUs can easily be separated from the bulk components of the sludge (e.g., zirconium and sodium). The status of the TRUEX processing of NCRW sludge has recently been described in detail (Lumetta and Swanson 1993a).

The largest uncertainty regarding the TRUEX process is how well the process will perform given widely different feed compositions. However, variability of feed will be an issue irrespective of the technology that is ultimately selected. The only reliable way to address this uncertainty is to test the TRUEX process on each waste type. Such tests will be conducted as tank waste samples become available.

A second uncertainty is the manner in which the TRUs will be stripped from the loaded solvent. Early TRUEX flowsheets for pretreating Hanford Site tank wastes called for using a 0.2 M HEDPA solution for stripping the TRUs before TRU extraction. Experimental results showed that this reagent was effective at stripping the TRUs from the TRUEX solvent. However, two issues have precluded its use. First, this reagent not only strips the TRUs from the solvent, but it also strips uranium. Because of the large inventory of uranium in the SSTs, it may be advantageous to separate the uranium from the TRUs before the TRUEX extraction. Selective stripping of TRU from uranium could not be achieved with HEDPA. Second, HEDPA contains two moles of phosphorus per mole of HEDPA. Because the TRUEX strip solution is a HLW, all of the phosphorus in the stripping agent would be in the feed to HWVP. Because of the low limits on phosphorus in the HWVP feed, using HEDPA would result in an excessive amount of glass being produced. Several alternative stripping methods currently are under consideration, but no decision has been made as to which is the best approach.

A third issue is interference by other sludge components, especially uranium, thorium, and bismuth. These three elements have been shown to be extracted by the TRUEX process solvent. If the TRUs must be separated from uranium and thorium, these two elements could be removed by extraction with TBP before extracting the TRUs with CMPO. Although much more extraction data are required for bismuth, preliminary extraction data suggest that the TRUs could be preferentially stripped, thus affecting a TRU/bismuth separation. The need to separate bismuth from the TRUs will depend on the impact that bismuth has on the HLW glass.

A fourth uncertainty is how well the TRUEX process will behave under continuous counter-current conditions. Plans are being made for the procurement of the equipment needed for such testing with actual Hanford Site tank waste.

A fifth uncertainty with TRUEX is the effect of solvent degradation products and the optimal method for removing them from the solvent.

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To date, no continuous counter-current tests of the TRUEX process have been performed using actual Hanford Site tank wastes. Small-scale tests (about 150L processed) have been conducted at ANL (Chamberlain et al. 1992) and on high-level liquid waste derived from the raffinate from PUREX processing of reactor fuel (Ozawa et al. 1992). Both of these tests gave promising results.

Strontium Removal by Solvent Extraction. Strontium -90 is present in many of the Hanford Site tank sludges. Separation of this radioisotope from the nonradioactive constituents of the waste is required to produce an LLW waste form because this would lower the radiological hazard associated with the LLW form. Because the sludges will be dissolved in acid for TRU separation processes, technologies are needed to extract the ⁹⁰Sr from acid solution.

The baseline process being considered for extracting strontium from acid-dissolved-sludge solutions is the strontium extraction (SREX) process (Horwitz, Dietz, and Fisher 1991). In this process, strontium is extracted from HNO₃ solutions using a solution of di-t-butylcyclohexano-18-crown-6 (DtBC18C6) in 1-octanol. Consideration will also be given to the combined TRUEX/SREX process being developed at ANL (Horwitz et al. 1992). The development of the SREX process will involve laboratory studies, bench-scale continuous counter-current tests, and pilot-plant tests.

Development of the the SREX process is just beginning. Initial work conducted by ANL indicates that this process is very promising for extracting strontium from dissolved tank sludges (Horwitz et al. 1991), but considerably more parametric data need to be collected to better define the operability of the process. An initial test of the SREX process with actual dissolved Hanford Site tank wastes resulted in a decontamination factor of 250 for strontium (Lumetta et al 1993b).

4.7.2.2 Reference System Enhancements. The following functions have been proposed as enhancements to the reference system that reduce the volume of HLW, reduce the volume and improve the type of low-level waste generated, and improve the types of secondary waste generated (Barker 1993). The proposed technology development programs would provide the basis for making final decisions on process deployment.

Alternate TRU Removal. System studies have indicated that the overall cost of disposal of the Hanford Site tank wastes can be reduced by implementing advanced pretreatment processes. The key element of this partitioning scheme is the separation of the TRUs from the bulk sludge components using the TRUEX process as a baseline as indicated in the preceding section. Since a major uncertainty regarding the TRUEX process is the effect of feed variability, there may be certain waste types that are not amenable to pretreatment using the TRUEX process. As further development work is performed, it may become apparent that TRUEX is not the best choice for the TRU separation process. Thus, the development of alternative TRU technologies as a backup to TRUEX is desirable.

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A recent review of TRU extraction technology has revealed only two strong alternative extractants for pretreating Hanford tank wastes (Orme 1992). These are dihexyl-N,N-diethylcarbamoylmethyl phosphonate (CMP) and tetraalkylmalonamides.

The process of using CMP to extract TRUs has been known for approximately 20 years. A systematic study of phosphoryl carbamoyl extractants revealed that phosphine oxides were superior to phosphonates as TRU extractants (Kalina et al. 1981; Horwitz et al 1982). More recently, it was suggested that CMP may hold some advantages over CMPO (Marsh and Yarbrow 1988). However, a recent comparison study by Kupfer concludes that even though the advantages of diamide and CMP are recognized, at the present stage of their development, CMPO is preferred over both diamide compounds and CMP for use in solvent extraction of TRU elements from acidified Hanford Site waste solutions (Kupfer 1993). A study is currently (FY 1993) underway at PNL to assess the use of CMP in pretreating Hanford Site tank wastes.

The tetraalkylmalonamides extractants are under development in France (Cullerier, Musikas, and Nigond 1993). These reagents show some promise, but development of these extractants is just beginning. The French workers have not yet made a final decision on which tetraalkylmalonamide is the best extractant. Potential problems with these extractants include high rates of hydrolytic degradation and the need for high nitrate content in the solvent extraction feed. A study is currently (FY 1993) underway at PNL to assess the use of tetraalkylmalonamides. The extractant to be used in this study will be provided by workers at LANL.

Strontium and TRU Removal on Basic Side. Strontium and TRU components are not generally very soluble in alkaline wastes unless complexants are present. Destruction of these complexants should solve much of the problem with strontium and TRU components in the alkaline waste. However, if the treatment goals outlined in the CLEAN option are adopted, strontium and TRU may have to be removed from alkaline wastes and sludge waste waters. Selective leaching of TRU components also may generate neutral to alkaline solutions containing significant amounts of TRU components and may require additional treatment.

A number of possible techniques for the basic side removal of TRUs and strontium have been identified (Orth and Kurath 1993; Kolaric 1991). Precipitation methods are the most promising of the processes identified. These precipitation method processes include the use of sodium titanate, ferric hydroxide, titanium hydroxide, and calcium phosphate as the precipitating agent. The use of ion exchange also has shown promise. Some of the ion exchangers that have been identified are sodium titanate, titanium-coated zeolites, and crystalline silico-titanates. There is evidence to show that some of the solvent extraction techniques (such as the dicarbolides) may work on the basic side.

Cesium Removal on Acid Side. Much of the cesium in the tank waste is expected to be soluble and will be removed from the sludge during the alkaline sludge washing step. However, it appears that significant amounts of cesium will remain in the sludge and will be acidified with the sludge for processing. Much of this cesium will have to be removed if it is determined that the LLW form must meet Class A LLW criteria.

Processes to remove cesium from acidified tank waste sludges are relatively undeveloped. While numerous technologies have been examined to remove cesium from acidic waste, few have focused on actual acidified sludges. As presented previously in Section 4.6.2, experiments were performed on various cesium removal technologies as part of a CC waste exploratory study (Lumetta et al. 1993c). These experiments were performed under limited conditions and focused on a limited number of technologies. Precipitation with sodium phosphotungstate showed the most promise. Additionally, the removal of cesium from acidic waste has not been scaled up. Only the use of sodium phosphotungstate to recover cesium from PUREX process HLW has been studied on a large scale at the Hanford Site.

Convert/Remove Nitrates. Nitrate is regulated as a toxic anion and may require destruction or removal from tank wastes to meet the requirements of LLW disposal. Nitrate has a limit of 10ppm in drinking water. The tank waste contains over 80,000 metric tons of nitrate. Currently, the majority of nitrates are expected to be disposed in grout as LLW. The effect of nitrate on grout performance with respect to stability and leachability is being evaluated using laboratory testing and performance assessments. If these studies determine that nitrate is creating an unacceptable risk, nitrate conversion or separation will be required.

Technetium Removal. Technetium is one of the major contributors to long-term risk associated with the disposal of LLW in grout. This is primarily due to its relatively long half-life (213,000 years) and relatively high mobility. To meet the Class A limit for technetium in grout, a decontamination factor (DF) of about 1.5 is required for DST waste. Technetium removal from SST waste is not required. However, As Low As Reasonably Achievable (ALARA) limits may require a total technetium DF of 100.

Separations processes are required for both caustic and acidic conditions because both soluble and insoluble technetium are expected. Potential processes to be investigated include anion exchange, solvent extraction, water-soluble chelating polymers (WSCP), and electrochemical methods. Initial experiments will be conducted with laboratory batch contacts to define key parameters and develop rough flowsheets.

A number of separations technologies have been investigated for removing technetium from acidic and alkaline media. Technologies investigated include solvent extraction, anion exchange, and electrolytic deposition. Much of the work has been directed at separation of technetium (VII) from acidic high-level waste (Kolaric 1991).

As previously discussed in section 4.6.2, laboratory batch contacts were conducted with simulant and actual CC waste (Lumetta et al. 1993a). Technetium distribution coefficients were measured for the TRUEX process and tetraalkylammonium salts using cyclohexanone or 1-octanol as diluents.

LLW Organic Destruction. The IPM is designed to process the safety tanks, including organic safety tanks. Other tanks that will not be processed by the IPM may require the organics to be destroyed before further processing or disposal. For example, complexants may be destroyed to precipitate complexed and soluble radionuclides or future feed pretreatment may require organic destruction in acid solutions. These tanks may have different organic

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constituents and destruction criteria than the IPM, and alternative organic destruction technologies may be more effective with respect to cost or schedule. When organic destruction criteria and technology have been selected for the IPM, the technologies not selected will be further evaluated with respect to the LLW organic destruction criteria.

Alternate Strontium Removal - Acid Side. Strontium-90 is present in many of the Hanford Site tank sludges. Separation of this radioisotope from the nonradioactive constituents of the wastes is desirable because this would lower the radiological hazard associated with the LLW form. Because the sludges will be dissolved in acid for TRU separation processes, technologies are needed to separate ⁹⁰Sr from acid solution. Currently, solvent extraction is considered to be the baseline approach to strontium removal. In this activity, the utility of other separation methods will be explored. For example, promising preliminary test results with extraction chromatographic materials for the separation of strontium from the Hanford Site tank wastes were conducted in FY 1992 (Lumetta et al. 1993c).

4.7.3 Development of Technology Alternatives

4.7.3.1 Sludge Leaching, Precipitation, or Solid Sorbents. Alternative processes and flowsheets are being evaluated for the treatment of tank sludges to provide an intermediate-term process for pretreating of tank sludges while minimizing the amount of glass produced. Most development efforts have been directed at the recovery of radionuclides from acidified sludges using solvent extraction (i.e., TRUEX). While this technology appears to be feasible, it will most likely require a new pretreatment plant, which is not expected to be online until after the year 2010. Feed for the HWVP is required shortly after the scheduled startup in December 1999. While this can be provided with a sludge washing process, the number of glass canisters produced is expected to be relatively high. The processes to be investigated in this planned pretreatment technology task are directed at providing feed to the HWVP until a new pretreatment plant is available, while minimizing the amount of glass produced. Processes are expected to be simple and could be performed in existing tanks or new tanks constructed of new materials.

Currently, flowsheets are being developed for sludge leaching processes, precipitation processes, and the use of solid sorbents. Sludge leaching is directed at either leaching inert compounds such as aluminum, chromium, zirconium, bismuth, and PO₄, or at leaching of radionuclides such as plutonium, americium, strontium, technetium, and cesium. Precipitation and solid sorbent methods are being examined for removing the radionuclides of interest from both alkaline supernatant liquors and acidified sludges.

4.7.3.2 Calcining and Leaching. This activity is being performed in conjunction with the calcining process as developed in the reference system technology, Section 4.7.2.1, for organic/ferrocyanide destruction. As calcination is developed as a method for organic/ferrocyanide removal, it becomes necessary to evaluate the characteristics of the remaining solids. This activity will investigate the water solubility and acid leachability of the remaining solids.

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Calcination also is proposed as an alternate approach to pretreatment, in place of the acid dissolution techniques currently advocated. To investigate the chemistry of the calcination/dissolution approach to processing, a program of literature and laboratory studies began in FY 1993. Following this phase, a testing program to investigate the chemistry of the actinides in sodium hydroxide melts and highly alkaline solutions will be pursued. The proposed testing program will then proceed through laboratory cold and hot tests. Finally, the need for further pretreatment will be identified and processes selected to achieve the desired separations. Pretreatment studies at this juncture will be directed to determine the applicability of the aqueous-based separations methods previously explored on the resulting calcined solids and liquids.

4.7.3.3 CLEAN Option. The CLEAN option is an alternative strategy and an alternative pretreatment system that applies more aggressive pretreatment of the tank wastes to reduce the quantity of HLW requiring vitrification and the radioactive and hazardous material content of the LLW product. The specific goals of the CLEAN option (Staalsund et al. 1992), which have been adopted to formulate an aggressive, but feasible strategy, are summarized below.

- The radioactivity will be removed from the bulk of the waste to the extent that the radionuclides in the remaining LLW will not exceed NRC Class A maximum allowable concentrations for shallow land burial of radioactive materials.
- The maximum allowable concentrations for technetium and iodine are further reduced below the Class A limits to ALARA levels.
- Additional radioactivity will be removed from the LLW where significant reductions can be achieved through minor modifications in the process scheme.
- Uranium will be separated at sufficient purity to be sent to a stockpile and will not become part of the HLW or LLW forms.
- The LLW will be disposed of in a manner that complies with the U.S. Environmental Protection Agency and Washington State regulations regarding hazardous wastes.
- The radionuclides that have been removed from the bulk of the waste will be disposed of within about 1,000 canisters of a borosilicate glass that meets current HWVP glass specifications.
- Waste minimization principles will be used to limit the volume of LLW.

The CLEAN option relies on the extrapolation of laboratory experience to industrial application. A committee of national technical experts (Staalsund et al. 1992) agreed that the process chemistry for a CLEAN option is feasible, and identified a set of technical issues to be resolved before a decision is made to consider implementing the CLEAN option.

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The major issues are divided into the following three areas of significant concern.

1. Feasibility issues that, if not resolved, make it impossible for the CLEAN option to meet its goals.
2. Key issues that, if not resolved, effect the ability of the CLEAN option to meet its goals.
3. Optimization issues where a high degree of confidence exists that a problem can be resolved with only minor development.

The feasibility issues were dissolution of solids, actual decontamination factors achievable in full-scale operating facilities, and liquid/solid separations. If heat generation is ignored, the amount and composition of the undissolved solids with TRU content greater than LLW limits may determine the number of glass canisters needed to dispose of tank waste. Actual decontamination factors achieved by the individual processes are uncertain. The conditions achievable in the laboratory or in pilot plants are often difficult to maintain in a full-scale facility. Reasons for this include cross-contamination, contaminant breakthrough, and solid carryover in the liquid/solid separation. However, improved online instrumentation or sequential processing with lag storage, where decontamination of individual batches is verified before moving on to the next step, should eliminate many of these problems.

The CLEAN option technology development is focused primarily on developing the reference system (see Section 4.7.2.1) and functional needs to a higher level of decontamination performance. These technology needs were described in Sections 4.7.2.1 and 4.7.2.2.

Currently, the technology needs of the CLEAN option, beyond the needs of the reference system and enhancements, have been identified base on the flowsheet analyses of pretreatment and disposal of Hanford Site tank wastes. The needs associated with the CLEAN option are being examined further in FY 1993. Pending results of these analyses, decisions will be needed regarding funding of the long-term development of technologies.

4.8 TREATMENT OF WASTE AFTER PRETREATMENT ACTIVITIES

4.8.1 Grout Treatment

Grout treatment is the process of mixing selected DST wastes with grout-forming solids, and possibly with liquid chemical additives, to form a grout slurry that is pumped into near-surface lined concrete vaults for solidification and permanent disposal. The waste is characteristically corrosive because of the high hydroxide ion concentration and is characterized as toxic because of the high concentrations of nitrite and hydroxide ions.

The grout disposal vaults are constructed to be hazardous waste disposal facilities. The vaults are surface impoundments which are to undertake final closure in the manner of landfills.

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4.8.2 Hanford Waste Vitrification Plant Project

4.8.2.1 The Hanford Waste Vitrification Plant. The HWVP will be used to immobilize high-level defense wastes, from the Hanford Site, by incorporating them into a vitrified (i.e., glass) waste form. The glass produced by the process will be poured into stainless steel canisters, which will then be sealed and decontaminated. Following temporary storage onsite, they will later be shipped to a federal geologic repository for permanent disposal.

The HWVP vitrification process comprises five major subsystems; feed receipt and preparation system, melter system, offgas treatment system, canister closure and decontamination system, and the waste handling system. The canister storage system, which formerly was also on this list of subsystems, has been removed from the HWVP Project, and is now treated as a separate project facility. The vitrification process subsystems of the HWVP will be operated remotely and maintained and will be located within process cells in the HWVP. Figure 4-7 provides a process flow schematic diagram for the HWVP. In the slurry receipt and adjustment tank (SRAT), dilute pretreated feed will be concentrated into a slurry by evaporation and chemically adjusted to facilitate slurry transport. In the slurry mix evaporator (SME) tank, glass formers, in the form of a (glass) frit will be added, to the waste feed slurry, and the resultant slurry will be further concentrated and chemically adjusted before being transferred to the melter feed tank (MFT). The resultant MFT slurry product will be fed to the joule-heated glass melter. The molten glass product will then be poured into stainless steel canisters, which will be subsequently dealt with as noted in the previous paragraph.

Cold chemical storage, utility systems, and personnel support services required to support the vitrification process will be located within buildings adjacent to the vitrification building. Wastes from the process and process support operations will be treated within the HWVP and non-TRU wastes will be discharged outside of the HWVP to an underground waste holding tank. The current baseline schedule for the HWVP Project (i.e., in place during this reporting period) lists December 1999 as the HWVP hot startup date, with cold operations testing and qualification testing scheduled during the preceding 18 months.

The HWVP process and storage facilities are designed for a 40-year operating lifetime, and they are also being designed to remain functional after design basis accidents caused by certain natural phenomena; (i.e., seismic disturbances (earthquakes), tornadoes, or ash fall from volcanic eruptions). The facilities provide for remote operation and maintenance of the process with appropriate biological shielding for operator safety. Heating, ventilation, and air conditioning systems provide additional confinement barriers to limit any potential spread of radioactive contaminants.

During the reporting period for this FY 1993 update, the design work for the HWVP has been in the "detailed" (i.e., final) phase of the design, according to the project planning baseline in place during this period. The HWVP Project baseline (i.e., for design and testing), during this reporting period, was still explicitly focused only on vitrification of HLW feed derived from processing the HLWs currently stored in the Hanford Site DSTs. The general waste types stored in these DSTs are NCAW, NCRW, CC wastes, and PFP

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HWVP Glass Production – Process Flow Schematic Diagram

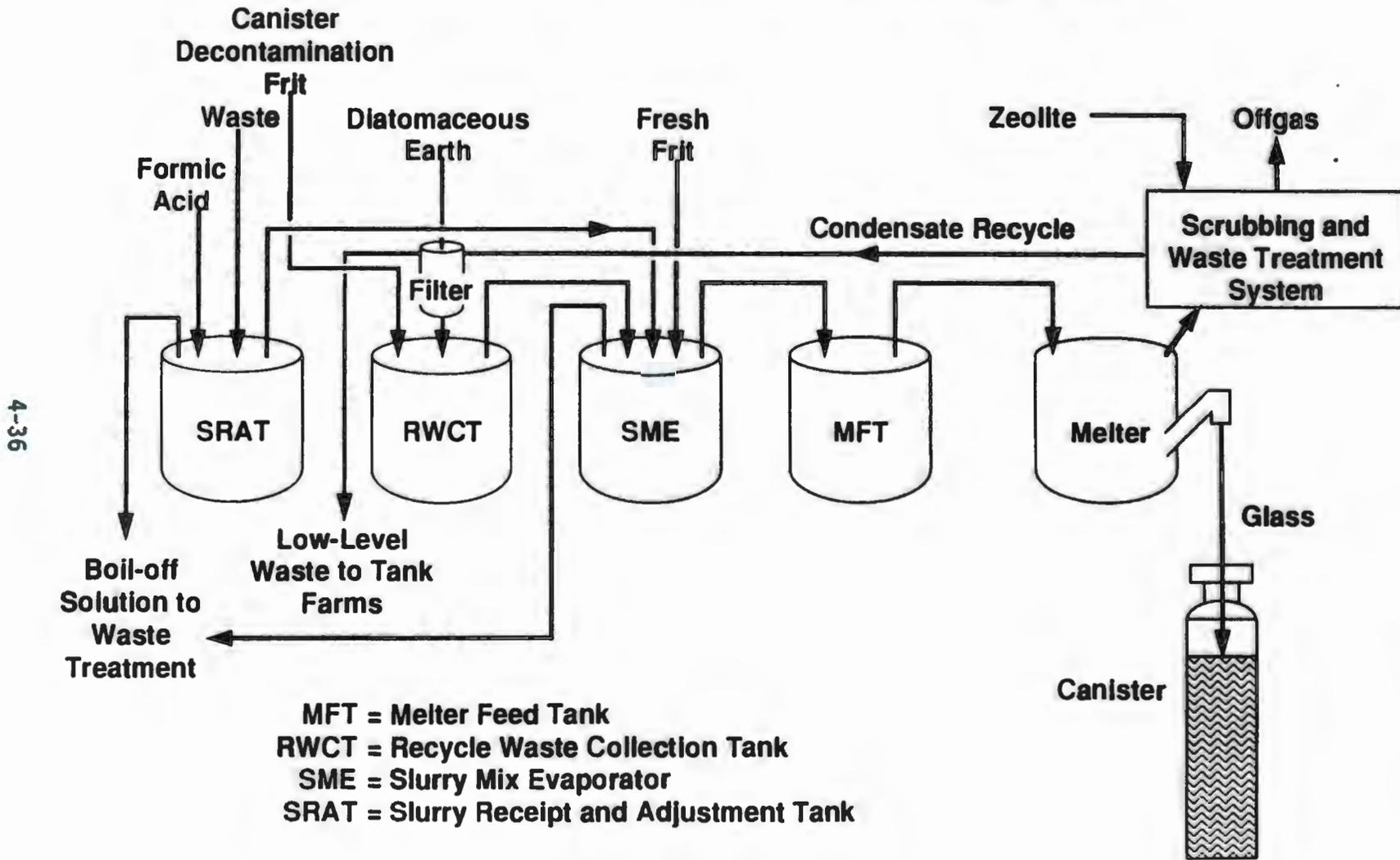


Figure 4-7. Hanford Waste Vitrification Plant Glass Production-
Process Flow Schematic Diagram.

wastes. Implicit to the baseline design program for the HWVP, however, was recognition of a need to incorporate design flexibility to facilitate processing adjustments that might be needed for vitrifying HLW feeds derived from other Hanford Site HLWs (i.e., wastes types not part of this current baseline, such as the SST wastes). During this reporting period the TWRS Program, of which "Immobilization" (e.g., the HWVP Project for vitrifying the high-level waste) is a functional element, has been in a rebaselining mode to address that topic. Namely, the DOE instruction to integrate the remediation of both the DST and SST wastes into one overall program, which will mean a new baseline for the HWVP design activity. Near the end of this reporting period, and as part of the TWRS Program rebaselining efforts, the HWVP Project did start work on a preliminary evaluation of the design feasibility of using a significantly high throughput feed preparation/melter system as part of the current basic design for the HWVP. The preliminary results of that effort indicate that such a higher throughput system (i.e., up to about 4 times the current rate) could be accommodated within the basic envelope of the plant design. Follow-on work on this topic is expected to continue into the next reporting period.

4.8.2.2 Waste Feed Processibility. The HWVP ultimately will process many different waste feed types, whose composition may not be fully characterized before the initial hot startup of the plant in December 1999. A composition variability study (CVS) is being conducted to characterize the relationship between glass composition and glass properties. The ability of the HWVP to produce a molten glass acceptable to melter operation, and then to produce a glass product acceptable to the permanent geologic repository is controlled by several properties and attributes of the glass. These properties and attributes include viscosity, electrical resistivity, thermal expansion, crystallinity, durability, liquidus temperature, radioactivity, heat generation, and concentrations of key components that may limit waste oxide loading in the glass. The current strategy, which provides maximum flexibility for handling variation in composition, is to define an envelope of acceptable glass compositions. This approach will be used to help determine the optimum waste oxide loading for all the vitrified waste forms (i.e., feeds from DST wastes and ultimately those from SST wastes).

In support of the general design requirements for the HWVP, which include WFQ requirements derived from the WAPS (see Section 7.3 for the WFQ discussion), testing and analysis work continued on the development of the CVS algorithms that relate the glass composition to selected properties and attributes of the glass waste form. This information is being used to define an acceptable composition range that will satisfy both the WFQ and the production requirements (e.g., production rate, waste loading fraction) for each waste (feed/product) type. The above information is also needed to conduct assessments of the waste feed processibility of the candidate waste types. Such processibility assessments have several important uses by the project, including for WFQ compliance basis planning for a given waste (feed/product) type. An update revision of the waste feed processibility assessment for the four general DST waste types was completed during the 1992 portion of this reporting period (May, et al. 1992).

4.8.2.3 Other Testing and Analysis Work. A considerable amount of technology development testing work was also conducted during this reporting period as part of the support work for the plant design work being done by Fluor Daniel. Such major topics as feed preparation behavior, melter performance and offgas system performance were addressed in this testing work. The final reporting for this work is still in preparation.

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5.0 TREATMENT OF EXISTING SINGLE-SHELL WASTES

5.1 DESCRIPTION OF SINGLE-SHELL TANK WASTES

One hundred and forty-nine SSTs contain portions of HLW, TRU waste, and LLW produced during Hanford Site operations before 1980. The current waste inventory of the SST system as of February 1993 is given in Table 5-1, which is taken from the *Tank Farm Surveillance and Waste Status Summary Report for February 1993* (Hanlon 1993). Interim stabilization efforts in support of Tri-Party Agreement interim milestone M-05-09 (Ecology et al. 1992) to remove pumpable liquid from the SSTs leaving salt cake, sludge, and interstitial liquid, are currently delayed because of criticality safety issues. These issues are discussed in greater detail in Section 9.0, Waste Tank Safety Issues. The remaining SST contents form the basis for future treatment efforts.

5.2 TREATMENT OF SINGLE-SHELL TANK WASTES

Currently, the major SST treatment objective is to resolve the tank safety issues pertaining to hydrogen generation, organic compounds, and ferrocyanide compounds, which can potentially react to evolve both heat and toxic gases (Borsheim and Kirch 1991). Eighteen of the 24 Hanford Site tanks which have been identified to contain high flammable gas concentrations are SSTs. All 28 tanks identified as having either potentially explosive mixtures of ferrocyanide or the potential for runaway organic-nitrate reactions are also SSTs. One additional tank safety issue pertains to a single SST (tank 106-C), which evolves sufficient radioactive decay heat to require periodic additions of cooling water.

The current SST waste volume inventory of the Hanford Site tank farms as of February 1993 is listed in Table 5-1. This information is available from the *Tank Farm Surveillance and Waste Status Summary Report for February 1993*, WHC-EP-0182-59 (Hanlon 1993). The volumes of both solids and liquids are recorded in cubic meters and thousands of gallons.

Table 5-1 also contains references to designations for waste types in SSTs. Complexant concentrate waste represents the concentrated product from the evaporation of dilute complexed (DC) waste. The concentrated phosphate (CP) waste is currently planned to be grouted directly. The non-complexed waste (designated NCPLX) is the general waste term applied to all Hanford Site liquors not identified as complexed waste.

The Pretreatment Technology Plan, previously discussed in Section 4.7, is applicable to both DST and SST waste pretreatment (Barker 1993). Therefore, the objectives for waste pretreatment processes also are identical.

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Table 5-1. Single-Shell Tank Inventory as of February 1993. (6 sheets)

Tank Number	Waste material ^a	Volume in kgal (m ³)			
		Total waste	Supernatant	Sludge ^b	Salt cake
101-A	DSSF	953 (3,607)	0	3 (11)	950 (3,596)
102-A	DSSF	41 (155)	4 (15)	15 (57)	22 (83)
103-A	DSSF	370 (1,400)	4 (15)	366 (1,385)	0
104-A	NCPLX	28 (106)	0	28 (106)	0
105-A	NCPLX	19 (72)	0	19 (72)	0
106-A	CP	125 (473)	0	125 (473)	0
101-AX	DSSF	748 (2,831)	0	3 (11)	745 (2,820)
102-AX	CC	39 (148)	3 (11)	7 (26)	29 (110)
103-AX	CC	112 (424)	0	2 (8)	110 (416)
104-AX	NCPLX	7 (26)	0	7 (26)	0
101-B	NCPLX	113 (428)	0	113 (428)	0
102-B	NCPLX	32 (121)	4 (15)	18 (68)	10 (38)
103-B	NCPLX	59 (223)	0	59 (223)	0
104-B	NCPLX	371 (1,404)	1 (4)	301 (1,139)	69 (261)
105-B	NCPLX	306 (1,158)	0	40 (151)	266 (1,007)
106-B	NCPLX	117 (443)	1 (4)	116 (439)	0
107-B	NCPLX	165 (625)	1 (4)	164 (621)	0
108-B	NCPLX	94 (356)	0	94 (356)	0
109-B	NCPLX	127 (481)	0	127 (481)	0
110-B	NCPLX	246 (931)	1 (4)	245 (927)	0
111-B	NCPLX	237 (897)	1 (4)	236 (893)	0
112-B	NCPLX	33 (125)	3 (11)	30 (114)	0
201-B	NCPLX	29 (110)	1 (4)	28 (106)	0
202-B	NCPLX	27 (102)	0	27 (102)	0
203-B	NCPLX	51 (193)	1 (4)	50 (189)	0
204-B	NCPLX	50 (189)	1 (4)	49 (185)	0
101-BX	NCPLX	43 (163)	1 (4)	42 (159)	0
102-BX	NCPLX	96 (363)	0	96 (363)	0
103-BX	NCPLX	66 (250)	4 (15)	62 (235)	0
104-BX	NCPLX	99 (375)	3 (11)	96 (364)	0
105-BX	NCPLX	51 (193)	5 (19)	43 (163)	3 (11)
106-BX	NCPLX	46 (174)	15 (57)	31 (117)	0
107-BX	NCPLX	345 (1,306)	1 (4)	344 (1,302)	0

Table 5-1. Single-Shell Tank Inventory as of February 1993. (6 sheets)

Tank Number	Waste material ^a	Volume in kgal (m ³)			
		Total waste	Supernatant	Sludge ^b	Salt cake
108-BX	NCPLX	26 (98)	0	26 (98)	0
109-BX	NCPLX	193 (731)	0	193 (731)	0
110-BX	NCPLX	199 (753)	1 (4)	189 (715)	9 (34)
111-BX	NCPLX	230 (870)	19 (72)	68 (257)	143 (541)
112-BX	NCPLX	165 (625)	1 (4)	164 (621)	0
101-BY	NCPLX	423 (1,601)	0	83 (314)	340 (1,287)
102-BY	NCPLX	341 (1,291)	0	0	341 (1,291)
103-BY	NCPLX	400 (1,514)	0	5 (19)	395 (1,495)
104-BY	NCPLX	406 (1,536)	0	40 (151)	366 (1,385)
105-BY	NCPLX	503 (1,904)	0	44 (167)	459 (1,737)
106-BY	NCPLX	642 (2,430)	0	95 (360)	547 (2,070)
107-BY	NCPLX	266 (1,007)	0	60 (227)	206 (780)
108-BY	NCPLX	228 (863)	0	154 (583)	74 (280)
109-BY	NCPLX	398 (1,506)	0	103 (390)	295 (1,116)
110-BY	NCPLX	398 (1,506)	0	103 (390)	295 (1,116)
111-BY	NCPLX	459 (1,737)	0	21 (79)	438 (1,658)
112-BY	NCPLX	291 (1,101)	0	5 (19)	286 (1,082)
101-C	NCPLX	88 (333)	0	88 (333)	0
102-C	DC	423 (1,601)	0	423 (1,601)	0
103-C	NCPLX	195 (738)	133 (503)	62 (235)	0
104-C	CC	295 (1,117)	0	295 (1,117)	0
105-C	NCPLX	150 (568)	0	150 (568)	0
106-C	NCPLX	229 (867)	32 (121)	197 (746)	0
107-C	DC	275 (1,041)	0	275 (1,041)	0
108-C	NCPLX	66 (250)	0	66 (250)	0
109-C	NCPLX	66 (250)	4 (15)	62 (235)	0
110-C	DC	187 (708)	0	187 (708)	0
111-C	NCPLX	57 (216)	0	57 (216)	0
112-C	NCPLX	104 (394)	0	104 (394)	0
201-C	NCPLX	2 (8)	0	2 (8)	0
202-C	EMPTY	1 (4)	0	1 (4)	0
203-C	NCPLX	5 (19)	0	5 (19)	0
204-C	NCPLX	3 (11)	0	3 (11)	0
101-S	NCPLX	427 (1,616)	12 (45)	244 (924)	171 (647)
102-S	DSSF	549 (2,078)	0	4 (15)	545 (2,063)

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Table 5-1. Single-Shell Tank Inventory as of February 1993. (6 sheets)

Tank Number	Waste material ^a	Volume in kgal (m ³)			
		Total waste	Supernatant	Sludge ^b	Salt cake
103-S	DSSF	248 (939)	17 (64)	10 (38)	221 (837)
104-S	NCPLX	294 (1,113)	1 (4)	293 (1,109)	0
105-S	NCPLX	456 (1,726)	0	2 (8)	454 (1,718)
106-S	NCPLX	543 (2,055)	0	32 (121)	511 (1,934)
107-S	NCPLX	368 (1,393)	6 (23)	293 (1,109)	69 (261)
108-S	NCPLX	604 (2,286)	0	4 (15)	600 (2,271)
109-S	NCPLX	568 (2,150)	0	13 (49)	555 (2,101)
110-S	NCPLX	390 (1,476)	0	131 (496)	259 (980)
111-S	NCPLX	596 (2,256)	10 (38)	139 (526)	447 (1,692)
112-S	NCPLX	637 (2,411)	0	6 (23)	631 (2,388)
101-SX	DC	456 (1,726)	1 (4)	112 (424)	343 (1,298)
102-SX	DSSF	543 (2,055)	0	117 (443)	426 (1,612)
103-SX	NCPLX	652 (2,468)	1 (4)	115 (435)	536 (2,029)
104-SX	DSSF	614 (2,324)	0	136 (515)	478 (1,809)
105-SX	DSSF	683 (2,585)	0	73 (276)	610 (2,309)
106-SX	NCPLX	538 (2,036)	61 (231)	12 (45)	465 (1,760)
107-SX	NCPLX	104 (394)	0	104 (394)	0
108-SX	NCPLX	115 (435)	0	115 (435)	0
109-SX	NCPLX	250 (946)	0	250 (946)	0
110-SX	NCPLX	62 (235)	0	62 (235)	0
111-SX	NCPLX	125 (473)	0	125 (473)	0
112-SX	NCPLX	92 (348)	0	92 (348)	0
113-SX	NCPLX	26 (98)	0	26 (98)	0
114-SX	NCPLX	181 (685)	0	181 (685)	0
115-SX	NCPLX	12 (45)	0	12 (45)	0
101-T	NCPLX	133 (503)	30(113)	103 (390)	0
102-T	NCPLX	32 (121)	13 (49)	19 (72)	0
103-T	NCPLX	27 (102)	4 (15)	23 (87)	0
104-T	NCPLX	445 (1,684)	3 (11)	442 (1,673)	0
105-T	NCPLX	98 (371)	0	98 (371)	0
106-T	NCPLX	21 (79)	2 (7)	19 (72)	0
107-T	NCPLX	180 (681)	9 (34)	171 (647)	0
108-T	NCPLX	44 (167)	0	44 (167)	0
109-T	NCPLX	58 (220)	0	58 (220)	0
110-T	NCPLX	379 (1,435)	3 (12)	376 (1,423)	0

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Table 5-1. Single-Shell Tank Inventory as of February 1993. (6 sheets)

Tank Number	Waste material ^a	Volume in kgal (m ³)			
		Total waste	Supernatant	Sludge ^b	Salt cake
111-T	NCPLX	458 (1,734)	2 (7)	456 (1,727)	0
112-T	NCPLX	67 (253)	7 (26)	60 (227)	0
201-T	NCPLX	29 (110)	1 (4)	28 (106)	0
202-T	NCPLX	21 (79)	0	21 (79)	0
203-T	NCPLX	35 (132)	0	35 (132)	0
204-T	NCPLX	38 (144)	0	38 (144)	0
101-TX	NCPLX	87 (329)	3 (11)	84 (318)	0
102-TX	NCPLX	113 (428)	0	0	113 (428)
103-TX	NCPLX	157 (594)	0	157 (594)	0
104-TX	NCPLX	65 (246)	1 (4)	0	64 (242)
105-TX	NCPLX	609 (2,305)	0	0	609 (2,305)
106-TX	NCPLX	453 (1,715)	0	0	453 (1,715)
107-TX	NCPLX	36 (136)	1 (4)	0	35 (132)
108-TX	NCPLX	134 (507)	0	0	134 (507)
109-TX	NCPLX	384 (1,453)	0	0	384 (1,453)
110-TX	NCPLX	462 (1,749)	0	0	462 (1,749)
111-TX	NCPLX	370 (1,400)	0	0	370 (1,400)
112-TX	NCPLX	649 (2,456)	0	0	649 (2,456)
113-TX	NCPLX	607 (2,297)	0	0	607 (2,297)
114-TX	NCPLX	535 (2,025)	0	0	535 (2,025)
115-TX	NCPLX	640 (2,422)	0	0	640 (2,422)
116-TX	NCPLX	631 (2,388)	0	0	631 (2,388)
117-TX	NCPLX	626 (2,369)	0	0	626 (2,369)
118-TX	NCPLX	347 (1,313)	0	0	347 (1,313)
101-TY	NCPLX	118 (447)	0	118 (447)	0
102-TY	NCPLX	64 (242)	0	0	64 (242)
103-TY	NCPLX	162 (613)	0	162 (613)	0
104-TY	NCPLX	46 (174)	3 (11)	43 (163)	0
105-TY	NCPLX	231 (874)	0	231 (874)	0
106-TY	NCPLX	17 (64)	0	17 (64)	0
101-U	NCPLX	25 (95)	3 (11)	22 (84)	0
102-U	NCPLX	374 (1,416)	18 (68)	43 (163)	313 (1,185)
103-U	NCPLX	468 (1,771)	13 (49)	32 (121)	423 (1,601)
104-U	NCPLX	122 (462)	0	122 (462)	0
105-U	NCPLX	418 (1,582)	37 (140)	32 (121)	349 (1,321)

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Table 5-1. Single-Shell Tank Inventory as of February 1993. (6 sheets)

Tank Number	Waste material ^a	Volume in kgal (m ³)			
		Total waste	Supernatant	Sludge ^b	Salt cake
106-U	NCPLX	226 (855)	15 (57)	26 (98)	185 (700)
107-U	DSSF	406 (1,537)	31 (117)	15 (57)	360 (1,363)
108-U	NCPLX	468 (1,771)	24 (90)	29 (110)	415 (1,571)
109-U	NCPLX	463 (1,753)	19 (72)	48 (182)	396 (1,499)
110-U	NCPLX	186 (704)	0	186 (704)	0
111-U	DSSF	329 (1,245)	0	26 (98)	303 (1,147)
112-U	NCPLX	49 (185)	4 (15)	45 (170)	0
201-U	NCPLX	5 (19)	1 (4)	4 (15)	0
202-U	NCPLX	5 (19)	1 (4)	4 (15)	0
203-U	NCPLX	3 (11)	1 (4)	2 (7)	0
204-U	NCPLX	3 (11)	1 (4)	2 (7)	0

^aSee next page for description.^bIncludes interstitial liquid.

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Table 5-1. Single-Shell Tank Inventory as of February 1993. (6 sheets)

Waste type abbreviation	Waste type	Description
CC	Concentrated complexant	Concentrated product from the evaporation of dilute complexed waste.
CP	Concentrated phosphate	Waste originating from the decontamination of 100 N Reactor. Concentration of this waste produces concentrated phosphate waste.
DC	Dilute complexed	Characterized by a high content of organic carbon including organic complexants. EDTA, citric acid, HEDTA, and IDA are the major complexants used. Main sources of DC waste are saltwell liquid inventory.
DSSF	Double-shell slurry feed	Waste evaporated just before reaching the sodium aluminate saturation boundary of 6.5 molar hydroxide in the evaporator. This form is not as concentrated as double-shell slurry.
NCPLX	Noncomplexed	General waste term applied to all Hanford Site liquors not identified as complexed.

EDTA = ethylenediaminetetraacetic acid
 HEDTA = hydroxyethylenediaminetriacetic acid
 IDA = iminodiacetate

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5.3 SUMMARY OF SINGLE-SHELL TANK WASTE TREATMENT STUDIES

The following information provides a summary of SST waste treatment activities completed or in progress. In many cases, activities being performed for the treatment of DST wastes also apply to the treatment of SST wastes, as previously inferred.

5.3.1 Pretreatment Strategies Options

Three major options currently are being evaluated for disposal of the DST and SST wastes to establish the preferred program for the Hanford Site. As stated previously in Section 4.7.1, these options include pretreatment processes ranging from minimal separations of the HLW and LLW to advanced separations processes that greatly reduce the volume of HLW and LLW produced and/or reduce the chemical toxicity of the LLW. The three optional systems, (1) developed (or minimum) pretreatment technology system, (2) draft reference pretreatment system, and (3) extensive pretreatment system with material recycle (CLEAN), form the basis for the current technology development program presented in the Pretreatment Technology Plan (Barker 1993).

5.3.2 Reference Pretreatment System Technology Program Development

The first phase of the reference pretreatment system technology development program consists of organic/ferrocyanide destruction to mitigate tank safety concerns. Since these concerns are of primary importance to SST waste pretreatment, recent progress in the development of methods to remove organics and ferrocyanide components from Hanford Site tank wastes are presented.

5.3.2.1 Removal of Organic and Ferrocyanide Components. Several promising processes are currently under evaluation and/or testing for the removal of organic and ferrocyanide compounds from Hanford Site tank wastes. One of these processes involves oxidizing the organic waste with ozone at ambient conditions of temperature and pressure to destroy the organic constituents of the waste. Ozonation is a process that destroys organic, and possibly ferrocyanide, compounds sufficiently to resolve safety concerns and does not add to the existing volume.

A laboratory-scale ozone reactor is being used to demonstrate the destruction of organic compounds and ferrocyanide compounds contained in Hanford tank waste. Current results indicate that the reactor can successfully destroy organic materials responsible for tank safety concerns in synthetic 101-SY Window E waste (Colby 1993). Ozonation of simulated waste contaminated with nickel ferrocyanide was not conducted during FY 1993 because of insufficient funding. However, a report of initial test results has been released (Colby 1992).

Ozonation process development activities initiated in FY 1992 have been extended in FY 1993. Continuing work conducted for IPM Project W-236A has demonstrated that other ozone reactor types with varying liquid flow and ozone gas feed rates can destroy certain organic contaminants. The organic carbon

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content of these contaminants has been reduced by ≥ 90 percent (Colby 1993). Test plans have been developed for laboratory experiments to determine the oxidizing characteristics of the ozonation process on radioactive 101-SY (DST) wastes in April and May of CY 1993. Grout testing of the radioactive ozonated waste also is planned during this timeframe. A large-scale ozonation process demonstration using simulated 101-SY waste is being planned to determine the feasibility of scaling up the process.

Calcination is a processing alternative that also is being considered for the destruction of organics, ferrocyanide, nitrites, and nitrates in the tank wastes. In this process, the waste is heated to dryness, and then to temperatures sufficient to oxidize organic and ferrocyanide compounds in the waste. Calcination processes are used in a variety of applications at temperatures varying from about 300 °C to 1,700 °C. The process typically produces a solid oxide product and offgases both inorganic and organic combustion products of lower molecular weight.

A plasma arc calcination process has been demonstrated that resolves tank safety issues and separates the transuranic fraction (TRU) into a relatively small volume. The results from testing small quantities of actual radioactive tank waste indicate that a calcination process is feasible. A plasma arc pilot scale demonstration using 2,270 kg (5,000 lb) of simulated waste was conducted early in FY 1993. This calcination process generated an 80 percent feedstock volume reduction with an electrical power requirement of 1000 kW-hr per gallon of waste processed (Colby 1993). Dissolution scoping studies for a large scale test are planned for FY 1993.

Other organic destruction concepts currently being tested include (1) electrochemical oxidation, (2) low pressure/temperature hydrothermal oxidation, and (3) high pressure/temperature hydrothermal oxidation.

In the electrochemical oxidation process, organic waste is introduced into an electrochemical cell containing high concentrations of nitric acid. The solution also contains a small quantity of silver, cerium, or other metal ion that, in its higher oxidation state, is a kinetically strong, rapid oxidizing agent. The metal ions are oxidized at the cathode surface of the cell and then reduced by reacting with and oxidizing other materials, such as organic or ferrocyanide molecules. Unless this process can be modified for use in high pH (basic) solutions, it will suffer the disadvantages of increases in waste volume that are associated with acidification and subsequent reneutralization of the waste.

A modification of the electrochemical oxidation process for use in highly basic solutions was developed in late FY 1992. The process demonstrated reduction of the organic carbon constituents in simulated tank wastes in early FY 1993. The test data suggests that organics are reduced to inorganic carbonates and small, carbon chain refractory organic compounds. Total organic carbon reduction, based on the initial process development testing, is greater than 90 percent. However, power efficiency is reduced as the total organic carbon is reduced. This is currently attributed to inefficient mass transport or difficult-to-oxidize refractory organics (Colby 1993). Plans are currently being made to demonstrate this process on one liter basic solution, using radioactive 101-SY waste late in FY 1993.

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The low pressure/temperature hydrothermal oxidation process entails introduction of the tank wastes containing organics into either a batch or continuous reactor that is heated to temperatures varying from 150 to 350 °C. The organics then react with abundant oxidants, such as nitrites, already present in the waste. The reaction produces hydrogen, carbon dioxide, methane, and ammonia. The test results demonstrated that the organics were transformed to carbonates at 350 °C (Jones et al. 1993).

The high temperature/high pressure hydrothermal oxidation process involves pressurization and heating the waste solution above the critical point of the mixture. At temperatures above the critical point, the nitrate/nitrite present in the waste will oxidize the organics and ferrocyanides present. Rapid, high-efficiency waste oxidation reactions occur in the temperature range of about 400 to 600 °C and approximately 210 to 350 kg/cm² (3,000 to 5,000 lb/in²). This process also has the potential to destroy nitrates and nitrites in the waste. Salts and metals precipitate out of the supercritical solution and can be subsequently treated.

5.3.2.2 Selective Leaching of SST Sludge. Selective leaching of alkaline-washed sludge from SST U-110 with 2 M HNO₃ at a temperature of 100 °C was found to dissolve the TRU content of the sludge without dissolving a large fraction of the sludge (Lumetta et al. 1993). The initial tests suggest that approximately 75 percent of the sludge from tank U-110 can be handled as LLW, with a resulting grout form meeting NRC Class C criteria for TRUs, ⁹⁰Sr, ¹³⁷Cs, and ⁹⁹Tc. The acid leach solution could be sent to HWVP directly or processed further to concentrate the TRUs.

It is expected that as more SST tank wastes are investigated, other wastes will be identified that could be pretreated using leaching methods.

5.3.2.3 Dissolution of SST Sludges. Laboratory sludge dissolution studies have been conducted on sludges from SSTs B-110 and U-110 (Lumetta et al. 1993). Good dissolution of the sludge solids from tank B-110 was obtained using HNO₃ and HNO₃/HF solutions. However, a large fraction of the sludge solids from tank U-110 did not dissolve in 2M HNO₃. In particular, most of the aluminum and silicon did not dissolve. The high molar ratio of Al to Si of about 5, suggested that there is an insoluble Al species present that is not an aluminosilicate. A significant fraction of the iron also did not dissolve. Additional acid leaching studies should be conducted on U-110 sludge. Variables should include HNO₃ concentration, temperature, and time of leaching.

Nevertheless, the results from these preliminary sludge dissolution were promising. Candidate reagents and procedures for making all of the various types of SST sludges soluble have been addressed by Schulz and Kupfer (1991).

5.3.3 Pretreatment Reference System Enhancements

Several functions were proposed in Section 4.1.2 as enhancements to the pretreatment reference system that are applicable to all Hanford Site waste tanks. These enhancements are intended to reduce the volume of HLW, reduce the volume and improve the type of low-level waste generated, and improve the

types of secondary wastes generated. Two enhancements unique to the SSTs are the removal of iodine and nickel, since the existing characterization data suggest that they are found only in SSTs (Straalsund 1992).

5.3.3.1 Iodine Removal. There is an estimated 30 kg of ^{129}I in the liquid and salt cake stored in Hanford Site SSTs at a concentration of 0.00006 nCi/g. Because of the long half-life of ^{129}I (17 million years), the mobility of soluble iodine species through the Hanford soil, and the inability of currently planned near-surface disposal options (i.e., grout) to immobilize ^{129}I when exposed to environmental conditions, a method might be needed to remove and concentrate radioiodine from the alkaline waste solutions stored at the Hanford Site, and possibly from aqueous wastes stored at other DOE sites. Such removal and concentration also will require development of a suitable waste form and strategy because no immobilization form currently exists.

This work objective, if it is determined that the iodine will require removal from the waste, would be to develop technologies for (1) separating radioiodine from alkaline wastes stored in underground radioactive waste storage tanks, and (2) alternative waste forms for long-term disposal of the resulting ^{129}I waste. The initial emphasis will be on anionic exchange resins and silver zeolites to recover and concentrate from the waste supernates. Other techniques to be investigated would include precipitation of insoluble iodine species such as silver iodide. To develop an immobilization form, previous technologies for preparing a waste form (silveriodide or other low-solubility iodides or iodates in cement or iodine immobilized in sodalite) would be evaluated.

Currently, no technology development activities are being conducted for this function. Additional analysis is required to determine whether iodine in tank wastes will require removal. Historically, some work has been done on separation and immobilization of radioiodine. This work would provide the basis for future technology development work, if required.

5.3.3.2 Nickel Removal. As stated in Section 4.7.3.4, the CLEAN option goals include removal of ^{99}Tc and ^{129}I on an ALARA basis because of their high mobility in the environment. However, several other instances exist where removal of other components (e.g., ^{63}Ni in SSTs) might be required because of variabilities in compositions among the tanks (Straalsund 1993). Removal of ^{63}Ni will need to be added to the list of components in future flowsheet development of the CLEAN option. The quantity of nickel present in SST waste is too high to include within the HLW criteria of 1,000 glass canisters. Furthermore, ^{63}Ni is present in some SST tanks (or groups of tanks) in quantities that would exceed the Class A limit in grout made from those tanks (or groups of tanks). Consequently, a different disposition method must be chosen for the separated nickel. Decay storage in a surface facility or repository disposal in an alternative waste form are possibilities for handling this special problem.

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6.0 EVALUATION AND SELECTION OF GROUT

Cement-based grouts are extensively used in the United States (U.S.) and worldwide as a vehicle for immobilization and near-surface disposal of solid and liquid LLWs. Formal selection of cementitious grout for disposal of selected liquid wastes in near-surface vaults was made in the *Hanford Waste Management Plan* (DOE-RL 1983). This selection was strongly influenced by the generally favorable Oak Ridge National Laboratory (ORNL) site grout hydrofracture disposal experience and by the Savannah River Laboratory (SRL) site evaluation and selection of a grout waste form for the disposal of certain aqueous LLW salt solutions. This selection was supported by an independent, comprehensive evaluation performed by Hanford Site scientists and engineers in 1980. This evaluation showed grout to be preferred over other known forms for immobilization and bulk disposal of Hanford Site liquid LLWs (RHO 1980).

The grout formulation process involves waste sampling, characterization, and product testing to ensure that the grout will meet strength and leachability criteria.

6.1 REGULATORY CHANGES AFFECTING GROUT

A change request was submitted to the EPA and Ecology in September 1992 proposing a change to Tri-Party Agreement Milestone M-01. The change request was denied in October 1992 and DOE-RL invoked a currently standing dispute resolution.

During February 1993, the Nuclear Regulatory Commission (NRC) denied a petition for rulemaking by the states of Washington and Oregon, which deals with the process and criteria for classifying radioactive waste materials at defense facilities as HLW or non-HLW.

6.2 STATUS OF ACTIVITIES IN PROGRESS

GTF Dangerous Waste Permit Application. The GTF permit application was completed and transmitted to Ecology in July 1992. Since that time, Ecology has prepared additional comments for inclusion in the permit application. Following comment inclusion, the permit application will be opened for public review and comment.

Final Safety Analysis Report. The final safety analysis report (FSAR) (WHC 1992) was transmitted by Westinghouse Hanford Company (WHC) to RL in November 1992. DOE-RL completed its review and transmitted the document to DOE-Headquarters (DOE-HQ) in December 1992. Brookhaven National Laboratory was tasked to review the FSAR for DOE-HQ. It is anticipated that DOE-HQ will approve the document in September 1993.

Performance Assessment. Approval of the performance Assessment (PA) for the GTF is currently the critical path item for the restart of the GTF. Extensive support and development of long-term facility, fate, and transport modeling has been conducted during the last year. The PA will be transmitted

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to DOE-RL in September 1993, to be followed by review by a DOE-HQ Performance Assessment Peer Review Panel. Approval of the PA by DOE-HQ is required to support facility restart.

Toxic Air Pollutant Notice of Construction. In September 1991, Ecology enacted controls for new sources of toxic air pollutants (TAPs), requiring that a notice of construction be submitted before the addition or significant modification of an atmospheric source emitting a toxic pollutant. Planned modification of Grout Disposal Facility (GDF) ventilation systems has been deemed to trigger notice of construction requirements for TAPs. A notice of construction, incorporating best demonstrated available technology (BDAT) review, has been prepared for submittal to Ecology in August 1993.

National Emission Standards for Hazardous Air Pollutants (NESHAP). In concert with the TAPs notice described above, a NESHAP application is in preparation to address radionuclide releases from increased ventilation of the GDF. The NESHAP modification is anticipated to be submitted to the U.S. Environmental Protection Agency in August 1993.

Grout Reformulation. Grout reformulation has been necessary to resolve issues of heat generation and poor wastefrom properties in earlier formulations. Pilot-scale operations conducted by WHC and PNL in mid-1992 proved to be successful in demonstrating desired process capability and product performance. Additional laboratory testing is proceeding with formulation verification on specific waste streams to support disposal Campaigns 102 and 103.

Waste Feed Transfer. During September and November through December 1992, wastes contained within tank 241-AN-106 were transferred to the grout feed tank 241-AP-102 in preparation for disposal of this waste in Campaign 102.

DST Waste Sampling. No additional waste tanks were sampled during the reporting period; however, preparations were completed to sample and analyze waste contained in tanks 241-AP-105 (March 1993), 241-AP-106 (March 1993), and 241-AP-102 (May 1993 following transfer from 241-AN-106).

Waste Scheduling. During November 1992, tank 241-AW-101 was declared a Watch List tank because of concerns with flammable gas generation. The contents of this tank were previously anticipated to be disposed in Campaigns 103 and 104. The material will not be released for grout disposal until safety concerns are addressed. In light of such a delay, the contents of 241-AP-105 have been accelerated in disposal scheduling to Campaign 103 while the contents of 241-AW-101 have been relieved for disposal to Campaigns 104 and 105.

Vault Construction. Vaults 102 through 105 have completed construction and will complete instrumentation in 1993.

Core Sampling. Laboratory testing of core samples extracted from the phosphate/sulfate waste (PSW) vault was completed in early 1993 and a report of the quality verification was prepared for April 1993 release. Fabrication

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of the grout sampling truck (Hanford Mobile Solidified Low-Level Radioactive Waste Sampling Unit) is underway with completion anticipated in 1993. Assembly of core sample transfer casks has begun.

Cold-Cap Formulation. Selection of a cold-cap formulation for the PSW vault was completed in 1992 following testing by the U.S. Army Corps of Engineers. Contractual agreements for supply of the cold-cap materials have been completed. Contractual agreements for a cold-cap placement truck are anticipated to be complete in June 1993. The PSW vault is anticipated to be cold-capped in August 1993.

Vault Equipment. A second portable instrument house (PIH) has been delivered. Each of the two PIHs currently are undergoing testing before acceptance. Design and fabrication of the exhauster for vaults 102 and 103 has been completed and the exhauster installed on the vaults. The exhauster is currently undergoing testing before acceptance.

Vault Hydrogen Issues. Extensive resources remain committed to resolution of issues of buildup and mitigation of grout vault hydrogen. Current work includes continued modeling of hydrogen buildup in the vault vapor space and leachate void space, physical testing of gas generation on material irradiation, and laboratory scale testing of catalytic oxidation of generated hydrogen. Safety analyses of the hydrogen gas generation issue is continuing with expected completion in FY 1993.

6.3 NEW ACTIVITIES

No significant new activities other than those described herein have been initiated during this reporting period.

6.4 WASTE GENERATION

The GTF did not operate during the time period covered by this report. During this period, a total of 7.7 m³ of mixed waste was generated due to rainwater infiltration and 0.007m³ of hazardous waste was generated with the disposal of out-of-date sealing material. Approximately 196.8 m³ of mixed low-level radioactive waste was generated in the two years previous to this report.

6.5 WASTE MINIMIZATION ACTIVITIES

A new waste minimization plan was issued in compliance with DOE Orders 5400.1 (DOE 1988b), 5400.3 (DOE 1989), and 5820.2A (DOE 1984) and under the guidance of the Washington Administrative Code (WAC 173-307).

Substitution of propylene glycol for ethylene glycol in the chiller system for makeup air at the Grout Treatment Facility (GTF) remains incomplete with planned completion in FY 1993.

Investigation is proceeding to replace aerosols and regulated solvent-based products currently being used.

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6.6 ESTIMATE OF PLANNED WORK ACTIVITIES FOR FY 1993

Much of the planned work effort for 1993 will be focused on the completion of major ongoing tasks (i.e., approval of Part B permit application, FSAR, and performance assessment, readiness review, and the resolution of hydrogen issues).

The contents of tank 241-AP-102, having been transferred from 241-AN-106, will be sampled and characterized. Small grout samples will be made with radioactive waste to ensure that the grouted waste will meet the processing and wasteform criteria (Riebling and Fadeff 1991).

A process waste assessment, geared toward waste minimization, required by the state of Washington and DOE-RL will be prepared.

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7.0 WASTE FORM QUALIFICATION ACTIVITIES

7.1 INTRODUCTION

This section on waste form qualification activities will provide pertinent background information and FY 1992 program updates on the following topics related to the remediation of HLW stored at the Hanford Site:

- Waste form selection
- Hanford Waste Vitrification Project.

7.2 WASTE FORM SELECTION

The DOE has initiated a remediation program for the disposal of high-level nuclear wastes currently stored in tanks at several DOE sites within the U.S. To date, the U.S. program has selected borosilicate glass as the waste form of choice for use in disposing of all, or at least a significant part, of such wastes that are stored at three of these sites; the Savannah River Site in South Carolina, the West Valley Demonstration Project in New York, and the Hanford Site in the state of Washington.

For the Hanford Site, DOE decided to use borosilicate glass as the waste form for the disposal of the HLW currently stored in DSTs (DOE 1988a). Although HLW is also stored in SSTs on the Hanford Site, final selection of the waste form for the HLW stored in SSTs had not been made during this reporting period. However, it should be noted that borosilicate glass is also one of the leading waste form choices for SST HLWs. The TWRS program for the Hanford Site currently is being rebaselined. One of the major objectives being addressed is that of creating a fully integrated program for the overall remediation of both DSTs and SSTs HLW. The TWRS program rebaselining is to be completed by March 1993.

7.3 HANFORD WASTE VITRIFICATION PLANT PROJECT WASTE FORM QUALIFICATION ACTIVITIES

The following waste form qualification documentation activities are important to the HWVP Project:

- Waste (form) acceptance specifications derived according to the needs of the repository project that will deal with disposing of the high-level waste form product
- Compliance planning by the waste form producer to meet the waste form acceptance specifications
- Waste (form) qualification reporting that documents the respective compliance basis for each waste form acceptance specification.

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BACKGROUND

In 1990, the repository program within the DOE Office of Civilian Radioactive Waste Management (DOE-RW) revised the acceptance specifications for the vitrified high-level waste form product, which in the standard form consists of sealed stainless steel canister filled with a borosilicate glass that is loaded with a mixture of waste constituents. Late in FY 1991 a July 1991 draft of the DOE-RW Waste Acceptance Preliminary Specifications (WAPS) became the subject of a high-level DOE-RW (Headquarters) review process that was supposed to culminate in 1992 in the baselining of the document. In November 1991, at the written request of RL, the HWVP Project began using the June 1991 draft of the (DOE-RW) WAPS to support project planning activities.

In July of 1992, the DOE-RW decided not to baseline the proposed draft of the "Waste Acceptance Preliminary Specification" (WAPS). Instead, RW departed from the documentation path outlined in the waste acceptance process description. As a replacement, RW created the "Waste Acceptance Systems Requirements Document" (WASRD), which is a broader scoped document than the July 1991 draft of the WAPS. In addition, the WASRD addresses the RW repository program waste (form) acceptance requirements for several types of waste forms (i.e., commercial power reactor spent fuel, transuranic wastes), as well as, the vitrified HLW. The WASRD was structured to provide a traceable path between each acceptance specification and higher levels of the technical document hierarchy for the Civilian Radioactive Waste Management System (CRWMS). The DOE-EM, in accordance with discussions with DOE-RW, then decided to prepare a waste acceptance specifications document that dealt only with the standard form of vitrified HLW (i.e., sealed stainless steel canisters filled with borosilicate glass that is loaded with the waste constituents). The resultant EM waste acceptance "product specifications" document, which somewhat confusingly has the same acronym (WAPS) but a slightly different title than that of the earlier DOE-RW WAPS document, contains specifications that are in nearly all cases topically and even specifically the same as the requirement found in the (DOE-RW) WASRD. The DOE-EM has the prerogative, in this arrangement, of adding specifications topics or changing the specification limits, but it is not allowed to make the specifications less restrictive (i.e., less conservative) than the requirements stated in the RW WASRD. The DOE-RL formally transmitted guidance, dated March 29, 1993, to WHC to implement these new documents within the HWVP Project.

During FY 1992, the HWVP Project prepared a plan that identified the major waste form qualification activities that are important to the HWVP Project and described the hierarchy of strategies being used to prepare the compliance basis for each of the acceptance specifications. Final publication and issuance of that document has been delayed pending completion of a cycle involving review and comment by the DOE-EM (Headquarters) and comment dispositioning and document revision by WHC. The report is planned to be published during the second half of FY 1993. This particular revision of the WFQ Program Plan, however, is based on the project planning baseline that was in place during the time of its initial FY 1992 preparation, and also will not, except by Preface discussion, address the specifics of the new DOE-EM WAPS in relation to the presentation of the respective compliance strategies.

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In addition to the WFQ Program Plan, the HWVP project prepared an initial draft (i.e., for WHC and RL internal review) of the Waste Compliance Plan, which describes how the project proposes to comply with each of the product acceptance specifications. Collectively, these two documents describe the hierarchy of topical activities that must be accomplished to ensure that the HWVP will produce a product that meets all of the acceptance specifications. These planning documents will be the subject of update revisions that will be produced several times during the life of the HWVP Project.

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8.0 ALTERNATIVE TREATMENT/DISPOSAL TECHNOLOGY

The UST-ID, funded by the Office of Technology Development (OTD) within DOE's Office of Environmental Restoration and Waste Management was created in February 1991 with a principal objective to develop and demonstrate technologies that will provide improvements or alternatives to the tank waste remediation baseline plan. The UST-ID will examine alternative technologies and technology systems for remediating USTs containing high-level, low-level, transuranic, and mixed wastes at five DOE participant sites: Fernald, Idaho National Engineering Laboratory (INEL), ORNL, Savannah River Laboratory (SRL), and Hanford Site. Activities currently included within the UST-ID at the Hanford Site are (1) characterization, (2) retrieval, transfer, and interim storage, (3) waste separation and pretreatment, and (4) low-level waste (LLW) form development. Listed below are UST-ID activities that relate to items 3 and 4. In some instances, Environmental Restoration and Waste Management (EM-30) has provided supplemental funding to these activities.

8.1 SLUDGE PARTITIONING AND TREATMENT

A key aspect in pretreatment of tank wastes will be to partition and treat troublesome constituents on a production basis. This task will be performed to develop an updated waste minimization process that has low risk and is cost effective, environmentally sound, and reliable. Tests will be conducted using existing technologies to determine the optimal subset that can work together to achieve a cost-effective production-scale waste minimization process. These same processes are under investigation by the Hanford TWRS, as described in the previous sections of this report, for possible incorporation into the TWRS technology baseline (Cruse 1993).

This task will address (1) the separation of sludges from supernates, (2) washing of the sludge and pretreatment of the dissolved portions, (3) acid dissolution of SST and DST sludges, and (4) partitioning (separating and concentrating) of TRU components.

8.1.1 Comprehensive Sludge Processing Flowsheet Development

A comprehensive sludge processing flowsheet will be developed and tested in an ORNL hot cell using hot wastes from the ORNL Melton Valley Storage Tanks (MVSTs). The comprehensive flowsheet developed in this task will provide the basis for design and operation of a pilot-scale waste processing facility to process the MVST wastes.

This work, using actual MSVT wastes similar to Hanford Site tank wastes and more easily retrievable, allows the hot verification tests to be conducted more quickly at ORNL than at the Hanford Site.

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8.1.2 Evaluation of Pretreatment Options for Hanford Tank Wastes

An evaluation of the pretreatment options for sludge taken from two different SSTs, tanks B-110 and U-110, was performed by workers at PNL, and is briefly described in Section 5.3.2 (Lumetta et al. 1993b). The pretreatment options examined for these sludges included (1) leaching of the TRU elements from the sludge, and (2) dissolution of the sludge followed by extraction of TRUs and ^{90}Sr . In addition, the TRU leaching approach was examined for a third tank waste type, neutralized cladding removal waste (NCRW) taken from DST tank 103-AW. The most recent results of the work on NCRW sludge also is described earlier in Section 4.4.

The major findings of this work are presented below:

- Carbonate/bicarbonate leaching (with and without oxidant) of tank sludges is not a promising approach to removing TRUs from the bulk waste components.
- After treatment of U-110 sludge with 2 M HNO_3 at 100 °C, the bulk of the sludge meets the NRC Class C LLW criteria for TRUs, ^{90}Sr , ^{137}Cs , and ^{99}Tc .
- Extraction of TRUs from the U-110 acid leach solution with CMPO will require adjustment of the process chemistry in order to avoid the formation of interfacial crud.
- The SREX process can be used to extract Sr from the dissolved B-110 sludge.
- The TRUEX process can be used to extract TRUs from B-110 sludge; in this case, minimal feed adjustment will be required to avoid interfacial crud.
- Data indicate that bismuth does extract into the TRUEX process solvent; however, bismuth separation from the TRUs might be achieved by adjusting the stripping conditions.

8.2 TRUEX MODEL DEVELOPMENT AND VALIDATION

This task will provide for transfer of the Generic TRUEX Model (GTM) to other DOE preapproved participants. These participants, which include PNL and WHC, will perform tests to validate the GTM using actual waste. ANL will provide consultation, as required by the validating participants. Validation testing will be conducted by ORNL.

Additional testing will be required for GTM application for the Hanford Site tank wastes. The FY 1993 activities will focus on collecting and analyzing samples. Model validation is planned for FY 1994.

8.3 TECHNICAL INTERCHANGE WITH THE FRENCH COMMISSARIAT L'ENERGIE ATOMIQUE (CEA)

Several countries (including France, Japan, and the United Kingdom) are pursuing programs directed at improving the chemical processes associated with the reprocessing of spent nuclear fuels. As part of these efforts, many of the countries are developing new technologies for separating specific fission products and actinides in waste streams. These activities are directed toward reducing the amount and radiotoxicity of the waste.

The primary area of interest is the Diamine process, a novel separation process that will separate TRU materials in a manner similar to TRUEX, but using a different flowsheet. Currently, the CEA is working on preliminary flowsheet development for the pretreatment of Hanford Site NCRW and CC wastes based on processes developed by the French Atomic Energy Commission. A report on this work, scheduled for delivery in FY 1993, provided no mass balance due to the preliminary stage of process development.

8.4 CALCINATION/DISSOLUTION OF TANK WASTES

As previously described in Section 5.3.2.1, a series of full-scale demonstrations is underway at a vendor site for calcining simulated Hanford Site waste using plasma arc technology to determine the feasibility of calcining in a production-scale process. A primary objective is to identify the combination of chemical dissolution and thermal processing that will destroy 99 percent each of the nitrates, organics, and ferrocyanides. A favorable feature of the plasma arc process is that it would separate the TRU material into a relatively small volume.

Activities supporting the FY 1993 testing will include detailed chemical analysis to better define the mass balance of the process and preparation of simulants for testing. Concurrent activities related to this project include chemistry development and residue leaching development. The chemistry development task will establish the current state of knowledge of the Hanford Site's tank wastes as it pertains to the chemical dynamics of the calcination and dissolution process steps.

8.5 BIOLOGICAL DESTRUCTION OF TANK WASTES

It is anticipated that existing biotechnology processes will be demonstrated as adaptable to HLW and LLW stored in USTs. The approach that appears feasible is denitrification (reduction of nitrate to N_2) and simultaneous separation of the remaining radionuclides and heavy metal constituents of the waste by biosorption (adsorption into bacterial biomass).

The existing processes were initially evaluated for their applicability to the conditions and characteristics specific to buried wastes at INEL. Testing concluded that microbes were capable of denitrification under conditions of salt concentrations up to 4M (Na + K) with acetic and phosphoric acids as the only added nutrients.

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The approach for FY 1993 will identify how bioremediation can best be implemented within the process flowsheets currently being developed for the TWRS pretreatment processes. This will include assessing tank waste characteristics, estimating potential impacts of anticipated advanced technologies, and identifying acceptable surrogate waste constituents. Further development work calls for demonstration of a laboratory-scale, continuous-flow bioreactor on simulated tank wastes (without metal contaminants) and assessing denitrification activity over a wide range of controllable conditions within the bounding conditions of the actual wastes.

8.6 CESIUM EXTRACTION TESTING

This task will support development of the cesium extraction CPU for application to a variety of Hanford Tank Waste streams as previously discussed in Section 4.7.2.1. The SRL, in coordination with PNL, is currently performing ion-exchange tests to obtain critical data needed for successfully designing and selecting the ion-exchange media for the CPU. Included in this task is the investigation of commercially available and foreign technology for cesium removal.

The SRL-developed resorcinol-formaldehyde resin for cesium removal has been demonstrated in testing at SRL, ORNL, and PNL. Other media for cesium removal either have lower capacity or are incompatible with the high pH and aluminum concentration of Hanford and Savannah River Site wastes. The SRL will provide technical data, bench-scale tests, and technical consultation for cesium ion exchange and radiolytic stability of the resin for this task. Recent concerns with the resorcinol-formaldehyde resin regarding the potassium level in the waste will be investigated fully and resolved.

8.7 NITRATE TO AMMONIA AND CERAMIC PROCESS

A patentable, inexpensive, and highly efficient method of decomposing the sodium nitrate component of tank wastes is being developed by ORNL. The supporting kinetic data for engineering use in pilot-scale design will be generated in bench-scale experiments followed by pilot-scale demonstrations. The process removes sodium nitrate by reactions creating ammonia as a by-product. The remaining waste volume is converted to a solid, inert, ceramic-like product, with the sodium incorporated into the ceramic matrix. Significant waste volume reductions (65 to 75 percent) may be possible relative to processing with current methods (e.g., grout). Initial bench-scale tests have been successful and further testing is planned for FY 1994.

8.8 TANK WASTE PROCESSING ANALYSIS

This task will evaluate pretreatment requirements of Hanford Site tank wastes on a tank-by-tank basis. Completion of this task will (1) identify the processing required for each tank to meet pretreatment criteria, (2) optimize the deployment of distributed processes for pretreatment. Data from other DOE-funded associated tasks will be factored into this task, as indicated by the UST-ID and other programs.

8.9 CESIUM EXTRACTION COMPACT PROCESSING UNIT (CPU)

A CPU for cesium ion exchange will be designed, built, and tested. Demonstration of the CPU concept is required before a decision to implement compact processing for the TWRS can be justified. The CPU for cesium ion exchange will address removal of cesium from Hanford Site tank waste supernates. PNL will develop conceptual design and a specification for the CPU and seek industry participation for detailed design and fabrication. PNL will interact with SRL and industry to obtain the necessary ion-exchange data to design this initial CPU for cesium ion exchange.

The current design concept is a single-pass, regenerative ion-exchanger using several columns, small feed tanks, and associated piping, pumps, valves, and instrumentation and control systems. This process system will be enclosed in a containment structure providing the shielding and containment necessary for installation and operation in the Hanford Site tank farms.

The development program began late in FY 1992 and is progressing favorably. The major work breakdown elements are as follows: (1) Environmental Compliance, (2) Design, (3) Fabrication, (4) Component Testing and Installation, (5) Nonradioactive Demonstration, and (6) Radioactive Demonstration.

The following primary design requirements for the CPU have been established.

- Capacity to process one million gallons of Hanford Site DST waste in one year.
- Cesium decontamination factor (DF) of 10,000; i.e., the concentration of ^{137}Cs remaining in the waste stream will be less than the NRC Class A limit of $\leq 1 \text{ Ci/m}^3$.
- Capable of operating acceptably and without significant maintenance for a minimum of one year.
- Design that permits using a construction crane and a transport trailer. The availability of various transport trailers suitable for CPU transport will be investigated when a firm design estimate of CPU weight and dimensions is available. Design targets for an approximate overall CPU size of less than 15 ft by 15 ft by 15 ft and weight less than 500 tons have been established to ensure that CPU transport is possible.

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9.0 WASTE TANK SAFETY ISSUES

9.1 INTRODUCTION

9.1.1 Purpose

This section is to provide a description, status, and plans for resolving pertinent safety issues (SIs) which may affect either the treatability of tank waste or the feasibility of using grout or glass (or another alternative) as a final disposal option.

9.1.2 Background

The U.S. Congress enacted Public Law 101-510, Section 3137, *Safety Measures for Waste Tanks at Hanford Nuclear Reservation (Safety Measures Law 1990)*, in November 1990, to address SIs concerning the handling of high-level radioactive waste in storage tanks at the Hanford Site. In response to this law, the Secretary of Energy reported to the U.S. Congress (DOE 1991) in June 1991 on actions being taken to promote tank safety and the timetable for resolving the SIs. Later in 1991, a second and more detailed report was issued that provided SI descriptions, as well as technical bases, alternatives, and an action plan for each SI identified in the *Report to Congress* (Wilson and Reep 1991).

Further review of all DOE waste storage sites by the DOE HLW tanks task force in 1992 identified additional SIs and a new category called system deficiencies (DOE 1992). The HLW Tanks Task Force report identified a total of 30 SIs and system deficiencies that must be addressed at the Hanford Site, Savannah River, Idaho Falls, and West Valley facilities. Of the 30 issues and deficiencies identified, 28 are applicable to the Hanford Site.

The SIs and system deficiencies encompass a broad spectrum of problem areas including:

- Reactivity of the tank waste in 49 tanks, and heat generation in one tank, which may have a serious potential for release of HLW due to uncontrolled increases in temperature or pressure. These 50 Watch List tanks (originally there were 53) were identified in accordance with the Safety Measures Law
- Potential for the release of harmful vapors and nuclear criticality in waste tanks
- Inadequate characterization of tank contents which does not allow full understanding of the chemical and radiological stability of the wastes, and tank integrity assessments to determine tank safe operating life
- No secondary containment for storage of waste in 149 tanks; 68 of these tanks are known or suspected to have leaked liquid radioactive waste to the ground

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- Deficient tank farm facilities and equipment which do not meet minimum requirements of consensus codes and standards, regulations, and DOE orders
- Deficient safety and operating documentation which does not meet minimum requirements of codes and standards, regulations and DOE orders.

The SIs associated with the first two problem areas above are the most serious SI since they deal with reactivity, heat generation, vapor releases, and nuclear criticality in the waste. These SIs are of primary concern because of their potential for release of radioactivity or harmful vapors, and their potential for impacting the treatability of tank waste. The SIs associated with these two problem areas are listed below. Four of these SIs involve unreviewed safety questions (USQs). The tanks affected by these most serious SIs are identified in Table 9-1.

- High flammable gas concentrations (also involves a USQ)
- Potentially explosive mixtures of ferrocyanide (also involves a USQ)
- Potential for runaway organic-nitrate reactions (also involves a USQ for tank 241-C-103)
- Water additions needed to cool SST
- Tank vapor release
- Potential for nuclear criticality in HLW tanks (also involves a USQ).

9.1.3 Impact on Waste Treatment

Activities are underway to resolve the SIs identified with the waste stored in Hanford Site waste storage tanks. These SIs resulted from past processes to treat the waste, and now pose a potential for release of high-level radioactive waste from 50 tanks (Watch List tanks) due to uncontrolled increases in temperature or pressure. In addition, the possibility of worker exposure to potentially harmful tank vapors and the potential for a nuclear criticality exists in tank farms.

In the process of resolving the tank waste SI much information on the behavior or the waste (radiolytic, chemical, and gas generation mechanisms) and character of the waste (radioactive and chemical content, and physical properties) is being generated. This information will be useful in developing process flowsheets for treating the waste, and operational strategies for handling the waste during disposal operations.

Safety Issue Title	Number of Tanks By Area and Tank Farm																	Total Tanks	
	200 East Area Tank Farms										200 West Area Tank Farms								
	DST					SST					DST		SST						
	AN	AP	AW	AY	AZ	A	AX	B	BX	BY	C	SY	S	SX	T	TX	TY		U
High Flammable Gas Concentrations	103 104 105		101			101	101 103					101 103	102 111 112	101 102 103 104 105 106 109	110			103 105 108 109	24
Potentially Explosive Mixtures of Ferrocyanide								102 106	103 104 105 106 107 108 110 111 112	108 109 111 112				107	118	101 103 104		20	
Potential for Runaway Organic-Nitrate Reactions								103			103		102	106		105 118		106 107	8
Water Additions Needed to Cool Single-Shell Tank											106								1
Tank Vapor Release		103	101	101 102	101 102	101 102 103 104 105 106		101 102 103 104 105 106 107 108 109 110 111 112	101 102 103 104 105 106 107 108 109 110 111 112	101 102 103 104 105 106 107 108 109 110 111 112	103 104 105 106 107 108 109 110 111 112		102	106	101 107	105 118	101 103 104	107 108	69
Potential for Nuclear Criticality in HLW Tanks	All Tanks										All Tanks							177	

Table 9-1. Most Serious Waste Tank Safety Issues and Tanks Affected.

Resolution of SIs is focusing on ways to ensure the safety of the SST and DST systems until appropriate treatment and disposal of their contents can be implemented. To ensure interim safety, extensive administrative and technical controls are maintained for the safety-issue related tanks identified in Table 9-1. A broad-based peer review of all planning and safety documentation by high-level oversight groups appointed by DOE-HQ is also being conducted. A high-level waste tanks task force and a high-level waste tanks advisory panel at the DOE in the Office of Environmental Restoration and Waste Management have been established. Together with the Hanford Site staff they ensure that the Hanford Site corrective action programs are technically adequate, have the proper priority, and are on an expeditious schedule for resolution. In addition, DOE approval of all actions relating to those tanks containing flammable gases and/or ferrocyanide compounds is required.

The hazardous characteristics of the existing SST and DST wastes, leading to their identification and control, currently are being evaluated on the basis of pertinent chemical literature, expert peer judgment, and limited sampling data. Mitigating factors, such as moisture content, presence of relatively inert diluents (e.g., sodium carbonate, sodium aluminate, and sodium phosphate) and any other conditions that could reduce reactivity of the wastes, are being analyzed.

Scenarios of significant concern associated with waste in tanks include the following.

- Potential for ignition of flammable gases, such as hydrogen-air and hydrogen-nitrous oxide.
- Potential for ignition of ferrocyanide-nitrate mixtures initiated by the radiolytic and/or chemical heating of dry salt cake.
- Potential for ignition of organic-nitrate mixtures initiated by the radiolytic and/or chemical heating of dry salt cake.
- Potential for tank leakage causing contaminant release to the environment while simultaneously meeting a requirement for addition of cooling water to tank 106-C to maintain its structural integrity.
- Potential for release of noxious vapors from waste tanks.
- Potential for nuclear criticality in waste tanks.

Administrative and technical controls are implemented to restrict activities which could cause any abnormal, undesirable events. For example, pumping of interstitial liquid from tanks containing ferrocyanide has been stopped to maintain present in-tank chemical stability. Nonsparking tools and use of electrical bonding techniques on tank instrumentation are also mandated. Normal activities for tanks at issue are limited to surveillance. Preparation of special safety analysis documents, which are extensively reviewed by the aforementioned peer groups, are prepared for all in-tank work activities.

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Comprehensive monitoring, characterization, and attendant applied research activities have been initiated to support resolution of the current key issues and any future safety concerns related to potential waste incompatibilities or actions from planned treatment and disposal of selected tank wastes. Such efforts will also provide a sound basis for near-term resolution of waste tank SIs, and will aid in defining the envelope of safety to support the disposal of all tank wastes at the Hanford Site. A plan to implement resolution of waste tank safety issues at the Hanford Site (Wilson and Reep 1991) and a report statusing these activities through March 1993 have been issued (Reep 1993).

9.2 STRATEGY FOR RESOLVING MOST SERIOUS SAFETY ISSUES

The overall strategy is to resolve the most serious waste tank safety issues as fast as resources can be effectively applied. The reason for emphasizing a strategy for the most serious safety issues is that 50 of the Watch List tanks pose a serious potential for release of high-level radioactive waste due to uncontrolled increases in temperature or pressure. In addition, the possibility of worker exposure to potentially harmful tank vapors and the potential for a nuclear criticality exists in the tank farms.

To provide for faster and more cost effective resolution of safety issues, a strategy has been implemented that divides tanks into groups having similar characteristics. The division of tanks into groups is based on review of available waste sample data and past processing records. The premise for this strategy is that tanks having similar waste characteristics will likely require similar steps to resolve the associated safety issue.

The overall approach for resolution of safety issues involves four steps, as follows:

1. Resolution by evaluating and defining the problem
2. Resolution in-tank with no treatment whenever possible
3. Resolution in-tank with treatment for remaining tanks whenever possible
4. Resolution out-of-tank for tanks not resolved by the above steps.

Resolution of the safety issue for a tank (or group of tanks) becomes progressively more difficult and costly as the steps increase. It is expected that the safety issues for most of the 50 Watch List tanks will be resolved in the first or second steps shown above. Resolution of the safety issues for the remaining Watch List tanks will be accomplished by in-tank treatment of the waste (resolution in-tank with treatment), or by removing the waste for storage in another tank (retrieval) with or without treatment (resolution out-of-tank). The strategy for resolving each of the six most serious SIs and USQs is summarized in Table 9-2.

Table 9-2. Strategy for Resolving Most Serious Safety Issues.

Safety issue	Grouping	Resolution strategy
High Flammable Gas Concentrations	SY Farm (Two Tanks)	Close USQ in FY-96. Mitigate tanks 241-SY-101 and 241-SY-103 by installing and operating mixer pumps or an alternative method, until new DSTs (Project W-236A) are available. Retrieve waste to new DSTs (Project W-236A). If necessary, treat waste in IPM (Project W-236B) to resolve SI.
	101-AW (One Tank)	Close USQ in FY-96. Mitigate tank 241-AW-101 as above until the waste is retrieved for feed to the Grout Treatment Facility. Treat waste in IPM (Project W-236B), if necessary, prior to feeding to Grout Treatment Facility.
	AN Farm (Three Tanks)	Close USQ in FY-97. Mitigate tanks 241-AN-103, 241-AN-104, and 241-AN-105 as above until the waste is retrieved for feed to the Grout Treatment Facility. Treat waste in IPM (Project W-236B), if necessary, prior to feeding to Grout Treatment Facility.
	SSTs (18 Tanks)	Close USQ and Safety Issue in FY-99. Complete evaluation and definition of flammable gas problem in 18 SSTs, and install monitoring equipment. Not expected to require treatment of waste either in-tank or out-of-tank to resolve SI.
Potentially Explosive Mixtures of Ferrocyanide	Two Tanks (Historical Review)	Close USQ in FY-93. Recommend removal of two SSTs from the Watch List based on review of historical records to resolve SI. Originally 6 tanks were included, but approval was granted in July 1993 to remove 4 of the tanks from the Watch List.
	14 Tanks (U Plant Flowsheet)	Close USQ in FY-94. Resolve SI by installing monitoring and moisture control equipment in 14 SSTs. Not expected to require treatment of the waste either in-tank or out-of-tank.
	Four Tanks (In-Farm Flowsheet)	Close USQ in FY-94. Mitigate tanks by installing monitoring and moisture control equipment as above. Retrieve waste to new DSTs and treat in IPM, if necessary, to resolve SI. The planning basis is that these tanks will not require out-of-tank resolution (i.e., retrieval and pretreatment).
Potential for Runaway Organic-Nitrate Reactions	103-C	Close USQ for tank 241-C-103 in FY-94. Pump out floating organic layer from 241-C-103 to resolve safety issue.
	Other Seven Organic Tanks	Mitigate remaining seven tanks by installing monitoring and moisture control equipment. Retrieve waste to new DST (Project W-236A), and treat in IPM (Project W-236B), if necessary, to resolve SI.
Water Additions Needed to Cool SST 106-C	106-C	Mitigate tank by reducing water additions to a minimum for safe storage. Retrieve waste to a DST in accordance with TPA Milestone M-07 to resolve SI.
Tank Vapor Release	103-C	Install area monitoring equipment on tank 241-C-103, and sample and characterize vapors. Mitigate tank with a vapor treatment system (in-tank resolution with treatment) to resolve SI.
	C Farm (Besides 103-C)	Install area monitoring equipment in 241-C Farm and sample and characterize vapors. If necessary, mitigate tanks with a portable vapor treatment system (in-tank resolution with treatment) to resolve SI.
	Remaining Tanks	Install area monitoring equipment in selected tank farms. If vapor release problems are identified mitigate as above to resolve SI.
Nuclear Criticality	Potentially All Tanks	Close USQ in FY-95. Gather data to show that nuclear criticality in a tank is not credible. Perform risk assessment and determine controls needed for SAR revision. To resolve SI, develop and test criticality monitoring and fissile material measurement equipment and demonstrate in tanks 241-SY-101 and 102 and 241-C-106 during retrieval of waste. Evaluate need for use in subsequent retrieval operations.

DST = Double-Shell tank
 SAR = Safety Analysis Report
 SST = Single-Shell Tank

IPM = Initial Pretreatment Module
 SI = Safety Issue
 USQ = Unreviewed Safety Question

9.3 STATUS AND PLANS FOR RESOLVING MOST SERIOUS SAFETY ISSUES

9.3.1 High Flammable Gas Concentrations

9.3.1.1 Description. Six DSTs and 18 SSTs have been identified as having a significant potential for flammable gas (hydrogen and nitrous oxide) accumulation, entrapment within the waste, and periodic gas releases. The possible presence of a flammable gas mixture, together with an ignition source, could provide the potential for a deflagration, leading to an increased risk of the release of radioactive waste. A lower potential risk is an unfiltered release of radioactivity to the environment from overpressurizing the ventilation system during a periodic gas venting. The waste tank that has been the most active, tank 241-SY-101, has released, during several of its venting periods, concentrations of hydrogen that, for a short period of time, exceeded the amount necessary to support combustion. During these releases, overpressurizations have been measured without resulting in any contamination spread. The venting of gases is expected to recur periodically until some form of in-tank treatment (mitigation) is taken. Resolution of the safety issue will most likely require retrieval of the DST waste and removal of some of the constituents (remediation). Operational restrictions have been imposed on the 24 waste tanks to reduce the potential for ignition sources.

A large number of options have been considered for mitigating (i.e., reducing the severity or intensity of the hazard) the flammable gas issue. A ranking of all concepts was conducted based on the following factors.

- Confidence in effectiveness of technology
- Achievable risk reduction
- Implementation risk
- Complexity of data/prototype modeling needs
- Implementation time required
- Operating time to achieve mitigation
- Maintenance, operational, and surveillance requirements
- Risk affecting disposal options.

The top four concepts selected for further evaluation were heating, dilution, sonic/ultrasonic agitation, and mixing with a horizontal jet pump.

The mitigation option that is selected is expected to take at least one (and probably several) years to instrument, obtain and characterize in-tank core samples, model and understand tank mechanisms, and complete National Environmental Policy Act (NEPA) documentation on the proposed mitigative options. Mitigative actions to eliminate accumulation and/or generation of flammable gas mixtures may require ventilation system replacement, additional DST space for diluting the waste, or sophisticated waste treatment processes to be developed, engineered, constructed, and operated for the remediation of all 24 high-level radioactive waste tanks that accumulate flammable gases. Meanwhile, near-term mitigative efforts will be directed towards emergency preparedness planning and eliminating the cyclic releases of flammable gas mixtures through sonic/ultrasonic agitation, in-tank mixing with a pump,

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dilution, heating, or some other method so that the gases generated within the waste tank will be continuously released at concentrations within safe limits.

9.3.1.2 Status. Work has continued to be focused on understanding the cyclic venting of flammable gases phenomena in tank 241-SY-101. This has included analyses of core samples, laboratory studies, modeling studies, tank upgrades, developing mitigation alternatives, and preparing for a mitigation test in tank 241-SY-101 using a mixer pump. Major accomplishments are listed below.

- A mixer pump was modified, tested, and installed in tank 241-SY-101. Four air lances and a bent thermocouple (TC) tree were removed from the tank. Ancillary equipment necessary to support the mitigation test was installed. This included a data acquisition and control system, multi-functional instrument tree (MIT), standard hydrogen monitors, and velocity-density-temperature trees. Planning for this activity is documented in the Tank 101-SY Flammable Gas Mitigation Test Project Plan (Lentsch 1992).
- A second core sample was obtained from tank 241-SY-101. The core sample analysis results are documented in reports on waste chemistry and physical properties (Reynolds 1992). A data analysis report on tank 241-SY-101 was also issued (Anantatmula 1992).
- A technical report was issued that closed out the issue of a potential for a crust burn in tank 241-SY-101 (Fox, et al, 1992).
- The Bureau of Mines study on the flammability of gas mixtures was issued (Cashdollar, et al, 1992).
- Accident consequence criteria and requirements for resolution of the flammable gas issue were documented (Christensen 1992).
- Excellent progress was made on modeling the behavior of tank 241-SY-101 waste.
- Methods were developed to analyze tank 241-SY-101 waste for chelating agents and to qualitatively identify low molecular weight degradation products.
- A high sensitivity mass spectrometer was installed and placed into routine operation in a PNL facility. Highly accurate analysis of gas samples from the vapor space of tank 241-SY-101 are being obtained.
- A data interpretation report for tank 241-SY-101 Window E core sample analysis was issued (Reynolds, 1993), and Window criteria for tank 241-SY-101 were revised.

9.3.1.3 Plans. Near-term plans (FY 1993 and 1994) include the following major activities.

- The pump installed in July 1993 will be tested at low speeds, followed by high speed tests. Results and recommendations will be documented.

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- A hazard assessment of tank 241-SY-103 will be completed.
- Near-term ventilation upgrades to tank 241-SY-101 will be completed and a modular exhauster will be procured for 241-SY and 241-AN tank farms.
- A gas monitoring cabinet will be installed on tank 241-SY-103 and three cabinets will be procured for 241-AN tank farm.
- Priorities will be assigned to flammable gas tanks based upon all available waste characterization data.
- Core sampling of tank 241-SY-103, or of another flammable gas tank which is determined to be of most concern after tank 241-SY-101.

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Long-term plans are focused on further evaluation and definition of the flammable gas SI by obtaining data on tanks and contents, developing tank safety criteria, and applying these criteria on a tank-by-tank basis. Current planning is based on the assumption that all six DST flammable gas tanks will require mitigation testing and mitigation, and that the 18 SSTs will not require mitigation. This assumption is based on historical records review. All 24 flammable gas tanks will be sampled, analyzed, and the data interpreted; and ventilation, monitoring, and instrumentation upgrades will be completed before the assumption can be validated.

Longer-term plans call for remediation of the safety issue. In order to resolve the safety issue for the 24 flammable gas tanks, all six DSTs will be retrieved, and two DSTs (241-SY-101 and 241-SY-103) may require treatment for organic destruction. Waste from 241-AW-101 and three 241-AN farm tanks will be retrieved and treated in the IPM to provide Grout feed. None of the 18 SSTs will be retrieved for safety issue resolution, but some need to be pumped for the purpose of interim stabilization.

9.3.2 Potentially Explosive Mixtures of Ferrocyanide

9.3.2.1 Description. 20 SSTs (originally these were 24 SSTs) may contain appreciable amounts of ferrocyanide precipitates (1,000 gram-moles [465 pounds] or greater). Estimated ferrocyanide content of the 20 tanks ranges from <1,000 g-moles (465 pounds) to approximately 83,000 g-moles (38,600 pounds) in tank 241-BY-104 (referred to as tank BY-104). During the early 1950's, in an effort to quickly obtain additional waste storage volume, a process was developed to reduce radionuclide concentration in the free-standing liquid tank wastes to a level low enough to permit disposal of the liquid to the soil. This process involved the addition of compounds containing ferrocyanide to the tanks to precipitate soluble radioactive nitrate constituents. Ferrocyanide compounds can react exothermically under certain conditions, including dryness, proper chemical concentration, and elevated temperatures. Explosive reactions can occur at 285 °C (545 °F). Organic materials (which some of these tanks may also contain) can produce an exothermic reaction in the temperature range of 220 to 250 °C (430 to 480 °F).

A 1990 General Accounting Office (GAO)-sponsored study postulated dose consequences that were two orders of magnitude greater than those stated in the 1987 EIS for a worst-case accident (Peach 1990). Because a bounding safety envelope may no longer be valid, the ferrocyanide issue was declared an USQ in October 1990 (Deaton 1990). Such a release is believed to have an extremely low probability of occurrence even from a localized "hot-spot," because the maximum temperatures measured inside the ferrocyanide tanks at the Hanford Site are at or below 55 °C (130 °F), thus providing a significant margin of safety. Tank temperatures have also been declining about 2 °C per year as the tank fission products continue to decay.

Three options are being considered to close the ferrocyanide USQ and resolve the SI: (1) demonstrate that the probability and consequences of a runaway chemical reaction are acceptably small and, therefore, no action other than surveillance of important tank parameters is required; (2) monitor and maintain moisture content of the waste to ensure that a ferrocyanide propagating reaction cannot occur and, therefore, no further action is required; and (3) if necessary, remove the waste from the tanks and destroy the ferrocyanide in the IPM (Project W-236B).

It is expected to take three to four more years to develop and install new instrumentation, obtain and characterize in-tank core samples, and complete a final NEPA document analyzing the proposed actions. Meanwhile, near-term efforts are required to determine if the tank constituents are stable. To determine if the tank constituents are stable, modeling, risk analysis, issue closure criteria, safety evaluations, chemical reaction studies, enhanced tank monitoring and modeling, waste characterization, and emergency preparedness planning activities are being conducted. Work is also underway to ensure that temperatures measured at various points in the tank are representative of the entire tank contents. Development of a moisture measurement system is also underway. This will further ensure that the tank contents are maintained well below temperatures that could cause exothermic reactions.

9.3.2.2 Status. Evaluation and definition of the ferrocyanide SI and USQ continued with vapor and full-depth core sampling and characterization; catalyst, initiator and diluent studies; sensitivity tests; adiabatic calorimetry screening tests; and hot spot modeling. New TC trees were installed in six tanks. The new TC trees are designed to have two or more TC elements in the waste and one or more elements in the vapor space. Connection of tank TCs to the Tank Monitor and Control System (TMACS) continued. Major FY 1992 and 1993 accomplishments are listed below.

- Four tanks (241-BX-110, 241-BX-111, 241-BY-101 and 241-T-101) were removed from the USQ and Watch List based on further review of historical records. This reduced the number of ferrocyanide tanks on the Watch List to 20. Two additional tanks are being further evaluated for removal from the Watch List, based on a review of historical records.
- Ten new TC trees were installed in ten tanks. The 10 remaining ferrocyanide tanks will have new TCs installed (or in the case of two of the tanks, the TC elements will be replaced) in FY 1994 and 1995.

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- Nine tanks were connected to the TMACS. A total of 14 ferrocyanide tanks are connected to the TMACS.
- Push-mode core sampling of three tanks (109-C, 112-C, and 107-T) was completed. Laboratory analysis of C-112 shows that moisture is at 50 weight percent (wt%); energetics are much lower than expected; and the cesium-137 is still insoluble.
- Spectral gamma scans were completed for cesium-137 and europium-154 in 12 tanks.
- Hot spot thermal modeling was completed on the credibility of thermal hot spots in ferrocyanide tanks. Modeling indicates that a rapid chemical reaction within the ferrocyanide waste due to a hot spot is incredible because the maximum waste temperature is limited to 120 °C, the boiling point of the waste liquor.
- The SA and environmental assessment (EA) for pumping leaking ferrocyanide tanks was issued for DOE review.
- Criteria for safe storage of ferrocyanide waste in situ was developed. Current assessments show that resolution of the ferrocyanide safety issue will not require mitigation or out-of-tank remediation for many of the tanks.
- A proof-of-principle infrared scan was completed in a non-Watch List tank. Sensitivity is better than expected and an existing hot spot could probably be detected if one existed.
- Energetic results from two known ferrocyanide tanks indicate that the material is even less energetic (and possesses less energetic potential) than the U Plant simulant. The exotherms recorded from waste obtained from tanks 241-C-109 and 241-C-112 do not exceed 13 cal/dry g of waste, and in several cases no discernable exotherm was observed. The minimum value established as a level of concern is 75 cal/g dry waste.
- Total cyanide assays performed on the wastes in these tanks suggest significant degradation of the ferrocyanide from the original waste condition. In 241-C-109 and 241-C-112, calculations based on historical records suggest that over 38,000 and 60,000 g-mols of ferrocyanide were deposited in each tank, respectively. Estimates based on core sample data indicate that approximately 7,100 g-mol and 8,700 g-mols remain, respectively. As a basis for comparison, the U Plant simulants possess a ferrocyanide concentration ranging between 4.3 to 8.6 wt%; the ferrocyanide concentration estimates (based on total cyanide results) for the tank waste range between 0.8 to 3.0 wt%.

Additional details on the status of the ferrocyanide SI can be obtained from the *Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 90-7 Quarterly Reports* (e.g., Cash and Dukelow 1992) and *Ferrocyanide Program Plan* (Dukelow 1992).

9.3.2.3 Plans. Near-term plans (FY 1993) include the following activities.

- Install TC trees in the remaining four non-leaker ferrocyanide tanks.
- Obtain DOE approval of the new method for installing TC trees in leaker tanks and order TC trees.
- Install TMACS in C, T, and BX tank farms, and connect new TC trees to the TMACS as they are installed in non-leaker ferrocyanide tanks.
- Complete demonstration of in-tank moisture monitoring using the enhanced neutron probe.
- Recalculate dose consequences for various postulated ferrocyanide burns.
- Update the ferrocyanide hazards assessment to the current state of knowledge and issue a revision to the report.
- Develop a fault-tree analysis for ferrocyanide hazard identification to resolve the ferrocyanide USQ.
- Complete data interpretation of core samples from tanks C-109 and T-107.
- Issue reports on hot spot thermal modeling; reaction sensitivity studies; ferrocyanide speciation method development; catalyst, initiator and diluent screening tests; ferrocyanide salt aging studies; microconvection modeling; cyanide speciation development at the 222-S Laboratory; reaction kinetics studies; and resolve the USQ.
- Core samples will be taken from tanks 241-C-108 and 241-C-111 by the Tank Waste Characterization Program.

Long-term plans are focused on resolving the ferrocyanide SI and closing the USQ by completing studies to confirm that resolution can be accomplished for these tanks without in-tank or out-of-tank treatment. In addition, instrumentation and monitoring upgrades will be completed. The planning basis is that no ferrocyanide-bearing tanks will require out-of-tank resolution (i.e., retrieval and treatment).

9.3.3 Potential For Runaway Organic Nitrate Reactions

9.3.3.1 Description. Eight SSTs at the Hanford Site may contain high concentrations of organic chemicals (e.g., total organic carbon content of more than 3 wt.% on a dry basis) mixed with nitrate/nitrite salts. Accurate concentrations for organic materials in these SSTs, and the chemical composition of the organic materials, are not known at present. Concentrated mixtures of organics with nitrate/nitrite salts could support an exothermic reaction at temperatures above approximately 180 °C (356 °F). In a scenario involving overheating of the waste in the tanks, an organic nitrate/nitrite

mixture might react exothermically, possibly compromising tank integrity and releasing radioactive materials to the environment. This is believed to have a low probability of occurrence, because the margin between the minimum ignition temperature [approximately 180 °C (356 °F)] and measured tank temperatures is large (tank temperatures in 1993 ranged from 26 °C (78 °F) to 50 °C (122 °F).

An eighth tank, 241-C-103, was added to the organic tanks Watch List due to the presence of a floating organic layer. The existence of this separable organic phase (floating layer) was declared a USQ in September 1992 because the consequences of this floating layer igniting and burning have not been fully analyzed.

Two options are being considered to resolve the organic-nitrate/nitrite issue: (1) demonstrate through waste characterization and laboratory testing that the probability of an exothermic reaction is acceptably small and that no action is required; or (2) retrieve the waste in order to treat the organic constituents using an appropriate organics destruction process.

It is expected to take up to six years to develop and install new instrumentation, obtain and characterize in-tank core samples, develop issue closure criteria, and complete NEPA and safety documentation analyzing the proposed remedial actions. Near-term efforts are focused on determining if the tank constituents are stable and, if so, whether they will remain so for a long period of time.

9.3.3.2 Status. Major emphasis has been on planning and developing a strategy for closure of the waste tank organic issue. Major FY 1992 and FY 1993 accomplishments are listed below.

- Installation and calibration of a high resolution mass spectrometer was completed (PNL).
- A report was issued on mechanisms that could concentrate waste constituents and increase the likelihood of a propagating reaction (Gerber et al. 1992).
- Mixing alternatives were studied. Mixing of organic-bearing waste will likely be required for either in-tank mitigation or ex-tank treatment for remediation.
- In preparation for waste aging studies, a literature search was completed on the effects of radiolysis and/or oxidation on waste organics and their analogs (PNL).
- Testing of organic waste surrogate energetics was completed by the U.S. Bureau of Mines and Fauske & Associates, Inc.
- Interim criteria were defined for organic tanks with the objective of determining requirements for placing tanks on, or removing tanks from, the organic tanks Watch List.
- A JCO and an EA were completed in support of tank 241-C-103 vapor and supernate (organic and aqueous) sampling.

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- An analytical plan for analysis of the tank 241-C-103 supernate sample was prepared. A data quality objectives process was conducted in support of the analytical plan.

9.3.3.3 Plans. Near-term plans (FY 1994) include the following activities.

- Obtain and analyze tank 241-C-103 supernate sample.
- Complete tank 241-C-103 Safety Analysis in support of USQ resolution. Resolve tank 241-C-103 USQ.
- Issue engineering study on retrieval and disposal of tank 241-C-103 organic layer.
- Issue an update to the *Waste Tank Organic Safety Program Plan* (WHC-EP-0502).
- Reassess 149 Hanford SSTs (against interim organic tanks Watch List criteria) for inclusion on the Watch List.
- Complete Hazards Analysis for organic Watch List tanks (tank 241-C-103 excepted).
- Initiate waste aging studies (PNL).
- Initiate organics solubility studies.
- Initiate organics concentration mechanism studies (PNL).
- Continue development of organic analytical methods (PNL).
- Continue organic waste surrogate/simulant energetics studies.

Long-term plans include (1) waste surrogate and waste simulant studies to determine if there is a potential for exothermic organic-nitrate/nitrite reactions; and (2) characterization of waste to determine if the Watch List tanks contain unacceptable concentrations of organic chemicals. All eight organic tanks will be core sampled, analyzed, and data will be interpreted. In addition, instrumentation upgrades will be completed.

Mitigation of tank 241-C-103 will be accomplished by pumping the floating organic layer from the tank. The planning basis assumes that mitigating tank 241-C-103 by removing the organic layer will resolve the SI for this tank. Mitigation of the other seven tanks will be accomplished by moisture monitoring and control. For these seven organic tanks (241-C-103 excluded), it is assumed that in-tank treatment (mitigation) will not resolve the safety issue but will ensure safe interim storage. Remediation of these seven organic tanks will require retrieval and treatment of the waste by an organic destruction process to resolve the organic safety issue. As waste characterization and tank monitoring information is collected and analyzed, the number of tanks needing retrieval and organic destruction may change.

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9.3.4 Water Additions Needed to Cool Single-Shell Tank

9.3.4.1 Description. Tank 241-C-106 is a 2.0-million-liter (530,000-gallon) capacity SST. The tank has been used for high-level radioactive waste storage since mid-1947 and currently is approximately half-full of waste. In the late 1960's, during the implementation of a program to recover heat-generating strontium and cesium from high-level radioactive waste in some of the SSTs, heat-generating sludge was inadvertently transferred to tank 241-C-106. Since mid-1971, water has been added periodically to tank 241-C-106 to keep the sludge wet and to promote heat removal by evaporative cooling to the vapor space. The cooling water is in addition to the other drainable liquids in the tank.

If tank 241-C-106 were to leak, the addition of cooling water could increase the amount of leakage to the ground. If cooling water additions to the tank are stopped, the sludge will heat to temperatures greater than established safety limits and may cause tank structural damage, possibly leading to dome failure and an unacceptable radioactive release to the environment. A Tri-Party Agreement milestone has been established to remove all the drainable liquid (which would eliminate the use of cooling water) and to interim-isolate tank 241-C-106 by September 1996.

Two options are being considered to mitigate this high-heat generation SI in tank 241-C-106: (1) partially remove, to DSTs, enough of the tank contents to reduce heat generation in tank 241-C-106 to an acceptable limit; and (2) provide a mechanical means of cooling the radioactive waste. The first option is currently the preferred alternative; however, transfer lines and DST space would be required for receipt of the removed waste which would impact tank space logistics.

It is expected to take up to three years to develop and install additional instrumentation and equipment, obtain and characterize in-tank core samples, and complete safety and NEPA documents to analyze the proposed remedial actions. For the near term, a contingency action plan will be followed in case of tank leak. Pending study results, DOE will work with regulators to select the best option to resolve this safety concern. The tank 241-C-106 high-heat SI is expected to be resolved by September 1998, by sluicing waste from the tank to reduce the heat generation in tank 241-C-106 to acceptable limits. The near-term mitigative measures being implemented by Waste Tank Safety Programs is being coordinated with the efforts of the Waste Retrieval Program to remediate tank 241-C-106 by sluicing.

9.3.4.2 Status. Major emphasis has been on developing plans for reducing the amount of water needed for cooling tank 241-C-106 and accelerating retrieval. The plan is to conduct a safety alternative process on tank 241-C-106 by stopping water additions. If the tank 241-C-106 safety alternative process is successful, then the amount of water needed for cooling the tank will be reduced to the minimum amount required, and possibly eliminated altogether. This would reduce the risk of releasing radioactivity to the environment in the event that tank 241-C-106 developed a leak prior to retrieval. Possible elimination of water addition requirements for tank 241-C-106 will be

coordinated with retrieval efforts. This action may alleviate the requirement to retrieve this tank first. Major FY 1992 accomplishments are listed below.

- Completed a detailed plan for accelerated retrieval of tank 241-C-106 using conventional sluicing techniques.
- Updated thermal and structural models of tanks 241-C-105 and 241-C-106 to support alternative cooling studies and waste retrieval.
- Completed the USQ screening process. No USQ exists for tank 241-C-106.

9.3.4.3 Plans. Near-term plans (FY 1993) include the following activities.

- Issue a program plan for high-heat safety program (DeFigh-Price and Wang 1993) [Completed]
- Retest existing TC tree in tank 241-C-106 and connect to TMACS. [Completed]
- Prepare a hazard assessment report.
- Update the contingency plan to cover the possibility of leaks from tank 241-C-106. [Completed, DeFigh-Price and Wang 1993].
- Stop water addition to tank 241-C-105 based on updated thermal analysis [Completed].

Long-term plans are focused on completing a safety alternative process in tank 241-C-106, upgrading instrumentation, and analyzing and interpreting data from core samples.

9.3.5 Tank Vapor Release

9.3.5.1 Description. Gases that pose health hazards may be present in waste tank vapor spaces (e.g., ammonia) and, ultimately, the work spaces. Such vapors have been found in tank 241-C-103. Nineteen exposure events, involving 34 people at the Hanford Site, occurred between July 1987 and May 1993. All of the vapor exposures involved first aid medical consultation, and some resulted in significant amounts of lost time to workers. Ten of these vapor exposure events, involving 18 people, were associated with the 241-C Tank Farm (many of these involved tank 241-C-103). A program plan (Osborne 1993) has been developed which focuses on tank 241-C-103 as a pilot program; the appropriate elements of the plan methodology can then be applied to other waste tank vapor issues.

On May 27 and 28, 1992, WHC hosted a tank vapor sampling conference attended by consultants from various national laboratories. The group defined a two-phase course of action to characterize tank vapors, beginning with tank 241-C-103. Characterization of vapors in other C Farm tanks will follow.

To resolve the safety issue, the hazards of potentially toxic tank vapors and implementing corrective actions commensurate with the level of hazard in each tank and/or tank farm will be evaluated. In-tank source sampling with a heated tube assembly of ferrocyanide and organic Watch List tanks, aging waste and actively ventilated DSTs, and any other high hazard (respiratory criteria) tanks, will be performed. Non-intrusive screening will be conducted for all remaining tanks, and the tank vapors will be analyzed to assess the industrial hygiene issue.

9.3.5.2 Status. Resolution of the tank vapor release safety issue includes evaluation and definition for tank vapor safety and in-tank resolution with treatment. Evaluation and definition of the problem includes: (1) vapor sampling of underground waste storage tanks; (2) characterization of tank vapors for chemical constituents, flammability, and aerosol issues; (3) epidemiology studies; (4) area monitoring of tank 241-C-103 for noxious vapors; (5) reduction of respiratory protection in tank farms; and (6) design of treatment systems for tank vapors. The workscope will be implemented in a phased approach: Phases 0, 1 and 2 address the characterization strategy for tank 241-C-103 and the development of analytical methods for analyzing toxic vapors. Phase 3 deals with the resolution of the vapor release problem in 241-C Tank Farm, and Phase 4 deals with resolution of any vapor release problems in the remaining tank farms. Initially, several vapor sampling techniques will be used simultaneously such as SUMMA^(R) canisters, sorbent tubes, and direct gas chromatography/mass spectrometer (GC/MS). A noxious odor advisory system (NOAS) pilot program has been implemented. Vapor sampling characterization studies; model development for air dispersion plume within 100 meters of the tank; microclimatic characterization; epidemiology study of past vapor exposures; and prospective occupational exposure studies will also be conducted.

In support of the characterization method development, a Development Mobile Laboratory 1 (DML1) was fabricated in FY 1993. Budget for FY 1994-1995 will support the design, specification, fabrication, and testing of DML2, 3 and 4. These mobile laboratories will be used to conduct Phase 3 and Phase 4 vapor characterization in the tank farms.

Early characterization methods development has shown that each tank may contain as many as 60 chemical constituents in the vapor space. This revelation has driven a requirement for extensive vapor database development. Complete characterization of all Hanford tanks, and the deployment of microclimatic weather stations, will generate hundreds of thousands of data points which must be correlated and analyzed. The vapor database development is, therefore, a critical component of tank vapor issue resolution.

In-tank resolution with treatment workscope includes alternate treatment approaches which will be evaluated based on the information generated in previous tasks. Alternatives will include one or a combination of the following: do nothing; develop work practices; treat by passive ventilation; treat by active ventilation; chemically treat; and/or remove waste from tank. For whatever corrective action is chosen, construction, instrumentation, and

¹SUMMA^(R) is a registered trademark of molectrics, Inc.

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installation design may be required. Depending on the action, functional design criteria, conceptual design report, and final design documentation may be required. Cost and schedule will vary depending on the action required.

Recent accomplishments (FY 1992-1993) are given below.

- A technical program plan was issued (Osborne 1993).
- A health and safety plan to evaluate hazards, risks, and worker exposures was issued.
- A tank vapor sampling team was assembled and a vapor sampling conference was held.
- Noxious Odor Advisory System Pilot Program was initiated.
- Developmental Mobile Laboratory 1 was completed.
- Completed tank 241-C-103 Phase 1A vapor sampling.

9.3.5.3 Plans. Near-term plans (FY 1993) include revising the technical program plan, the development of a characterization methodology, and a mobile vapor sampling laboratory. Specifically, the definitive and exhaustive vapor characterization of tank 241-C-103 will be accomplished in FY 1993. Other initiatives, such as epidemiological studies, toxicology, analytical methods development, portable weather stations, and technical integrating contractor concepts will also be initiated.

Long-term plans will focus on developing analytical methods for analyzing vapors and developing and installing vapor treatment systems on tanks that release vapors. Phase 3 (241-C Farm) vapor sampling and Phase 4 (remaining tanks) will be completed, and routine periodic sampling will be initiated.

9.3.6 Potential for Nuclear Criticality in HLW Tanks

9.3.6.1 Description. The Hanford SARs address a nuclear criticality but conclude that nuclear criticality in the Hanford Site waste tanks is not credible. However, a review by offsite experts concluded that, while a criticality accident is probably not an imminent risk, uncertainties in the fissile material inventories and distribution within the tanks do exist. The historical records are incomplete and predictions based on these limited records often disagree significantly with sample information. As a result of these findings this issue was determined to be an USQ since there was inadequate analysis to support the conclusion that a nuclear criticality in waste tanks was incredible. Efforts are underway to (1) gather additional data to evaluate the SAR position that criticality is not credible; and (2) perform a risk assessment and determine controls that would be the basis of a revised SAR to include a criticality event.

9.3.6.2 Status. The Justification for Continued Operation (JCO) resulting from the declaration of the USQ was written by WHC and approved for implementation by the Program Secretarial Officer (PSO) on August 31, 1992.

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The JCO required further evaluation for stabilization and some waste-intrusive activities. The evaluation for stabilization is underway; however, most of the intrusive activities are not identified or scheduled.

WHC-EP-0563, *Upgrade Activities for the Criticality Safety Program of Hanford High-Level Radioactive Waste Tank Farms* (Vail 1992), describes the plan for implementing resolution of the findings and recommendations identified by the review team of offsite experts, as well as the activities to resolve the USQ. The status of activities is given below.

- USQ Resolution:
 - A Dose Consequence Analysis was issued.
 - The Risk Assessment is in progress. The identification of a scenario resulting in a criticality is proving difficult.
- Resolution of findings and recommendations:
 - The Waste Tank Characterization Plan has been modified for consideration of criticality safety issues.
 - Criticality Safety Evaluations are being updated for the SSTs and DSTs.
 - Alternative methods of evaluating the fissile material inventory and distribution in the tanks have been narrowed to four separate groups. This effort is continuing.

9.3.6.3 Plans. Final closure of the USQ will be accomplished after completion of a safety analysis describing the risk assessment, and after procedures have been approved and put in place. Closure of the USQ is funded by ADS TDD 1100-NC, Corrective Activities.

Additional work is needed to implement recommendations included in the U.S. Department of Energy Nuclear Criticality Safety Review of Hanford High-Level Radioactive Waste Tank Farms. Recommendation B states, in part: "Alternative measurement methods and analyses should be adopted to estimate fissile material inventories and distributions within the waste tanks...In addition to core sampling, alternative measurement techniques should also be considered."

Recommendation I states, in part: "Investigations of tank anomalies should include monitoring for short-lived isotopes to determine if a criticality occurred, and detection criteria should be developed to ensure that monitoring would detect in-tank criticality accidents."

Implementation of the above recommendations is needed to fully resolve the nuclear criticality safety issue.

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The plan for resolving this safety issue is to develop and install fissile material measurement and criticality monitoring equipment on three tanks (241-SY-101, 241-SY-102, and 241-C-106) and their receiver tanks. The purpose is to demonstrate that the waste from these tanks can be safely retrieved with respect to a nuclear criticality. The operating controls and equipment demonstrated in these tanks will be evaluated for the need to establish nuclear criticality controls during subsequent waste retrieval activities.

9.4 POTENTIAL IMPACT ON TREATMENT

Extensive requirements for peer review and associated approvals for any intrusive action in listed tanks (Table 8-1) could impact both cost and schedule associated with treatment of tank wastes. In addition, the existence of potentially incompatible mixtures of chemicals in the tanks will impose temperature limitations on the retrieval operations and might require modification of pretreatment flowsheets to either destroy reactive components or to require separation of fuel from oxidizers.

The waste tank safety program has recommended that temperature limitations be imposed on all aspects of retrieval to limit edge-of-tool temperatures to below 150 °C (302 °F). As work progresses, the program will determine the degree to which the listed tanks do indeed pose a near-term or inherent safety problem with respect to safe storage. Many of the mitigation and/or remediation strategies that are being evaluated for tank 101-SY should be broadly applicable to other tank wastes. The focus for the ferrocyanide program is more clearly defined as an envelope of risk for an explosion of heated tank wastes. The organic program planning effort is continuing and remediation alternatives currently are being evaluated. Remediation alternatives for tank 106-C are also being evaluated.

The safety program is actively working with the SST and DST treatment and disposal programs to ensure that engineering approaches considered accommodate the potential risk associated with the Watch List tanks.

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LIST OF TERMS

ALC	airlift circulator
BAT	best available technology
CAW	current acid waste
CY	calendar year
D&D	decontamination and decommissioning
DOE	U.S. Department of Energy
DOE-HQ	U.S. Department of Energy, Headquarters
DMF	Dry Materials Facility
DSSF	double-shell slurry feed
DST	double-shell tank
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
EDTA	
FFTF	Fast Flux Test Facility
FY	fiscal year
GDF	Grouted Waste Disposal Facility
GPF	Grout Processing Facility
GTF	Grout Treatment Facility
HVAC	heating, ventilation, and air conditioning
HWVP	Hanford Waste Vitrification Plant
IEM	Interim Examination and Maintenance (Cell)
LLW	low-level waste
MAP	mixed activation products
MASF	Maintenance and Storage Facility
MCI	megacuries
MFP	mixed fission products
NCAW	neutralized current acid waste
NCRW	neutralized cladding removal waste
NZAW	neutralized zirflex acid waste
OA	outside air
OSR	Operational Safety Report
PFP	Plutonium Finishing Plant
PNL	Pacific Northwest Laboratory
PRICE	Productivity Improvement and Cost Effectiveness Program
PRF	Plutonium Reclamation Facility
PUREX	Plutonium/Uranium Extraction (Plant)
RCA	radiation controlled areas
RL	U.S. Department of Energy, Richland Field Office
RLWS	Radioactive Liquid Waste System
RMC	Remote Mechanical C-Line
RMW	radioactive mixed waste
SCA	surface contamination areas
SST	single-shell tank
SWL	saltwell liquor
TRU	transuranic (waste)
TSD	temporary storage and disposal
UNH	uranyl nitrate hexahydrate
WAC	Washington Administrative Code

LIST OF TERMS (continued)

WESF
Westinghouse
Hanford

Waste Encapsulation and Storage Facility
Westinghouse Hanford Company

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A.1.0 100 N AREA

This section documents the studies, activities, and issues which occurred in the 100 N Area during the period of March 1, 1992, through February 28, 1993.

A.1.1 INTRODUCTION

The principal facility in the 100 N Area is the dual-purpose N Reactor, which was designed to produce special nuclear materials and steam for generating electricity. Support facilities for N Reactor include a water-filled fuel storage basin and decontamination systems for both the reactor and fuel storage basin.

The three primary types of waste generated at this facility during operation are

- N Reactor decontamination waste
- Ion-exchange regeneration waste
- Sand filter backwash.

Because of the standby status of the N Reactor, no new waste from reactor operations was generated during the period from March 1992 through February 1993.

A.1.2 SUMMARY OF MARCH 1992 THROUGH FEBRUARY 1993 ACTIVITIES

Generation of 136 m³ (36,000 gal) of Waste. This section traces the processing of the remaining waste stored in the fuel storage basin which would have generated an estimated 136 m³ (36,000 gal) of waste as mentioned in Section 1.2.2, Appendix A, of the 1990 *Annual Report of Tank Waste Treatability* (Karnesky 1990).

The generation of this waste will not take place for two reasons.

- There is limited 200 Area tank space.
- The need for ion-exchange column use and regeneration has been eliminated because of a reduction of storage basin water radionuclide concentrations experienced since the completion of irradiated-fuel transfers to the K-Basins in December 1989.

A.1.3 STATUS OF 1993 ACTIVITIES IN PROGRESS

A sand filter is used to remove entrained solids from the fuel storage basin water before treatment with ion-exchange during normal operations. The sand filter backwash is primarily an inorganic sludge generated during

periodic filter flushing to remove accumulated solids. The sand filters at 107-N have been shut down. The system will not be used again until basin cleanup activities commence in the 1994/1995 time period.

A.1.4 CURRENT INVENTORY AND/OR AMOUNTS GENERATED

The regenerative waste tank in 107-N is currently holding 75.7 m³ (20,000 gal) of sulfate waste that will be shipped to the tank farms in fiscal year (FY) 1995.

A.1.5 WASTE MINIMIZATION ACTIVITIES

No new waste minimization activities are in place.

A.1.6 ESTIMATE OF PLANNED WORK ACTIVITIES FOR 1993

The following work activities were originally planned to occur during the FY 1991/1992 timeframe, but have not been included in the budget to date. Thus, the completion of these activities will not occur before FY 1995, but resolution of higher priority issues and availability of tank and Evaporator 242-A space may further extend the completion date.

- 56.8 m³ (15,000 gal) of liquid wash-down waste is expected from tank cleanout and layup activities.
- The operation of the sand filters mentioned previously in Section A.1.3 necessitates backwashes which add to the sludge volume in the backwash settling tank. The sludge hold-up volume is estimated to be 3.8 m³ (1,000 gal). This sulfate waste is projected to be shipped in FY 1995, but will require additional liquid for dilution due to the fissile content and high dose rate levels experienced from the concentration of radionuclides present in the settling tank constituents. The requirement for dilution is estimated to be 340.6 m³ (90,000 gal).
- Previously, N Reactor had received a FY 1991 shutdown order. Therefore, decontamination and decommissioning (D&D) of the inactive production reactors would represent a potential large-scale activity in the 100 Area which would generate an presently undetermined quantity of decontamination-related waste.

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A.2.0 CURRENT WASTE GENERATORS IN THE 300 AREA

This section documents the studies, activities, and issues which occurred in this area during the period of March 1, 1992 through February 28, 1993.

A.2.1 DESCRIPTION OF FACILITIES AND TYPES OF WASTES GENERATED

In the 300 Area, tank waste is generated in seven different laboratory facilities and transferred to the 340 Waste Handling Facility for shipment to the tank farms for storage, any necessary treatment, and ultimate disposal. The liquid waste is disposed of via transport directly to the 340 Facility where it is transferred directly into the holding tanks. Alternatively, the liquid waste is delivered to the 340 Facility by transfer of the liquid into a Radioactive Liquid Waste System (RLWS) drain line which is directly connected to the holding tanks.

Descriptions of the seven individual laboratory facilities and the 3000 Area facilities, the 340 Facility, and their respective individual waste streams, are presented in this section. A composite analysis of the tank waste generated in the 300 and the 3000 Areas is included in the discussion of the 340 Facility.

A.2.1.1 324 Chemical Engineering Laboratory

The 324 Chemical Engineering Laboratory contribution to tank waste is principally from two groups of shielded hot-cells and their service and operations galleries. Liquid wastes that are produced during the operation of these hot-cell facilities are pumped from vault tanks through the RLWS line to the 340 Facility for temporary storage before transfer by rail tank car to the tank farms.

The 324 Chemical Engineering Laboratory's contribution to tank waste for FY 1993 is considerably lower than the waste volumes generated in previous years. This is due to the continuing emphasis on total cleanout of their waste holding tanks from previous programs. Consequently, there are only small amounts of material remaining in these tanks. The remaining tank contents are expected to be transferred to the 340 Facility in 1993. Waste streams from the 324 Facility consist mainly of small project waste as follows:

- Volume--114L/yr (30 gal/yr)
- Chemical composition--mainly water
- Predominant radionuclides--¹³⁷Cs and ⁹⁰Sr with mixed fission products (MFP) and mixed activation products (MAP).

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A.2.1.2 325 Radiochemistry Laboratory

The 325 Radiochemistry Laboratory is a multipurpose laboratory facility with two different sets of hot-cells and several analytical laboratories. Waste volumes have been relatively stable since the last 1992 Tank Waste Treatability Report. The future waste volumes may fluctuate depending on the priorities of the single-shell tank (SST) double-shell tank (DST) tank core characterization activities.

The hot cells located in the east wing of the 325 Building (325A) are used to handle highly radioactive materials for a variety of processes and materials testing programs. The inorganic waste produced in the cells generally consists of rinse water and dissolved irradiated fuel sample sections. The hot-cells are also used to extrude and blend core samples from the tank farms. A description of the waste that will be generated in the process research hot-cells (325A) is as follows:

- Volume--757 L/yr (200 gal/yr)
- Chemical composition--inorganic compounds, water
- Predominant radionuclides--¹⁴⁴Ce, ⁶⁰Co, ¹³⁴Cs, ¹³⁷Cs, ¹⁰⁶Ru with MFP and MAP.

The hot-cells in the west wing of the 325 Building (325B) are used to prepare fuel component samples, tank cores, and other solid samples for various chemical analyses. The waste that is generated in these hot cells is primarily rinse water. A description of the waste generated in the 325B Building is as follows:

- Volume--3,028 L/yr (800 gal/yr)
- Chemical composition--traces of inorganic and organic constituents, water
- Predominant radionuclides--¹⁴⁴Ce, ⁶⁰Co, ¹³⁴Cs, ¹³⁷Cs, and ¹⁰⁶Ru with MFP and MAP.

The analytical laboratory waste generated in the 325 Building is sent directly to the 340 Facility via a RLWS drain located within the building. Most of the waste is generated from fuel rod analysis and tank core characterization programs. A general description of the waste produced from laboratory analytical work is as follows:

- Volume--2,460 L/yr (650 gal/yr)
- Chemical composition--inorganic, organic (trace), and analytical waste
- Predominant radionuclides--¹⁴⁴Ce, ⁶⁰Co, ¹³⁴Cs, ¹³⁷Cs, and ¹⁰⁶Ru with MFP and MAP.

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A.2.1.3 326 Materials Technology Laboratory

Most of the work performed in the 326 Materials Technology Laboratory involves the study of metallurgical, chemical, and physical behavior of reactor components and fuel materials. Three of these laboratories were used for a tritium research program during the past year. A small amount of non-hazardous scintillation cocktail solution were transferred from these laboratories.

The metallography laboratory, where radioactive waste is generated, is used to prepare metal coupons for survey in an electron microscope. The coupons are prepared by washing them in several different acid baths. A general description of the waste that is generated in this section of the 326 Building is as follows:

- Volume--38 L/yr (10 gal/yr)
- Chemical composition--solutions containing trace quantities of perchloric acid, acetic acid, and methanol. Other liquid wastes contain a non-hazardous liquid scintillation solution
- Predominant radionuclides--⁵⁵Fe, ⁵⁴Mn, tritium, ¹⁴C, ⁶³Ni, ⁶⁰C, ⁹³Zr, and ⁹⁹Tc.

A.2.1.4 327 Post-Irradiation Testing Laboratory

The 327 Postirradiation Testing Laboratory is used for destructive and nondestructive examination of irradiated reactor fuel and structural materials. These examinations and the associated testing are carried out in 12 shielded hot cells, several of which drain to the 340 Building via the RLWS. Wastes from the cell drains are filtered to prevent solids from entering the RLWS piping. Most of this waste is generated during cutting operations, performed on irradiated fuels and materials, and during cleaning and rinsing operations of equipment in the cells. The following is a general description of the waste that is generated by the 327 Laboratory:

- Volume--3,028 L/yr (800 gal/yr)
- Chemical composition--water mixed with decontamination materials (traces of detergents, cleaners, surfactants), low concentrations of isobutanol and methanol
- Predominant radionuclides--¹⁴⁴Ce, ¹³⁷Cs, ⁹⁰Sr, and ⁶⁰Co.

A.2.1.5 329 Physics Science Laboratory

The 329 Physics Science Laboratory includes laboratories for radioanalysis and low-level detection and measurement of radioisotopes. Radioactive sources are also manufactured in this laboratory.

The experiments or processes used in the radiochemical portion of the 329 laboratory include dissolution of solids, ion-exchange and precipitation partitioning, and liquid extractions. The following is a description of the waste typically generated in the radiochemistry portion of the 329 Laboratory:

- Volume--341 L/yr (90 gal/yr)
- Chemical composition--nitrate, carbonate, oxalate, sulfate, fluorine, sodium, and ammonia solutions
- Predominant radionuclides--²⁴¹Am, ⁶⁰Co, ¹³⁷Cs, ⁵⁵Fe, ^{93m}Nb, ⁶³Ni, ²³⁹Pu, ²⁴⁰Pu, and ⁹⁰Sr.

Only a small amount of waste is produced in the low-level detection facility. The following is a general description of the waste produced:

- Volume--19 L/yr (5 gal/yr)
- Chemical composition--water
- Predominant radionuclides--⁶⁰Co, ¹³⁷Cs, and ⁹⁰Sr.

A.2.1.6 3720 Building

Several laboratories are housed in the 3720 Building. Work in the Geochemistry group generates radioactive waste as a result of the study of radioactive grouts and their leachates. The small amount of radioactive waste generated in the 3720 Building (and also at the lysimeter site north of the 300 Area) is collected in drums and transported to the 340 Facility where it is added to the storage tanks.

A general description of the waste generated in 3720 Building is as follows:

- Volume--38 L/yr (10 gal/yr)
- Chemical composition--varies depending on experiment, mainly groundwater with small amounts of chemical indicators
- Predominant radionuclides--tritium, ⁶⁰Co, ¹⁴C, ⁹⁹Tc at or below detection levels.

A general description of the waste that is generated from the lysimeter studies is as follows:

- Volume--2,498 L/yr (660 gal/yr)
- Chemical composition-- varies depending on experiment. Mainly groundwater with trace levels of indicators such as ethylenediametetraacetic acid (EDTA) and Bromcresol purple
- Predominant radionuclides--¹²⁵I and ⁹⁹Tc.

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A.2.1.7 331 Life Sciences Laboratory

The 331 Life Sciences Laboratory is used for a variety of biological and ecological research studies. A small amount of waste generated at the 331 Building was sent to the 340 Facility in 1991 via the RLWS drain in the 325 Building. A general description of the waste generated in the 331 Building is as follows:

- Volume--303 L/yr (80 gal/yr)
- Chemical composition--biological liquid wastes containing low concentrations of sodium nitrate, sodium phosphate, and other inorganic compounds
- Predominant radionuclides--tritium, ^{239}Pu , ^{14}C .

A.2.1.8 3000 Area Facilities

The two facilities in the 3000 Area (LSL-II and RTL) mainly generate liquid scintillation counting waste (non-hazardous) in support of biological and geochemical research programs. The wastes are shipped to 325 Building or the 329 Building and disposed via the RLWS drains. A general description of the waste generated in the 3000 Area Facilities is as follows:

- Volume--568 L/yr (150 gal/yr)
- Chemical composition--biological and geochemical wastes containing non-regulated scintillation cocktail solutions with low concentrations of organic acids
- Predominant radionuclides--tritium, ^{14}C , ^{60}Co , ^{63}Ni .

A.2.1.9 340 Waste Handling Facility

A.2.1.9.1 Description. The 340 Facility is a liquid waste handling facility. Waste is received from Pacific Northwest Laboratory (PNL) via underground pipelines or transported to the 340 Facility in drums and added into the 340 storage tanks. The 340 Facility transfers the waste into 75,700-L (20,000-gal) railcars and ships them to the DSTs via the 204AR unloading facility. As part of operating the facility, small quantities of liquid waste are generated.

A.2.1.9.2 Summary of Activities During March 1992 through February 1993. Following a railcar loading operation, waste transfer lines are flushed to reduce contamination and radiation levels. Each transfer generates approximately 189 L (50 gal) of waste. In the past year, the 340 Facility has made four transfers adding 757 L (200 gal) to the tank waste inventory.

Periodic decontamination activities (i.e., sampling hood, floor sump, and equipment repairs) have resulted in some waste generation. For the past year

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it is estimated approximately 378.5 L (100 gal) of waste was added to the tank waste inventory. Safety shower flushes generated an additional 5,677 L (1,500 gal) of liquid waste.

A.2.1.9.3 Listing of Applicable Documents. None.

A.2.1.9.4 Status of 1993 Activities in Progress. Due to the evaporator shutdown, no large liquid waste generating activities are planned. Once the evaporator is made operational again, the 340 Facility plans to flush out the auxiliary storage tanks to reduce the radiation dose levels. The area is currently categorized as a controlled radiation area with average dose rates exceeding 50 mrem/hr.

A.2.1.9.5 Waste Minimization Activities. Generation of liquid waste is being strictly managed by the Radioactive Liquid Waste Task Team. Waste generating activities are reviewed on a continuing basis, with minimization being a key decision-making component before granting disposal approvals.

A.2.1.9.6 Estimate of Planned Work Activities for 1994. The six 340A auxiliary storage tanks are planned to be flushed of residual solids. It is anticipated that this effort will generate 30.3 to 37.85 m³ (8,000 to 10,000 gal) of additional waste.

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A.3.0 CURRENT WASTE GENERATORS AT THE 400 AREA

This section documents the studies, activities, and issues which occurred in this area during the period of March 1, 1992, through February 28, 1993.

A.3.1 DESCRIPTION OF FACILITY AND TYPES OF WASTE GENERATED

The 400 Area contains the Fast Flux Test Facility (FFTF), a U.S. Government-owned nuclear reactor specifically designed for the irradiation and testing of nuclear reactor fuels and materials. Prior to being placed on standby status on April, 1992, the FFTF played a key role in the development and testing of fuels and materials for application in fast neutron flux reactors and in testing fusion reactor materials.

This 400-MW fast-breeder reactor is located in a shielded cell in the center of the containment building. The heat generated by the fission process is removed from the reactor by liquid sodium circulating under low pressure through three primary coolant loops. An intermediate heat exchanger in each of these three loops separates the radioactive sodium in the primary system from the nonradioactive sodium in the secondary system. The radioactive primary sodium does not leave the Reactor Containment Building. Three secondary sodium loops transport reactor heat from the intermediate heat exchangers to the air-cooled tubes of the 12 dump heat exchangers.

The FFTF also includes facilities for receiving, conditioning, storing, and installing core components and test assemblies. Examination and packaging capabilities for onsite and offsite shipments and radioactive waste handling are also available at the facility.

A.3.2 GENERATION OF TANK WASTES IN THE 400 AREA

In the 400 Area, radioactive liquid wastes are generated primarily in conjunction with the removal of residual sodium from irradiated reactor components and fuel assemblies in the Interim Examination and Maintenance (IEM) Cell and by the cleaning and decontamination activities conducted in the Maintenance and Storage Facility (MASF). Wastewater, which is generated during the cleaning processes, is stored in a 18.9-m³ (5,000-gal) tank at the FFTF and in two 18.9-m³ (5,000-gal) tanks at the MASF. The wastewater is moved from the FFTF to the MASF via an 30.3 m³ (8,000-gal) railcar and then transferred to the 200 Area Tank Farms via a 75.7-m³ (20,000-gal) rail tank car. A shipment of the contaminated wastewater to the 200 Area Tank Farms occurs approximately once every two years.

During the past year, 27,253 L (7,200 gal) of wastewater was generated in the 400 Area. This volume is currently stored in the FFTF and MASF storage tanks. These amounts are consistent with the generation rate over the last several years.

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A.3.3 TANK WASTE MINIMIZATION AT THE FAST FLUX TEST FACILITY AND AT THE MAINTENANCE AND STORAGE FACILITY

The design of the cleaning systems used in the IEM Cell enables the washwater to be recirculated to the greatest extent possible, which minimizes the amount of radioactive tank waste generated by the facility. Current practices generate about 1,892 L (500 gal) of contaminated water with each cleaning episode. The total quantity of wastewater generated each year in the IEM Cell is dependent on the number of reactor assemblies washed.

An annual hydrostatic test is required for the 30.3-m³ (8,000-gal) tank car which is used to ship waste from the FFTF to the MASF. The testing method includes filling the tank with water. After the test is complete, the water used in the test is shipped to the 200 Area Tank Farms. The amount of washwater generated annually by the IEM Cell and the MASF is less than what is required to perform the test. To further minimize the amount of tank waste generated in the 400 Area, procedures have been upgraded to allow the use of existing wastewater from the two 18.9-m³ (5,000-gal) tanks at the MASF to help fill the tank car for the required annual hydrostatic test. This results in a substantial reduction in the wastewater volume generated annually.

To further minimize the tank waste generated at the T Plant in the 200 West Area, 36.3 m (9,600 gal) of liquid waste were shipped from the MASF to T Plant for use in hydrostatic testing of a 75.7-m³ (20,000-gal) tank car. The use of the low-level waste (LLW) from the 400 Area to partially fill the 75.7-m³ (20,000-gal) tank car reduced the new waste generated at T Plant by 36.3 m³ (9,600 gal).

A.3.4 FUTURE TANK WASTE GENERATED AS A RESULT OF THE FAST FLUX TEST FACILITY SHUTDOWN OPTION

Since April 1, 1992, FFTF has been on hot standby status; therefore, the future of FFTF and the MASF is undetermined at this time. If the reactor is to be permanently shutdown, the amount of wastewater generated would vary greatly depending upon the method of sodium disposal selected. The possibility exists that up to 1,892.5-m³ (500,000 gal) of radioactive 50 percent sodium hydroxide waste solution from reacting the liquid sodium drained from FFTF with water will be generated from shutdown activities. This solution will need to be treated as radioactive waste. In addition, 946.3 m³ (250,000 gal) of slightly contaminated, low-level radioactive rinse water or alcohol could be generated as a result of sodium removal operations in FFTF piping and components after the bulk sodium is drained. If FFTF is to remain on standby or resume operation, the waste generation rate would remain at historic levels.

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A.4.0 TANK FARMS

This section documents the studies, activities, and issues which occurred in this area during the period of March 1, 1992 through February 28, 1993.

A.4.1 INTRODUCTION

The tank farms located in the 200 East and 200 West areas of the Hanford Site were built for storing and managing liquid radioactive and chemical wastes generated by various production and laboratory operations. The tank system consists of 177 tanks grouped in 18 tank farms as shown in Figure A.4-1. The underground, reinforced-concrete steel-lined tanks are of two different types; SSTs and DSTs.

A.4.2 DESCRIPTION OF THE FACILITIES

A.4.2.1 Single-Shell Tanks

Between 1943 and 1964, 149 SSTs were built for storing radioactive wastes. These SSTs are located in 12 tank farms, with each tank farm consisting of 4 to 18 SSTs.

The SSTs have volumes of 208 to 3,785 m³ (55,000 to 1,000,000 gal). One hundred thirty-three of the SSTs are 22.9 m (75 ft) in diameter and 9.1 to 16.5 m (29.75 to 54 ft) high, with nominal capacities of 1,893 to 3,785 m³ (500,000 to 1,000,000 gal). Sixteen of the SSTs are smaller units of similar design; 6.1 m (20 ft) in diameter and 7.8 m (25.5 ft) high with capacities of 208 m³ (55,000 gal) each.

The tanks are located below grade with at least 1.9 m (6 ft) of soil covering the tanks to provide shielding and minimize the radiation exposure to tank farm operating personnel. Most of the 1,893- and 2,839-m³ (500,000- and 750,000-gal) SSTs were built in the form of "cascades" of three or four SSTs each. Waste was transferred to the first SST in the cascade and allowed to overflow into each of the successive SSTs in the cascade through inlet and overflow lines located near the top of the steel liner within in each SST.

Access to each of the SSTs is provided by risers penetrating the domed top of the SSTs. These risers vary in diameter from 10.2 to 106.7 cm (4 to 42 in.). Each of the SSTs have up to 11 risers, with the majority of the SSTs having 3 to 5 risers.

Radioactive waste generated during the various Hanford Site operations was not placed into SSTs after November 1980. While the SSTs are considered to have been taken out of service in November 1980, the 149 tanks continue to hold approximately 140,045 m³ (37 Mgal) of saltcake, sludge, and interstitial liquid.

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A.4.2.2 Double-Shell Tanks

Between 1968 and 1986, 28 DSTs were constructed. Three of these tanks are located in the 200 West Area (241-SY Tank Farm) and 25 tanks are located in the 200 East Area (241-AN, -AP, -AW, -AY, and -AZ Tank Farms). All of these DSTs were constructed at least 5 ft below grade to provide shielding and minimize the radiation exposures to operating personnel. Table A.4-1 provides a chronology of the DST construction.

The four 241-AY and -AZ tanks each have a 3,785 m³ (1-Mgal) capacity and are designed to store the high-heat-generating neutralized current acid waste (NCAW) from the Plutonium-Uranium Extraction (PUREX) process. These tanks are referred to as aging waste tanks and have airlift circulators for mixing and a vessel ventilation system designed to remove and condense steam.

Table A.4-1. Chronology of the Double-Shell Tank Construction.

Tank farm	Year constructed	Number of tanks	Tank volume m ³ (Mgal)	Comment
241-AY	1968-70	2	3,785 (1.00)	Aging waste tank
241-AZ	1971-77	2	3,785 (1.00)	Aging waste tank
241-SY	1974-76	3	4,315 (1.14)	-
241-AW	1978-80	6	4,315 (1.14)	-
241-AN	1980-81	7	4,315 (1.14)	-
241-AP	1983-86	8	4,315 (1.14)	-

The DSTs use a tank-within-a-tank design to provide double containment for the radioactive liquid and solid wastes. This design ensures that if a leak in the primary shell occurs, the liquid waste will be fully contained within the outer shell.

The freestanding primary tank is about 22.9 m (75 ft) in diameter and 14 m (46 ft) high at the dome crown. The carbon steel in the bottom of the tank ranges from 1.3 to 2.5 cm (0.5 to 1 in.) thick. The primary tank wall thickness ranges from 1.3 to 1.9 cm (1/2 to 3/4 in.) with the dome thickness at 1.0 cm (3/8 in.).

An annular space of 0.76 m (2.5 ft) is provided between the primary tank and the secondary steel tank that allows room for installation of liquid-level and leak detection devices, inspection equipment (such as periscopes), television cameras, photographic cameras, ventilation air supply and exhaust ducts, and equipment for pumping liquid out of the annular space.

Tank dome penetrations in the primary tank and annulus allow for various monitoring and processing activities. Primary tank monitoring activities include measurement of liquid level, sludge level, temperature, and pressure.

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A.4.3 DOUBLE-SHELL TANKS OPERATION (MARCH 1992 THROUGH FEBRUARY 1993)

The tank farm facilities at the Hanford Site receive radioactive wastes generated by other Hanford Site waste generators. Tank farm operations are typically characterized as a waste receiver rather than a waste generator. However, in the operation of the tank farms, a variety of additions are made that increase the volume of the wastes in the tanks. These streams are identified because their minimization has the overall effect of reducing the volume requiring treatment for final disposal. Waste from these streams is addressed for the period from March 1992 through February 1993.

1. Saltwell Liquor. The SSTs hold moist solids (salts and sludges) that contain interstitial liquid. Saltwell pumping can remove a portion of the interstitial liquid called saltwell liquor (SWL) from these solids. Through calendar year 1990, 105 SSTs have been interim stabilized, leaving 44 SSTs to be interim stabilized by the end of FY 1995 [Tri-Party Agreement milestone M-05 (Ecology et al. 1990)].

During the time period from March 1, 1992 through February 28, 1993, no pumpable liquid was removed from the SSTs and transferred to DSTs. However, it is predicted that 15,140 m³ (4,000,000 gal) will be removed from the SSTs by FY 1995 when the saltwell pumping program is expected to be completed.

2. Airlift Circulator (ALC) Flushes. Salts are periodically flushed from the ALCs in the aging waste DSTs using raw water. The volume of ALC water flushes for the specified time period totaled 222 m³ (58,700 gal). The water flushes were transferred to tanks 241-AZ-101 and 241-AZ-102.
3. Aging Waste Ventilation System De-entrainer Flushes. No deentrainer flushes were performed from March 1, 1992 through February 28, 1993.
4. Jet Pump Transfers. Waste transferred from catch tanks to DSTs using a jet pump added 32 m³ (8,500 gal) of motive water to the DSTs.
5. The DST 241-AZ-101 Aging Waste Steam Condensate. The DST 241-AZ-101 contains steam coils to boil water from the aging waste. To prevent these steam coils from freezing during winter weather, a small amount of steam must be allowed through the coils. The aging waste steam coils were not operated during this reporting period and did not add any water to the DSTs.
6. Tank Car Waste Flushing and Water from Recertification. Radioactive waste is shipped by rail tank car to the 200 East Area DSTs from the 100 N, 300, and 400 Areas. The tank car used to transport this waste must be flushed and recertified. The volume of waste water added to DST's due to the activities at the 204-AR facility during this reporting period totaled 90 m³ (23,700 gal).

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7. Equipment Flushes and Washes. Water is used to periodically wash accumulated solids and salts from measurement equipment. Other equipment must be flushed after use or for maintenance. The volume of waste water added to the DST's from these activities was 87 m³ (22,900 gal) for this reporting period (March 1, 1992 through February 29, 1993).
8. 242-A Evaporator Restart Water Additions. During this reporting period, activities associated with the restart of the 242-A Evaporator Facility resulted in the addition of 1,011 m³ (267,000 gal) of water to the DSTs.

The total increase in waste volume transferred to the DSTS during this reporting period, including all generation, transfers, and losses, was 1,606 m³ (424,000 gal).

A.4.4 LISTING OF APPLICABLE DOCUMENTS

Information pertaining to the Tank Farms activities discussed in the preceding sections was obtained primarily from Tank Farm Operations surveillance data sheets.

Tank liquid levels and other information related to the status of the tank system are issued monthly in the Tank Farm Surveillance and Waste Status Summary Report (WHC-EP-0182).

A.4.5 WASTE MINIMIZATION ACTIVITIES

As part of the concern over diminishing DST space at Tank Farms, the limit for the total volume of waste accepted into the DST system from the various waste generating facilities (B-Plant, PUREX, 222-S) was reduced from 91,000 gallons/month to 64,000 gallons/month. To meet this goal, the generating facilities are currently transferring wastes to the DST system at an average rate thus far in FY 1993 of less than 40,000 gallons/month.

A.4.6 ESTIMATE OF PLANNED WORK ACTIVITIES FOR FY 1993

Preparations are underway to transfer wastes from two additional SSTs this year. Tanks BX-111 and BX-110 are expected to initiate waste transfers to the DST system in the July-August 1993 timeframe. The transfer of wastes from tanks 241-BY-102 and 241-BY-109 is also being considered for later in CY 1993.

A.5.0 EVAPORATORS

This section documents the studies, activities, and issues which occurred in this area during the period of March 1, 1992, through February 28, 1993.

A.5.1 INTRODUCTION

Since the early 1950's, eight evaporator facilities have been used to treat tank wastes at the Hanford Site. The only evaporator facility that is planned for continued operation is the 242-A Evaporator-Crystallizer located in the 200 East Area.

A.5.2 DESCRIPTION OF EVAPORATOR FACILITIES

The evaporator building is divided into rooms housing particular process components or support facilities. The main process rooms are the evaporator room, containing the reboiler and vapor-liquid separator, the condenser room, housing the overhead vapor condensers and condensate collection tank, and the pump room, which contains the slurry pumps. Support rooms include the control room, loading room, heating, ventilation, and air conditioning (HVAC) room, and changerooms.

The 242-A Evaporator is used to reduce the volume of radioactive mixed waste requiring storage in the DSTs. The evaporator uses forced circulation through the reboiler and vapor-liquid separator to heat the waste under vacuum, causing vaporization of water and other volatiles. The vapors from the separator are condensed, retained, and then treated before disposal. The slurry product stream is sent back to the DSTs from the evaporator. The volume of the slurry-product stream is significantly less than the volume of the waste feed stream.

A.5.3 TYPES OF WASTE GENERATED

The operation of the 242-A Evaporator-Crystallizer 242-A does not generate new tank waste except when there is a process upset. The following streams are generated:

- Double-shell slurry feed (DSSF), which is returned to DSTs
- Steam condensate from reboiler, which is sent to the 216-B-3 Pond
- Process condensate, which is held for treatment
- Cooling water from the process condenser, which is sent to the 216-B-3 Pond
- Small volume, intermittent wastes such as de-entrainer wash, which are sent to the evaporator pot.

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The slurry returned to the DSTs is not considered an original waste stream for the tank farms.

The small-volume, intermittent wastes such as de-entrainer wash, are sent to the evaporator pot where their identity is lost during evaporation with DSSF.

If there is an upset condition and process condensate becomes contaminated with radionuclides, the process condensate may be returned to a DST. Upset conditions seldom occur and the process condensate is typically not considered a tank waste.

A.5.4 STATUS OF 1993 ACTIVITIES IN PROGRESS

The 242-A Evaporator is scheduled to resume operations in July, 1993. Presently, three tanks are characterized to be processed through the facility. Tanks 102-AW, 106-AW, and 103-AP are scheduled to be processed with an anticipated reduction in waste volume (amount of liberated tank space) of 9,500 m³ (2,500 kgal) during the first campaign. A second campaign, using characterized wastes from tanks 101, 107, and 108-AP as feed, is currently planned to begin shortly after the completion of the first campaign. However, an official date for the start of the second campaign has not been established.

A.5.5 WASTE MINIMIZATION

Many upgrades have been made to the 242-A Evaporator since the facility was shutdown in April 1989. The most significant upgrade, in terms of waste minimization, was the replacement of the primary condenser. The old condenser allowed raw water used for cooling to leak into the process condensate, which a listed waste. In past years, this practice resulted in the production of excessive volumes of process condensate. Other recent upgrades include the replacement of steam-heated and vessel vent heaters with electrically heated units. These replacements reduced the quantity of steam condensate that is produced and a subsequent requirement for disposal.

A.5.6 ESTIMATE OF PLANNED WORK ACTIVITIES FOR 1993

In addition to the processing goals outlined in Section A.5.3, a major upgrade project is scheduled to be completed at the 242-A Evaporator facility by October 1997, as part of a site-wide effort to minimize the quantity of liquid effluent discharges to the soil column. The 242-A Evaporator cooling system will be converted from a "once-through" cooling system to a closed loop, recirculating water cooling cycle. Presently, the "once-through" cooling system uses approximately 2,600 gal/min of raw water to condense process vapors. The noncontact cooling water is processed through a series of three

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condensers before discharge into the 216-B-3 Pond System. The makeup water for the planned, closed-loop cooling system will be composed of other intermittent sources that were also previously discharged into the 216-B-3 Pond System. A minimal amount of blowdown (about 50 gpm) would then be collected with contributions from other facilities before treatment and disposal, as required. Presently, this upgrade project is in the design phase.

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A.6.0 PLUTONIUM FINISHING PLANT

This section documents the studies, activities, and issues which occurred in this area during the period from March 1, 1992, through February 28, 1993.

A.6.1 INTRODUCTION

The Plutonium Finishing Plant (PFP) is located in the 200 West Area of the Hanford Site. The PFP has the primary mission of plutonium processing, handling, and storage. Stabilization of plutonium scrap to plutonium oxide, waste treatment, product storage, and packaging for shipment are the principal operations conducted at the PFP. Plutonium metal will not be produced at the PFP because of changes in the defense production mission at the Hanford Site.

A.6.2 RECAP OF MARCH 1, 1992 THROUGH FEBRUARY 29, 1993 ACTIVITIES

A.6.2.1 Planned Treatment of Plutonium Finishing Plant Waste

Present plans are to develop and use a PFP Waste Solidification Process (Project C-130) where the process waste will be treated for the removal of organics, nitrates, and water, and then solidified. The resultant solids will either contain transuranic (TRU) or low level amounts of TRUs which will be solidified into 208 L (55-gal) drums and certified for final emplacement at the WIPP site in Carlsbad, New Mexico, or for burial at the Hanford low level burial Site. Project C-130 was planned as a FY 1995 line item, which means that the design for the PFP Waste Solidification Process was scheduled to start in FY 1995. Funding for the project was not provided in the FY 1993 budget. The project has not been canceled but has been placed on hold again until funding is allocated.

A.6.2.2 Plutonium Reclamation Facility Process Modification

Bypassing of the Outside Air (OA) Column during plutonium-only and uranium depletion operations, as described in the 1990 *Annual Report of Tank Waste Treatability*, is still scheduled when the Plutonium Reclamation Facility (PRF) starts up. The PRF is scheduled for restart in the latter part of calendar year (CY) 1993.

A.6.2.3 Project C-031H

Project C-031H, the PFP Liquid Effluent Treatment Facility Upgrade, originally consisted of removal and replacement of four of the five waste tanks in Building 241-Z. The concrete tank vaults containing these tanks were to be repaired and each vault lined with stainless steel. Redundant tank level measuring devices were to be installed on the new tanks. Four new

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encased and monitored transfer lines from the plant to the 241-Z Building were also scheduled for installation in FY 1992. This installation was completed in CY 1992, since the issuance of the last report. The old transfer lines were left in place.

A final decision on the replacement of the Building 241-Z waste tanks is still pending. Presently, it appears that the existing tanks will be left in place and used until the planned Plutonium Reduction Facility (PRF) campaign is completed. After completion of the campaign, two 1,892 L (500-gallon) storage/treatment tanks may be installed in Building 241-Z above the existing tanks. A 189 L (50-gallon) receiver tank will also be installed below grade outside Building 241-Z and connected to the encased transfer lines.

The existing waste tanks are used for storage and treatment of transuranic aqueous wastes from the PRF, the Remote Mechanical C-Line (RMC) and the Development and Analytical Laboratories. After treatment, the wastes are transferred to Tank Farms.

A.6.3 WASTE GENERATED AND CURRENT INVENTORY

Approximately 45.6 m³ (12,050 gal) of liquid wastes were transferred from PFP to Tank Farms in CY 1991 that were not reported in last year's report. A total of 3,713 m³ (981 gal) of treatment chemicals were added to the waste tanks prior to the transfers. There were approximately 3.0 m³ (795 gal) of wastes in the D-4,-5,-7, and-8 waste tanks on December 31, 1992.

A.6.4 WASTE MINIMIZATION ACTIVITIES

A.6.4.1 Plutonium Reclamation Facility Process Modification

In addition to the modifications previously described in earlier versions of this annual report, the following modifications for the abatement of CCl₄ emissions are being investigated:

- When the PRF starts operations a "water cap" will be in place between the CCl₄ and the air pulser on the pulse extraction columns to minimize the emission of CCl₄. The extraction columns are known to be a major source of CCl₄ emissions.
- Investigations are continuing to find a replacement solvent for CCl₄ which is more environmentally acceptable.

A.6.4.2 PFP Waste Minimization

Waste minimization activities described in the 1990, 1991, and 1992 reports are continuing. Additional activities to those previously described are:

- The volume of routine aqueous samples from the PFP crib was reduced from one liter to 1/2 liter. The PFP Analytical Laboratory further reduced this volume by converting the required samples to a dry mount sample system. Liquid samples are now collected, dried, and mounted on filter media paper at the PFP labs, thus reducing the hazard of handling and transporting liquid samples from PFP to the 222-S Laboratory. Approximately 1,100 kg of liquid waste was avoided with this system change.
- The areas of radioactive surface contamination in 234-5Z and 241-ZA were changed from surface contamination areas (SCA) to radiation controlled areas (RCA) after an extensive cleanup effort by plant personnel. The total reduction of contaminated surface area was 3,530 m² (38,000 ft²), allowing waste from offices, laboratories, and nonprocess rooms to be managed as as nonradioactive wastes. Additionally, work practices were implemented to reduce the quantity of materials and equipment entering the smaller SCA areas thereby reducing the amount of radioactive waste generated. These practices resulted in avoiding the generation of 20,000 kg of additional radioactive waste.

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A.7.0 PUREX PLANT

This section documents the studies, activities, and issues which occurred in this area during the period of March 1, 1992, through February 28, 1993.

A.7.1 INTRODUCTION

The PUREX Plant was designed to reprocess irradiated nuclear reactor fuels for the recovery of uranium and plutonium. The last fuel reprocessing run (the stabilization run) was completed in March 1990. The PUREX Plant entered into the cold standby mode in October 1990 until December 21, 1992, when DOE directed that PUREX be deactivated.

A.7.2 DESCRIPTION

A.7.2.1 Facility

The PUREX Plant is located in the southeast corner of the 200 East Area of the Hanford Site. The PUREX Plant comprises several buildings and support facilities.

The primary structure is the 202A Building. The 202A Building is a reinforced concrete canyon structure 304 m (1,000 ft)-long, 36.3 m (119 ft)-wide (at its maximum width) and 30.4 m (100 ft)-high, with approximately 12.2 m (40 ft) of this height below grade. It contains a "canyon" with processing cells, a laboratory, various support systems and galleries, and administrative offices.

Several other buildings associated with the PUREX Plant complex include the following; several mobile office trailers, structures associated with various support functions, two long storage tunnels, two small tank farms, warehouses, and several materials storage areas.

A.7.2.2 PUREX Process

The PUREX process and associated equipment were designed to chemically extract plutonium and uranium from irradiated metal nuclear reactor fuel. Because of the radioactive materials being reprocessed, the system has been designed for remote operation and maintenance. The reprocessing equipment is located in the process cells within the PUREX canyon. The PUREX Plant is currently configured to reprocess zircaloy clad fuel from N Reactor.

Plutonium and uranium separation begins with the batch removal of the fuel cladding followed by batch dissolution of the spent reactor fuel itself. The dissolved fuel is then fed into a continuous aqueous/organic where the mixed fission products are separated from the plutonium and uranium. The plutonium and uranium are then separated from each other and purified in subsequent reprocessing operations. The final products are uranyl nitrate hexahydrate (UNH) and either plutonium oxide or plutonium nitrate.

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A.7.2.3 Waste Types

The wastes produced by the PUREX Plant fall into four general types: NCAW, neutralized cladding removal waste (NCRW), miscellaneous wastes, and solvent recovery wastes. The NCAW is the aqueous high-salt waste from the first-cycle solvent extraction column in the solvent extraction process system. The NCAW is also referred to as neutralized zirflex acid waste (NZAW). The NCRW results from removal of the zircaloy cladding from the spent N Reactor fuel by means of the zirflex batch dissolution process. The miscellaneous wastes come from various sources throughout the plant. The solvent recovery wastes result from washing and regenerating the nonregulated organic solvent (tributyl phosphate/normal paraffin hydrocarbon) used in the PUREX solvent extraction process.

The NCAW, NCRW, and the miscellaneous waste are all radioactive mixed wastes regulated by the U.S. Environmental Protection Agency (EPA) and the Washington State Department of Ecology (Ecology). The solvent recovery wastes are radioactive wastes controlled administratively by the U.S. Department of Energy (DOE). The pH of all wastes is adjusted to a value greater than 12. Sodium nitrite is then added to the waste solution for purposes of corrosion control before transfer to the DSTs for interim underground storage.

During transition-to-standby and cold standby and deactivation, the principal type of waste generated is miscellaneous waste. A small amount of solvent recovery waste may also be produced. The NCAW and NCRW are only generated during fuel reprocessing and will not be generated during cold standby or deactivation.

A.7.3 RECAP OF ACTIVITIES FROM MARCH 1992 THROUGH FEBRUARY 1993

In October 1990, the U.S. Department of Energy, Richland Operations Office (RL) put the PUREX Plant on cold standby. Cold standby may be defined as placing the plant into a safe and environmentally sound condition that does not compromise future fuel reprocessing capability. In December 1992, the PUREX Plant received official notification to begin deactivation and terminal cleanup activities.

The plant has been in a cold-standby mode of operation for this entire reporting period. The plant activities have included equipment maintenance, isolation of water, steam, and chemical lines, and general surveillance.

A.7.4 LISTING OF APPLICABLE DOCUMENTS

The notification of shutdown of the PUREX Plant is referenced in the following letter:

- Letter, W. W. Bixby and Duffy, L.P., to J.D. Wagoner, "Termination of the Plutonium-Uranium Extractraction (PUREX) Plant and Guidance to Proceed with Shutdown Planning and Terminal Cleanout Activities," dated December 21, 1992.
- The PUREX Plant annual waste minization report provides the annual goals for the amount of tank waste that is expected to be generated. The quarterly waste minimization reports provide updates to the total quantity of material transferred to Tank Farms and progress towards achieving the goal set for the current fiscal year.

A.7.5 STATUS OF CY 1992 ACTIVITIES IN PROGRESS

As part of the standby activities, various plant systems are being isolated from the steam and water supplies to reduce waste generation. System isolation is continuing and essential material inventories are being reduced. The waste volume being saved is estimated at 1,079 m³ (285,000 gal) per year.

A.7.6 CURRENT INVENTORY AND AMOUNTS GENERATED

A.7.6.1 Tank Waste Inventory

The tanks used to collect the NCAW and NCRW are permitted as 90-days accumulation tanks and do not store waste. The solvent recovery tanks contain radioactive nonregulated materials and do not require permitting. As a matter of operating practice, solvent recovery wastes are also transferred to tank farms within 90 days. The miscellaneous waste tanks and tank TK-F18 are permitted for the treatment and storage of waste.

A.7.6.2 Tank Waste Generated

Between March 1, 1992, and February 29, 1993, the following types and amounts of tank wastes were transferred from the PUREX facility to the tank farms DSTs:

- NZAW waste: 0 m³
- NCRW waste: 0 m³
- Miscellaneous waste: 255 m³ (67,357 gal)
- Solvent recovery waste: 0 m³.

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A.7.7 WASTE MINIMIZATION ACTIVITIES

To reduce the volume of water entering the canyon from condensation in water and steam lines, those lines that are inactive during standby status have been blanked. Before blanking the lines, the water that entered the canyon because of condensate from these leaking pipes became waste and, thus had to be sent to tank farms for disposal/storage in the DSTs. The amount of tank waste volume being conserved is not readily quantifiable at the present time.

**A.7.8 ESTIMATE OF PLANNED WORK ACTIVITIES
FOR FISCAL YEAR 1993**

The primary activity involving tank wastes at the PUREX Plant is the completion of the Process Waste Assessments.

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A.8.0 B PLANT

This section documents the studies, activities, and issues which occurred in this area during the period of March 1, 1992, through February 28, 1993.

A.8.1 DESCRIPTION OF FACILITY

B Plant is designed to remotely process radioactive materials with minimal radiation exposure to operators. The first mission of B Plant was to reprocess spent fuel between 1945 and 1952 using the bismuth phosphate process. B Plant was refurbished for Mission 2 (1965 to 1985) to recover and purify cesium and strontium from newly generated current acid waste (CAW) and from NCAW stored in waste tanks. The B Plant canyon as well as other major areas of the facility have initiated general cleanup activities.

A.8.2 STATUS OF CURRENT ACTIVITIES

A.8.2.1 Support to the Waste Encapsulation and Storage Facility for Storage of Cesium and Strontium Capsules

B Plant currently provides demineralized water to the Waste Encapsulation and Storage Facility (WESF) for pool-cell storage of cesium and strontium capsules. B Plant also provides treatment for low-level radioactive liquid waste produced at WESF, as well as lag storage for radioactive solid waste generated at WESF.

A.8.2.2 Management of an Existing Inventory of Radioactive Liquid Waste

Radioactive liquid waste is currently in storage at B Plant. This waste includes organic solutions containing cesium and strontium as well as some organic solvents. These liquid wastes exist at B Plant as a result of previous missions. Activities are underway to remove the liquid inventory from B Plant.

A.8.2.3 Management of an Existing Inventory of Radioactive Solid Waste

B Plant currently stores drums of radioactive solid waste in cell 4. These drums of waste, as well as used jumpers, miscellaneous piping, and used equipment stored on the canyon deck and in process cells, are the result of both past and current operations at B Plant and WESF.

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There are currently several megacuries (MCI) of radioactively contaminated materials in B Plant. Buried HEPA filters, the process equipment, and the structure itself are the major sources of radiation. Strontium-90, and ¹³⁷Cs, deposited during Mission 2, are the principal radionuclides contributing to the radiation dose levels in B Plant.

A.8.2.4 Treatment of Low-Level Waste Generated by Operation of Plant Ventilation Systems

The pH of low-level radioactive liquid wastes generated in B Plant and WESF (primarily steam condensate) is chemically adjusted to meet DST acceptance criteria, before transfer to the DSTs.

A.8.2.5 Process Condensate Treatment Facility

Treatment required for the process condensate which is generated as a result of B Plant concentrator operation will be provided with the implementation of recommendations resulting from the best available technology (BAT) engineering report.

A.8.3 WASTE MINIMIZATION ACTIVITIES

Several waste minimization activities associated with the B Plant low-level waste have continued during this reporting period.

A.8.3.1 Suspend Tank Farm Flushes

Past operations procedures at B Plant provided for flushing the transfer line to tank farms after each waste transfer to prevent solids buildup in the transfer line. This procedure added about 14.1 m³ (3,750 gal) of supplemental waste to each transfer of waste to the DSTs. Current procedures call for suspension of flushing prior to the receipt of solids testing results and to flush only when the solids content of the waste exceeds 4 percent.

A.8.3.2 Minimize Tank Liquid Heel Replacement

Tank liquid heels, also known as water seals, have been maintained with demineralized water according to previous operating procedures at B Plant. These water seals were used to prevent contamination between tanks connected to a common ventilation system. This practice was discontinued in June 1990. The maintenance of tank liquid heels is now accomplished with low-level radioactive liquid waste.

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**A.8.3.3 Rerouting of Waste and Elimination
of Steam Jet Dilution**

Low-level liquid waste has been rerouted through tanks equipped with water pumps rather than using steam jets; (i.e., tank 24-1 to tank 25-1 vs. tank 24-1 to tank 23-3 to tank 23-1 to tank 25-1). This practice has eliminated the need for steam jetting, which, in turn, has eliminated a source of liquid dilution.

A.8.4 CURRENT INVENTORY AND/OR AMOUNTS GENERATED

During the reporting period from March 1, 1992 through February 28, 1993, B Plant transferred 490 m³ (129,543 gal) of low-level radioactive waste to the DSTs. This waste consists primarily of steam condensate which is generated by operation of essential plant ventilation systems.

A.8.5 ESTIMATE OF PLANNED WORK ACTIVITIES

Activities currently planned for B Plant are as follows:

- Cleanup of the B Plant canyon deck and support areas of the facility will continue.
- Operation of the LLW concentrator will allow for the system optimization and characterization of the B Plant process condensate and steam condensate effluent streams.
- Preparation for future missions will be initiated by cleanout and stabilization of the B Plant canyon and hot-cells.
- Operation of the LLW concentrator will provide system optimization and characterization of the B Plant process condensate and steam condensate effluent streams.
- Solid waste volume reduction will be implemented by use of a jumper cutter.

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A.9.0 222-S LABORATORY COMPLEX

This section documents the studies, activities, and issues which occurred in this area during the period of March 1, 1992, through February 28, 1993.

A.9.1 DESCRIPTION OF LABORATORY-COMPLEX FUNCTION, FACILITIES, AND WASTE

A.9.1.1 Laboratory-Complex Function

The 222-S Laboratory Complex (222-S Complex), in the southeast corner of the 200 West Area, consists of the 222-S Laboratory (222-S), the 222-SA Standards Laboratory, and several ancillary facilities. The main facility of the complex consists of the 222-S Laboratory, which provides analytical chemistry and radiological services.

The current mission of the 222-S Complex is to provide quality analytical services supporting the Hanford Site processing units with current emphasis on waste management, chemical processing, and environmental functions for the following facilities:

- B Plant
- U Plant
- Tank farms
- 242-A and 242-S Evaporators
- GTF
- WESF
- PUREX
- PFP.

Quality analytical services are also provided in support of general process development/upset activities.

Currently the 222-S Complex is being upgraded to support *Resource Conservation and Recovery Act of 1976* analytical protocols and programs for environmental restoration and DST characterization activities for the Hanford Site.

A.9.1.2 Facilities

The 222-S Laboratory is a two-story, aboveground building, 98-m (322-ft) long and 32.6-m (107-ft) wide. This structure is divided into laboratory support spaces, offices, a multi-curie wing, and supplemental service areas. It has facilities for waste disposal and decontamination, and systems for ventilation, radiation monitoring, and fire protection, including alarms.

The first floor of 222-S is divided into three general sections; west, east, and central. The west section contains a lunchroom, offices, and changerooms. This section is kept free of radioactivity and toxic chemicals.

The central section has service areas and laboratories where toxic chemicals and low-level radioactive materials are analyzed, and intermediate-level radioactive samples are also analyzed occasionally. The east section, commonly known as the multi-curie section, contains laboratories and cells in which intermediate-level radioactive materials are analyzed.

The 219-S Waste Handling Facility (219-S) has three storage tanks in which liquid waste from 222-S can be received, stored temporarily, and neutralized. From this facility, neutralized waste, which may contain radionuclides, is transferred to the tank farms. A 2.65 m³ (700-gal) sodium-hydroxide supply tank is also located in this facility.

A.9.1.3 Waste

Most waste generated at the 222-S Complex derives from analytical activities in 222-S. Waste from 222-S is gravity fed to the 219-S Waste Handling Facility. There are three tanks in 219-S (TK-101, TK-102, and TK-103) that receive hazardous and radioactive liquid waste. Waste solution from 222-S flows to either TK-101 or TK-103. From these tanks, the waste is transferred to TK-102 for pH adjustment using sodium hydroxide. As needed, sodium nitrite is added to the solution, which raises its nitrite concentration to levels meeting tank farm specifications. Then to ensure adequate mixing of the waste constituents, the solution is agitated. After these steps are completed, the neutralized waste is ready for transfer to the tank farms for long-term storage until it can be disposed of permanently.

The types and respective concentrations of wastes typically resulting from laboratory activities are shown in Table A.9-1. Figure A.9-1 illustrates typical concentrations of 222-S waste. The volumes of waste generated, chemical compositions, radionuclide constituents and concentrations, and amounts of solids may vary depending on the analytical activities used to support different programs.

Intermediate-level radioactive waste streams flows to tank-101 of 219-S. These streams originate from hood drains, decontamination hood No. 16, hot laboratory sinks, and inductively coupled plasma analyzers.

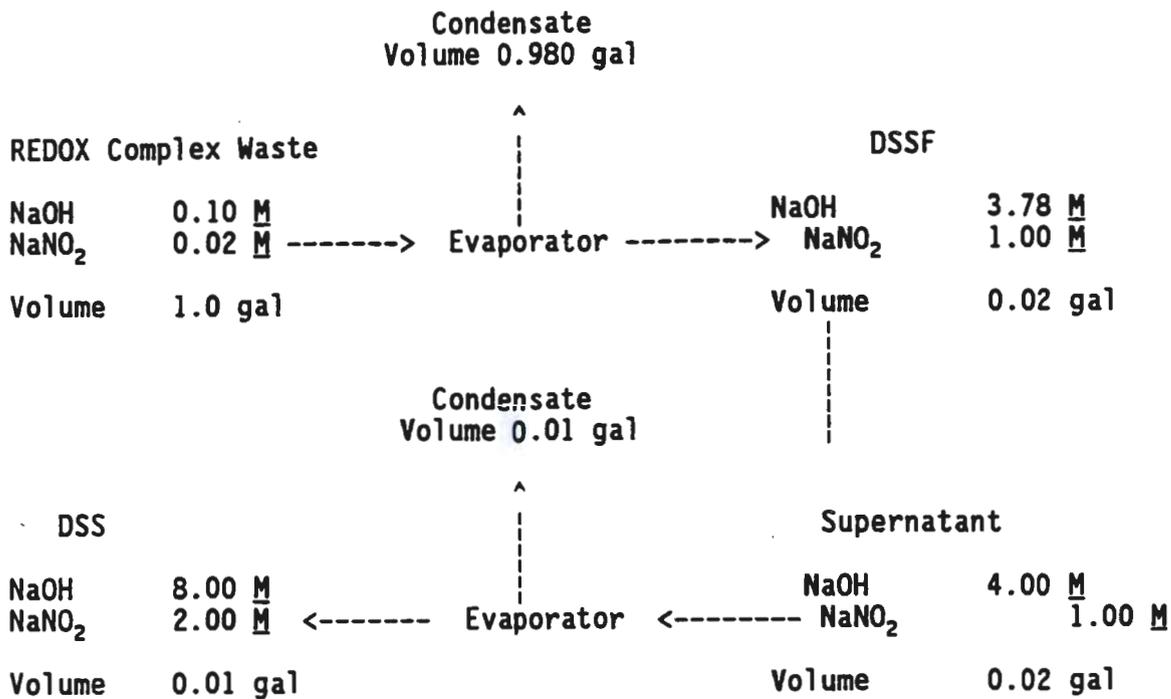
High-level radioactive waste streams are transferred to tank-103. These streams originate from hot-cell drains, jet-suction vacuum (slurping) operations performed at decontamination hood No. 16, the 1-F manipulator-repair hood drain, the atomic-absorption spectrophotometer hood drain, and from the hot tunnel sumps.

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Table A.9-1. 222-S Laboratory Waste Composition.

Chemical	Composition
Liquids	
Fluoride	4.00 E-03 M
Sulfate	3.90 E-03 M
Phosphate	1.45 E-03 M
Nitrite	3.30 E-02 M
Nitrate	9.65 E-02 M
Hydroxide	5.00 E-01 M
Sodium	7.80 E-01 M
Radionuclides	
Total alpha	2.63 E-06 Ci/L
Total beta	8.02 E-05 Ci/L
¹³⁷ Cs	4.83 E-07 Ci/L
^{89,90} Sr	8.05 E-06 Ci/L
^{239,240} Pu	3.70 E-07 Ci/L
Americium	9.04 E-08 Ci/L
Uranium	3.41 E-09 Ci/L
Solids	
Percent	0.00 E+0

Figure A.9-1. Concentration of 222-S Laboratory Waste.



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A.9.2 WASTE MINIMIZATION

Waste minimization plans affecting the 219-S tanks are currently being investigated to help reduce the amount of liquids being disposed of to the tanks. Two examples of waste minimization activities currently being considered are:

- Reducing the amount (volume) of sample being sent by the waste generator. This procedure would minimize the quantity of sample waste because the total delivered sample volume is not always used in the laboratory analysis.
- Returning unused sample portions to the generator of the sample for disposal, which would result in a reduction of aqueous sample volumes being dumped to the waste tanks.

A.9.3 STATUS OF ACTIVITIES IN PROGRESS

The projected volumes of waste are based on facility operating plans, target waste-generation rates, and the SST and DST characterization schedules.

The following schedule represents the anticipated number of SST and DST core samples to be analyzed at the 222-S Laboratory FY 1994 through FY 1998. These projections will be adjusted as required to reflect any changes in the current schedule.

FY	Number of Core Samples
94	21
95	29
96	46
97	62
98	28

In addition to the core samples, other analyses performed will include those required for supporting grout, DST dip samples, and Part B compliance analysis for temporary storage and disposal (TSD) facilities on site.

During the 12-month period from March 1, 1992 through February 28, 1993, 63.74 m³ (16,839 gal) of liquid waste was transferred to tank 204 AR in the 200 East Area Tank Farms.

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A.10.0 T PLANT

This section documents the studies, activities, and issues which occurred in this area during the period of March 1, 1992, through February 28, 1993.

A.10.1 FACILITY DESCRIPTION

T Plant is located in the 200 West Area of the Hanford Site. The T Plant's primary mission is equipment decontamination and refurbishment. The head end of the 221-T canyon building houses the Containment Systems Test Facility. This facility was used to perform experimental testing which requires containment or isolation. The T Plant waste system handles radioactive liquid waste from decontamination activities in the hot-cells, the railroad tunnel, the 2706-T Building, and the head end. The railroad tunnel generates waste from decontaminating railroad cars and multipurpose transfer boxes. During sorting and repackaging of Tank Farms "unknown" waste, low-level radioactive waste, and radioactive mixed waste is generated in the railroad tunnel.

Most of the waste from cells in T Plant consists of water with settled solids generated during decontamination activities. Each cell in the 221-T Canyon has a 15-cm-dia. drain line that allows wastewater to drain into the canyon's 61-cm-dia. sewer line. Potentially contaminated wastes from the head end are also drained through a 15-cm line into the canyon's 61-cm-dia. sewer line. This line empties into tank 5-7 in the canyon. The waste in tank 5-7 is transferred to tank 15-1. In tank 15-1, the waste is sampled, analyzed, then sent to tank farms via the cross-site transfer line or by certified railcar. If the waste is to be delivered via the cross-site transfer line, it is chemically treated to meet tank farms' storage specifications before the transfer operation.

A.10.2 SUMMARY OF MARCH 1992 THROUGH FEBRUARY 1993 ACTIVITIES AND WASTE GENERATED

During this time period, T Plant was under limited operational status and generated only 100.5 m³ (26,792 gal) of waste. The majority of this waste was generated from the addition of water to the rail cars for purposes of railcar certification. The composition of this waste is presented in Table A.10-1. The radioactivity levels of this waste is given in Table A.10-2 for the most significant radionuclides. These data, obtained from process sample data, represent an arithmetic average of the laboratory analysis results. Since April 3, 1991 protocol samples also have been taken, but no analytical data has been made available during this reporting period.

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Table A.10-1. T Plant Waste Chemical Characteristics.

Chemicals	Composition
PO ₄	3.97 E+00 ppm
NO ₂	6.50 E-05 M
NO ₃	4.23 E+02 ppm
Si	2.11 E+03 ppb
Ni	1.99 E+02 ppb
Ca	3.62 E+03 ppb
Cr	9.34 E+01 ppb
P	7.04 E+03 ppb
S	9.58 E+03 ppb
Mg	7.44 E+02 ppb
Na	1.45 E+05 ppb
B	7.82 E+02 ppb
K	9.52 E+03 ppb
Mn	2.43 E+02 ppb
Cl	6.08 E+00 M
pH	5.4
Specific gravity	0.395
Percent solids	0.316
Separable organics	None

Table A.10-2. T Plant Waste Radiological Characteristics.

Radionuclides	Concentration
²³⁸ Pu	1.57 E-08 g/L
^{239/240} Pu	8.90 E-06 g/L
²⁴¹ Pu	1.47 E-08 g/L
²⁴² Pu	3.60 E-09 g/L
²³⁴ U	9.94 E-07 g/L
²³⁵ U	1.14 E-04 g/L
²³⁶ U	4.79 E-06 g/L
²³⁸ U	1.80 E-02 g/L
¹³⁷ Cs	1.12 E+00 uCi/L
¹⁵⁴ Eu	7.13 E-01 uCi/L
¹⁵² Eu	4.16 E-01 uCi/L
¹⁵⁵ Eu	1.99 E-01 uCi/L
⁶⁰ Co	1.15 E-02 uCi/L
¹³⁴ Cs	3.47 E-03 uCi/L
^{89/90} Sr	2.19 E+00 uCi/L
²⁴¹ Am	7.63 E-08 g/L
Total alpha	4.11 E-01 uCi/L
Total beta	2.68 E+01 uCi/L

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A.10.3 STATUS OF ACTIVITIES IN PROGRESS

T Plant decontamination operations are still in a limited operational mode while planned facility upgrades are being completed and operating procedures are being updated and revised.

A.10.4 CURRENT INVENTORY AND/OR AMOUNTS GENERATED

The current tank waste inventory is 23.9 m³ (6,300 gal). Until decontamination operations are resumed, the waste volumes produced will be limited.

A.10.5 WASTE MINIMIZATION ACTIVITIES

The use of plastic and paper for contamination control during work activities within the tunnel has resulted in a reduction in the requirements for post-job decontamination. This, in turn, has reduced the total amount of waste generated.

Liquid LLW generated by T Plant also is used for hydrotesting of railcars, which reduces the amount of water that must be added to the railcar for these tests.

A.10.6 ESTIMATE OF PLANNED WORK ACTIVITIES FOR FISCAL YEAR 1994

As previously stated, T Plant decontamination operations have been limited during FY 1993. The following activities are planned for FY 1994:

- Complete the Readiness Review and resume operations at 2706-T
- Conduct a Canyon Operations Readiness Review.

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A.11.0 HANFORD WASTE VITRIFICATION PLANT

The Hanford Waste Vitrification Plant (HWVP) currently is scheduled for start up in 1999. The low-level waste generated at this facility will be returned to the DST farms for storage treatment and for disposal as grout waste.

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A.12.0 GROUT TREATMENT FACILITY

This section documents the studies, activities, and issues which occurred in this area during the period of March 1, 1992, through February 28, 1993.

A.12.1 DESCRIPTION OF FACILITY AND TYPES OF WASTE GENERATED

A.12.1.1 Description of Facility

The GTF, located in the 200 East Area of the Hanford Site, has the primary mission of permanently disposing of LLW. These LLWs will be blended with cementitious materials for immobilization and solidification in below-ground vaults. The GTF includes the Dry Materials Facility (DMF), the Grout Processing Facility (GPF), and the Grout Disposal Facility (GDF).

The DMF has the primary purpose of receiving, storing, and blending the dry cementitious grout materials. Materials used in this facility include portland cement, fly ash, and blast furnace slag. No radioactive materials are handled at the DMF.

The GPF has the main purpose of receiving radioactive liquid LLW from the 241-AP Tank Farm feed tank, mixing it with the dry-blend materials from the DMF, and transferring the resultant grout mixture to a disposal vault.

The GDF is where the grout disposal vaults are located. The grout slurry mixture is pumped into the vault and cures into a hardened grout product. Liquid waste generated by the grout process or excess water and leachate liquid from the vault during the setting and curing process is returned to the tank farms for processing. Flush liquid results in additional liquid waste to be recycled.

A.12.1.2 Type of Waste Generated

The GTF has generated small quantities [approximately 7.7 m³ (2,035 gal)] of mixed, low-level radioactive and chemically hazardous liquid waste as result of rainwater infiltration to the LCT/MM. In addition, the GTF generated 7.7 L (2 gal) of chemically toxic waste with the disposal of out-of-date sealing material.

A.12.2 WASTE MINIMIZATION ACTIVITIES

The waste minimization plan has the primary purpose to reduce the volume, weight, or toxicity of all regulated waste generated at the GTF to the extent practical. Areas addressed in the plan include;

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organizational responsibilities, employee training, employee participation and incentive programs, and incorporation of waste minimization as part of the design process for new projects or designs.

A.12.2.1 Employee Training

As part of general training for new employees, waste minimization training is included. General waste minimization training is provided to all employees of the GTF via waste minimization team awareness presentations and for hazardous waste shippers as part of the Hazardous Waste Shipment Certification training. Specific training and application of waste minimization techniques will be provided on an individual or group basis, as appropriate, by the respective manager or supervisor. The manager or supervisor is responsible for establishing employee responsibilities, assignments, and goals. Each group will keep a record of waste minimization training.

A.12.2.2 Employee Participation and Incentive Program

An employee participation and incentive program is part of the waste minimization plan at the GTF. Promotion and application of employee incentives appear to be a good way to minimize waste generation and to maximize the use of good operating procedures. The incentive program has several components.

- Encourage employees to submit suggestions as Productivity Improvement and Cost Effectiveness Program (PRICE) proposals or Great Ideas.
- Encourage employees to submit suggestions to the Westinghouse Hanford waste minimization specific incentive program (currently being developed).
- Encourage employees to submit on-the-job waste minimization ideas directly to the GTF Waste Minimization Team with certificates and other rewards for this program.

A.12.2.3 New Projects and Designs

New projects and designs will be required to include waste minimization as an integral part of the design process. To accomplish this, the GTF waste minimization representative will review any proposed new construction and major grout process changes to ensure that waste minimization has been considered. New construction presently includes four grout disposal vaults and modification to tank 241-AP-104 for use as a second feed tank. New construction under consideration is a Grout Failed Equipment Handling Facility to stage contaminated failed equipment.

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A.13.0 REFERENCES

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Karnesky, 1990, *Annual Report of Tank Waste Treatability*, WHC-EP-0365, Westinghouse Hanford Company, Richland, Washington.

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