1 of 3

Pretreatment Status Report on the Identification and Evaluation of Alternative Processes

Milestone Report No. C064

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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Date Published
September 1993

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Sta #10 SEP 2 1993	ENGINEERING DATA TRANSMITTAL	Page 1 of 1 1. EDT 155420
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2. To: (Receiving Organization) Distribution	3. From: (Originating Organization) Pretreatment Engineering	4. Related EDT No.:
5. Proj./Prog./Dept./Div.: TWRS/PRETREATMENT	6. Cog. Engr.: D. G. Sutherland	7. Purchase Order No.: N/A
8. Originator Remarks: Release the "Pretreatment Status Report on the Identification and Evaluation of Alternative Process"		9. Equip./Component No.: N/A
		10. System/Bldg./Facility: N/A
11. Receiver Remarks:		12. Major Assm. Dwg. No.: N/A
		13. Permit/Permit Application No.: N/A
		14. Required Response Date: N/A

15. DATA TRANSMITTED					(F)	(G)	(H)	(I)
(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	Impact Level	Reason for Trans- mittal	Originator Dispo- sition	Receiver Dispo- sition
1	WHC-SD-WM-PRS-012		0	Pretreatment Status Report on the Identification and Evaluation of Alternative Processes	4	2		

16. KEY		
Impact Level (F)	Reason for Transmittal (G)	Disposition (H) & (I)
1, 2, 3, or 4 (see MRP 5.43)	1. Approval 4. Review 2. Release 5. Post-Review 3. Information 6. Dist. (Receipt Acknow. Required)	1. Approved 4. Reviewed no/comment 2. Approved w/comment 5. Reviewed w/comment 3. Disapproved w/comment 6. Receipt acknowledged

(G)	(H)	17. SIGNATURE/DISTRIBUTION (See Impact Level for required signatures)						(G)	(H)
Reason	Dis- p.	(J) Name	(K) Signature (M) MSIN	(L) Date	(J) Name	(K) Signature (M) MSIN	(L) Date	Reason	Dis- p.
	1	Cog. Eng. D. G. Sutherland		9/3/93					
	1	Cog. Mgr. W. B. Barton		9/3/93					

18. D. G. Sutherland Signature of EDT Date Originator	19. _____ Authorized Representative Date for Receiving Organization	20. W. B. Barton Cognizant/Project Date Engineer's Manager	21. DOE APPROVAL (if required) Ltr. No. ☐ Approved ☐ Approved w/comments ☐ Disapproved w/comments
--	--	---	--

Date Received: 9/9/93	INFORMATION RELEASE REQUEST	Reference: WHC-CM-3-4
Complete for all Types of Release		
Purpose ☐ Speech or Presentation ☐ Full Paper (Check only one suffix) ☐ Summary ☐ Abstract ☐ Visual Aid ☐ Speakers Bureau ☐ Poster Session ☐ Videotape		☐ Reference ☒ Technical Report ☐ Thesis or Dissertation ☐ Manual ☐ Brochure/Flier ☐ Software/Database ☐ Controlled Document ☐ Other
		ID Number (include revision, volume, etc.) WHC-SD-WM-PRS-012, Rev. 0
		List attachments.
		Date Release Required 9/22/93

Title Pretreatment Status Report on the Identification and Evaluation of Alternative Processes		Unclassified Category UC-	Impact Level 4
New or novel (patentable) subject matter? ☒ No ☐ Yes If "Yes", has disclosure been submitted by WHC or other company? ☐ No ☐ Yes Disclosure No(s).		Information received from others in confidence, such as proprietary data, trade secrets, and/or inventions? ☒ No ☐ Yes (Identify)	
Copyrights? ☒ No ☐ Yes If "Yes", has written permission been granted? ☐ No ☐ Yes (Attach Permission)		Trademarks? ☒ No ☐ Yes (Identify)	
Complete for Speech or Presentation			
Title of Conference or Meeting		Group or Society Sponsoring	
Date(s) of Conference or Meeting	City/State	Will proceedings be published?	☐ Yes ☐ No
		Will material be handed out?	☐ Yes ☐ No
Title of Journal			

CHECKLIST FOR SIGNATORIES			
Review Required per WHC-CM-3-4	Yes	No	Reviewer - Signature Indicates Approval
			Name (printed) Signature Date
Classification/Uncontrolled	☐	☒	
Nuclear Information	☐	☒	
Patent - General Counsel	☒	☐	<u>S. W. Berglin</u> } <u>[Signature]</u> <u>9/16/93</u>
Legal - General Counsel	☒	☐	<u>S. W. Berglin</u>
Applied Technology/Export Controlled	☐	☒	
Information or International Program	☐	☒	
WHC Program/Project	☒	☐	<u>W. B. Barton</u> } <u>[Signature]</u> <u>9-8-93</u>
Communications	☐	☒	
RL Program/Project	☒	☐	<u>S. T. Burnum</u> } <u>[Signature]</u> <u>9/14/93</u>
Publication Services	☒	☐	<u>L. Orgill</u> } <u>by M. Boston per telecon</u> <u>9/27/93</u>
Other Program/Project	☐	☒	
Information conforms to all applicable requirements. The above information is certified to be correct.			

Yes No References Available to Intended Audience ☒ ☐ Transmit to DOE-HQ/Office of Scientific and Technical Information ☒ ☐ Author/Requestor (Printed/Signature) <u>D. G. Sutherland</u> <u>[Signature]</u> Date <u>9-8-93</u>	INFORMATION RELEASE ADMINISTRATION APPROVAL STAMP Stamp is required before release. Release is contingent upon resolution of mandatory comments.
Intended Audience ☐ Internal ☐ Sponsor ☒ External Responsible Manager (Printed/Signature) <u>W. B. Barton</u> <u>[Signature]</u> Date <u>9-8-93</u>	Date Cancelled	Date Disapproved

SUPPORTING DOCUMENT		1. Total Pages 244
2. Title Pretreatment Status Report on the Identification and Evaluation of Alternative Processes	3. Number WHC-SD-WM-PRS-012	4. Rev No. 0
5. Key Words Pretreatment Alternative Processes Candidate Processes Waste Treatment	6. Author Name: D. G. Sutherland Signature Organization/Charge Code 7E822/D34D4	
7. Abstract This supporting document provides a status report for the identification and evaluation of alternative processes for the pretreatment of Hanford DST/SST waste. Included are four independent flowsheet studies, and brief accounts of pretreatment activities being performed by others.		
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9. Impact Level 4

**APPROVED FOR
PUBLIC RELEASE**
M. Boston 9/27/93
Information Release Administration

EXECUTIVE SUMMARY

This report is a presentation of candidate technologies for pretreatment of Hanford Site tank waste. Included are descriptions of studies by the Pacific Northwest Laboratory of Battelle Memorial Institute (PNL); Science Applications International Corporation (SAIC), an independent consultant; BNFL, Inc. (BNFL) representing British technologies; Numatec, representing French technologies; and brief accounts of other relevant activities.

OBJECTIVES

This report presents fiscal year (FY) 1993 activities that identify and assess processes currently being considered for pretreatment of Hanford Site tank waste, and establishes decision criteria for prioritizing the candidate processes. Included is the discussion of a study in which SAIC used similar criteria to identify, evaluate, prioritize, and select the candidate processes that comprise the study's proposed pretreatment flowsheet. The other FY 1993 studies that developed alternative pretreatment flowsheets were completed near year-end, therefore relative rankings were not made for these processes due to time constraints.

This report also identifies, in a single document, various processes being considered for pretreatment of Hanford Site high-level waste. We intend for the report to facilitate future reviews and evaluations of the integrated processes described herein, as well as assessments of the numerous other unit processes being considered for high-level waste pretreatment.

BACKGROUND

The Tank Waste Remediation System (TWRS) was established in 1991 to safely manage and immobilize Hanford Site tank waste, and in March 1993 a new technical strategy was established to carry out the TWRS mission. A systems engineering approach currently is being implemented to support this mission. Five major decision criteria comprised of eighteen subcriteria were developed for TWRS and will serve as top-down requirements for pretreatment evaluations.

Two bounding technology approaches for waste pretreatment and immobilization were defined, one for high-capacity vitrification and the other for extensive separations. These technologies range from mature to emerging processes and provide diverse levels of performance. The TWRS New Technical Strategy (NTS) seeks to implement disposal actions as early as practicable on selected supernates, while developing new technologies for later pretreatment of other supernates, salt cake, and sludge. Program flexibility is achieved by the ability to overlap adjacent phases consistent with the progress of technology development.

STUDIES REPORTED

Pretreatment technologies were surveyed during FY 1993 by contracting organizations that, in the aggregate, could bring a fresh, encompassing view to Hanford Site tank waste pretreatment. These organizations were SAIC, PNL, BNFL, and Numatec. The studies produced a diversity of perspectives. SAIC was requested to survey processes, national and international, that have potential applications for Hanford Site waste pretreatment. Contracts with

BNFL and Numatec augmented the ongoing U.S. Department of Energy (DOE) effort to involve foreign firms that have developed significant nuclear programs in the determination of a Hanford Site pretreatment process.

The contracting strategy was to create a task variety such that the composite of all studies would be global in perspective. The independent consultant was given a broad latitude, not only to assess candidate processes but also to develop and implement a structured decision methodology by which the preferred flowsheet was established. The survey of pretreatment technologies provided by SAIC and the international perspective inherent in the BNFL and Numatec studies is complemented by the process-oriented approach of PNL. The PNL study focused on simple technologies that hold a potential for near-term application. Precipitation, ion exchange, and leaching were investigated. The work complemented the other studies by ensuring that inherently simple operations are not overlooked in favor of exciting new technologies.

PROCESSES SELECTED

The SAIC pretreatment process is a combination of ozonation to destroy complexants; ion exchange with titanium-treated zeolite (as applied at the West Valley Site) to remove cesium, strontium, and transuranic waste (TRU); and strong-base anion exchange to remove technetium. BNFL recommends removing complexants from the waste by whatever oxidation process the current Hanford Site development activities decide is appropriate, separating cesium and strontium by ion exchange, and separating TRU by the transuranic extraction (TRUEX) process. Numatec favors electrolysis or hydrogen peroxide treatment.

for organic complexant destruction, ion-specific extractants for cesium and strontium removal, and the diamide extraction (DIAMEX)¹ process for TRU. Using a combination of precipitation, ion exchange, and bulk leaching, PNL developed four different flowsheets. One of these approaches, a combination of aggressive sludge dissolution and ion exchange, came impressively close to meeting goals of the extensive separations alternative of the TWRS NTS (i.e., CLEAN), perhaps an important new development. Figure ES-1 is a quick reference, comparing processes selected by each study.

Figure ES-1. Processes Selected by Composite Study.

		CC/FeCN Destruction		Cs Separation	Sr Separation	TRU Separation	Tc Separation	Other
Bulk Treatment	Precipitation	Acid	Not in Scope	Phosphotungstic Acid	Sulfuric Acid and Pb(NO ₃) ₂	Oxalic Acid and CaSO ₄	No Treatment	Not in Scope
		Alkaline		Crystalline Si-Titanates	Crystalline Si-Titanates	Crystalline Si-Titanates	Na ₂ S	
	Solid Sorbents	Acid		Ammonium Phosphomolybdate	Sr Spec	Sr Spec and TRU Spec	No Treatment	Not in Scope
		Alkaline		Resorcinol Formaldehyde	IRC-718	No Treatment	Reillex	
	Leach	Acid		Ion X Resin Elution with HNO ₃	No Treatment	No Treatment	No Treatment	No Treatment
		Neutral or Alkaline		Act-de-con	Act-de-con	Act-de-con		
Independent Consultant		Ozonation	WVDP	WVDP	WVDP	ISO 100	No Treatment	
			Ion X Ti-Treated Zeolite	Ion X Ti-Treated Zeolite	Ion X Ti-Treated Zeolite	Ion X Strong Base Anion Resin		
British Technology		Calcination or Hydrothermal (IPM)	Sellafield	Sellafield	Solvent EX TRUEX	No Treatment	U Solvent EX PUREX	
			Ion X SIXEP	Ion X SIXEP			F, Al, Zr Precip. EARP	
French Technology		H ₂ O ₂ or Electrolysis [Ag(I) or Co(II)]	Solvent EX Macrocyclic	Solvent EX Macrocyclic	Solvent EX DIAMEX	No Treatment	U, Ce Solvent EX DIAMEX	

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¹DIAMEX is a trademark of the French Atomic Energy Commission.

Decisions made with regard to sludge dissolution dictate the options for removal of radionuclides. If the waste requiring vitrification is to be minimized, aggressive acid dissolution is the choice. If the designer chooses to avoid uncertainties associated with acid dissolution, the choice may be water and dilute caustic wash to remove soluble ions and aluminum. The PNL and SAIC studies made different choices, PNL choosing aggressive acid dissolution and SAIC favoring benign washes.

The PNL sludge processing sequence consists of water wash, caustic leach, and two dissolution steps, first with boiling nitric and oxalic acids and next with boiling nitric and hydrofluoric acids. Leaching and dissolution produce an acid and an alkaline stream. A significant uncertainty inherent in this approach is the effectiveness of sludge dissolution. Other questions requiring further development include material compatibility under the acidic conditions imposed and solid-liquid separations.

The conservative approach taken by SAIC results in a significantly larger volume of high-level waste produced, but eliminates the need for a separate series of processes to separate radionuclides from acidic solutions. After decanting supernate, the sludge is washed with caustic solution and the resultant solids immobilized as high-level waste. The intent is to follow the Savannah River Site sludge washing and agitation process using quad-volute pumps that SAIC believes can be applied at the Hanford Site.

BNFL and Numatec were tasked to consider complexant concentrate (CC) and neutralized cladding removal waste (NCRW). Neither study chose an initial sludge wash step, preferring to avoid the need for alkaline-side processes.

BNFL and Numatec followed a common approach for nitric acid dissolution based on work by PNL but differing somewhat with one another. In the Numatec study, solids remaining after dissolution are combined with the treated waste going to grout. The preliminary BNFL study apparently includes the undissolved solids in the feed stream going to vitrification.

There was not a clear consensus in the studies on organic destruction methods recommended. SAIC proposed ozonation, BNFL favored following the lead of Hanford Site technology developments, and Numatec chose either electrolysis or oxidation using hydrogen peroxide. Organic destruction was outside the PNL study scope. Both SAIC and Numatec considered several options in making their process decisions. Three organic destruction processes (ozonation, calcination, and hydrothermal processing) were evaluated by SAIC. Organic destruction processes considered by Numatec were oxidation with hydrogen peroxide, subcritical wet oxidation, supercritical wet oxidation, and electrolytic oxidation.

CONCLUSIONS AND RECOMMENDATIONS

From the pretreatment flowsheet studies described in this report, taken in context with other recent investigations, several conclusions can be drawn. Each study suggested technologies it determined can be developed to perform sufficiently well to satisfy projected pretreatment flowsheet needs, yet the technologies selected by the studies differed significantly from one another. These independent investigations by four highly qualified organizations with widely differing backgrounds determined not only that process candidates exist that can be developed to pretreat Hanford Site tank waste, but also that there

are several good ones from which to choose. The studies selected not only different processes, but also different unit operations. Figure ES-1 shows that for radionuclide removal, SAIC selected all ion exchange separations (for strontium, cesium, transuranic elements, and technetium), Numatec selected all solvent extraction separations, and BNFL selected a combination of ion exchange and solvent extraction. The unit operations investigated in the PNL studies were predetermined to be precipitation, ion exchange, and leaching.

This composite study augments the conclusions reached by previous investigations that many technology uncertainties must be resolved before a final assessment of pretreatment alternative processes can be made. The seven flowsheets developed were quantified to differing degrees, largely due to variations in technology maturity. Firm life-cycle costs could not be determined at this time due to these factors, as well as to uncertainties associated with waste feed to the pretreatment process and with immobilized waste form and manner of disposal.

Three of the four studies described in this report reached similar conclusions as to which radionuclides needed to be removed from the high-volume low-level waste fraction. This task was outside the PNL scope. All four studies targeted strontium, cesium, and the transuranic radionuclides of plutonium and americium for removal from the low-level waste fraction (Figure ES-1). The two studies that addressed NCAW (by SAIC and PNL) also targeted technetium removal.

The composite study did not produce a technical consensus regarding sodium salt treatment. SAIC considered several methods, but did not suggest

treatment of inert salts. Neither BNFL nor Numatec suggested a process for sodium salt treatment, possibly because their experience is based on a waste much lower in salts than Hanford Site waste. The potential treatment of sodium salts was not in the PNL scope.

The report suggests that sufficient technology identification searches have been conducted to justify beginning a meaningful prioritization activity, and proposes the development of a decision model specific to the evaluation of pretreatment processes. It would explicitly model uncertainty. All identified technologies, preferred and not currently preferred, would be tracked, and data pertinent to their prioritization would be electronically managed. The pretreatment decision model would be patterned after the overall Site systems model, interfaced with and subordinated to controls from the systems model, and designed specifically to satisfy pretreatment needs. The result would be a decision rationale that makes clear the bases for recommendations, and can be defended, if necessary, in a public arena.

Only a finite quantity of technical specialists, cold and hot test facilities, funding, and time exists to satisfy the Hanford Site pretreatment mission. In order that uncertainties be reduced and eventually eliminated, this finite quantity of resources must not be diluted to the extent that realistic candidates fail to be brought to maturity in a timely manner. By implementing a structured prioritization system, the highest-rated process candidates can be elevated in stature to a preferred "short-list." Given a commitment by relevant WHC and PNL organizations to make such a system work, resources can be focused on pretreatment "short-list" processes until each is understood sufficiently well that the conceptual design stage can begin.

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LIST OF TERMS

A/O	aqueous phase to organic phase volume ratio
ALARA	as low as reasonably achievable
ANL	Argonne National Laboratory
APM	ammonium phosphomolybdate
BNFL	BNFL, Inc.
CC	complexant concentrate
CFR	<i>Code of Federal Regulations</i>
CLEAN	Extensive Separations Pretreatment Option
CMPO	octyl (phenyl)-N, N-diisobutylcarbamoyl-methylphosphine oxide
COGEMA	Compagnie Generale des Matieres Nucleaires
CPU	Compact Processing Units
CST	crystalline silicotitanate
CSTR	continuous stirred tank reactor
CVS	Compositional Variability Study II
DF	decontamination factor
DIAMEX	diamide (family of solvents) extraction
DOE	U.S. Department of Energy
DOE-HQ	U.S. Department of Energy-Headquarters
DPL	Decision Programming Language
DSSF	double-shell slurry feed
DST	double-shell tank
DT&E	demonstration, test, and evaluation
EARP	Enhanced Actinide Removal Plant
Ecology	Washington State Department of Ecology
EDTA	ethylenediaminetetraacetic acid
EM-30	Office of Waste Management
EM-40	Office of Environmental Restoration
EM-50	Office of Technology Development
ESPIP	Efficient Separations and Processing Integrated Program
FY	fiscal year
GTF	Grout Treatment Facility
GTM	Generic TRUEX Model
HEDPA	1-hydroxyethane 1,1-diphosphonic acid
HLW	high-level waste
HTP	hydrothermal processing
HWVP	Hanford Waste Vitrifaction Plant
IBM	International Business Machines
ICPP	Idaho Chemical Processing Plant
IPM	Initial Pretreatment Module
ITEP	International Technology Exchange Program
KEH	Kaiser Engineers Hanford Company
LANL	Los Alamos National Laboratory
LLW	low-level waste
MAU	Multiaattribute Utility Theory
MBE	moving bed evaporator
MVST	Melton Valley Storage Tank
NCAW	neutralized current acid waste
NCRW	neutralized cladding removal waste
NRC	Nuclear Regulatory Commission
NTS	new technical strategy
O/A	organic phase to aqueous phase volume ratio

LIST OF TERMS (cont)

ORNL	Oak Ridge National Laboratory
PA	performance assessment
PNL	Pacific Northwest Laboratory
PTA	phosphotungstic acid
PUREX	Plutonium-Uranium Extraction (Plant)
R&D	research and development
RCRA	<i>Resource Conservation and Recovery Act of 1976</i>
RDDT&E	research, development, demonstration, test, and evaluation
RL	U.S. Department of Energy, Richland Operations Office
SAIC	Science Applications International Corporation
SGN	Saint-Gobain Nucleaire
SIXEP	Site Ion Exchange Plant (British)
SLF	supported liquid film
SNL	Sandia National Laboratory
SREX	strontium extraction
SRS	Savannah River Site
SST	single-shell tank
SWFTP	separations and waste-form technologies and processes
TBP	tributyl phosphate
TEDF	Treated Effluent Disposal Facility
TOC	total organic carbon
TRAC	track radionuclide components
TRU	transuranic waste
TRUEX	transuranic extraction
TWRS	Tank Waste Remediation System
UST	underground storage tank
UST-ID	Underground Storage Tank-Integrated Demonstration
VE	value engineering
WAC	<i>Washington Administrative Code</i>
WHC	Westinghouse Hanford Company
WVDP	West Valley Demonstration Project

TRADEMARKS

The following is a list of the trademarks that appear in this document with the respective owners of the trademark.

<u>Trademark</u>	<u>Owner</u>
4th Dimension (registered), 4D Compiler, 4D Draw	Acius, Inc.
Act-de-con	Bradtec-US, Inc.
Amberchrom, Amberlite, Cs-100, Duolite, IRC-718	Rohm and Haas
Apple File Exchange, Macintosh (registered),	Apple Computer, Inc.
ASPEN Plus II, ASPEN Speed Up	ASPEN Technologies
CALEX, DIAMEX, DIAGNOLEX, PAREX, SIMULEX	The French Atomic Energy Commission
Decision Programming Language	Applied Decision Analysis, Inc.
Delphi	Rand Corporation
Design/IDEF (registered)	Meta Software Corporation
Dowex-1	Dow Chemical Company
IBM	International Business Machines Corporation
IONSIV IE-96, IONSIV TIE-96	UOP (Union Carbide Corporation)
Kepner-Tregoe	Kepner-Tregoe, Inc.
LEAFLASH	French Atomic Energy Commission
Logical Decision	Logical Decisions
Mathematica	Wolfram Research, Inc.
Reillex	Reilly Tar and Chemical Company
Sr•Spec, TRU•Spec	El Chrom Ind., Inc.
Supertree	Strategic Decisions Group
Tiron	LaMotte Chemical Products Company

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**PRETREATMENT STATUS REPORT ON THE IDENTIFICATION AND
EVALUATION OF ALTERNATIVE PROCESSES**

DOE-HQ MILESTONE REPORT NO. C064

1.0 INTRODUCTION

This status report summarizes evaluations of alternative processes for pretreatment of Hanford Site defense high-level waste (HLW) that were performed by or for the Pretreatment Engineering organization of the Westinghouse Hanford Company (WHC). The report is submitted to satisfy requirements of the U.S. Department of Energy-Headquarters (DOE-HQ) class milestone (control number C064) entitled "Issue Report on Pretreatment Alternative Process Evaluation."

Pretreatment, as used in this document, refers to the processing of radioactive wastes now stored at the Hanford Site in underground tanks into separate HLW and low-level waste (LLW) fractions. Following pretreatment, HLW is to be vitrified as borosilicate glass, and LLW is to be incorporated into a solid grout form. The report is based on information received by August 1, 1993, and every effort has been made to consider salient developments that surfaced during later stages of document preparation.

1.1 OBJECTIVES

An objective of this report is to present the activities conducted during fiscal year (FY) 1993 to identify and assess the processes currently being considered for the pretreatment of Hanford Site tank waste, and to establish criteria for prioritizing the alternative processes. These criteria, recommended for FY 1994 prioritization activities, are reviewed. Included is the discussion of a study in which Science Applications International Corporation (SAIC) used similar criteria to identify, evaluate, prioritize, and select the candidate processes that comprise the study's recommended pretreatment flowsheet.

Another report objective is to identify, in a single document, various processes that have been proposed for pretreatment of Hanford Site HLW. It is intended that this presentation will facilitate future reviews and evaluations of the integrated processes described herein, as well as the assessment of numerous other individual or unit processes being considered for HLW pretreatment.

1.2 PURPOSE

The purpose of this report is to support the development and demonstration of a pretreatment system that will (1) destroy organic materials and ferrocyanide in tank wastes so that the wastes can be stored safely, (2) separate the high-activity and low-activity fractions, (3) remove radionuclides and remove or destroy hazardous chemicals in LLW as necessary to

meet waste form feed requirements, (4) support development and demonstration of vitrification technology by providing representative feeds to the bench-scale glass melter, (5) support full-scale HLW vitrification operations, including near-term operation, by providing feed that meets specifications, and (6) design and develop pretreatment processes that accomplish the above objectives and ensure compliance with environmental regulations (Wodrich 1993).

1.3 SCOPE

Seven separate flowsheets for the pretreatment of Hanford waste were developed and evaluated by four independent studies. The studies were conducted by the Pacific Northwest Laboratory (PNL); SAIC; BNFL, representing British technologies; and Numatec, representing French technologies. The recommended technologies, technical issues, and technology development requirements for each study are discussed herein.

Criteria recommended for FY 1994 prioritization activities are presented. Because the studies referenced above were of year-long duration (final reports for five of the seven flowsheets were not available at the time of status report preparation), these criteria could not be applied to the flowsheets during FY 1993. Although the final selection of a specific integrated pretreatment process is beyond the scope of this report, a comprehensive prioritization and selection activity using structured decision methodologies was conducted and is documented herein as an integral part of the independent consultant study.

1.4 REPORT ORGANIZATION AND CONTENT

The report is organized into ten sections of text, a reference section, and an appendix, as described briefly below.

Section 1.0, **INTRODUCTION**, is a summary-level view of Hanford Site pretreatment strategy based on overall systems requirements, and includes a synopsis of relevant historical factors.

Section 2.0, **CONCLUSIONS AND RECOMMENDATIONS**, builds on a digest of FY 1993 activities and is intended to assist the U.S. Department of Energy (DOE) in allocation of resources to essential pretreatment efforts.

Section 3.0, **NEW TECHNICAL STRATEGY**, defines the overall pretreatment approach, flowsheets, and individual processes within the flowsheets currently envisioned to satisfy the pretreatment function.

Section 4.0, **INDEPENDENT CONSULTANT STUDY**, summarizes a study performed by SAIC to identify potential alternative processes for waste pretreatment, develop a methodology for prioritization of the alternative processes, and prepare a material balance flowsheet for the number one process.

Section 5.0, **BULK TREATMENT**, summarizes a study performed by the PNL for waste pretreatment by bulk precipitation, ion exchange, nonradionuclide leach, and radionuclide leach processes.

Section 6.0, **BRITISH TECHNOLOGY**, summarizes a study performed by BNFL, a wholly-owned subsidiary of British Nuclear Fuels, for the application of British technology to the pretreatment of neutralized cladding removal waste (NCRW) and complexant concentrate (CC).

Section 7.0, **FRENCH TECHNOLOGY**, summarizes a study performed by Numatec, an affiliate of the French Atomic Energy Commission (Comissariat L'Energie Atomique), for the application of French technology to the pretreatment of NCRW and CC.

Section 8.0, **ASSESSMENT OF ALTERNATIVES**, summarizes an initial evaluation of pretreatment processes presented in Section 4.0 through Section 7.0 using classical engineering evaluations combined with the criteria-driven approach of Section 9.0, subject to the time constraints of FY 1993.

Section 9.0, **DECISION ANALYSIS**, discusses the application of decision analysis to the evaluation of pretreatment processes. Included is a discussion of decision analytic aspects of the various independent studies that are a part of this report, a description of evaluative criteria, and recommended FY 1994 decision analytic activities.

Section 10.0, **TECHNOLOGY IDENTIFICATION AND MANAGEMENT**, summarizes efforts made to survey global technologies, with an aim towards identifying processes potentially applicable to Hanford Site waste treatment and towards managing the data.

Section 11.0, **REFERENCES**, are provided.

Appendix A, **PRETREATMENT ACTIVITIES OUTSIDE OF REPORT SCOPE**, identifies relevant pretreatment activities being conducted in support of the Hanford Site cleanup that are not within the scope of this report, which will be documented in detail elsewhere.

The independent consultant study used information obtained from various sources, including an electronic literature search by the PNL Technical Library of the chemical abstracts and DOE files for the 5-year period from 1988 through 1992; international papers obtained through the International Technology Exchange Program (ITEP); WHC; the Initial Pretreatment Module (IPM) study performed by Kaiser Engineers Hanford Company (KEH); and from researchers at various other locations. The flowsheet studies by the BNFL and Numatec contributors identified processes that, based on their respective technologies, would satisfactorily treat Hanford Site HLW while the PNL study targeted bulk treatment or, more specifically, separations by selective leaching, precipitation, and ion exchange.

In addition to the information from this contracted work, it has been the intent to identify, on a "global" basis, all technologies that have sound potential for Hanford Site application. The information presented in this report represents the current "state of the art" to the extent that it is documented and available in national or international publications or in the DOE technical literature, or has been otherwise available to the WHC staff. The identification and organization of candidate processes and the electronic compiling and management of the information obtained is discussed in Section 10.0 of this report.

The winnowing of nonapplicable papers from the computer search, selection of candidate processes, and narrowing or focusing of attention on a relatively few top contenders for each process function is addressed in Sections 2.0 and 9.0 of the report. This selection process is ongoing and will be tracked with the use of the electronic data-management tools described in Section 10.0. A discussion of the current status of preliminary comparisons and evaluations of candidate processes is presented in Section 8.0. Selection of a final specific integrated pretreatment process is beyond the scope of this report; however, methodology is available for performing an objective screening of candidate processes and was used during one study to identify a preferred integrated pretreatment process (see Section 4.0). Also, a discussion of decision analysis theory and application is presented in Section 9.0. Included is a discussion of how decision analysis methodology could be used to determine a preferred "short list" of candidate pretreatment processes. In addition to providing an objective, rational selection, decision methodology provides a defensible rationale for the recommendation.

Decision methodologies were used by each of the study groups that developed pretreatment processes (Section 9.3). The specific criteria used by each group and the importance applied to each criterion, however, differed. Section 9.4 compares the sets of selection criteria used by the various study groups with each other and with the criteria identified in the integrated technology plan for the Tank Waste Remediation System (TWRS) (Wodrich 1993). This document identified 18 criteria in five categories, as discussed in Section 9.4.

1.5 BACKGROUND

The DOE Hanford Site in eastern Washington State has stored HLW in large underground tanks since 1944. Approximately 232,000 m³ (61 Mgal) of alkaline liquids, slurries, salt cakes, and sludges are currently stored in 177 tanks. In addition, significant amounts of ⁹⁰Sr and ¹³⁷Cs previously removed from tank waste are now stored onsite in double-encapsulated metal containers. The DOE and WHC are evaluating technical strategies for remediating these wastes.

Methods for treatment and disposal of Hanford Site tank waste have been under study for more than 15 years. In 1977, *Alternatives for Long-Term Management of Defense High-Level Radioactive Waste, Hanford Site Reservation, Richland, Washington* (ERDA 1977) was issued. It considered 27 different methods to treat and dispose of the tank waste. These methods were refined and studied further, as reported in *Technical Aspects of Long-Term Management Alternatives of High-Level Defense Waste at the Hanford Site* (RHO 1980). In 1983 the DOE published a notice of intent to prepare an environmental impact statement (EIS) on disposal of radioactive defense HLW and transuranic waste (TRU) at the Hanford Site. As a result, engineering support data for the methods considered in the EIS were documented in the *Hanford Defense Waste Disposal Alternatives: Engineering Support Data for the HDW-EIS* (RHO 1985). Subsequently, the final EIS (DOE 1987) and Record of Decision (Federal Register, Volume 53, p. 12449 [53 FR 12449]) were issued. Since then, engineering studies have developed and evaluated additional alternatives (Boomer et al. 1991 and 1993).

The selection of a technical strategy for remediation of tank waste is a complex task requiring the evaluation of a large quantity of data using common criteria as they relate to decision values held by different stakeholder groups. To accommodate this dynamic situation, a tailored systems engineering approach recently has been initiated to structure and analyze technical strategy candidates (Johnson et al. 1993). The key priorities for pretreatment are to (1) develop and employ the technologies necessary for resolution of tank safety issues, and (2) develop early technology that will enable decision-makers to select the degree of separations to be implemented and determine the capacity requirements of the HLW vitrification system.

The currently proposed technical strategy (Section 3.0) focuses first upon the mitigation or resolution of tank safety issues and the establishment of a safety envelope for continued operations. The strategy addresses early progress by processing supernate and/or salt cake for radionuclide removal through either the IPM or compact processing units. For the more difficult sludge waste, two boundary alternative approaches will be developed in parallel until sufficient technical data are available to allow decision makers to select a pretreatment flowsheet. The two boundary approaches are extensive separations and high-capacity vitrification.

In the extensive separations pretreatment (CLEAN) approach (Sections 3.0 and A8.0), pretreatment uses yet undeveloped technologies to separate the tank waste into a small-volume HLW fraction and a large-volume LLW fraction. HLW could be processed into glass in a vitrification plant smaller than the currently envisioned Hanford Waste Vitrification Plant (HWVP). The LLW fraction radionuclide concentration would be within the *Code of Federal Regulations*, Title 10, Part 61 (10 CFR 61) Class A waste limits, would have reduced chemical toxicity, and would be disposed of onsite as grout.

In the high capacity vitrification approach, pretreatment uses current technologies to separate tank waste into HLW and LLW fractions. A melter capacity greater than the currently sized HWVP melter would be required to effectively immobilize the larger volume of HLW. A new, very large capacity melter could be developed to vitrify the LLW to produce an improved LLW form for onsite disposal. The LLW fraction would meet regulatory requirements, but would contain higher radionuclide concentrations than produced by the extensive separations approach.

As development and evaluation of the two boundary technologies progress, a preferred alternative may develop that is between the two bounds using an intermediate level of separations and an appropriately sized vitrification facility.

Cleanup and disposal of the quantity of radioactive and hazardous waste stored in tanks at the Hanford Site is an unprecedented undertaking. The engineering information that is necessary to develop such a program is obtained from various sources. Most of the information is based on comparisons with chemical processing industries that do not routinely work with radioactive nuclides. Some of the information is based on development work that has been demonstrated on a laboratory scale, but not on a pilot plant or production scale, while other information results from the experience gained by contractors responsible for the original radiochemical separation processes. All of these considerations introduce a level of uncertainty about

the reliability of data being used to select the ultimate pretreatment flowsheet and individual processes comprising the flowsheet, and increase the risks associated with making a final selection. Other uncertainties that inhibit the decision-making process include tank waste composition and immobilized waste form and manner of disposal.

2.0 CONCLUSIONS AND RECOMMENDATIONS

Conclusions and recommendations resulting from the studies described herein, taken in context with prior WHC and PNL investigations, are summarized in this section.

2.1 CONCLUSIONS

The studies presented in this report have identified and examined technologies that can be developed to successfully pretreat Hanford Site tank waste. However, important uncertainties impact virtually each technology. Many processes can do the job, but the selection of a specific approach depends to a great extent on timing and risk of the operating process. If technical justification can be found to narrow the list of candidate processes under investigation, structured prioritization tools exist to assist in the selection of primary and backup processes for each processing task.

2.1.1 Candidate Pretreatment Processes

Comprehensive surveys and studies of national and international technologies with potential application to Hanford Site waste pretreatment have been conducted over the past few years, as identified in Section 10.0. A method to organize and document relevant data from these surveys and studies is being developed, and test cases run to date indicate the alternative processes model can be electronically linked with the ASPEN Plus and Mathematica models. This overall network, after it has been developed more thoroughly, can significantly assist personnel working with pretreatment alternative technologies during the research, development, demonstration, test, and evaluation (RDDT&E) cycle.

From the pretreatment flowsheet studies described in this report, taken in context with other investigations by WHC and PNL, several conclusions can be drawn. Each study concluded that the suggested technologies can be developed to perform sufficiently well to satisfy currently projected pretreatment flowsheet needs. Yet, the technologies selected by the studies differed significantly from one another. One PNL study, a combination of aggressive sludge dissolution and ion exchange, produced a lower glass volume that came impressively close to meeting the goals of the CLEAN option.

A dominant conclusion suggested by the composite study is that independent investigations by four highly qualified organizations with widely differing backgrounds have determined not only that process candidates exist that can be developed to pretreat Hanford Site tank waste, but also that there are several good ones from which to choose. The studies selected not only different processes, but also different unit operations. Table 8-1 shows that for radionuclide removal, SAIC selected all ion exchange separations (one each for strontium, cesium, TRU, and technetium). Numatec selected all solvent extraction separations, and BNFL selected a combination of ion exchange and solvent extraction. The unit separations for the PNL studies were predetermined to be precipitation, solid sorbent treatment, and leaching.

A second dominant result of all four studies augments the conclusions reached by previous investigations, that many important technology uncertainties must be resolved before a final assessment of pretreatment alternative processes can be made. These uncertainties are identified in Sections 4.3, 5.2.4, 5.3.4, 5.4.4, 6.4, and 7.4 of this report.

2.1.2 Radionuclides and Nonradioactive Elements Requiring Separation Processes

Three of the four pretreatment studies described in this report arrived independently at similar conclusions as to which radionuclides needed to be removed from the high volume LLW fraction. Each study considered radionuclide concentrations in the waste feed and radionuclide separation factors, evaluating them against Class A disposal LLW radionuclide concentration limits. For two of the four studies, those by BNFL and Numatec, NCRW and CC waste were specified as feedstock. NCRW was selected because this waste has been characterized to a higher level of confidence than have other waste types, and CC waste was chosen in order to determine if BNFL and Numatec technologies could augment current Hanford Site activities directed toward the resolution of tank safety issues. In addition to these two waste types, SAIC also studied neutralized current acid waste (NCAW) to provide WHC with process technologies suitable for technetium separations and to address the more severe strontium separation requirement of NCAW. The feed selected for the PNL studies was a composite of total single-shell tank (SST) and double-shell tank (DST) waste. This composite allowed comparisons to be made later with prior, relevant Hanford Site studies (i.e., Boomer et al. 1991) and was not an independent assessment of radionuclide separation requirements.

All four studies targeted strontium, cesium, and the TRU elements of plutonium and americium for removal from the LLW fraction (Table 8-1). The two studies that addressed NCAW (by SAIC and PNL) also targeted technetium removal. BNFL and Numatec concluded that the waste feeds specified for their studies, NCRW and CC waste, did not contain sufficient technetium to justify its removal. However, both the BNFL and Numatec evaluations recommended additional waste treatments. BNFL suggested that the level of uranium in NCRW be reduced before vitrification and that fluorides and beta/gamma activity be reduced to allow improved grout disposal. Numatec also proposed the removal of uranium, and cerium is automatically separated in their diamide extraction (DIAMEX) process. It was concluded from these combined studies that separation processes for strontium, cesium, technetium, and the TRUs should be further developed for treatment of Hanford Site tank waste, and the potential treatment of fluorides, aluminum, zirconium, uranium, and beta/gamma contributors be further evaluated.

2.1.3 Organics, Ferrocyanide, and Sodium Nitrate Treatment

Safety issue resolution. Two of the four studies identified processes for the destruction of organics and ferrocyanide, with the processes differing from one another. Processes selected were ozonation by SAIC (Figure 4-1), and either hydrogen peroxide treatment or electrolytic oxidation by Numatec (Figure 7-3). A specific choice between the two Numatec candidates was deferred to a later date. After addressing the issue, BNFL concluded that

they do not have superior technology in this area and chose to recommend the technology eventually to be selected by the IPM project. Safety issue resolution was not in the PNL scope of work. Based on the results of these two studies, combined with the separate but relevant investigation by the IPM project for hydrothermal and calcination processes, we concluded that the process candidates currently identified can be developed to satisfactorily destroy organics and ferrocyanide compounds.

Sodium nitrate treatment. The composite study represented by this report did not produce a technical consensus of the advantages and disadvantages for sodium salt treatment, nor did it draw a conclusion regarding sodium nitrate removal versus nitrate destruction. SAIC considered several methods for nitrate destruction or removal, including CLEAN salt and the nitrate to ammonium and ceramic processes, but did not suggest treatment of inert salts. This direction was influenced by their cost-minimization approach. Neither BNFL or Numatec suggested a process for the treatment of sodium salts, possibly because their waste is normally lower in salts than Hanford Site waste, therefore their experience base in this specific technology would not be large. The potential treatment of sodium nitrate was not in the PNL scope of work.

2.2 RECOMMENDATIONS

Based on the conclusions presented in Section 2.1, it is suggested that sufficient technology identification activities have been conducted to begin a meaningful technology prioritization activity. A small quantity of preferred pretreatment processes would be separated from a much larger quantity of currently less-preferred processes. All technologies, preferred and not currently preferred, would be tracked, and data pertinent to their prioritization would be electronically retrievable (Section 10.0). Decision methodologies would form the basis of prioritization activities. The pretreatment decision analysis model would be patterned after the overall Hanford Site systems model, would interface with and be subordinate to controls from the systems model, and would be designed specifically to satisfy waste pretreatment needs.

2.2.1 Prioritization of Alternative Processes

We propose to develop a decision analysis model specific to the evaluation of pretreatment processes that is consistent with the TWRS rebaselining model. It would be based on the Multiattribute Utility Theory (MAU), and would explicitly model uncertainty. This methodology integrates stakeholder judgements of what objectives are important, with engineering judgement and data of how well the alternatives meet these objectives. The result will be a decision rationale that will make clear the basis for recommendations, which can be defended, if necessary, in a public arena. Furthermore, the proposed process for the selection of alternatives and the creation of the model is designed so as to develop a broad-based consensus throughout the Hanford Site.

The proposed model also will support decisions concerning the relative merits of continued research and development (R&D) versus implementing

existing technology. The analyses necessary to support these decisions are made possible by the explicit modeling of uncertainty. It also will support characterization by identifying a rationally justifiable and prioritized list of characterization requirements.

In addition, the model will take on the form of a decision support tool that can be modified and updated over time, as necessary. This will make it possible to evaluate additional processes that are subsequently identified and compare them with those initially evaluated. It also will make it possible to revise the model to reflect changes in policy and/or technology.

The proposed model and the processes necessary for its creation are described in Section 9.0.

2.2.2 Support Activities

The goal for developing the pretreatment alternative processes model is to bring order to the complex list of candidates that have been and will be identified. FY 1994 activities should include updating process information in the database as new technologies surface and existing technologies mature; building the database management capability; documenting prioritization criteria, evaluations, and actions; and exploiting interface relationships with the ASPEN Plus and Mathematica models. ASPEN Plus is used to do mass-flow calculations and other chemical process flow calculations, and Mathematica is used as a tool for parametric analysis.

Table 9-2 lists pretreatment process candidates that have been identified in recent flowsheet studies, including those examined in this report. Section 9.0 discusses how these processes can be made a starting point for the development of an alternative processes short list from which the ultimate pretreatment flowsheet will eventually evolve. It is recommended that the processes listed in Table 9-2 be further studied and prioritized in accordance with the decision analysis methodologies presented in Section 9.0.

2.2.3 Resolution of Uncertainties

Only a finite quantity of technical specialists, cold and hot RDDT&E facilities, funding, and time exists for satisfying the Hanford Site pretreatment mission. In order that uncertainties be reduced and eventually eliminated for pretreatment short-list candidates, it is necessary to ensure that this finite quantity of resources will not be diluted by an extensive separations program to the extent that favored candidates fail to be brought to maturity in sufficient time to meet the pretreatment conceptual design commitment.

It is recommended that resources be focused on pretreatment short-list candidates until each is understood sufficiently well that the conceptual design stage can begin. It is anticipated that short-list candidates will change from time to time, as criteria and/or criteria weightings evolve, and as new test data and study results develop. To satisfy this need, it appears necessary that the technology strategy for the extensive separations option be prioritized to first develop short-list technologies.

3.0 NEW TECHNICAL STRATEGY

Pretreatment of tank waste is necessary to resolve safety issues by destroying reactive chemicals in specific tanks and to separate wastes into high-activity and low-activity fractions that constitute acceptable feeds for the HLW and LLW solidification processes, respectively. This includes removal of radionuclides and hazardous and/or chemically incompatible substances from supernates, salt cakes, and sludges.

The specific objectives of pretreatment are to (1) destroy organic materials and ferrocyanide in tank wastes so that the wastes can be stored safely, (2) separate the high-activity and low-activity fractions, (3) remove radionuclides and remove or destroy hazardous chemicals in LLW as necessary to meet waste form feed requirements, (4) support development and demonstration of vitrification technology by providing representative feeds to the bench-scale glass melter, (5) support full-scale HLW vitrification operations, including near-term operation, by providing feed that meets specifications, and (6) design and develop pretreatment processes that accomplish the above objectives and ensure compliance with environmental regulations (Wodrich 1993).

The pretreatment reference system strategy associated with these objectives consists of a four-phased approach:

1. Tank safety issue resolution
2. Early pretreatment demonstration to expedite LLW disposal
3. Evaluation and implementation of technologies to pretreat supernates and salt cakes
4. Evaluation and implementation of sludge pretreatment technologies.

Development of the four-phased pretreatment strategy is represented by the Figure 3-1 logic diagram. This strategy seeks to implement disposal actions as early as practicable on selected supernates, while completing additional technology development for pretreatment of other supernates, salt cakes, and sludges. The four phases of the pretreatment strategy are described below.

3.1 PHASE 1--TANK SAFETY ISSUE RESOLUTION

3.1.1 Strategy

The highest priority of pretreatment is to resolve tank safety issues by treating selected wastes to remove or destroy the reactive chemicals that are causing safety concerns. Currently, pretreatment is required to destroy organic complexants and ferrocyanides in as many as 18 tanks to resolve tank safety issues. A number of technologies that could be applied are being evaluated, with current emphasis placed on calcination and two approaches to

Figure 3-1. Pretreatment Strategy Logic Diagram.

Safety Issue Resolution

Early Pretreatment for Tank Space

Supernatant/Salt Cake Separations

Sludge Separations

Melter Development

BTFO30093.18
Rev. Date 03/19/93

hydrothermal processing. These technologies have been selected by a team of technical experts as having the greatest chance of near-term deployment for the destruction of safety-issue chemical compounds.

3.1.2 Process Functions

Organic destruction involves breaking down organic compounds to reduce hydrogen-generating constituents. A near-term, moderately efficient process is needed. If the near-term process is not sufficient to meet LLW performance requirements for levels of organic contaminants, then an additional long-term, highly-effective process for almost total destruction of organic materials in grout feed will be provided by the later phases of pretreatment.

Because ferrocyanide is reactive and may be present in sufficient quantities to be classified as a safety concern in the SSTs, processes are being investigated to break the ferrocyanide down into nonhazardous materials before waste disposal.

3.2 PHASE 2--EARLY PRETREATMENT

3.2.1 Strategy

Limited pretreatment capabilities will be implemented to provide suitable feed for the grout disposal of LLW to make DST space available. Early pretreatment will strive to provide feeds to the LLW disposal facility sufficiently free of radionuclides to result in a grout product that meets 10 CFR 61 Class A limits. Processes will focus on double-shell slurry, double-shell slurry feed, and other DST waste, and are envisioned to be performed in-tank or in modular equipment using the best technologies available. The specific process functions will include cesium removal. Nitrate destruction or removal and/or organic destruction also may be implemented in the early pretreatment phase.

3.2.2 Process Function

The main functional needs envisioned for the early pretreatment phase are alkaline-side cesium removal and the destruction of organics and nitrates (Wodrich 1993). These functions will likely be performed in-tank or within compact processing units (CPU) external to and near the tank. Additional technologies will be deployed if needed in the near term for the destruction of organics and/or nitrates. The need for these additional technologies is not clearly established at this time, based upon regulatory requirements.

3.3 PHASE 3--SUPERNATE AND SALT CAKE PRETREATMENT

3.3.1 Strategy

Supernates, sludge wash solutions, and dissolved salt cakes may be pretreated to remove hazardous chemicals and radionuclides. The extent of this need will be established through a systems engineering analysis of available technologies, including their costs and benefits, and will be impacted by the strategy selected for sludge treatment. This third phase supports the overall treatment capability for all supernates and salt cakes by providing additional treatment capacity and radionuclide removal over the first two phases. A goal of Phase 3 is to implement processes that provide feeds to the LLW disposal facility sufficiently free of radionuclides to result in a grout product that meets 10 CFR 61 Class A limits or better, to produce a nearly benign LLW form. These new facilities may include processes for the removal of cesium and/or TRUs, and possibly for the removal of strontium and/or technetium. Nitrate destruction or recycle and organic destruction also may be included.

3.3.2 Process Function

The major functions for the supernate and salt cake pretreatment phase are similar to those for the early pretreatment phase, except that these technologies will be developed to a greater extent and the separations levels may be higher. Solid-liquid separations, the physical separation of solid phases from liquid phases, could include settling, decanting, filtration, centrifugation, and flocculation.

Alkaline-side cesium removal likely will be performed using well-known cation exchange processes. Both inorganic and organic exchange materials need to be investigated. Methods for removal of TRU components from complexed, alkaline solutions need to be explored. Candidate processes include precipitation and solid sorption. Other methods that remove TRU components from acidified supernates and salt cakes (e.g., solvent extraction) also should be developed.

Processes that remove strontium from alkaline waste solutions may need to be developed, particularly for wastes that contain organic complexants. Destruction of organic complexants will precipitate previously complexed elements (e.g., TRU and strontium) from alkaline solutions, which will assist in providing an acceptable feed for LLW immobilization and disposal. Several potential precipitation and sorption processes are candidates. Also, separation of technetium from alkaline supernates and dissolved salt cakes may be required. Investigation of strong base anion resins, as well as other candidate processes, is needed.

The wastes contain large quantities of nonradioactive chemicals. In addition, many of the separation systems identified require that significant quantities of chemicals be added to the process. As appropriate, these chemicals should be separated from various waste streams and recycled. The destruction of nitrates may be deployed to recover and recycle nitric acid

from pretreatment processes, thus significantly reducing the volume of LLW. Nitrate destruction may reduce the environmental impact of the grout LLW form.

3.3.3 Enhancement

A potential enhancement to Reference System Phase 3 is aluminum and sodium removal. This function could serve as a supernate and salt cake preconditioning step before cesium removal. This precaution would guard against the cesium ion exchange resin becoming fouled by aluminum precipitates if supernate pH becomes low.

3.4 PHASE 4--SLUDGE PRETREATMENT

3.4.1 Strategy

Sludges constitute the major HLW disposal volume associated with tank wastes, and most of this volume is comprised of nonradioactive chemical compounds of iron, phosphorus, bismuth, aluminum, silicon, barium, lanthanum, cesium, and sodium. Decontaminating sludges will allow their disposal in the LLW product stream, significantly reducing HLW volume. However, sludge treatment technologies are not mature. The degree of sludge pretreatment selected will depend upon technology availability for both pretreatment and vitrification, as well as overall constraints on the disposal system. The goal for sludge pretreatment technology is to develop and implement processes that can substantially minimize the volume of HLW, because of the estimated high cost of disposal and the uncertainties associated with the geological repository.

3.4.2 Process Function

The fourth pretreatment phase consists of blending; sludge wash and leach; sludge dissolution; removal of cesium, strontium, TRUs, technetium, and possibly other radionuclides from the dissolved sludge solutions; as well as the possible treatment of sodium salts and the separation of inert chemical combinations such as actinides and lanthanides, and barium and strontium.

Blending. This is the physical combination of solids, liquids, and slurries to (1) make feed more homogeneous by mixing wastes, (2) make feed available sooner by allowing slow SST retrieval processes to work on several tanks simultaneously, and (3) provide feeds to the melter that have better glass-making characteristics.

Sludge washing. This process removes water-soluble non-TRU compounds (e.g., salts of cesium, sodium, and potassium) from the waste by successive mixing of tank sludge with water or inhibited water. This process can be used as the sole treatment for the insoluble waste fraction, or as a precursor to additional pretreatment, and most likely would be performed in-tank.

Selective leaching. This consists of a group of intermediate-term processes that remove minor components from the bulk solids. Depending on the

process involved, selective leaching may be applied to feeds for LLW and HLW immobilization. Low-activity feeds would be selectively leached to remove radionuclides (e.g., cesium and technetium) or metals that are regulated in near-surface disposal processes. High-activity feeds would be selectively leached to remove components that have a deleterious effect on waste glass formulation (e.g., phosphates, sulfates, and chromates).

Sludge dissolution. This process involves dissolving waste solids in an acid (such as nitric acid) to allow minimization of the mass of material fed to the HLW vitrification process by performing separations on the dissolved sludge solution. This function will require solid-liquid separation to remove undissolved solids from the acid stream. Undissolved solids will be immobilized as either the HLW or LLW form, depending on the radionuclide content.

Acid-side TRU removal. This separates TRU radionuclides from the acidic-dissolved HLW. Products from this function will include (1) a stream containing the bulk of the dissolved solids, which after additional processing steps, will be fed to the LLW immobilization facility; and (2) a stream containing TRU materials, which is to be vitrified as HLW.

Acid-side strontium removal. Process requires acid-side strontium to be removed from acidic dissolved sludge solutions. The separated strontium will be vitrified, and the pretreated feed stream will be processed further to remove other radionuclides before grouting as LLW.

Acid-side cesium removal. Some waste sludges, especially from ferrocyanide tanks, may still contain 30 to 50% of the cesium after sludge washing. Sludge dissolution will release the cesium into the acidic stream. Although certain technologies look promising for acid-side cesium removal, they may produce too much glass or require a very narrow range of acidity to work. This is an important technology development area.

Acid-side technetium removal. In acidic processes, technetium exists in the form of pertechnetate, a mobile component in grout. Although the quantity of ^{99}Tc in SST and DST waste is small relative to nuclides such as ^{90}Sr and ^{137}Cs , a process for its removal may be required to meet LLW disposal specifications.

Uranium and iodine removal. It is uncertain at this time if uranium and/or iodine will be removed from the LLW stream. The question of uranium recovery is economics driven--the cost for its removal vs. the improvement in environmental acceptability of the LLW grout form. The potential for iodine removal will be influenced by the level of iodine found to be present in wastes during characterization investigations yet to be performed.

Actinides and lanthanides. These may be co-extracted in the TRU separation step. The lanthanides are separated from the actinides and disposed of in the LLW stream. This function could decrease the volume of HLW produced.

Barium and strontium. Nonradioactive barium could be co-extracted with strontium in dissolved sludge pretreatment. Separating barium from strontium and disposing of barium in the LLW stream can reduce the volume of HLW

produced but the small quantity of barium in the waste may not justify this process operation. Also, if barium was separated from strontium and the separation stream contained >100 mg/L barium, the stream would be less amenable for disposal.

3.4.3 Enhancement

A potential enhancement to Phase 4 is the recovery of noble metals. If noble metal concentrations in treated waste are high, several problems may be imposed onto the vitrification process, including the generation of hydrogen during feed preparation and the precipitation of conductive metals in the melter. Should this scenario be judged credible, noble metals would be removed from the glass feed and sent to LLW immobilization and disposal or recovered for economic value.

3.4.4 Alternative Concepts

Calcination and leach is a process in which waste solids and liquids are introduced into a high-temperature furnace (calciner). Temperatures within the vessel cause the liquids to evaporate, and solid materials are reacted to their oxide state. Organic materials are broken down principally to carbon dioxide and water. Nitrates and nitrites are converted to nitrogen, oxygen, and nitrogen oxides. The nitrogen oxides are then scrubbed from the offgas, or destroyed before the offgas stream is released.

Bulk leach is a group of intermediate-term processes that remove major components from the bulk solids and could be used to reduce the amount of feed sent to vitrification. Feed streams would be bulk leached to remove components that can be easily separated from the waste (e.g., aluminum, zirconium, iron).

3.5 PRETREATMENT SYSTEM BOUNDARIES

Figures 3-2 and 3-3 are functional flow diagrams for the high-capacity vitrification and the extensive separations approaches, respectively, that span the anticipated range of viable technologies being considered for the pretreatment of Hanford Site SST and DST waste (Wodrich 1993). These technologies range from mature to emerging processes and provide diverse levels of radionuclide separation, hazardous material reduction, and HLW minimization.

The figures define major pretreatment functional needs and the highest-priority candidate technologies to fulfill the functional needs. The functional needs and candidate technologies were initially identified by the TWRS Pretreatment Technology Working Group during the TWRS National Technology Workshop held in June 1992 and have been updated in the Pretreatment Technology Plan (Barker 1993). Only those technologies that were planned to receive funding during FY 1993 are included. The full list of candidate technologies is included in the proceedings from the TWRS National Technology Workshop.

Figure 3-2. Pretreatment Functional Flow Diagram for High-Capacity Vitrification Approach.

Figure 3-3. Pretreatment Functional Flow Diagram for Extensive Separations Approach.

3.6 REFERENCE PRETREATMENT SYSTEM

The current reference pretreatment system, represented by the Figure 3-4 functional flow diagram, is a four-phased approach over the duration of the TWRS Program, including (1) tank safety issue resolution, (2) early pretreatment demonstrations to expedite LLW disposal, (3) evaluation and implementation of technologies to pretreat supernates and salt cakes, and (4) evaluation and implementation of sludge pretreatment technologies. This option includes the minimum required 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. Although not included on the flow diagram, it may also be necessary to remove technetium. Several unit operations are candidates to provide these more aggressive separations, although specific processes have not yet been selected. The four phases of reference system deployment will allow resolution of tank safety issues as a priority and bring mature technologies on line in the near term, while other required technology development activities are being completed.

Figure 3-4. Pretreatment Functional Flow Diagram for Current Reference System.

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4.0 INDEPENDENT CONSULTANT STUDY

SAIC was contracted to perform an independent assessment to determine and recommend a pretreatment flowsheet for Hanford Site tank waste. This section summarizes the SAIC final report (Beary et al. 1993), which contains the detailed descriptions and accomplishments of this study.

4.1 INTRODUCTION

The SAIC study included activities to develop or adapt existing methodology for prioritizing alternative pretreatment processes. This section briefly describes the "Delphi" technique that was employed and the recommended integrated pretreatment process resulting therefrom.

Literature Research. An important preliminary to any study of the type discussed in this section is information gathering. Information sources included WHC, the PNL Technical Library, international literature via the ITP, and references and papers obtained from individual researchers. Information provided by WHC included the IPM report by KEH and reports on specific processes, particularly on the subjects of salt removal and organic destruction. The PNL Technical Library performed an electronic literature search of the chemical abstracts files and the DOE files for the radionuclides of interest for the 5-year period from 1988 to 1992. The abstracts that were provided by PNL were reviewed for applicability; of the 405 citations, 50 were deemed to be potentially applicable to the pretreatment study. Twenty-one additional citations addressed the use of ferrocyanides and hexacyanoferrates for separation of cesium, and numerous others addressed analytical separation techniques. The 50 references of potential applicability were reviewed in more detail; many of these references described the same process, and numerous others described processes that had not been demonstrated on a plant scale. The final selection included representative reports of those processes with demonstrated effectiveness in performing the separations functions. Primary reasons for dropping processes from consideration were safety (e.g., those involving the use of ferrocyanide), complexity or nonapplicability to large-scale operation, and the absence of evidence of at least pilot-scale demonstration.

Evaluation Methodology. The methodology used for prioritizing the pretreatment process options, the Delphi technique, was developed by the Rand Corporation in 1975 for use in support of technological forecasting for the U.S. Department of Defense. This technique has an advantage over "round-table" discussions in that the inputs are prepared independently by a panel of experts (respondents), compiled by an independent facilitator, and returned to the panel of respondents for further evaluation. Thus, the authors of the inputs and comments are anonymous and not subject to pressure by each other. Furthermore, writing of one's comments and ideas permits a more rational, comprehensive presentation of information than is possible in a round table discussion.

A panel of ten knowledgeable and experienced engineers and scientists¹ reviewed the available technical information on the various process options and provided their evaluations via response to Delphi questionnaires. The respondents were also encouraged to draw from their own knowledge and resources for information. The Delphi method consisted of a series of three successive questionnaires that progressively narrowed the options to the final selected, integrated process. Emphasis during the technical reviews and recommendations was on the use of currently proven technology. While cost was considered in general terms, no attempt was made to obtain life-cycle cost information to provide a firm basis for cost comparisons.

4.1.1 Objectives

SAIC performed an independent assessment of the pretreatment technologies by assembling a group with a broad range of technical skills and experience. Considerable latitude was given SAIC in performing this task. The objectives of the SAIC study were to identify potential alternative processes for waste pretreatment to develop a methodology for prioritization of waste pretreatment alternative processes and to prepare a material balance flowsheet on the number one process.

The prioritization methodology used to assess the relative merits of the waste pretreatment alternatives identified was a Delphi study. Delphi is a series of questionnaires. The first questionnaire asks individuals that make up the respondent panel a broad question. Each subsequent questionnaire is built upon responses to the preceding questionnaire. The process stops when consensus is approached among the respondents, which in this case was an integrated pretreatment process.

4.1.2 Scope

Identification of waste pretreatment technologies, both national and international, began with processes that have already been identified by previous reviews such as the IPM study. Additional information on pretreatment process was obtained by literature searches and discussion with researchers in the field. The ITP was identified as a good source of Russian technological information. The pretreatment technologies presented at the Waste Management Symposium was expected to be a part of the known information, but a review was done to ensure that relevant technology was not overlooked. References were checked for additional process details, level of development, and process effectiveness. The information on pretreatment processes that were judged to be safe and viable were resources used in the Delphi study to determine the best pretreatment process for the Hanford Site.

¹The Delphi respondents included three individuals with Ph.D. degrees in chemical engineering, four with M.S. degrees in chemical engineering, and three with B.S. degrees in chemical engineering or related fields. The combined professional and technical experience of the panel totaled over 300 years.

The key to the classic Delphi methodology is the Delphi question submitted to a respondent panel of people knowledgeable in the field. All members had Hanford Site experience and unique background or experience of value to the Delphi study. Three general areas of expertise were represented in panel members: radiochemical operations and safety, regulatory compliance, and testing and scale-up. Three respondents were Ph.D.'s in chemical engineering, and four had extensive Hanford Site experience including operation of B Plant for the recovery of cesium and strontium; operation of both Hanford Site fuel reprocessing plants, the Plutonium-Uranium Extraction (PUREX) Plant and the Reduction Oxidation Plant; and construction management of the cesium and strontium encapsulation plant.

The Delphi questionnaire can consist of as many as five questions or more typically, three. The three questionnaire approach was used in the evaluation of pretreatment alternatives:

1. Questionnaire 1: Requested that the respondent panel members select a preferred integrated process from pretreatment alternatives identified that would destroy organics and remove cesium, strontium, technetium, and TRUs. Written justification was requested.
2. Questionnaire 2: Requested that each of the respondent panel members review the integrated processes identified in questionnaire 1 and revise the integrated pretreatment process that panel members had originally proposed, then rank each pretreatment process proposed against criteria (see Section 4.1.3).
3. Questionnaire 3: Requested that each of the respondent panel members rank the processes from questionnaire 2 and provide supporting arguments.

The scope of the Delphi respondents was broadened beyond the actual Delphi evaluation to rank against the established criteria for each pretreatment process associated with each removal step, i.e., all processes identified for cesium removal. A proposed solvent extraction process for using chlorinated cobalt decarbolyde to remove cesium and strontium, and transuranic extraction (TRUEX) for TRU, was rated low by Delphi respondents. Justification in writing for this low rating was requested and provided.

A process flowsheet and material balance for the pretreatment of SSTs and DSTs was prepared on the top-ranked integrated pretreatment process.

The material balance on the preferred process provides the process operating conditions, time sequencing for batches, and a listing of raw materials. The material balance shows the composition and flow of secondary waste streams generated by the process. The process material balance will give the composition of the two pretreatment product streams: the concentrated radionuclide stream going to vitrification and the relatively clean stream going to the Grout Treatment Facility (GTF). A comparison can then be drawn between the feed-stream specifications for these facilities and the pretreatment process products.

4.1.3 Criteria

A set of criteria was given to the Delphi respondents to use in selecting the various unit process for organic destruction and the removal of cesium, strontium, and TRU. To compare the processes, a numerical range of 1 to 5 was applied to each criteria. A value of 5 meant that a process would easily meet the criteria, and a value of 1 meant that the process would meet the criteria only by applying additional resources. The endpoints of the numerical range 1 and 5 were defined to assist the respondent in rating the processes and to give the rating a common reference (see Table 4-1).

4.2 INTEGRATED PRETREATMENT PROCESS

This section describes the SAIC integrated process for pretreatment of Hanford Site defense HLWs. Process flowsheets and material balances are also included.

4.2.1 Process Overview

The proposed integrated process for pretreating the tank waste in preparation for final waste form production includes the following five basic steps:

1. Tank waste retrieval and solids washing
2. Organic destruction by oxidation with ozone (ozonation)
3. Cesium, strontium and TRU removal by ion exchange using titanium-treated zeolite
4. Technetium removal by ion exchange, using a strong-base anion resin and recovery of the acid from the eluate product
5. Reconcentration of the resulting dilute LLW stream.

These steps are discussed briefly in Section 4.2.2 and in more detail in Section 4.3.

The material balanced flowsheet is, in essence, a test of the selection by the Delphi respondent panel of the pretreatment process. This process meets the stated goal of producing a treated LLW that, when mixed with grout, can meet the requirements of 10 CFR 61 Class A limits. Titanium-treated zeolite was the Delphi panel consensus in the three-question approach for the removal of cesium, strontium, and plutonium. The Delphi technique, as employed in this study, did not involve the engineering analysis required to determine process efficiency or cost.

The Delphi panel did make some judgements on the effectiveness of titanium-treated zeolite based on information from the West Valley project that was provided to the panel members. This information was provided in the Task 1 report (Contract No. MMW-SVV-067914) (Beary et al. 1993). The determination of process effectiveness in meeting 10 CFR 61 Class A

Table 4-1. Criteria With Endpoints Chart.

Criteria	Range of Endpoints
Minimize health and safety impact on workers	5 - Simple design, benign, fail-safe, room temperature operation 1 - Extensive, complicated design to control reaction rate and explosion hazard
Minimize total life-cycle cost	5 - Minimum special features, inexpensive process chemicals 1 - Numerous special features, expensive process chemicals
Minimize volume of HLW generated	5 - Produce small number of glass canisters 1 - All waste into glass canisters
Comply with Federal and state regulations	5 - Straight forward extensions of previous licenses (best available control technology) 1 - Controversial licensing process
Minimize campaign duration	5 - High throughput in small facility 1 - High throughput in large facility
Provide maximum flexibility for incorporating improved technology	5 - New technologies easily incorporated 1 - Impossible to incorporate new technologies
Minimize technical risk	5 - History of operation in radioactive environment 1 - Analytical approach requiring scale up
Meet output specifications	5 - Process has the capability to exceed specifications 1 - Process has marginal capability to exceed specifications
Maximize reliability and maintainability	5 - Good operating record in a radioactive environment 1 - Undemonstrated reliability; challenging remote maintenance
Minimize generation of secondary waste	5 - Minimum addition (i.e., <15% additional neutralized salts etc.) to grout and solid waste 1 - Maximum addition (i.e., >25% additional neutralized salts etc.) to grout and solid waste
Treat a broad range of chemical and chemical compositions (wide range of input specification)	5 - Process has the capability to treat wide range of waste compositions. (See Appendix H of Questionnaire 1) 1 - Process has the capability to treat average waste compositions. (See Appendix H of Questionnaire 1).

requirements depends on analysis of the characteristics of the waste and of the ion exchange media, i.e., radionuclide concentration, pH, sodium, and concentration. Judgement can only provide direction and approximations.

The separations effected in the pretreatment process are estimated in the preparation of the material balance. Processing different types of waste, e.g., CC, NCRW, or NCAW will give different results, with some waste being more of a challenge for the pretreatment process to meet specifications. The CC was initially selected as the waste to use in the preparation of a material balance. The high total organic carbon (TOC) content of this waste makes it obviously a challenge for the organic destruction step of the process, ozonation. The levels of cesium, strontium, and plutonium in the CC, however, were relatively low in comparison to other Hanford Site wastes, like the NCAW, and no technetium was listed. A comparison of the radionuclide concentrations in the three different types of waste--CC, NCRW, and NCAW--is found in Table 4-2.

Table 4-2. Radionuclide Concentration in the Neutralized Cladding Removal Waste, Complexant Concentrate, and Neutralized Current Acid Waste.

Radionuclide	NCRW moles/L ($\mu\text{Ci/mL}$)	CC (convective layer-liquid) $\mu\text{Ci/mL}^a$	NCAW $\mu\text{Ci/mL}$
^{137}Cs	4.85 E-6 (58)	6.45 E+02	4.7 E+03
^{90}Sr	Below limits	5.0	4.0 E+03
^{99}Tc	Below limits	Below limits	4.5 E-01
Plutonium	2.80 E-5 ^b (1.6)	1.5 E-04 ^b	3.2 E-01

^aConversion from $\mu\text{Ci/g}$ to $\mu\text{Ci/mL}$ by multiplying by density of 1.5 g/mL.

^bTotal ^{239}Pu and ^{240}Pu ; specific activity of ^{240}Pu used for conversion from grams to curies.

Verification of the capability of the SAIC pretreatment process to remove the cesium, strontium, technetium, and TRU was considered to be the primary purpose of the material balance. The NCRW is inadequate as a test case because it lacks both strontium and technetium. Obviously the NCAW is a severe test, and it was selected as the feed for the radionuclide removal processing units. The NCAW is low in TOC, hence, bypassing the ozonation process with this waste is likely. The most challenging waste for ozonation is the CC because of the high level of TOC. Thus, the flowsheet presented in Section 4.3 includes an ozonation step as well as radionuclide removal steps that used waste composition that would test process effectiveness. Researching a worst case Hanford Site waste composition by a comprehensive review of all underground storage tank (UST) analyses was not performed.

4.2.2 Process Summary

The operations and equipment requirements for the waste retrieval step have been studied previously, and this step was not a part of this study.

Waste retrieval is addressed herein to provide a complete package and because of the potential impact of retrieval methods on subsequent processing. Retrieval of the HLW from the USTs involves a number of steps, but is basically a liquid-solids separation and liquid transfer operation. The concentrated supernate is decanted from the storage tank and remaining sludge and consists mostly of soluble nitrate salts and insoluble sulfate and phosphate salts washed in situ. In the case of the NCAW, or aging waste, in the 241-AZ Tank Farm, the numerous (22) air lift circulators in these two tanks may inhibit slurrying and washing of the sludge; however, the current thinking is that in situ washing can be accomplished.

Organic destruction by oxidation with ozone will use high-efficiency venturi injectors to obtain intimate mixing and high mass transfer of ozone into the solution and, thus, minimize the ozone requirement. Several injectors are used, and the HLW solution is recycled through each injector a number of times to achieve the desired degree of organic decomposition. The greater number of injectors used, the lower the recycle rate will be. The separation of the spent offgas from the solution is accomplished in a cyclone separator. Following separation, the liquid drains to the succeeding pump tank and the residual ozone in the offgas is decomposed in a reactor vessel before final filtration and discharge to the environment. The ozone treated effluent is sparged with carbon dioxide to lower pH from the 13 to 14 range to the 12.2 to 12.5 range (nominal pH is 12.2). During recent testing, engineers observed that aluminum precipitation did not occur until ~pH 11 was reached, and separate preliminary tests did not experience precipitation until a pH of <12.0 was reached. The SAIC-integrated process is based on pH 12.2 to be compatible with the experience of the West Valley Demonstration Project.

Removal of the radionuclides from the HLW supernate and sludge wash solutions is accomplished with ion exchange using multiple, fixed-bed columns. The multiple-column arrangement permits continuous operation, high resin loading, and high decontamination performance. The cesium, strontium, and TRU are removed by passing the diluted, solids-free solution through multiple beds of titanium-treated, granular zeolite media. The product stream from the ozonation step or, if organic destruction is not required, the diluted HLW solution is filtered before ion exchange, and the solution is cooled to 10 °C. The conceptual cesium, strontium, and TRU ion exchange system will use four columns (or beds) of titanium-treated IONSIV IE-96 granular zeolite. The four-column system will permit loading of the first column to nearly 100% breakthrough, while the effluent from the third column in the series is virtually free of radionuclides (except for technetium). The fourth column is off-line for media replacement, while the other three are in a loading mode. Two of the columns will contain untreated zeolite, IE-96, and the third column will contain titanium-treated IE-96. The spent zeolite--loaded with cesium, strontium, and TRU--is slurried from the column into a holding tank for subsequent blending with the insoluble HLW solids for vitrification.

Technetium is removed from the solution by adsorption onto strong-base anion resin. The conceptual system will use two columns; one will be operating in a loading cycle, while the second is in an elution and resin regeneration cycle. The acidic product stream (eluate) from the technetium elution cycle is reacted with formic acid to destroy the nitric acid, then concentrated and stored for ultimate blending with the solids slurry feed to the vitrification plant.

The product stream from ion exchange is concentrated and routed to the grout feed system. The radionuclide content of the low-level salt waste stream is projected to be below the Nuclear Regulatory Commission (NRC) Class A limits for near-surface disposal of LLW.

4.2.3 Process Description

4.2.3.1 HLW Retrieval and Sludge Wash. The HLW is retrieved from the storage tanks by pump decanting into a second empty, solids-free DST. The decantation is (presumably) performed using a specially designed pump. After completion of decanting of the supernate, the sludge will be washed by at least two successive batches of dilute caustic solution ($\sim 1M$). The washes will be at a 3:1 liquid-to-solids volume ratio for the DSTs and a 4:1 liquid-to-solids volume ratio for the SSTs. Studies have shown that the overall wash dilution must be equivalent to a 15:1 water to settled solids volume ratio or greater. Two successive washes, each at a 3:1 water to settled solids volume ratio, will provide greater dilution of the soluble salts than a single 15:1 ratio wash. The solids wash solutions are added to the supernate, supplying a portion of the water necessary to dilute the supernate to the required 1.8 to 2.0M sodium concentration for the subsequent organic destruction step. The supernate decanting, washing (sluice-mixing), and subsequent settling of the sludge is expected to require considerable time and should be initiated several months before the planned hot startup of the pretreatment plant. The washed sludge is not subjected to acid dissolution and is routed to the HWVP for immobilization and disposal.

4.2.3.2 Organic Destruction. Ozone has been demonstrated to effectively destroy organic complexants in Hanford Site Defense HLW solutions. These demonstration studies, performed at Hanford Site in a continuous stirred tank reactor (CSTR), indicated that, under the strongly alkaline conditions of this waste solution, the oxidation of organic complexants by ozone is rapid, but the ozone requirement is high. Ozonation under strongly alkaline conditions promotes the formation of hydroxyl radicals that are the very powerful key oxidizing species of the organic decomposition reaction. The high pH catalyzes the oxidation reaction but also promotes the decomposition of ozone. Therefore, the amount of ozone required for the oxidation of ethylenediaminetetraacetic acid (EDTA) is much higher under high pH conditions ($O_3/EDTA = 30$) than under acidic conditions ($O_3/EDTA = 10$). Other factors that affect ozone consumption are the presence of oxidizable inorganic salts such as nitrite and free radical quenchers such as carbonate, and the degree of mixing of the gaseous and liquid phases (contactor design).

To minimize the ozone requirement (ozone decomposition) while maintaining a high ozone mass transfer, and thereby a high rate of EDTA oxidation, the use of high efficiency venturi injectors in combination with gas separators is recommended for the ozone treatment. Although the objective is different, this technology is similar to the one used for the ozone treatment of a 170 gal/min flow of 5% solid aqueous slurry medical waste.

The recommended flowsheet for full-scale treatment of the HLW supernate is as outlined in Figure 4-1. The ozone contractor treatment system outlined in Figure 4-1 consists of three assemblies of pump: injector, gas separator, and reservoir loop units. The number of these loop units in the system may

Figure 4-1. Ozonation Pretreatment Flowsheet for Organic Destruction Using Three (N - 3) Injector Passes.

vary from 2 to 10 or more. The recommended number of loop units for the purpose of this report is nine, consisting of three systems of three loop units each.

The ozone treatment system outlined in Figure 4-1 stores the diluted HLW waste in the waste storage tank. The diluted waste is withdrawn from the waste storage tank by the suction of the pump of the first pump-injector-gas separator-pump reservoir loop unit. Once the process equilibrium is reached, the loop unit will recirculate the waste solution at a rapid rate. One of the key components of the loop unit is the recirculation pump that provides the driving force for the system and the energy for the high shear mixing of ozone gas into the dilute waste. During each pass through the loop, the waste solution is treated with ozone in the injector. After a few seconds of contact time in the pipes, the offgas is removed by the cyclone separator, and the treated waste is collected in the pump reservoir ready to be recycled again through the loop. After passing through a multiple of ozone treatment cycles, the waste passes into the next loop unit and so on until it is finally discharged into the treated waste tank, and from there into the ion exchange treatment process.

When the treatment process employs a total of nine loop recycle units and the fresh diluted waste is fed into the treatment system at the rate of 60 gal/min, the recirculation flow rate in each of the loop units is 960 gal/min and the fully ozone-treated waste is discharged from the ninth loop unit into the treated waste tank at the rate of 60 gal/min.

The high efficiency venturi injector allows the introduction of more gas at a lower pressure differential ($\Delta P = \text{inlet} - \text{discharge}$), and therefore, at a lower power input than it is possible with the standard venturi injector. A high shear violent mixing of gas and liquid occurs in the throat of the injector. The pressurized operation of the injector promotes rapid mass transfer. The pressure is the single most important parameter for increasing the solubility and therefore the mass transfer of ozone.

An in-line mechanical mixer (CSTR) could also be used in the place of the injector. However, the mixer would not allow operations under pressure in excess of the pressure of ozone feed. It would be larger in size, require more maintenance and more power, and the efficiency would be lower and/or the residence time longer.

The separation of spent offgas from the diluted supernate and sludge wash solution can be accomplished very rapidly in the proposed cyclone gas separator. Other more conventional gas separators could also be used, but they require more residence time and are larger in size.

The ozone contractor consisting of the previously described injector and cyclone gas separator offers the following advantages for this project:

1. Operation under 5 to 50 lb/in² (gage) pressure, which can use the output of standard commercially-available ozone generators that operate in the range of 2 to 15 lb/in² (gage).
2. Small size and small floor space requirement.

3. Low power requirement.
4. Low cost.
5. Low maintenance, no moving parts.

The proposed ozone contractor has not been tested using Hanford Site nuclear waste. It is, therefore, recommended that a program be initiated at an early date to test the device using nonradioactive simulated and/or actual CC from tank 241-SY-101.

The feed to the ion exchange columns must be free of solids to avoid column plugging. Therefore, a solids removal step, using a hydropulse filter, is provided following organic destruction. The filtration step is delayed until after organic destruction because of the probability of precipitation of small quantities of solids during this operation. In addition, by delaying filtration until after organic destruction, it is possible to provide backup strontium removal capability by adding crystalline silicotitanate (CST) to the solution and allowing a brief settling period before filtration.

4.2.3.3 Radionuclide Removal. The radionuclides of concern that are present in the HLW solution--cesium, strontium, TRU, and technetium--are all removed by ion exchange. Before ion exchange, the feed is adjusted to a pH of 12.2 by sparging the ozone-treated effluent with carbon dioxide. The cesium, strontium, and TRU are co-adsorbed onto an inorganic cation-exchange medium, and the technetium is adsorbed onto strong-base anion resin. The two ion-exchange steps are addressed separately in the following discussion in that different ion exchange media are used.

4.2.3.4 Cesium, Strontium, and TRU Removal. The recommended integrated process for removing cesium, strontium, and TRU (plutonium and americium) from the HLW supernate is ion exchange using IONSIV IE-96, a granular zeolite pretreated with titanium. The titanium-treated IE-96 zeolite has a high affinity for all of these elements, with distribution ratios (R_d)² ranging from about 230 for cesium to 1,000 for strontium and 2,200 for plutonium at 6 °C, pH = 12.5, and Na⁺ concentration of 2.25M. The process will use a four-column system so that three columns will always be available for loading. When the first column in the series is loaded to the maximum extent practicable, it is removed from the flow system, and the next column in the series becomes the initial feed column. The zeolite is removed from the loaded column and replaced with new zeolite. The column is then placed back in service as the last column in the series and functions as a "polishing" column to remove any traces of radionuclides that escape from the previous column. The loaded zeolite is slurried into a holding tank and is held for eventual blending with the insoluble sludge from the HLW storage tank for feed to the HWVP. The flowsheet for cesium, strontium, and TRU removal by ion exchange is shown in Figure 4-2.

$$^2R_d = \text{cesium}/C_e, \text{ mL/g}$$

where cesium = concentration of radionuclide adsorbed on the zeolite,
g(or curies)/g of anhydrous zeolite

C_e = concentration of radionuclide remaining in solution after
batch contact, grams (or curies) of radionuclide/mL.

Figure 4-2. Ion Exchange Pretreatment Flowsheet for the Removal of Cesium, Strontium, and Plutonium.

Ion exchange was the process of choice of the majority of respondents in the Delphi study on the basis of simplicity of equipment, process and operational control, and minimization of secondary waste generation. Adsorption onto finely divided ion exchange media followed by gravity settling of the media ("precipitation") appears to be the simplest process; but it is a batch process and requires a liquid and solids separation step, which could be very time consuming. Moreover, the process is relatively inefficient--equivalent to a single equilibrium stage. The maximum separation factor that can be achieved is equal to the distribution coefficient for the adsorbing material, whereas the separation (or decontamination) factor achievable with multicolumn ion exchange is many orders of magnitude higher than the distribution coefficient. If a true precipitant is used, then the separation factor is a function of the solubility product constant of the precipitate.

Solvent extraction is a powerful process, capable of achieving a high degree of separation and purification. The liquid-liquid contactors and ancillary equipment, and the instrumentation required to control the process and the operation of the contactors, however, are complex and expensive. If individual product species of high purity are required, solvent extraction could easily be the most desirable process. For pretreatment of the HLW supernate, however, neither high product purity, nor separation of the various radionuclides, is desired. The real need is for near quantitative removal of radionuclides from the HLW supernate, low contamination of the radionuclides with inert materials, and the generation of as little secondary waste as possible. For this case, solvent extraction would be an expensive and complicated method for accomplishing a task that can be handled much more simply and cheaply with ion exchange. Another disadvantage of solvent extraction is the fire hazard associated with the use of large quantities of organic and the problem of disposing of the large quantities of mixed waste generated (all of the spent organic will be classified as mixed waste).

4.2.3.5 Technetium Removal. Technetium is removed from the HLW supernate and wash solutions by adsorption as the pertechnetate ion on a strong-base anion resin. Of the readily-available commercial resins, Duolite A101 and Amberlite IRA 401 appear to have the greatest affinity for technetium, with R_d values in the range of 325 to 390 at a Na^+ concentration of 5.0M, a $\text{NO}_2^- + \text{NO}_3^-$ concentration of ~3.5M, and a pH >12. The IRA 401 resin appeared to have a slightly more favorable adsorption rate than other anion resins.

A two-column system will be used to remove the technetium; one column will operate on a loading cycle while the other column is operating on the elution cycle. Between 100 and 150 column volumes of feed can be processed in a loading cycle. This will load the column to ~90% breakthrough ($C/C_0 = 0.90$). Elution of technetium from the resin is accomplished with four column volumes of 8M nitric acid. To avoid undue heating and gassing of the column, the loaded column is washed first with water to displace the alkaline supernate then with dilute nitric acid solution. Following the elution step, the nitric acid is displaced with water (at least two-column volumes), then the column is pretreated with dilute caustic to preclude gassing during the loading step. The flowsheet for technetium removal by ion exchange is shown in Figure 4-3.

Figure 4-3. Technetium Ion Exchange Flowsheet.

A review of the available analyses and estimates of technetium concentration in the various HLW solutions indicates an average decontamination factor (DF) of 2 will be required (assuming the total waste is homogeneously mixed) to enable the grouted LLW to meet NRC Class A limits. However, technetium is believed to be contained within relatively few tanks in higher concentrations than the average value. Similarly, many tanks contain such low concentrations of technetium that the waste can bypass the technetium removal step. The actual DF required would be greater, and the technetium level of these tanks needs to be addressed either by processing or by blending the waste feed.

4.2.3.6 Eluate Concentration, Denitration, and Acid Recovery. Following elution, the technetium-bearing, acidic eluate and subsequent acid wash solution are concentrated to 8.0M nitric acid and reacted with formic acid to destroy the nitric acid. They are then concentrated to a minimum volume and held in the concentrator for the next batch. All of the technetium from the NCAW³ (~206 kg) can easily be stored in a single batch of concentrate. A modestly-sized evaporator (boiloff of ~5 gal/min or a steam load of ~2500 lb/h) will accomplish this task.

The oxides of nitrogen that result from the nitric acid-formic acid reaction are absorbed in a standard, commercially available NO_x absorption tower. The recovered acid is reused for subsequent elution of the ion-exchange column. The nitric acid destruction and recovery flowsheet is shown in Figure 4-4.

4.2.3.7 LLW Concentration. The final step in the pretreatment process, reconcentration of the diluted supernate and solids wash solution to the grout feed specification limit of ~4.2M sodium, is accomplished in a large thermosyphon evaporator sized for a boiloff capacity of ~40 gal/min (a steam load of ~20,000 lb/h). The LLW concentrate is transferred to one of the feed tanks for the GTF. The condensate is recycled to the ozonation feed tank as dilution water or to the receiver tank for the treated effluent from ozonation as wash water.

4.2.4 Material Balance Summary

A material balance for key cations, anions, and radionuclides, including flow rates, batch sizes, and cycle times is provided in the SAIC Task 3 final report.

4.3 UNCERTAINTIES

The SAIC integrated pretreatment process was selected to minimize uncertainties; there are, however, a number of areas that would benefit from additional information. The greatest uncertainty at this time is the composition of the various waste types. The only data available for most of

³A review of the available data regarding technetium concentration in the various types of HLW indicates the NCAW to be the only waste requiring technetium removal.

Figure 4-4. Nitric Acid Recovery Flowsheet.

the SSTs and some of the DSTs are the volume and specific gravity of the supernatant liquid and the volumes of the sludge and salt cake. Chemical and radionuclide inventories of the SSTs are based on total inputs to the HLW storage system and are not applicable to a single tank.

Another uncertainty that applies to the SAIC flowsheet is the processing of NCRW. The reported studies of the waste have addressed the preparation of an acidic solution suitable for feed to a TRUEX solvent extraction cycle. The dissolution characteristics of the NCRW solids in a lower concentration of nitric acid are not known. The behavior of the plutonium in the solution of dissolved solids at intermediate pH levels is also not known.

Another uncertainty that may have a major bearing on the final process selection is that of life-cycle cost and the attendant balance between capital and operating costs. Finally, an uncertainty that may have a very substantial bearing on the final process selection is the cost of producing and storing the canisters of vitrified HLW.

4.4 ADVANTAGES AND DISADVANTAGES

The basic process described in Section 4.2, namely organic destruction by ozonation followed by radionuclide removal by ion exchange, was the process of choice of nine of the ten experts on questionnaire 2. Only details remained to be resolved in questionnaire 3. In general, process safety, simplicity, and current status of the technology of the selected process were the primary factors driving the selection. Of particular note is that all of the radionuclides of primary concern are adsorbed onto the same ion-exchange medium, thus greatly reducing the number of unit operations required. Moreover, the various individual processes are mutually compatible.

The advantages and disadvantages of the integrated process and of the individual unit operations are categorized according to the evaluation criteria presented in Section 4.1.3. In the evaluation of strengths and weaknesses, only those criteria for which the integrated process and separate unit operations rated above 3.5 out of a possible 5 (a rating of 5 representing the highest rating) were considered to be advantages. Ratings of 3.5 or lower were considered to be disadvantages.

The evaluations are shown below:

4.4.1 Integrated Process

Advantages

- Impact to the health and safety of the facility workers will be minimal. Rating = 4.75.
- The impact on the total life-cycle cost was judged to be low. Rating = 4.5.

- The process was judged to be capable of complying with, and producing effluents that will comply with, Federal and State regulations. Rating = 3.88.
- The process was judged to be capable of meeting production schedules. Rating = 4.0.
- The process was judged to provide for reasonable flexibility for incorporating new technology. Rating = 3.75.
- The process was judged to be of a low technical risk, overall. Rating = 4.5.
- The process will produce HLW and LLW streams that meet output specifications. Rating = 4.25.
- The reliability and maintainability of the equipment for the integrated process was judged to be good. Rating = 4.5.
- The generation of secondary waste from the integrated process was judged to be acceptably low. Rating = 4.0.
- The integrated process was judged to be capable of treating a broad range of feed compositions. Rating = 4.0.

Disadvantages

- The primary weakness of the integrated process is that the volume of HLW will not be minimized. Just how much the zeolite resin will increase the ultimate volume of glass is currently unknown. If the zeolite (essentially a form of sodium aluminosilicate) can be used to replace some of the inert additives, the actual impact may not be great. Rating = 3.5.

4.4.2 Unit Operations--Ozonation

Advantages

- The reliability and maintainability of the process equipment should be good. Rating = 4.3.
- Process should be capable of treating a broad range of feed compositions. Rating = 4.1.
- Generation of secondary wastes will be minimized. Rating = 4.1.
- The process and effluent streams should be in compliance with Federal and State regulations. Rating = 4.0.
- The technical risk should be low. Rating = 3.8.
- The impact on worker health and safety should be acceptably low. Rating = 3.8.

- The volume of HLW should not be adversely affected. Rating = 3.8.
- The production schedule should not be adversely affected.
Rating = 3.6.

Disadvantages

- The total life-cycle cost will be high for this operation.
Rating = 3.3.
- The flexibility for incorporating new technology into this operation was judged to be somewhat low. Rating = 3.5.
- While ozonation has demonstrated the capability to destroy organic complexants, allowing removal of radionuclides (a definite strength), the capability of the ozonation process to reduce the TOC to the specification limits for GTF feed has not been demonstrated.
Rating = 3.5.

4.4.3 Cesium, Strontium, and Transuranic Removal with Titanium-Treated Zeolite

Advantages

- The impact on the health and safety of the facility workers should be very low. Rating = 4.5.
- The technical risk of this operation should be low. Rating = 4.3.
- The reliability and maintainability of the equipment should be very good, as all equipment pieces are standard, "off-the-shelf" items.
Rating = 4.3.
- The generation of secondary waste should be near minimum.
Rating = 4.1.
- The life-cycle cost should be reasonably low. Rating = 4.0.
- The process should be in full compliance with the regulations.
Rating = 3.9.
- The HLW and LLW streams should be in full compliance with specifications. Rating = 3.8.
- The process should not have an adverse effect on production schedules or overall campaign duration. Rating = 3.8.
- The process is capable of treating a relatively broad range of feed compositions. Rating = 3.8.
- The flexibility for incorporating improved technology is judged to be acceptable. Rating = 3.7.

Disadvantages

- The only noticeable weakness of this process is its impact on the generation of HLW. Rating = 3.3.

4.4.4 Technetium Removal with Strong-Base Anion Resin

The review of the selected technetium removal process to the listed criteria showed no exceptional strengths or glaring weaknesses. The ratings ranged from a high of 4.1 (for minimal impact to worker health and safety, meeting output specifications, and reliability and maintainability) to a low of 3.7 (for minimizing volume of HLW generated, compliance with Federal and State regulations, and impact on campaign duration).

5.0 BULK TREATMENT

This section of the report describes preconceptual engineering studies of alternative pretreatment systems for Hanford Site tank waste. Flowsheets were prepared and evaluated for processes using ion exchange, bulk precipitation, nonradionuclide leaching, and radionuclide leaching. Specific processes selected for each of these flowsheets were based on the potential of the technology to achieve adequate separations of ^{137}Cs , ^{90}Sr , ^{99}Tc , plutonium, and americium. Primary pretreatment goals were to (1) meet NRC Class A limits for the grout feed, (2) minimize the volume of grout and glass produced, (3) minimize potential safety and environmental problems by minimizing the addition of organics and hazardous chemicals, and (4) select processes that minimize the need for complex chemical adjustments and the number of process steps.

5.1 INTRODUCTION

The processes selected for these flowsheets are in various stages of development. For example, much laboratory data is available for ^{137}Cs removal using a resorcinol-formaldehyde ion exchange column. On the other hand, there was no data available on sulfide precipitation of ^{99}Tc in alkaline solutions. Therefore, assumptions and major technical uncertainties are discussed with the presentation of each flowsheet. A major technical uncertainty common to all flowsheets is the partitioning of components between the solid and liquid phases after water washing, caustic leaching, or acid dissolution.

The bulk precipitation flowsheet used the following precipitants: CST for alkaline ^{137}Cs , ^{90}Sr , and TRUs; Na_2S for alkaline ^{99}Tc ; phosphotungstic acid (PTA) for acidic ^{137}Cs ; lead sulfate for acidic ^{90}Sr ; and oxalic acid for acidic TRUs. This flowsheet resulted in an estimated glass production of 18,300-183,000 canisters and an estimated grout volume of $9.11 \times 10^5 \text{ m}^3$.

The ion exchange flowsheet used the following ion exchange materials: resorcinol-formaldehyde for alkaline ^{137}Cs ; IRC-718, an organic chelating resin, for alkaline ^{90}Sr ; Reillex for alkaline ^{99}Tc ; ammonium phosphomolybdate (APM) for acidic ^{137}Cs , Sr•Spec for acidic ^{90}Sr and plutonium; and TRU•Spec for acidic americium. This flowsheet resulted in an estimated glass production of 2,500-8,300 canisters and an estimated grout volume of $1.05 \times 10^6 \text{ m}^3$.

The nonradionuclide leaching flowsheet used the following materials: resorcinol-formaldehyde for ^{137}Cs ; IRC-718, an organic chelating resin, for alkaline ^{90}Sr ; Reillex for alkaline ^{99}Tc ; NaOH for aluminum and phosphorus leaching, and 0.1M NaOH and KMnO_4 for chromium leaching. This flowsheet resulted in an estimated glass production of 19,900-26,100 canisters and an estimated grout volume of $9.04 \times 10^5 \text{ m}^3$.

The radionuclide leaching flowsheet used the following materials: resorcinol-formaldehyde for ^{137}Cs ; IRC-718, an organic chelating resin, for alkaline ^{90}Sr ; Reillex for alkaline ^{99}Tc ; a mixture of H_2O_2 , alkaline and alkali carbonates, and EDTA for leaching actinides, strontium, cesium, technetium, and potentially lead. This flowsheet resulted in an estimated glass production of 14,000 to 101,000 canisters and an estimated grout volume

of $8.03 \times 10^5 \text{ m}^3$. However, the Class A requirements for strontium in grout were exceeded based on the assumed separation factors, but it would meet the NRC Class C limits. A summary of projected grout and glass production produced by each pretreatment flowsheet is tabulated in Table 5-1.

Table 5-1. Summary of Flowsheets.

Flowsheet	Grout volume (m^3)	Glass volume* (number of canisters)	Σ Fraction of Class A limit in grout
Bulk precipitation	$9.11 \text{ E}+5 - 6.5 \text{ E}+6$	18,300-183,000	1.0
Ion exchange	$1.05 \text{ E}+6 - 9.44 \text{ E}+6$	2,500-8,300	1.7
Nonradionuclide leaching	$9.04 \text{ E}+5 - 2.14 \text{ E}+6$	19,900-26,100	5.0
Radionuclide leaching	$8.03 \text{ E}+5 - 6.55 \text{ E}+6$	14,000-101,000	734

*Glass volume per canister is assumed to be 0.62 m^3 , which corresponds to a mass of 1,650 kg.

Ranges are given for the grout and glass volumes that reflect the considerable uncertainty associated with the design of these flowsheets. The lower grout volume corresponds to a reference loading of 5M sodium salts in the grout feed, and the higher grout volume corresponds to the volume of grout that would result if the most restrictive component limits for the grout feed were to be applied. The lower glass canister estimates correspond to a reference loading of 25 wt%, and the higher estimates correspond to the amount of glass that would be produced if certain restrictive limits were applied to the waste loading in glass.

The sum of the fraction of NRC Class A limits for the LLW grout indicates that none of the flowsheets will produce a grout that meets these requirements (i.e., a sum of fractions less than 1.0). It is believed that, with a reevaluation of some of the assumptions used in the development of the flowsheets, a grout could be produced that meets the Class A limits for the bulk precipitation, ion exchange and solid sorbent, and nonradionuclide flowsheets. Specifically, no credit was taken for the fact that much of the complexed ^{90}Sr and TRU components will precipitate during the organic destruction step reducing the alkaline supernatant liquid decontamination requirements. It is believed unlikely that the radionuclide leaching flowsheet could achieve a level of decontamination that would result in a grout that meets the Class A limits, primarily because of the difficulty in leaching ^{90}Sr and the relatively low limits applied to this radionuclide.

Pretreatment using sludge washing and cesium ion exchange would result in an estimated $23,750 \text{ m}^3$ of glass (38,300 canisters) and $977,000 \text{ m}^3$ of grout (Boomer et al. 1993). All four of these alternative flowsheets have the potential to reduce the cost of disposal compared to sludge washing alone. Of

these flowsheets, the ion exchange and solid sorbent flowsheet appears to have the most impact on reducing the volume of HLW glass produced. Considerable data on sludge dissolution, the separation processes, and optimization of the waste loading in grout and glass are needed to obtain a more accurate assessment of these flowsheets.

5.1.1 Objective

The objective of this study was to conduct Hanford Site preconceptual engineering studies of alternative pretreatment systems for the tank wastes. This included the preparation and evaluation of flowsheets using ion exchange and solid sorbents, precipitation, nonradioactive leaching, and bulk radionuclide leaching for the pretreatment of tank wastes.

5.1.2 Scope

Four separate flowsheets for the pretreatment of Hanford Site tank waste were developed and evaluated. These flowsheets include a precipitation flowsheet, a solid sorbent flowsheet, a bulk nonradionuclide leaching flowsheet, and a bulk radionuclide leach flowsheet. The radionuclides of interest are ^{137}Cs , ^{90}Sr , ^{99}Tc , and the TRU components (plutonium and americium). The flowsheets track most of the components in the tank waste and chemical additions, and estimate the quantities of grout and glass that would result from each process. Technical issues and technology development requirements are identified and discussed.

5.1.3 Criteria

The following criteria were considered in the development of the process flowsheets:

- Minimize the radionuclides disposed of in the grout waste form (NRC Class A limits were applied to the grout feed)
- Maximize the radionuclides going to glass
- Minimize the volume of grout and glass (the impact of this was to promote the selection of processes that add a minimum of chemicals and to add chemicals that do not have restrictive limits in the final waste forms)
- Minimize potential safety and environmental problems by minimizing the addition of organics and hazardous chemicals
- Minimize complexity (the impact of this was to promote the selection of processes that did not require complex chemical adjustments and that minimized the number of process steps).

5.1.4 Assumptions

Some assumptions apply to all flowsheets, while others apply only to precipitation and ion exchange.

Assumptions Common to All Flowsheets

1. **Waste Composition.** The waste composition data used for this study indicate an average composition based on 99% of the SST and DST inventories. SST inventories are based on normalized track radionuclide components (TRAC) data, and DST inventories are estimated from characterization data.
2. **Retrieval.** The waste processing rates in the material balances are based on a processing time of about 10 years with an online efficiency of 60% for a total of 2,192 processing days. Ion-exchange effluent and grout evaporator overheads will be reused for retrieval and/or washing.
3. **Sludge Wash and Dissolution.** The sludge wash process will be an in-tank settle and decant process: an initial decant followed by two batch washes. Sludge washing operations will be performed with water at three times the mass of the settled sludge. The settled sludge from all washings or solid-liquid separations will have a 1:1 liquid to solid mass ratio. Sufficient filtration will be provided to result in negligible solids carryover into the liquid product from solid-liquid separations.
4. **Pretreatment.** An organic destruction step is included in each flowsheet to eliminate complexing agents that would prevent efficient separation of cations with a valence of +2 (i.e., ⁹⁰Sr, plutonium, americium). It is assumed that the organic destruction process does not add or remove any inorganics to or from the waste stream.
5. **Disposal Criteria.** Composition variability study models (Piepel et al. 1993), HWVP minor component limits, a constant waste loading value of 25 wt%, and other applicable factors were used to estimate the amount of glass produced. The number of glass canisters was calculated using a weight of 1,650 kg/canister.

Grout volumes were determined using a 5M sodium concentration specification, as well as the reference grout specifications for chemical limits. In addition, the flowsheets were optimized as needed to meet NRC Class A limits, if reasonable.
6. **Equipment Design.** The waste will be retrieved to new stainless-steel tanks with a large volume. The new tanks have agitation that provides good mixing throughout the tank volume. Tanks used for caustic leach and acid dissolution will be capable of being heated to 100 °C.

Assumptions Common to Precipitation and Ion Exchange

Dissolution-related assumptions common to the precipitation and ion-exchange flowsheets only are given in Section 5.2 and 5.3 of this report.

5.1.5 Approach

Four separate flowsheets (pretreatment systems) were developed and evaluated using ASPEN flowsheet modeling software. An average tank waste composition based on normalized TRAC data for the SST wastes and actual characterization results for the DST wastes was used. This average composition was split into two streams, one representing the aqueous fraction and one representing the washed solids (i.e., sludge). The aqueous fraction included the supernates, dissolved salt cake, and sludge wash waters. The solids fraction consisted of those materials that are generally considered to be insoluble in alkaline solutions. The process steps included in the flowsheets were sludge washing, solid and liquid separation, solids dissolution, organic destruction, removal of the radionuclides, and conversion to the final waste form (i.e., grout and glass). Material balances were developed using partitioning factors for each of the components for each unit operation. Where possible, these partitioning factors are based on known chemistry of the waste components. Existing grout and glass specifications were used to assess the process performance.

5.2 PRECIPITATION

Figure 5-1 is a block flow diagram of the bulk precipitation process, and the supporting information is listed in Table 5-2. The following text summarizes the processes that make up the diagram. The diagram assumes that an organic destruction process has been previously conducted to destroy the complexants that prevent radionuclides from precipitating. The effectiveness of subsequent precipitation steps depends on adequate removal of organic complexants.

It is recognized that sorption onto a finely divided solid media is sorption rather than precipitation. However, it is anticipated that solid sorbents will be separated from the liquid phase by gravity settling (possibly followed by filtration of the liquid stream), therefore the simplifying term "precipitation" has been used throughout this section of the text.

Extensive sludge dissolution is necessary to minimize the amount of glass produced from HLW and meet Class A grout disposal requirements for the LLW. Therefore, a process sequence using water washes, a caustic leach, and two successive acid dissolution steps is assumed to minimize residual solids that would be vitrified, thus maximizing the amount of material dissolved that would be sent to a grout treatment facility after removal of radionuclides.

*Two-step acid dissolution
 Step 1 - Nitric Acid and Oxalic Acid
 Step 2 - Nitric Acid and HF

Figure 5-1. Bulk Precipitation Block Flow Diagram.

Table 5-2. Bulk Precipitation Flowsheet Assumptions.

Base-Side Processes	
Cesium, Strontium, and Plutonium Removal	
Precipitant	Crystalline silicotitanate
Precipitant amount added	0.0092 kg/L solution ^a
Cesium DF	1,000
Strontium DF	>10 ⁴
TRU DF	1,000
References	Bray, Carson, Elovich 1993
Technetium Removal	
Precipitant	Na ₂ S
Precipitant amount added	2 moles/mole technetium
Technetium DF	100
Reference	O'Kelly 1987
Acid-Side Processes	
Cesium Removal	
Precipitant	Phosphotungstic acid ^b
Total precipitant amount added	2 moles/mole cesium
Overall cesium DF	10 ⁴
References	Bray, Wise, Meyers 1984
Strontium Removal	
Precipitant	Pb(NO ₃) ₂ , H ₂ SO ₄ ^c
Final sulfate concentration	1.5 M SO ₄
Amount of lead added	0.02M solution
Strontium DF	10 ⁴
References	Bray and Van Tuyl 1961 Richardson 1965
TRU Removal	
Precipitant	Oxalic acid
Precipitant concentration	0.2M oxalic acid
Coprecipitant	0.03M Ca(NO ₃) ₂
Plutonium DF	10
Americium DF	350
References	Bokelund et al. 1991

^aAssumes four batch contacts with a K_d of 2,000.

^bAssumes two successive precipitation steps. It is assumed that potassium, silver, and rubidium will be quantitatively precipitated.

^cAssumes three precipitation steps.

The solid stream from the water washes is then combined with solids recycled from the second acid dissolution step and the phosphotungstate salts generated by the acid-side cesium precipitation step. A 50 wt% caustic solution is then added to the solids in an amount that results in a free hydroxide concentration of 3M in the resulting solution. The purpose of this caustic leach step is to dissolve compounds containing aluminum and silicon and to convert some insoluble phosphates to hydroxides. The caustic leach is followed by decanting and a water wash. The decanted liquid streams are combined with the liquid from the initial decant and water wash steps and sent to the base-side cesium precipitation step.

The undissolved solids from the caustic leach are contacted with a nitric acid solution and an oxalic acid solution. Oxalic acid is added to complex with cations enhancing the dissolution. Undissolved solids from the first acid dissolution step are contacted with a nitric acid solution and a hydrofluoric acid solution. Hydrofluoric acid is also added to complex cations and thus provide for a more complete dissolution.

After each of these dissolution steps, the tank contents are allowed to settle, and the resulting liquid is decanted. Any remaining solids and interstitial liquid are washed once after each dissolution step according to the assumptions described previously. The liquid streams from acid dissolution and subsequent wash steps are combined and sent to the acid-side cesium precipitation step. Ninety percent of any undissolved solids are recycled to the caustic leach step. The remaining 10% of undissolved solids are combined with solids from the precipitation steps, washed, and sent to vitrification.

One of the largest technical uncertainties in all the flowsheets is the amount of solids that will dissolve in the leaching and dissolution steps. There have been few dissolution tests on actual tank waste, and dissolution is expected to vary significantly over the wide range of sludges to be treated. Therefore, the amount and nature of solids that would remain undissolved by the process described here is not known.

5.2.1 Base-Side Precipitation

The combined liquid streams from initial water washing and caustic leaching are contacted with CST to precipitate cesium, strontium, plutonium, and americium. CST is a new ion exchange material that shows great promise for removal of radioactive cations from alkaline solutions. For the conditions of this flowsheet, it is assumed that the batch distribution coefficients (K_d 's) for cesium, strontium, and TRUs are 2,000, $>10^5$, and 2,000, respectively. A total of 0.0092 kg of CST is added per liter of solution (in four separate contacts of 0.0023 kg/L), with total DFs of cesium, strontium, and TRUs assumed to be 1,000, 5×10^4 , and 1,000, respectively. Use of one precipitation step for removal of multiple radionuclides greatly simplifies the overall flowsheet, but appears to require a huge mass of CST material.

Removal of technetium from alkaline streams by bulk precipitation has not been investigated as much as ion exchange processes. Technetium solution chemistry is not very well known. Precipitation by formation of insoluble sulfides may be one of the few precipitation options available for technetium removal (O'Kelly 1987).

After adding precipitant in each of these steps, the tank contents are allowed to settle. The decontaminated liquid from base-side processing is evaporated to produce a grout waste stream. The evaporated water can be recycled back to the wash steps. The precipitated solids are combined with solids from other steps for vitrification.

5.2.2 Acid-Side Precipitation

The combined liquid streams from the acid dissolution steps are sent to acid-side processing. First, the liquid is contacted with PTA for cesium precipitation. The remaining liquid is then contacted with sulfuric acid and lead nitrate for strontium precipitation. Next, the remaining liquid is contacted with oxalic acid and calcium sulfate to precipitate TRUs. The precipitated solids from each of these steps are combined with other solid waste streams and sent to vitrification. The decontaminated liquid stream is evaporated to recover water for water washes and then sent to the GTF.

Lead sulfate precipitation is then used to remove strontium from the liquid remaining from the PTA precipitation step. Lead sulfate precipitation was the only precipitation method identified in a recent literature search to assess methods for separating strontium from acidic media (Orth and Kurath 1993). This process was used on a large scale to recover strontium from PUREX waste as a strontium crude product that was further processed by ion exchange. In laboratory studies (Bray and Van Tuyl 1961) and pilot studies (Richardson 1965), over 95% of the strontium was precipitated at 80 °C and a pH between 0.4 and 4.0.

Oxalate precipitation using a calcium carrier was the most promising precipitation method identified in a recent literature search to assess methods for separating TRUs from Hanford Site tank waste. DFs of 10 and 350 for plutonium and americium, respectively, were assumed.

5.2.3 Summary of Material Balances

The bulk precipitation flowsheet results in the production of 18,300 canisters of glass based on 25 wt% waste loading and $9.11 \times 10^5 \text{ m}^3$ of grout (based on 5M Na+). A comparison of the radionuclide concentration in the LLW and the Class A limits is found in Table 5-3. The grout production assuming different limiting components is in Table 5-4. The estimated number of glass canisters varies as shown in Table 5-5 depending on the constraints used to project the waste loading. The HLW resulting from this flowsheet is different than the NCAW wastes evaluated in the Compositional Variability Studies (CVS), and the limits may not be the same. The limiting category in the CVS model is sulfur. This would limit the vitrification feed to 11.7 wt% waste and increase the number of canisters to about 41,900 canisters.

Table 5-3. Low-Level Waste Radionuclide Concentrations at 5M Na⁺--Precipitation Flowsheet.

Radionuclides	Class A limits, Ci/m ³	Concentration, Ci/m ³	Fraction of limit
¹³⁷ Cs	1	0.17	0.17
⁹⁰ Sr	0.04	0.0095	0.24
⁹⁹ Tc	0.3	0.0096	0.03
¹²⁹ I	0.008	2.55 E-5	0.003
²⁴¹ Am	TRU	--	--
²³⁹ , ²⁴⁰ Pu	TRU	--	--
TRU	10 nCi/g	5.8 nCi/g	0.58
Σ Fractions	--	--	1.02

Table 5-4. Low-Level Waste Production--Precipitation Flowsheet.

	Sodium concentration (M)	Volume of grout (m ³)	Vaults	Limiting component
Reference loading	5	9.11 E+5	235	Sodium
Grout feed criteria	0.7	6.5 E+6	1670	Arsenic
--	1.9	5.61 E+6	1450	Sulfur

Table 5-5. High-Level Waste Production--Precipitation Flowsheet.

	Waste loading (wt%)	Mass of glass (kg)	Canisters	Limiting component
Reference loading	25	3.02 E+7	18,300	N/A
HWVP reference feed criteria	2.5	3.02 E+8	183,000	TiO ₂
CVS II model	11.7	6.90 E+7	41,900	Sulfur

Titanium is the limiting component using the HWVP reference feed criteria and is present due to addition of CSTs. The estimated grout volume is shown in Table 5-4 for various limiting components.

5.2.4 Uncertainties

The bulk precipitation process contains many uncertainties because of the variability of the waste composition and form. The technology to dissolve most of the tank sludges using caustic leach and a two-step acid dissolution has not been demonstrated. The effectiveness of solid-liquid separations using settling and decanting on a large scale is also yet to be determined.

The individual precipitation processes are in various stages of development. The greatest uncertainty is using sodium sulfide to precipitate ^{99}Tc , which has not been demonstrated on any scale. Even for processes that have been demonstrated on a large scale, it is uncertain whether precipitation will achieve large DFs for individual tank wastes in which the radionuclide of interest is much more dilute than the average concentration for all tank wastes combined. For this reason, increased quantities of precipitants may have to be added to achieve desired overall DFs. Alternatively, higher concentrations of radionuclides would be sent to the GTF.

The waste that would be sent to the vitrification plant varies considerably from NCAW waste and other waste for which glass formulation have been studied extensively. This may create glass formulation problems causing additional canisters to be produced as compared to glass with a 25% waste loading. It could also allow glass with higher waste loadings, which would reduce the canisters produced.

5.2.5 Advantages and Disadvantages

The advantages of the bulk precipitation flowsheet are simple operation, minimal capital investment, and processing that could be started on an accelerated schedule compared to facility options. Lead sulfate precipitation and PTA precipitation have been implemented on a large scale for other wastes. CST has shown great promise for removal of radioactive cations from alkaline solutions.

The main disadvantage of this flowsheet is that a relatively large amount of glass may be produced. Also, more quantities of hazardous chemicals (i.e., lead, sulfuric acid) are added to the waste than with the other flowsheets. The use of corrosive and hazardous chemicals are required for both dissolution and bulk precipitation steps. Although this process could be performed in tanks, new tanks of more expensive materials than carbon steel would be required.

5.3 ION EXCHANGE AND SOLID SORBENTS

Figure 5-2 is a block flow diagram representing the ion exchange process, and assumptions regarding DFs are shown in Table 5-6. The following text summarizes the processes that make up the diagram. We assume that ion

5.3 ION EXCHANGE AND SOLID SORBENTS

Figure 5-2 is a block flow diagram representing the ion exchange process, and assumptions regarding DFs are shown in Table 5-6. The following text summarizes the processes that make up the diagram. We assume that ion exchange materials will be used in columns, because column operations are much more efficient than batch contacting.

The sorbents selected for this study are summarized below:

<u>Radionuclide Removed</u>	<u>Sorbent</u>
Cesium in basic solution	Resorcinol-formaldehyde
Strontium in basic solution	IRC-718
Technetium in basic solution	Reillex
Cesium in acid solution	Ammonium phosphomolybdate
Strontium/plutonium in acid solution	Sr•Spec
Americium in acid solution	TRU•Spec

For these material balance calculations, each of the ion exchange materials is used one time and removed from the system loaded with radionuclides, except for the base-side cesium ion exchanger and the acid-side Sr•Spec, which is eluted and reused. Due to concerns about storing cesium-loaded organic ion exchange resin, the cesium is eluted from an organic ion exchange resin used for base-side processing and that resin is reused. After several loading and elution cycles, the resin is eluted for the final time and discarded as LLW. The ability of the organic ion exchanger to achieve high DFs after several elution and loading cycles is uncertain. Therefore, the resin may need to be discarded after each elution or after fewer elutions. This would result in more volume (of spent resin) sent to LLW.

The Sr•Spec columns will also be eluted and reused. In addition to strontium, barium and lead will be quantitatively sorbed onto the Sr•Spec column. Strontium and barium will be eluted with water. Lead will subsequently be eluted with dilute sulfuric acid. The Sr•Spec resin is then reused for another loading cycle. The benefits of elution include (1) separating the lead from the HLW stream and (2) avoiding the high cost using once-loaded Sr•Spec.

5.3.1 Base-Side Ion Exchange

Cesium is removed from the combined alkaline liquid waste using a resorcinol-formaldehyde ion exchange resin developed at the Savannah River Site (SRS) and available from Boulder Scientific Company. Although the batch distribution factors for resorcinol-formaldehyde are not as high as with the CST discussed earlier, resorcinol-formaldehyde was chosen because CST has not been fabricated into pellets suitable for column operation.

Figure 5-2. Ion Exchange Block Flow Diagram.

Table 5-6. Ion Exchange Flowsheet Assumptions.

Base-Side Processes	
Cesium Removal	
Process Sorbent DF Cesium capacity, column volumes/cycle References	Elution with HCOOH Resorcinol-formaldehyde 10" 220 Bibler and Wallace 1990 Bray et al. 1990
TRU Removal	
Process Sorbent DF Reference	Elution with HCOOH Resorcinol-formaldehyde 10 Lumetta et al. 1993b
Strontium Removal	
Process Sorbent DF Strontium capacity, column volumes/cycle Reference	Once-through loading IRC-718 10,000 2,000 Swanson 1993
Technetium Removal	
Process Sorbent DF Technetium capacity, column volumes/cycle	Once-through loading Reillex 100 250
Acid-Side Processes	
Cesium Removal	
Process Sorbent DF Cesium capacity References	Once-through loading Ammonium phosphomolybdate-- $(\text{NH}_4)_3\text{P}(\text{MO}_3\text{O}_{10})_4$ 2,000 50 mg cesium/g sorbent Faubel and Ali 1986 Swanson 1993
Strontium and TRU Removal	
Process Sorbent DF for Strontium Plutonium Capacity References	Elution with water and acid Sr•Spec 10,000 10,000 0.1 moles/L sorbent Horwitz, Chiarizia, Dietz 1992 Orth and Kurath 1993
Americium Removal	
Process Sorbent Americium DF Capacity Reference	Once-through loading TRU•Spec 100 0.0375 moles/L sorbent Lumetta et al. 1993a

Other inorganic ion exchangers, such as IE-96, were not selected because the additional sodium and aluminum would significantly increase the waste volume. Resorcinol-formaldehyde was chosen over other organic ion exchangers, such as Cs-100, due to its superior cesium capacity observed from tests to date.

It is assumed that some of the plutonium and americium is also removed to a limited extent by the resorcinol-formaldehyde resin, although this is speculative. Limited experimental data obtained by batch contacts with CC waste simulant (Lumetta et al. 1993b) indicates that the resin was found to have a K_d of 14 for americium and a K_d of 450 for plutonium. Additional experiments with actual waste indicate that the material had a K_d of 12 for plutonium. While these K_d 's are considered low, it should be noted that the presence of complexants in the waste probably suppressed the K_d 's significantly. Column loading and elution experiments were not performed. If the TRU components are not removed with the resorcinol-formaldehyde resin, it is possible to add a sorption step with sodium titanate to remove the plutonium and americium. This addition would probably increase the glass volume since the material would be used on a once-through basis.

The decontaminated liquid from base-side processing is evaporated to produce a grout waste stream that is $5M Na^+$. The evaporated water can be recycled back to the wash steps. The loaded IRC-718 and Reillex columns are combined with solids from other steps for vitrification.

5.3.2 Acid-Side Ion Exchange

The combined liquid streams from the acid dissolution steps are sent to acid-side processing. First, cesium is removed from the acid solution by ion exchange onto an APM ion exchange column. The cesium-loaded APM is added to the caustic leach step, where the solids are dissolved. Cesium dissolved from the loaded APM is removed from the waste in the base-side resorcinol-formaldehyde ion exchange step. Next, strontium and TRUs are removed from the acid solution using the Sr•Spec sorbent. Then, americium is removed using the TRU•Spec sorbent. The decontaminated liquid stream is evaporated to recover water for water washes and then sent to the GTF.

APM ion exchange and ferrocyanide ion exchange were identified as the most promising ion exchange technologies in a recent literature review to assess methods for separating cesium from acidic media. Other exchange materials considered in the previous study included other phosphates, oxides, polyantimonic acid, macrocyclic ligands, and zeolites.

Sr•Spec was identified in a recent technology review as the most promising solid sorbent material for acid-side strontium removal (Orth and Kurath 1993). Sr•Spec is a chromatographic resin consisting of an octanol solution of 4,4'(5')-bis(t-butyl-cyclohexano)-18-crown-6 sorbed on an inert polymeric support. Sr•Spec exhibits a high selectivity over other metal cations in concentrated nitric acid solutions ($>1M$) except barium, lead, and tetravalent neptunium. Polonium and plutonium sorbent are greater than that of strontium at $3M HNO_3$. Therefore, Sr•Spec can also be used for plutonium removal.

For this flowsheet, a strontium DF of 10,000 and a plutonium DF of 10,000 are assumed. It is also assumed that barium and lead will quantitatively sorb onto the column. The total column capacity is assumed to be about 0.1M of sorbent. Strontium and barium can be subsequently eluted with a small volume of water (five column volumes). Lead is then eluted with dilute acid ($0.1M\ H^+$), and this solution is combined with the LLW stream. The eluted Sr•Spec can be reused several times before final disposal as solid LLW. It is assumed that Sr•Spec can be used for at least five loading and elution cycles.

TRU•Spec was selected for removing americium from the acid-side solution. TRU•Spec is a chromatographic resin consisting of octyl (phenyl)-N, N-diisobutylcarbamoyl-methylphosphine oxide (CMPO) and tributyl phosphate (TBP) sorbed on an inert polymeric support (Amberchrom CG-71). TRU•Spec exhibits a high selectivity over bulk sludge components such as zirconium, sodium, or aluminum. Although TRU•Spec has a high capacity for actinides such as americium and plutonium, experiments have also demonstrated a high affinity for uranium. About 90% of the uranium in a dissolved NCRW sludge was loaded onto the resin. Relatively low DFs for americium (about 2.4) were attributed to competition from uranium (Lumetta et al. 1993a). Therefore, a separate uranium step would be required to minimize the amount of resin required and uranium sent to HLW. Alternatively, a technique would have to be developed that permits the americium to be separated from uranium during an elution process.

For this flowsheet, an americium DF of 100 was assumed. It is also assumed that all the other lanthanides will quantitatively sorb onto the column, and about 90% of the uranium will be sorbed onto the column. The total column capacity is assumed to be about 0.0375 moles of trivalent cations per liter of sorbent. The column would be once-loaded and disposed of as HLW. Since a once-loaded process using this resin is expensive, it would be desirable to develop an elution technique, especially a method that would facilitate separation of uranium and americium.

Alternative ion exchange techniques were considered for americium removal. Organic cation exchange has been tested, but separations between americium and other bulk trivalent ions (iron, aluminum, chromium) are very poor. Efforts to improve this separation by reducing the Fe^{3+} to Fe^{2+} , or using complexing agent such as oxalic acid to selectively load or elute americium, have resulted in limited success. A chromatographic ion exchange technique, band ion exchange, has been developed for selectively eluting americium from other trivalent cations, including other lanthanides (Wheelwright 1979). However, this approach was successful for purifying a reasonably large amount of americium from fission products and may not be successful with tank waste containing low concentrations of americium and high concentrations of competing cations. In addition, band ion exchange is significantly more complex than the simple bulk processing desired for this study.

5.3.3 Summary of Material Balances

A comparison of the radionuclide concentration in the LLW and the Class A limits is found in Table 5-7. As formulated, these flowsheets do not meet the Class A limits for grout feed because the sum of fractions is greater than 1, although limits for individual radionuclides are met. This is due largely to the cesium and TRU components in the alkaline waste stream. The grout production assuming different limiting components is in Table 5-8.

The ion exchange flowsheet results in the production of an estimated 2,500-8,300 canisters of glass and $1.05 \times 10^6 \text{ m}^3$ of grout (based on 5M sodium). The estimated number of glass canisters varies as shown in Table 5-9, depending on the constraints used to project the waste loading. The HLW resulting from this flowsheet is different than the NCAW wastes evaluated in the CVS studies, and the limits may not be the same. The limiting category in the CVS model is the "other." This would limit the vitrification feed to 19 wt% waste and increase glass volume to about 3,400 canisters. The composition of the "other" is much different than studied for NCAW, which could change the amount of waste that could be incorporated into the glass. The lanthanides are the limiting components for glass production under the HWVP reference feed criteria. The estimated grout volume is listed in Table 5-8.

Table 5-7. Low-Level Waste Radionuclide Concentrations at 5M Na⁺--Ion Exchange Flowsheet.

Radionuclides	Class A limits, Ci/m ³	Concentration, Ci/m ³	Fraction of limit
¹³⁷ Cs	1	0.95	0.95
⁹⁰ Sr	0.04	9.0 E-3	0.23
⁹⁹ Tc	0.3	8.5 E-3	0.028
¹²⁹ I	0.008	2.2 E-5	0.0028
²⁴¹ Am	TRU	--	--
^{239,240} Pu	TRU	--	--
TRU	10 nCi/g	4.4 nCi/g	0.44
Σ Fractions	--	--	1.65

Table 5-8. Low-Level Waste Production--Ion Exchange Flowsheet.

	Sodium concentration (M)	Volume of grout (m ³)	Vaults	Limiting component
Reference loading	5.00	1.05 E+6	271	sodium
Grout feed criteria	0.80	6.53 E+6	1690	arsenic
--	0.56	9.44 E+6	2440	molybdenum

Table 5-9. High-Level Waste Production--Ion Exchange Flowsheet.

	Waste loading (wt%)	Mass of glass (kg)	Canisters	Limiting component
Reference loading	25	4.15 E+6	2500	N/A
HWVP reference feed criteria	7.6	1.37 E+7	8300	Lanthanides
CVS II model	19	5.58 E+6	3400	"other"

5.3.4 Uncertainties

The ion exchange process contains many uncertainties because of the variability of the waste composition and form. The technology to dissolve most of the tank sludges using caustic leach and a two-step acid dissolution has not been demonstrated. The effectiveness of solid-liquid separations using settling and decanting on a large scale is also yet to be determined.

The individual ion exchange processes are in various stages of development. Capacities and selectivities of these exchangers need to be confirmed for the wide variety of waste to be treated. If the overall DF that can be achieved is less than the DF possible for the average composition of all tank wastes, more radionuclides will be sent to grout. Other major uncertainties are listed below:

- The DFs assumed in this study are dependent on the process operating conditions and can vary significantly, depending on how the processes are operated. Significant process variables include the loading flow rate, the number of columns, and the extent of elution and regeneration.

- Achievable DFs for americium using TRU•Spec. Initial tests indicate interference by uranium that is not observed for the TRUEX process (Lumetta et al. 1993a). An additional process for uranium removal may be necessary to use this technology and meet pretreatment objectives.
- The capability of the resorcinol-formaldehyde resin to remove plutonium and americium is largely unproven. Batch contacts indicate that the material has a useable capacity and the level of TRU in the alkaline waste is probably not as great as assumed for this study, which reduces the required performance. However, column loading and elution experiments examining the behavior of americium and plutonium have not been completed.
- The capacity of resorcinol-formaldehyde after repeated loading and elution cycles.
- The efficacy of Reillex in alkaline solutions. Laboratory studies have only been performed in acid solutions. Also, column demonstration is needed.

The waste that would be sent to the vitrification plant varies considerably from NCAW waste and other wastes for which glass formulation has been studied extensively. This may create glass formulation problems, causing additional canisters to be produced as compared to glass with a 25% waste loading. It could also allow glass with higher waste loadings, which would reduce the canisters produced. Vitrification of some ion exchange resins has been demonstrated, but implementation of this mode of operation would require changes in the design and operation of the vitrification plant.

5.3.5 Advantages and Disadvantages

The primary advantage of the ion exchange flowsheet is that less glass is produced than for the other flowsheets considered by PNL.

The main disadvantage of this flowsheet is that large quantities of corrosive and hazardous chemicals are added to maximize dissolution of radionuclides. Also, operation will be more complex than the other flowsheets, requiring operations external to tanks. In addition, the kinetics are slow for the IRC-718 ion exchange process.

5.4 SELECTIVE LEACHING

The selective leaching flowsheets considered methods for simple in-tank leaching of specific components from the waste to reduce the quantity of HLW glass required and produce a feed stock for grout that meets NRC Class A requirements and current grout requirements for chemical components. The advantages of the leaching flowsheet are simple operation and minimal capital investment, and the process could be started on an accelerated schedule compared to facility options. Also, the bulk leach only needs to be used on

specific wastes types for maximum benefit if the waste can be blended before being transferred to HWVP. The following text summarizes the selective leaching concept.

The potential disadvantages for the bulk leaching are that the separations are not as good as with other options and glass volume is not minimized as much as facility processing.

The major technical issue with the leaching flowsheets is partitioning factors. Only selected tanks have been tested, and the other tanks may not behave in a similar manner. The other major technical issue is the development of a glass that has the majority of the compounds outside of the previously studied glass envelope. The waste loading allowed in the glass based on available information could vary substantially.

Selective leaching was considered from two perspectives. One option was leaching of nonradioactive compounds. The goal of nonradioactive leaching is to remove certain nonradioactive components from the sludge that would otherwise result in the production of large quantities of glass. The other option would be to concentrate on leaching TRUs and fission products from the waste. This radioactive leach process would allow the remaining sludge to be grouted and the leachate vitrified. These two concepts could be combined; however, with the limited amount of data available at this time, there are no incentives to combine the leaching steps. These flowsheets start with the waste "as retrieved" from the tanks and then in decanted form, which removes a large portion of cesium from the tank. Organic destruction would be required for waste that contains complexants that could interfere with the removal of ^{90}Sr or the TRU components. The supernate would then be processed through ion exchange columns to remove cesium, strontium, and technetium, and possibly plutonium and americium.

5.4.1 Nonradionuclide Leach

The nonradioactive leach subjects the sludge to various chemical treatments that reduce the mass of the sludge without removing significant quantities of TRU or radionuclides other than cesium and technetium, which are normally soluble in the alkaline waste. In addition to the selective leaching, a method is required to remove cesium, strontium, technetium, and TRU components from the supernate and possibly some leachates to make them acceptable grout feeds. Ion exchange was selected as the most appropriate process to combine with the selective leaching processes for treatment of the supernates and leachates. The ion exchange processes are the same as chosen for the ion exchange flowsheet and are discussed in Section 5.3.

The nonradioactive leach block flow diagram in Figure 5-3 uses caustic and reducing agents to remove aluminum, phosphorous, and chromium. Leaching steps are arranged so the pH starts high and is then lowered in successive process steps. The high pH solutions contain the most sodium, and need to be washed so the addition of sodium does not cause an increase in glass production. The flowsheet uses a 3M NaOH solution for the dissolution of aluminum and phosphorous. Then a solution of 0.1M NaOH and KMnO_4 is used to remove chromium. A summary of assumptions used for the process is shown in

Figure 5-3. Nonradioactive Leach Block Flow Diagram.

Table 5-10. The leaching flowsheets assume all solid-liquid separations are performed by settle-decant in large tanks. The chemical leaching is carried out in the large tanks under controlled temperature conditions over extended periods of time.

The initial flowsheet step is a settle-decant of supernate and water used during retrieval. After the initial decant, the sludge is washed again with 0.1M NaOH, and the resulting supernate is decanted. The initial decanted liquid and the supernate from the first wash are sent to the ion-exchange columns for removal of cesium, strontium, technetium, and TRU components. The ion exchange processes for treatment of the alkaline liquids are the same as those described in Section 5.3.

The canisters of glass produced (reference loading) are estimated to be approximately 19,900. Using the NCAW glass component limits used for the HWVP glass envelope, the number of canisters would be 26,100. If additional phosphorous and zirconium could be removed, the number of canisters could be reduced further.

Summary of Material Balances. A comparison of the radionuclide concentration in the LLW and the Class A limits is found in Table 5-11. The grout production, considering selected nonradioactive limiting components, is in Table 5-12. The nonradionuclide leach flowsheet results in the production of 26,100 canisters of glass and 2.14×10^6 m³ of grout, based on the most realistic limits. The estimated number of glass canisters varies as shown in Table 5-13, depending on the constraints used to project the waste loading. The HLW resulting from the leaching process is different than the NCAW wastes evaluated in the CVS studies, and the limits may not be the same. After the nonradionuclide leach, the limiting components are still phosphorous, although a large quantity is removed. If the phosphorous leaching efficiency was better than assumed in the flowsheet, the waste loading would increase and the number of canisters would be reduced. The next limiting category in the CVS model is the "others." This would limit the glass composition to 24 wt% waste, and the number of canisters would be about 18,000. The composition of the "others" is much different than studied for NCAW, which could change the amount of waste that could be incorporated into the glass. However, it also might allow the phosphorous limits to be increased.

Uncertainties. The nonradionuclide leach process contains many uncertainties because of the variability of the waste composition and form. The ability to leach aluminum, phosphorous, and chromium has been demonstrated on a few tanks with little carryover of actinides and strontium. The performance of the leaching process has been conservatively extrapolated to perform on the other waste tanks. The waste that would be sent to the vitrification plant varies considerably from NCAW waste and other waste for which glass formulation have been studied extensively. This may create glass formulation problems causing additional canisters to be produced as compared to glass with a 25% waste loading. It could also allow glass with higher waste loadings, which would reduce the canisters produced.

Table 5-10. Nonradionuclide Leach Flowsheet Assumptions.

Soluble Leachate Processes--Base-Side Processes	
Cesium Removal	
Process Sorbent DF Cesium capacity, column volumes/cycle References	Elution with HCOOH Resorcinol-formaldehyde resin 10 ⁴ 220 Bibler and Wallace 1990 Bray et al. 1990
Strontium Removal	
Process Sorbent DF Strontium capacity, column volumes/cycle Reference	Once-through loading IRC-718 100 2,000 Swanson 1993
Technetium Removal	
Process Sorbent DF Technetium capacity, column volumes/cycle reactant/waste volume ratio	Once-through loading Reillex 100 250 0.70
Aluminum Removal	
Process Reactant Converts to soluble form Al P Tc Is Cancrinite L reactant/L waste	Bulk leach in 3-5M NaOH 19M NaOH 85% 50% 80% 50% 50% 0.70
Chromium Removal	
Process Reactant Converts to soluble form Cr ⁺³ to Cr ⁺⁶ Na Al Am, Pu, La, Np, Bi, Sr kg reactant/kg Cr ⁺³	Bulk leach 0.1 M NaOH and 50% excess KMnO ₄ 84% 92% 0.0 0.1% 4.6

Table 5-11. Low-Level Waste Radionuclide Concentrations at 5M Na⁺--Nonradionuclide Leach Flowsheet.

Radionuclides	Class A limits (Ci/m ³)	Concentration (Ci/m ³)	Fraction of limit
¹³⁷ Cs	1.00	1.33	1.33
⁹⁰ Sr	0.04	0.12	2.89
⁹⁹ Tc	0.30	0.008	0.027
¹²⁹ I	0.008	2.44 E-5	0.003
²⁴¹ Am	TRU	--	--
²³⁹ , ²⁴⁰ Pu	TRU	--	--
TRU	10 nCi/g	6 nCi/g	0.6
Σ Fractions	--	--	4.9

Table 5-12. Low-Level Waste Production--Nonradionuclide Leach Flowsheet.

	Sodium concentration (M)	Volume of grout (m ³)	Vaults	Limiting component
Reference loading	5.0	9.04 E+5	230	sodium
Grout feed criteria	2.1	2.14 E+6	550	fluorine
--	3.1	1.47 E+6	380	arsenic

Table 5-13. High-Level Waste Production--Nonradionuclide Leach Flowsheet.

	Waste loading (wt%)	Mass of glass (kg)	Canisters	Limiting component
Reference loading	25	3.3 E+7	19,900	N/A
HWVP reference feed criteria	19	4.3 E+7	26,100	P ₂ O ₅
CVS II model	19	4.3 E+7	26,100	P ₂ O ₅

The grout from the nonradionuclide leach does not meet NRC Class A requirements. The initial assumption used to split the soluble and insoluble fractions of americium and strontium are estimates based on available data and may not represent a large fraction of the tanks. The solubility of these components in the leach solution has not been tested on the majority of the tanks. A portion of the radioactivity in grout feed originated in the leach solutions, and most could be removed by routing this stream through ion exchange. The DF used for cesium is 10,000, which may require additional polishing columns to achieve. The characterization of at least the waste types--which are high in aluminum, phosphorus, and chromium--is needed to fully evaluate this process. The behavior of arsenic during the leaching is not known, and it is the most limiting chemical component for the grout based on the current requirements. The behavior of arsenic in the waste or in the grout could change the quantity of grout produced significantly.

The uncertainties associated with ion exchange treatment of the alkaline wastes also apply to this flowsheet (see Section 5.3.4).

Advantages and Disadvantages. The advantages of the nonradionuclide leach flowsheet are that simple operation, minimal capital investment, and processing could be started on an accelerated schedule compared to facility options. The use of corrosive and potentially hazardous organic chemicals is minimized, and the bulk leach only needs to be used on specific wastes types for maximum benefit.

The potential disadvantages for the bulk leaching are that the separations are not as good as with other options, and the glass and grout volumes are not minimized as much as facility processing. The bulk treatment still requires ion exchange for the supernate decontamination. The quantity of chemicals used, but not recycled, is large as reflected in the total grout volumes.

5.4.2 Radionuclide Leach

The radionuclide leach process is based on the Act-de-con process, which uses a combination of oxidants, carbonates, and EDTA to selectively remove plutonium, uranium, americium, and strontium. The assumptions used in estimating grout and glass volumes are listed in Table 5-14. The process has been used on contaminated soils, but not on Hanford Site tank waste. Another option for this type of process is to use 0.1M Tiron as an extractant with the resulting solution sent directly to the vitrification plant. However, the Tiron contains a significant amount of sulfur, which has a low limit in glass. The Act-de-con chemicals add sodium to the glass, but the actual quantity is not known. The block flow diagram (Figure 5-4) assumes a TRU and strontium removal efficiency similar to laboratory tests using Tiron. The process probably will not remove enough strontium, cesium, and TRU from the sludge to meet NRC Class A limits, although it should meet Class C limits. Information on soil decontamination tests indicate the process can achieve DFs of 10-20 with two contacts. A DF of 6.7 was used for the flowsheet. The quantity of reactants is not known at this time, so engineering judgement was used to select the same volume of reactants as there is sludge for each reactant contact. The amount of inert solids that will dissolve is also unknown, and a value of 20 wt% was investigated.

Table 5-14. Radionuclide Leach Flowsheet Assumptions.

TRU Leaching Process	
Process	Bulk leach of TRU and strontium
Reactant	2 wt% H ₂ O ₂ , 8 wt% EDTA, 89 wt% water, 1 wt% mixed carbonates
Converts to soluble form	
Pu, U	85%
Am	95%
Sr	75%
Cs	10%
Cl, F, NO _x	90%
Bulk solids	20%
Na, K	90%
kg reactant/kg waste	1

The initial flowsheet step is a settle-decant of supernate and water used during retrieval just like the other flowsheets. After the initial decant, the sludge is washed again with water, and the resulting supernate is decanted. The initial decanted liquid and the supernate from the first wash are sent to the ion-exchange columns for removal of cesium, strontium, and technetium. The ion-exchange resin chosen for cesium is resorcinol formaldehyde as in the ion exchange flowsheet. The resin is to be eluted with nitric or nornic acid and regenerated with NaOH.

After the ion exchange, the sludge is left in the tank for TRU leaching. The decanted solutions are combined and sent to an evaporator to concentrate the solution before sending it to the vitrification plant. The solutions contain a significant amount of sodium that impacts the quantity of glass produced. The sludge, low-level ion-exchange stream, and overheads from the evaporator are sent to grout.

The radionuclide leach would probably not be performed in existing tanks because of the organics used. New large underground tanks equipped with adequate mixing and ventilation systems should be appropriate for the processing.

The grout volume produced based on chemical limits results in $6.5 \times 10^6 \text{ m}^3$ of grout feed. The volume could be reduced significantly with additional relaxation of constraints, and the grout quality would be probably still meet the requirements proposed in the performance assessment.

5.4.3 Summary of Material Balances

The radionuclide flowsheet results in the production of 14,000 to 101,000 canisters of glass, and $8.03 \times 10^5 \text{ m}^3$ of grout based on a 5M sodium concentration. A comparison of the radionuclide concentrations in the LLW and Class A limits is found in Table 5-15 and grout production in Table 5-16. The grout from the radionuclide leach does not meet Class A requirements for cesium, strontium, and TRU. The initial assumption used to split the soluble

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Figure 5-4. Radionuclide Leach Block Flow Diagram.

Table 5-15. Low-Level Waste Radionuclide Concentrations at 5M Na⁺--Radionuclide Leach Flowsheet.

Radionuclides	Class A limits (Ci/m ³)	Concentration, Ci/m ³	Fraction of limit
¹³⁷ Cs	1.0	9.6	9.6
⁹⁰ Sr	0.04	28.7	720.0
⁹⁹ Tc	0.3	0.01	0.035
¹²⁹ I	0.008	2.9 E-05	0.003
²⁴¹ Am	TRU	--	--
^{239, 240} Pu	TRU	--	--
TRU	10 nCi/g	40 nCi/g	4.0
Σ Fractions	--	--	734.0

Table 5-16. Low-Level Waste Production--Radionuclide Leach Flowsheet.

	Sodium concentration (M)	Volume of grout (m ³)	Vaults	Limiting component
Reference loading	5.0	8.03 E+5	210	N/A
Grout feed criteria	0.6	6.55 E+6	1700	arsenic
--	1.9	2.13 E+6	550	fluorine

and insoluble fractions of cesium, strontium, and TRU are estimates based on available data and may not represent a large fraction of the tanks. The leaching efficiency of these components in the leach solution has not been tested on Hanford Site waste. Differences between the assumptions used in this report based on soil washing test and the reality could allow this process to meet NRC Class A limits or indicate the radionuclides in the supernates are much too high to send to grout without further treatment. Additional treatment was not added to this flowsheet because no simple bulk treatment processes could be identified. The behavior of arsenic during the leaching is not known and is a limiting chemical component for the grout based on the current requirements. The behavior of arsenic in the waste or in the grout could change the quantity of grout produced significantly. If the arsenic was removed and the radionuclides did not limit the quantity of grout, the fluorine would restrict the grout volume. The limit for fluorine is based on past experience and could probably be increased.

The estimated number of glass canisters varies as shown in Table 5-17 depending on the constraints used to project the waste loading. The HLW resulting from the leaching process is very different than the limits

Table 5-17. High-Level Waste Production--Radionuclide Leach Flowsheet.

	Waste loading wt%	Mass of glass, kg	Canisters	Limiting component
Reference loading	25.0	2.31 E+7	14,000	N/A
HWVP reference feed criteria	3.5	1.66 E+8	101,000	P ₂ O ₅
CVS II model	3.5	1.66 E+8	101,000	P ₂ O ₅

evaluated in the CVS studies based on NCAW wastes. After the radionuclide leach, the majority of components going to glass are sodium from the leach solution and phosphorous assumed to leach with the leachate. The phosphorous is the most limiting compound only allowing a 3.5 wt% waste loading. Using a 25% waste loading, the number of canisters is reduced to 14,000 canisters. Therefore, if 50% phosphorous as assumed does not leach with actinides or the phosphorous is removed before the radionuclide leach, the number of canisters could probably be reduced. The "other" category is the most limiting after phosphorous and it would reduce the waste loading to 21 wt%. But the composition of the "others" category is much different than studied for the CVS studies, and this may allow a higher waste loading to be reached. Therefore, using a waste loading of 25 wt% appears to be the most realistic based on available data. The glass waste loading could be limited by the sodium added as part of the leach solution, if the concentration of sodium is higher than assumed for this flowsheet. The actual quantity of sodium in the leach solution is not known, because the information is proprietary. The actual quantity of reactants could have a significant effect on the quantity of waste generated from this process.

5.4.4 Uncertainties

The radionuclide leach process contains the same uncertainties because of the variability of the waste composition and physical form. The ability to leach actinides, strontium, and cesium has not been demonstrated on Hanford Site waste. The performance of the leaching process has been predicted based on soil washing tests and actinide extractant data. Data on the solubility of inert components also is not available. Actual data is needed to project feasibility. Also needed is the identification (or development) of suitable in-line instrumentation to control the process.

The HLW stream from this process that would be sent to the vitrification plant varies considerably from NCAW waste and other waste for which glass formulation has been studied. Specifically, the phosphorous could be very high. The amount of phosphorous that would carry over with leach solution is unknown, and the results will have a large effect on the amount of canisters produced.

The grout from the radionuclide leach does not meet Class A requirements, but the leaching efficiency assumption used to split cesium, strontium, and TRU are estimates based on very limited data. The grout limits for arsenic and fluorine could probably be elevated with further testing of grout formulations, and this would allow the reference waste loading of 5M sodium to be achieved.

The uncertainties associated with ion exchange treatment of the alkaline wastes also apply to this flowsheet (see Section 5.3.4).

5.4.5 Advantages and Disadvantages

The advantages of the radionuclide leach flowsheet are that simple operation, minimal capital investment, and processing could be started on an accelerated schedule compared to facility options. The use of corrosive compounds is minimized.

The potential disadvantages for the radionuclide leach are that the separations are not as good as with other options, and the glass and grout volumes are not minimized without additional processing to remove phosphorous or reprecipitation of nuclides from the leachate. The grout produced would not meet the more restrictive grout requirements that may be applied in the future such as NRC Class A requirements.

6.0 BRITISH TECHNOLOGY

During 1991 BNFL, Inc., a wholly-owned subsidiary of British Nuclear Fuels, was contracted by WHC to perform an engineering study of the Hanford Site waste pretreatment mission. This activity addressed both process and facility concepts. During 1993 BNFL was tasked with developing a means to pretreat Hanford Site NCRW and CC wastes, which is the activity discussed in this report. However, the contract was not placed sufficiently early to allow BNFL enough time to bring their study very far along at the preparation of this status report. We anticipate that BNFL will contribute more to the pretreatment program than Section 6.0 indicates.

6.1 INTRODUCTION

The development of radioactive waste pretreatment flowsheets draws on numerous years of BNFL experience in PUREX and chemical separations technologies developed around the world to support reprocessing. The development of a modern PUREX flowsheet is based on solid experimental and operational data gained from over 40 years of commercial, government, and development programs. The basic feed streams to a PUREX process are well characterized and defined. The risk to plant operations due to uncertainties in process performance is very small. Changes in operational or feed requirements can, in most cases, be quantified through literature searches.

However, the development of processes to separate radioactive waste species into narrow bands for differing disposal criteria is not on such firm ground or solid experience base. The suggested flowsheets described in this report, and the previous work performed by PNL and WHC, can only be viewed as a starting point. There is a tremendous need for laboratory and pilot scale development, with both chemical simulants and radioactive materials, to define precisely the performance and equations that drive performance of these flowsheets. This work must be done at an early stage to ensure the designers have confidence in the performance of the selected equipment, processes, and flow rates. Without a detailed development plan, supported by pilot work and a detailed waste characterization program, the flowsheets developed, by anyone, are speculative at best.

6.1.1 Objective

The objective of this study was to conduct a preconceptual engineering study of alternative pretreatment systems for Hanford Site NCRW and CC waste, based on BNFL technology and experience. This included the preparation and discussion of mass balanced flowsheets.

6.1.2 Scope

Two flowsheets for the pretreatment of Hanford Site tank waste were prepared, one for the processing of NCRW and the other for processing CC waste. Each flowsheet was discussed in the BNFL report (BNFL 1993), and a technical description given for the individual processes that make up the

flowsheets. By contracting BNFL to perform this study, steps have been taken to ensure that BNFL technologies potentially relevant to Hanford Site pretreatment needs have been identified.

6.1.3 Criteria

In the development of any new plant, process, or project, BNFL develops selection criteria to aid the designer in reaching objectives. The criteria are established by both management and the users of the facility. The criteria are assigned weights, again agreed to in advance of design work, to allow a documented selection process to be implemented. Often tools like Kepner-Tregoe are used. Paramount to the BNFL approach, regardless of the tools used, is the agreement by all parties to the criteria that will be used to judge the selection process. This must absolutely be established at the outset, or designers will have no clear path, nor a valid, documented means to judge results. Without agreed criteria, process selection may merely be done based on personality of the presenter or skillful presentation of less than detailed results. This will eventually result in a plant or project that does not live up to the operations requirements.

A generic set of criteria that BNFL would use initially is as follows:

1. Reasonable chance of successful development within a reasonable timescale
2. Proved at pilot scale with active species
3. Demonstrated safe with little uncertainty
4. Conventional engineering with little novel or untried equipment
5. Demonstrated compatibility with associated plants
6. Simple, easy-to-control process with minimum process steps and unit operations
7. Demonstrated acceptable lifetime costs.

This set of criteria, amplified by others, would be used to select among competing processes. Many of the processes will have been taken to active pilot-scale work to fully understand their performance. In the case of the NCRW and CC work, included would be the meeting of HWVP and grout feed specifications with an option of meeting Class A LLW definition. These criteria would be bounded by BNFL criteria 5.

6.1.4 Assumptions

DFs in this report are defined as the ratio of species flowrate at the input to a stage divided by the species flowrate from the stage in the stream that has been 'cleaned.'

The DFs for ion exchange are those found in practice in BNFL's Site Ion Exchange Plant (SIXEP) plant. The values of 10 for ^{60}Co , ^{95}Nb , ^{95}Zr , ^{106}Ru , ^{125}Sb , ^{144}Ce , ^{154}Eu , and ^{155}Eu are assumed on the basis that apart from the DFs on alpha, strontium, and cesium, there is a DF of 500 on total beta.

The DFs for the floc precipitation plant are generally based on those predicted for BNFL's Enhanced Actinide Removal Plant (EARP) plant.

The values of 10 for the cations aluminum, chromium, lanthanum, magnesium, molybdenum, and zirconium are assumed and require confirmation.

Because the liquor from NCRW sludge is much more concentrated than the feed to EARP, it is likely that relatively more precipitate will form when treating NCRW.

6.1.5 Engineering Philosophies

Several aspects of the BNFL approach to nuclear waste processing, as they relate to the Hanford Site HLW pretreatment study, are briefly stated below. These bases have been broken down into systems engineering and facility design considerations.

Systems Engineering. The main computer model used for design of chemical processes is ASPEN Plus II for static system evaluation and ASPEN Speed Up for dynamic system modeling. Both software are commercially available in the United States through ASPEN Technologies. Extensive modification of each software package has been conducted for specialized application to nuclear fuel reprocessing and waste management processes.

In addition to computer simulations, BNFL has adopted a company philosophy that incorporates systems engineering principles throughout the duration of a project. Approximately 300 personnel at the Sellafield Site are trained in a value engineering (VE) process, which is very similar to the systems engineering methods being used at Hanford Site. Personnel from all disciplines are actively involved. The VE process is chaired by a person not directly related to the project, but who works at any of the Sellafield facilities. The VE process evaluates each project and provides recommendations to the project manager for incorporation. All recommendations are tracked, and feedback on incorporation is conducted. A centralized group handles mainly administrative activities such as personnel training, arranging for project reviews, and monitoring benefits of the VE program. Although a consulting agency was initially used to establish the VE program and train core personnel, all VE work is now done internal to BNFL.

Facility Design. The BNFL nuclear waste processing facilities were designed and constructed to recover fissionable materials from 5-pint fuel rods for recycling. Secondary waste minimization is an important criteria. The facility life is set as a business decision. Process equipment is designed as much as possible to be reliable for the life of the facility. BNFL prefers enclosed cells over canyons, and designs mechanical equipment such that motors and drive systems requiring periodic maintenance can be located outside the cells for access.

Overall design decisions are made on the basis of life-cycle costs. Much time is spent preparing specifications for the process and facility. Once the cost of the facility is established, the manager has strict control of the money and has to build the facility within the estimated budget. Reprocessing contracts are established based on estimated facility costs. BNFL performs the design of the facility and manages the construction. They will use design and build contracts for some equipment. They provide specifications to a subcontractor who may perform some design and constructs the equipment. The equipment performance is tested, and the subcontractor is held responsible for meeting the specifications for the equipment performance.

6.2 NEUTRALIZED CLADDING REMOVAL WASTE

This section is a summary of the flowsheet and material balance discussions presented in the report (BNFL 1993).

6.2.1 Flowsheet Summary

Hanford Site NCRW is currently stored in mild steel tanks under alkaline conditions. Only the sludge, not the supernate, is to be considered for treatment. The basic processing required is the separation of the sludge into streams suitable for vitrification and grouting.

It should be noted that limits for vitrification and grouting are not available for all the cations and anions present in NCRW. The GTF acceptance criteria shows, for example, the limit for calcium metal, whereas the limit for fluorine is expressed as the fluoride ion. BNFL questions that their interpretation of such limits is always correct.

Separation is to be achieved by sludge dissolution in nitric acid followed by the TRUEX process to separate TRU elements from other species. The TRU stream is suitable for vitrification in terms of its activity content, and the raffinate from the TRUEX process will be low enough in actinides for grouting. It is suggested that both TRUEX outlet streams should be made alkaline with nitrite addition for storage in mild steel tanks before their later vitrification and grouting when plants are available.

Examination of preliminary mass balances for normal concentration and maximum concentration NCRW indicates that the TRU streams plus undissolved solids are too high in phosphorous and uranium for vitrification. Making these streams alkaline with NaOH and NaNO₂ for storage puts the sodium and nitrite contents above acceptable limits for vitrification. The combined raffinate and wash streams from the TRUEX process, which are intended for grouting, are too high in fluoride and beta/gamma activity to give satisfactory grout. The initial approach to solving the problems encountered has been to look for ways of making the TRU plus undissolved residue streams suitable for vitrification, and then to look at the stream intended for grouting. Neither of these streams can be considered in isolation as further processing results in additions to both streams and the redirection of some species from one stream to the other. However, the approach adopted by BNFL offers a solution to the problem which, with further development, they expect to be capable of treating both NCRW and CC waste.

An underlying assumption in the preparation of this flowsheet is that there is no low active effluent disposal route to the sea as is available to BNFL. Instead, all process materials including water end up in glass or grout. Whenever possible, recycled reagents including water should be used to reduce the burden on the grout stream. This may mean an evaporation stage to produce low activity clean condensate for recycle, and/or reuse of nitric acid, sodium hydroxide, or sodium carbonate that have been used in the washing of solvents (or chemical compounds from any other source).

The split of components through the TRUEX process has been modeled statically using ASPEN Speed Up. However, there are many gaps in the detailed solvent to aqueous concentration ratios. Quantified ratios are needed for a successful model, which for now must be obtained by intelligent guess-work since no better information is available. Therefore the ASPEN Speed Up model (an attachment of the BNFL draft report) has been run to converge into a single solution, and the resulting input stream to output stream ratios over the whole TRUEX process for each species have been transferred to the current spreadsheet model.

If the spreadsheet model is used for normal concentrations of NCRW with only sludge dissolution, filtration, pH adjustment, and TRUEX processing followed by separately making the streams alkaline, then the uranium and phosphorous contents of the stream for vitrification are too high. These levels of uranium and phosphorous can be reduced by separating out the uranium in another process stage (PUREX process) and adding calcium and iron to dilute the phosphorous and the remaining uranium.

If the stream for vitrification is made alkaline using NaOH with nitrite addition, the resulting stream is too high in sodium and nitrite for vitrification. The fluoride and beta/gamma contents of the stream intended for grouting are too high for grouting.

Excessive aluminum can be diluted by the addition of calcium and iron, which reduces or eliminates the need for uranium separation in the stream for vitrification. Additionally, the stream for grouting contains too much TOC.

The process stages that make up the overall Hanford Site waste pretreatment flowsheet, Figure 6-1, are as follows.

6.2.1.1 Dilution, Neutralization, and Filtration. Dilute and neutralize the NCRW sludge with water and nitric acid (15.7M). Use an air sparge to mix the water, acid, and sludge. The air sparge will assist in the removal of the CO₂ and NO_x. BNFL does not anticipate problems driving off ammonia, which will mix with the NO_x to form ammonium nitrate in the offgas ductwork. The sparge air containing NO_x and CO₂ will be scrubbed using NaOH. The scrub liquors are added to the stream for grouting after the proposed floc precipitation. About 5% of the sludge will not dissolve. These solids will be separated using filtration. The solids will be washed with nitric acid and water, and the washings added to the filtrate.

6.2.1.2 Solvent Washing. The filtrate contains TOC as materials for which no quantitative details are available. Provision has been made to wash the filtrate with a suitable organic solvent to remove as much TOC as possible. It is not known what effect TOC will have on the TRUEX solvent, but excess TOC is likely to rapidly reduce the efficacy of the TRUEX and increase TRUEX solvent makeup rate.

A filtrate and solvent separation stage is required. The solvent will be recovered, probably by distillation, but this depends on the solvent selected. Solvent rich in TOC will be disposed of by the same process as required for disposal of spent TRUEX solvent.

6.2.1.3 TRUEX Extraction Process. After TOC removal, the filtrate and washings will be adjusted for acid and relevant species molarity by the addition of nitric acid and/or water in preparation for TRUEX processing. The TRUEX process raffinate and Na_2CO_3 wash streams will be combined.

6.2.1.4 Uranium Separation. The TRUEX strip stream containing the TRU elements will be subjected to the PUREX process to remove uranium, if necessary, before being combined with the undissolved solids from the filtration stage. The TRU stream will be stored as a suspension in acid conditions and will be kept in long-term suspension.

Before vitrification, the TRU stream will be slurried with calcium and iron to dilute species (aluminum and phosphorous), which otherwise are above the levels permitted for vitrification. Ion exchange and floc precipitation solids also will be added. BNFL was informed by WHC that phosphorous content of the TRU stream cannot yet be quantified accurately.

6.2.1.5 Fluoride Precipitation. Provision has been made to add calcium to the TRUEX raffinate and wash streams to precipitate CaF_2 . BNFL believes that the CaF_2 remains insoluble at the pH of grout and suggests that the CaF_2 content should not be counted as part of the calcium limit. If the limit in GTF feed acceptance criteria (Hendrickson 1991) were for Ca^{2+} , there would be no doubt on this matter. How much beta/gamma activity comes down with the CaF_2 precipitate is not known.

The amount of beta/gamma activity that the following ion exchange and floc precipitation processes can remove is insufficient as yet, based on BNFL's experience with their effluents, to achieve a stream that meets all the limits imposed by the grout acceptance criteria.

6.2.1.6 Ion Exchange. Following calcium addition and separation of the precipitate, the filtrate pH will require adjustment before passing through an ion exchange plant for principally removing cesium and strontium. The system will be similar to BNFL's SIXEP plant or the plant proposed for the IPM project, which is a two-stage plant suitable for treating effluents with high sodium content. The spent ion exchange medium containing the cesium and strontium could be vitrified. Alternatively it may be shown to be preferable to operate an ion exchange system in alkaline conditions and to put the system after the precipitated floc separation.

6.2.1.7 Floc Precipitation. Following ion exchange, the permeate will be treated with NaOH to precipitate a floc of aluminum and zirconium. Additional iron will be added if required, as will sodium nickel ferrocyanide to assist in cesium precipitation. This process stage will be generally similar to BNFL's EARP plant. The concentrations in the EARP feed streams are different to and generally lower than for the NCRW stream. It is possible that much higher quantities of beta/gamma activity will be taken out into the floc precipitate than those predicted from EARP.

Addition of carbonate may be used to precipitate strontium carbonate which would be separated with the floc. This would reduce the need for an ion exchange for removal of strontium. The precipitated floc will be separated by ultrafiltration, and the concentrated floc could be vitrified.

6.2.1.8 Waste Solvent Treatment. The waste solvents from the initial filtrate washing of TRUEX degradation products and from the separation of uranium by the PUREX process may be treated by successive washings. Suitable wash reagents would be nitric acid, sodium hydroxide, and sodium carbonate. Washing would be followed by one of the following:

1. Solvent destruction using boiling alkaline hydrolysis (a plant operating this process is proposed and is being designed for BNFL's Solvent Treatment Plant)
2. Destruction using calcination (the French Atomic Energy Commission process)
3. Burning.

Any of these processes will result in an organic stream that requires burning, followed by water scrubbing of the offgas and a stream high in phosphorous that will be sent for grouting. A selection of the best process (1, 2, or 3) might be governed by the following:

- A. Process will best suit a solvent of low activity
- B. Process will produce a large amount of liquid effluent that must be grouted
- C. Process is possibly the most suitable in the circumstances as we currently understand them.

6.2.2 Material Balance Summary

An overall spreadsheet has been developed that provides the mass balance for both NCRW and CC waste (BNFL [1993] Table 5). This spreadsheet can model the processing of any combination of NCRW at normal or maximum concentrations with any relative quantity of normal or maximum concentration CC, and the CC can be any ratio of sludge to supernate.

The BNFL (1993) shows that for normal concentration NCRW and without any of the following--TOC removal, uranium removal, calcium or iron additions to HWVP, and calcium fluoride precipitation--zirconium is twice too much for

optimum glass waste loading, and fluoride ion is 5.7 times too much for optimum grout loading. The figures for active species can be reduced nominally by ion exchange and floc precipitation DFs based on BNFL's SIXEP and EARP plants. At a later date, it must be determined how much calcium and iron are added to the process.

Similarly, Table 2 of BNFL (1993) showed the results for NCRW at maximum concentration. Aluminum was too high for vitrification by a factor of 1.4. Fluoride ion was still too high, now by a factor of 4.

Dilution or moving one species from the vitrification stream to the grout stream or vice versa should solve the problems of meeting the vitrification and grout specifications. The flowsheet and mass balance show the results of diluting the stream for vitrification with calcium and iron in HWVP. Calcium and iron were chosen because the NCRW sludge is well below the vitrification limits for these two species, and they are both readily available. Dilution was chosen as a technique because BNFL is unaware of any process that will satisfactorily take aluminum or zirconium from one stream to another without carrying with it a large proportion of the activity in the stream.

For the mass balance calculations, we assume that at the initial dilution and neutralization stage, the slurry will be neutral and not acidic. We realize that in practice the slurry will be acid, which is the reason for assuming all the carbonate and nitrite are driven off as CO_2 and NO_x . Undissolved solids were assumed to be 5%.

We assumed that 15.7M acid is used with water for washing the filtered solids. Dilute acid cannot give a 1.8M acid solution from neutral solids. When the zirconium concentration is high enough, it is diluted.

A stage for removing TOC is included between filtration of the undissolved solids and the TRUEX extraction. We assumed that a solvent can be found that will remove substantial amounts of the TOC, although the TOC is not yet defined. The amount of solvent required to carry out the TOC to a solvent treatment plant has been set at 1% of the volume of aqueous feed to this stage for normal, and at 5% for maximum concentration TOC.

Mass balance tables as backup to the flowsheet for treating NCRW at normal and maximum concentrations are presented in BNFL (1993). They show that the effluent streams for vitrification and grouting will probably meet the required specifications. Assumptions made for DFs must be achieved to meet the specifications that require verification, as the NCRW material is substantially different from the BNFL streams on which the DFs are based.

The fractional split through the TRUEX process is given in the bottom block of the BNFL (1993) spreadsheet. Essentially all the uranium, plutonium, and americium go into the strip stream and are subsequently vitrified. TRUEX makeup solvent will be required, and the rate has been set at 1% of the aqueous feed to the TRUEX process. The amounts of active and inactive species that will be carried out in the waste solvent streams will be low and is currently set at zero.

Tables 3 and 4 of BNFL (1993) for normal and maximum concentration NCRW show the effects of calcium and iron additions and total dry mass flow to

HWVP. The need for a uranium extraction stage using the PUREX process system when treating NCRW appears to depend on the incremental cost of vitrification. The preliminary mass balance showed that if the TRUEX strip and undissolved solids were combined and then neutralized and treated with sodium nitrite for storage in mild steel tanks before vitrification, then the sodium level would be too high for vitrification. This mass balance does not repeat that neutralization; it assumes that acid storage will be used. BNFL does not believe there will be any problems using stainless steel for storage of this acid slurry.

The combined wash and raffinate streams from the TRUEX process are treated with calcium to precipitate CaF_2 . The CaF_2 will be separated off to leave a clear solution for the subsequent ion exchange stage. The CaF_2 is returned to the stream for grouting before neutralization. The quantity of other species, active or inactive, which will be in the CaF_2 stream is as yet not quantified, nor is the quantity of liquid required to carry the CaF_2 .

It is assumed that an ion exchange system can be found that, in conjunction with a floc precipitation system, will have adequate DFs for the active species to give a satisfactory effluent for grouting. The flowsheet shows an ion exchange plant operating in acid conditions upstream of the alkaline floc precipitation plant. It is possible that the order of the ion exchange and floc precipitation may be reversed, and that the ion exchange system should be under alkaline conditions after floc precipitation.

The values for DF given in the spreadsheet are derived from BNFL's SIXEP and EARP plants for ion exchange and floc precipitation. The streams flowing into the proposed ion exchange and floc precipitation plants for NCRW are very different from BNFL's streams to SIXEP and EARP. The SIXEP stream is much lower in sodium, hence the plant for NCRW may be like that proposed for the IPM process (i.e., two stage). The EARP stream is much more dilute than the stream for NCRW. This implies that better DFs may be obtainable for NCRW than in EARP, as more will precipitate at a higher concentration. The amount of ion exchange medium required is quantified based on SIXEP at 1 m^3 for $1.8 \times 10^{14} \text{ Bq}$ total alpha and beta. The aqueous effluent from HWVP returned for grouting is assumed to have a high DF of at least 1×10^5 , derived from evaporation, to prevent recontamination of the stream for grouting.

The spent solvents from washing the initial filtrate to remove TOC from TRUEX and PUREX will be combined. On the basis of BNFL's Solvent Treatment Plant, we assumed that the spent solvent will be washed successively with 0.1M nitric acid 1:1 volume ratio, 0.25M sodium carbonate 1:1 volume ratio, and 23% NaOH 1:3 aqueous:solvent volume ratio. Subsequently, the solvent will be destroyed by boiling alkaline hydrolysis, calcination, or burning as described in Section 6.2.1 of this report.

For the mass balance, it is assumed that 10 times the volume of solvent will be produced as aqueous effluent at the solvent destruction stage. This effluent will be suitable for adding to other streams for grouting. It is assumed that the volume of solvent leaving the treatment stage for burning is the same as that entering the destruction stage. The burnt gasses will require scrubbing and the quantity of scrub liquor, possibly very dilute acid, is assumed to be 15 times the volume of solvent being burnt. The scrub liquor is assumed to return to the floc precipitation neutralization stage.

Attention has been given to the amount of water required for the various cleanup stages, and reagents have been accounted for at maximum concentrations. In practice, more dilute reagents may be required. It is suggested that dilution water and all the water required in the whole process is obtained as far as possible by recycling water. Fresh water should, in principle, only be used for the burnt gas scrubber and the NO_x offgas scrubber, as the gaseous effluents are assumed to be discharged to the atmosphere. Candidate streams for evaporation and the reuse of the condensate are those from HWVP. Such evaporations have not been shown on the process flowsheet or in the mass balance spreadsheet.

BNFL (1993) report Tables 5 and 6 show the overall result of the treatments proposed on normal and maximum concentration NCRW. In each case, the effluents for vitrification and grouting are within feedstock specifications. In these two tables, the DFs in the right hand columns are obtained from values in the bottom block columns 20 and 21, and are now DFs that must be achieved.

The DFs that have been changed to values that must be achieved are those for ¹⁰⁶Ru, ¹²⁵Sb, ¹³⁴Cs, and ¹³⁷Cs. BNFL believes that the plant differences between the proposed NCRW treatment and BNFL's plants should make such DFs possible, although development work is essential.

6.3 COMPLEXANT CONCENTRATE WASTE

The BNFL contract was placed during FY 1993 at a late date; therefore, BNFL has not yet had an opportunity to prepare a CC waste report. After investigating several concepts for safety issue resolution, BNFL concluded that none of their approaches were inherently superior to those presently being considered for Hanford Site application. At this time, BNFL intends to adopt the oxidation technologies being developed for the IPM program, specifically calcination and hydrothermal treatment.

This section, when completed, will be a summary of the flowsheet and material balance discussions presented in future BNFL documentation.

6.4 UNCERTAINTIES

Before the development of detailed flowsheets or process diagrams, BNFL would require characterization of the waste. Characterization is performed to achieve the following:

1. Develop process options from retrieval to disposal
2. Provide radiochemical and chemical data for process flowsheet and plant design
3. Provide data for safety case (safety analysis) work
4. Formulate simulants for inactive fullscale process development trails and plant commissioning work

5. Define waste variability for process design and quality assurance
6. Specify effluent treatment and particulate filtration needs.

For this small project, BNFL used professional judgement and supplied data for the process flowsheet. There was insufficient time to develop multiple flowsheets for subjection to decision analysis tools to pick a 'best.' The work described should then be considered as a first cut, with the recognition that additional effort and sampling programs are required..

As the program by WHC proceeds, it is recognized that a comprehensive sampling and characterization program needs to be implemented, along with detailed pilot work tied to specific process selection criteria that will result in a successful plant.

7.0 FRENCH TECHNOLOGY

In 1992 Numatec was contracted to make processing recommendations for Hanford Site NCRW and CC waste, based on French experience. This section summarizes the results of a study (Numatec 1993) performed by Numatec's affiliate, the French Atomic Energy Commission, and contains preliminary processing recommendations for the above Hanford Site tank waste. The study concluded that it is feasible to pretreat NCRW and CC waste from Hanford Site waste tanks before solidification. Pretreatment removes alpha emitters and fission products with extractors from the diamide family and macrocyclic compounds using the DIAMEX and CALEX 19.5 (or CAMELS) process. Each of the two use a separate process of the French Atomic Energy Commission.

7.1 INTRODUCTION

A substantial amount of data was taken from Swanson (1993) in developing recommended conceptual process flow sheets for treatment of the NCRW and CC waste. This is particularly the case for NCRW, which is the subject of the majority of published studies. Some of the recommended process flow sheets described in this section are identical to those proposed by Swanson (1993). In particular, the design of the reliable process appears to be conditioned on dissolving the sludge as completely as possible by nitric acid dissolution and liquid-liquid treatment of the resulting solution to separate the radionuclides from the inactive elements.

7.1.1 Objective

The objective of this study was to conduct a preconceptual engineering study of alternative pretreatment systems for Hanford Site NCRW and CC waste, based on French technology and experience. This included the preparation and discussion of flowsheets.

7.1.1.1 Neutralized Cladding Removal Waste. The objective of NCRW pretreatment is to separate the waste into two streams:

1. One stream containing most of the inactive components of the waste and from which alpha, beta, and gamma emitters have been removed to a level permits grout treatment and near-surface disposal
2. One stream containing the majority of alpha-emitting radionuclides, certain beta/gamma emitters, and a small amount of the waste's inactive components, which will be vitrified for disposal in a deep geologic repository.

Studies performed by PNL have demonstrated that this objective requires almost total dissolution of the waste in a nitric acid medium so that decontamination by liquid-liquid separation is possible. If the upper limit for alpha activity in the waste before pretreatment is assumed to be 3.75 Ci/ton, and if the target for residual alpha activity after pretreatment is 0.05 Ci/ton, then a DF of 75 must be achieved for plutonium and americium.

7.1.1.2 Complexant Concentrate. The objective of CC treatment is the same as for NCRW. However, different constraints must be taken into consideration:

1. Treatment relates to the suspension liquid in the case of CC, whereas the relatively uncontaminated supernatant in the tanks containing NCRW does not need treatment
2. The wide variety of organic compounds in significant concentrations must be destroyed before pretreated CC can be grouted.

The average alpha activity of the suspension (solids + supernatant) is estimated to be 0.55 Ci/ton. Therefore, to achieve the target for residual alpha activity of 0.05 Ci/ton, the DF to be achieved for alpha is 11. The required efficiency for the alpha decontamination process for CC waste is therefore about seven times lower than the efficiency required for NCRW.

7.1.2 Scope

Two flowsheets for the pretreatment of Hanford Site tank waste were prepared, one for the processing of NCRW and the other for processing CC waste. Each flowsheet was discussed, as were technical issues relevant to the individual processes that make up the flowsheets. The principal ions contained in the sludges were addressed:

- Na(I), Zr(IV), K(I), Si(IV), Al(III);
- F^- , OH^- , NO_3^- , NO_2^-

The principal radionuclides in the sludges also were addressed:

- Alpha emitters: plutonium and americium (733 μ Ci/L);
- Fission products: ^{134}Cs , ^{137}Cs , ^{144}Ce , ^{106}Ru , ^{125}Sb , ^{95}Nb , ^{95}Zr ;
- Activation product: ^{60}Co .

7.1.3 Criteria

The Numatec proposal did not specifically list criteria. However, various parts of the text referred to process considerations regarding criteria and are summarized in Section 9.0.

7.1.4 Assumptions

The Numatec proposal did not specifically list assumptions. However, the extensive number of uncertainties listed in Section 7.4 of this report gives insight into assumptions they will have made.

7.1.5 Engineering Philosophies

Several aspects of the Numatec approach to nuclear waste processing, as they relate to the Hanford Site HLW pretreatment study, are briefly stated below. These bases have been broken down into systems engineering and facility design considerations.

Systems Engineering. Several computer models are used to assist in facility design, process evaluation, and training of personnel. A computer model of the PUREX flowsheet (PAREX) has been developed and was used to assist in the design of the La Hague facility. The PAREX model is based upon actual laboratory results and includes actual facility data. A computer model (SIMULEX) is used to simulate the solvent extraction process for training of personnel. A diagnostic program (DIAGNOLEX) is being developed to incorporate expert knowledge into troubleshooting systems.

The main computer model used for design of chemical processes is ASPEN Plus II for static system evaluation and ASPEN Speed Up for dynamic system modeling. Both software are commercially available in the United States through ASPEN Technologies. Extensive modification of each software package has been conducted for specialized application to nuclear fuel reprocessing and waste management processes.

Facility Design. The French design their facilities to use simple equipment that can be easily changed using remote operations to minimize facility down time. The French reprocessing facilities were constructed to recover uranium and plutonium for French, German, and Japanese utilities, so the French also have a strong profit motive which drives their decisions. Processes and equipment are selected to recover and recycle highly energetic nuclear material (uranium and plutonium) in highly reliable equipment that provides safe operation of the process while minimizing secondary waste generation and environmental discharges. Stringent standards regarding worker exposure are imposed.

The French start with uranium and plutonium product and waste form specifications and design their processes, equipment, and facilities to meet these specifications. The waste forms produced must be licensed by the French safety authorities for interim storage and must meet foreign disposal specifications, because the waste glass is returned to the utility customer along with the uranium and plutonium. Identification of product and waste form specifications is an iterative process involving regulatory agencies and customers. One goal in their decision approach is to implement processes that condition wastes as they are produced, rather than store the wastes for future processing.

Chemical processes are selected that improve the decontamination of recyclable materials and contain the beta/gamma activity in the highly active part of the plant. They use laboratory, bench, and pilot scale testing to develop processes and equipment that reduce uncertainty as much as possible before designing the facility. The amount of testing performed is proportional to the uncertainty in the process and equipment. Consideration is also given to improving extraction system performance, minimizing secondary waste generation, and concentrating streams for vitrification.

The nuclear materials companies, COGEMA (Compagnie Generale des Matieres Nucleaires) and Saint-Gobain Nucleaire (SGN), have the engineering resources to design their own facilities. They also act as the manager for construction and testing of the facility. Their approach to facility design is to (1) define the basic design, (2) perform a preliminary cost estimate (+20%), (3) review the process to see where costs can be reduced, (4) redo the cost estimate, and (5) establish bonuses and penalties for design and construction.

Factors that constrain their designs include engineering principles, safety, maintenance needs, process parameters, equipment replacement considerations, environmental discharge limits, economics, and impacts of abnormal operations. Separate cells are preferred over canyon facilities. They try to standardize equipment designs so equipment can fit into standard casks, and design to avoid the need for special tools.

Cost-effectiveness of the facility is sought through equipment reliability. An equipment design program is followed which involves identifying specifications, testing equipment performance, and developing an equipment performance qualification file to provide reliability. Selection of facility life is a business decision based on the cost to provide a particular capacity and consideration of the total material that needs to be processed. Reliable equipment is then defined as performing without failure for the facility life. When reliability cannot be ensured, equipment is designed for remote removal.

7.2 NEUTRALIZED CLADDING REMOVAL WASTE

This section consists of discussions of the NCRW flowsheet and material balance.

7.2.1 Flowsheet Summary

The basic process flow sheet for NCRW is shown in Figure 7-1, and the principal process steps are described in the following paragraphs.

7.2.1.1 Nitric Acid Dissolution. After the addition of water, fluidization of the mixture, and removal from the tanks, the sludges are subjected to nitric acid dissolution to solubilize as many solids as possible. Sulfamic acid must be added to the dissolution medium to avoid the production of nitrous vapors due to the presence of nitrite ions in the sludges.

7.2.1.2 Solid-Liquid Separation. The sludge dissolution liquid is clarified in a second stage which generates two streams: the residual solid, which is approximately 5% by weight of the initial sludges and contains 3% of their total alpha emitters; and the dissolution liquid containing 95% of the sludges, most of the beta/gamma emitters, and 97% of the alpha emitters.

There are two treatment options for the residual solid: route it to the vitrification process or combine it with the inactive elements in the dissolution liquid, which will be decontaminated at the tail end of the extraction cycles and routed to grout treatment.

Figure 7-1. Process Flowsheet for Neutralized Cladding Removal Waste.

The second option looks attractive because it drastically reduces the amount of waste to be vitrified, and therefore, the cost. Numatec did not feel this was the best solution because it gave an alpha DF of 33 for all waste combined, far below the specified DF of 75. Consequently, only the first option was presented, i.e., routing of the dissolution liquid to the extraction cycles (see Figure 7-1).

7.2.1.3 Actinide Extraction with the DIAMEX Process. The feed must be adjusted to achieve the specified feed composition for the DIAMEX process. The composition of the feed to be processed after adjustment is provided in Figure 7-2. Detailed data, assumptions, and calculations relevant to feed adjustment are given in the Numatec draft report (Numatec 1993).

Flocculation and clarification appear to be necessary for successful extraction operations, especially when they rely on centrifugal extractors. The formation of interphase crud has been observed when TRUEX solvent contacts the adjusted, but untreated, dissolution liquid, which could also occur in the DIAMEX process. It is possible that the crud consists of siliceous compounds, in which case flocculation with a gelatin additive may resolve the problem. After clarification, the solid could easily be routed to grout treatment.

The liquid from the preceding step is treated by liquid-liquid separation with a diamide solvent to extract the alpha emitters. In addition to removing plutonium and americium, the solvent also extracts uranium and the lanthanide isotope ^{144}Ce . Following the extraction cycle, the actinides and lanthanides are routed to the vitrification process, while the extraction raffinate, which has been decontaminated in alpha emitters, is routed to the cesium extraction cycle.

To avoid partial co-extraction of Fe(III) and especially of Zr(IV) , the loaded organic phases will probably require rinsing with an aqueous solution containing a strong complexant of metallic ions.

The uranium, plutonium, and americium actinides in the feed are extracted by counter-current contact of the feed with a solvent consisting of a solution of 0.5M diamide in an aliphatic carbide: hydrogenated tetrapropylene. An aqueous phase to organic phase volume (A/O) ratio of 0.33 at extraction was used, which should give an adequate actinide extraction factor. The lanthanides present in the feed, consisting of the ^{144}Ce radionuclide and the inactive elements lanthanum and neodymium, are co-extracted with the actinides.

A fraction of the Zr(IV) , Fe(III) , and fluorine ions present in the feed may end up being co-extracted. The loaded solvent must therefore be rinsed in an aqueous solution (first rinsing cycle, A/O = 1) containing a complexant high in Zr(IV) and Fe(III) . Oxalic acid was chosen as an example, even though it could cause certain problems, such as precipitation of Zr(IV) . It is probably better to choose another complexant that does not create this concern and which, like oxalic acid, is a good complexant for Zr(IV) and Fe(III) in an acidic medium without complexing the actinides. The other complexant should be able to be destroyed as a gaseous compound.

Figure 7-2. Material Balance for Neutralized Cladding Removal Waste Treatment by the DIAMEX Process.

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To reflux the complexant added during the first rinsing cycle, which would have been partially co-extracted, to the aqueous phase, the loaded solvent must be rinsed with a 4M nitric acid solution (second rinsing cycle; organic phase to aqueous phase volume [O/A] = 1.66).

A third rinsing cycle (O/A = 5) of the loaded solvent will substantially lower its concentration of HNO_3 before reextracting the actinides.

Actinide reextraction is achieved by contact between the loaded solvent and a 0.3M solution of sodium carbonate. The active lanthanide, ^{144}Ce , and inactive lanthanides lanthanum and neodymium are reextracted along with the actinides. This solution is then routed to the vitrification process. A special solvent treatment step does not seem necessary at this stage of the process; most of the solvent's properties should be restored after the actinide reextraction stage.

The raffinate, cleaned up of actinides and lanthanides, contains most of the inactive substances from the initial sludge. A new solute is present, the complexant added during the first rinsing cycle. This will either be destroyed during concentration of the effluent produced by the cesium extraction cycle, or it will be partially present in the neutralized solution, which contains primarily sodium nitrate, and released to the environment. The raffinate, decontaminated in alpha emitters, is routed to the cesium extraction cycle.

7.2.1.4 ^{137}Cs Extraction Cycle. The liquid from the DIAMEX process cycle is treated by liquid-liquid separation using a solvent containing a macrocyclic compound with a strong affinity for cesium. It should be noted that no feed adjustment stage is included. For the chemical conditions of the effluent exiting the DIAMEX process, the affinity of cesium for the solvent must be high.

Two streams exit this extraction cycle: (1) a minor stream consisting of the solution from reextraction of cesium, which is routed to the vitrification process, and (2) a major stream from which cesium has been removed. Several options are available for the treatment of the latter stream, as briefly described in the Numatec (1993) report, page 33. The draft report also contains a description (page 37) for cesium extraction on a calixarene-coated film (the CAMELS process) and for centrifugal extraction (the CALEX process).

7.2.1.5 Coprecipitation Process. The streams exiting the actinide and cesium extraction operations still contain radioelements. Numatec did not hazard estimates of the residual radiochemical composition of these streams at this time without prior testing. However, they assumed that the majority of the actinides, cerium, and europium will have been extracted by this stage. What remains in the effluent, therefore, are cobalt, ruthenium, antimony, and the $^{95}\text{Zr-Nb}$ pair.

The first treatment objective is to insolubilize these radioelements in order to solidify them; the residual nitrate solution is released or undergoes additional treatment. Coprecipitation therefore offers the advantage of reducing the volumes of waste to be solidified.

Treatment consisting of neutralization and the addition of complementary reagents will precipitate most of the salts from the initial sludges as well as the soluble salts, such as nitrate and sodium fluoride, remaining in the supernatant. It is preferable to completely insolubilize the fluorides if the effluent is to undergo thermal treatment before release.

In summation, the recommended process is as follows:

- Addition of hydrazine hydrate to destroy any remaining nitrites in an amount that is stoichiometric in relation to the effluent's nitrite concentration
- Addition of Ti^{4+} in sulfate form to entrain residual alpha and antimony, and decontamination by precipitation of the titanium in the form of the hydroxide $Ti(OH)_4$
- Neutralization of the effluent to a pH of 8 using lime to facilitate fluoride precipitation from the solution
- Addition of cobalt sulfate and sodium sulfide to form a precipitate of cobalt sulfide, which will entrain the ruthenium and cobalt
- Possible addition of a flocculent to refine precipitation.

For the La Hague effluent, this type of treatment results in a DF of 25 to 100 for ruthenium and 10 to 50 antimony.

7.2.1.6 Selection of Denitrification Process. Thermal denitrification on a fluidized bed would appear to be difficult for effluents as complex as those of the Hanford Site, given the risk of fouling. In this case, the LEAFLASH process is recommended because it is less sensitive to this phenomenon if hygroscopic salts are controlled.

Treatment consists of simultaneous injection of the effluent and microspherical alumina in the process equipment in an amount that is stoichiometric in relation to the nitrates. Under these conditions, the nitrates convert to sodium aluminate, which is collected at the foot of the column and in the equipment's tray filter. The salts contained in the effluent are also extracted at this stage. The nitrous vapor produced by decomposition of the nitrates is diluted in the flow of hot air injected into the head of the dryer and may be processed after passing through a filter.

7.2.2 Material Balance Summary

A material balance for key cations, anions, and radionuclides during the different steps of the DIAMEX process is given in Figure 7-2. The Numatec draft report did not include a mass balance for the remainder of the suggested pretreatment flowsheet.

7.3 COMPLEXANT CONCENTRATE WASTE

7.3.1 Flowsheet Summary

The basic process flowsheet for the treatment of CC waste is shown in Figure 7-3. The main steps in the process are described below.

7.3.1.1 Nitric Acid Dissolution. The biphasic mixture in the storage tanks is mixed to fluidize it and then transferred to the reaction vessel, where solids are solubilized by the addition of nitric acid. According to studies performed in the United States, there is no difficulty in dissolving the solids and solubilizing the radiocontaminants. The presence of large amounts of nitrite ions in the mixture requires that either an antinitrite reagent be added to the feed before acid dissolution, or that nitrous vapor be recovered to reconstitute the nitric acid for recycling.

7.3.1.2 Solid-Liquid Separation. The dissolution liquid for CC waste is clarified; however, the residual solid content represents only a small proportion of the sludge contained in the initial waste. Thus, in view of the average alpha DF of 11 to be achieved for the entire process, it should be possible to route this residual solid content to grout treatment after mixing it with decontaminated saline components produced by liquid-liquid separation of the solution after acid dissolution. However, the preferred approach is to route this solid residue to the vitrification process (see Figure 7-3). The clarified dissolution solution is routed to the organics destruction process before the extraction cycles.

7.3.1.3 Destruction of Organics. The presence of a wide variety of complexing organics raises a certain number of problems in the later stages of the process:

- Potential variation in the actinide distribution coefficient during extraction with the DIAMEX process
- Potential variation of strontium distribution coefficients in the extraction cycle with macrocyclic extractor
- Incompatibility with feed specifications for grout treatment.

It is preferable to destroy the organics completely before extraction. Although the actinide extraction cycle in the DIAMEX process requires a rinsing solution containing an organic complexant (which will itself be destroyed before the decontaminated solution is sent to grout treatment, as discussed later), it is preferable to destroy organics before actinide extraction, which gives better control over the process.

Several processes may be used to destroy organics:

- Reaction with an electrogenerated oxidizing reagent, in which case the mediator pair must be chosen. For the Ag(I)/Ag(II) pair, it is clear that a silver recovery stage would have to be added to the

Figure 7-3. Process Flowsheet Complexant Concentrate.

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process, given the cost of this reagent. If the Co(II)/Co(III) pair is selected, it may not be necessary to recover cobalt, which would then be added to the residues to be routed to grout treatment.

- Reaction with hydrogen peroxide.
- Wet oxidation.

Additional details for destruction of organics are given in the final report (Numatec 1993).

Having undergone oxidation, the liquid is routed to the actinide extraction cycle. After the organics destruction step, the plutonium should have oxidized in the form of Pu(VI); in addition, the chromium will be in the form of Cr(VI).

7.3.1.4 Alpha Emitter Extraction Cycle with the DIAMEX Process. Following organic destruction, the solution is adjusted so that its composition meets the feed specifications for alpha emitter extraction using the DIAMEX process. Processing is not expected to pose any difficulty. All of the alpha emitters, plutonium isotopes, and ^{241}Am will be co-extracted with uranium. The organic phase, which is loaded with actinide ions, will probably have to be rinsed with an aqueous phase containing a complexing series such as oxalic acid and/or a reducing series to reflux any partially co-extracted Fe(III) and Cr(VI) to the aqueous phase. Unseparated beta/gamma emitting ^{90}Sr and ^{137}Cs are contained in the raffinate from the DIAMEX process.

After processing, which requires minimal alpha emitter decontamination, the alpha emitters and the uranium end up in an aqueous reextraction solution that is routed to the vitrification process, while the primary stream of materials in the extraction raffinate is routed to the cesium and strontium extraction cycles.

7.3.1.5 ^{90}Sr and ^{137}Cs Extraction Cycle with Macrocyclic Extractors. The liquid exiting the DIAMEX process, from which the alpha emitters have been removed, undergoes strontium and cesium extraction using macrocyclic extractors. It may be necessary to adjust the nitric acidity of the liquid to be processed by the addition of sodium carbonate before operation of the extraction cycles. After the extraction cycles, beta/gamma emitters are contained in a small volume of aqueous reextraction solution, which is routed to the vitrification process. The extraction raffinate containing the inactive substances initially present in the CC is routed to the concentration and denitrification step.

7.3.1.6 Nitric Acid Concentration, Denitrification, and Recycling. The raffinate from the extraction cycles, from which alpha and beta/gamma emitters have been removed, is concentrated to reduce the volume of effluent to be grouted and to remove the nitric acid. The raffinate is routed to a concentration column and the concentrated regenerated acid is recycled into a new batch of CC. The concentrate, which contains the inactive mineral components of the CC and residual nitric acid, is routed to grout treatment.

7.3.1.7 Grout Treatment. The concentrate from the previous stage is neutralized with sodium carbonate in preparation for grout treatment.

7.4 UNCERTAINTIES

The Numatec (1993) report did not address uncertainties, per se. The information below was taken from Section 6, "Additional R&D Requirements."

7.4.1 DIAMEX Process

Several studies should be performed to strengthen the conceptual flow sheets recommended in this report. A preliminary list of such studies includes the following.

7.4.1.1 Laboratory Tests using Simulated NCRW and CC Solutions. For simulated solutions whose average composition is the same as the NCRW and CC dissolution solutions, the partitioning of radionuclides and inactive solutes at various stages in the process should be studied:

1. Extraction

- Study of the distribution coefficients of actinides (alpha emitters and uranium), fission products, and activation products
- Study of the distribution coefficients of inactive solutes (cations and anions)
- Formation of interphase crud during contact between aqueous solutions and the diamide solvent
- Formation of the third phase
- Study of the possibility for kinetic extraction (in a centrifuge extractor)

2. Rinsing of the complexing agent

- Study of the influence of the type and concentration of the complexing agent on the partitioning of Fe(III) and Ar(IV), in the case of NCRW, and of the actinides

3. Actinide reextraction

- Determination of the actinide distribution coefficients as a function of the concentration of sodium carbonate.
- Perform kinetic extraction and reextraction studies (important for implementation of the process in centrifuge extractors, as well as solvent decomposition and regeneration studies.)

7.4.1.2 Laboratory Tests Using Actual NCRW and CC. Actual waste must be available to confirm the data obtained with the simulated solutions. Studies to be performed are similar to those listed above; however, a more limited number of tests may be necessary.

7.4.1.3 Pilot-Scale Tests Using Simulated NCRW and CC Solutions. Tests on counter-current treatment in the DIAMEX process should be performed with simulated NCRW and CC solutions in a battery of laboratory-scale centrifugal extractors. The use of pulse columns may be better suited to the treatment of these solutions, which are likely to contain precipitate. Assuming this technique is selected, pilot-scale treating in pulse columns should be performed.

7.4.1.4 Pilot-Scale Tests Using Actual NCRW and CC Solutions. Tests identical to those mentioned above will most certainly be necessary. Their implementation will no doubt be highly complex due to problems of availability of actual waste in the required amounts.

7.4.2 Organic Effluent Destruction Processes

7.4.2.1 Electrolytic Oxidation. There are two types of studies that should be performed relative to the destruction of solutes of organic complexing agents contained in CC by electrolytic oxidation: (1) process-related studies and (2) equipment-related studies.

Process-Related Studies. Process-related studies will help determine the characteristics of the destruction of organic compounds (quantitativity, kinetics) as a function of process operating parameters.

Equipment-Related Studies. Given the very large volume of CC to be treated, it would be advantageous to be able to use electrolytic destruction of the organic compounds in a continuous electrolyzer whose size would be much smaller than equipment designed for batch treatments. A substantial amount of work would no doubt be necessary for the development, design, and fabrication of such equipment.

7.4.2.2 Other Oxidation Processes. As previously indicated, reaction conditions should be optimized by parametric testing on a batch basis in an autoclave available to the French Atomic Energy Commission. The purpose of the tests would be to determine destruction kinetics and efficiencies, based on certain reaction parameters: temperature, pressure, catalyst concentration, and reagent addition. The tests would include detailed identification of any residual organic compounds.

At the laboratory level, studying effluent decontamination by radioelement insolubilization, by controlling pH and adding mineral entrainers, appears to be attractive. While the first stage may consist of inactive tests, the second naturally requires active testing on a representative effluent with tracers.

Full-scale demonstration of the feasibility of the process requires testing in a pilot that is sufficiently large to allow for dynamic testing. This would involve studying the physiochemical behavior to the phases inside the reaction vessel and related equipment.

7.4.3 Coprecipitation Process

The recommended process was based on studies performed by the French Atomic Energy Commission for treatment of La Hague effluent. In this case, a field of acceptable parameter variation was defined; for example, nitric acid content of the effluent from 0 to 2 N, nitrite content below 200 mg/L, or TBP content limited by solubility.

However, the Hanford Site effluent is substantially different, and the impacts of this should be examined, particularly with respect to the following points:

- DFs for ^{60}Co
- Influence of nitrite content
- Influence of the presence of fluoride, oxalate, phosphate, and ammonia
- Influence of traces of solvent.

7.4.4 Fission Product Extraction with Macrocyclic Compounds

The uncertainties associated with the use of calixarenes for solvent extraction of cesium and strontium are outlined below and were further investigated during a joint field trip by WHC and PNL investigators to the relevant French facilities. The low maturity of calixarene technology is further discussed in Section 8.0 in the cesium and strontium acid-side separations.

Cesium Extraction. Since calixarene is a recent invention, several experiments should be performed:

- Study of the influence of various parameters (e.g., acidity, salinity) on the extractive properties of calixarene
- Study of decomposition by hydrolysis (in a highly acid medium or with high nitrate content) and by radiolysis
- Modifications to calixarene to increase its solubility in diluent
- Selection of optimum extraction or transport conditions (calixarene concentration in the aqueous phase)
- Stability of the films under irradiation. These films must be optimized to achieve a high cation transport while maintaining good stability.

Strontium Extraction. Strontium extraction must be improved and verified by optimizing the following:

- Diluent
- Concentration of crown in the organic phase
- Selectivity, to avoid competition from inactive cations (H_3O^+ , Na^+ , Ca^{2+} , etc.).

7.5 ADVANTAGES AND DISADVANTAGES

The separate items below are listed randomly, and therefore are not in order of decreasing or increasing importance.

Advantages. The potential advantages offered by the DIAMEX processes were suggested by the proposal to include the following:

- Low probability of crud formation after interaction of waste dissolution liquids with products from solvent decomposition, which is particularly important for process implementation in centrifugal extractors
- Little influence from solvent decomposition products on actinide extraction or reextraction
- Simple actinide (Figure 7-4) reextraction without a complexing agent containing phosphorus, which creates problems for secondary waste disposal
- Probable elimination of a special solvent treatment step, which occurs at the same time as actinide reextraction
- No secondary solid waste produced with the use of the diamide extractor because of potential decomposition of this molecule in gaseous compounds.

The use of new macrocyclic compounds (CALEX, CAMELS processes) should make it possible to improve cesium DFs.

In principle, complexing organic compounds such as the CC waste may be destroyed by electrolytic oxidation. However, this option required the development of high-efficiency, continuous reaction equipment.

In addition, effluent denitrification in the LEAFLASH process should lower the volume of waste to be disposed of in a near-surface repository and allow nitric acid recycling.

Disadvantages. The Numatec (1993) report did not list any disadvantages. However, the uncertainties mentioned in Section 7.4, "Uncertainties," represent potential disadvantages of the Numatec technology.

Figure 7-4. Actinide Extraction from Complexant Concentrate Waste Using the DIAMEX Process.

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While the NCRW and CC waste treatment flowsheets recommended in this report represent realistic solutions, their implementation will nonetheless require substantial additional R&D.

To the extent that testing of actual waste would take place in France, the transport of HLW must be considered. As an alternate approach, French researchers could be brought to the Hanford Site to perform tests with actual wastes. This could be costly in terms of relocation expenses, and there are contracts with Numatec to consult with French experts still in France.

8.0 ASSESSMENT OF ALTERNATIVES

8.1 BASES FOR INDEPENDENT STUDIES

8.1.1 Objectives

FY 1993 work surveyed pretreatment technologies by contracting with organizations that in the aggregate could bring a fresh, encompassing view of pretreatment processes for Hanford Site waste. The organizations contracted to do this overview--SAIC, BNFL, and Numatec brought to the task a diversity of perspectives; the contracts to these organizations were written to encourage this diversity. SAIC was requested to survey processes, national and international, that have potential applications for Hanford Site waste pretreatment. The contracts with BNFL and Numatec augmented the effort to involve foreign firms that have developed significant national nuclear programs in the determination of a Hanford Site pretreatment process.

PNL was also contracted to conduct a preconceptual engineering study of pretreatment alternatives involving ion exchange, bulk precipitation, and nonradioactive and radioactive leaching. The survey of pretreatment technology provided by SAIC and the international perspective provided by BNFL and Numatec is complemented by the process-oriented approach of PNL. The PNL request was intended to consider simple processes, i.e., precipitation, leaching, and ion exchange.

8.1.2 Scope

The contracting strategy was to vary the task statements for each pretreatment study so that the composite of all studies was global in perspective. Identification of the integrated pretreatment alternatives required a selection process. For each unit process making up the integrated process, material balances were prepared. The material balance is an important first step in predicting process performance.

The independent consultant, SAIC, was given broad latitude to survey the technical literature for candidate pretreatment processes, develop a selection methodology, and prepare a material balance and flowsheet for the selected integrated process. SAIC surveyed the international, as well as national literature for processes that have potential application for Hanford Site waste pretreatment, as mentioned in Sections 1.1 and 4.1.

To ensure that foreign technology was not overlooked, BNFL and Numatec were asked for their recommendations based on their respective experience. The Russians have also made significant contributions in radiochemistry. Inclusion of the British, French, and Russian (via SAIC) technologies in the pretreatment alternatives selection process helps to ensure that important foreign technologies have not been overlooked.

The PNL study is different than the other studies, which attempt to reflect a global perspective i.e., the PNL study focuses on operationally simple technologies for the pretreatment of SST and DST waste. Ion exchange,

bulk precipitation, and leaching of the nonradioactive and radioactive components were investigated, and four different pretreatment alternatives incorporating combinations of these processes were prepared and evaluated. Operational simplicity is attractive because of the potential for rapid implementation. The PNL study complements the other studies by ensuring that simple operations like precipitation are not overlooked in favor of new technology.

8.1.3 Criteria

Three of the studies (SAIC, PNL, and BNFL) listed the criteria used in evaluating process options. While specific criteria are not explicitly stated in the Numatec report, factors that influenced process decisions are addressed, and these, along with the criteria used in the other studies, are presented in Table 9-1.

A dominant criteria addressed in the PNL report for each specific process was waste minimization in terms of the number of glass canisters and grout volume produced.

High repository costs have been the incentive to minimize glass canister production; however, it is not obvious that there is a direct correlation between the repository storage space and the number of canisters. Canisters with a high content of radionuclides are high heat sources that may require greater spacing between canister storage locations than low heat canisters.

Heat generation is also important in the size and operation of an interim monitored retrievable storage facility should the need for such a facility occur. High heat canisters may result in high life-cycle cost because of the cooling fan power requirement.

Minimization of life-cycle costs is a criteria common to the TWRS Rebaseline Study and the PNL, SAIC, and British studies. Actual estimates of life-cycle cost, while a part of these criteria, are not included because of the limited scope of the studies. Although life-cycle costs are crucial in the final evaluation, the number of glass canisters produced and the number of grout vaults required does not present the complete picture.

8.2 PROCESSES SELECTED

The SAIC, PNL, BNFL, and Numatec pretreatment alternatives are described in Sections 4.0, 5.0, 6.0, and 7.0, respectively. The SAIC pretreatment process is a combination of ozonation and ion exchange: ozonation to destroy complexants, and ion exchange with titanium-treated zeolite as applied at the West Valley DOE site to remove cesium, strontium, and TRU. BNFL recommends removing complexants from the waste in a manner yet to be determined, separating cesium and strontium by ion exchange, and removing TRU by the TRUEX process. Numatec favors electrochemical or hydrogen peroxide oxidation for organic complexant destruction, macrocyclic extractants for cesium and strontium removal, and DIAMEX process for TRU. Using a combination of

selective leaching, ion exchange, and precipitation, PNL prepared four different flowsheets. Figure 8-1 is a quick reference comparing processes prescribed in each study, the radionuclide(s) removed by each process, and the approximate status of process maturity.

All seven flowsheets representing the individual studies discussed in this report address levels of pretreatment separations that fall between the two boundary limits of the new technical strategy (NTS), minimum separations (high-capacity vitrification), and extensive separations. None of the studies directed their efforts along the process approach of either extreme. The SAIC, BNFL, and Numatec studies were free to choose the separations they felt should be performed, given specific Hanford Site waste types and disposal conditions (i.e., NRC Class A LLW). Although the specific radionuclides to be separated were preselected for the PNL studies, specific approaches to solids dissolution and acid-side versus alkaline-side separation processes were left open for the study.

The SAIC study settled on an approach closer to the NTS minimum separations (early pretreatment) boundary than did the others. This approach targeted high-maturity, forgiving technologies, at the expense of a larger HLW glass volume. Although the BNFL and Numatec studies appear to comply with the intent of the NTS boundary limits, they do not satisfy the precise definition of the region within the boundary limits in that neither performs an initial wash nor an alkaline-side cesium separation. BNFL and Numatec experiences independently led their studies to an initial acidification of all waste, thereby negating the need for alkaline-side processes. A primary purpose of this composite study was to bring "global" thinking to the Hanford Site pretreatment mission; therefore, the BNFL and Numatec process concepts are considered in this report to be totally responsive.

The PNL studies of four simple but different bulk processes produced a diversity of results with respect to the NTS. By combining aggressive sludge dissolution with advanced ion exchange treatments of both alkaline- and acid-side waste, the HLW glass volume produced came impressively close to meeting goals of the NTS CLEAN option. Conversely, the same aggressive sludge dissolution combined with either precipitation or with radionuclide leaching, while also complying with the HWVP reference feed criteria, produced an unacceptably large glass volume with little commensurate reduction in low-level waste. The low waste loading in glass for the precipitation concept was due to the titanium constraint (from the addition of crystalline silicotitanates), and for the leach concept the limiting constraint was phosphorous. The PNL studies scope did not provide for modification of the waste forms to minimize the impacts of these limiting chemicals. It appears that with proper waste form development these processes could result in limited high level waste production.

8.2.1 Sludge Wash, Dissolution, and Leaching

Decisions made with regard to the supernatant and sludge dictate the option for removing radionuclides. If the waste requiring vitrification is to be minimized, then aggressive acid dissolution is the choice. If the designer is concerned with the uncertainty associated with acid dissolution, then the

		CC/FeCN Destruction		Cs Separation	Sr Separation	TRU Separation	Tc Separation	Other
Bulk Treatment	Precipitation	Acid	Not in Scope	Phosphotungstic Acid	Sulfuric Acid and Pb (NO ₃) ₂	Oxalic Acid and CaSO ₄	No Treatment	Not in Scope
		Alkaline		Crystalline SI-Titanates	Crystalline SI-Titanates	Crystalline SI-Titanates	Na ₂ S	
	Solid Sorbents	Acid		Ammonium Phosphomolybdate	Sr Spec	Sr Spec and TRU Spec	No Treatment	Not in Scope
		Alkaline		Resorcinol Formaldehyde	IRC-718	No Treatment	Reillex	
	Leach	Acid		Ion X Resin Elution with HNO ₃	No Treatment	No Treatment	No Treatment	No Treatment
		Neutral or Alkaline		Act-de-con	Act-de-con	Act-de-con		
Independent Consultant		Ozonation	WVDP	WVDP	WVDP	ISO 100	No Treatment	
British Technology		Calcination or Hydrothermal (IPM)	Sellafield	Sellafield		No Treatment	U Solvent EX PUREX	
French Technology		H ₂ O ₂ or Electrolysis [Ag(I) or Co(II)]				No Treatment	F, Al, Zr Precip. EARP	
			Solvent EX Macrocycle	Solvent EX Macrocycle	Solvent EX DIAMEX	No Treatment	U, Co Solvent EX DIAMEX	

Key:

Laboratory with Simple Simulants

Laboratory Complete, No Pilot Plant Work

Proven in Pilot Plant or Plant with Non-Hanford HLW

Proven in Plant Scale with Hanford HLW

Figure 8-1. Processes Selected and Their Maturity.

choice is likely to be water and dilute caustic (or carbonate) wash to remove soluble ions and some aluminum. The PNL and SAIC teams, faced with the initial selection of a sludge treatment process, made different choices, with PNL choosing aggressive dissolution of the sludge and SAIC favoring water and dilute caustic wash.

The PNL processing sequence consists of water wash, caustic leach, and two successive acid dissolution steps. Two batch water washes of the sludge at a 3 to 1 water-to-sludge ratio are proposed in new stainless steel tanks. Solids are settled and wash liquor decanted. After decanting the wash water, the solids are mixed with 50 wt% caustic and heated to boiling to dissolve aluminum hydroxide and sodium aluminosilicates. Acid dissolution follows in two separate steps. In the first step, nitric and oxalic acids are used, and in the second step, nitric and hydrofluoric acids are used. Both acid dissolution steps are accompanied by heating to the boiling point and maintaining this temperature for several hours. Solid-liquid separation is by gravity-settling and decanting the dissolvent; 90% of the solids are recycled back to caustic leaching. This process of leaching and dissolution produces an acid stream and an alkaline stream. The alkaline stream would be combined with supernate decanted off the sludge.

The uncertainty associated with the decision to minimize glass production is the effectiveness of solid dissolution. Dissolution testing of actual tank waste is limited. Other questions requiring further development are material compatibility with the nitric-hydrofluoric acid dissolvent and the waste dissolved in this solution. Reliance on gravity settling of the solids remaining after leaching or dissolution may provide inadequate separation. The SRS is planning to precipitate cesium in the waste tanks and separate precipitate from the treated liquor by cross-flow filtration.

A less aggressive approach is taken by SAIC that results in a greater number of glass canisters being produced. However, a process simplification is achieved by caustic leaching only. This eliminates a separate system for radionuclide separations from acid solutions. After decanting of the supernate, the sludge is washed by two batch contacts with caustic solution at a 3 to 1 solution-to-sludge ratio for DSTs and a 4 to 1 ratio for SSTs. The intent is to follow the work that has been done at the SRS in sludge washing. For example, sludge washing and sludge agitation by the quad-volute pumps is a SRS development that could be applied at the Hanford Site. The alkalinity condition of both processes, SAIC and SRS, should eliminate material compatibility problems.

The SAIC sludge washing process, like the PNL process, lacks the data needed to project process effectiveness in dissolving solids. The SRS is anticipating that the original settled sludge volume will be reduced by as much as 50% by caustic leaching (Goslen et al. 1985). The variability in the Hanford Site waste rules out any similar expectation. Thus, there is a need for sludge dissolution data for caustic and nitric acid.

The BNFL and Numatec tasks were more specific in the type of waste to be processed than the SAIC and PNL tasks. The former considered CC and NCRW. In the preliminary reports of BNFL and Numatec, a common approach of nitric acid dissolution based on the work by PNL is proposed (Sections 6.0 and 7.0). There are some minor variations, however; BNFL treats the NCRW sludge and

supernate as a single stream in a blend of 1 to 4 volumetric ratio, while the Numatec process appears to be limited to NCRW sludge. The disposition of the NCRW supernate is unclear in the Numatec flowsheet. It appears that it would have to be acidified along with the sludge. The sludge is dissolved with nitric acid in both studies, and the two studies differ in the treatment of the nitrogen oxides generated in the dissolution process. BNFL sparges the dissolvent with air to remove nitrogen oxides and carbon dioxide, which are removed in a caustic scrubber. Numatec avoids the generation of nitrogen oxides by the addition of sulfamic acid. The solids remaining after dissolution are combined, in the Numatec process, with the treated waste going to grout. The preliminary BNFL study apparently includes the undissolved solids in the feed stream going to vitrification.

8.2.2 Organic Destruction

There was no consensus in the studies on organic destruction methods recommended. SAIC proposed ozonation and Numatec, electrolytic oxidation or oxidation using hydrogen peroxide. BNFL investigated several potential processes and, although the final report has not yet been prepared, the current BNFL intent is to rely on the organic destruction work being done for the IPM project. Organic destruction was outside the scope of the PNL study. Both SAIC and Numatec considered several options in making this process decision. Three organic destruction processes (ozonation, calcination, and hydrothermal) were initially proposed by the SAIC panel of respondents. Seven of the ten panel members proposed ozonation, two proposed calcination, and one proposed hydrothermal. Organic destruction processes considered by Numatec were oxidation with hydrogen peroxide, subcritical wet air oxidation, supercritical wet oxidation, and electrolytic oxidation.

The use of either hydrogen peroxide treatment or electrolytic oxidation is indicated on the Numatec flowsheet for the pretreatment of CC waste. This specific electrolytic oxidation process was developed for the dissolution of refractory plutonium dioxide using Ag (II) in nitric acid. The process was successfully extended to destruction of TBP, anion exchange resins, and organic complexing agents (using Co (III)).

The effectiveness of different methods in destroying complexants was evaluated by Numatec. A short reaction time and complete destruction are desirable. The supercritical process is inherently the most likely of the organic destruction alternatives to satisfy these conditions. Numatec discarded this option, however, because of the high temperature and pressure involved and the difficulty in managing and separating the solid, liquid and gaseous phases.

Wet air oxidation was tested by Numatec using a 0.5 L Hastelloy reaction vessel for tests on polyethylene, polystyrene, polyvinyl chloride, and acetic acid. For acetic acid, the residual concentration is reduced by increasing the temperature to 320 °C or by adding a catalyst. Tests were performed in neutral or alkaline conditions, rather than the acidic condition that is produced in the dissolution. Locating this process before dissolution more closely matches test conditions. If the organic complexant cannot be removed

before sludge dissolution because of interference of the sludge, then the use of hydrogen peroxide is proposed. No wet air oxidation tests have been performed on a nitric acid stream. There are uncertainties in applying wet oxidation in an acid medium that cannot be resolved without further testing.

Ozonation, the proposed SAIC process, was successfully demonstrated to be effective in a hot cell test for the destruction of organic complexant present in CC waste samples obtained from tank 241-SY-101. In this test, the CC waste was first treated with ozone to destroy the complexant and then treated by precipitation and ion exchange to remove radionuclides. The efficiency with which the radionuclides were removed from waste was a demonstration of the effectiveness of the ozonation process.

Ozonation has proven effective in removing other components found in the Hanford Site waste. TBP, the extractant used in the PUREX process, and ferrocyanide, a component in some of the SST wastes, have been removed by treatment with ozone. Large (30,000 lb/day) ozone generating plants have been built and even larger ones (115,000 lb/day) are under consideration for the treatment of community water supplies.

8.2.3 Radionuclide Removal

As discussed previously, the sludge treatment processes proposed in the four reports produce either an acidic or an alkaline feed stream to the radionuclide removal steps. The radionuclide removal processes proposed by SAIC are alkaline based, whereas the processes proposed by BNFL and Numatec produce acidic streams. The sludge treatment process proposed by PNL produces both alkaline and acidic streams.

In the SAIC process, the supernate is decanted and the sludge is "washed" with two successive water (or dilute caustic) contacts at a liquid-to-sludge volume ratio of 3 to 1 for the DST wastes (4 to 1 for the SST wastes). The wash solution is combined with the supernate, and the combined solution diluted to a sodium concentration of $\sim 1.5M$. After treatment for organic destruction, as necessary, the solution is filtered through a hydropulse filter before radionuclide removal.

In the PNL process, the supernate is decanted and the sludge washed with water in the same manner as described in the SAIC process. Following the water washes, the sludge is leached with $3M$ sodium hydroxide to dissolve the aluminum and silicon compounds and convert some of the phosphates to hydroxides. These solutions are all combined and constitute the feed for the alkaline processing steps. The remaining sludge is contacted with nitric-oxalic acid and nitric-fluoride solutions. The residual solids are washed with water (at a 3:1 volume ratio) after each acid contact and the wash solutions are combined with the acid dissolvents and routed to the acid waste processing steps.

The BNFL and Numatec processes acidify the combined supernate and sludge, yielding solutions with nitric acid concentrations of $1.8M$ and $2.0M$.

The two different process approaches--alkaline and acidic--are assessed separately in the following discussion.

8.2.4 Cesium Removal

8.2.4.1 Alkaline Processes. The two alkaline processes proposed by PNL both use ion-exchange media--resorcinol-formaldehyde resin for the process using standard, flow-through ion exchange columns, and CST powder for the "precipitation" process. The ion exchange resin is regenerated and reused, but PNL reports a 5-20% loss in capacity after seven loading cycles. Taking this loss into account, the average capacity per cycle is estimated at 220 column volumes. The resin would require either replacement or supplementation with additional resin after seven to ten column volumes are processed. Assuming these estimates are valid, and applying some conservatism because of the paucity of data for actual plant conditions, it should be possible to process a full tank of HLW supernate plus sludge leach solution through a three-column system of 1,000 gal of resin per column before resin replacement is required. This assumes the tank contains 750,000 gal of supernate and 250,000 gal of sludge, and the sludge is leached with two batches of solution at a 3 to 1 solution-to-sludge volume ratio.

Column experiments on simulated SRS alkaline waste (Bray et al. 1990) have demonstrated cesium DFs of greater than 10,000, the figure that was assumed in material balance calculations.

The PNL "precipitation" process uses CST powder mixed with the waste solution in the same manner as a precipitant, and is separated from the solution by settling and decanting and/or filtration. The CST is a powerful adsorbent because it has a strong affinity for strontium and TRU, as well as for cesium, with values of K_d reported to be of the order of 2,000, $>10^5$ and 2,000 for cesium, strontium and TRUs, respectively. A distinct disadvantage, however, is that the K_d for cesium decreases substantially with increasing pH. At the conditions of the Hanford Site tank supernate ($[OH^-] = \sim 0.6M$), the K_d for cesium is about 100. The CST is added to the salt waste at a ratio of 9.2 g powder/L of waste solution in each of four separate contacts. This calculates to be a total of 173 ton/Mgal storage tank, using the same assumptions as described in the previous paragraph. This would be expected to provide an overall cesium DF of 1,000, which should be sufficient to meet the NRC Class A limits with NCAW. This waste is presumed to contain the highest concentration of radionuclides of all of the Hanford Site defense HLW solutions.

Although the CST sorbent has only been produced in the powder form to date, it should be pointed out that a goal of the program is to manufacture a family of CST sorbents in a bead or pellet form suitable for use in commercial ion exchange-type equipment. If the program is successful, it is reasonable to anticipate that these sorbents might be placed into an existing process after the process has been operational for some time with a different sorbent, providing that sufficient operational flexibility has been designed into the system.

The SAIC study proposed using the titanium-treated zeolite ion-exchange process used by West Valley Nuclear Services at West Valley, New York. After dilution to $\sim 1.5M$ sodium concentration, the waste solution (combined supernate and sludge wash solutions) is pumped through three ion-exchange columns in a series, and the treated effluent is reconcentrated to $\sim 5M$ in sodium

concentration and solidified in grout. This process achieved cesium DFs as high as 10^5 at West Valley, and the resultant concreted waste meets the requirements of the 10 CFR 61 for Class A LLW.

The SAIC flowsheet uses NCAW as the feed stream. Flowsheet material balance calculations based on the higher radionuclide concentrations in this waste (see Section 4.2.1) provided a greater degree of assurance that the SAIC integrated process would produce a high-salt, LLW stream meeting NRC Class A limits. With a capacity of 450 column volumes of diluted waste solution (135 column volumes of concentrated waste), approximately 25 tons of the zeolite material would be required to treat a million gallons of HLW.

A comparison of the three cesium removal processes using ion exchange, considered separately from the respective integrated pretreatment processes, indicates that the multiple-column processes have a clear advantage over the bulk silicotitanate "precipitation" process with respect to both cesium removal effectiveness and media use. Both the resorcinol-formaldehyde resin, with a DF reported in laboratory studies of greater than 10^4 (Section 5.3.1), and the titanium-treated zeolite, with a demonstrated DF of greater than 10^5 (Section 4.2.3), have the capability of producing NRC Class A waste. With the silicotitanate "precipitation" process (with a reported DF of $\sim 2,000$, Section 5.3.1), this capability is questionable.

With respect to cesium removal effectiveness (mass of material required per unit volume of HLW processed), the resorcinol-formaldehyde resin has the clear advantage: ~ 0.5 g of resin is required per liter of combined supernate, wash, and leach solution. Use of titanium-treated zeolite would require ~ 2.7 g/L of combined waste. The PNL study using crystalline silicotitanates, Table 5-2, shows a total addition of 9.2 g/L applied in four successive batch contacts.

The comparisons are summarized in Table 8-1. In summary, the resorcinol-formaldehyde resin developed at the SRS appears to have a slight advantage over the titanium-treated zeolite because of its high capacity and capability for limited regeneration and reuse. A distinct disadvantage of resorcinol resin is the same as is experienced by all organic ion exchange resin, instability in a high hydroxide environment. While not sufficient to cause process problems, the safety ramifications of its use would require consideration. The demonstrated capacity and effectiveness of the zeolite material should be considered a strong plus to offset the disadvantage of increased solids routed to HWVP.

8.2.4.2 Acid Processes. The acidic processes proposed by PNL are ion exchange using granular APM mixed with a granular alumina dispersant and precipitation using PTA as the precipitant. PNL assumed a DF of 10^4 by using multiple columns in a series. The loaded ion exchange material is removed from the column and slurried to the caustic leach tank where the APM "solids" are dissolved.

Table 8-1. Cesium Removal Effectiveness of Ion Exchange Media.

Adsorption medium	Cesium DF	MTL Requirements	
		(g/L)	(tons/tank)
Resorcinol-formaldehyde	$\sim 10^4$	0.5	4.7
Titanium-treated zeolite	10^5	2.7	25.0
Crystalline silicotitanate	$\sim 10^3$	9.2	87.0

Precipitation with PTA was the process used at B Plant for recovering cesium from PUREX Plant acid waste. In a study of PTA treatment of West Valley alkaline waste, overall DFs of 10,000 were consistently obtained with two successive precipitations with 1:1 molar ratios of PTA to cesium. The only other precipitant PNL identified that was comparable to PTA in effectiveness was ferrocyanide, and this chemical was not considered because of safety concerns. Ferrocyanides react violently with nitrates and nitrites at elevated temperatures, a characteristic that would require additional safety measures for downstream processing, especially at the HWVP. SAIC dropped ferrocyanides from consideration for the same reason.

CSTs were not selected for sorption of cesium, although research is progressing rapidly. Based upon existing Los Alamos National Laboratory (LANL) data, a K_d of 3,000 to 6,000 has been measured in acid. CST is a promising candidate for Cs removal that will require additional research and development before it is demonstrated to be operationally ready.

The BNFL draft report specified ion exchange and recommended either their SIXEP or the plant proposed for the IPM, but did not identify a specific ion exchange resin.

The Numatec proposal for cesium removal is solvent extraction using calixarene, a microcyclic or "crown" ether as a solvent. The calixarene would be supported as a thin film or "membrane" in pores of a hollow fiber material, which also separates the aqueous strip solution (demineralized water) from the high-salt waste solution. Extraction of greater than 90% of the cesium is claimed for this "supported liquid film" (SLF) process, but this is not equated to an overall cesium DF. The use of centrifugal contactors is suggested for the processing of large volumes of waste, but a problem with the density of the organic diluent (only slightly greater than 1.0) would have to be resolved.

Although the calixarenes have great flexibility for extraction molecule formulation, their level of maturity at this point in time is primitive. When Numatec was questioned about the performance of calixarenes for particular ions; the position was that a molecule could be synthesized for that purpose. This would entail a great deal of development work to test many molecules. The Numatec study did not produce a statement that they have one molecule that gives good performance for a particular class of elements.

In summary, three completely different processes have been proposed: precipitation, ion exchange, and solvent extraction using a macrocyclic (or "crown") ether extractant on a supported liquid membrane. These involve two types of processes, batch and continuous. While continuous processes have some advantage with respect to process uniformity and equipment use, there is considerable difference in the maturity and viability of the three processes. Development requirements vary from minimal for the PTA precipitation process to very substantial for the SLF process. The disadvantage of the PTA process is that it would cause a significant increase in the amount of waste. The waste volumes are less for ion exchange, but the unknowns are greater and considerable development work is needed to identify a more suitable substrate for the APM ion exchange media.

8.2.5 Strontium Removal

8.2.5.1 Alkaline Processes. The adsorbent materials proposed by PNL for strontium removal are CST for "precipitation" and IRC-718, a macroreticular organic resin for ion exchange. As discussed previously for "cesium removal" the CST is added as a powder to the waste solution. At an addition ratio of 9.2 g of CST/L of waste, an overall strontium DF of $>10^4$ is used by PNL.

The ion exchange resin proposed by PNL for strontium removal, IRC-718, is a macroreticular resin made of polystyrene crosslinked with divinyl benzene. A strontium DF of 10^4 and a once-through capacity of 2,000 column volumes are claimed for this resin. The adsorption kinetics are relatively slow, however, and equipment design to accommodate the long residence time and, concurrently, provide the needed throughput could be a problem.

The strontium removal process proposed by SAIC is a combination of adsorption-precipitation and ion exchange. An optional adsorption-precipitation step is provided before the waste clarification and filtration step. This "precipitation" step uses amorphous sodium titanate powder to effect partial removal of the strontium in the same manner as the PNL alkaline precipitation process using CST. The sodium titanate is added in a single batch contact at a ratio of 40 g of powder per liter of waste solution. This addition is expected to provide a DF of about 250 and would generate an additional 375 tons of waste per million-gallon tank. As stated previously, the sodium titanate adsorption step is optional and would be employed only as required for pretreating wastes with high strontium concentrations.

The subsequent ion exchange process using a combination of natural zeolite (EI-96) and titanium-treated zeolite (TIE-96), as described previously for cesium removal, will provide a DF of about 350. The combined DF for the two processes is $\sim 9 \times 10^4$.

A comparison of the alkaline processes for strontium removal reveals an apparent advantage for the macroreticular resin, IRC-718. If this resin can be blended with the other HLW material and safely fed to the HWVP melter, its high capacity coupled with its destruction by oxidation and resultant low contribution to the HLW volume would seem to favor its use for strontium removal. The primary question regarding this material that was not addressed in the PNL report and, presumably, has not been studied is the stability of the resin to radiation. Organic ion exchange resins are generally much more

stable in an alkaline environment than in an acidic one, but the high radiation level and the presence of nitrate ion would be expected to cause resin deterioration. One of the primary disadvantages of the resorcinol-formaldehyde resin for cesium removal is its susceptibility to radiolysis and the resultant safety concerns. There is no apparent reason that the same concern is not warranted for the IRC-718 resin.

Of the other two processes, the use of CST adsorbent would appear to hold a slight edge on the basis of less solids contribution to the HLW volume. However, the flexibility of the combination of in-tank and fixed-bed column adsorption processes proposed by SAIC has merit because the use of the in-tank adsorption step would not be required for the major part of the HLW inventory.

In summary, the advantages and disadvantages of the three processes appear to be about balanced and the ultimate choice will depend on the relative importance accorded the selection criteria.

8.2.5.2 Acid Processes. The large differences in the various proposals for strontium removal from acidic waste solutions constitute a "testimony" to scientific ingenuity (but may not reflect the use of the best engineering judgement). Carrier precipitation, ion exchange, and solvent extraction processes are proposed, as discussed in the following paragraphs.

The PNL proposes carrier precipitation using lead sulfate as the carrier precipitant for strontium sulfate. Lead nitrate is added first, to a concentration of 0.02M in the waste solution. Sulfuric acid is then added to a final waste solution sulfate concentration of 1.5M. Pilot studies have shown a DF of over 20 with this process. According to the information in the PNL report⁴, this would result in the addition of ~38 tons of lead and 35.5 tons of sulfate to the HWVP, and 23 tons of nitrate and 900 tons of sulfate to grout for each tank of HLW processed.

For their acid-side ion exchange process for strontium removal, PNL proposes the use of Sr•Spec, a chromatographic resin. DFs of 10⁴ were assumed for strontium and plutonium, at a capacity of 0.1 moles/L sorbent. These DF values are dependent on process operating conditions and can vary significantly depending on how the processes are operated.

BNFL also proposes ion exchange for strontium removal, but does not identify the ion exchange medium nor, for certain, whether the strontium ion-exchange system is to operate in an acidic or an alkaline medium. Due to the lack of substantive information, assessment of the BNFL proposal for strontium removal was not possible.

The Numatec study proposed solvent extraction using a macrocyclic "crown" ether (calixarene) in the form of an SLF. The approach is similar to their proposal for cesium removal, as described in Numatec (1993), Section 10.2.2.4, "Acid Processes." The low maturity features of calixarenes applicable to

⁴Carrier precipitation using lead sulfate as the carrier precipitate was used to provide a strontium "crude" feed to the B Plant purification process. However, the precipitation was followed by metathesis and wash steps to reduce the lead and sulfate content of the crude.

cesium extraction would apply equally to strontium extraction. As an alternative to the SLF, the use of centrifugal contactors is implied. The absence of test data of any kind on the use of centrifugal contactors with a solvent of this type is a major uncertainty, as is the use of the SLF concept in a high-throughput, highly radioactive environment.

In summary, three different types of processes are proposed for the acid-side removal of strontium--carrier precipitation, ion exchange, and solvent extraction with a "crown" ether--and none appear to be without major disadvantages or uncertainties. The sulfate precipitation process using lead sulfate as a carrier precipitant, proposed by PNL, would result in large quantities of sulfate and lead, a toxic, semivolatile metal being processed into glass. The solubility of sulfate in the vitrified waste is low, with an established limit in the HWVP feed of less than 1% of the oxides, and handling of the excess could be a serious problem. Also, the addition of 900 tons of sulfate (per million-gallon waste tank) to the grout feed inventory would be difficult to justify, particularly with the relatively low strontium removal efficiency reported.

The use of ion exchange for strontium removal from an acid solution would, at the present time, appear to be very risky. The only medium for which substantive laboratory data are available is polyantimonic acid. The adsorption kinetics of this material are apparently slow, however, which could cause problems in column design, and the disposition of the loaded media is not addressed. In addition, its lack of selectivity may reduce its effectiveness for strontium removal. The only other possibility mentioned, Sr•Spec, a macrocyclic ligand sorbed onto an inert substrate, was reported to have high specificity for strontium, but was dropped from consideration in favor of polyantimonic acid with its broad-spectrum exchange capability.

The only solvent extraction process proposed, the use of a crown ether in a suitable nonpolar diluent and supported as a thin film on a hollow fiber support, appears to show promise on a laboratory scale. DFs of 200 to 400 were obtained in tests. It was acknowledged in Numatec (1993), however, that the use of SLFs may be limited to small-scale operations. Processing rates such as projected for the Hanford Site pretreatment facility would probably require the use of large columns or centrifugal contactors. No development or scaleup information is currently available regarding the use of crown ether solvents in standard solvent-extraction equipment.

8.2.6 Transuranic Removal

8.2.6.1 Alkaline Processes. The titanium-based adsorbents--CST, sodium titanate, and titanium-treated zeolite--all remove the TRU elements, as well as strontium and cesium from alkaline waste solutions. The PNL process, using a 3M caustic wash, limits the solubility of the hydroxides of plutonium and americium, holding them in the sludge for later dissolution in the acid washes. The SAIC process, using "tempered" water (dilute caustic), follows the approach used at West Valley and SRS. The trace quantities of TRU in these washes are removed by the sodium titanate and/or titanium-treated zeolite.

The CST used by PNL to remove cesium and strontium from the alkaline waste also provides a DF of about 1,000 for TRU, which should be more than adequate to remove the trace of TRU dissolved in the caustic wash. DFs calculated by SAIC for TRU, of at least 10 and 80 for sodium titanate and titanium-treated zeolite, respectively give a combine DF of 800. This is nearly comparable to the DF of 1,000 for CST.

8.2.6.2 Acidic Processes. The range of options for TRU removal from acid solutions is quite large. The PNL, with their stated limitation to precipitation and ion exchange processes, selected oxalic acid for precipitation and a combination of Sr•Spec and TRU•Spec for ion exchange. The BNFL and Numatec studies both proposed solvent extraction processes.

Oxalate carrier precipitation using calcium oxalate as the carrier precipitate was the most promising precipitation method identified by PNL. Calcium sulfate is first added to the waste solution at a ratio of 0.03 moles/L of solution. Oxalic acid is then added to the solution and plutonium, americium and calcium precipitate as the hydrous oxalate, DFs of 10 and 350 are quoted by PNL for this process.

One of the ion exchange mediums selected by PNL for the removal of TRU, Sr•Spec, is the same material as was selected for strontium removal. Other ion exchange media were considered, but were not selected because of their inability to adsorb strontium, as well as plutonium and americium. The DF quoted using Sr•Spec for plutonium removal was 10,000 of a capacity of 0.1 moles/L sorbent. Using TRU•Spec for americium removal, the DF quote was 100 of a capacity of 0.0375 moles/L sorbent. Other elements in the waste compete for ion exchange sites, which results in the low DFs. Tests with waste simulants and actual waste are important in determining if Sr•Spec and TRU•Spec can effectively treat Hanford Site waste.

TRUEX, the process proposed by BNFL, is a relatively new liquid-liquid extraction process developed at Argonne National Laboratory for the removal of all actinides from acidic (nitrate or chloride) nuclear waste solution. The TRUEX solvent, a complex organic phosphine oxide (CMPO), is a new actinide-lanthanide selective extractant. When processing nitric acid waste solutions, TBP is added to the TRUEX process solvent to prevent the formation of a second organic phase. The basic features of the TRUEX process are the same regardless of the application, i.e., extraction of actinides from a feed high in nitrate or chloride, a scrub step to achieve additional decontamination from impurities and a strip performed at low nitrate or chloride concentration aided by the presence of a complexing agent such as fluoride or oxalate ion.

In addition to actinides, CMPO extracts trivalent light lanthanides and, to a lesser extent, zirconium, technetium, palladium and iron. Thus scrubbing of the CMPO solvent with 0.25M HNO₃ is necessary to prevent iron accumulation. The composition and amount of scrub solution used may be a function of the type of waste being processed. The BNFL flowsheet calls for stripping or back extraction of TRU with 0.2M 1-hydroxyethane 1,1-diphosphonic acid (HEDPA) followed by washing of the process solvent with 0.25M sodium carbonate. The stripping agent HEDPA and the sodium impact the waste loading in the glass.

A molten salt accumulation in the melter can be caused by sulphate, phosphate, or halide addition in excess of feed specification. Blending the

waste with additional glass frit may be required to prevent this molten salt layer from forming. At a minimum, waste loading would be expected to be lower than 25%. There have been some concerns in the past that a molten salt layer could result in a steam explosion. This possibility was dismissed, but the introduction of large quantities of phosphorus into the melter could cause this issue to be raised again.

Recent tests indicate that the concentration of HEDPA can be significantly reduced by combining the HEDPA and Na_2CO_3 , thus reducing the possibility of phosphorous impacting the waste loading of the glass.

Last, a wash of aqueous carbonate solution removes degradation products of both TBP and CMPO, as well as any uranium that is co-extracted.

The efficacy of the TRUEX process to remove TRUs to levels required by LLW is well established. The BNFL material balance shows that essentially all the uranium, plutonium, and americium are removed by the TRUEX process. The TRU removal effectiveness quoted by BNFL is derived from the work at PNL. Development of the TRUEX process at Hanford Site has proceeded to the point where countercurrent testing using 4-cm centrifugal contactors are the proposed next step.

Numatec has developed their own TRU removal process that provides alternative process steps. In the event the development program for one process encounters major problems, it may be circumvented by the features of the other process.

The Numatec process called DIAMEX was developed to remove plutonium isotopes and americium while minimizing the generation of secondary waste. The other development objective was to find extractant molecules that could be destroyed, producing a gaseous waste. These requirements were met by the development of the diamide family of molecules which contain only the elements carbon, hydrogen, nitrogen, and oxygen.

The extractant currently considered to be the best, a malonamide compound, can be made in industrial quantities at one-tenth the cost of CMPO. In a test of the DIAMEX process, medium-level waste was treated successfully in that the DF for alpha emitters was 12,600. The overall effectiveness of the process was similar to the TRUEX process for treatment of an effluent with a similar composition.

Like the TRUEX process, the DIAMEX process extracts elements other than those in the actinide family. Zirconium (IV) is a constituent of the NCRW that would be extracted from the acid waste. Iron (III) and fluoride ion are also expected to be co-extracted to some extent. Oxalic acid was selected to scrub the Zr(IV) and the Fe(III) from the solvent, even though it could cause precipitation of Zr(IV). The identification and testing of other complexants is a R&D requirement. The ideal complexant would not complex actinides and its destruction would yield gaseous products.

A second scrub with 4M HNO_3 is performed to remove partially co-extracted complexant. This is followed by contact with a third scrub solution to reduce the HNO_3 acid in the solvent and, finally, the actinides are back-extracted (or stripped) by contacting the loaded solvent with a 0.3M solution of sodium

carbonate. The complexant added during the initial scrub is either destroyed during concentration of the effluent from the cesium extraction cycle, or it will be partially present in the neutralized sodium nitrate solution and is released to the environment (presumably as grout).

The potential advantages offered by the DIAMEX process include the following:

- Low probability of crud formation after interaction of the dissolved sludge solution with products from solvent decomposition, which is particularly important for process implementation in centrifugal extractors
- Little influence from solvent decomposition products on actinide extraction or back-extraction
- Simple actinide back-extraction without a complexing agent containing phosphorus (which would create problems for secondary waste disposal)
- Probable elimination of a special solvent treatment step, which occurs at the same time as actinide back-extraction
- No secondary solid waste produced with the use of the diamide extractant, due to potential decomposition of this molecule in gaseous compounds.

8.2.7 Technetium Removal

Technetium is presumed to exist in waste streams on the Hanford Site in the form of pertechnate (TcO_4^-), a relatively mobile component in grout. This radionuclide is considered to be a significant contributor to doses for individuals in performance assessments. Therefore, a process for removing technetium from grout feeds may be required.

The removal of technetium from waste streams was addressed by two of the four studies, those by SAIC and by PNL. The source of technetium in the SAIC study was NCAW, at a technetium concentration of $4.5 \times 10^{-1} \mu\text{Ci/mL}$. The PNL study was based on a composite DST and SST waste with a technetium concentration of $6.0 \times 10^{-2} \mu\text{Ci/mL}$. Four separation processes were incorporated into five of the seven overall study flowsheets. These processes were strong base anion exchange by SAIC and by PNL; Na_2S alkaline precipitation and alkaline ion exchange using Reillex resin. No acid-side processes were identified by either SAIC or PNL. All processes reviewed in this section take place in alkaline conditions.

Technetium removal was not a part of the BNFL and Numatec reports. The feed streams studied in each case were NCRW and CC waste, neither of which contains technetium at a high enough level to require treatment. NCRW was selected for the studies because it has been characterized to a higher level of confidence than the other waste types, and CC waste was chosen to determine if British and/or French technologies could augment current Hanford Site activities directed toward the destruction of organics and ferrocyanide.

8.2.7.1 Strong Base Anion Exchange (SAIC). Technetium is removed from the HLW supernate and wash solutions in the SAIC flowsheet design by adsorption, as the pertechnetate ion, on a strong-base anion resin. Of the readily-available commercial resins, Duolite A101 and Amberlite IRA 401 were judged to have the greatest affinity for technetium.

The SAIC study resulted in a two-column system being selected for use in technetium removal, one column operating on a loading cycle while the other column is operating on the elution cycle. Between 100 and 150 column volumes of feed can be processed in one loading cycle. This operation is further detailed in Section 4.0 of this report, including breakthrough values and the recommended elution procedure.

The overall technetium ion exchange system proposed by SAIC is a low risk design which has given attention to technology maturity and commercial experience. Additional benefit also should result from commonality of the unit operation selected for technetium removal (column ion exchange) with that selected for removal of strontium, cesium, and TRUs (column ion exchange). Besides simplifying the logistics of plant consumables, the benefits of commonality would include operator training effectiveness and the expected high plant availability that likely would result.

8.2.7.2 Bulk Precipitation (PNL). The alkaline-side bulk precipitation flowsheet PNL developed assumes an organic destruction process has been previously conducted to destroy the complexants that prevent radionuclides from precipitating. The effectiveness of subsequent precipitation steps depends on adequate removal of organic complexants. The combined liquid streams from initial water washing and caustic leaching are subjected to cesium, strontium, plutonium, and americium precipitations (Section 5.2) before technetium treatment.

Removal of technetium from alkaline streams by bulk precipitation has not been investigated as much as ion exchange processes. Technetium solution chemistry is not well known, and precipitation by formation of insoluble sulfides may be one of the few precipitation options available for technetium removal. It was assumed during the study that addition of twice the stoichiometric amount of sodium sulfide theoretically required to precipitate technetium will result in a DF of 100. Side reactions have not been included, although it is not known if sulfide will be oxidized by nitrate before it can react with the pertechnetate. Considering the abundance of cations, other than technetium, in the waste competing for the sulfide, the assumption that a technetium ion will find a sulfur ion while the latter still remains unreacted must be considered fragile.

The use of sodium sulfide to precipitate technetium has not been demonstrated on any scale. Even for processes that have been demonstrated on a large scale, it is uncertain whether precipitation will achieve large DFs for individual tank wastes in which the radionuclide of interest is much more dilute than the average concentration for all tank wastes combined. For this reason, increased quantities of precipitants may have to be added to achieve desired overall DFs. Alternatively, higher concentrations of radionuclides would be sent to grout. Without these potential problems surfacing, it is estimated that the total DST and SST inventory of 2,000 kg of technetium will require the addition of 9,000 kg of Na_2S precipitant.

Also of concern, the addition of significant quantities of sodium sulfate to the process raises several issues with regard to melter operations. A molten salt accumulation in the melter can be caused by an excess of sulfate. Blending of vitrification feed with additional glass frit may be required to prevent a molten salt layer from forming. At a minimum, waste loading would be expected to be lower than 25%. Concerns have been voiced in past years that a molten salt layer could result in a steam explosion (Holton and Sommer 1984). This possibility now has been dismissed, but the introduction of large quantities of sulfate into the melter could result in raising this issue again.

8.2.7.3 Ion Exchange (PNL). Ion exchange materials are intended to be used in columns, since column operations are much more efficient than batch contacting. These exchange systems will consist of two or more columns operating in series. To maximize column loading, material in the front column in each series can be replaced for every loading cycle, at which time the second column would be moved to the first column in position.

As with the other PNL flowsheets, an organic destruction step was assumed prior to ion exchange processing. The purpose of organic destruction is to eliminate complexants that prevent radionuclides from sorbing the ion exchange materials. The next step in the overall ion exchange flowsheet is an in-tank settle and decant process to separate the liquid from the solids, which is followed by a caustic leach and washing step. The liquid stream from each of these operations is sent to alkaline-side processing.

After cesium and strontium separations are performed, technetium is removed from the alkaline waste using Reillex, an organic anion exchange resin. Batch tests in nitric acid have demonstrated a TcO_4 capacity four times greater than that of Dowex-1, an alternative anion exchange material. This resin has also been selected due to its greater stability toward radiation exposure and oxidants than alternative materials. However, Reillex has not been demonstrated to perform efficiently in alkaline solutions. The capacity assumed for the PNL flowsheet was presented as an educated guess and assumed the concentration of nitrate ion to be the most important variable in determination of TcO_4 capacity. A loading of 250 cycle volumes and a DF of 100 was assumed.

The decontaminated liquid from base-side processing is evaporated to produce a grout waste stream that is 5M sodium. The evaporated water can be recycled back to the wash steps. The loaded Reillex resin is combined with solids from other steps for vitrification.

8.2.7.4 Selective Leaching (PNL). The advantages of the selective leaching approach are simple operation, minimal capital investment, and could be started on an accelerated schedule compared to facility options. Also, bulk leach only needs to be used on specific waste types for maximum benefit, if the waste can be blended before being transferred to HWVP.

The potential disadvantages for bulk leaching are that the separations are not as good as with other options, and glass volume is not minimized as much as facility processing.

The major technical issues with the leaching flowsheets is partitioning factors. Only selected tanks have been tested, and the other tanks may not behave in a similar manner. Another serious technical issue is the development of a glass that has the majority of the compounds outside of the previously studied glass envelope. The waste loading allowed in the glass, based on available information, could vary substantially.

The selective leaching concept was considered from two perspectives. One option was leaching of nonradionuclides to remove certain nonradioactive components from the sludge that would otherwise result in the production of large quantities of glass. The other option would be to concentrate on leaching TRUs and fission products from the waste.

The nonradionuclide leach subjects the sludge to various chemical treatments that reduce the mass of the sludge without removing significant quantities of radionuclides other than cesium and technetium, which are normally soluble in the alkaline waste. While this operation could prove effective for the concentration of TRUs and strontium, its performance to remove inert, soluble salts from cesium and technetium radionuclides would be limited.

In addition to the selective leaching summarized above, a method is required to remove technetium from the supernate and possibly some leachates to make them acceptable grout feeds. Ion exchange was selected as the most appropriate process to combine with the selective leaching processes for this technetium removal step. The ion exchange process is the same as chosen by PNL for the ion exchange flowsheet previously discussed.

The radionuclide leach process is based on the Act-de-con process, which uses a combination of oxidants, carbonates, and EDTA to remove select radionuclides. The process has successfully removed plutonium, uranium, americium, and strontium from contaminated soils, but has not been tested on Hanford Site tank waste.

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9.0 DECISION ANALYSIS

Decision analysis is an integral aspect of the systems engineering approach that is being used by WHC for the evaluation and implementation of TWRS strategic technical alternatives (Boomer et al. 1993). This section will describe the decision analytic process and discuss FY 1993 decision analytic activities directed to the evaluation of pretreatment processes. These activities include an analysis, from a decision analytic perspective, of each of the independent studies funded by WHC; some additional analysis of the SAIC data; a discussion of the evaluative criteria used by the independent studies; and, recommended FY 1994 activities directed to the further evaluation of pretreatment flow processes. A preliminary engineering evaluation of the flow processes identified in FY 1993, and discussed earlier in this report, is presented in Section 8.0.

9.1 FISCAL YEAR 1993 APPLICATION OF DECISION ANALYSIS

This section provides a summary of FY 1993 decision analytic activities directed toward the identification and evaluation of pretreatment processes.

The primary emphasis in FY 1993 has been on the identification, by independent contractors, of potential pretreatment process alternatives. The contractors have only made these processes available for evaluation towards the end of the fiscal year. Thus, the FY 1993 application of decision analysis has been mostly in the preliminary and planning stages. The major exception is that WHC has worked closely with SAIC to provide a quantitative ranking of processes based upon evaluation criteria. SAIC's initial plan was to use the Delphi procedure (see Section 4.1) with criteria playing a qualitative role of guiding the thinking, but not being used explicitly in a formal evaluation. It was important that SAIC retain autonomy of their study; but, at WHC request, criteria were developed to a greater extent, and both integrated and unit processes were evaluated on these criteria. WHC also directed SAIC to perform a preliminary analysis based upon the evaluations. This was in addition to the identification of the best processes through the Delphi technique. The results of this analysis are summarized in Section 8.3.1.

WHC has also analyzed the decision methods used by the independent contractors. Each of the four contractors used some method to identify and evaluate pretreatment processes. The type of formal decision analytic process used, and the extent to which it was employed, varied greatly. The decision analytic aspects of these studies is summarized and discussed. This analysis has the potential for providing insights into possible reasons for differences in results between contractors and lays the foundation for a more formal evaluation of all the flow processes identified by the contractors. These analyses are summarized in Section 9.3.

WHC has also begun an initial analysis of the FY 1993 pretreatment processes. At present this is based primarily upon an engineering analysis of the differences in the flow sheets, with the focus being on the assumptions such as waste characterization and separations efficiencies. This provides an

understanding of the differences and commonalities, which is a necessary prerequisite to a more formal evaluation. These processes are reviewed in Sections 4.0, 5.0, 6.0, and 7.0. An initial assessment is given in Section 8.0.

WHC has begun to develop a methodology for the formal evaluation of the various pretreatment processes. This methodology will be based upon decision analysis which is a part of the systems engineering approach that has been adopted by TWRS for the evaluation of technical strategies. A description of decision analysis is presented in Section 9.2. The proposed methodology is to develop a decision analytic model that will create a framework for defensible evaluations of pretreatment processes. The model will support a variety of analyses that will allow the explicit consideration of risk, differences in stakeholder values, and other analyses that make explicit the rationale for selecting the preferred pretreatment process. The model will be in the form of a decision support system that can be modified and updated as the need arises. The decision model will also provide analyses that can support the decision of when to start the implementation of a particular process or set in motion a pretreatment strategy.

One initial effort directed toward a formal evaluation of all processes will be to determine their performance on grout volume, number of glass canisters, and fraction of Class A limits in grout. Performance on these criteria is given by PNL for the bulk treatment processes they identified. All FY 1993 processes need to be evaluated on these criteria. This is just one aspect of performance, but it is a start in the process of gathering data for a more comprehensive comparison.

WHC is also developing a comprehensive set of criteria to be used in the decision analysis model. This process was initiated by reviewing the criteria identified by all investigators with the goal of developing a set of criteria that is consistent with those of TWRS but specific to the evaluation of pretreatment processes. Section 9.4 provides a summary of this effort to date. WHC has also begun to identify the key uncertainties. These are uncertainties that are important to include in the evaluation of pretreatment alternatives and may also be important to resolve before the final selection of a pretreatment process. Finally, WHC is exploring the extent pretreatment can leverage off the TWRS rebaselining decision analysis model. This decision model was designed to evaluate technical strategies, of which pretreatment is a part. The decision analysis activities of FY 1993 lay the foundation for a comprehensive and systematic evaluation to be carried out in FY 1994.

9.2 METHODOLOGY

The evaluation of flow processes will be carried out using the methods of decision analysis. (See, for example, Keeney and Raiffa 1976 or von Winterfeldt and Edwards 1986.) The methodology is presented here for reference and will be referred to in subsequent sections. Decision analysis has its theoretical foundation in a set of axioms that capture the basic principles of rational decision making, and the decision rules are derived as a consequence of these axioms (see von Neumann and Morgenstern 1947 and Savage 1954). The methodology of decision analysis incorporates both judgments of uncertainty and judgments of preference. When these judgments incorporate the

best available engineering data and reflect the values of stakeholders, the resulting decision is a logically defensible consequence; and the decision logic will be clearly specified and available for open discussion. The approach is especially appropriate when decision outcomes depend on technological uncertainties.

9.2.1 Logic of Decision Analysis

Decision analysis creates logically defensible decisions in a complex decision environment by decomposing the process into a series of simpler judgments. These judgments are then resynthesized to arrive at an overall evaluation. The process is made possible by quantifying both preferences and uncertainties. Some of the more notable features of decision analysis are briefly discussed below.

9.2.1.1 Defensible Decisions. Decision analysis documents the decision process so that it is open for all to see, as opposed to "intuitive" or less well specified decision procedures, in which the method for arriving at the decision may be unclear. By objectively specifying what factors are to be considered, how they are to be measured and evaluated, and their relative importance, decision makers clearly understand the basis for their decisions. This makes it possible to have open discussion and "fine tuning" of the decision process. The final result is a decision that is well understood and that can be clearly explained and justified in a public arena if the need should arise.

9.2.1.2 Decomposition. Decision analysis is based upon the assumption that the best strategy for complex decisions is to analyze the various components separately and then integrate the individual judgments to arrive at an overall decision. This ensures that all the relevant factors are identified and their relative importance is considered. The procedures for obtaining the individual judgments, and the decision rules for combining them and identifying the best alternative, have both theoretical and empirical foundations in mathematics, economics, and psychology.

9.2.1.3 Quantification. Numbers rather than qualitative expressions are used to construct scales, represent preferences, and express uncertainties. The relationship between qualitative preference structures and quantitative scales is given a precise and rigorous description in the mathematical discipline of measurement theory (Krantz et al. 1971). Measurement theory is incorporated into the theoretical underpinnings of decision analysis. Quantification also fosters clear and precise communication. Numerous studies have documented the ambiguity of verbal expressions when used to express likelihood. See, for example, Bryant and Norman (1980).

9.2.2 Elements of Decision Analysis

The process of decision analysis consists of first identifying the objectives to be achieved, developing measures and value functions for those objectives, determining the relative importance of the various objectives, identifying and evaluating alternatives with respect to the various measures, and determining the overall value of an alternative via an objective function

that rolls all the information into a single number. It is an iterative process both within and across the various steps and terminates only when sensitivity analysis has shown the decision to be robust to the satisfaction of the decision maker. Decision analysis is a way of thinking carefully about difficult decisions and is not a substitute for hard thinking. The steps in this process are further described below.

9.2.2.1 Alternatives. Alternatives are the various courses of action under consideration. The richer the set of alternatives that are identified for evaluation, the better are the odds of choosing one that is optimal. Techniques exist for fostering creativity in the identification of alternatives. It is common initially to identify one or two options that serve as anchors and prevent a broad range of ideas from being explored. Clearly specifying objectives and the means of achieving them is one technique for identification of alternatives (Keeney 1992). Alternatives need to be precisely defined if they are to be evaluated.

9.2.2.2 Objectives. Objectives should capture stakeholder's concerns and preferences. Stakeholders include the decision maker and all groups with a legitimate and/or perceived interest in the outcome. Developing a set of objectives for the evaluation of alternatives can be quite challenging. However, the effort is well spent and will pay dividends in the end. Well thought out objectives are essential if there is to be a logical basis for the decision, and if the chosen alternative is to have the highest expectation of meeting the requirements of the decision situation. Objectives that are clearly specified in advance can also provide a basis for identifying a broad range of alternatives, thus increasing the likelihood of making an optimal decision. Objectives are statements of what we want to achieve (Keeney 1992). For evaluation purposes, objectives are put into a hierarchical form, starting with the overall goal and the fundamental objectives. Fundamental objectives are objectives that are of basic importance to the decision situation. They are ends in themselves; however, they should not be too broad in scope for the decision situation. When constructing the goal hierarchy, fundamental objectives are further broken down into more specific aspects of those objectives. This process continues until one arrives at a level at which the objectives can be quantifiably measured. The objectives at this level are called criteria.

9.2.2.3 Criteria. Criteria are also known as performance measures or attributes. These measure the degree to which the objectives are achieved by the various alternatives. The criteria make possible a quantitative evaluation of alternatives. Project duration measured in years is an example of a well-defined criterion. Years is a natural scale. Often natural scales are not available, in which case scales must be constructed. Scales should be constructed so as to minimize ambiguity as to what is meant by a given level of performance. A measure of the objectivity of scales is whether they can pass the clarity test (Howard 1983). The clarity test is said to be met if a clairvoyant with knowledge of all events past and future would be able to unambiguously assign the performance level for a given alternative. Notice that this requires that both the scales and the alternatives be well specified. Scales that depend on quantifiers such as high, medium, and low, unless further qualified, are especially ambiguous in that one person may evaluate an alternative as high, while another evaluates it as medium, even though they both had the same underlying performance in mind.

9.2.2.4 Value Functions. Value functions measure the importance of a single criteria. They take as their range the various levels of performance and typically map it into $[0,1]$. One reason for mapping the performance into value space is that an objective's importance may not be linear with its scale. Another reason for transforming performance measures into value space is that it provides a common metric for comparing the relative importance of different criteria. This also makes possible an overall assessment of alternatives with a single number. Value functions are called utility functions if they contain risk preference information.

9.2.2.5 Weights. Whereas value functions capture the importance of a single criteria, weights capture the relative importance among several criteria. Typically, alternatives that improve performance on one criteria do so at the expense of some other criteria. Weights logically depend on the ranges in performance over which the alternatives vary. A common mistake is to nominally specify the relative importance of objectives without considering the ranges in performance.

9.2.2.6 Objective Function. This is a mathematical formula that rolls up all the above judgments into a single number by which the alternatives can be compared. The appropriateness of its functional form depends upon whether certain assumptions concerning preferential independence are satisfied. Often an additive linear model will be appropriate; this will be more likely if a hierarchical value structure is developed, as described above, in which each further specification of the value tree is mutually exclusive and exhaustive (i.e., a partition).

9.2.2.7 Sensitivity Analysis. Sensitivity analysis explores the robustness of the decision under various assumptions or conditions. It should be carried out to whatever extent is necessary until the decision maker is satisfied that the best alternative has been identified. Various types of sensitivity analysis are possible. The most common is sensitivity on the criteria weights. This is typically carried out for each of the performance measures to determine the relationship between the weight placed upon that criterion and the overall performance of the various alternatives. Of particular interest is to what extent the optimal alternative is sensitive to a particular criterion's weighting. In a similar vein, sensitivity analysis can be used to explore the sensitivity of decisions to the different values of various stakeholders. One can extend this analysis to determine dominant options in a multiple stakeholder preference space. Sensitivity analysis can also be used to determine the impact of various variables on the outcome measures. This is especially valuable when modeling uncertainty and will be described in the next section on uncertainty.

9.2.3 Uncertainty

For many decision situations, the procedure sketched above will provide all the necessary analysis for evaluators to make an optimal decision. Often the relationship between an alternative and its level of performance on a given criterion is uncertain due to uncertainties about other events and/or variables that bear on the outcome. In such cases, it may be valuable to model explicitly the uncertainty associated with the performance measures.

This makes it possible to identify uncertainties having the greatest impact and to determine the risk associated with various alternatives. What follows is a brief description of the process of including uncertainty in the decision model.

9.2.3.1 Structuring Decisions. Structuring is the process of determining the relationships among decisions, aleatoric variables, and the outcome measures. This can profitably be done using influence diagrams (Howard and Matheson 1981). (Structuring also includes the identification of alternatives, objectives, and criteria; here the primary concern is with the decision structure as it relates to uncertainty.) An influence diagram is a decision analytic tool that was developed at Stanford University for the purpose of representing complex decision problems in a form that is intuitive to understand, has a compact representation, and yet provides the structure for a quantitative decision-analytic model. The elements of an influence diagram consist of decision nodes, uncertainty nodes, deterministic nodes, and outcome nodes. Arrows connecting the nodes provide additional structural information. For example, an arrow from one uncertainty node to another shows probabilistic dependence or unknown interdependence, and the lack of an arrow implies probabilistic independence. An arrow into a decision node from an uncertainty node means that the uncertainty has been resolved and the actual state of uncertainty is known by the decision maker at the time the decision is made. Thus an influence diagram is a method for representing the relationships among the decision variables. An example influence diagram is shown in Figure 9-1.

9.2.3.2 Deterministic Models. The purpose of a deterministic model is to define the quantitative relationship between the input variables and the outcome variables. This relationship may be defined in an influence diagram environment using special purpose decision analytic software, but it is often developed in an electronic spreadsheet environment, which then interfaces with the decision software. The model's inputs are the decision alternatives and the possible values for the uncertainties, and the outputs are the alternatives' levels of performance on each of the criterion. Thus, it calculates performance criteria for alternatives conditional on the state of uncertainties.

9.2.3.3 Sensitivity Analysis. When modeling uncertainty, sensitivity analysis is used to determine which of the variables in the deterministic model need to be carried forward to the probabilistic model. Sensitivity analysis determines the amount of influence the uncertain variables have on the performance measures. It is especially important to know whether the optimal decision would be different depending on the potential value of some input variable. Variables with little impact on the outcomes can be treated deterministically by setting them at their nominal values. The sensitivity analysis consists of computing the value of a performance criterion for a given alternative with all input variables set at their nominal value, except for one that is allowed to vary from its lowest to highest level. The calculated impact on the performance criterion can then be observed. The importance of an uncertainty depends on both the performance criterion and the alternative being evaluated.

Figure 9-1. Influence Diagram Model for Number of Glass Logs.

9.2.3.4 Probabilistic Models. Those variables that are determined by sensitivity analysis to have a significant impact on the decision are carried forward to a probabilistic modeling of the decision situation. Probabilistic modeling is used to determine the combined impact of the technical uncertainties on the performance measures. The probabilistic model computes the expected value for each combination of decision alternatives. For calculation purposes, the probabilistic model is often represented as a decision tree. Each branching of the tree represents possible decision alternatives or possible outcomes of some uncertain variable. A probability distribution must be developed for each uncertain event in the probability model. These can be derived from any historical data that may be available: by constructing simulations, either computer or bench scale, and from expert judgment. The decision tree analyses consist of rolling the tree back to determine the expected value (or utility) of the various alternatives, and rolling forward to determine the risk profiles of each alternative. The risk profile is often presented as a cumulative probability distribution of the criterion outcome values. This allows an assessment of the range of possible outcomes and their probabilities, as well as the expected outcome.

9.2.3.5 Value of Information Analysis. Probabilistic modeling lends itself to additional analysis that can answer the question of whether it is worthwhile to gather more information so as to reduce the uncertainty of some variable. The value of perfect information is the difference between the expected value if all uncertainties were resolved before making a decision and the expected value given the uncertainty. Typically, additional information does not completely resolve uncertainty; it only reduces it. Consequently, the value of information is less than the value of perfect information, which sets an upper limit on how much one should be willing to pay to obtain additional information so as to reduce uncertainty.

9.3 DECISION METHODOLOGIES EMPLOYED IN THE VARIOUS STUDIES

Decision analysis was used to varying extents for the identification and evaluation of pretreatment processes by the various research groups. This section summarizes the decision methodologies used in each of the studies. Also, this section helps to clarify where additional analysis is needed. It also lays the foundation for an integrated analysis across the studies by clarifying the extent of existing analyses, their commonalities and differences, and their strengths and weaknesses.

9.3.1 Independent Consultant (SAIC)

9.3.1.1 Delphi Method. This study used a structured decision methodology for the generation and evaluation of alternative flow processes. The methodology centered around the Delphi technique, which is an excellent procedure for obtaining judgments from many minds and arriving at a single evaluation that reflects the best collective thoughts of the group. A valuable aspect of the method employed was having each expert make explicit the relative merits of the alternatives as they relate to various evaluative criteria that were developed in the study. By having the decision rationale of each member

available to all the other members--and preserving anonymity--the strongest arguments tend to win the day, and the best alternatives prevail. Thus, the Delphi method creates a collective consciousness that taps the best in the minds of all the experts.

9.3.1.2 Synthetic Evaluation. The primary result of this study was a ranking of the integrated flow processes. The ranking was based upon holistic judgments by each member of a team of experts. The experts considered the relative merits of each process based upon arguments that were put forth as to their impacts on the various criteria. The experts also considered the relative importance of the criteria as they saw it. They then made overall (holistic) judgments of which process is best, second best, and so on. These results are reported in Beary et al. (1993) and are summarized in Section 4.0. An additional analysis, based upon an analytical evaluation, is presented in the next three subsections.

9.3.1.3 Analytical Evaluation. In addition to rankings based on holistic judgments, performance evaluations were also made with respect to the individual criterion. This was done both for the three final contending integrated pretreatment processes, as well as for the alternatives identified for each of the unit operations. The analytical evaluation of the integrated pretreatment processes agrees with the holistic Delphi judgments in picking ozonation and ion exchange as the best process. Thus, evaluation of the processes on the individual criterion and aggregation of the results produces the same result as the more intuitive evaluations.

The initial analysis assumed that all the criteria were given equal weighting. It turns out that the same results would occur regardless of the judged relative importance of the different criteria. Sensitivity analysis shows that ozonation and ion exchange dominate the other two processes on all criteria except for one. The one exception is Provide Maximum Flexibility for Incorporating Improved Technology; if this criteria is given 75% (rather than 9%) of the weight then "ozonation/ion exchange + nitrate destruction" would be the best option. Thus, the results of SAIC's evaluation of the integrated pretreatment processes are very robust. It should be pointed out that the magnitudes of the differences in the overall analytical ratings of the three integrated processes are not that much different. This is in part explained by the fact that processes are not that radically different from each other--usually differing by one or two unit operations. Also, what was being evaluated were the resulting best three processes that had been culled from all the earlier possibilities. Thus, it is not surprising that there was not much difference among the top three.

9.3.1.4 Evaluation of Unit Operations. In addition to rating the integrated pretreatment processes, ratings for each of the alternatives that were identified for the unit operations were also obtained on individual criterion. There were six unit operations identified by SAIC, which when strung together form an integrated pretreatment process. For each of these unit operations, three to six alternatives were identified. The result is as follows: if the best unit operations, as determined by ratings on the individual criteria, are strung together to form an integrated process, it not only results in an overall process that is analytically feasible, but it is the same process that was rated best using the holistic Delphi judgments.

9.3.1.5 Summary Observations. The results obtained by SAIC show a remarkable consistency when the holistic Delphi ratings are compared with the analytical evaluations based on the individual criterion. Not only does the same integrated flowsheet (ozonation and ion exchange) receive the highest evaluation in each case; but, this same integrated process emerges as the best when the processes are evaluated as unit operations. Ozonation and ion exchange emerges as a clear winner in the SAIC study (not in the overall seven flowsheet studies of this report); however, it is not possible to know how the other processes, identified in the SAIC study but not evaluated, would have done with different criteria weightings. This is especially important for decisions such as this one, which will be subject of public scrutiny. The Delphi method is an excellent procedure for identification of alternatives; it can be even better when combined with an analytical evaluation process.

9.3.2 Bulk Treatment (PNL)

PNL developed flow sheets for four types of processes which are summarized in Section 5.0. Criteria were considered in the development of the processes; however, no attempt was made to develop scales for the criteria or to evaluate formally the performance of the processes on the criteria. Rather, the pros and cons of each process are summarized. It is worth noting that these summary arguments consider additional criteria besides those explicitly listed for consideration in the development process. Also, while the relative merits of each process are discussed, no attempt is made to directly compare the processes. However, material balance calculations are developed. These calculations allow for a summary of the resulting grout volumes, glass volumes, and fraction of Class A limits in grout. A direct comparison of the processes on these variables is provided. A consideration of only these variables would seem to favor the ion exchange process because of the minimal amount of glass, but there are additional technical uncertainties that make this conclusion problematic. A formal evaluation of these processes, using well defined criteria, would be very valuable. This would allow comparison of the four identified flow sheets as well as a comparison with processes that have been identified by other researchers.

9.3.3 BNFL, Inc.

BNFL developed mass balance spreadsheets for processing NCRW and CC waste (BNFL 1993), which are summarized in Section 6.0. These processes were to be based on methods and practices that BNFL would use if the waste streams were in the United Kingdom. The spreadsheets allow for "what if" questions and should prove useful in exploring the strength of the process. The report outlines the decision methodology that BNFL normally uses in the development of any new plant, process, or project. As a general rule, BNFL develops selection criteria up front of design projects. These criteria are developed from an initial set of generic criteria that BNFL created for this purpose. The generic criteria primarily address technical assurance, safety, simplicity, and cost. In this case, the criteria were augmented by criteria suggested by WHC that included meeting HWVP and grout feed specification, and meeting NRC Class A limits. Also, BNFL generally assigns criteria weights in advance. They use decision tools like Kepner-Tregoe to evaluate alternatives. They would also normally characterize the waste before developing a flowsheet.

This is all done in an attempt to create an objective evaluation of proposed designs. Because of the limited time, they used professional judgment and supplied data, and only one flowsheet was developed. Thus, with only one alternative it was not possible to use decision analysis to pick a "best" process from multiple options. The criteria used by BNFL are a subset of those collectively identified by other researchers. The process identified by BNFL would benefit from a formal evaluation in which it was compared to the other processes that have been developed. In addition, the mass balance spreadsheets should make it relatively easy to determine the flowsheet's performance on grout volume, number of glass canisters, and fraction of Class A limit in grout. Thus, a comparison with processes identified by PNL should be possible. It may also be possible to obtain this information for the SAIC study and possibly the Numatec study. This would provide the beginnings of an objective comparison across the various studies. However, it will be necessary to ensure that similar assumptions are being observed to carefully qualify any conclusions.

9.3.4 Numatec

Numatec made recommendations for processing NCRW and CC waste (Numatec 1993), which are summarized in Section 7.0. These processes were to be based on methods and practices that the French Atomic Energy Commission would use if the waste streams were in France. Numatec did not specifically list criteria or discuss a specific decision methodology to be used in the identification and evaluation of alternatives. Their recommendations are based upon technical considerations of the composition of the waste streams and required output specifications.

Numatec separately considered pretreatment objectives for NCRW and CC waste. In both cases, they described the overall objective as the separation of the waste into two waste streams: (1) one stream containing inactive components that will form grout and be stored near the earth's surface, and (2) the other stream containing the majority of the radionuclides to be vitrified and put in a deep geologic repository. They also describe the special technical requirements for NCRW and CC waste. These are shown in Table 9-1.

The processes identified by Numatec would benefit from a formal evaluation in which they are compared to the other processes that have been developed. The mass balance sheets in the draft report are incomplete; however, it still should be possible to determine the flowsheet's performance on grout volume, number of glass canisters, and fraction of Class A limit in grout. This would be the start of a more comprehensive comparison with processes identified by other contractors.

9.3.5 Tank Waste Remediation System Rebaselining

Decision analysis was an integral part of the FY 1993 TWRS rebaselining (see Johnson et al. 1993). The purpose of the rebaselining decision analysis is the evaluation and selection of a technical strategy for treatment and

Table 9-1. Comparison of Pretreatment Criteria. (4 sheets)

TWRS Rebaseline Criteria	PNL Criteria	SAIC Criteria	BNFL Criteria	Numatec Criteria
Public and worker health and safety				
<ul style="list-style-type: none"> • Minimize worker radiological exposure • Minimize public radiological exposure • Minimize worker industrial hazards • Minimize public transportation hazards 	Minimize potential safety and environmental problems by minimizing the addition of organics and hazardous chemicals.	Minimize health/safety impact.	Demonstrated safe with little uncertainty.	
Environmental impact				
<ul style="list-style-type: none"> • Minimize long-term environmental contamination • Minimize offsite HLW volume 	<p>Minimize potential safety and environmental problems by minimizing the addition of organics and hazardous chemicals.</p> <p>Minimize the volume of grout and glass (the impact of this was to promote the selection of processes that add a minimum of chemicals and to add chemicals that do not have restrictive limits in the final waste forms).</p>	Minimize volume of HLW generated.		One stream containing the majority of alpha emitting radionuclides, certain beta/gamma emitter and a small amount of the waste's active components.

Table 9-1. Comparison of Pretreatment Criteria. (4 sheets)

TWRS Rebaseline Criteria	PNL Criteria	SAIC Criteria	BNFL Criteria	Numatec Criteria
<ul style="list-style-type: none"> Minimize onsite LLW volume Minimize system generated waste volume 	<p>Minimize the radionuclides disposed of in the grout waste form (NRC Class A limits were applied to the grout feed).</p> <p>Maximize the radionuclides going to glass.</p>	<p>Minimize generation of secondary waste.</p> <p>Minimize generation of secondary waste.</p>		<p>One stream containing most of the inactive components of the waste and from which alpha, beta, and gamma emitters have been removed to a level that permits grout treatment and near-surface disposal.</p>
Technology assurance				
<ul style="list-style-type: none"> Maximize operability and reliability 	<p>For selection of the individual separations processes, sufficient laboratory data must be available to indicate that the process can work and to allow an estimate of the separation performance.</p>	<p>Maximize reliability and maintainability.</p>	<p>Conventional engineering with little novel or untried equipment.</p>	<p>A NCRW DF of 75 must be achieved for plutonium and americium.</p>

Table 9-1. Comparison of Pretreatment Criteria. (4 sheets)

TWRS Rebaseline Criteria	PNL Criteria	SAIC Criteria	BNFL Criteria	Numatec Criteria
<ul style="list-style-type: none"> Maximize use of mature processes 	Minimize the radionuclides disposed of in the grout waste form (NRC Class A limits were applied to the grout feed).	Minimize technical risk.	Proved at pilot scale with active species.	A CC DF for alpha is 11.
<ul style="list-style-type: none"> Maximize flexibility to incorporate improved technology Avoid regulatory uncertainty 	<p>Minimize complexity (the impact of this was to promote the selection of processes that did not require complex chemical adjustments and that minimized the number of process steps.</p> <p>Maximize the radionuclides going to glass.</p>	<p>Maximize flexibility to incorporate improved technology.</p> <p>Treat a broad range of chemicals and compositions.</p> <p>Comply with Federal and State regulations.</p> <p>Meet output specifications.</p>	<p>Simple, easy to control process. Minimum process steps and unit operations.</p> <p>Demonstrated compatibility with associated plants.</p>	
Cost				
<ul style="list-style-type: none"> Minimize life-cycle cost Minimize discounted costs 		Minimize life-cycle cost.	Demonstrated acceptable lifetime costs.	

Table 9-1. Comparison of Pretreatment Criteria. (4 sheets)

TWRS Rebaseline Criteria	PNL Criteria	SAIC Criteria	BNFL Criteria	Numatec Criteria
Schedule				
<ul style="list-style-type: none"> • Minimize time duration for resolving safety issues • Minimize time duration for resolving environmental concerns 		Minimize health and safety impact, comply with regulations	Reasonable chance of successful development within a reasonable timescale.	
<ul style="list-style-type: none"> • Minimum campaign duration • Maximize early immobilization for disposal progress 		Minimize campaign duration		

disposal of Hanford Site wastes. This decision has a much broader scope than the selection of a pretreatment process. However, the alternative technical strategies that were considered include the specification of pretreatment processes; consequently, the decision methodology is summarized here.

9.3.5.1 Decision Methodology. The decision methodology used by TWRS Rebaselining Decision Analysis is MAU theory. The rebaselining decision analysis is noted for explicitly treating uncertainty in the evaluation of alternatives. The steps in the decision analysis process include the following:

- Defining strategic alternatives
- Identifying measurable performance criteria
- Identifying uncertainties that impact outcomes
- Developing a decision model that relates the alternatives and uncertainties to performance criteria
- Performing sensitivity analysis to determine which variables to model probabilistically
- Developing a probability model
- Evaluating alternatives to determine the alternative with the highest expected value and its associated risk.

9.3.5.1.1 Alternatives Evaluated. The decision alternatives considered evolved from those identified in the *Tank Waste Technical Options Report* (Boomer et al. 1993). These alternatives address three of the four level 2 functions that were identified: (1) manage tank waste, (2) process waste, and (3) manage system generated waste and excess facilities. The alternatives considered by the decision analysis model are a combination of a pretreatment process, a pretreatment facility, a LLW form, and a HLW form. Thus, the alternatives combine treatment and disposal options. Four categories of pretreatment were considered: (1) no pretreatment, (2) minimum pretreatment, (3) advanced pretreatment, and (4) extensive separations, which was not evaluated. Nine categories of waste are identified (five for DSTs and four for SSTs). The decision model allows for the pretreatment processes to be individually specified for each waste type.

9.3.5.1.2 Criteria Development. Criteria used in the decision analysis model evolved over time from the criteria in the *Systems Engineering Study for the Closure of SSTs* (Boomer et al. 1991) and the *Tank Waste Disposal Program Redefinition* (Grygiel et al. 1991). These criteria were developed within a MAU analysis paradigm using input from a variety of stakeholders. There are 18 criteria in 5 categories. The five categories include the following:

1. Public and worker health and safety
2. Environmental impact
3. Technology assurance
4. Schedule
5. Cost.

These criteria are further defined below in Section 9.4. The weights of the criteria were determined using a swing weighting procedure so that they reflect their importance relative to the variation in the alternatives being considered.

9.3.5.1.3 Uncertainty. The TWRS decision analysis model is most notable for its explicit consideration of uncertainty. Technical uncertainties were identified in a series of workshops. Waste composition was assumed to range $\pm 30\%$ of TRAC3 data. Also considered was the technical risk associated with a pretreatment process. This risk was incorporated into the model by computing the expected value of a reference pretreatment process and its backup. So if a reference option was not successfully developed and/or deployed, then a backup option was assumed to be used. The expected value was calculated as the value of the reference option on the criterion, assuming it to be a success, times the probability it would be a success, plus the value of the backup option times its probability of being deployed (which is one minus the probability of the reference being successful). The model identifies those technical uncertainties that have the greatest impact on the criteria and uses them in a more detailed analysis.

9.3.5.1.4 Deterministic Model. The decision analysis model interfaces with a deterministic spreadsheet model that acts as a subroutine. The deterministic model relates decision alternatives and uncertainties to performance criteria. It takes as input the technical strategy alternatives, various uncertainties such as waste characterization, probability of success for an alternative, the separations efficiency, year of pretreatment facility availability, and others and outputs performance levels on the criteria.

9.3.5.1.5 Sensitivity Analysis. Sensitivity analysis was used to determine which uncertainties make a difference and which have a marginal impact and can thus be eliminated from further analysis. One important result of the analysis was a listing, for each criteria, of the alternatives for which each of the identified uncertainties is important. This information is not only valuable for further analysis of technical strategies, but also provides guidance to pretreatment. This guidance can help with the identification of uncertainties that pretreatment should consider as well as to identify areas in which further study by pretreatment can make a difference.

9.3.5.1.6 Probabilistic Modeling. The TWRS decision analysis model does probabilistic modeling to determine the combined impact of the technical uncertainties on the performance measures. Only technical uncertainties that were determined by sensitivity analysis to be important are carried forward into the probabilistic modeling. The probabilistic model considers the possible states of the technical uncertainties and their probabilities, and computes the expected value for each combination of alternatives. In addition to expected values of alternatives, it also provides an analysis of the risk of alternatives. The risk analysis is presented as a cumulative probability distributions of the criterion outcome values. This allows an assessment of the range of possible outcomes and their probabilities as well as the expected outcome. It also makes it easy to determine whether one alternative dominates another.

9.3.5.2 Findings. As a result of the analysis, the two bounding strategies for pretreatment are to be carried forward: extensive separations and high-capacity vitrification. A selection between the two approaches will be made when supporting technologies are sufficiently developed to understand the uncertainties associated with each approach. Identified technical uncertainties that are relevant to pretreatment include the successful development of an extensive pretreatment process, composition of tank wastes as compared to TRAC3 data, successful development of a TRUEX process, year pretreatment facility is operational, and pretreatment facility process throughput. The decision model as described in March 1993 is incomplete in that it evaluates a subset of the 18 performance criteria. These are the HLW volume, LLW volume, number of new DSTs, life-cycle cost, time for resolving safety issues, campaign duration, and HLW facility startup date. The relationship between alternatives and outcome measures still need to be defined for the remaining criteria. The decision analysis model calculates for each alternative a probability distribution of its performance on each of these criteria.

9.3.5.3 Significance for Pretreatment. Decision analytic efforts that are developed for pretreatment need to be consistent with the TWRS decision plan. The impacts of alternative pretreatment processes should be evaluated on the criteria developed for TWRS to the extent that it is appropriate to do so. Pretreatment should also be cognizant of the significant uncertainties that the TWRS decision plan has identified and either try to resolve them or develop strategic alternatives that address these uncertainties. A further discussion of proposed TWRS decision analysis interfaces is in Section 9.5.

9.4 DECISION CRITERIA

Decision criteria were considered by each of the researchers that developed pretreatment flow processes reviewed in this report. In some cases, the criteria were used to formally evaluate alternatives, and in some they were used informally to provide guidance in the development and selection of processes. The scope of the criteria also varied from including a broad base of public concerns to a focus on technical performance. A comparison of the various criteria are shown in Table 9-2.

The 18 criteria identified by TWRS are the most complete set and have been subject to the most public scrutiny and review by stakeholder groups. The stakeholder groups include the following:

- The States of Washington and Oregon
- U.S. Environmental Protection Agency
- Yakima Indian Nation
- WHC
- PNL
- DOE-HQ
- DOE Richland Operations Office (RL).

The criteria have also been endorsed by the TWRS Leadership Council and subjected to review by DOE-HQ and RL. As can be seen in Table 9-1, those criteria identified by the other researchers are a subset of the TWRS

Table 9-2. Studies from Which Processes for Preliminary Short List Were Taken.

	CC & FeCN Destruction	Cesium Separation	Strontium Separation	TRU Separation	Technetium Separation	Other Separations
Redefinition Study (Grygiel et al. 1991)	early study	Ion exchange (basic)	Solvent extraction (strontium extraction [SREX])	Solvent extraction (TRUEX)	TBD	TBD
Tank Closure Study (Boomer et al. 1991)	early study	Ion exchange (basic)	Solvent extraction (SREX)	Solvent extraction (TRUEX)	Ion exchange (basic)	NONE
Initial Pretreatment Module (Bailey 1992)	hydrothermal or calcination	Ion exchange (basic)	NONE	NONE	NONE	NONE
Bulk Precipitation Study	Not in scope	Precipitation (acidic, basic)	Precipitation (acidic, basic)	Precipitation (acidic, basic)	Precipitation (basic)	Not in scope
Bulk Ion Exchange Study	Not in scope	Ion exchange (acidic, basic)	Ion exchange (acidic, basic)	Ion exchange (acidic)	Ion exchange (basic)	Not in scope
Bulk Leach Study	Not in scope	Leach (acidic, basic)	Leach (Act-De-Con)	Leach (Act-De-Con)	NONE	Leach Al, Cr
Independent Consultant Study (Beary et al. 1993)	Ozonation	Ion exchange (Ti-treated zeolite)	Ion exchange (Ti-treated zeolite)	Ion exchange (Ti-treated zeolite)	Ion exchange (anion resin)	NONE
British Technology Study (BNFL 1993)	calcination or hydrothermal (IPM)	Ion exchange (SIXEP)	Ion exchange (SIXEP)	Solvent extraction (TRUEX)	NONE	Precipitation F, Al, Zr
French Technology Study (Numatec 1993)	H ₂ O ₂ or electrolysis [Ag(I) or Co(II)]	Solvent extraction (macrocycle)	Solvent extraction (macrocycle)	Solvent extraction (DIAMEX)	NONE	Solvent extraction U, Ce

criteria. The TWRS criteria were developed for evaluating technical strategies for managing tank wastes. As such, they may be too broad in scope for evaluating pretreatment flow processes; or at least the operational definitions may need to be modified. Also operational definitions that were suitable for the TWRS decision model were not developed for all of these criteria. Consequently, pretreatment is in the process of further developing these criteria so that they will be specifically tailored to the evaluation of pretreatment processes while retaining all the broad concerns of TWRS. The criteria in their current state of development are shown in Figure 9-2.

9.5 PROPOSED FISCAL YEAR 1994 APPLICATION

This section describes decision analysis activities that will be conducted to identify, screen, and evaluate pretreatment alternatives. We propose to develop a decision analysis model that is specific to pretreatment. Specific analyses are proposed, and a description is given of their potential benefits. Activities necessary for the realization of the model and to carry out the analyses are also identified.

9.5.1 Benefits to Creating a Pretreatment Decision Analysis Model

The benefits to creating a pretreatment decision analysis model include (1) providing decision methodology whereby decisions can be communicated and defended in a public arena, (2) showing the relative merits of additional R&D versus existing technology, and (3) creating a decision support tool that can be modified over time as policy requirements and/or technology changes.

9.5.1.1 Defends Decision Methodology. The decision methodology will integrate stakeholder values with scientific and engineering judgment. It will make the decision rationale explicit and make it possible to explore the strength of the decision to changes in assumptions and tradeoffs between competing objectives (e.g., cost vs. schedule). The process is designed to develop consensus among Hanford Site scientists and engineers.

9.5.1.1.1 Integrates Engineering Judgment and Stakeholder Values. The decision methodology integrates engineering judgment and/or data with stakeholder values. Stakeholder values are reflected in the criteria used to evaluate alternatives and the relative importance given to the criteria. Engineering judgment is used to determine how well the different flow processes perform on the criteria. Where possible, hard analytical data based on mass balance sheets will be the basis for assigning performance levels. The criteria used will be a refinement of the criteria used in the TWRS rebaselining decision analysis model. These criteria have evolved over time and been subject to review of the major stakeholders. The criteria were developed to evaluate strategic technical options that include pretreatment. These criteria need to be reviewed and revised as necessary to ensure that they can be distinguished among options that are specific to pretreatment. It may be necessary to add criteria more specific to pretreatment that are a means to achieving some of the more general criteria identified for TWRS rebaselining.

Figure 9-2. Decision Criteria for the Evaluation of Pretreatment Processes.

9.5.1.1.2 Develops Consensus Among Scientists and Engineers. The proposed process is designed to develop consensus among scientists and engineers. This consensus will be developed throughout the Site (and wider as deemed appropriate) by involving key personnel from a variety of pretreatment programs in model development. Activities targeted for involvement will include refining scales and criteria, selecting processes to be evaluated, and obtaining judgments or data for performance of the alternatives. The latter will include development of performance models used to evaluate alternatives on each of the criteria.

9.5.1.1.3 Makes Explicit Basis for Relative Rankings. The rationale for recommending one flow process over another is clearly specified. The overall performance of each process is quantified; consequently, whether one process is only slightly better than another, or a lot better, is clear. Also, processes can be compared on each of the criterion; thus, relative performance of processes on each objective is explicitly given. In addition, the relative weight given to the criterion is stated explicitly as is the value of various levels of performance on a given criterion. The relationship between alternatives and their performance on criteria is specified; or at least, the factors that were considered in making the judgments is specified. Thus, all the value judgments and all the engineering judgments that form the basis for the evaluations are clearly stated. If there are differences of opinion, they can be resolved at the level of engineering judgment and value.

9.5.1.1.4 Supports Sensitivity Analysis. The pretreatment decision analysis model will make it possible to explore key decision drivers and the strength of the solutions to new parameter estimates, and help the decision maker understand critical aspects of the decision. This will make it possible to determine the strength of the decision and to identify areas in which data inputs should be further explored.

9.5.1.2 Creates a Decision Support Tool. The model will be in the form of a computer-based decision support tool that can be modified and updated as the need arises. Thus it will be possible to evaluate alternatives that are identified subsequent to the initial analysis and compare them to those alternatives in the initial evaluation. If there are policy changes in which the relative importance of criteria changes, then the model can be adjusted accordingly. If new issues develop that were not captured by the original criteria, criteria can be added and it will not be necessary to perform an entirely new analysis. Also, if technological breakthroughs change performance levels on a criterion, appropriate modifications can be made and the impact on the alternatives' rankings observed. In summary, as policy and/or technology changes, the model can be modified to reflect the changes, and there is no need to bring together a large group of experts for an entirely new evaluation.

9.5.1.3 Provides Stopping Information. One of the biggest issues facing TWRS is when to stop gathering more data and evaluating alternatives and start the commitment of resources to a particular alternative. This decision is difficult because future technology always holds out the promise of a better outcome. The key to being able to make this decision is a defensible estimate of what would be gained by continuing to gather more information. A comparison of potential gains with extra costs and delay in schedule makes clear the tradeoffs involved. Estimates can also be made of the potential

risks associated with promised technologies not being developed. These issues can be addressed with respect to both alternative process development and characterization requirements.

9.5.1.4 Addresses Characterization Needs. The model will identify uncertainties that have the greatest impact on outcomes and make a difference with respect to the optimal alternative. Thus, it will be possible to provide a rational basis for characterization needs. This will ensure that pretreatment's needs are given full consideration in sampling and analysis plans.

9.5.2 Model Description

This section describes the proposed pretreatment decision analysis model.

9.5.2.1 Theoretical Description. The proposed decision analysis model will be based on MAU and will model uncertainty. This theoretical approach is described in Section 9.2.

9.5.2.2 Computer Realization. The decision software used to model performance on each of the criteria will be either Decision Programming Language (DPL) produced by Applied Decision Analysis, Inc., or Supertree created by Strategic Decisions Group. Both programs are capable of representing decisions as either decision trees or influence diagrams. DPL was initially developed to include an influence diagram and is capable of a composite representation that makes both representations more parsimonious. DPL also has excellent graphical abilities. Furthermore, DPL is not limited in the number of uncertain variables that it can include in the probabilistic phase of the analysis; whereas, Supertree is limited to six or seven uncertain variables. Supertree was used in the TWRS rebaselining decision analysis. Both programs also allow the user to interface with spreadsheets, which act as subroutines for the decision program. Spreadsheets will be used for complex calculations of performance, such as those based upon mass balance sheets.

The MAU analysis will be carried out using Logical Decision, which is produced by Logical Decisions. This is a user friendly MAU software package. It is capable of a number of useful analyses and provides a variety of graphical displays that clarify the results.

9.5.3 Analyses Made Possible by Model

This section describes anticipated analyses that can be carried out and the type of decisions that they will support.

9.5.3.1 Quantitative Analysis of Performance. The model will compute the overall value for each integrated flow process. These results can be displayed graphically to clearly see the relative standings of the different processes. This analysis is an aggregation over all of the criteria and is based upon the relative importance of the criteria (weights). The model will also allow processes to be compared on each of the individual criterion and/or criteria categories. For example, the processes could be compared on the amount of HLW generated or the more general criteria of environmental impact.

Additionally, for each process, a performance profile can be generated that shows graphically--using bar graphs--performance of each criterion. If the heights of the bars represent levels of performance on the individual criteria, and the width represents the weight given to the criterion, then the area in each bar is the contribution of that criterion to the overall value of the process. The total area for all bars is the overall value of the process. An example of a performance profile is shown in Figure 9-3. A comparison of these profiles for different processes can provide some interesting insights.

9.5.3.2 Identification of Key Uncertainties. The performance outcome of a pretreatment flow process depends on which process is chosen and various uncertainties such as waste characteristics. It is important to distinguish uncertainties having a large impact on outcomes from those that make little difference. Those having minimal impact can be treated as a constant in further analysis. The other, key uncertainties can be carried forward into a probabilistic model that captures risk information. The key uncertainties are also candidates for further studies directed to their resolution. A sensitivity analysis during the deterministic phase of decision analysis model will make it possible to identify key uncertainties.

A description of sensitivity analysis is given in Section 9.2.3.3. Two general types of analysis will be useful. One, is a "comparison" sensitivity. It compares changes in criterion value as a function of the extreme values of the relevant uncertain variables. This can be displayed graphically, for each combination of criterion and flow process, as a tornado diagram. The changes in criteria values are represented as horizontal bars for each of the uncertain variables. If the bars are ordered vertically from most to least important, the resulting diagram has the funnel shape of a tornado. An example tornado diagram is shown in Figure 9-4. This clearly shows the relative importance of the uncertain variables that enter into the calculation of performance levels.

Another sensitivity analysis is to explore the relationship of a single uncertain variable to the value of some performance criterion. The criterion's values can be calculated for a representative set of the values for the uncertain variable. DPL will display this information as a colored graph, in which the changes in colors represent different optimal alternatives that depend on the value of the uncertain variable.

9.5.3.3 Risk Information. Risk information is made possible by probabilistic modeling of the decision situation. Probabilistic modeling is described in Section 9.2.3.4. Risk information provides a more complete description of potential outcomes than is provided by the point estimate given by a deterministic model. It shows all the possible outcomes and their associated probabilities. Thus, the decision maker can evaluate processes based not only on the best estimate of what will happen, but on the likelihood of potential adverse consequences. It is possible that a process with a lower performance point estimate will be judged more desirable than some other process with a higher point estimate, but have potentially worse outcomes. This information becomes especially clear if the cumulative probability distributions for several processes are plotted on the same graph. If the distribution lines

Figure 9-3. Performance Profile for Integrated Process.*

* Fictitious Data

Figure 9-4. Tornado Diagram Showing Comparative Impact of Uncertainties on Number of Glass Logs.*

* Fictitious Data

cross, then risk tradeoffs are required. If two distribution lines do not cross, then one process stochastically dominates the other, i.e., no matter what values the uncertainties take on, one process is always better. Figure 9-5 shows the cumulative probability distributions for three flow processes. Process C stochastically dominates the other two, and process A is riskier than process B.

9.5.3.4 Elimination of Dominated Alternatives. A valuable analysis is the elimination of dominated alternatives. One process dominates another if it is better on all the dimensions being considered. Stochastic dominance was described above under Section 9.5.3.3, "Risk Information." Another potentially valuable analysis will be to compare processes on two dimensions: cost and value, where value is all the criteria "rolled up" except cost. Processes that cost more and provide less value than some other processes can be screened from further consideration as dominated options. If the options are plotted in the two-dimensional space of cost and value, the set of dominated options becomes apparent. The choice of a process to be implemented would be among the set of nondominated options. To choose among these options, the decision maker should start by considering the least costly nondominated process. The decision maker would decide if the increase in value for the next most costly process is worth the additional cost. The procedure would continue until the answer is no. At this point, the decision maker has found the preferred tradeoff between cost and value.

9.5.3.5 Sensitivity Analysis. Sensitivity analysis is an integral part of any decision analysis and will be carried out using the pretreatment decision analysis model. It consists of playing "what if" games to determine the strength of the recommended alternative. It is important that Pretreatment be satisfied that the optimal process does not depend on small variations in judgments of value for some variable. If the optimal process is sensitive to small changes in judged value for some variable, then it may be desirable to spend more time gathering data and/or considering the value of that variable.

It will be most important to perform sensitivity analysis on the criteria weights because these judgments are the most difficult to make and the most subjective. Criteria weights that decision makers are least sure of or stakeholders disagree with are especially important to consider. Sensitivity analysis will be explored to determine crossover points, which are the weighting values for which the recommended and next best processes reverse places. If these values are far from the judged weight, then pretreatment can be confident in the recommendation. If the crossover point is close to the judged value for some weight, then additional thought will be given to the judged value until Pretreatment is confident in their recommendation. This type of analysis is easily performed by MAU software packages, which provide a graphical display of the results. Figure 9-6 shows a typical display. For this fictitious example, process B does best for the weight put on this attribute. If less weight is used, process C can be best. If more weight is put on this attribute, process A can be best.

In addition to sensitivity analysis on criteria weights, sensitivity analysis will also be performed on the judged value of other key variables and probabilities to the extent necessary.

Figure 9-5. Performance Distributions for Three Flow Processes on High-Level Waste.

Figure 9-6. Sensitivity Analysis on Weight for Technical Assurance.

Technical Assurance

9.5.3.6 Impact of Stakeholder Values. Of particular interest may be the impact of differing values of stakeholders. This is best explored by simply performing successive evaluation of the options with the differing criteria weights as input. These results can be displayed graphically so as to make clear what impact, if any, the differing stakeholder values would have on how the processes would be ranked. Figure 9-7 is an example display.

9.5.3.7 Stopping Information.

9.5.3.7.1 Search for Processes. The decision as to when to make a commitment to a particular process alternative can be addressed by a "value of control" analysis. What is required is a comparison of the value of a reference process that is best for near-term implementation to other processes that promise more but require additional development time. The basic rationale assumes that these promising processes are successfully developed and that their outcomes can be controlled to provide all that they promise. The value of these promising processes can be compared to the reference process and a decision made as to whether this additional value is worth the extra time, cost, and risk.

9.5.3.7.2 Characterization. An issue confronting Pretreatment is whether the lack of reliable characterization data should delay the selection of a pretreatment process. Value of information analysis can be used to help answer this question and to determine which characterization needs really impact the decision outcomes. Initially, a value of perfect information analysis can be carried out. The essence of this analysis assumes process decisions are made subsequent to resolving characterization uncertainties. The value calculated under this assumption is then compared to expected value when the characterization information is not known in advance; the difference is what it would be worth to resolve the uncertainties. If this analysis is used to address multiple characterization needs, then the information can be used to rank various uncertainties according to the value of their resolution and/or aid in the decision of which uncertainties to resolve. Analytical methods are also available for valuing characterization needs that take into account the unreliability of the data.

9.5.4 Alternative Pretreatment Processes

9.5.4.1 Need for Screening. A wide variety of processes need to be evaluated in order that the analysis will be defensible. The richer the set of candidates to be evaluated, the greater are the chances of selecting an alternative that maximizes potential performance on criteria. If too narrow a range of alternatives is considered, then there exists a potential to fault the selected process as not being as good as some process that were not considered. However, if a wide variety of processes are considered, then the chances are that any process that might be pointed up as a better alternative than the one selected is just a variation on one that was considered.

There is a very large number of potential integrated processes. At least six separate operations have been identified as making up an integrated process. For each of these unit operations, four or more methods have been identified as potential candidates. Thus, there are a large number of possible combinations of integrated processes that potentially could be

Figure 9-7. Example Analysis of Impact of Stakeholder Values.

evaluated using the decision analysis model. The number of potential candidates is too large for it to be practical to evaluate them all because of limitations of time and resources. Thus, some method of initial screening is necessary.

While it is possible to separately evaluate the alternatives for the unit operations; ultimately, evaluation of alternatives needs to be at the integrated process level. The collection of unit processes, which are judged best separately, do not necessarily make the best combination for an integrated process. This collection may be incompatible in the sense that they create an output at one stage of the integrated process that is less than ideal for input to a subsequent process. Another reason for evaluating integrated processes is that there are also other factors to be considered that may only emerge when the integrated process is evaluated as a whole. These factors may not be apparent when considering the unit processes individually. Thus, the evaluation of pretreatment alternatives needs to take place at the integrated process level, and this is assumed in the proposed screening strategy.

9.5.4.2 Screening Strategy. The essence of the proposed screening strategy is to let qualified organizations that have been tasked to develop and/or evaluate pretreatment processes do the screening for us. Table 9-2 lists the preferred integrated pretreatment processes that have been identified by various organizations in the past 3 years. This is the initial list of candidate processes to be considered for evaluation. This list will be circulated for review by qualified organizations concerned with Hanford Site waste treatment. These organizations will be allowed to nominate additional processes. The favored process for many organizations is already on the list, so the number of additions should not be too great. If the total number of candidates is 12 or less, then it should be possible to evaluate them all. If the number becomes too great, then an additional screening strategy will be developed. If an additional screening strategy is needed, it will be decided upon after the initial list is generated. Whatever additional screening is proposed, it will give due consideration to the nature of the initial list of candidates. One possible strategy is for a two-staged evaluation. This would evaluate classes of more generic processes first to choose a particular category of process, then would subsequently evaluate candidates within a particular type. Another possibility is to eliminate candidates that do poorly on some subset of criteria, possibly in the form of constraints.

9.5.4.3 Processes to be Evaluated. The initial short list of candidate processes that Pretreatment proposes to evaluate in FY 1994 is shown in Table 9-2. This list is subject to review and change as discussed above. Evaluation and analysis of the FY 1994 short list may indicate that a defensible process for the cleanup of Hanford Site tank waste has been identified. It is also possible that additional processes will come to light that will require evaluation. The decision analysis model will make additional evaluations relatively painless.

A consideration in the need for additional evaluations is that the processes identified so far have been developed for processing NCRW, CC waste, and combined tank waste. There are seven additional categories of tank waste (Section 9.3.5.1.1). It may be that additional processes will be identified specific to the pretreatment of these waste streams. It may also be that it

will be necessary to evaluate the performance of currently identified processes on these other waste streams. In any case, additional analysis may be desirable in subsequent years. As more data becomes available, it will be possible to update the decision model to determine whether the selected alternative still represents the best course.

9.5.5 Fiscal Year 1994 Activities

This section summarizes the activities that are necessary to develop a pretreatment decision analysis model and carry out the proposed evaluations and analyses. This decision analysis model, like any other model, is only as good as the data from which it is developed. Consequently, the focus of this discussion is on data collection. The physical realization of the model is in the form of three off-the-shelf software packages as described above. Time must be allowed for programming this software and subsequent analysis; however, the majority of the resources will be for data collection as this involves input from a variety of personnel. All of these data collection activities will be carried out in a manner designed to develop consensus among experienced Hanford Site process engineers and organizations concerned with Hanford Site waste treatment.

9.5.5.1 Steps Needed to Create Model. The steps involved in creation of the pretreatment decision analysis model and the evaluation of alternatives are as follows:

1. Identify process alternatives to be evaluated
2. Identify criteria
3. Develop scales
4. Determine relative weight of criteria
5. Determine value functions for criteria
6. Develop performance models for criteria as needed
7. Obtain initial input data (alternative evaluations and uncertainty inputs) for deterministic model
8. Analyze data and perform deterministic sensitivity analysis
9. Revise model to create probabilistic model
10. Solicit appropriate probability distributions
11. Run model to evaluate processes based upon risk
12. Perform additional analysis as desired
13. Perform additional sensitivity analysis

14. Revise model as needed until all are satisfied that the model accurately reflects the essential features of the pretreatment process decision
15. Present findings and recommendations for review.

Identifying alternatives and criteria is an interactive process. As criteria are identified, objectives become clearer, and additional means to achieving the objectives may be identified. The entire decision analysis process is interactive and may go through several revisions. Also, value is gained, in the form of additional insight for the decision maker, at each stage in the model development. To present defensible results, the model needs to be developed at least through its deterministic phase. The extent of performance modeling required will be determined for each criterion individually. What follows is a brief description of those activities that merit further comment.

9.5.5.2 Consensus Building. A major objective in creating a decision analysis model for pretreatment will be to develop consensus as to its validity. Consequently, at each stage in its development, model building activities will be planned and implemented so as to obtain input from as many groups as is practical. Pretreatment intends to identify systems engineering groups and other technical organizations that are participating in the development of pretreatment processes. The particular involvement strategy will vary with the type of activity and will be decided upon on a case-by-case basis. One possibility is to have a workshop dedicated to the activity with attendees having a broad-based representation. Each product would subsequently be circulated for review. Alternatively, Pretreatment would develop it first and then circulated it for review, or some combination.

9.5.5.3 Refine Criteria and Scales. Section 9.4 compares the criteria used in past studies and presents an initial refinement specific to pretreatment. The TWRS rebaselining criteria are the most inclusive. They have evolved over time and have been reviewed by a broad spectrum of stakeholders.

Additional work is needed to develop a set of criteria that are specific to pretreatment. Criteria must be broad enough to address all the concerns of stakeholders and yet be specific enough to capture the important distinctions among the various processes. Scales must be developed that are clearly specified and that provide a workable evaluative measure for pretreatment. At the same time, they need to remain consistent with the TWRS rebaselining criteria developed to evaluate more general alternatives.

The refine scales and criteria activity will also include development of value functions and weights. These were discussed in Section 9.2.

This activity will solicit a broad spectrum of active involvement in the development and/or review of criteria and scales. A strawman version will be developed in house. This will either be circulated for review and comment or else a workshop will be held for this purpose.

9.5.5.4 Identify Candidate Processes. The method for identifying processes to be evaluated is discussed above. The current initial list of candidate processes is shown in Table 9-2. This list will be circulated for review. We

will identify qualified groups and/or organizations to take part in the review. Qualified organizations will be allowed to nominate one candidate process for inclusion in those to be evaluated. This will ensure that a variety of candidate processes are evaluated and that the favorite processes of qualified organizations are included among them. In addition we will solicit the names of other organizations that should be included in the review process. Every attempt will be made to identify all organizations that may be proponents of some pretreatment process.

9.5.5.5 Performance Modeling. For each of the identified criterion, not only must there be a defensible scale, in addition, there must be a way of establishing an alternatives level of performance on that scale. For each criterion, a model will be developed to capture the relationship between the alternative and its performance contingent on the value of relevant uncertainties. This is part of the structuring process that was discussed in Section 9.2.3.1. These models will be initially developed using influence diagrams such as the one shown in Figure 9-1. The influence diagram captures the essential relationships on a qualitative level and represents them in a manner that can be easily understood by a variety of stakeholders. For some criterion, such as "number of glass logs," these relationships can be further quantified based on mass balance sheets and made explicit in a spreadsheet model. For other criterion, such as "worker health and safety," the quantitative relationship will not be possible to capture in a mathematical formula and will require engineering judgment. The influence diagram model will make explicit all the factors that need to be considered and will result in judgments with greater validity and reliability. A major activity we propose is to consider each of the criteria separately and develop a model of the factors that enter into the determination of performance and the interrelationships among those factors. This will greatly enhance the validity of the decision analysis model and make possible additional analyses and insights into the performance of alternatives.

Performance modeling is an activity in which we want to leverage off the work of others to the extent possible. Where mass balance sheets have already been developed, we will use them. If a group has already developed an algorithm for calculating a particular performance measure, such as the number of glass logs, we will adapt it for our purposes. We will also leverage the TWRS rebaselining decision analysis model whenever possible and involve groups with technical or specialized expertise on a particular criterion if it is feasible. For example, when modeling safety issues, we will solicit help from tank safety groups as well as groups that specialize in risk analysis.

The performance model will include best estimates and 90% confidence intervals for all key uncertainties.

9.5.5.6 Evaluate Alternatives. Alternatives will be evaluated by individuals that pretreatment identifies as being most qualified to make the necessary technical judgments. Most likely this will be done in a workshop environment. The workshop will begin with a general discussion of the its purpose and objectives. Participants will be presented with a criteria and scales and the performance models that will have been developed for each of the criterion. They will also be presented with a complete description of each of the alternatives. In some cases, the experts will make a direct assessment of the performance level for each of the alternatives; the performance model will be

used to prime their thoughts with the relevant factors that should be considered in making their judgments. Also, these judgments may be conditional on the value of key uncertainties, which will require that several conditional judgments be made. In other cases, the experts will provide the necessary information for the calculation of performance level by a spreadsheet model.

Later, a decision will be made as to whether all experts should make judgments on all criteria, or just in their areas of expertise.

10.0 TECHNOLOGY IDENTIFICATION AND MANAGEMENT

The technology assessment activities described in this section use the following strategy: identify > organize > manage > evaluate > select/reject > document. Currently, candidate pretreatment technologies are being identified, characterized, and organized into a function-oriented matrix. Also, a related effort is underway to develop new tools to electronically manage the data that supports the decision-making process effectively, while accommodating the shifting of criteria values that may occur with the passage of time.

10.1 IDENTIFICATION OF ALTERNATIVE PROCESSES

An ongoing effort has been conducted over the past several years to bring new technologies into consideration, national and international, that have potential application to the Hanford Site tank waste pretreatment mission. A wide range of processes have been surveyed, from the destruction of safety issue chemical compounds, to radionuclide separations, to the treatment of inert materials for waste volume reduction. Most of the separation processes remove select radionuclides from waste, but several remove inerts from the radionuclides. Some processes can be used in-tank, others near-tank, while many would require a central processing facility(s). Hanford Site experience has primarily consisted of processes operating in a crane-remote (canyon) structure. Other domestic and international sites have used vastly different facility strategies ranging from no maintenance, to contact maintenance, to hybrids that attempt an integration of the best features that each concept offers.

Information sources that have provided useful data to the pretreatment technology searches include the following:

- Technical library literature surveys
- Database surveys
- Technical conference papers and proceedings
- DOE Defense Complex technology exchanges, facility tours, etc.
- National Technology Workshop in June 1992 for TWRS technology
- DOE programs sponsored by the Office of Technology Development
- DOE programs sponsored by EM-30, DOE Office of Waste Management, and EM-40, DOE Office of Environmental Restoration
- RL and WHC contract to LANL for technology development
- RL and WHC contract to Sandia National Laboratory for cesium and strontium separations technology development
- WHC contract to SAIC for overall pretreatment technology study

- WHC contract to BNFL for British experience
- WHC contract to Numatec, Inc. for French experience
- Technical meetings with Russian engineers and scientists
- Inspections of British, French, and Russian waste processing research centers.

References that identify and/or address the potential pretreatment technologies currently being considered include: Barker et al. 1993, *Pretreatment Technology Plan*; Beary and Nicholson 1993a, *Identification of Alternative Processes for Waste Pretreatment*, Vol. 1; Boomer et al. 1993, *Tank Waste Technical Options Report*; and Holton 1993, *PNL TWRS Pretreatment Technology Development FY 93 Project Work Plan*.

Attention has also been given to the new technical strategy, where four separate phases of pretreatment technology development are identified with respect to the time period when new processes need to be available. Timing has been an important overall search criteria, as have potential performance and relevancy.

10.2 ORGANIZATION OF ALTERNATIVE PROCESSES CHART

All current alternative process candidates have been incorporated into one chart (Appendix B). The following text is an explanation of how the chart data are labeled and organized.

10.2.1 Alternative Process Blocks

Alternative processes in the charting database are represented as rectangular boxes when drawn on the chart. Each process block is labeled with a descriptive, unique process name in the center of the block. Thermometer bars are drawn and filled on the outside of the process block, depending on the values of the corresponding fields for the database record. Abbreviations for the company, DOE site, or country in which the process is being developed appear along the top of the box. An asterisk '*' is used beside the upper right-hand corner of the process block to indicate that the record has been added or modified since the last time the chart was drawn. A unique surrogate record number is displayed near the upper left corner of the block.

The thermometer bars, which are drawn on the outside of the process block, correspond to the three fields in the database structure that represent (1) the maturity or confidence in the process, (2) DOE funding for the project, and (3) the potential benefit gained from the process. If the process has been proven full scale at the Hanford Site, the process block is completely surrounded with a solid filled box. Processes that have been proven full scale at other sites are bounded by an empty rectangle. Thermometer bars are drawn for processes that have not been proven on a full-scale process. The left side bar corresponds to the value of the potential benefit field, the right side bar corresponds to the DOE funding level. If the process is in the demonstration, test, and evaluation stage (DT&E), then

the process is in the demonstration, test, and evaluation stage (DT&E), then the confidence bar is drawn on top of the process block. When the process is still in the R&D stage, the confidence bar is drawn on the bottom of the process block. The bars are filled according to the value of the appropriate field. The value is low, medium, or high, and the bar for the field will be empty, half-filled, or completely filled, respectively. The explanations presented in this paragraph are also displayed as a legend at the bottom of the chart.

10.2.2 Chart Structure

The chart is organized into five areas from top to bottom. These areas include the following: (1) reference system schematic diagram, (2) new technology strategy process boundary concepts and reference system, (3) proven processes, (4) alternative processes, and (5) legend. These areas are optional and can be electronically drawn or hidden as desired by the user, with the exception of the alternative processes section which will always be drawn. From left to right, the chart is organized by columns of processes that belong to a category of species separations or a related function (i.e., dissolution and separation). Rows and columns are drawn if there are processes in the database that are in these rows or columns, or if the user asks the database to display empty rows or columns. When drawing a subset of the records in the database, many rows and columns may be empty.

The reference flowsheet, when drawn, appears at the top of the chart. The flowsheet is drawn with the blocks that are tagged as being in the reference flowsheet, and the mass-flow streams of the flowsheet are drawn to and from the appropriate process blocks. Arrows on the streams indicate the direction of flow. Each process block appears in the same column in the flowsheet as in the alternative processes section. The flowsheet is drawn for the currently selected set of flowsheet blocks, and streams are routed according to the existence of the input and output process blocks in the flowsheet.

The new technical strategy rows are drawn below the reference system schematic diagram. Each process has a set of boolean flags to identify if the process is included in one of the reference studies. Alternative processes that are included in any of the three options will appear in the appropriate study rows.

The proven processes rows are two rows composed of processes from each column that have been proven full scale either for Hanford Site or elsewhere. The first proven row contains the processes proven full scale at the Hanford Site and are drawn with a filled box surrounding the process label. The second proven row contains the processes proven full scale outside of the Hanford Site. These processes are drawn with an empty box surrounding the process label.

The alternative processes section is always drawn for the chart. This section draws all of the currently selected records in the database. Process blocks that appear in the three previous sections are copies of the process blocks drawn in this section. The rows of the alternative processes can be

organized in a number of ways. The most common way is to draw the rows by the original row name given to the processes. The processes can also be organized into rows by using the following categories:

- **Confidence** or maturity of the process, with the highest confidence at the top and lowest at the bottom
- **Country** that developed the process, in the same order as the pick list used to select the country
- **DOE Site** that developed the process, in the order defined by the DOE Site list
- **Company** that developed the process, in the order defined by the Company list
- **Technology Category**, such as extraction or precipitation, in the order defined by the Technology Category list
- **DOE Funding level**, with the highest funding level in the first row and the lowest at the bottom
- **Potential Benefit**, with the highest potential benefit in the first row and the lowest at the bottom.

The legend is drawn at the bottom of the screen when requested, and displays the symbols used to draw the process blocks.

The rows and columns are drawn only for those rows and columns which contain process records in them, or if the user elects to have the program show all empty rows and columns. A maximum column width can also specify the maximum number of boxes wide a column can be. If the number of process blocks in a particular row for a particular column exceeds the maximum column width, then the row will be widened as needed to draw all of the process blocks in the row and column. The paper size can be specified as one of the common American National Standards Institute or architectural sizes, or any custom size desired. The margins for the paper can also be specified by the user. The aspect ratio of the boxes remains constant when the chart is drawn, and the program will automatically size the boxes to fit on the constraining width or length of the page.

10.3 DATABASE

The bringing forward and acceptance or rejection of candidate pretreatment technologies over the next few years may be a dynamic process where documented information plays a key role. Toward this end, considerable attention has been given to selection of a versatile database capability.

10.3.1 4th Dimension and 4D Draw

The decision to use the relational database 4th Dimension on the Macintosh was made on the basis of availability, capability, and flexibility. In addition to the usual database functionality common to databases, 4th Dimension has a very easy and powerful interface for designing database structures, input and output layouts, and a script language for automating database tasks. Many add-on modules have been created to support 4th Dimension, including the module 4D Draw, which contains the procedures to create and draw graphics. Also available is the 4D Compiler, which compiles a database into a form that is much faster than the interpreted database.

10.3.2 Database Structure

There are a number of fields associated with each process record. The primary field is the unique, indexed name for each process. The Process Name field is a 40-character text string that is displayed as the label in the center of each process block when it is drawn. The other fields in each process record include the following:

- **Proof Status** is a required 40-character field that identifies if a process has been proven full scale or has not been fully proven. This field is used to determine if a full rectangle is drawn around a process block.
- **Stage** is the proof stage for processes that have not been fully proven and is either DT&E or R&D. This determines if the Confidence bar is drawn on the top or bottom of a process block.
- **Funding Level** is the level of DOE funding for the process or project that has not been proven full-scale. The funding level is either high, medium, or low, and is drawn on the right-hand side of the process block.
- **Benefit** is the potential benefit gained from using the process to treat Hanford Site wastes. The benefit is either high, medium, or low, and is drawn on the left-hand side of the process block.
- **Confidence** is the maturity or confidence in the process, and is either high, medium, or low. The bar for this field is drawn on the top or bottom of the process block according to the Proof Status above.
- **Description** is a text description associated with the process.
- **Documentation** is a list of documents that are associated with the process. Each document has a field for the Title of the document, Type of document, Dates published, ID Number for identification, Work Package ID number where applicable, and Authors of the document.

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- **USTI Demo** is a 30-character field related to the status of the process in the Underground Storage Tanks Integrated Demonstration. This field may be removed in the future.
- **Company** is a list of companies that are working on the process.
- **DOE Site** is a list of DOE sites that are working on the process.
- **Country** is a list of countries that are working on the process.
- **Dependent** is a field that is no longer used.
- **Reference** is a boolean (true or false) flag to indicate if the process is in the reference flowsheet.
- **Row** is the name of the original row the process is in.
- **Comments** are text comments about why a process was or was not included in the list of alternatives considered for further investigation by SAIC.
- **Surrogate Key** is a unique integer record number for further identifying process blocks. This number is drawn to the upper left of a process block.
- **Advantages** is a text description of the advantages of a process.
- **Disadvantages** is a text description of the disadvantages of a process.
- **Requirements** is the 30-character field that specifies what column each process block is in and corresponds to the type of separation or mixing that is involved. This is related to the Requirements information for each category.
- **Hyper Clean** is a boolean flag to indicate if the process is in the CLEAN technical strategy.
- **Mega Glass** is a boolean flag to indicate if the process is in the High Capacity Vitrification technical strategy.
- **PreTreat Study** is a boolean flag to indicate if the process is in the Reference Case technical strategy.
- **Tech Category** corresponds to the technology category the process belongs to. This would be extraction, precipitation, or other chemical engineering methods.
- **Last Date Mod** and **Last Time Mod** are the last date and time a process record was added or edited. This information is used to determine if an asterisk '*' should be drawn in the upper right-hand corner of the process block to indicate that data has been recently added or modified.

- **Optimum pH** is the optimum pH factor for the process.

The database also has requirements information for each category of **Requirements**. The information for each category has three text fields for the description, advantages, and disadvantages of each category of separation. The streams represented in the flowsheet also have a database file. Each stream has a unique 20-character **Name**, **To Process**, and **From Process**. The **To Process** and **From Process** fields are related to the process name of a process. Based on the source and destination of a stream, the stream is classified as an input, output, or intermediate stream. A database file of abbreviations is also used for labeling process blocks when drawn on the chart. The **Country**, **DOE Site**, and **Company** fields for each process are related to the abbreviations.

10.3.3 Row and Column Modifications

Original rows and columns for the chart can be added and deleted with menu commands. The original rows and columns can also be positioned relative to each other with menu commands. This allows flexibility in drawing the standard charts. Moving rows will not have an effect on charts that are drawn by any method other than by original rows. When the chart is redrawn, the database automatically recalculates the positions of the process blocks on the chart.

10.3.4 Incorporation of Consultant Data

Data being provided on a separate contract by SAIC will be incorporated into the chart when it is available. SAIC will submit data in delimited text form, which is a standard for translating data between spreadsheets. This form can be imported directly into the database and appended to the records of the database. If the data source is an International Business Machines (IBM) computer, the data file is simply read from an IBM formatted disk using the Macintosh utility Apple File Exchange and converted to Macintosh format. To produce the list of possible processes applicable to Hanford Site cleanup, SAIC did a literature search of available articles. The result of the literature search included many articles that would not directly apply to the Hanford Site and will not be included in the data provided for import into the database. However, the complete results of the literature search will be incorporated into another database for historical recording purposes.

10.3.5 Future Additions to the Database

Rating and prioritizing measures will be part of the data eventually supplied by SAIC. When the structure of this data has been determined, the database will be modified to include fields for these measures. The database will also be modified to calculate ratings based on priorities and weights given to each measurement. This will allow the database to calculate the rating for each process relative to the priority given to each measure.

10.4 FLOWSHEET MODELING

10.4.1 Flowsheet Definition

The charting database flowsheet is defined as a set of process blocks connected by a set of streams. For each process block in the flowsheet, the field **Reference** is set to **True** to indicate that the process blocks appear in the flowsheet. Streams are defined between the processes that appear in the flowsheet. Each stream has a **From process** and **To process** field that specifies what the source and destination are for each stream. A stream is also categorized as an input, output, or intermediate stream on the basis of the source and destination of the stream. Streams that have no process as a source are input streams, streams that have no process destination are output streams, and streams that have both a source and a destination are intermediate streams.

10.4.2 Flowsheet Drawing Algorithm

When the charting flowsheet is drawn, each process block in the flowsheet is drawn in the column directly above the position of the block in the alternative processes section. For each column, one process block per flowsheet row is drawn. The position of each row vertically on the page is determined by the number of streams that pass between that row and the previous row.

Streams are drawn between blocks according to the positions of the source and destination blocks in the flowsheet. For input streams, the stream is drawn from the left margin of the flowsheet to the destination block. If the destination is in the first column, then the stream is drawn straight from the left margin to the process block. When an input stream destination is not in the first column, the stream is drawn below the row the destination block is in and then splits the column in front of the destination block to enter the destination block. Output streams are drawn in a similar fashion from the source block to the right-hand side of the chart. Output streams in the last column are drawn straight to the right margin, while output streams that are not in the last column are drawn below the row of the source process.

Intermediate streams are drawn depending on the number of columns between the source and destination process blocks. When the source and destination blocks are in neighboring columns, then the column between the two blocks is used to draw the intermediate stream and no rows are split. When the difference between the source and destination is greater than one, the stream will be drawn between rows above or below the destination block depending on the row position of the source and destination. The appropriate columns by the source and destination blocks will be split accordingly.

Before the flowsheet is drawn, all of the block and stream positions are calculated. When this is done, the number of streams splitting each row and column is calculated. The number of streams that are drawn in the space between adjacent process boxes in the same row are also calculated. This

allows the charting algorithm to draw stream lines that do not overlap. All intersections between stream lines on the flowsheet will be at right angles to each other.

10.4.3 Flowsheet Translation and Calculation

As part of the work for the Separation Technologies database, an investigation was made into data translation of chemical process flowsheets to and from various software applications. These applications are used to create and calculate flowsheets for design and analysis. In particular, Design/IDEF is used to create hierarchial flowsheets, ASPEN Plus is used to do mass-flow calculations and other chemical process flow calculations, and Mathematica is used as a tool for parametric analysis. The relationship between the applications and the data translation process is shown in Figure 10-1.

A prototype database was developed with 4th Dimension that will automate the data translation process. Files exported from Design/IDEF can be read into the database, converted to a single-page form used by the other programs, then drawn on the screen by the database. Chemical components, input inventories for the components, separation factors, and reaction yields for each stream output from each block are input by the user or imported from a spreadsheet table created by the database. The database will also check the definition of the separation factors and reaction yields to verify that the mass-flows will balance for each block in the flowsheet.

After the database has verified the mass balances, the mass flows for the flowsheet can be calculated. The database can calculate these mass flows, or the database can create an input file for ASPEN Plus. After the ASPEN Plus program is run with the input file, an output table of mass-flows is created that can be imported back into the data translator database.

The final flowsheet representation that can be produced by the data translation database is a Mathematica notebook file. Mathematica is an application that does numeric and symbolic algebra and is commonly used for parametric analyses. The mass flow for each chemical component for all of the process blocks and streams is represented as a linear equation in terms of the separation factors and the input inventories. Mathematica is then used to create curves diagramming the behavior of the flowsheet with respect to any of the parameters of the system.

Figure 10-1. 4th Dimension Data Translator.

* ASPEN Plus is a trademark of Aspen Technology.
 ** Design/IDEF is a registered trademark of Meta Software Corporation.
 *** Mathematica is a trademark of Wolfram Research.
 **** 4D Draw is a trademark of Acius, Inc.

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APPENDIX A

**PRETREATMENT ACTIVITIES OUTSIDE
OF REPORT SCOPE**

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APPENDIX A

PRETREATMENT ACTIVITIES OUTSIDE OF REPORT SCOPE

A1.0 INTRODUCTION

A broad base of activities relevant to cleanup of the Hanford Site was performed during fiscal year (FY) 1993 throughout the Defense Complex and government laboratories, within private industry, at universities, and in foreign nations. Pretreatment-related activities that do not fall within the scope of this report and will be reported in detail elsewhere, are identified and briefly summarized below. The text is based largely on planning documents in place during early FY 1993 and, as such, reflect work intended at that time to be done. For an accurate account of work that was completed, the final report for each specific activity should be consulted when these reports become available.

A1.1 WESTINGHOUSE HANFORD COMPANY PRETREATMENT DEVELOPMENT

The Pretreatment Development organization of Westinghouse Hanford Company (WHC) manages a significant activity aimed at the identification, evaluation, and development of pretreatment technology in a cost-effective, timely manner. A description of this activity is contained in the Pretreatment Technology Plan (Barker 1993). Several pretreatment options are being evaluated for disposal of tank wastes to establish the preferred flowsheet. These options include pretreatment processes ranging from minimal separations of the high-level waste (HLW) and low-level waste (LLW) to advanced separation processes that dramatically reduce the volume of HLW and LLW produced and/or reduce the chemical toxicity of the LLW.

Presented in this section are the planned developmental activities by functional need for candidate pretreatment processes, which include tasks to be performed by WHC, Pacific Northwest Laboratory (PNL), and outside contractors working through WHC and PNL.

A1.1.1 Reference Technology

The reference pretreatment system is the phased technology deployment strategy presented in Section 3.0. The technology development program for each reference technology function is summarized below.

A1.1.1.1 Sludge Washing. Sludge washing studies will be conducted on actual tank sludge samples over a period of 7 years. The objective of these studies will be to determine the effect of sludge washing on the composition of the sludge. The composition of each washed sludge (e.g., radionuclides, chromium, aluminum, iron, bismuth, and phosphorus contents) will be determined, as will the composition of the wash solutions. These data will be used to make

decisions as to further processing of the sludges, i.e., direct vitrification, intermediate processes, or advanced pretreatment.

A1.1.1.2 Cesium Removal by Ion Exchange. Batch equilibrium studies initiated during FY 1992 will be concluded during FY 1993 to provide a comprehensive reference of equilibrium behavior for the ion-exchange media under consideration. As the Initial Pretreatment Modular (IPM) project progresses and additional design basis information requirements are identified, it is anticipated that further Design Basis Experiments will be completed. For example, during FY 1994, Phase 1 is planned to verify the baseline IPM flowsheet on a bench scale. In FY 1995, it is anticipated that project design, safety, and regulatory documents will have identified issues requiring resolution through laboratory studies.

A1.1.1.3 Organics and Ferrocyanide Destruction. Laboratory studies will be conducted by WHC, PNL, and outside contractors on selected technologies to provide data necessary to narrow technology choices. The tasks include establishing testing standards, and performing preliminary laboratory tests using synthetic wastes (based on the contents of an organic and a ferrocyanide watch list tank) and preliminary laboratory tests with actual wastes (from both an organics 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. Engineering evaluations of the data from the laboratory tests and from operating the pilot plant will be completed to support decisions on the final technology and the design, fabrication, and operation of a radioactive pilot facility. Operation of the hot 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.

A1.1.1.4 Selective Leaching of Sludge. Two general types of leaching methods are being considered: (1) leaching of nonradioactive components (e.g., aluminum, silicon, chromium) from the tank sludges, and (2) leaching of transuranics (TRU) 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 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.

A1.1.1.5 Blending. Development of computer software to examine benefits of blending, which incorporates all of the tank waste compositions and explores the impact of various assumptions and constraints, 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. The completed software will provide an optimum treatment strategy for a given set of constraints and will allow "what if" studies to be readily performed. Continued use of the software by systems personnel is desirable for feedback to the software development.

A1.1.1.6 Sludge Dissolution. 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, ongoing through FY 2000. The tank sludges investigated in any given fiscal year will be obtained from tank core samples taken in the previous year. For example, sludges from tanks core sampled in FY 1992 will be investigated in FY 1993. The results from the laboratory-scale dissolution tests will be used to plan scale-up and will be an integral part of bench- and pilot-plant scale solvent extraction tests.

A1.1.1.7 TRU Removal by Solvent Extraction. Development of the TRU extraction (TRUEX) process will involve laboratory studies, bench-scale continuous counter-current tests, and pilot-plant tests. The scope of the solvent extraction laboratory studies includes (1) preliminary batch contacts of actual dissolved sludge solutions with the TRUEX process solvent, (2) design of 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 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 30 L of waste per hour; however, shakedown tests will be conducted with simulated waste before tests with actual waste are done.

A1.1.1.8 Strontium Removal by Solvent Extraction. The baseline process being considered for extracting strontium from acid-dissolved-sludge solutions is the strontium extraction (SREX) process. Consideration will also be given to the combined TRU/SREX process being developed at Argonne National Laboratory (ANL). Development of the SREX process will involve laboratory studies, bench-scale continuous counter-current tests, and pilot-plant tests.

A1.2 PRETREATMENT 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 LLWs generated, and improve the type of secondary wastes generated. The proposed technology development programs would provide bases for making final decisions on process deployment.

A1.2.1 Alternate Transuranic Removal

The development of alternative solvent extraction processes for TRU removal involves laboratory studies, bench-scale continuous counter-current

tests, and pilot-plant tests. The scope of the solvent extraction laboratory studies include the following:

- Identifying potential extractants
- Defining the extraction systems by measuring distribution coefficients for the various sludge constituents
- Choosing the most promising alternative extractant
- Making preliminary batch contacts of actual dissolved sludge solutions with the candidate extractant
- Designing process flowsheets for individual waste streams
- Testing 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 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 30 L of waste per hour. Again, shakedown tests will be conducted with simulated waste before tests with actual waste are done.

A1.2.2 Strontium and Transuranic Removal on Basic Side

The scope of this task will include (1) batch contacts with actual sludge wash solutions, (2) development of process flowsheets, and (3) testing of the flowsheets using batch contacts. If an ion exchange method or a precipitation method proves to be a viable technology, laboratory-scale testing will be performed with simulated wash solutions. If a solvent extraction process is identified, bench-scale testing with actual wastes will be performed using continuous counter-current solvent extraction.

A1.2.3 Cesium Removal on Acid Side

The scope of this task includes (1) batch contacts with actual dissolved sludge solutions, (2) developing process flowsheets, and (3) testing the flowsheets using batch contacts. The process flowsheets will then be demonstrated with laboratory-scale equipment. If a solvent extraction process is the chosen technology, a bench-scale test will be performed with continuous counter-current solvent extraction equipment using actual wastes. If a precipitation or ion exchange method is chosen, laboratory-scale testing will be performed with waste simulants (assuming the acidified sludge can be adequately characterized and waste simulants developed) rather than with actual wastes.

A1.2.4 Convert or Remove Nitrates

The ongoing laboratory studies and performance assessments will be monitored and evaluated. If the studies determine that nitrate conversion or removal is required, the criteria for nitrate conversion or removal will be determined and a demonstration program established. Candidate destruction technologies to be considered include thermochemical, thermal, electrochemical, and catalytic. Possible separation technologies include anion exchange, liquidalalysis, membrane separations, and crystallization.

A1.2.5 Iodine Removal

No method has been identified or developed for separating radioiodine from alkaline aqueous wastes stored at the Hanford Site or at other U.S. Department of Energy (DOE) sites, nor has a technology or strategy been developed that will ensure long-term disposal of the ^{129}I . The objective of this work, if it is determined that the iodine will require removal from the waste, would be to develop technologies for (1) separating radioiodine from alkaline aqueous 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.

A1.2.6 Technetium Removal

Separation processes are required for 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, and electrochemical methods. Initial experiments will be conducted with laboratory batch contacts to define key parameters and develop rough flowsheets. A technology assessment will be conducted in parallel with the laboratory work and will define the treatment requirements for technetium removal from both acidic and alkaline waste streams. This technology assessment will provide recommendations on further development needs for the processes. If a solvent extraction process is the chosen technology, a bench-scale test will be performed with continuous counter-current solvent extraction equipment. Other technologies that may be chosen will be demonstrated with laboratory-scale equipment.

A1.2.7 Low-Level Waste Organics Destruction

The overall requirements for organics destruction will be determined and compared to the requirements for the IPM. Organics destruction requirements that are outside the scope of the IPM will be further refined and performance criteria established. Organics destruction technologies will be developed to meet the performance criteria and may include adapting IPM organics destruction technologies or developing new technologies.

A1.2.8 Alternative Strontium Removal--Acid Side

A study will be conducted in FY 1993 to identify strontium separation processes that have potential application in pretreating Hanford Site tank wastes. Laboratory tests will be conducted to evaluate the utility of these processes. Eventually, one or more strontium separation methods will be chosen for further development, which will include bench-scale tests with actual wastes and pilot-plant tests, if warranted.

A1.3 TECHNOLOGY ALTERNATIVES

A1.3.1 Sludge Leaching, Precipitation, or Solid Sorbents

This task includes developing flowsheets for sludge leaching processes and precipitation processes, and using solid sorbents for radionuclide separation. Laboratory work will be required where insufficient data are available to develop flowsheets.

A1.3.2 Calcination and Leach

To investigate the chemistry of the calcination and 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 is being pursued. The testing program will 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 point will be directed to determine the applicability of the aqueous-based separations methods previously explored on the resulting calcined solids and liquids.

A1.4 CLEAN OPTION

The extensive separations pretreatment option (CLEAN) is an alternative pretreatment system that applies more aggressive pretreatment of the tank wastes to reduce the quantity of HLW requiring vitrification and the radionuclide and hazardous material content of the LLW product. The CLEAN option technology development is focused primarily on developing the reference system and enhanced system functional needs to a higher level of decontamination performance. The specific goals of the CLEAN option that have been adopted to formulate an aggressive, but feasible, strategy, are summarized below.

- The radioactivity will be removed from the bulk of the waste so that the radionuclides in the remaining LLW will not exceed U.S. Nuclear Regulatory Commission (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 as low as reasonably achievable (ALARA) levels.
- Additional radioactivity will be removed from the LLW where significant reductions can be achieved through minor modifications to 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 form.
- The LLW will be disposed of in a manner that complies with 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 as 1,000 canisters of a borosilicate glass that meets current Hanford Waste Vittrification Plant (HWVP) glass specifications.
- Waste minimization principles will be used to limit the volume of LLW.

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A2.0 WESTINGHOUSE HANFORD COMPANY WASTE MANAGEMENT ENGINEERING

During FY 1993 an engineering study was made of the technology options for disposal of tank waste at the Hanford Site (Boomer et al. 1993). The study assessed waste characterization, safety issue resolution, waste retrieval, separations of the mixed waste into HLW and LLW fractions, treatment of the HLW fraction for disposal in a geologic repository, and treatment of the LLW fraction for disposal onsite. Additionally, although not a part of Tank Waste Remediation System (TWRS), the report examined closure options for the tank systems. Data presented in this subsection is a summary of the pretreatment-related portions of the above study, and served as one of several key reports that provide input to the definition of Section 3.0, "New Technical Strategy."

A2.1 PREPARATION OF FLOWSHEETS

Eighteen criteria were developed to analyze the technical options. These criteria were grouped into the following five categories:

- Public and worker health and safety
- Environmental impact
- Technology assurance
- Cost
- Schedule.

Additionally, the analysts developed detailed material balances (at the pump, tank, and filter level) that provided the basis for equipment lists and cell layouts. These, in turn, provided the basis for facility layouts, which then provided the basis for capital cost estimates. From the facility layouts and material balances, material and staff estimates were prepared.

The analysts produced 12 options to separate the waste into fractions for offsite (HLW and TRU waste) and onsite (low-level radioactive waste). A suite of technology candidates for defining the options was developed using information from literature searches and technology exchanges. The number of technologies was reduced using engineering judgment to eliminate those technologies with minimal development and/or clear technical disadvantages. From the remaining candidates, specific process technologies were selected (e.g., cesium ion exchange) as being representative for analysis of the options. Analyses of the relative options to the 18 criteria were then performed.

A2.2 ANALYSES OF FLOWSHEETS

Twelve separations flowsheets were analyzed. These flowsheets ranged from no separations of the tank waste to acidifying all of the waste for processing by advanced separations. The flowsheets were divided into two categories, sludge washing and solvent extraction. Both types of flowsheets used ion exchange to remove radionuclides from the alkaline solution. The solvent extraction flowsheets dissolved the sludge and used solvent extraction

processes to reduce radionuclides in the dissolved sludges that were neutralized and routed to LLW. The solvent extraction processes resulted in a smaller volume of HLW for treatment and repository disposal than sludge washing processes.

The 12 separations process options analyzed include the following:

- No separations
- In-tank sludge wash A
- In-tank sludge wash B
- Sludge wash A
- Sludge wash B
- Sludge wash C
- Sludge wash D
- Solvent extraction A
- Solvent extraction B
- Solvent extraction C
- Solvent extraction D
- CLEAN.

The process options provide varying levels of radionuclide recovery from the waste. The Sludge Wash A option accomplishes the least amount of partitioning by separating salt cake and sludge. The CLEAN option accomplishes the greatest amount of separations. Figure A-1 shows the process steps used for each option.

A2.3 COST ANALYSES OF PROCESSING OPTIONS

Analyses of this function showed the following two strategies to reduce the overall cost for separation and disposal of the waste:

- Dissolve the sludge to allow radionuclide removal
- Increase disposal container size.

Sludge dissolution options (i.e., solvent extraction and CLEAN process options) significantly reduced the volumes of waste requiring repository disposal compared to the sludge washing options. If the HLW fraction is sent to the repository in the reference (0.62 m³) canister, sludge dissolution results in a significant reduction in the repository disposal costs (Table A-2). However, increasing the disposal container size to reduce the number of containers requiring disposal also reduced repository disposal costs significantly, as shown in Table A-2.

The disposal cost advantages for using extensive waste separations were found to be eliminated by the use of large containers. The combined costs for separations, treatment, and repository disposal are approximately the same for both the sludge washing options and solvent extraction (TRUEX) options if a large glass container (1.4 m³ versus 0.62 m³) is used for the sludge washing options. The total disposal mission cost for options that employ no separations are also competitive with the separations options if large (approximately 11 m³) casks are used to contain the vitrified waste.

Figure A-1. Separations Options.

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Table A-2. Waste Volume and High-Level Waste Disposal Costs for Separation Process Options.

a. Waste Volume and Number of High-Level Waste Canisters for the Separations Options

	Separations process			
	CLEAN	Solvent extraction	Sludge washing	None
Waste volume, m ³	1,240	6,820	23,600	135,000
Number of containers:				
0.62 m ³ canisters ^a	2,000	11,000	38,000	218,000
1.4 m ³ canisters		4,900	16,800	96,400
Large casks ^b		800	2,360	12,300

b. Disposal Costs for the Separations Options (millions of dollars)

Canister size	Separations process			
	CLEAN	Solvent extraction	Sludge washing	None
0.62 m ^{3a}	360	2,160	7,000	44,000
1.4 m ³		1,060	3,650	23,700
Large casks ^b		1,400	3,710	12,700

^aReference Hanford Waste Vittrification Plant canister size.^bAssumes 8.5 m³, 10 m³, and 11 m³ casks, respectively, for solvent extraction, sludge washing, and no separations.

The costs of the following two strategies for improving the environmental performance of the LLW form were determined:

- Extensive separations (CLEAN)
- Improved waste form performance coupled with in-tank separations processes (in-tank sludge wash B, glass in sulfur, LLW).

Extensive separations improve the performance by removing long-lived radionuclides and hazardous components from the LLW stream. However, improving the release properties of the LLW form such that the waste form is effectively resistant to environmental dispersion also can improve the environmental performance. The glass in sulfur LLW form can result in significant reduction of total costs when coupled with processes such as solvent extraction D or in-tank separations processes.

A2.4 OTHER SEPARATIONS TECHNOLOGIES

Other separation technologies under research that held potential benefits were identified, but because of their low technical maturity did not offer sufficient basis for full development of the flowsheet and facility requirements, at the time of the study (Boomer et al. 1993). It was suggested that as these technologies become better defined, they may be evaluated. The separations technology options that lacked sufficient maturity to evaluate include the following:

- Calcination and dissolution
- Fractional crystallization
- Radio frequency plasma torch and plasma centrifuge
- In-tank separations processes.

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A3.0 PACIFIC NORTHWEST LABORATORY

The TWRS Pretreatment Technology Development Project (Project) was established in FY 1992 within PNL to manage all technology development and demonstration activities within PNL associated with the safe storage and disposal of Hanford Site's 177 underground tanks. The overall objectives of the Project are to coordinate and manage all pretreatment technology development activities within PNL funded by EM-50, DOE Office of Technology Development, and EM-30, DOE Waste Management Operations. This subsection describes the work within PNL sponsored by EM-30.

The FY 1993 activities for the Project are divided into the following five technical areas:

- Process Engineering and Evaluation
- Fission Product Separation Technology Development
- Sludge Treatment and Extraction Technology Development
- Organic Destruction Technology Development
- Pretreatment Materials Evaluation.

The activities within each project element are summarized below. Additionally, a detailed description of the work scope for each element is available in the PNL Project Work Plan (Holton 1993).

A3.1 PROCESS ENGINEERING AND EVALUATION

The Process Engineering and Evaluation Task provides engineering analysis of pretreatment systems including the 'Strawman' Reference TWRS Pretreatment System, enhancements, and alternatives to the Reference Pretreatment System. These analyses and evaluations are completed by preconceptual and conceptual engineering evaluation of data obtained from literature reviews and experiments conducted as part of this project. This task also conducts literature reviews to identify technology alternatives and technology advancements to support the overall identification and evaluation of Pretreatment Technology options for the TWRS. This task interacts with the Fission Product Separations Technology Development Task and Sludge Treatment and Extraction Task to assess the impact of experimental data on the TWRS pretreatment system and, thereby, provide guidance on the overall pretreatment technology development approach.

A3.2 FISSION PRODUCT SEPARATION TECHNOLOGY DEVELOPMENT

The Fission Product Separation Technology Development Task is focused on establishing technical data, through experimentation, to support the identification and evaluation of processes to remove soluble and partially soluble radionuclides and hazardous components for alkaline tank wastes. The initial efforts of this task are to establish radiochemical flowsheets for the removal of ^{137}Cs from neutralized current acid waste (NCAW) supernatants, complexant concentrate (CC) supernatants, and double-shell slurry feeds (DSSF). The primary technology being evaluated by this task is absorption via ion-exchange.

A3.3 SLUDGE TREATMENT AND EXTRACTION TECHNOLOGY DEVELOPMENT

The Sludge Treatment and Extraction Technology Task is focused on establishing technical data, through experimentation, to support the identification and evaluation of processes to remove the following:

- Soluble salts and radionuclides from tank sludge using water as a leachate
- Selective removal of radionuclides and chemicals from sludge using oxidative and complexant processes
- Acidic dissolution of sludge to solubilize the majority of chemical and radioactive components, and decontamination of dissolved wastes by extraction and sorption processes.

The extraction processes to be evaluated will include liquid-liquid extraction using several extractants and chromatographic extractions. The sorption processes will include ion-exchange and carrier precipitation processes.

A3.4 ORGANIC DESTRUCTION TECHNOLOGY DEVELOPMENT

The Organic Destruction Technology Task is focused on experimentally evaluating technologies for the destruction of organics and ferrocyanide (FeCN) in tank wastes. The Hanford Site tanks contain two classes of chemical components which, because of their reactive nature, are believed to require destruction to ensure the safe storage of Hanford Site tank wastes. These are organic complexants and their byproducts and several ferrocyanide compounds. The objectives of this task include the following:

- Establish the basis for organic destruction requirements
- Identify simulant compositions that can be used for process development testing
- Evaluate technologies that can be used to destroy these two chemical species.

Hydrothermal processing (HTP) will be the primary technology evaluated during FY 1993. Evaluation of HTP will involve laboratory testing with simulated and actual wastes and pilot-scale vendor tests using waste simulants. Alternative organic destruction technologies that could represent a significant enhancement, if successful, will also be experimentally evaluated, including the following:

- Heat and digestion
- Corona discharge
- Electrochemical oxidation processes.

This work will support final selection of an organic destruction treatment technology for the IPM.

A3.5 PRETREATMENT MATERIALS EVALUATION

The Pretreatment Materials Evaluation Task is focused on evaluating and recommending materials of construction for pretreatment process vessels. The chemical processes being examined for organic destruction and pretreatment operations (sludge leaching and dissolution, extraction, and absorption) will convert the stored wastes to corrosive solutions. This task evaluates the corrosiveness of the pretreatment solutions and gasses and evaluates materials of construction for the proposed process vessels. Methods of measuring and controlling corrosiveness of pretreatment solutions also will be identified.

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A4.0 LOS ALAMOS NATIONAL LABORATORY

The TWRS Technology Applications Program, established in FY 1993, is one of three components of the Los Alamos National Laboratory (LANL) Hanford Site Support Activities, the other two being Tank Safety and Independent Engineering Reviews. Within the TWRS Technology Applications Program are activities that fall under the following:

- Pretreatment
- Characterization
- Tank safety.

This subsection addresses only pretreatment activities. The overall objectives are to coordinate and manage LANL technology projects directed at resolving Hanford Site tank safety issues, and providing technology for the pretreatment of Hanford Site wastes. The seven major technical tasks being conducted are summarized below.

A4.1 SYSTEMS ANALYSIS

The Systems Analysis task applies comprehensive process flow simulations developed for the DOE Complex 21 Program to TWRS technologies developed or proposed at LANL, and elsewhere within TWRS as requested. Special emphasis is placed on chemistry-specific systems analyses, up- and downstream effects of process changes, waste minimization, and technology incompatibilities for the Tank 241-SY-102 Flowsheet Project and the CLEAN option for pretreatment technology. This task is integrated with overall tank 241-SY-102 project activities.

A4.2 PHYSICAL SEPARATIONS

This task focuses on the application of high-gradient magnetic separation technology to tank wastes, particularly sludges. It is expected that significant waste volume reduction can be achieved through the separation of sludge particulates on the basis of their magnetic susceptibility. Such a process would have distinct advantages for pretreatment in that volumes are reduced without the addition of processing reagents or further complication of downstream processes. Initially, small scale high-gradient magnetic separation tests were to be conducted on individual neutralized cladding removal waste (NCRW) waste simulant components. Once individual behavior was understood, the simulant components were to be combined to more accurately reflect tank waste compositions, and tests performed. Finally, separations of actual NCRW will be performed.

A4.3 TANK 241-SY-102 FLOWSHEET DEVELOPMENT

This task will produce a flowsheet for the remediation and treatment of wastes in tank 241-SY-102. This tank was chosen for a number of reasons as follow:

- The tank waste composition closely resembles the type of waste regularly produced at the LANL Plutonium Facility
- Technologies are currently in use at LANL to treat such waste on an operating plant scale
- These technologies do not require an operating vitrification plant
- The tank is located next to tank 241-SY-101, a serious safety concern tank because of hydrogen generation, making tank 241-SY-102 available for remediation of tank 241-SY-101 if desirable
- Tank 241-SY-102 is currently used as a transfer tank for other tank remediation activities, and removing the existing sludge would eliminate possible incompatibilities with future waste transfers
- The early demonstration of tank remediation will establish credibility for TWRS and DOE in affecting timely successes at the tank farms.

The approach is to remediate the tank and place the LLW in grout on-site, and the TRU in a form suitable for long-term storage. This eliminates the requirement for an operating vitrification plant before beginning tank remediation. Tests will be performed first on waste simulants with scale-up being performed using the Advanced Testing Line for Actinide Separations facility at LANL.

A4.4 CATION EXCHANGE STUDIES

Although conventional cation exchange resins can remove certain trace impurities from waste streams, they often provide poor selectivity. Other cation exchange materials, such as inorganic absorbers and resins with phosphoric acid functionality, are expected to offer greater selectivity. The objective of this study is to measure the distribution coefficients of selected radionuclides onto cation exchange resins and potentially useful inorganic and composite cation absorbers from solutions that simulate the supernatant and dissolved sludge portions of tank 241-SY-102. The selected radiotracers represent important fission products, key matrix elements, and actinides. The initial scope of this study has been expanded slightly to include one anion exchange resin and a series of commercially available extractants to provide useful reference points.

A4.5 FISSION PRODUCT PARTITIONING

This task is focused on establishing separation methods for technetium from tank wastes, including the following:

- Supernates
- Dissolved salt cake
- Sludge washes and leaches
- Dissolved sludge
- Pretreatment solutions.

Primary consideration is being given to the use of improved ion exchange resins and/or solvent extraction systems from basic solutions. The goal is to design a technetium partitioning system as follows:

- Is robust to acids, bases, and radiolysis
- Interfaces with the pretreatment chemical separations of tank waste
- Reduces the amount of residual waste associated with the baseline method.

A small effort will be expended to provide support to EM-50 research efforts on the dicarbollide solvent extraction system for cesium and strontium separations.

A4.6 HYDROTHERMAL DESTRUCTION OF ORGANICS, FERROCYANIDES, NITRITES, AND NITRATES

The objective of this task is to demonstrate, test, and evaluate the safety, reliability, and cost and benefits of HPT technology for the treatment of undesired chemical components in Hanford Site tank wastes. These components are organic complexants and their byproducts, and several ferrocyanide compounds. Additionally, the presence of large quantities of nitrates and nitrites can lead to excessive final waste volumes. HPT of these wastes will be evaluated using waste simulants representing tank 241-SY-101. Experiments will be performed at both the pilot and laboratory scale. A 300 gal/day pilot-scale processing unit will be designed, built, and tested using both nonradioactive and radioactive simulated waste. A process model will be developed to allow evaluation of operation at full scale. Both pilot and laboratory-scale experiments will be performed to obtain data necessary for development and validation of the model. The safety hazards and other risks associated with HPT will be determined.

A4.7 SAMPLE TRANSPORTATION

This task is focused on determining the processes and equipment (e.g., transportation containers) necessary for the transport of up to 25-L samples of Hanford Site tank wastes to LANL. Included in this task is the possible consolidation of efforts with a separately funded activity tasked with designing and constructing transportation containers for shipment of

radioactive sludge-like material from the Nevada Test Site. Also included is the obtaining of required permits for the receipt of Hanford Site tank waste samples (e.g., a State of New Mexico Treatability Studies Permit).

A5.0 SANDIA NATIONAL LABORATORY

The Sandia National Laboratories (SNL) presently conduct a program to develop and implement technologies that support resolution of Hanford Site waste pretreatment needs for cesium, strontium, and TRU separations, and for the destruction of safety issue chemical compounds. These radionuclide separation are based on crystalline silicotitanate (CST) technology. Safety issue activities employ the steam-reforming process.

A5.1 RADIONUCLIDE SEPARATIONS USING CRYSTALLINE SILICOTITANATES

Tasks 1, 2, and 3 focus on development and qualification of basic-side CST processes. The focus of tasks 4, 5, and 6 are production scaleup and engineered form development, chemical and physical property studies, and acid-side processing capability, respectively.

A5.1.1 Task 1--Separations for Double-Shell Slurry Feeds

The goal of task 1 is to develop cesium removal technology applicable to DSSF by processes using CSTs, on a time scale consistent with Hanford Site waste pretreatment needs, using either in-tank precipitation, column processing, or hybrid processing. The major task effort is to prepare and characterize a range of CSTs, and apply this information to develop processes for DSSF waste treatment. Efforts are being directed at developing a treatment to reduce the cesium curie content sent to grout by at least a factor of ten. Research and development (R&D) activities include initial laboratory-scale evaluation of synthesis conditions such as the following:

- Concentration
- Mixing
- Reaction time
- Temperature
- Cooling rate.

For selected CSTs, ion exchange properties such as K_d measurements, and stability in high pH solutions will be evaluated. A baseline composition will be selected for more detailed characteristics and performance testing, including tests at PNL with waste simulants and actual DSSF waste.

A5.1.2 Task 2--Separations for the Initial Pretreatment Module

The goal of task 2 is to demonstrate that column ion-exchange processes based on CSTs should be used as the baseline technology for the IPM or other compact processing units (CPUs). The major task effort is to reduce cesium,

strontium, and TRU curie contents in treated Hanford Site waste to below the Class A limits. Activities include the following:

- Development of improved materials, engineered forms, and synthesis techniques
- Selection of baseline materials and processes
- Measurement of important chemical and physical properties.

A5.1.3 Task 3--Separations for Future Hanford Site Pretreatment Processes

The goal of task 3 is to further develop CST capabilities for basic-side processing of Hanford Site wastes to support future pretreatment processes. This robust technology would apply to treatment of all Hanford Site waste forms, including sludges, so that it can be used by post-IPM installations. The major task effort is to reduce cesium, strontium, and TRU curie contents in treated Hanford Site waste to below the Class A limits. Activities include the following:

- Development of improved materials, engineered forms, and synthesis techniques
- Selection of baseline materials and processes
- Measurement of important chemical and physical properties.

A5.1.4 Task 4--Production Scaleup and Engineered Form Development

The initial synthesis of CST materials is performed using 20-mL laboratory reactors. For the most promising materials and synthesis techniques, a technical basis for production scaleup and engineered form generation is required. The following three important subtasks were initiated at the beginning of FY 1993:

- Employing 300-mL (~0.1-gal), 1-gal, and 20-gal reactors at Texas A&M University to investigate scaleup issues
- Developing a commercialization strategy for identifying and developing a commercial partner to make large quantities of CST materials
- Developing an engineered form of the material appropriate for column use.

The first subtask was to evaluate optimum reaction conditions and compositions for production scaleup. Use of cost-efficient feed materials as an alternative to more costly feed materials was also investigated. The second subtask, to select a commercial partner, included activities for patent protection and a Commerce Business Daily announcement. As the synthesis

program proceeds and significant quantities of materials were prepared, the third subtask was to select a composition(s) for formulation into an engineered form such as a pellet or bead. The engineered form was to be evaluated for cesium removal and stability, not only by laboratory analyses but also in batch and column tests. Solution compositions and other conditions that simulate a DSSF cesium removal process were to be used to develop test parameters.

A5.1.5 Task 5--Fundamental Chemical and Physical Knowledge

Task 5 will develop a fundamental understanding of the chemical and physical properties of CSTs by testing several compositions, using a variety of test techniques and procedures. Activities will focus on understanding the ion exchange mechanism, the kinetics of the ion exchange, whether a means to regenerate can be found, and the stability in chemical and radiation environments. X-ray diffraction, transmission electron microscopy, Raman spectroscopy, and other techniques will be used to characterize the chemical bonding and crystal structure. The long-term goal of this effort is to develop the capability to predict the performance and stability of CSTs in chemical and radiation environments.

A5.1.6 Task 6--Radionuclide Separations From Acidic Solutions

To date, most CST R&D effort has focused on cesium removal in high pH solutions. Limited studies have shown that CSTs are stable in low pH (acidic) solutions, and will remove cesium under these conditions. Batch K_d measurements for cesium removal will be conducted on selected CST materials for acid conditions. The chemical stability of the CST in these solutions also will be evaluated.

A5.1.7 Late Fiscal Year 1993 Status Update

Because the development of CST technology has proceeded at a rapid pace, the following information is provided. The text is representative of the state of development at the time this status report was prepared.

A baseline CST composition has been selected and five lots of CST have been prepared in a 1-gal autoclave at Texas A&M University. Each batch yielded approximately 175 g of CST that has been shown to have a cesium K_d of about 1,000 mL/g in solution with 77 ppm Cs, 5.1M NaNO_3 , and 0.6M NaOH. This would translate to a K_d of about 2,000 mL/g in tank 241-AW-101 simulant. A synthesis run has also been completed in a 5-gal autoclave that yielded approximately 800 g of CST with a K_d of slightly over 1,000 mL/g. No problems have been encountered in the scaleup from a 100-cm³ reactor to a 5-gal reactor. During scaleup, CST performance has increased and material quality as assessed by X-ray diffraction and transmission electron microscopy has improved.

A preliminary experiment has shown that CST can be prepared in an engineered form using 25% aluminosilicate binder. A flow test at 3 CV/h showed a breakthrough of cesium at about 250 CV at 40 °C. The cesium capacity will increase at lower temperatures and lower flow rates. Tests to determine the stability of CST in 1.6M NaOH have shown no degradation in K_d over 100 days in pH 14 waste simulants.

A limited test has shown that CST, both as a powder and cesium-loaded to simulate use conditions, is stable to 10^6 rads. Tests to measure rad stability to 10^7 rads will be undertaken in the near future.

Tests have shown that CST is not regenerated in 1M HCOOH and 3M HNO₃. Chemically efficient regeneration of CST using chemicals compatible with Hanford Site operations is currently not practical. These tests indicate that CSTs have significant promise for removing cesium from highly acidic solutions.

SNL and Texas A&M University are evaluating potential suppliers for CST and CST engineered form and will announce the potential partner in September 1993. On the basis of discussions with potential suppliers, laboratory quantities of these materials will be available within a few months after the agreement is reached. We project that 50 kg quantities of bulk CST will be available 6 months after an agreement is reached with the partner and 50 kg quantities of a CST in an engineered form will be available for test and evaluation about 12 months after the agreement. It is anticipated that scaleup to 10,000 kg quantities of CST in an engineered form would require another year and negotiation of a purchase agreement with the organization requiring the CST.

A5.2 SAFETY ISSUE RESOLUTION USING STEAM REFORMING

The SNL is conducting a program for treatment of Hanford Site tank waste that makes use of a moving bed evaporator (MBE) to gasify organics, destroy ferrocyanides, and decompose nitrates. Gasified organics from the MBE are destroyed in a detoxifier unit. A developmental MBE with a throughput capacity of ~0.5 gal/min successfully processed Hanford Site surrogate waste during FY 1992 and has continued to be used during FY 1993 to perform cold simulant laboratory experiments. One major purpose of the FY 1993 effort was to provide sufficient information regarding the steam reforming process to the Hanford Site IPM project for its technology downselection decision May 24 through 27, 1993. The IPM project did not select steam reforming, because it had concerns that they felt could not be addressed by steam reforming technology within the scope and time frame of IPM compared to the technologies that were selected. The SNL steam reforming program will be continued during FY 1993 to provide the necessary technical, regulatory, and infrastructure framework for laboratory-scale (~0.5 gal/min) and pilot-scale (5 gal/min) hot-simulant and actual waste testing of the steam reforming process. Such testing would be performed after March 1994.

A6.0 UNDERGROUND STORAGE TANK-INTEGRATED DEMONSTRATION

The Underground Storage Tank-Integrated Demonstration (UST-ID) Program was created in February 1991 with a principal objective to develop and demonstrate technologies that will provide improvements or alternatives to the remediation baseline plan. The program is focused on the needs of several DOE sites simultaneously, thus maximizing the potential to apply these new technologies at more than one site. Activities currently included within the UST-ID are (1) characterization, (2) retrieval, transfer, and interim storage, (3) waste separation and pretreatment, and (4) LLW form development. This subsection focuses on the waste separation and pretreatment area, summarizing the currently funded technology development projects. In this area, several CPU are being developed to effect near-term demonstration and deployment of promising processes in actual tank environments. Because this overall report is process driven and does not focus on facility concepts per se, detailed CPU information is not included herein but can be found in the literature (Cruse 1993).

A6.1 SLUDGE PARTITIONING AND TREATMENT

This task addresses the following:

- Separation of sludges from supernates
- Washing of the sludge and pretreatment of the soluble portions
- Acid dissolution of the sludge
- Partitioning of TRU components.

A comprehensive sludge processing flowsheet will be developed and tested in an Oak Ridge National Laboratory (ORNL) hot cell using radioactive waste from the ORNL Melton Valley Storage Tanks (MVST). This waste is similar to Hanford Site tank waste and is easily retrievable, allowing hot verification tests to be conducted more quickly at ORNL than at Hanford Site. The flowsheet developed will provide the basis for design and operation of a pilot-scale waste processing facility, which in turn will provide the design basis for a production-scale facility to process the MVST waste.

A6.2 TRANSURANIUM EXTRACTION MODEL DEVELOPMENT AND VALIDATION

Under this task, the Argonne National Laboratory (ANL) will transfer the Generic TRUEX Model (GTM) to ORNL participants, who will perform tests to validate the GTM using actual waste. The ORNL, as part of its radioisotopes program, collects and refines significant amounts of americium from irradiated Savannah River Site (SR) targets. The process produces an acid waste that is good feed stock for piloting TRUEX, and ORNL personnel will conduct hot-cell validation runs using this waste as feed. This waste stream is different in chemical and radiochemical composition compared to Hanford Site wastes; therefore, these tests will be used only for validation of the model. Additional testing will be required for GTM application to Hanford Site waste. Sample collection and analysis is scheduled for FY 1993, and model validation is planned for FY 1994.

A6.3 TECHNICAL INTERCHANGE WITH THE FRENCH ATOMIC ENERGY COMMISSION

Several nations, including France, Japan, and the United Kingdom, are developing new technologies for separating specific fission products and actinides from radioactive waste streams. In this task, a technical staff member will be assigned to one of the French Atomic Energy Commission sites for a period of approximately 1 year. The assignee will work as a member of a French Atomic Energy Commission team working on R&D activities within mutually agreed upon technical areas. The primary area of interest is the diamine process, a novel technology that will separate TRU materials in a manner similar to TRUEX, but using a different flowsheet. Also, the assignee will develop a broad understanding of French waste management programs as a whole.

A6.4 CALCINATION AND DISSOLUTION PROCESS DEVELOPMENT

A series of full-scale demonstration tests is underway at a vendor site for calcining simulated Hanford Site waste using plasma arc technology. A primary objective is to identify the combination of chemical dissolution and thermal processing that will destroy 99% each of the nitrates, organics, and ferrocyanide compounds. Activities supporting the tests include detailed chemical analyses to better define the mass balances 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 Hanford Site tank waste as it pertains to the chemical dynamics of the calcination and dissolution process steps. Laboratory testing will be used to verify and optimize process parameters and material balances. The residue leaching task will determine additional treatment techniques to further concentrate the TRU residue left from the calcination and dissolution operations.

A6.5 BIOLOGICAL DESTRUCTION OF TANK WASTES

Existing biotechnology processes will be investigated to determine if they are adaptable to DOE liquid HLW and LLW wastes stored in USTs. Included will be denitrification (reduction of nitrate to N_2) and simultaneous separation of the remaining radionuclide and heavy metal constituents of the waste by biosorption (adsorption into bacterial biomass). The approach for FY 1993 will identify how bioremediation can best be implemented within the process flowsheet currently proposed for pretreatment of Hanford Site tank waste.

A6.6 CESIUM SEPARATION TESTING

This task will support development of the cesium separation CPU for application to a variety of Hanford Site tank wastes. In coordination with PNL, the SRS will perform ion-exchange tests to obtain data needed to design and select the ion-exchange media for the CPU. The SRS has developed a resorcinol-formaldehyde resin for cesium removal that has demonstrated high

performance in testing at SRS, ORNL, and PNL. Technical data and bench-scale tests, along with technical consultation, will be provided by SRS for cesium ion exchange and radiolytic stability of the resin.

A6.7 NITRATE TO AMMONIA AND CERAMIC PROCESS

An efficient and inexpensive method to decompose the sodium nitrate component of tank waste 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 the sodium nitrate by reactions that create ammonia as a byproduct. The remaining waste is converted to a solid, inert, ceramic-like product, with the sodium incorporated into the ceramic matrix. Significant waste volume reductions (65 to 75%) may be possible, relative to processing with grout. Initial bench-scale tests have shown success, and further bench-scale testing is planned during FY 1993 to allow selection of a reactor design. Engineering drawings are being prepared to support pilot-plant construction and demonstration activities scheduled for FY 1994.

A6.8 TANK WASTE PROCESSING ANALYSIS

This task will evaluate pretreatment requirements of Hanford Site tank wastes on a tank-by-tank basis. Completion of the task will accomplish the following:

- Identify the processing required for each tank to meet pretreatment criteria
- Evaluate the effects of change in pretreatment criteria on processing requirements
- Optimize the deployment of distributed processes for pretreatment. Relevant data from other DOE-funded activities will be factored into the task.

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A7.0 EFFICIENT SEPARATIONS AND PROCESSING INTEGRATED PROGRAM

The role of the Efficient Separations and Processing Integrated Program (ESPIP) is four-fold:

1. Provide separations and waste-form technologies and processes (SWFTP) to treat and immobilize a wide spectrum of radioactive and hazardous defense wastes
2. Where appropriate, transfer demonstrated SWFTP technologies developed by DOE to the U.S. industrial sector
3. Explore the potential uses of separated radionuclides
4. Coordinate SWFTP R&D efforts within DOE.

ESPIP has been implemented to ensure that SWFTPs are developed and ready when they are needed for waste processing and environmental restoration across the DOE complex, and to ensure that technologies developed for one waste will be used to the widest possible extent on other wastes. Specific emphasis is given to the Hanford Site, Idaho, and Rocky Flats sites, and current ESPIP anticipated accomplishments correspond with the anticipated startup date for the HWVP in FY 2000.

Major short-term goals of ESPIP include the following:

- Respond to EM-30 and EM-40, DOE Office of Environmental Restoration, separations and processing needs by identifying required R&D to meet those needs
- Demonstrate the utility of new, simple-to-operate solid-based separation technologies in efficiently separating radionuclides and other hazardous materials from wastes without generating unacceptable quantities of secondary wastes
- Develop a systems tool to define processes and evaluate the cost, required R&D, potential savings, and secondary waste generation of radionuclide processing options
- Establish a separations and processing network to coordinate DOE separations efforts and ensure against redundant pursuits
- Select and develop the most appropriate waste form for Idaho Chemical Processing Plant (ICPP) HLW.

Intermediate and long-term goals include developing SWFTP to save \$30 to 35 billion in remediating Hanford Site tank wastes and \$2 to 10 billion in remediating ICPP HLW calcine. Goals also include helping Rocky Flats meet its separations-related commitments to the State of Colorado.

The five generic technologies listed below are the central thrust of ESPIP.

A7.1 PRETREATMENT SLUDGE SCIENCE AND TECHNOLOGY

Much of the defense HLW across the DOE complex is in the form of chemically complex sludges containing small quantities of radionuclides. Separating the radionuclides from the nonradioactive components is essential because of the high cost of handling HLW. Such pretreatment may include water washing, acid leaching, caustic leaching, and acid dissolution. This part of the program will address the treatment of HLW solids by coupling thermodynamic modeling with experimental measurements in the laboratory. Successful implementation will result in optimum treatment of the solids to ensure proper HLW feedstock for the HWVP.

A7.2 AQUEOUS PRETREATMENT PROCESSES

ESPIP will measure and evaluate the performance of promising new chemical agents for separating cesium, strontium, and TRUs from HLW waste. Included in this part of the program are the sequestering-agent design and synthesis and research, development, demonstration, test, and evaluation activities required to successfully extract small quantities of TRUs, strontium, cesium, technetium, organics, *Resource Conservation and Recovery Act of 1976* (RCRA) metals, noble metals, iodine, ^{14}C , and ^3H for the waste stream. Some of these technologies are expected to apply to LLW and mixed waste, groundwater, contaminated-soil and decommissioning cleanup, as well as to HLW and LLW. Technologies from industry and universities will be jointly developed to meet some of the aqueous needs.

A7.3 PYROCHEMICAL SEPARATIONS PROCESSES

Some HLW, such as Idaho calcine and unprocessed defense fuel elements, may be more amenable to pyrochemical processes, where separations are accomplished at high temperatures, rather than to aqueous processes. For example, Idaho calcine waste contains large quantities of zirconium which, if volatilized, would decrease the volume of HLW from this source that requires geologic disposal by a factor of 20-30. Therefore, a component of this program will address pyrochemical separations.

A7.4 IMPROVED WASTE FORMS (CONDITIONAL)

We anticipate that the development of new separations processes will open up other avenues for associated development of improved waste forms. When the separations processes have been developed to the point that waste-form options can be identified, ESPIP will develop new waste forms as needed to take full advantage of the new separations process. Currently, borosilicate glass is the contemplated waste form for most HLWs. However, other forms, for example phosphate glass, ceramics, or metals, may be preferable. The form for Idaho HLW has yet to be selected. ESPIP will include R&D toward this selection. In addition, if pretreatment processes developed under ESPIP produce small quantities of unique HLW, corresponding HLW forms will be developed.

The LLW waste at the Hanford Site is contemplated to be cementitious grout. However, some concerns merit additional R&D. In particular, curing processes must be carefully controlled, or certain constituents in the grout will be leachable. Heat generated by excessive radioactive cesium would raise the curing temperature to the point of destroying the holding power of the grout. This could in turn increase the likelihood that nitrates and nitrites, technetium, and perhaps cesium, would leach into the adjacent soil and perhaps the groundwater. Thus, there is an incentive to destroy leachable components before the grout is formed and/or to extract cesium and technetium before cementation. It is possible that after the nitrates and nitrites are destroyed, a calcined or ceramic waste could be formulated. ESPIP will include R&D to improve the LLW form.

A7.5 SYSTEMS INTEGRATION AND ANALYSIS

A systems-oriented effort will consist of two levels of analysis: (1) a global decision tool and (2) unit-process tools. The unit-process tools will guide R&D in separations technology development and will integrate the data for use by the global decision tool. This tool in turn will develop pretreatment process options that include retrieving (technology not developed by ESPIP), separating, and packaging individual tank wastes into acceptable low-level and high-level fractions. The effort will integrate tasks in robotics (not developed by ESPIP), chemical and physical separations, in situ and in-line instrumentation (not developed by ESPIP), and final waste-form generation and will also identify voids or weaknesses in separations technologies that make up the process. Key data from all R&D efforts will be fed into the database used by the systems model.

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A8.0 EXTENSIVE SEPARATIONS OPTION

CLEAN is one of a number of possible approaches for pretreatment of the Hanford Site tank wastes before vitrification of HLW for permanent storage in the geologic repository. Pretreatment advantages include the following:

- Reduction in the quantity of HLW to be vitrified and stored
- Elimination of various hazardous materials (e.g., nitrates, organics) from waste streams
- Greatly reduced radioactivity and toxicity in the LLW that will constitute the majority of the separated wastes.

The specific goals of CLEAN with respect to HLW and LLW are to develop technology necessary for the following:

- Accommodate the HLW fraction of the Hanford Site tank waste in a minimum number of canisters--approximately 1,000
- Separate radionuclides from the LLW waste stream to the point that the LLW (grout) can meet NRC Class A limits (10 CFR 61.55); and, in addition, remove technetium, iodine, and uranium because of their mobility in groundwater
- Reduce the chemical toxicity of the LLW through the destruction of nitrates and organics and the immobilization of heavy metals
- Achieve the above objectives with no increase in the volume of LLW.

A8.1 OBJECTIVES AND MISSION

Major objectives of the CLEAN option include the following:

- Minimize the radioactivity and chemical hazard from tank waste left onsite to the point that it does not represent major concern
- Minimize the volume of HLW resulting from tank waste remediation so as to reduce demands on the geologic repository.

The mission of the option is to (1) define and provide the information and technology required to achieve these objectives at an acceptable cost and (2) permit an informed decision on deployment of the technology. Two major decisions are anticipated by proposed technology development activities. These are expected to take the form of recommendations based on cost and benefit considerations, and on processing and disposition of (1) supernates and salt cakes in the fall of 1996 and (2) sludges in early 1999.

A8.2 SUPERNATE DEVELOPMENT NEEDS

Process requirements and process sequences should be evaluated for supernate liquids. Questions to be addressed include the following:

1. Is ion exchange before organic destruction acceptable in all cases, or is it necessary for some liquids to undergo organic destruction first in order to separate strontium to Class A levels?
2. Are there complexed TRUs in any of the supernates that would require polishing, and how should they be dealt with?

Answers to such questions will determine if a process encompassing both nitrate and organic destruction would be acceptable in all cases, or if there are instances where separate processes might be required. Answering such questions will require tank-by-tank analysis plus selected laboratory tests, such as on CC waste.

Costs, safety, permitability, and performance of cesium removal, strontium removal, organic and nitrate destruction, and technetium and iodine removal process steps need to be established through specific demonstration projects. Estimates are required for total system processing costs as a function of LLW cleanliness (e.g., how much is strontium and cesium removal alone as compared to strontium/cesium + technetium removal). This needs to be done for the least expensive and lowest risk processing configurations, which are not yet known; therefore estimates should be done for both compact processing and central plant approaches. Estimates should involve formulation of arrays and sequences of compact processing units; itemization of logistics requirements such as maintenance facilities, piping, and transportation; and then estimation of corresponding costs, operational manpower, and safety needs.

Stability and compatibility of the LLW form need to be demonstrated. It is expected that grout will probably be the cheapest and possibly the best form for the wastes after radioactivity, nitrates, and organics are removed. However, the compatibility of solids from extensive separation processing and grout and also the advisability of neutralization of the OH⁻ with, perhaps, carbonate must be determined. The required effort is probably a paper study plus a small number of laboratory leachability tests.

Methods for LLW waste processing that are compatible with the distributed processing concept should be explored with the goal of exploiting the potential advantages in being able to create LLW packages in the field. Studies should be performed at least through a conceptual design activity or, preferably, to actually demonstrate distributed processing concepts. Demonstrations will provide the most useful and convincing evidence that the unit processes produce an acceptable waste. Estimates of the benefits of extensive separation LLW will be required to weigh against cost to make a decision. A limited number of performance assessment (PA) studies to develop comparisons on risk, and a study to determine if barrier costs and PA (the complete one for permitting) costs can be reduced through the extensive separation strategy should be performed. These studies should be done as a function of degree of cleanliness.

The ongoing effort on potential reduced costs through introduction of advanced materials should be continued. Advanced materials, expected to be developed by ESPIP over the next several years, could substantially reduce processing costs either through increased throughput in existing ion exchange column designs or through simpler schemes, such as selective precipitation in a tank or selective precipitation followed by filtration in a process unit. Demonstrations may be necessary to support the introduction of the newer materials if potential cost savings warrant.

A8.3 SALT CAKE DEVELOPMENTAL NEEDS

We assume that the salt cakes are basically dried out supernate and that the chemistry is identical. This assumption should be confirmed or modified based on data and analysis. The required effort is mostly a paper study focused on process requirements. Some laboratory experimentation should be required.

A retrieval-dissolution-filtration system for salt cake that is compatible with nominal compact processing flow rates should be developed and demonstrated. Compact processing array and flow rates for the salt cake should be optimized.

Total system processing costs should be developed in a fashion similar to that proposed above for supernates. An initial estimate of salt cake processing costs would probably be necessary to factor into the estimate for supernates before a large amount of effort is expended on the retrieval-dissolution-filtration system demonstration. This is because the decision on the extent of distributed processing would probably need to be made for salt cakes and supernates at the same time, even though the actual processing of salt cakes could lag that of supernates.

A8.4 SLUDGE DEVELOPMENTAL NEEDS (PHASE I EFFORT-- INITIAL 3-4 YEARS)

The feasibility of sludge dissolution needs to be verified and the process chemistry (dissolution behavior and evaluation relative to subsequent processing) needs to be explored extensively. This is a feasibility issue for the extensive separation approach and is one of the most important unknowns for the reference system as well. As many as 200 samples need to be investigated (about 10 samples from about 20 different types of sludge). What is involved is not a single measurement from each sample, but in effect an experimental program on each sample to determine processability as well as composition. Dissolution and leaching includes both basic and acid treatments.

The feasibility of sludge calcination followed by subsequent dissolution needs to be determined, and corresponding flowsheets developed. This alternative approach to dissolution has some potential advantages including the possible production of a stabilized waste suitable for interim storage before final processing. The suitability of interim storage of the sludge after initial caustic leaching should be determined. During this process, cesium would be leached, and ferrocyanides and some organics would be

destroyed. After drying, the original 20 Mgal of sludge would be reduced to about 2 Mgal that might be stored for future processing.

Acid-side chemistry alternatives to those currently in the extensive separation flowsheet should be developed. These alternatives would offer simplification, cost reduction, or reduced intermediate secondary wastes. Both individual process and flowsheet development activities need to be carried out in an interactive manner. Acid-side conceptual process designs are needed to develop schemes that permit progressive or staged processing a step at a time, each step getting closer to the end result, or permit schemes that will allow distributed processing. An example is storage of partially treated sludge. Such schemes are needed to reduce technical risk.

Conceptual equipment designs that enable distributed processing, e.g., a continuous compact dissolver, are needed to enable distributed "conventional" processing of sludge. Failure to demonstrate a feasible conceptual design would rule out the possibility of distributed processing for sludge, at least using the conventional route of dissolving followed by separation.

One of the major problems with the extensive separation as it relates to sludge is the technical risk, which is largely associated with process complexity. Changes in the waste package, ranging from minor changes in the specifications in borosilicate glass to changes in waste package design, have the potential of enabling major process simplifications. A study of HLW package, process, and form optimization is needed to explore this potential.

Characterization of the repository interface is needed to support the waste package and process optimizations and to determine the value of repository space. Technical working sessions are needed between process developers and repository developers to explore such areas as potential cost reduction.

Phase I of the CLEAN option is expected to lead to the following:

1. Initial conceptual flowsheets and implementation scenarios, roughly comparable to the present state of development for salt cakes and supernates
2. Formulation of the key elements requiring demonstration similar to the present stage of development for salt cakes and supernates
3. Rough processing cost estimates
4. An idea of the potential benefits of the extensive separation goal of minimum canisters.

Phase I results will form the basis for entering into Phase II, which is similar in nature to the demonstration program proposed for salt cakes and supernates. The anticipated Phase II deliverables are process layout recommended deployment strategy; demonstration of engineering feasibility and data to support cost vs. canister count; and risks, to support decisions to implement the extensive separation approach.

A8.5 ADDITIONAL DEVELOPMENTAL NEEDS

Detailed planning is currently in progress to establish the following developmental activities.

Experimental Logistics. As many as 200 samples of sludge need to be characterized in terms of composition and processing characteristics in the next 3 years. Samples and sludge types need to be identified, and means developed and executed to get the sludges into the hands of performing organizations. Some common understanding of testing standards needs to be developed. Surrogates need to be developed in the interim. Questions to be answered in the near term include the following.

1. Should different groups get different classes of sludge, or should it go by process scheme or some combination?
2. Who should collect the samples and transport them?
3. How do we obtain needed priorities?
4. From the experimentalist's perspective, what types, numbers, and sizes of samples are needed?
5. Are sampling, transport, and experimental capacities adequate to support required schedules.

Permitting. Individual process demonstrations will probably have their own permitting activity. However, an early-on involvement of the state and other interested parties in the entire extensive separation strategy may speed the permitting process. A "rollover" permitting process might be developed for some of the compact processing units if they are deployed in the same form as the demonstration.

Safety and Risk Analyses. Analyses will probably be needed on a task-by-task basis except for those involving generic issues such as transportation and piping systems.

Final Closure. While this issue might be deferred, the extensive separation cannot be logically pursued in a total sense without considering final closure and the residual radioactivity. These factors will eventually have to be considered, and the need to do so should at least be acknowledged early on.

Integration With Other Pretreatment Activities. Extensive separation is one of several pretreatment options under consideration. Some options will have R&D as well as analysis needs in common and should have common key milestones for decisions. There should be an activity to integrate extensive separation development with other similar activities.

A8.6 OVERALL PROJECTION

The extensive separation approach could evolve over the next 30 years for three broad categories of waste: supernates, salt cakes, and sludges. The

overall scheme is based on the observation that the supernates and salt cakes require only basic processing, which is better developed than the acid media methods that will be needed for sludge dissolution and separations.

A9.0 INITIAL PRETREATMENT MODULE

The IPM will be the first in a series of radiochemical process facilities designed to pretreat Hanford Site tank waste in preparation for final disposal as grout and glass. To handle the waste safety issues, its primary function, the IPM facility will chemically process tank wastes by destroying or modifying the constituents that cause the safety issues. In addition, a second function (a cesium recovery process) is included to decontaminate the soluble salt stream before using as feed in HWVP.

This project will address gas generation, explosive mixtures of oxidizers and ferrocyanides, and organic-nitrite reactions. High-heat generation will be resolved by retrieving tank 241-C-106 contents through another project. The selected IPM processes will be sized to allow the full contents of tank 241-SY-101, the highest priority safety tank, to be processed in 1 year, after an initial hot startup period.

Follow-on pretreatment modules will expand the capacity of the initial module, and/or provide any additional processes needed to treat retrieved SST and DST wastes before disposal. The follow-on modules may be implemented as modifications to the first module, expansions of the basic facility, separate facilities, or a combination of these options.

A9.1 IDENTIFICATION OF PREFERRED ALTERNATIVE

Eleven candidate oxidation processes and three cesium extraction processes were evaluated to arrive at the most viable oxidation cesium extraction options. The first evaluation exercise reduced the oxidation processes to a short list of ozonation, wet-air oxidation, and calcination. Additional data was developed in the form of process flow diagrams and mass balance schedules. The second process selection exercise reviewed the data developed for the short list processes and arrived at the ozonation process as the most viable alternative for oxidation. A subsequent evaluation eliminated ozone and reinstated calcination, also adding a new process, hydrothermal treatment. Currently, the latter two technologies are competing in a down selection process to determine the IPM preferred approach.

Cesium extraction by ion exchange is the preferred cesium treatment alternative. Various modes exist for operating an ion exchange process. The engineering study is based on using a regenerative resin column. Subsequent studies will include an evaluation of a once-through ion exchange (nonregenerative resin column) and electrochemical ion exchange.

A9.2 ENVIRONMENTAL PERMITTING

RCRA, Part B. A RCRA, Part B Permit application for the Hanford Site has been submitted to Washington State Department of Ecology (Ecology). Subsequently, Ecology has issued a draft permit for the Hanford Site which will eventually address each operating unit that treats, stores, or disposes of dangerous waste based on information submitted for the units. Information for the DST farms has already been submitted to Ecology, and the DSTs are

currently covered by the draft permit. It is expected the Ecology's approval, via amendment of the Sitewide RCRA permit, will be required before start of construction.

Clean Air Act Permitting. The IPM will be a potential source for radioactive emissions and emissions of other toxic pollutants to the atmosphere. Permitting under the Federal Clean Air Act and State Of Washington regulations will be required before start of construction.

Liquid Effluent Permitting. By agreement between DOE and Ecology, discharges of liquid effluent to the soil column will be permitted under WAC 173-216. Currently, efforts are underway on the Hanford Site to terminate independent plant discharges of liquid effluent to the soil column by either modifying plant processes to terminate existing streams, or by diverting current liquid effluent to the Treated Effluent Disposal Facility (TEDF), which will be permitted separately under WAC 173-216. The TEDF will be operational in 1995. If liquid effluent from the IPM is routed to TEDF, no separate permitting activity will be required. If the IPM discharges liquid effluent to the soil column, a separate permitting process will be required for a state-approved water treatment system. In either case, discharged liquid effluent will have to meet cleanliness standards of Ecology or the TEDF.

A9.3 METHODS OF PERFORMANCE

Offsite Architect-Engineer Work. An offsite architect-engineer will provide definitive design (Title I and Title II) engineering services during construction and acceptance inspection services on this project.

Procurement. The operating contractor will procure and provide the long-lead items as owner-furnished material to the construction contractor. The balance of equipment for this project will be purchased and installed by the construction contractor.

Construction Work by Offsite Contractor. Construction work will be performed under a fixed-price contract by the engineering and construction contractor who will also provide construction management.

Work by Operating Contractor. The operating contractor will provide overall project management during design, procurement, and construction of the project.

A9.4 RISKS AND ASSESSMENTS

Outline of Organics and Ferrocyanides. To meet the present project schedule, which mandates a plant startup by December 1999, every phase of the design effort will proceed at technical risk (before receiving process technology development results required to confidently start each design phase). A well-planned and expedited technology development program must be

put in place to support the design effort. At a minimum, the following activities must be included in the development program:

- Bench-scale tests with actual waste samples to determine the optimum reaction parameter.
- Pilot-plant scale tests with synthetic wastes.
- Pilot-plant tests with actual wastes.

Cesium Extraction through Ion Exchange. Cesium extraction through ion exchange is a well-established technology, including 15 years of experience at Hanford Site. No difficulty is anticipated in applying the existing technology to treat the Hanford Site wastes.

Waste Retrieval. The underground storage tank waste retrieval technology is at an early stage of development. This provides considerable uncertainty about IPM feed. Any delay in the development of the technology to support an industrial scale process by the year 1999 could have a serious impact on the IPM project. If this occurs, additional feed could be provided from nonsafety watch tanks for cesium ion exchange to continue providing HWVP and grout feed.

Fluidic Pumps and Mixers. The IPM design is based on using mechanical, motor driven, and fluidic pumps and mixers for agitating and propelling the wastes. This equipment was developed by the British nuclear-chemical industry using commercially-available fluidic components that have been used successfully with slurries as well as liquids. With no moving parts to fail, fluidic pumps and mixers are extremely reliable maximizing the facility's total operating efficiency and minimizing operating and maintenance costs.

The fluidic pumps and mixers need to be tested with simulated, highly viscous, Hanford Site wastes to verify satisfactory operation. Testing needs to be performed before start of detailed design to minimize the impact of any problems that might be discovered.

Programmatic Risks. Any success in meeting the schedule established for project W-236B will require an aggressive plan and the cooperation of all agencies involved with the design, procurement, construction, and permitting of the facility. Meeting the optimistic schedule established for completing the facility will depend heavily on twelve programmatic factors that are summarized in Bailey (1992), pages 92-94.

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Destruction	NaOH/HNO3 Recycle	NaNO3 Removal	Water Wash, Sol/Liq Separation		Dissolution and Separation	
			906 Hydramic Filter Sol/Liq Separation	907 Water Wash		
			906 Hydramic Filter Sol/Liq Separation	907 Water Wash	910 Solids Dissolution (DST)	909 Solids (DST)
*	905	906	906	907	910	909

REFERENCE SYSTEM (TYP1

NEW TECHNI

Tec
Sep

Separation	TRU Separations (Acidic)	Tc & U Pre-Separation (Acidic)	Strontium Separation (Acidic)
99			
911			
912			
913			
914			

RETREATMENT ALTERNATIVE PROCESSES CHART

EM (TYPICAL) SCHEMATIC DIAGRAM

TECHNICAL STRATEGY

	Technetium Separation (Acidic)	Cesium Separation (Acidic)	Cesium Separation (Basic)	Technetium Separation (Basic)	Strontium Separation (Basic)
ic)			916 Cs Separation (Basic)		
			916 Cs Separation (Basic)		
	914 Te Separation (Acidic)	915 Cs Separation (Acidic)	916 Cs Separation (Basic)	917 Te Separation (Basic)	918 Sr Separation (Basic)

TRU Separation (Basic)	Halogen Separation	Uranium Separation	Heavy Metals Separation	Noble Metals Separation	Actinide/Lanthanide Separation
919 TRU Separation (Basic)	920 Iodine Removal	921 Uranium Separation	922 Heavy Metals Separation	923 Noble Metals Separation	924 Actinide/Lanthanide Separation

Rows displayed by original rows

Barium/Strontium Separation	Other Separations	Disposal	
			High Capacity Vitrification
		<div> <div> <div>WV7</div> <div>WV7</div> </div> <div> <div>WV8</div> <div>WV8</div> </div> </div>	Reference System
<div> <div>WV3</div> <div>WV3</div> </div>		<div> <div>WV7</div> <div>WV7</div> </div> <div> <div>WV8</div> <div>WV8</div> </div>	Extensive Separations
			Proven for Hanford HLW

Verification			
Reference System		003 CE/FeOH Destruction	
Extensive Separations		003 CE/FeOH Destruction	004 MS Destruction
Proven for Hanford HLW			
Proven for Non-Hanford HLW	006 H/Am/Plu Separation	01 Ag 11 PROCESS	00 ALKALINE HYDROLYSIS
Generic Processes		003 CE/FeOH Destruction	004 MS Destruction
Pacific Northwest Laboratory		00 CE/FeOH DESTRUCTION HYDROTHERMAL	077 PWL MS Destruction (PWL)
Westinghouse Hanford Company		06 CE/FeOH DESTRUCTION CALCINATION	70 MOLTEN SALT PYROLYSIS (on)
		070 NWC CE & FeOH Destruction Destruction	000 NWC CE/FeOH Destruction Destruction
USTID FY-93	006 Selective Tumb Analysis	007 Metallurgical Destruction	
Contractor, IBC Adv. Techs.			
Contractor,		27 ELECTRO-	79 H2O2 WET OXIDATION

			006 Hydrophilic Filter SOL/Liq Separation	007 Water Wash	010 Sludge Classification (SST)
003 HCl Destruction	005 NaOH/NaNO ₂ Recycle	006 NaNO ₂ Removal	009 Hydrophilic Filter SOL/Liq Separation	007 Water Wash	010 Sludge Classification (SST)

			19 WMC WATER WASH SETTLE-DECANT	20 WMC HYDROPLUSE FILTER	
			21 CENTRIFUGE	000 Hydrophilic Filter SOL/Liq Separation	
			007 Water Wash		
			22 SMB WATER WASH (SST)	23 WATER WASH (SST)	
			24 FRA SLUDGE SEPARATION SST-3		

003 HCl Destruction	005 NaOH/NaNO ₂ Recycle	006 NaNO ₂ Removal	009 Hydrophilic Filter SOL/Liq Separation	007 Water Wash	010 Sludge Classification (SST)
PHL HCl Destruction (PHL)	076 PHL NaOH/NaNO ₂ Recycle (PHL)	078 PHL NaNO ₂ Removal (PHL)			05 PHL SST SOLIDS DISSOLUTION (PHL)
					07 SST SOLIDS SEPARATION (PHL)
25 ELECTRO- CHEMICAL ION X	11 CLEAN SALT PRECIPITATION	12 CALCINATION NITRATE DESTRUCTION	19 WMC WATER WASH SETTLE-DECANT	20 WMC HYDROPLUSE FILTER	08 SST SOLIDS DISSOLUTION (WMC)
	34 FREEZE CRYSTALLIZATION	100 HCl PYROLYSIS MOLTEN SALT (WMC)	21 CENTRIFUGE	000 pH Control Wash	01 SST SOLIDS SEPARATION (WMC)
	29 HCl TO HCl & CEAMIC		000 Sludge Wash SOL/Liq Separation		107 Sludge Classification
36 NITRATES SALT SPLITTING	27 NITRATES DESTRUCTION	100 NITRATES SEPARATION			

	912 ㊟ To Pre-Separation (Solid)	913 ㊟ To Separation (Solid)			916
	918 ㊟ To Pre-Separation (Solid)	919 ㊟ To Separation (Solid)	914 ㊟ To Separation (Solid)	915 ㊟ To Separation (Solid)	916

PROVEN PROCESSES

		139 WHC ㊟ To EXTRACTION (WHC)			916
133 PRA ㊟ TRU TITRANT PRECIPITATION		143 ㊟ To ION X	144 ㊟ To PRECIPITATE LA TRAPILTRAT ON		150
		145 PRA ㊟ To Solid PRECIPITATION			150

ALTERNATIVE PROCESSES

	912 ㊟ To Pre-Separation (Solid)	913 ㊟ To Separation (Solid)	914 ㊟ To Separation (Solid)	915 ㊟ To Separation (Solid)	916
104 TRU SOLID SORBENT	126 ㊟ To ADSORPTION (PML)	93 ㊟ To SELECTIVE LEACH	982 ㊟ SPRAX	979 PML ㊟ To Aids Separation	979 PML ㊟ To Aids Separation
		90 ㊟ To PRECIPITATION	102 ㊟ To SOLID SORBENTS (PML)		
105 TITANATE TRU SEPARATION	120 ㊟ To ADSORPTION (WHC)	130 WHC ㊟ To EXTRACTION (WHC)	130 ㊟ TITANATE To REMOVAL	982 WHC ㊟ To Aids Separation (WHC)	982 WHC ㊟ To Aids Separation (WHC)
991 WHC ㊟ TRUOX (WHC)		141 ㊟ CORAL 7 DICARBOLITE (SP)			
		918 ㊟ To EXTRACTION (LUTIO)			
	124 ㊟ To MOLECULAR RECOGNITION (Tc6U)	125 ㊟ U MOLECULAR RECOGNITION	140 ㊟ To MOLECULAR RECOGNITION		
		142 ㊟			

Uranium Separation	922 Heavy Metals Separation	923 Noble Metals Separation	924 Actinide/Lanthanide Separation	925 Thorium/Strontium Separation		927 Immobilization in Grout

	187 ULTRAFILT. CENTRIFUGE AND FLOCCULATION	188 FRA Pu SEPARATION			186 C14 SEPARATION CAUSTIC SCRUB	208 VITRIFICATION (60)
						210 FRA VITRIFICATION

Uranium Separation	922 Heavy Metals Separation	923 Noble Metals Separation	924 Actinide/Lanthanide Separation	925 Thorium/Strontium Separation		927 Immobilization in Grout
PNL U Separation	887 PNL Heavy Metals Separation (PNL)	888 PNL Noble Metals Separation (PNL)	883 PNL Actinide/Lanthanide Separation	884 PNL Pu/Sr Separation	174 CEPOD	200 TRANSFORMATION
	177 HEAVY METALS EXTRACTION C0104				178 CR LEACH	201
					885 WMC Al Precipitation	203 TRANSFORMATION
						195 LEACH
	181 HEAVY METAL MAGNETIC FILTER				43 FTS PROD ELECTRO-CHEMICAL 1 X	
					180 ELECTROCHEMICAL ION X	
401 LANL				900 LANL	Or, Nd, Fe Magnetic Separation	205

925 * Series/Stratification Separation		927 * Immobilization in Grout	926 * Vitrification to Glass	Extensive Separations
				Proven for Hanford HLW
	186 G14 SEPARATION CAUSTIC SCRUB	208 * VITRIFICATION (GB)	209 * GROUT (GB)	Proven for Non-Hanford HLW
		210 * FRA VITRIFICATION (Japan)	211 * FRA LLW IN BITUMEN	
925 * Series/Stratification Separation		927 * Immobilization in Grout	926 * Vitrification to Glass	Generic Processes
884 * PNL Au/Sr Separation	174 CEPOD	200 * TRANSMUTATION (PNL)		Pacific Northwest Laboratory
	178 CR LEACH	885 * WHC Al Precipitation	201 * WHC HMVP	Westinghouse Hanford Company
			202 * WHC GROUT	
		203 * TRANSMUTATION (WHC)		
		195 LLW POLY-ETHYLENE ENCAPSULATION		USTID FY-93
				Contractor, IBC Adv. Techs.
48 FIS PROD ELECTRO-CHEMICAL I X	180 ELECTROCHEM ION X			Contractor, Bradtec
900 LANL * Op. M. for aqueous separation		205 * SAS DWPF	206 * SAS GROUT (Other)	Other Defense Complex Tech.

		870 WMC * CC & FeCN Destruction, Oxidation	898 WMC * CC/FeCN Destruction, Electrodes	
USTID FY-93	888 * Selective Toxin Analysis	887 * Biological Destruction		
Contractor, IBC Adv. Techs.				
Contractor, Bradtec		27 ELECTRO- CHEMICAL OXIDATION	78 H2O2 WET OXIDATION	
Other Defense Complex Tech.	888 * TV/Amibio Suppression	80 INEL * BIOLOGICAL DESTRUCTION	130 * CC OZONIZATION	
		131 * SUPER- CRITICAL WATER OXIDATION	132 * H2O2 CC OXIDATION	
Other Domestic Technology				
Foreign, Britain		81 * Ag II PROCESS	82 * ALKALINE HYDROLYSIS	
		83 ELECTRO- CHEMICAL INCINERATION	84 WET OXIDATION	
Foreign, France		86 FRA * ORGANICS DESTRUCTION (P)		
Foreign, Japan (OMEGA)				
Foreign, Britain & Japan		87 ELECTRO- CHEMICAL ORGANICS TO CO2 & H2O		
Foreign, Russia				

		<div>103 TO NH3 & CERAMIC</div>	<div>Sludge Wash Sol/Liq Separation</div>	<div>197</div> <div>Sludge Dissolution</div>
	36	27	189	
	<div>NITRATES SALT SPLITTING</div>	<div>NITRATES DESTRUCTION</div>	<div>NITRATES SEPARATION</div>	
		171		22
		<div>NH3 PYROLYSIS MOLTEN SALT (DRUM)</div>	<div>SRS</div> <div>WATER WASH (SWS)</div>	
<div>PRELIMINARY INFO.</div>				
			23	
			<div>WATER WASH (W)</div>	
			24	
			<div>FRA</div> <div>SLUDGE SEPARATION STE-3</div>	
	/			
		28	3	28
		<div>NITRATES TO H2 & H2O ELECTRO CHEM IX</div>	<div>SBR ELECTRO- FLOCCULATION</div>	<div>SBR ELECTRO- FLOTATION</div>
			172	
			<div>SLUDGE DEWATERING ELECTRO- OSMOSIS</div>	

<div>50</div> <div> <div>MoT104 ACIDIC</div> </div>			
<div>109</div> <div> <div>SUBSTITUTED MALONAMIDES</div> </div>			
<div>110</div> <div> <div>TRU FLOC ULTRA- FILTRATION</div> </div>		<div>143</div> <div> <div>3⁺ ION X</div> </div>	<div>144</div> <div> <div>3⁺ PRECIPITATE ULTRAFILTRATI ON</div> </div>
<div>111</div> <div> <div>FRA</div> <div>TRU T1 (DM 4) PRECIPITATION</div> </div>	<div>112</div> <div> <div>Pu Am ALKYLDIAMIN E EXTRACTION</div> </div>	<div>145</div> <div> <div>FRA</div> <div>3⁺ DMSO PRECIPITATION</div> </div>	
<div>113</div> <div> <div>OMG</div> <div>DIOXA (ACID)</div> </div>	<div>114</div> <div> <div>OMG</div> <div>TRUEX (Japan)</div> </div>	<div>146</div> <div> <div>OMG</div> <div>3⁺ REMOVAL</div> </div>	
	<div>127</div> <div> <div>ELECTRO- CHEMICAL URANIUM SEPARATION</div> </div>		
<div>152</div> <div> <div>CIS</div> <div>TRANS Pu ION X</div> </div>	<div>153</div> <div> <div>CIS</div> <div>TRANS Pu ION X CHROMA- TOGRAPHY</div> </div>	<div>166</div> <div> <div>CIS</div> <div>3⁺ EXTRACTION CROWN ETHER</div> </div>	<div>167</div> <div> <div>CIS</div> <div>3⁺ EXTRACTION w/CHC6O1C</div> </div>
<div>170</div> <div> <div>CIS</div> <div>TRANS Pu EXTRACTION w/CHC6O1C</div> </div>			

KEY TO SYMBOLS

MATURITY

PO

BENCH SCALE
REALISTIC SIMULANTS

FULL SCALE
REALISTIC SIMULANTS

PILOT PLANT

PROVEN IN AN
OPERATING
FULL-SCALE
FACILITY FOR
PROCESSING LOCAL

PROVEN IN AN
OPERATING
FULL-SCALE
FACILITY FOR
PROCESSING HANFORD

	182	✱	1 REMOVAL WITH Ag MORDENITE	184	✱	HEAVY METAL EXTRACTION					
	184	✱	Removal by Cu ²⁺ Precipitation	185	✱	1 REMOVAL VIA Ag ZEOLITE	187	✱	ULTRAFILT. CENTRIFUGE HM FLOCCU- LATION		
	190	FRA	✱	100% SEPARATION			188	FRA	✱	Pu SEPARATION	
							182	OMG	✱	Pu Pu Pu RECOVERY	
						184	✱	ELEC CHEN 12 TRACE METAL SEPARATION	183	✱	ELECTRO- CHEMICAL Pu DEPOSITION

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T REVISION

				207 * TRANSMUTATI ON (Other)	Complex Tech.	
		44 * CC PHASE SEPARATION	45 * BIOLOGICAL SEPARATION	204 * AEROSOL LLW IN POLYETHYLEN E	Other Domestic Technology	
		92 * PUMPS BIOLOGICAL DESTRUCTION	163 * LANTHANIDE EXTRACTION (Other)			
		898 * A3 & 2 Precipitation	188 * C14 SEPARATION CAUSTIC SCRUB	208 * VITRIFICATION (GB)	209 * GROUT (GB)	Foreign, Britain
		189 * FRA LANTHANIDE EXTRACTION (Fr)	191 * FRA MACROCYCLE SEPARATIONS	210 * FRA VITRIFICATION (Japan)	211 * FRA LLW IN BITUMEN	Foreign, France
				214 * OMG TRANSMUTATI ON (Japan)		Foreign, Japan (OMEGA)
		46 * ELECTRO- FILTRATION				Foreign, Britain & Japan
	/	7 * C18 LANTHANIDES EXTRACTION w/CHROMIC	41 * ALKALI EARTHS ION X CHROMA- TOGRAPHY	10 * C18 LLW IN SILICA		Foreign, Russia
		42 * LANTHANIDES ION X CHROMA- TOGRAPHY	175 * C18 LANTHANIDES ION X			

FIGURE B-1 HANFORD DST & SST WASTE PRETREATMENT
ALTERNATIVE PROCESSES CHART

Foreign, Britain

83 11 PROCESS

84 ALKALINE
HYDROLYSIS

83 ELECTRO-
CHEMICAL
INCINERATION

84 WET
OXIDATION

Foreign, France

86 FRA
ORGANICS
DESTRUCTION
PM

Foreign, Japan
(OMEGA)

Foreign, Britain
& Japan

87
ELECTRO-
CHEMICAL
ORGANICS TO
CO₂ & H₂O

Foreign, Russia

KEY TO SYMBOLS

MATURITY				POTENTIAL

		186 Ca ION L, BR	187 Ca ION L, BR ALTRAP/ULTRAFS ON	184 Y ₂ EXTRACTION		
		188 PFA Ca ION L, P		189 PFA Y ₂ SEPARATION (H)		
		189 OHG Ca REMOVAL		190 OHG Y ₂ SEPARATION (H)		
		9 Ca EXTRACTION w/CHROMIC	9 Ca ION L PERMUTANIDE			

SYMBOLS

POTENTIAL BENEFIT	DOE FUNDING	PREPARED BY: DO FRANK DG SUTHERLAND MSIN L4-72 DATE: _____
<div>R&D</div> <div>DT&E</div> <div>HIGH</div> <div>HIGH TIMELY</div> <div>MEDIUM</div> <div>MODERATE TIMELY</div> <div>LOW</div> <div>LOW, UNTIMELY, OR INACTIVE CONCEPT</div>	<div>R&D</div> <div>DT&E</div> <div>HIGH</div> <div>SIGNIFICANTLY ADVANCED MATURITY</div> <div>MEDIUM</div> <div>MODERATELY ADVANCED MATURITY</div> <div>LOW</div> <div>NEGLECTIBLE ADVANCE OF THE MATURITY</div>	APPROVED BY: WB BARTON DATE: _____ * INDICATES CHANGE SINCE LAST CHART REVISIO

[illegible]

FIGURE B-1 HANFORD DST & SST WASTE PRETREATMENT ALTERNATIVE PROCESSES CHART

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APPENDIX B

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1 / 7 / 94

END